Dedication

To my beloved family for their love and support, Nakurun Lapsetry for supporting my education throughout

DECLARATION

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

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List of Abbreviations

1°C/h	One degree centigrade per hour
^{1}HNMR	Proton Nuclear Magnetic Resonance
APCI-MS	Atmospheric Pressure Chemical Ionization Mass Spectrometry
ASTM	American Society for Testing and Materials
B100	Neat biodiesel
BHP	Brake Horse Power
BS	British standards
BSFC	Brake Specific Fuel Consumption
BTE	Brake Thermal Efficiency
Btu	British thermal units
Cal.	Calories
CFPP	Cold Filter Plugging Point
CI	Compression Ignition
cm	Centimeters
cm^{-1}	Per centimeter
CME	Croton Methyl Esters
CN	Cetane Number
cSt	Centistokes
DF2	Grade two diesel fuel
DIN	German Institute for Standardization
ELSD	Evaporative Light Scattering Detection
Eq.	Equation
FAME	Fatty Acid Methyl Esters
FFA	Free Fatty Acid
Fig.	Figure
FID	Flame Ionization Detector
GC	Gas Chromatography
g/cc	Grams per cubic centimeters

g/kWh	Grams per kilowatt hour
HPLC	High Performance Liquid Chromatography
I_2	Iodine
ISO	International Standard Organization
IR	Infrared
j	Joules
JIS	Japanese Industrial Standards
JME	Jatropha Methyl Esters
KEBS	Kenya Bureau of Standards
Kg	Kilograms
KHP	Potassium Hydrogen Phthalate
KOH	Potassium Hydroxide
LTFT	Lower Temperature Flow Test
m	Meter
MeOH	Methanol
mg	Milligrams
Mj/Kg	Mega joules per kilogram
MSD	Mass Spectrometer Detector
$NaOCH_3$	Sodium Methoxide
NaOH	Sodium Hydroxide
NIR	Near Infrared
NMR	Nuclear Magnetic Resonance
No. 1-D	Grade number one diesel fuel
No. 4-D	Grade number four diesel fuel
OPEC	Organization of the Petroleum Exporting Countries
OSI	Oils Stability Index
PAD	Pulsed Amperometric Detection
ppm	Parts per million
PPO	Pure Plant Oil
SG	Specific Gravity
SFC	Specific Fuel Consumption

SVO	Straight Vegetable Oils
THF	Tetrahydrofuran
UNFAO	United Nation Food and Agriculture Organization
Vs	Versus

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ABSTRACT

The main objective of this project was to study biodiesel production from two local non-edible plant feedstocks namely *Jatropha curcas* and *Croton megalocarpus*. The oil from the above plant seeds were mechanically extracted using a screw pressing machine and the oil yield determined. Preliminary test were done on the neat oil to ascertain their quality, these included; viscosity, density, acid value, iodine and calorific value. The oils were then converted into biodiesel through trans-esterification process using methanol and potassium hydroxide as a catalyst. The factors governing the trans-esterification process investigated included; reaction time, amount of base catalyst (potassium hydroxide) per liter of oil, amount of methanol per liter of oil and reaction temperature. Biodiesel yield of 87.5 % CME and 71.3 % JME were obtained at methanol/oil ratio of 5:1, temperatures of 60°C, reaction time of one hour while KOH/liter oil was 0.75 wt% croton oil and 1.5 wt% jatropha oil respectively.

Blends consisting of *Jatropha curcas* methyl esters (JME) and *Croton megalocarpus* methyl esters (CME) were also prepared and tested in the proportions; 25%JME and 75%CME, 50%JME and 50%CME and 75% JME and 25%CME. The above mixtures were further separately blended with commercial diesel to obtain B5, B10 and B20 blends. The individual esters were separately blended with grade 2 diesel (DF2) to obtain B5, B10 and B20. Both esters and their blends with DF2 were characterized with respect to specific gravity, kinematic viscosity, iodine value, acid value and calorific value. The kinematic viscosities of all blends of the esters were lower than those of JME (B100) and CME (B100) at all temperatures. Blending the above fuel esters with commercial DF2 lowered the specific gravity and kinematic viscosity significantly.

The acid values for all the neat fuel esters and their blends were found to be within the allowed maximum limit of 0.8mgKOH/g. The calorific values decreased with increase in percentage of biodiesel in the blends. The iodine values for both the SVO, neat fuel esters and their blends were within the allowed maximum limits of $115gI_2/100g$ oil and $120gI_2/100g$ oil except for SVO from *Croton megalocarpus* which gave a high iodine value of $133gI_2/100g$ oil. The fatty acid methyl ester composition from CME determined using gas chromatography showed it to contain primarily the three fatty acid methyl esters of methyl palmitate, methyl stearate and methyl oleate. The engine performance tests of neat esters and their blends as investigated included; brake specific fuel consumption, thermal efficiency, brake horsepower and exhaust temperatures. The results obtained were comparable to those of commercial DF2.

CHAPTER ONE

GENERAL BACKGROUND INFORMATION

The concept of using vegetable oil as an engine fuel dates back to when Rudolf Diesel (1858-1913) developed the first engine to run on 100% peanut oil (Nitske et al, 1965). This was demonstrated as early as 1900 at the World Exhibition in Paris. Diesel promoted the use of vegetable oil as fuel by suggesting that it would greatly benefit the development of agriculture in countries that utilized this potential.

The adoption of petroleum-based fuel as the primary fuel for the diesel engine was largely influenced by the cheaper costs of petroleum at the time. The driving force for large-scale use of biodiesel has been the need to reduce the harmful emissions that result from the burning of petroleum oil as well as our dependence on diminishing reserves of petroleum oil. The similarity in properties of biodiesel and petroleum diesel fuel, along with its economic and environmental benefits, has made it an attractive choice.

Vegetable oils have been proposed as diesel engine fuels as they are widely available from a variety of renewable sources (Boehman, 2005; Wan Nik et al., 2005). However, greater viscosity results in sticking of piston rings, injector deposits and oil thickening (Baldwin et al., 1982; Fuls et al., 1984; Ryan et al., 1984; Van Der Wat and Hugo, 1982). Conversion of the oils to their alkyl esters reduced the viscosity and produced fuels with properties similar to petroleum based diesel fuel capable of use in existing engines without modifications.

Increasing concerns regarding environmental impacts, the soaring prices of petroleum products together with the depletion of fossil fuels have prompted considerable research to identify alternative fuel sources. Biofuels have recently attracted attention because of its renewability, better gas emissions and its biodegradability.

The use of edible vegetable oils and animal fats for biodiesel production is of great concern because such compete with use as food (Arjun et al., 2008). Onyari and Munavu (1981) studied the oil content and properties of over 15 non-conventional local seed oils which included *Jatropha curcas*. Azam et al., (2005) studied the prospects of using fatty acid methyl esters (FAME) of some 26 non-traditional plant seed oils including Jatropha.

as potential biodiesel and found these to be suitable for use as biodiesel. Subramanian et al., (2005) reported that there are over 300 different species of trees identified as producers of oil bearing seeds. Thus, there is a significant potential for non-edible oil source from different plants for biodiesel production as an alternative to petro-diesel. Often the vegetable oils investigated for their suitability as biodiesel are those which occur abundantly in the locality.

The fuel and energy crises of the late 1970's and early 1980's as well as accompanying concerns about the depletion of the world's non-renewable resources provided the incentives to seek alternatives to conventional, petroleum-based fuels. From the mid-1980s to September 2003, the inflation adjusted price of a barrel of crude oil was generally under $25/barrel. Then during 2004, the price rose up to $50/barrel. The prices then exceeded $75/barrel in the middle of 2006. Prices reached $99.29/barrel by December 2007. On February 29, 2008, oil prices peaked at $103.05 per barrel, and reached $110.20 on March 12. Prices on June 27, 2008, were $141.71/barrel before declining to about $110. The most recent price per barrel maximum of $147.02 was reached on July 11, 2008. OPEC's president predicted prices may reach $170 by the end of the year, 2008. An important contributor to price increases has been the slow down in oil supply growth, which has continued since oil production surpassed new discoveries in 1980 (http://en.wikipedia.org/wiki/Oil_price_increases_of_2004-2006).

Kenya does not have locally produced fossil fuels as for now and therefore it is a net importer. Oil imports for the year 2005/06 cost Ksh.95.188 billion which was 7.4% of the GDP and 25% of the foreign exchange earnings. The Economic Survey 2007, indicates that the petroleum import bill increased by Ksh.18 Billion from Ksh.95.7 billion in 2005 to Ksh.113.7 Billion in 2006 (an increase of 18.8%). It also reported that importation of diesel in the year 2006 constituted 57% of the total oil imports.

The energy pattern in the country demonstrates the need to diversify the energy economy to ensure that a majority of Kenyan people access more sustainable and cost effective energy products. According to the United Nations Food and Agriculture Organization (UNFAO), wood is amongst the main forms of energy in most rural homes in the developing world. Burning wood fuel still accounts for 70% of Kenya's energy supply.

Efforts should therefore be made to diversify energy sources especially for the ordinary Kenyan, only less than 2% of who have access to electricity.

The consumption and demand of diesel is anticipated to go up due to an increase in population and economic activity. The introduction and promotion of Biodiesel fuel will therefore aid in cutting government expenditure on fossil fuel enhance energy security and solving fuel crisis characterized by uncertain interruptions that may disrupt economic growth targets and increase inflation. Promotion of biofuels from non-edible oils will also diversify rural economies, improve rural incomes and contribute to afforestation and biodiversity conservation efforts. The production of bio-fuels as a sustainable energy alternative for Kenya is untapped or at very emerging stages. This research work evaluated the properties of biodiesel obtained from *Jatropha curcas*, *Croton megalocarpus*, blends between the two methyl esters and with commercial DF2, as well as engine performance tests.

1.1 DIESEL ENGINES

The first diesel engine that ran at 26% efficiency was constructed by Rudolph Diesel in 1893 and ran on peanut oil. The diesel engine is termed as compression-ignition (CI) engine because after injection of diesel fuel it is ignited by the heat of compression in a diesel engine. A diesel engine takes in air, compresses it and then injects fuel into the compressed air. The heat of the compressed air lights the fuel spontaneously. In contrast, gasoline is spark-ignited. The differences in the ignition processes entail significant differences in chemical composition and physical properties of the fuels. The ignition quality of diesel fuel is measured by ASTM D613 and reported as the cetane number (CN). Ignition quality is defined by the ignition delay time of the fuel in the engine. The shorter the ignition delay time the higher the CN. Diesel engines can be grouped into two types as described below;

1.1.1 Direct Injection Engine:

Air inducted in the engine is compressed and the fuel is injected directly into the combustible chamber where the heat caused by compression of air ignites the fuel.

1.1.2 Indirect Injection Engine:

In this engine diesel fuel is injected into a small pre-combustion chamber where combustion is initiated. A narrow passage connects this to the main combustion chamber above the piston

1.2 BIODIESEL

Biodiesel is defined as the mono-alkyl esters of fatty acids derived from vegetable oils or animal fats. It is the product obtained when a vegetable oil or animal fat is chemically reacted with an alcohol to produce fatty acid alkyl esters. A catalyst such as sodium or potassium hydroxide is required. Glycerol is produced as a co-product (Van Gerpen et al., 2004). Research has also made it possible for the use of other catalysts such as enzymes (biocatalyst) and acids catalysts. Biodiesel can be used in any internal combustion diesel engine in either its pure form, which is referred to as "neat" biodiesel or B100. However, it is often blended with petroleum-based diesel fuel and when this is done the blend is designated "BXX" where XX is the percentage of biodiesel in the blend. For example, B20 is a blend of 20% biodiesel and 80% petroleum diesel fuel.

There are several primary reasons for encouraging the development of biodiesel especially in developing countries without fossil oil reserves.

1. It provides a market for excess production of vegetable oils and animal fats.
2. It decreases the country's dependence on imported petroleum and thus enhances energy security.
3. Biodiesel is renewable and does not contribute to global warming due to its closed carbon cycle.
4. The exhaust emissions from biodiesel are lower than with regular diesel fuel.
5. Biodiesel has excellent lubricating properties.
6. Jobs creation and diversification of rural economies.
7. Afforestation, biodiversity conservation and carbon trading opportunities.

The main advantages of using biodiesel fuels as 100 % mono alkyl esters of vegetable oil and animal fat or biodiesel blends (up to 20 % blend to the diesel fuel) are producing less smoke and particulates and having higher cetane numbers (Antolin et al., 2002; Encinar et al., 2007). The use of biodiesel present some technical challenges such as low volatility, high pour and cloud points and cold filter plugging temperature. They also contribute to high emission of nitrogen oxide (NO_x) than DF2 which is due to oxygen content of the biodiesel. Oxygen content in the biodiesel tends to provide additional oxygen for the NO_x formation (Crutzen et al., 2008). Biodiesel essentially contain no sulfur; therefore, greatly reduce sulfur dioxide emissions from diesel vehicles (Alptekin and Canakci, 2008; Saifuddin and Chua, 2004). As an alternative to diesel fuel, biodiesel must be technically feasible, economically competitive, environmentally acceptable and readily available. Nowadays, biodiesel fuel is used in public traffic for performing farm engines, lighting and heating of rooms in specific conditions (Haas, 2005; Schlautman et al., 1986; Tomasevic and Siler-Marinkove, 2003). However economic reasons have impaired the widespread use of biodiesel as the cost of biodiesel is higher than the petroleum-derived diesel due to the high cost of virgin vegetable oil. Therefore, it is necessary to explore ways to reduce production cost of biodiesel starting with minimizing the cost of raw materials. According to Nelson et al., (1994), the most important factor in biodiesel breakeven price was feedstock cost. As in the case of conversion of vegetable oils or fats to their esters, the resulting glycerol co-product with a potential market of its own may offset some of the costs.

1.3 OBJECTIVES

1.3.1 Broad Objective

To investigate the properties of alkyl monoesters of fatty oil from *Jatropha curcas*, *Croton megalocarpus* and their blends as an alternative source of oil to diesel fuel.

1.3.2 Specific Objectives

1. To extract oil from *Jatropha curcas* and *Croton megalocarpus* plant seeds and compare oil yields.
2. Convert the oil into biodiesel using methanol, through the process of trans-esterification using conventional technologies.
3. To prepare biodiesel blends of *Jatropha curcas* and *Croton megalocarpus* and determine the properties of the biodiesel blends as a function of temperature.
4. To perform engine performance tests on new biodiesel samples, blends and compare results with commercial diesel.
5. To determine fatty acid composition of the biodiesel using gas chromatography.

CHAPTER TWO

LITERATURE REVIEW

2.1 DESCRIPTION OF PLANT RESOURCES

2.1.1 *Jatropha curcas*

This is a shrub whose oily seeds or nuts are also called Barbados or Physic nut. *Jatropha curcas* belongs to the Euphorbiaceae or spurge family (pictured). Curcas is one member of the Jatropha genus, of which there are about 175 members. Its origins are thought to be Central America, or perhaps the Caribbean, but it is now grown in Asia, Africa and other parts of the world. The genus Jatropha possesses more than 70 shrub species, such as *Jatropha pohliana, Jatropha gossypiifolia* and *Jatropha curcas*, which produce seeds with high oil contents (Shah et al., 2005).

It is resistant to a high degree of aridity (it can be planted even in the desert) and as such does not compete with food crops. It's considered poisonous (to some degree,) as its seeds or nuts are non-edible. Boateng and Kusi (2008) investigated and revealed that *Jatropha curcas* oil is toxic to both *Callosobruchus maculatus* (Coleoptera: Bruchidae) and its Parasitoid, *Dinarmus basalis* (Hymenoptera: Pteromalidae); which is a cosmopolitan cowpea beetle under laboratory conditions. They suggested that it is possible to incorporate the oil in a well designed pest management program. Rakshit et al., (2008) also investigated the toxicity of *Jatropha curcas* oil in rats which was due to the presence of toxic phorbol esters and lectin. (Wilhelm and Mittelbach 2000, Martínez et.al. 2006, Gubitz et.al 1999) also confirmed similar results that *Jatropha curcas* oil contains phorbol esters which cause biological effects such as tumor and inflammation to animals and human.

There are more than 200 names for it all over the world, which indicates its significance to man and the various possibilities of its use (Anamika, 2006). Pant et al., (2006) reported that the oil content in *Jatropha curcas* varied with the altitude at which it is grown. They showed that the average oil contents in *Jatropha curcas* at the elevation ranges of 400-600m, 600-800m and 800-1000m were 43.19%, 42.12% and 30.66% of their seed weight respectively.

In Kenya, *Jatropha curcas* has been largely used as a live fence because livestock cannot brows them and is distributed in most parts of the country. Kimilu (2007) studied the viability of *Jatropha curcas* seeds that were locally collected from different parts of Kenya as an alternative fuel for diesel engines.

2.1.1.1 Cultivation and environmental importance

- *Jatropha curcas* can grow in wastelands and grows almost anywhere, even on gravelly, sandy and saline soils. It can thrive on the poorest stony soil.
- It doesn't need much water to survive - only about 10 inches (250 mm) of rainfall per year, thus can be grown in arid regions and will grow well on marginal land;
- Once grown, it has a long life, about 40-50 years and needs little maintenance. It doesn't have to be plowed under each year; it produces nuts about three years or earlier after planting.
- Seeds or cuttings can be directly planted in the main field. Sometimes the seedlings are grown in polybags and then transplanted in the main field
- Approximately yield of 1200 Kg seed per hectare may be obtained from irrigated plantation in comparison to 750 kg seed (per hectare) from rain fed plantations. This is expected from third year onwards after planting (Anamika, 2006).
- Approximately 5-6 Kgs of seed is adequate to raise 1 hectare of plantation. The spacing maintained is about 2m ×2m and for high density planting 2m × 1m distance can be recommended.
- It can stop land degradation and reverse deforestation.
- It can be grown alongside food crops
- As a perennial (doesn't die every year) it can sequester carbon too.

2.1.1.2 Properties and suitability of *Jatropha carcus* oil as a diesel engine fuel

Most research work has established that fatty acid composition of *Jatropha curcas* classifies it as Linoleic or Oleic acid types, which are unsaturated fatty acids (Arjun et al., 2008, Gubitz et al., 1999, Hawash et al., 2009, Jefferson et al., 2009, Liang et al., 2006). The fatty acid compositions of Jatropha consist of Myristic, Palmitic, Stearic, Arachidic, Oleic and Linoleic acids. Table (2.1) below summarizes the fatty acid composition of Jatropha carcus oil. Table (2.2) shows the fatty acid composition of other naturally occurring plant oils. Some of the important physical and chemical properties of Jatropha carcus oil are as shown in table (2.3) below.

Table 2.1: Fatty acid composition of *Jatropha curcas*

Acid	Carbon number/Number of double bonds	Source 1 Amount in %	Source 2 Amount in %	Source 3 Amount in %	Source 4 Amount in %
Lauric	C12:0	5.90		0.31	
Myristic	C14:0	2.7			
Palmitic	C16:0	13.50	18.22	13.38	1-15.30
Patmitoleic	C16:1			0.88	0-1.3
Stearic	C18:0	6.10	5.14	5.44	7-9.80
Oleic	C18:1	21.80	28.46	45.79	34.3-45.80
Linoleic	C18:2	47.40	48.18	32.27	29.0-44.20
Others		2.70		1.93	

Source 1: Jefferson et al., 2009

Source 2: Hawash et al., 2009

Source 3: Arjun et al., 2008

Source 4: Gubitz et al., 1999

Table 2.2: Fatty acid composition of other naturally occurring plant oils

	% Composition of Fat							
Fatty acid	Carbon number/Number of double bond	PNO	RSO	CRO	PO	SUO	TLO	SNO
Lauric	12:0						0-0.2	
Myristic	14:0	0-1		0-7	0.5-6		2-8	
Palmitic	16:0	6-9	1-3	8-12	32-45		24-37	4.67
Stearic	18:0	3-6	0.4-3.5	2-5	2-7	3-6	14-29	1.45
Arachidic	20:0	2-4	0.5-2.4			1-3	0-1.2	7.02
Behenic	22:0	1-3	0.6-2.1			0.6-4		1.45
Palmitoleic	16:1	0-1.7	0.2-3	0.2-1.6	0.8-1.8	0-0.8	1.9-2.7	0.37
Oleic	18:1	53-71	12-24	19-49	38-52		40-50	52.64
Eicosenic	20:1		4-12			14-43		23.85
Erucic	22:1		40-50					1.09
Linoleic	18:02	13-27	12-16	34-62	5-11	44-75	1.5	4.73
Linolenic	18:03	-	7-10					1.94

Source: Arjun et al., 2008 and Allen, C.A.W 1998.

Note: PNO-Peanut Oil; RSO-Rapeseed Oil; CRO-Corn Oil; PO-Palm Oil; SUO-Sunflower Oil and TLO-Tallow, SNO-Soap Nut oil.

Table 2.3: Physical and Chemical Properties of neat *Jatropha curcas* oil and diesel

Properties	**Source 1**	**Source 2**	**Source 3**	**Source 4**	**Diesel**
Density (g/cc), 30 ^{0}C	0.9180	0.9329	0.9215	0.9136	0.840
Kinematic Viscosity (cSt), 15 ^{0}C	49.900	52.760	30.686	40.400	4.560
Calorific value (Mj/Kg)	39.774	38.000	40.310		42.390
Flash Point	240	210			75
Cetane number	45	38			45-55
Carbon residue	0.44				0.10
Saponification value		198		195	
Iodine number		94		101.7	
Pour point (^{0}C)			-2		
Acid value (mgKOH/g)			8.45	3.50	

Source 1: Arjun et al., (2008)
Source 2: Pramanik (2003)
Source 3: Jefferson et al., (2009)
Source 4: Surendra and Subhash (2008)

Since the 1980's several tests have been done with unmodified diesels running on *Jatropha curcas* oil. Short term tests, with duration in the order of 36 hours, did not give any problem at all, all engines did run perfectly. After running around 400 to 500 hours however, several engines broke down due to clogged material in the diesels. It is important that long term running of diesel engines on pure plant oil (PPO), for example jatropha oil, is sustainable, i.e. the engines might have some more maintenance than usual, but they should not break down. There are two major parameters that determine proper operation on pure plant oil (PPO), the quality of the pure plant oil (PPO) and the type and state of the diesel engine (Jan et al., 2007).

Senthil et al., (2000) indicated that use of vegetable oils in diesel engines leads to slightly inferior performance as compared to petro-diesel and higher smoke emissions due to their high viscosity and carbon residue. Stewart et al., (1981) observed that straight vegetable oil led to filter plugging and cold starting difficulties along with higher specific consumption, this is due to the higher viscosity and lower calorific value of vegetable oils. The performance of vegetable oil can be improved by modifying vegetable oil to its mono alkyl esters by transesterification process. Conversion of the oils to their alkyl esters reduces the viscosity of *Jatropha* oil to near the diesel fuel levels and produces a fuel with properties that are similar to petroleum based diesel fuel and which could be used in existing engines without modifications (El Diwan et al., 2009).

2.1.2 *Croton Megalocarpus*

Croton megalocarpus; Hutch (pictured) belongs to the family euphorbiaceae. It occurs in tropical East Africa, at altitudinal range of 4,000 to 6,700 feet and commonly used as a shade tree in coffee plantations. It may reach a height of 120 ft; with a clear cylindrical bole 40 to 60 ft in length, free of buttresses; with trunk diameters of 2 to 4 ft (Bolza and Keating, 1972). Seeds 2 × 1 × 0.7 cm, ellipsoid, shallowly rugulose, slightly shiny, yellowish-grey; caruncle minute. *Croton megalocarpus* start bearing nuts at 3 years and matures at about 11 years.

2.1.2.1 Facts about *Croton megalocarpus*

- This tree is indigenous to East Africa, and has been widely grown in its mountainous regions as an ornamental for generations. The center of its endemism in Kenya is the Aberdare Mountains. It is therefore almost inconceivable that an ecological catastrophe could be triggered.
- It is propagated by direct sowing. It can also be propagated from seedlings and wildlings. It has high oil content (30%)
- The Croton nut is inedible, and therefore cannot directly affect edible oil prices.
- When mature, the tree has relatively open-architecture, that is, a significant amount of sunlight penetrates the canopy to reach the ground. Other crops can in principal be grown under the trees in a two-tiered agro forestry system. Thus there is no reason to fear competition with food crops.
- The tree grows and produces well at rainfall accumulations of 800 mm/year without need for irrigation. Because it has deep tap roots, it can access sufficient soil nutrients so that fertilization is not required. Therefore the trees will augment the soil, in that root exudates will enrich the soil with minerals and leaf litter with organic carbon.
- At the end of the trees' productive life, approximately 50 years from planting, they can be felled; the timber is usable for furniture production, thus continue to temporarily store carbon. .
- Unlike the other feedstocks, *Croton megalocarpus* simply drops its seedpods 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.

(Additional information on croton was taken from Lenard Milich; Environmental Comparisons of *Croton Megalocarpus* vs. Other Tropical Feedstocks, www.africabiofuel.com/files/B)%20feedstocks.doc; *accessed online on 16th April 2009 at 5:13Pm)*

2.2 DIESEL ENGINE FUEL REQUIREMENTS

2.2.1 Background on Diesel Combustion

Diesel combustion is the process that 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. When fuel is injected into the turbulent compressed air inside the engine cylinder, it does not ignite immediately. There is a time period called the ignition delay, during which the fuel heats up, vaporizes, mixes with air, and undergoes chemical pre-combustion reactions that produce the radicals necessary for spontaneous ignition or auto-ignition. The classical notion of ignition delay calls the heating, vaporization and mixing processes the "physical delay" and the pre-reactions the "chemical delay". This can be deceptive in that both processes can be, and probably are, occurring simultaneously. After sufficient time has elapsed, ignition will occur spontaneously at multiple locations.

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

2.2.2 Properties of Engine Fuel

2.2.2.1The fuel must ignite in the engine

One of the most important properties of a diesel fuel is its readiness to autoignite at the temperatures and pressures present in the engine cylinder when the fuel is injected. The laboratory test that is used to measure this tendency is the Cetane Number Test (ASTM D

613). Fuels with a high cetane number will have short ignition delays and a small amount of premixed combustion since little time is available to prepare the fuel for combustion. The cetane number however does not accurately reflect the auto-ignition conditions in modern turbocharged engines and particularly with alternative fuels.

2.2.2.2 The fuel must release energy when it burns

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

The actual heating value for diesel fuel will vary depending on the refinery in which it was produced, the time of year, and the source of the petroleum feedstock. It also depends on the composition of the fuel, for example diesel fuels with high percentages of aromatics tend to have high energy contents per gallon even though the aromatics tend to have low heating values per pound. Biodiesel fuels do not contain aromatics but they contain fatty acids with different levels of unsaturation. Fuels with more unsaturation tend to have slightly lower energy contents (on a weight basis) while those with greater saturation tend to have higher energy content is more dense than the diesel fuel, the energy content is only 8% less on a per gallon basis.

Tests have shown that the actual efficiency at which the energy in the fuel is converted to power is the same for biodiesel and petroleum-based diesel fuel reference. Therefore, the brake specific fuel consumption (BSFC) is most often used by engine manufacturers to characterize fuel economy.

2.2.2.3 The fuel must not limit the operability of the engine at low temperatures

Diesel fuel contains small amounts of long chain hydrocarbons, called waxes that crystallize at temperatures within the normal diesel engine operating range. If temperatures are low enough, these wax crystals will agglomerate and plug fuel filters and prevent engine operation. At a low enough temperature, the fuel will actually solidify. Additives, known as pour point depressants, are used to inhibit the agglomeration of the wax crystals, which then lowers the point at which fuel filter plugging occurs.

2.2.2.4 The fuel must not contribute to corrosion

Many of the parts in the diesel fuel injection system are made of high-carbon steels and are prone to corrosion when in contact with water. Water damage is the leading cause of premature failure of fuel injection systems. Many diesel engines are equipped with water separators that cause small water droplets to coalesce until they are large enough to drop out of the fuel flow where they can be removed. Diesel fuel containing excessive water that enters the injection system can cause irreversible damage in a very short time. Some compounds in diesel fuel, especially sulfur compounds, can be corrosive. Since copper compounds are particularly susceptible to this type of corrosion, copper is used as an indicator of the tendency of the fuel to cause corrosion.

2.2.2.5 The fuel must not contain sediment that could plug orifices or cause wear

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

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

2.2.2.6 The fuel should not cause excessive pollution

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

2.2.2.7 The fuel properties should not deviate from the design specifications

This property is determined by the viscosity of the diesel fuel. The fuel viscosity must be specified within a fairly narrow range. Hydrocarbon fuels in the diesel boiling range easily meet this viscosity requirement.

2.2.2.8 The fuel should be intrinsically safe

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

2.3 DIESEL FUEL SPECIFICATION

The American Society for Testing and Materials (ASTM) identifies five grades of diesel fuel described below (Van Gerpen et. al., 2004).

2.3.1 Grade No. 1-D and Low Sulfur 1-D:

A light distillate fuel for applications requiring a higher volatility fuel for rapidly fluctuating loads and speeds like light trucks and buses. The specification for this grade of diesel fuel overlaps with kerosene and jet fuel and all three are commonly produced from the same base stock. One major use for No. 1-D diesel fuel is to blend with No. 2-D during winter to provide improved cold flow properties.

2.3.2 Grade No. 2-D and Low Sulfur 2-D:

A middle distillate fuel for applications that do not require a high volatility fuel. Typical applications are high-speed engines that operate for sustained periods at high load. 2-D, or No. 2 diesel fuel, is more dense than 1-D and so it provides more energy per gallon. This makes it the preferred fuel for on-highway trucks.

2.3.3 Grade No. 4-D:

A heavy distillate fuel that is viscous and may require fuel heating for proper atomization of the fuel. It is used primarily in low and medium speed engines.

2.4 FUEL PROPERTIES AND THEIR MEASUREMENT

The methods and standards used in determining the fuel properties in a given fuels were put forth by American Society for Testing and Materials (ASTM). The following are some of the properties used to characterize diesel fuels needed to provide acceptable engine operation (Kinast, 2003).

2.4.1 Flash point

It determines the flammability of fuel. The flash point can be defined as the lowest temperature at which an applied ignition source will cause the vapors of a sample to ignite. Therefore, it is a measure of the tendency of a sample to form a flammable mixture with air. The standard procedure for measuring the flash point for diesel and biodiesel fuels is ASTM D93. The flash point is determined by heating a sample of the fuel in a stirred container and passing a flame over the surface of the liquid. If the temperature is at or above the flash point, the vapor will ignite and an easily detectable flash can be observed (Van Gerpen et.al., 2004). The flash point needs not to correspond to a sustained flame. The "fire point" is sometimes used to designate the fuel temperature that will produce sufficient vapor to maintain a continuous flame.

2.4.2 Water and Sediment

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

2.4.3 Calorific Value

The calorific value (or heat of combustion) of a fuel is the quantity of heat units produced by a unit mass of a sample when burned with oxygen in an enclosure of constant pressure and temperature. 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.

Calorific value (or heat of combustion) as measured in a bomb calorimeter denotes the heat liberated by the combustion of all carbon and hydrogen with oxygen to form carbon dioxide and water including the heat liberated by the oxidation of other elements such as sulfur which may be present in the sample.

Heat measured in a bomb calorimeter may be expressed either as calories (cal), British thermal units (Btu) or Joules (j).

1cal = 4.1868 absolute joules which is equivalent to heat energy required to rise the temperature of gram of water one degree Celsius at 15°C.

Btu = 251.996 calories which is equivalent to the energy required to raise one pound of water one degree Fahrenheit at 60°F.

The results obtained from test in a bomb calorimeter represent the gross heat of combustion of a sample, which includes the heat of vaporization given up when the newly formed water vapor produced by oxidation of hydrogen is condensed and cooled to the temperature of the bomb. This water usually escapes as steam and is not available for useful work. To compensate for this loss, net heat of combustion is calculated by subtracting the latent heat of vaporization from this gross value obtained. This requires knowledge of the hydrogen content of the sample but because of the difficulty in accurately determining the hydrogen content of the sample, and the fact that the hydrogen content of most fuels is fairly low, the gross heat of combustion is usually reported.

The American Society for Testing and Material (ASTM) has developed a series of standard methods for testing both solid and liquid fuels in a oxygen bomb calorimeter, these include; ASTM D205, ASTM D3286, ASTM D4809, ASTM D2382, ASTM E711 ASTM E144.

International Standard test method; ISO 1928-1976 (E), 1976-12-01, ISO 9001 certification

German standard test method; DIN 51 900, Tel 1, 2 & 3

British test methods; BS1016: Part 5

Japanese industrial method; JIS M 8814-1975

2.4.4 Kinematic Viscosity

Kinematic viscosity is defined in terms of dynamic viscosity (or simply viscosity). Viscosity which is also called dynamic viscosity (η) is the ease with which a fluid will flow. There is a hydrodynamic definition of viscosity as well; technically it is the ratio of the shear stress to the shear rate for a fluid. Dynamic viscosity is measured in units called "centipoise".

In contrast the kinematic viscosity (ν) is the resistance to flow of a fluid under gravity. Therefore, the kinematic viscosity of a fluid is related to the dynamic viscosity through the density (ρ), i.e., $\nu = \eta/\rho$, and is measured in "centistokes". The standard procedure for measuring kinematic viscosity in diesel or biodiesel fuels is given in ASTM D 445. Viscosity impacts the operation of components such as the fuel pump. Higher viscosity interferes with injector operation, resulting in poorer atomization of the fuel spray, and has been associated with increased engine deposits.

A number of experimental methods are available for measuring viscosity. Many are based upon measuring the amount of time (t) it takes for a given amount of fluid to flow through the capillary of a calibrated viscometer under a reproducible driving head and at a closely controlled and known temperature. An equivalent measurement is carried on a fluid of known viscosity (usually water is used as reference). The unknown viscosity is then calculated using the expression;

$$\frac{\eta_1}{\eta_2} = \frac{\rho_1 t_1}{\rho_2 t_2}, \qquad (2.1)$$

Where

ρ_1 is the density of the sample

ρ_2 is the density of water

η_1 is the viscosity of sample

η_2 is the viscosity of water

However, if the viscometer constant is known then there is no need of using a reference, viscosity of sample is calculated using the following expression (Nathan et al., 2006);

$$\eta = t\rho C_0 \qquad (2.2)$$

Where

η = Viscosity of sample
t = time taken for the liquid sample to flow through the viscometer
ρ = density of sample at a particular temperature
C_0 = Viscometer constant

Viscosity varies with temperature, generally becoming smaller as temperature is elevated. This trend occurs because the increased kinetic motion at higher temperatures promotes the breaking of intermolecular bonds between adjacent layers. A considerable amount of research has been carried out in an attempt to understand the exact nature of the temperature variation of viscosity. One relatively simple model assumes that the viscosity obeys an 'Arrhenius-like' equation of the form

$$\eta = Ae^{\left(\frac{E_a}{RT}\right)}, \qquad (2.3)$$

Where
A is the pre-exponential factor

E_a can be interpreted as the activation energy for viscous flow

A and E_a are constants for a given fluid.

The equation above can be written in the logarithmic form

$$\ln \eta = \ln A + \left(\frac{E_a}{R} \right) \frac{1}{T}. \qquad (2.4)$$

If a fluid obeys the above equation then a plot of viscosity versus reciprocal absolute temperature should be linear and the slope can be used to determine the activation energy for viscous flow.

2.4.5 Ash content

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

2.4.6 Sulfur

Measures the amount of sulfur in diesel fuels. As part of the fuel, sulfur is converted to sulfur oxides and sulfuric acid, affecting the emissions of the engine. The lack of detectable sulfur in the biodiesels would result in a reduction in the particulate emissions, in comparison to diesel. The current test procedure for amount of sulfur in biodiesel is given in D2622, but there is need to change to a new method when low levels of sulfur are required because it allows diesel fuel to contain up to 0.5% (5000 ppm) yet this value is to be lowered to 15 ppm.

2.4.7 Copper Strip Corrosion

Measures the degree to which the fuel can have a corroding effect on various metals. Biodiesel easily meets this diesel requirement for low corrosion impacts. The standard test procedure for determining the corrosion abilities of diesel fuels is defined by ASTM D 130.

2.4.8 Cetane Number (CN)

This is a measure of the fuel's ignition delay. Higher Cetane numbers indicate shorter times between the injection of the fuel and its ignition. Higher numbers have been associated with reduced engine roughness and with lower starting temperatures for engines; all biodiesel have been found to contain higher cetane number values, so they would tend to improve operation of the engine with respect to pure diesel (based on this value alone). However, both too high and too low CN can cause operational problems (in case of too high CN, combustion can occur before the fuel and air are properly mixed, resulting in incomplete combustion and smoke; in case of too low CN, engine roughness, misfiring, higher air temperatures, slower engine warm-up and also incomplete combustion occur). The cetane number standard test procedure is defined by ASTM D613.

The cetane number can be estimated empirically by using the cetane index. However it does not provide accurate indication of cetane number if the fuel contains cetane improving additive. Two ASTM methods are available for computing the cetane index and they take into account the distillation temperature of the fuel (Van Garpen et al., 2004).

ASTM standard D 976 gives the following empirical equation for the cetane index:

Cetane Index $= 454.74 - 1641.416\,D + 774.74\,D^2 - 0.554\,T_{50} + 97.803[\log_{10}(T_{50})]^2$

Where (2.5)

D = fuel density at 15°C in g/ml.

T_{50} = the temperature corresponding to the 50% point on the distillation curve in degrees ^{0}C.

ASTM standard D 4737 gives the cetane index according to the following four-variable equation:

Cetane Index $= 45.2 + 0.0892(T_{10}N) + 0.131(T_{50}N) + 0.0523(T_{90}N) + 0.901B\,(T_{50}N) - 0.420B\,(T_{90}N) + 4.9x10\text{-}4(T_{10}N)^2 \text{-} 4.9x10\text{-}4(T_{90}N)^2 + 107B + 60\,B^2$ (2.6)

Where

$T_{10}N = T_{10} - 215$

$T_{50}N = T_{50} - 260$

$T_{90}N = T_{90} - 310$

When T_{10}, T_{50}, and T_{90} are temperatures at 10%, 50%, and 90% volume distilled in degrees C and $B = [\exp^{(-3\ 5DN)}] - 1$ when DN = density at 15°C (kg/liter) - 0.85

2.4.9 Carbon Residue of Petroleum Products

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

2.4.10 Specific Gravity (SG)

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, ρ, to a reference density, ρ_{ref}. The equation for the specific gravity (SG) is $SG = \rho/\rho_{ref}$. 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.

2.4.11 Acid Number

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

2.4.12 Iodine Value of Drying Oils and Fatty Acids

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

2.4.13 Low-Temperature Properties

The low-temperature properties of biodiesel and conventional petroleum diesel are extremely important. Unlike gasoline, petroleum diesel and biodiesel can freeze or gel as the temperature drops. If the fuel begins to gel, it can clog filters on dispensing equipment and may eventually become too thick to pump. Important low-temperature performance metrics for handling and blending of B100 are as follows (National renewable energy laboratory report 2008):

- **Cloud point;** The temperature at which small solid crystals are first visually observed as the fuel is cooled. Below the cloud point, these crystals might plug filters or could drop to the bottom of a storage tank. However, fuels can usually be pumped at temperatures below cloud point. ASTM D2500 gives the standard test procedure.
- **Pour point;** The temperature at which the fuel contains so many agglomerated crystals that it is essentially a gel and will no longer flow. Distributors and blenders use pour point as an indicator of whether the fuel can be pumped, even if it would not be suitable for use without heating or taking other steps.
- **Cold filter plugging point (CFPP);** This is the temperature under a standard set of test conditions, as defined in ASTM D6371, at which a fuel filter plugs. The CFPP test employs rapid cooling conditions. CFPP results more than 10°C below the cloud point should be viewed with suspicion, because they may not reflect the true low temperature operability limit. The test simulates the performance of an average or typical vehicle and is not protective of the most challenging fuel system designs from a low-temperature operability standpoint, which make up roughly one-third of heavy-duty vehicles or one-fifth of light-duty vehicles.
- **Low-temperature flow test (LTFT);** this test also reports a temperature under a standard set of conditions, defined in ASTM D4539, at which a fuel filter plugs. LTFT employs slow cooling at one degrees centigrade per hour (1°C/h) and simulates the most severe (and common) fuel system designs in North American heavy-duty trucks from the standpoint of low-temperature operability

2.5 EMPIRICAL APPROACH IN PREDICTING BIODIESEL PROPERTIES

Many of the properties are directly measured by chemical analysis, or are calculated from the ester composition in the fuel. Specifically, the kinematic viscosity, cetane number, and cloud point of the fuel are ester composition dependent. The total glycerin and free glycerin values can also be determined by compositional analysis. It is possible that the acid number and copper strip corrosion values may also be correlated with the detailed compositional analysis. The use of chemical composition and structure as the basis for estimating physical, thermodynamic and transport properties was first done by (Prausnitz et al., 1987). They showed how chemical structure can be used to compute properties for pure components. They also discussed mixing rules to estimate properties for mixtures.

2.5.1 Density

The density of hydrocarbons as a function of temperature is best estimated using an empirical equation, based upon corresponding states theory, called the modified Rackett equation (Prausnitz et al., 1987). This approach has been applied to fatty acids and to methyl esters of fatty acids (Janarthanan, et al., 1996) with good accuracy. A simpler method for estimating the density of methyl esters of fatty acid however is to use the empirical relation developed by Janarthanan, et al. (1996).

$$\rho_i = \alpha_i \mathrm{t} + b_i \qquad (2.7)$$

Where t is the temperature in °C and the component dependent empirical constants are reported in Table 2.4. The density of a mixture of these components can be estimated using a simple linear mixing rule, as shown in the equation below;

$$\rho_{mix} = \sum x_i \,(\alpha_i \mathrm{t} + b_i) \qquad (2.8)$$

Where x_i is the mass fraction

Table 2.4: Empirical constants used to estimate methyl ester density

Ester	Constant a	Constant b	Temperature Range, °C
Palmitate	-7.4608E-4	0.879094	26.7 - 98.9
Stearate	-6.9247E-4	0.877325	48.9 – 110
Oleate	-6.8563E-4	0.888357	26.7 – 110
Linoleate	-7.2226E-4	0.900981	37.8 – 110

Source Clements 1996

2.5.2 Viscosity

Viscosities of hydrocarbon mixtures, at a specified temperature, can be estimated from their densities and average molecular weights. Riazi and Al-Otaibi (2001) proposed a method as shown in the equation below to estimate viscosity of liquid hydrocarbons and petroleum mixtures at various temperatures from their refractive index (I).

$$1/\eta = A + B/I \qquad (2.9)$$

Where: A and B are constants specific for each compounds

I - is the refractive index

The primary parameters for viscosity estimation are esters composition and temperature. Viscosity can be estimated using values for the individual components, or based on measured viscosities for biodiesel from different feedstocks (Van Garpen et al., 2004). Janarthanan, et al. (1996) presented experimental data for a number of esters. They also tested a number of empirical expressions for representing the temperature dependence of liquid viscosity. The liquid viscosity for methyl palmitate, stearate and oleate follow the expression;

$$\ln \eta = A + B/T + C/T^2 \qquad (2.10)$$

And the viscosity of methyl linoleate is represented best by the expression,

$$\ln \eta = A + BT + C/T \qquad (2.11)$$

Where the empirical constants for A, B, C and T are empirical constants that depend on the material and are given in Table 2.5.

Table 2.5: Empirical constants for estimating methyl ester viscosity

Ester	Constant A	Constant B	Constant C	Temperature range ^{0}C
Palmitate	-17.7087421	0.0194820	4095.98793	26.7 - 98.9
Stearate	-12.2620883	0.0109932	3310.50996	48.9 – 110
Oleate	-9.6133497	0.0075371	2739.10625	26.7 – 110
Linoleate	-0.5705778	-680.80715	396575.647	37.8 – 100

Source Clements 1996

The estimation of the viscosity of mixtures is one of the most difficult problems in the entire domain of property estimation. A number of expressions have been suggested. Clements 1996 suggested the following expressions;

$$\ln \eta_{mix} = \sum x_i f(\eta) \qquad (2.12)$$

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

The best equation used to estimate the viscosity of mixture is;

$$\ln \eta_{mix} = \sum x_i (\ln \eta)^{1/3} \qquad (2.13)$$

Allen et al., (1998) suggested the expressions below (equations) for estimating viscosity of individual saturated fatty acid methyl ester (FAME) and the mixture, at 40°C respectively;

$$\eta = 1.05 \times 10^{-4} M^2 - 0.024M + 2.15 \qquad (2.14)$$

$$\ln \eta = \sum y_i \ln \eta_i \qquad (2.15)$$

Where y_i is the mass fraction and M is the intrinsic molecular mass.

2.5.3 Cetane Number

The cetane number of a diesel fuel is a measure of its ignition quality under compression ignition conditions. This property can easily be estimated by simply using the Kay's rule mixing equation (Clements 1996);

$$P_{mix} = \sum x_i CN_i \qquad (2.16)$$

Where CN_i is the pure component cetane number as given in Table (2.6)

2.5.4 Heating Value

The fuel heating value is important as a measure of the potential power to be derived from combustion. The components in biodiesel have nearly identical heating values. Similarly, the heating value can be estimated by using the Kay's rule mixing equation of the form below;

$$H_{mix} = \sum x_i H_i \qquad (2.17)$$

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

Table 2.6: Major pure component property data for fatty acid methyl esters

Ester	Density, g/cc @15.5 ^{0}C	Viscosity @ 40 ^{0}C, cSt	Cetane number	Heating value, Mj/Kg	Melting value, 0C
Palmitate	0.867	4.37	74	39.4	30.6
Stearate	0.867	5.79	75	40.1	39.1
Oleate	0.878	4.47	55	39.9	-19.8
Linoleate	0.89	3.68	33	39.7	-35
Source	Jonarthanan et al., 1996	Jonarthanan et al., 1996	Bagby & Freedman, 1989	Bagby & Freedman, 1989	Toh & Clements 1988

2.6 OIL EXTRACTION FROM VEGETABLES

The seeds for oil extraction should always be dried to the right moisture content; reducing their moisture content to approximately 10 to 11 percent by weight is normally preferred. Since most oil bearing seeds have an outer kernel, they must be decorticated to remove the outer shell. The seeds must be cleaned of foreign materials such as sticks, stems, pods, tramp metal, sand, and dirt. The seeds are then weighed because the final oil yield is reported as percentage by weight of the seeds. Oil can be extracted from plant seeds by either of the following methods;

2.6.1 Mechanical oil Extraction

Historically, oils have been extracted by wrapping seeds in cloth, and then using devices operated by stones and levers to exert pressure on them. An improved form of mechanical device involves the use of hydraulically operated rams: a simple, hand-operated cylinder pump is used to press flat plates or hollow cages attached to the hydraulic ram against a fixed-position ram. This type of press developed into a motorized hydraulic pump system that pressed the seed bag and then released a press cake. The next improvement in extracting oil was the screw press or expeller. Screw presses use an electric motor to rotate a heavy iron shaft, which has flights, or worms built into it to push the seeds through a narrow opening. The pressure of forcing the seed mass through this slot releases part of the oil, which comes out through tiny slits in a metal barrel fitted around the rotating shaft. Expellers have a continuous flow of seed through the machine in contrast to the hydraulic system, which uses small, individual packages or batches of seed. To release as much oil as possible, the seeds must be dried to rather low moisture content. The major disadvantages of screw press or expeller is overheating of the meal which affects the color of the oil and leave too much of the high value oil in the seed cakes.

2.6.2 Solvent oil Extraction

The seeds are normally prepared for solvent extraction by the following operational principals: cracking, de-hulling/hull removal, conditioning, and flaking. After cracking the seeds are conditioned (i. e., make them pliable and keep them hydrated). Conditioning is necessary to permit the flaking of the chips and to prevent them being broken into smaller particles. Flaking allows the oil cells to be exposed and the oil to be more easily extracted.

The extraction process consists of "washing" the oil from the flakes with hexane solvent in a countercurrent extractor or any other solvent that boil fairly at low temperatures. Then the solvent is evaporated (i.e., desolventised) from both the solvent/oil mixture (micella) and the solvent-laden, defatted flakes. The oil is desolventized by exposing the solvent/oil mixture to steam (contact and non-contact). Then the solvent is condensed, separated from the steam condensate, and reused. Residual hexane not condensed is removed with mineral oil scrubbers. The desolventized oil, called "crude" oil, is then refined. Solvent extraction recovers almost all the oil, leaving only one percent or less oil in the flakes.

In configuring the solvent extraction plant, pre-pressing may be involved in which case seeds are lightly pressed leaving about 14% to 18% oil in pressed cake. Solvent extraction will further process these cakes and leave only 1% oil or less in the final cake (meal). This method results in higher capacity; Lower power consumption, lower wear and tear / maintenance and high extract efficiency. Thus it could be used as complement equipment to extract the oil remained in cakes.

2.7 BIODIESEL PRODUCTION

Research has emphasized that the various problems associated with using straight vegetable oils as fuel in compression ignition (C.I.) engines are mainly caused by their high viscosity (Agarwal (1998); Sinha and Misra (1997); Roger and Jaiduk (1985). The high viscosity is due to the large molecular mass and chemical structure of vegetable oils. The following problems have been identified to occur when using straight vegetable oils (SVO) in diesel engines (Adam 2002);

i. Cooking and trumpet formation on the injectors to such an extent that fuel atomization does not occur properly or is even prevented as a result of plugged orifices.
ii. Carbon deposits.
iii. Oil ring sticking.

iv. Thickening and gelling of the lubricating oil as a result of contamination by vegetable oils.
v. Lubricating problems.
vi. High viscosity.
vii. Lower volatilities content which causes formation of deposits in engines due to incomplete combustion and incorrect vaporization characteristics.

Therefore, a reduction in viscosity is of prime importance to make vegetable oils a suitable alternative fuel for diesel engines. The problem of high viscosity of vegetable oils has been tackled by the following method;

- Pyrolysis/cracking.
- Dilution or blending with other fuels.
- Micro-emulsification.
- Trans-esterification.

2.7.1 Pyrolysis

This refers to a chemical change caused by the application of thermal energy in the absence of air or nitrogen. The liquid fractions of the thermally decomposed vegetable oil are likely to approach diesel fuels. Khotoliya et al., (2007) found out that pyrolyzate had lower viscosity, flash point and pour point than diesel fuel and equivalent calorific values. The cetane number of the pyrolyzate was lower.

2.7.2 Micro-emulsification

The formation of microemulsions (co-solvency) is one of the methods for solving the problem of vegetable oil viscosity. Microemulsions are defined as transparent, thermodynamically stable colloidal dispersions in which the diameter of the dispersed-phase particles is less than one-fourth the wavelength of visible light. Microemulsion-based fuels are sometimes also termed "hybrid fuels," although blends of conventional diesel fuel with vegetable oils have also been called hybrid fuels (Georing et al., 1982).
The components of microemulsions can be conventional DF, vegetable oil, an alcohol, a surfactant and a cetane improver. Microemulsions are classified as non-ionic or ionic, depending on the surfactant present. Microemulsions containing for example, a basic

nitrogen compound are termed ionic while those consisting for example, only of a vegetable oil, aqueous ethanol, and another alcohol, such as 1-butanol, are termed non-ionic. Non-ionic microemulsions are often referred to as detergentless microemulsions, indicating the absence of a surfactant. Viscosity-lowering additives were usually with C_{1-3} alcohols length while longer-chain alcohols and alkylamines served as surfactants. Faletti et al.,(1984) performed engine tests using micro-emulsified fuel and found out that these fuels burned faster with higher levels of premixed burning due to longer ignition delays and lower levels of diffusion flame burning than DF, resulting in higher brake thermal efficiencies, cylinder pressures, and rates of pressure rise. He further noted that NO_x and CO emissions increased with these fuels, while smoke and unburned hydrocarbons decreased.

2.7.3 Dilutions

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

However mixed results have been achieved with this technology, engine problems similar to those found with neat vegetable oils as fuels were observed

2.7.4 Trans-esterification

Transesterification is the general term used to describe the important class of organic reactions where an ester is transformed into another through interchange of the alkoxy moiety. When the original ester is reacted with an alcohol, the trans-esterification process is called alcoholysis (Ulf et al., 1998). In biodiesel industry trans-esterification refers to the reversible reaction of a fat or oil (both of which are composed of triglycerides and free fatty acids) with an alcohol in the presence of a catalyst to form fatty acid alkyl esters and glycerol. The catalyst may be acidic, basic (KOH, NaOH, $NaOCH_3$, etc.), or enzymatic (lipase) (Van Gerpen et al., 2004).

All vegetable oils and animal fats consist primarily of triglyceride molecules such as that shown schematically below.

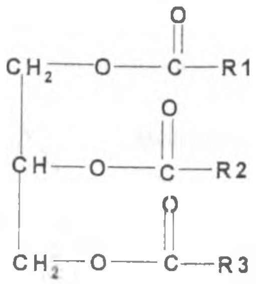
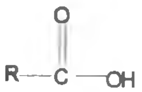


Fig. 2.1: Triglyceride

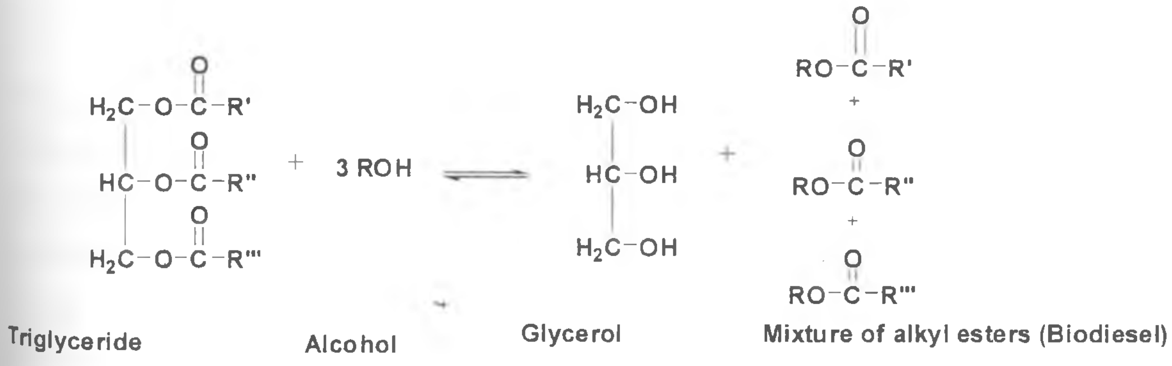
R_1, R_2, and R_3 represent the hydrocarbon chains of the fatty acyl groups of the triglyceride. In their free form, fatty acids have the configuration shown below where R is a hydrocarbon chain > 10 carbon atoms.



$R-C(=O)-OH$

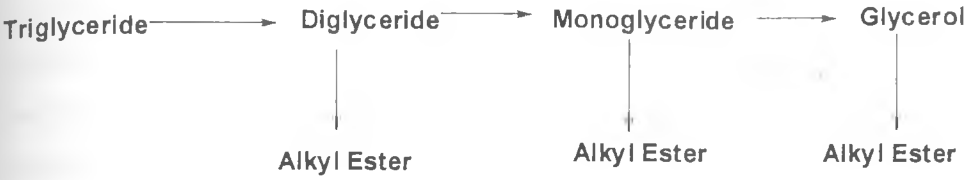
Fig. 2.2: Fatty Acid

Scheme 2.1 below shows the general catalyst aided trans-esterification process.



Scheme 2.1: Catalyst aided trans-esterification process

The mixture of alkyl esters produced by this reaction is referred to as **biodiesel.** Any short chain alcohol can be used for trans-esterification. The fuel properties of biodiesel are determined by the amounts of each fatty acid in the feedstock used to produce the esters. The basic chemical process that occurs during the trans-esterification reaction is indicated in scheme 2.2 below



Scheme 2.2: Chemical process that occur during trans-esterification reaction

The triglycerides are converted to diglycerides, which in turn are converted to monoglycerides, and then to glycerol. Each step produces a molecule of alkyl ester of a fatty acid. The trans-esterification is an equilibrium reaction as shown in scheme 2.3 below. In order to achieve a high yield of the ester the alcohol has to be used in excess to push the reaction to the right.

$$RO-\overset{\overset{O}{||}}{C}-R' + R''OH \xrightleftharpoons{\text{Catalyst}} R''O-\overset{\overset{O}{||}}{C}-R' + ROH$$

Scheme 2.3: Equilibrium representation of trans-esterification reaction

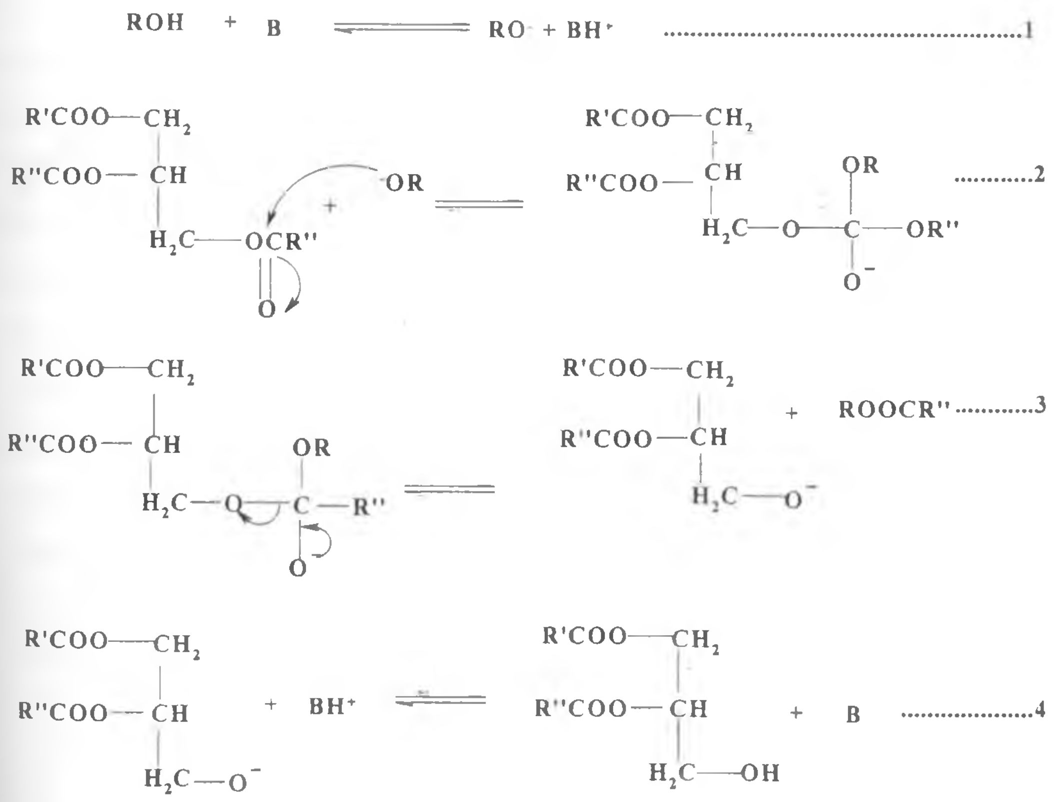
2.7.5 Trans-esterification without using catalysts

The trans-esterification reaction can also take place without the use of a catalyst. This eliminates the need for the water washing step. However, high temperatures and large excesses of methanol are required (Saka and Kusdiana 1999, 2001; Saka et al,, 2004; Dasari et al., 2003 and Diasakou et al., 1998). The reaction is performed under conditions in which the alcohol is in a supercritical state. Vivek and Giridhar (2007) synthesized biodiesel from plant oils using supercritical methanol and ethanol without using a catalyst. Chincholkar et al., (2005) prepared biodiesel in various supercritical alcohol treatments with methanol, ethanol, 1-propanol, 1-butanol, or 1-octanol to study trans-esterification of rapeseed oil and alkyl esterification of fatty acid at temperatures of 300 and 350°C. The results obtained showed that in trans-esterification the reactivity was greatly correlated to the alcohol; the longer the alkyl chain of alcohol, the longer was the reaction treatment. Hawash et al., (2009) studied the trans-esterification of Jatropha oil using supercritical methanol in absence of a catalyst. The results revealed that over 98% of methyl esters were obtained at a temperature of 350°C and 43:1 molar ratio of methanol to oil within four minutes. However when a co-solvent was incorporated the reaction system decreased the operational temperature, pressures and increased the conversion efficiency of methanol (Jian-Zhong et al., 2008). They reported that under the supercritical conditions, the maximum methyl ester yield exceeded 98% when the molar ratio of methanol to oil was 42:1 and the reaction temperature ranged from 260°C to 350°C. Upon using CO_2 or hexane as co-solvent in the reaction system at 300°C, there was a significant increase in the methyl esters yield. With the optimal reaction temperature of 160°C and methanol to oil ratio of 24:1, a 98% yield of methyl esters was observed in 20 min.

2.7.6 Base catalyzed transesterification

The base-catalyzed transesterification of vegetable oils proceeds faster than acid or enzyme catalyzed transesterification. In addition alkaline catalysts are less corrosive than acidic compounds hence industrial processes usually favor base catalysts, such as alkaline metal alkoxides and hydroxides as well as sodium or potassium carbonates. Alkaline metal alkoxides (as CH_3ONa for the methanolysis) are the most active catalysts, since they give very high yields in short reaction times even if they are applied at low molar concentrations. However, they require the absence of water which makes them inappropriate for typical industrial processes. Alkaline metal hydroxides (KOH and NaOH) are cheaper than metal alkoxides, but less active. Nevertheless, they are a good alternative since they can give the same high conversions of vegetable oils just but at a higher catalyst concentration. However, even if a water-free alcohol/oil mixture is used, some water is produced in the system by the reaction of the hydroxide with the alcohol. The presence of water gives rise to hydrolysis of some of the produced ester, with consequent soap formation. This undesirable saponification reaction reduces the ester yields and makes it considerably difficult for the recovery of the glycerol due to the formation of emulsions. Potassium carbonate gives high yields of fatty acid alkyl esters and reduces the possibilities of soap formation because bicarbonate are formed instead of water which does not hydrolyze the esters.

The mechanism of the base-catalyzed transesterification of vegetable oils is shown in Scheme 2.4 below. The first step (Eq. 1) is the reaction of the base with the alcohol, producing an alkoxide and the protonated catalyst. The nucleophilic attack of the alkoxide at the carbonyl group of the triglyceride generates a tetrahedral intermediate (Eq. 2), from which the alkyl ester and the corresponding anion of the diglyceride are formed (Eq. 3). The latter deprotonates the catalyst, thus regenerating the active species (Eq. 4), which is now able to react with a second molecule of the alcohol, starting another catalytic cycle. Diglycerides and monoglycerides are converted by the same mechanism to a mixture of alkyl esters and glycerol (Schuchardt et al., 1998).



Scheme 2.4: Base catalyzed transesterification process

Drawbacks of base catalyzed transesterification;

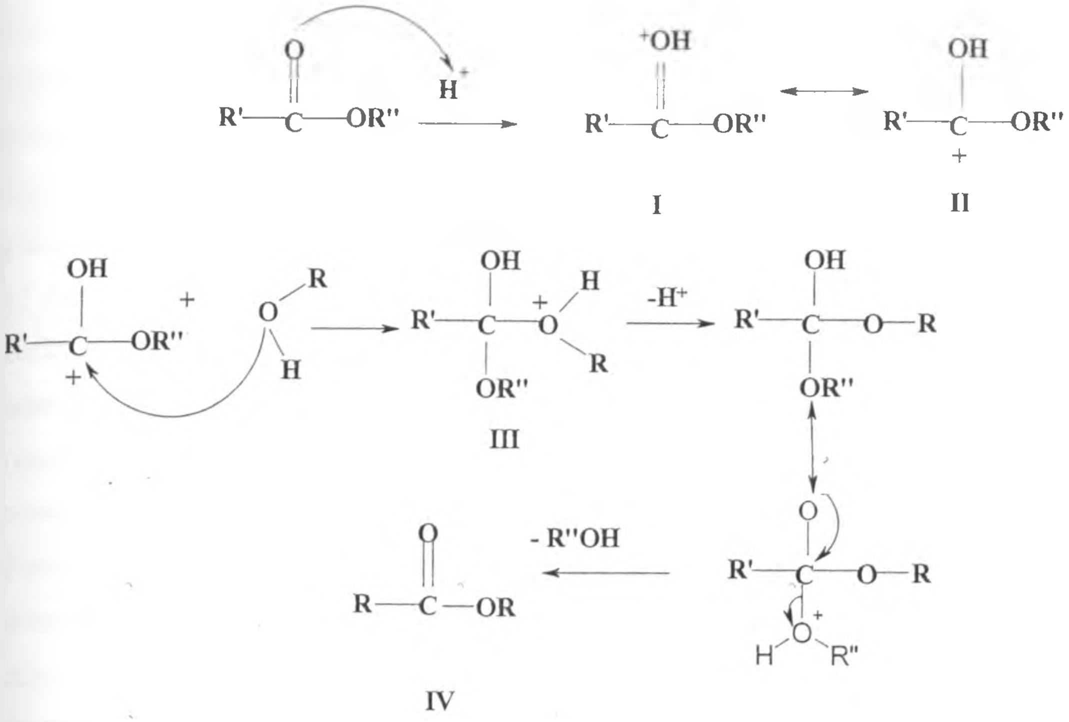
Although chemical transesterification using an alkali catalyzed process gives high conversion levels of triglycerides to their corresponding alkyl esters in short reaction times, the reaction has several drawbacks (Devanesan et al., 2007; Hideki et al., 2001; Mamoru et al., 2001);

- Its energy intensive.
- Recovery of glycerol is difficult.
- The alkaline catalyst has to be removed from the product.
- Alkaline wastewater requires treatment.
- Free fatty acids and water interfere with the reaction and leads to soap formation.

2.7.7 Acid catalyzed transesterification

The transesterification process is catalyzed by Bronsted acids, preferably by sulfonic and sulfuric acids. These catalysts give very high yields in alkyl esters, but the reactions are slow, requiring, typically, temperatures above 100°C and more than 3 h to reach complete conversion hence proving to be uneconomical (Ulf et al., 1998).

The mechanism of the acid-catalyzed transesterification of vegetable oils is shown in Scheme 2.5 for a monoglyceride. However, it can be extended to di- and triglycerides. The protonation of the carbonyl group of the ester leads to the carbocation II which, after a nucleophilic attack of the alcohol, produces the tetrahedral intermediate III, which eliminates glycerol to form the new ester IV, and to regenerate the catalyst H^+. According to this mechanism, carboxylic acids can be formed by reaction of the carbocation II with water present in the reaction mixture. This automatically suggests that an acid-catalyzed transesterification should be carried out in the absence of water, in order to avoid the competitive formation of carboxylic acids which reduce the yields of alkyl esters.



Where

R'' – Glyceride, R' – Carbon chain of the fatty acid, R – Alkyl group of the alcohol

Scheme 2.5: Acid catalyzed transesterification.

2.7.8 Enzymatic catalyzed transesterification by lipase

Due to their ready availability and the ease with which they can be handled, hydrolytic enzymes have been widely applied in organic synthesis. They do not require any coenzymes, are reasonably stable, and often tolerate organic solvents. Their potential for regioselective and especially for enantioselective synthesis makes them valuable tools. Enzyme catalyzed transesterification overcomes the problems posed by alkali catalyzed process in particular the byproduct glycerol, can easily be recovered without complex processing and also the free fatty acids that may be contained in oils and fats can be completely converted to alkyl esters without forming contaminants like soap (Mamoru et al., 2001). Lipase is isolated primarily from four major microorganisms: *Candida antarctica*, *Rhizopus oryzae*, *Mucor miehei*, and *Pseudomonas cepacia* (George and Terry 2007). In order for the lipase to maintain its activity for repeated reactions (stability and reusability), either the enzyme or the entire cell must be immobilized (Devanesan et al., 2007, Hideki et al., 2001, Mamoru et al., 2001).

One major problem of lipase-catalyzed transesterification is that glycerol competitively inhibits lipase activity by blocking the active sites. However, use of acyl acceptors has proved to alleviate this problem because they produce more useful and less detrimental byproducts. An acyl acceptor functions as the new attachment of fatty acid chains, in place of glycerol. Du et al (2004) used methyl acetate as an acyl acceptor, the byproduct of this reaction is triacetylglycerol, which has no negative effects on the reaction, can easily be separated from the biodiesel product and has a higher value than glycerol for later use. Modi et al., (2007) used ethyl acetate and acyl acceptor. The use of ethyl acetate results in biodiesel composed of ethyl esters. The extra carbon in the ester increases the cetane number, as well as the heat content. This leads to lower cloud points, improved flash and combustion points, which improve engine starting in the cold, one of the current downfalls of biodiesel produced by methanol transesterification. Use of methyl acetate or ethyl acetate as substrate would allow lipase to be used repeatedly significantly reducing the cost of production.

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

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

Solvent use results in high yields obtained by relatively low amounts of enzyme. Despite the advantages that are associated with this technique, large scale production and industrial application is still ineffective because of the high cost of lipase.

2.8 STEPS IN BASE CATALYZED PRODUCTION OF BIODIESEL BY TRANSESTERIFICATION

2.8.1Mixing of alcohol and catalyst

The catalyst typically sodium hydroxide (NaOH) or potassium hydroxide (KOH) is dissolved in the alcohol e.g. methanol or ethanol using a standard agitator or mixer to obtain the respective methoxide or ethoxide. The amount of KOH or NaOH is normally reached based on the amount needed to neutralize the free fatty acids in the oil as determined by titration.

2.8.2 Reaction

The predetermined volume of oil is heated to temperatures just below the boiling point of the alcohol in a reactor. The alcohol/catalyst mix is charged into a closed reaction vessel containing the oil under stirring at a predetermined speed. Vigorous mixing at the beginning of the reaction improves reaction rates. The temperature of the reaction mix is kept just below the boiling point of the alcohol to speed up the trans-esterification reaction for a given reaction time. Near the end of the reaction mixing, the speed must be reduced to improve separation of glycerin and the reaction would proceed faster in the top layer. Excess alcohol is normally used to ensure total conversion of the fat or oil to its esters.

2.8.3 Separation

Once the trans-esterification reaction is completed, the mixture is transferred into a separating funnel to achieve separation of the two major products, glycerin and biodiesel. The glycerin phase is much denser than biodiesel phase and the two can be gravity separated with glycerin simply drawn off the bottom of the settling vessel. Due to the low solubility of glycerol in the esters, this separation generally occurs quickly.

2.8.4 Alcohol Removal

After separation from the glycerol, the alkyl esters enter a neutralization step and then pass through an alcohol stripper, usually a vacuum flash process or a falling film evaporator, before water washing. Acid is added to the biodiesel to neutralize any residual catalyst and to split any soap that may have formed during the reaction. Soaps will react with the acid to form water soluble salts and free fatty acids. The salts will be removed during the water washing step, and the free fatty acids will stay in the biodiesel. The alcohol is recovered using distillation equipment and is re-used. Care must be taken to ensure no water accumulates in the recovered alcohol stream.

2.8.5 Glycerin Neutralization

The glycerin by-product contains unused catalyst and soaps that are neutralized with an acid and sent to storage as crude glycerin. Water and alcohol are removed to produce 80-88% pure glycerin. Purification of the glycerine is normally done using sorbent materials and properties monitored using spectroscopic methods such as NMR and IR spectroscopy.

2.8.6 Alkyl Ester (Biodiesel) Wash

Once separated from the glycerin, the biodiesel is purified by washing gently with warm water. The water washing step is intended to remove any remaining catalyst, soap, salts, methanol, or free glycerol from the biodiesel. Neutralization before washing reduces the water required and minimizes the potential for emulsions to form when the wash water is added to the biodiesel.

2.8.7 Methods of biodiesel washing;

Keith (2007) gave a brief description of the main washing methods;

2.8.7.1 Mist washing

The process involves a super fine spray of water made above the wash tank. This sends mist of water droplets down onto the surface of the biodiesel, which sinks down the biodiesel washing, creating zero agitation. However it's slow and uses a lot of water which cannot be reused. It can also mask poor biodiesel quality as agitation is minimal, a process that can promote emulsification of the biodiesel and indicator of poor biodiesel.

2.8.7.2 Bubbling Washing

This method utilizes a small air pump usually an aquarium aerator pump with a bubble stone. Water is added to the biodiesel in the wash tank (usually a quarter to half as much water as biodiesel), the water sinks to the bottom, the bubble stone is thrown in and also to the bottom. The pump is then switched on air bubbles rise through the water and into the biodiesel carrying a film of water around them which washed the biodiesel around the bubble. On reaching the surface the air bubble breaks and the water sinks back down washing the oil again. Its advantage is its simple and easy to use; however it is time consuming and can mask an incomplete reaction. Its other major disadvantage is the tendency to cause fuel oxidation and polymerization.

2.8.7.3 Stir Washing

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

(Additional information on biodiesel washing techniques was obtained from http://www.make-biodiesel.org/washingtec/ 'How to make biodiesel; Techniques for Water Washing Biodiesel' *accessed on 3rd May 2009 at 7:30pm)*

2.8.8 Biodiesel Drying

2.8.8.1 Vacuum driers

The biodiesel is subjected to a highly reduced pressure. This allows the water in the biodiesel to evaporate at a low temperature. Vacuum driers can be either batch or continuous in which the biodiesel is dried in batches or continuously, respectively.

2.8.8.2 Falling film evaporator

Here a thin film of biodiesel runs down a heated surface of the evaporator. The direct contact with the heated wall evaporates the water rapidly. Falling film evaporators allow for rather high heating and evaporation rates. Caution is however taken to avoid high temperatures that lead to darkening of the biodiesel, which is a sign of polymerization of the poly-unsaturated alkyl esters.

2.8.8.3 Bubble drying

Uses same principle as bubble washing with the exception that there is no water, air is bubbled through the biodiesel enhancing the evaporation of water in the biodiesel. It has the same disadvantages of oxidizing and polymerization as occurs in bubble washing.

2.8.8.4 Evaporation

Biodiesel when left in the open for a day or longer clears on its own. The process can be accelerated by heating the biodiesel to 100°C any water present in the biodiesel will evaporate.

2.9 BIODIESEL QUALITY TESTING

Keith (2007) proposed the following tests as quality checks where standard tests are not available;

2.9.1 Wash tests

150 ml of unwashed biodiesel is mixed with 150 ml of water in a half a liter glass jar, the lid is screwed tightly and the jar shaken vigorously for ten or more seconds until a homogeneous mixture is formed. The mixture is then left to settle. For a good quality biodiesel the biodiesel is supposed to separate from the water in half an hour or less, with amber biodiesel on top and milky water below. If it turns into something like mayonnaise and won't separate or separates slowly with a white creamy layer sand-witched between water and biodiesel, the fuel is of poor quality which may be due to;

- Use of too much catalyst and made excess soap.
- Incomplete reaction with poor conversion which leaves half-processed monoglycerides and diglycerides, fuel contaminants that also acts as emulsifiers.

- Both; too much catalyst as well as poor conversion.

Poor conversion is much more likely to cause a severe emulsion that does not separate than excess soap formation.

2.9.2 Reprocessing Test

The reprocessing test is a simple check that tells you if the process went far enough, with good completion of the reaction and good conversion. If not, there will still be unconverted and partly converted material in the fuel, such as diglycerides and monoglycerides, fuel contaminants that can emulsify the fuel when you wash it so that it won't separate from the wash-water. A small amount of the finished biodiesel is reprocessed again as if it were neat vegetable oil. If more glycerin drops out then the fuel is not of good quality.

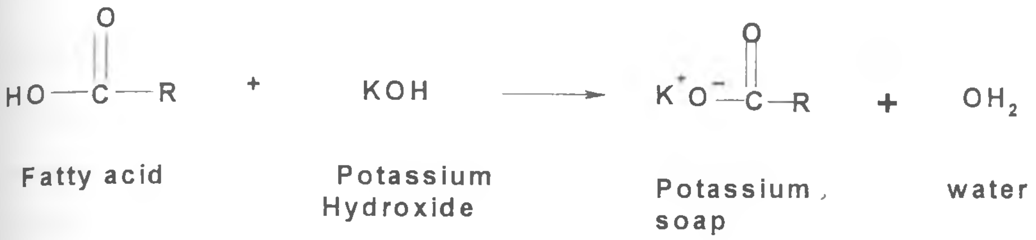
2.9.3 Methanol Test

Take exactly 25 ml of biodiesel and dissolve it in exactly 225 ml of methanol in a measuring glass. The biodiesel should be fully soluble in methanol, forming a clear bright phase. If not there is contamination of the biodiesel. This method gives indication of impurities in the biodiesel. It is valid only for biodiesel made from vegetable oils and animal fats and is not valid for biodiesel made from oils with a very wide fatty acid pattern such as fish oils.

2.10 VARIABLES AFFECTING TRANSESTERIFICATION REACTION

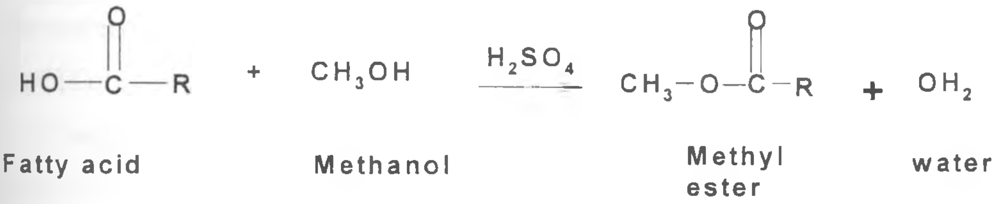
2.10.1 Effect of free fatty acid and moisture

To carry the base catalyzed reaction to completion, a free fatty acid (FFA) value lower than 3% is needed. If the oil or fat contains sufficient amounts of FFA, special processes are required. Used cooking oils typically contain 2-7% FFAs and animal fats contain from 5-30% FFAs. Some very low quality feedstocks, such as trap grease, can approach 100% FFAs. When an alkali catalyst is added to such feedstocks, the free fatty acids react with the catalyst to form soap and water as shown in the reaction scheme 2.6 below; (Jon Van Gerpen, 2005).



Scheme 2.6: Reaction between free fatty acid and potassium hydroxide

The soap created during the reaction is either removed with the glycerol or is washed out during the water wash. When the FFA level is above 5%, the soap formed inhibits separation of the glycerol from the methyl esters, causes an increase in viscosity of the biodiesel, reduces catalytic efficiency and contributes to emulsion formation during the water wash. For these cases, an acid catalyst such as sulfuric acid can be used to esterify the FFAs to methyl esters as shown in reaction scheme 2.7 below; (Jon Van Gerpen, 2005).



Scheme 2.7: Esterification of free fatty acids using acid catalyst

This process can be used as a pretreatment to convert the FFAs to methyl esters and thereby reduce the FFA level. Then, the low FFA pretreated oil can be transesterified with an alkali catalyst to convert the triglycerides to methyl esters (Jon Van Gerpen, 2005). As shown in the reaction, water is formed and, if it accumulates, it can stop the reaction well before completion. Any water presence or addition to the entire system quenches a proportional amount of the catalyst. One part of water can quench up 4.67 parts of catalyst (Charles et al 1996). This calls for use of more base catalyst for compensation hence making the process to be uneconomical. Therefore for alkali catalyzed transesterification, the oil and alcohol must be substantially anhydrous.

2.10.2 Catalyst type and concentration

Catalysts used for the transesterification of triglycerides are classified as alkali, acid, enzyme or heterogeneous catalysts, among which alkali catalysts like sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide are more effective. If the oil has high free fatty acid content and more water, acid catalyzed transesterification is suitable. The acids could be sulfuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid. Ma et al., (1998) studied methanolysis of beef tallow with NaOH and NaOMe catalysts and after comparing the results of the two catalysts, NaOH was significantly better than NaOMe. They all reached their maximum activity at 0.3 and 0.5% w/w of the beef tallow respectively. However, NaOMe has been found to be more effective presumably because a small amount of water is produced upon mixing NaOH with methanol. As a catalyst in the process of alkaline methanolysis, mostly sodium hydroxide or potassium hydroxide have been used, both in concentration from 0.4 to 2% w/w of oil. Basic alkaline-earth metal compounds have been used in the transesterification processes but still they exhibit low catalytic activity as compared to NaOH or KOH.

Although chemical transesterification using an alkaline catalysis process gives high conversion levels of triglycerides to their corresponding methyl esters in short reaction times, the reaction has several shortcomings: it is energy intensive, recovery of glycerol is difficult, the acidic or alkaline catalyst has to be removed from the product, alkaline waste water require treatment, and free fatty acid and water interfere the reaction (Devanesan et al., 2007). The above drawbacks can be overcome using enzymatic catalysts like lipases which are able to effectively catalyze the transesterification of triglycerides in either aqueous or non-aqueous systems (Fuduka et al., 2001). In particular, the by-products, glycerol can be easily removed without any complex process, and also that free fatty acids contained in waste oils and fats can be completely converted to alkyl esters. On the other hand, in general the production cost of a lipase catalyst is significantly greater than that of an alkaline one

2.10.3 Molar ratio of alcohol to oil

The stoichiometric ratio for transesterification requires 3 moles of alcohol and 1 mole of triglyceride to yield 3 moles of fatty acid alkyl esters and 1 mole of glycerol. Since transesterification is an equilibrium reaction large excess of alcohol is required to shift the equilibrium to the proposed product, methyl ester. Higher molar ratios result in greater ester conversion in a shorter time. Freedman et al., (1984) studied the effect of molar ratios (from 1:1 to 6:1) on ester conversion with vegetable oils. Soya bean sunflower, peanut and cotton seed oils all behaved in the same way, with the highest conversion being achieved at a 6:1 molar ratio. Anh and Tan (2008) also confirmed the dependence of biodiesel yield on methanol/oil ratio. Their results showed that as the ratio increased from 5:1 to 8:1 conversion increased the from 50% for the ratio of 5:1 to 64% for the ratio of 8:1. However the high molar ratio of alcohol to vegetable oil interferes with the separation of glycerin because there is an increase in its solubility (Meher et al., 2004; Anh and Tan 2008). When glycerin remains in solution, it helps drive the equilibrium back to the left, lowering the yield of alkyl esters since transesterification is an equilibrium dependent process.

2.10.4 Effect of reaction time

The conversion rate increases with reaction time. Freedman et al., (1984) transesterified peanut, cotton-seed, sunflower and soybean oil under the following conditions; methanol/oil molar ratio 6:1, 0.5% sodium methoxide catalyst and 60 ^{0}C. They observed an approximate yield of 80% after 1 min for soybean and sunflower oils. After 1 h, the conversion was almost the same for all four oils (93-98%). Ma F et al., (1998) studied the effect of reaction time on transesterification of beef tallow with methanol. The reaction was very slow during the first minute which they said was due to mixing and dispersion of methanol into beef tallow. From one to 5 min, the reaction proceeded very fast. The production of beef tallow methyl esters reached the maximum value at about 15 min.

To achieve reaction in shorter times, non conventional heating methods can be employed. Nezihe and Aysegul (2007) performed transesterification of cotton seed by microwave irradiation in the presence of methanol and potassium hydroxide (KOH). To compare the heating systems conventional heating was also employed in transesterification. As a result, 7 min reaction time, 333 K temperature and 1.5% catalyst–oil ratio were obtained as optimum reaction parameters for microwave heating. Similar results were found out for conventional heating but 30 min of reaction time. Saifuddin and Chua (2004) reported similar results. During their study they noted that while the conventional process required 75 min, the microwave assisted process only required 4 min to complete the transesterification reaction. The use of microwave-assisted transesterification process contributes to dramatic save of time. Hence, microwave irradiation accelerates the chemical reaction and high product yields are achieved within a short time. Shorter reaction times with high yields of biodiesel can also be achieved when transesterification is carried out in supercritical conditions and use of co-solvents (Vivek and Giridhar, 2007; Hawash et al., 2009 and Zhou et al., 2003).

2.10.5 Effect of temperature

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

Anh and Tan (2008) studied the effect of temperature on the conversion of waste cooking oil to biodiesel at the methanol/oil ratio of 8:1 in the presence of 0.75 wt% KOH. They observed that by increasing the temperatures from 30°C to 50°C, the conversion increased by 10–13%. However, when the temperature was increased up to 70°C, a slight reduction in the conversion was observed. This is because high temperature enhances both transesterification and saponification reactions.

2.10.6 Mixing intensity

Mixing is very important in the transesterification reaction, as oils or fats are immiscible with sodium hydroxide-methanol solution. Once the two phases are mixed and the reaction is started, stirring is no longer needed (Meher et al., 2004). Ma et al., (1998) studied the effect of mixing on transesterification of beef tallow. No reaction was observed without mixing and when NaOH/MeOH mixture was added to the melted beef tallow in the reactor while stirring, stirring speed was insignificant. Reaction time was the controlling factor in determining the yield of methyl esters.

2.10.7 Effect of using organic cosolvents

Meher et al., (2004) reported that the methoxide base catalyzed methanolysis of soybean oil at 40°C (methanol-oil molar ratio 6:1) to form methyl esters proceeds approximately more slowly than butanolysis at 30°C. This is interpreted to be the result of a two phase reaction in which methanolysis occurs only in the methanol phase. Low oil concentration in methanol causes the slow reaction rate; a slow dissolving rate of the oil in methanol causes an initiation period. Intermediate mono- and di-glycerides preferentially remain in the methanol, and react further, thus explaining the deviation from second order kinetics. In order to conduct the reaction in a single phase, the use of cosolvents like tetrahydrofuran (THF), 1,4- dioxane and diethyl ether was studied. At the 6:1 methanol-oil molar ratio the addition of 1.25 volume of tetrahydrofuran per volume of methanol produced an oil dominant one phase system in which the rate of methanolysis increased dramatically and occurred as fast as butanolysis. In particular, THF is chosen because its boiling point of 67°C is only two degrees higher than that of methanol. Therefore at the end of the reaction the unreacted methanol and THF can be co-distilled and recycled (Boocock et al., 1996). Similar results were again reported by Boocock et al., (1998), they carried out transesterification of soybean oil using THF with methanol at different concentrations of sodium hydroxide. The ester contents after one minute for 1.1%, 1.3%, 1.4% and 2.0% sodium hydroxide were 82.5%, 85%, 87% and 96.2%, respectively.

2.11 ANALYTICAL MONITORING OF TRANSESTERIFICATION REACTION

Various analytical methods can be employed to analyze mixtures containing fatty acid esters and mono-, di-, and tri-glycerides obtained by the transesterification of vegetable oils;

2.11.1 Gas chromatographic method (GC)

A gas chromatographic method for the simultaneous determination of glycerol, mono-, di-, and tri-glycerides in vegetable oil methyl esters has been developed, (Meher et al., 2004). In principle, glycerol, mono-, di-, and tri-glycerides can be analyzed on highly inert columns coated with polar stationary phase without derivatization. The inertness of the column, required to obtain good peaks and satisfactory recovery, cannot be easily maintained in routine analysis. Trimethylsilylation of the free hydroxyl groups of glycerol, mono- and di-glycerides, however, ensures excellent peak shapes, good recoveries and low detection limits and enormously improves the efficiency of the procedure, (Meher et al., 2004). For complete silylation of glycerol and partial glycerides, the conditions of the derivatization reaction have to be controlled carefully (Meher et al., 2004).

Most reports on the use of GC for biodiesel analysis employ flame-ionization detectors (FID), although the use of mass spectrometric detector (MSD) would eliminate any ambiguities about the nature of the eluting materials since mass spectra is unique to individual compounds would be obtained (Knothe, 2001).

2.11.2 High performance liquid chromatography method

A general advantage of High performance liquid chromatography (HPLC) compared to gas chromatography (GC) is that time and reagent consuming derivatization are not necessary, which reduces analysis time. The first literature on HPLC method describes the determination of overall content of mono-, di- and tri-glycerides in fatty acid methyl esters by isocratic liquid chromatography using a density detector, (Trathnigg and Mittelbach, 1990). The separation was achieved by coupling a cyano-modified silica column with two gel permeation chromatography (GPC) columns; chloroform with an ethanol content of 0.6% is used as an eluent. This system allowed for the detection of mono-, di- and tri-glycerides as well as methyl esters as classes of compounds. The system was useful for the study of degree of conversion of the transesterification reaction (Trathnigg and Mittelbach, 1990).

HPLC with pulsed amperometric detection (the detection limit is usually 10-100 times lower than for amperometric detection whose detection limit is 1 mg/g) was used to determine the amount of free glycerol in vegetable oil esters. The HPLC-PAD method has proved to be simple, rapid and accurate (Lozano et al., 1996). The major advantage of this method is its high sensitivity. The simultaneous detection of residual alcohol is also possible with this technique (Knothe, 2001).

(Holcapek et al., 1999), used reverse phase high performance liquid chromatography (RP-HPLC) to determine compounds that were formed during the production of biodiesel from rapeseed oil with various detection methods which included; UV detection at 205 nm, evaporative light scattering detection (ELSD) and atmospheric pressure chemical ionization mass spectrometry (APCI-MS) in positive ion mode. The results showed that the linearity of each detection method varied with the individual triglycerides. ELSD and APCI-MS has decreased sensitivity with increasing number of double bonds in the fatty acid methyl esters. However, the sensitivity of UV detection was also different for individual triglycerides. APCI-MS is stated to be the most appropriate detection method for the analysis of rapeseed oil biodiesel. Komers et al., (2001) studied HPLC method of quantification of mono-, di-, tri-glycerides and esters using UV detection method at the region of 205 nm for methanolysis of rapeseed oils. Noureddini and Zhu (1997) used a HPLC equipped with a refractive index detector for the analysis of biodiesel produced from soybean oil. The HPLC mobile phase consisted of acetone and acetonitrile. Mono-, di-, and tri-glycerides were quantified to study the reaction kinetics for transesterification reaction.

2.11.3 Proton Nuclear Magnetic Resonance (^{1}H NMR) method

The first report on spectroscopic determination of the transesterification reaction utilized ^{1}H NMR depicting its progressing spectrum was developed by Gelbard et al., 1995. The signal due to methylene protons adjacent to the ester group in triglycerides appear at 2.3 ppm and after the reaction the methoxy protons of the methyl esters appear at 3.7 ppm. These areas of the signals of methylene and methoxy protons have been used to monitor the yield of transesterification reaction (Gelbard et al., 1995).

2.11.4 Near Infrared (NIR) spectroscopy

Knothe (1999), used NIR spectroscopy to monitor the transesterification reaction. The basis for quantization of the turn over from triglyceride feedstock to methyl ester product is different in the NIR spectra for these classes of compounds. At 6005 cm^{-1} and 4425 cm^{-1} - 4430 cm^{-1}, the methyl esters display peaks, while triglycerides display only shoulders. Ethyl esters could be distinguished in a similar fashion (Knothe (1999). The absorption at 6005 cm^{-1} gave better result than the one at 4425 $cm.^{-1}$ The mid range IR spectra of triglycerides and methyl esters of fatty acids are almost identical and offer no possibility for distinguishing.

2.11.5 Viscometry

Naoko et al., (2008) used acoustic wave solid state viscometer to continuously monitor the transesterification reaction to its end-point by measuring changes in the viscosity of the reaction mixture. The acoustic wave solid state viscometer allowed in situ measurement of the viscosity as the methyl ester conversion took place in a reactor. The progress of the reaction as indicated by the results they got clearly showed decrease in the viscosity of the mixture; the viscosity reached a plateau once the reaction had attained steady state.

The progress of the transesterification can be followed by monitoring the viscosity of the mixture in the reactor based on the compositional change because the reactants and the products have different viscosities (Naoko et al., 2008). The viscosity difference forms the basis of viscometry as an analytical method, applied to determine the conversion of vegetable oil to methyl ester (De Filippis et al., 1995). For example, the viscosity of soybean oil is 32.6 mm^2/s (at 38°C) and that of methyl soyate is 4.41 mm^2/s (at 40°C) (Knothe et al., 1997).

2.12 BIODIESEL STABILITY

Vegetable oil derivatives especially tend to deteriorate owing to hydrolytic and oxidative reactions. Their degree of unsaturation makes them susceptible to thermal and/or oxidative polymerization, which may lead to the formation of insoluble products that cause problems within the fuel system, especially in the injection pump (Meher et al., 2004).

Stability of fuels can refer to two issues: long-term storage stability or aging (or oxidative stability) and stability at elevated temperatures or pressures as the fuel is re-circulated through an engine's fuel system (or thermal stability). For B100, storage stability is the paramount concern; thus, D6751 includes an oxidation stability requirement. The oxidation stability test, EN14112 (also referred to as the Oil Stability Index (OSI) or the Rancimat test), involves heating a specified quantity of B100 to 230°F (110°C) while air is bubbled through at a specified flow rate. The air then passes through a water bath that collects the volatile acids formed in oxidation. A conductivity meter is used to monitor the water.

A stable B100 can go for many hours under these conditions without forming volatile oxidation products. This period of time, before oxidation products form, is called the induction time or induction period. The stability requirement in D6751 is that B100 have a minimum three-hour induction time. In biodiesel, fuel aging and oxidation can lead to high acid numbers, high viscosity, and the formation of gums and sediments that clog filters. If the oxidation stability, acid number, viscosity, or sediment measurements exceed the limits in ASTM D6751, the B100 is degraded to the point where it is out of specification and should not be used. Biodiesel with high oxidation stability (longer induction time) will take longer than biodiesel with low oxidation stability to reach an out-of-specification condition. Monitoring the acid number and viscosity of B100 over time is necessary to indicate whether it is oxidizing, (Meher et al., 2004).

2.13 ENGINE PERFORMANCE TESTS

The performance of a diesel engine fueled by formulated biodiesel blends are evaluated on the basis of the following parameters;

2.13.1 Brake Specific Fuel Consumption (BSFC);

This is the ratio of the engine fuel consumption to the engine power output as measured at the flywheel. BSFC has units of grams of fuel per kilowatt-hour (g/kWh).

2.13.2 Thermal Efficiency;

This is the relationship between actual heat energy stored within the fuel and power produced in the engine (indicated horsepower). It indicates the amount of potential energy contained in the fuel that is actually used by the engine to produce power.

2.13.3 Specific Fuel Consumption (SFC);

Specific Fuel Consumption is a measure of the fuel consumed by an engine. It is the rate of fuel consumption divided by the power produced.

2.13.4 Brake Horsepower (BHP);

This is measured by a dynamometer and represents the power output of the engine.

CHAPTER THREE

MATERIAL AND METHODS

3.1 BIODIESEL FEEDSTOCKS

The plant feedstocks used in this research were *Jatropha curcas* and *Croton megalocapus. Croton megalocapus* seeds were collected around Chiromo campus. The seeds were sun dried to a point where the kernel containing the seed cracked and the seeds easily came out. At this point it was assumed that the required dry weight and moisture content were attained. The seeds were then decorticated manually to remove the outer shell. 156.00 kilograms of dried seeds with the required moisture content were obtained. Oil extraction was done using a screw pressing machine at Jomo Kenyatta University of Agriculture and Technology. 42 liters of oil were obtained from the seeds which translated to 28% (v/w) oil yield per total weight of the seeds. The extracted oil was well sieved using canvas bags to remove solid impurities and packed in clean air tight containers ready for biodiesel making.

The *Jatropha curcas* seeds were obtained from a commercial supplier from Arusha, Tanzania and 20 liters of clean oil obtained using a mechanical pressing machine. Preliminary tests such as density, viscosity and acid value were done to ascertain the quality of the oil. The tests were determined in the laboratory using the standard methods and techniques. Density and viscosity were done at room temperature. The acid value was done to aid in determining the amount of base that would be required per liter of the oil during transesterification and also to determine percentage free fatty acid composition (%FFA). It is reported in most research work that high FFA content of crude vegetable oils lead to soap formation and lower yields of biodiesel.

3.2 BIODIESEL MAKING (TRANSESTERIFICATION)

The process of transesterification was done in the science workshops, School of physical sciences, University of Nairobi. The preliminary study to determine the optimum conditions for transesterification which included; amount of base catalyst per liter of oil, amount of alcohol (methanol) to be used per liter of oil, reaction time and reaction temperature was done. The optimum conditions obtained were adopted for transesterification.

3.2.1 Determining the amount of base required for transesterification

Potassium Hydroxide (KOH) was chosen in this process because of its high solubility in methanol as compared to Sodium hydroxide. To find out the amount of base required per liter of the oil, the following titration process was used;

- 1g of KOH was dissolved in 1 liter distilled water to make 0.1% w/v KOH solution.
- 1ml of the oil was dissolved in 10ml of pure isopropyl alcohol (propan-2-ol) in a 100ml conical flask.
- The beaker was warmed gently on a hot plate till all the oil dissolved in the alcohol and the mixture turned clear.
- 2 drops of phenolphthalein indicator were added.
- The oil – alcohol – phenolphthalein solution was titrated against the 0.1%w/v KOH solution with continuous swirling of the beaker.
- KOH was added until the solution stayed pink for 20 minutes
- The volume of KOH used was taken and recorded.

The KOH used had a purity of 85% and therefore there was need to adjust the volumes of KOH used in each oil to correspond to 100% pure KOH. The constant used to adjust the volume was that proposed by Keith (2007). Therefore for each volume of KOH used, 4.9ml was added. The corrected volume was equivalent to the amount of KOH in grams required to transesterify one liter of oil. However, confirmation experiment was carried out to investigate if the above value yields high biodiesel conversion during transesterification. Similarly, other reaction conditions were optimized as described below:

3.2.2 Optimizing parameters for biodiesel production from crude oils

The reaction was investigated step by step. The optimal value of each parameter involved in the process was determined while the rest of the parameters were kept constant. After each optimal value was attained, these values were adopted for the optimization of the next parameter.

3.2.3 Effect of catalyst concentration

The effect of potassium hydroxide concentration on the transesterification of the jatropha and croton oils was investigated. The amount was arrived at based on the amount of base required to neutralize one gram of oil by titration. Considerations were also taken from literature review. KOH was investigated with its concentration varying from 0.5 to 2.0 wt% for Jatropha oil and 0.5 to 1.0 wt % for croton (based on the weight of raw oil).

Neat oil was heated to 60°C and 10ml transferred into a 50ml vial. The 60°C reaction temperature was arrived after taking into consideration the boiling point of methanol which is 65°C. Separately, the amount of base to be investigated was dissolved in equal amount of methanol (based on 200 ml methanol per liter of oil). 2 ml of the resulting mixture was withdrawn and mixed with the hot oil and shaken for 35 min with regular immersing in a hot water bath at 80°C to maintain the reaction temperature of 60°C. The vial containing the mixture was put on a rack to allow separation to take place. The biodiesel layer was subjected to the wash test to determine the completeness of the reaction. The procedure was repeated for all KOH concentrations for the two oils.

3.3.3 Effect of methanol/oil molar ratio

The amount of methanol required for base-catalyzed transesterification was analyzed in terms of volumetric ratio. Stoichiometrically, the methanol/oil molar ratio required is 3:1 but in practice this is not sufficient to complete the reaction. Higher amount of alcohol is required to drive the reaction to completion at a faster rate. Although it takes 110 – 160 ml of methanol per liter of oil to form the methyl ester molecule, use of excess of methanol to push the conversion to completion is recommended. The effect of alcohol amount on yield of the transesterification experiments was conducted with different amounts of methanol to oil in the range of 120–240 ml per liter of oil at intervals of 20 ml. Wash test method was performed to determine which volume of methanol gave the best conversion.

3.3.4 Effect of reaction temperature

Transesterification can occur at different temperatures, depending on the properties of oils. It could be at ambient temperature or at a temperature close to the boiling temperature of the alcohol used for transesterification. The optimized catalyst concentration as obtained in the above section was adopted. Temperatures of 40, 50, 60, 70 and 80°C were investigated. Observations were made on the separation ability after the reaction and thereafter wash test was carried to determine reaction and conversion efficiency.

3.3.5 Effect of reaction time

In order to achieve an effective interaction between the catalyst and the oil during transesterification, it is essential that they must be stirred well at constant rate for a good duration of time. The effect of reaction time was investigated over 90 minutes. The reaction was stopped after every 15 minutes, each time a small amount of the reacting mixture was taken for analysis to determine the quality of the biodiesel using wash test method.

3.4 TRANSESTERIFICATION

3.4.1 The reacting vessel

The reacting vessel shown was fabricated at Bama Jua Kali Center in Nairobi; it had a maximum capacity of 5 liters. The Key features of the vessel included;

- An electrical heating coil.
- Thermostat (black knob).
- Mixing shaft (stirrer).

The lid was tight fitting to prevent heat loss. The conditions optimized above were adopted for the transesterification process. The vessel was calibrated to establish at what thermostat settings gave a reaction temperature of 60°C. In this study 200ml of methanol was used per liter of oil. The amount of KOH used per liter of each oil was as optimized above. Two liters of oil was processed per batch.

3.4.2 Transesterification of Croton oil

The transesterification process was done as outlined below and as described by Kimilu (2007);

i. 14g of KOH were measured out using an electronic top-pan balance then transferred to an air tight container to prevent it from absorbing water from the atmosphere which can interfere with biodiesel reaction.
ii. 400ml of methanol was measured using a measuring cylinder and transferred into a 1000ml volumetric flask and corked.
iii. The KOH was then transferred into the volumetric flask and shaken continuously until it all dissolved.
iv. 2 liters of croton oil was measured using a clean measuring cylinder into the reacting vessel.
v. The thermostat was set at 80°C and the mains switched on. At this thermostat setting, the maximum temperature attained by the oil was 60°C.
vi. After the thermostat had switched off, the mixture of methanol and KOH was carefully added into the oil.
vii. The stirrer was inserted through the lid, and the lid was tightly fitted on the reacting vessels using screws.
viii. The stirrer was then fixed onto the mixing machine and was switched on. It was operated at a speed of 1100 rpm for one hour both. Since the reaction is exothermic the thermostat setting was changed from 80°C to 60°C as the reaction progressed.
ix. After mixing for one hour the reaction was stopped, the mixture was transferred into a 2.5 liter separating flask and allowed to separate. Separation occurred immediately into two distinct liquid phases; crude methyl ester at the top and glycerol phase at the bottom. But to achieve effective separation a settling time of four hours was allowed.

x. The glycerin was run out through tap and the biodiesel transferred into a clean container awaiting washing.

xi. The process was repeated for twenty liters of oil.

3.4.3 Transesterification of Jatropha oil

i. 30.7g of KOH were measured out using an electronic top-pan balance then transferred to an air tight container to prevent it from absorbing water from the atmosphere which can interfere with biodiesel reaction.

ii. Steps (ii) to (xi) above were repeated.

3.4.4 Biodiesel washing

Biodiesel washing was done in a transparent 5 liter plastic bottle. 1.5 liters of water was used per 2 liters of oil in the washing process. Water was heated to temperature between 45°C and 50°C. 1.5 liter of water was then gently poured into the bottle containing the oil and the bottle shaken vigorously until the oil and water uniformly mixed. It was then placed into a hot water bath for two hours because the water forms tiny bubbles in the biodiesel that take time to settle out hence the hot water will make them clear faster. The biodiesel was carefully separated from the milky water. The washing process was repeated until the wash water was clear.

3.4.5 Biodiesel Drying

Washed biodiesel was very cloudy, much lighter in colour than the original biodiesel and needed drying. Drying of the obtained biodiesel involved heating the oil to 110°C. Since biodiesel is water washed, there is a possibility of water remaining during separation process, hence at this temperature all the water present in the biodiesel evaporated. The presence of water was detected by the presence of bubbles in the oil. The cloudiness of the biodiesel cleared after it cooled. Care was taken not to heat the oil to extreme temperatures that could adversely affect the quality of the biodiesel.

3.5 DETERMINATION OF BIODIESEL PHYSICOCHEMICAL PROPERTIES

3.5.1 Specific Gravity

The specific gravity of a substance is a comparison of its density to that of water. Specific gravity is a special case of relative density. In this case the density of a substance is divided by the density of water at 4 F (0°C). Since water has a density of 1 gram/cm3, and since all of the units cancel, specific gravity is the same number as density but without any units (a dimensional). The method used to determine the specific gravity was that of the relative density where relative density is the number of times a substance is heavier than water. This test was to investigate the effect of temperature on the density of biodiesel. A density bottle of 25ml capacity was used. The empty bottle was cleaned and dried in the oven and weighed using an optical beam balance and its mass recorded. The bottle was filled with distilled water and corked, the excess water escaped through the hole in the cork and what remained was exactly 25mls. The test temperatures investigated were from 15°C to 60°C with an increment of 5°C.

As described by Kimilu (2007), the bottle was immersed in the water bath and remained in the bath for 15-20 minutes to attain uniform temperature. It was then removed and dried of any water on its surface and reweighed, from which the mass of water was determined by subtracting the mass of the empty bottle. This process was done for all temperatures investigated. The fuels under study were tested using the same method as the water and their masses at different temperatures were determined and recorded. Three readings were taken for each sample and the average taken.

The relative density was calculated from the relation;

$$\rho = M_{oil}/M_{water} \qquad (3.1)$$

Where

ρ = density

M_{oil} = mass of oil

M_{water} = mass of water

The specific gravity of the test fuels at each temperature was determined as the ratio of the mass of the fuel to that of water at the same temperature.

3.5.2 Viscosity

The method used to determine the viscosity is as described by Kimilu (2007). The Ostwald viscometer size D BS/U 790 was used to determine the viscosity. The viscometer was cleaned and rinsed with distilled water and dried in the oven. It was then clamped in a temperature controlled water bath in a vertical position, such that the marks 'a' and 'c' were below the water level and clearly visible through the water bath. 15ml of distilled water was pippeted into the wider arm which could fill the upper bulb 'b' between the two marks and at the same time leaving the lower bulb 'B' a least 1/3 full. The temperature of the bath was adjusted to 15°C using ice cold water with the help of a thermostatic thermometer and left for between 15-20 minutes to reach thermal equilibrium.

The water was sucked up through tube 'T' to a level above mark 'a' and allowed to flow down. The time taken for the meniscus to pass from 'a' to 'c' was determined (Fig. 3.1). This was repeated three times and averaged. The procedure was repeated for the temperatures 15°C to 60°C at increment of 5°C and three readings were taken for and the average value recorded. This procedure was done to all the test fuels and the viscosities of the fuels were determined using the relationship below;

$$\upsilon_f / \upsilon_w = \rho_f t_f / \rho_w t_w \qquad (3.2)$$

Where

υ_f = viscosity of the fuel sample at a given temperature

υ_w = viscosity of water at a given temperature

ρ_f = density of the fuel sample at a given temperature

ρ_w = density of water at a given temperature

t_f = time taken for fuel sample to run between 'a' and 'b'

t_w = time taken for water to run between 'a' and 'b'

The water viscosity and density values at the required temperatures were obtained from the Hand book of Chemistry by Lange (1941).

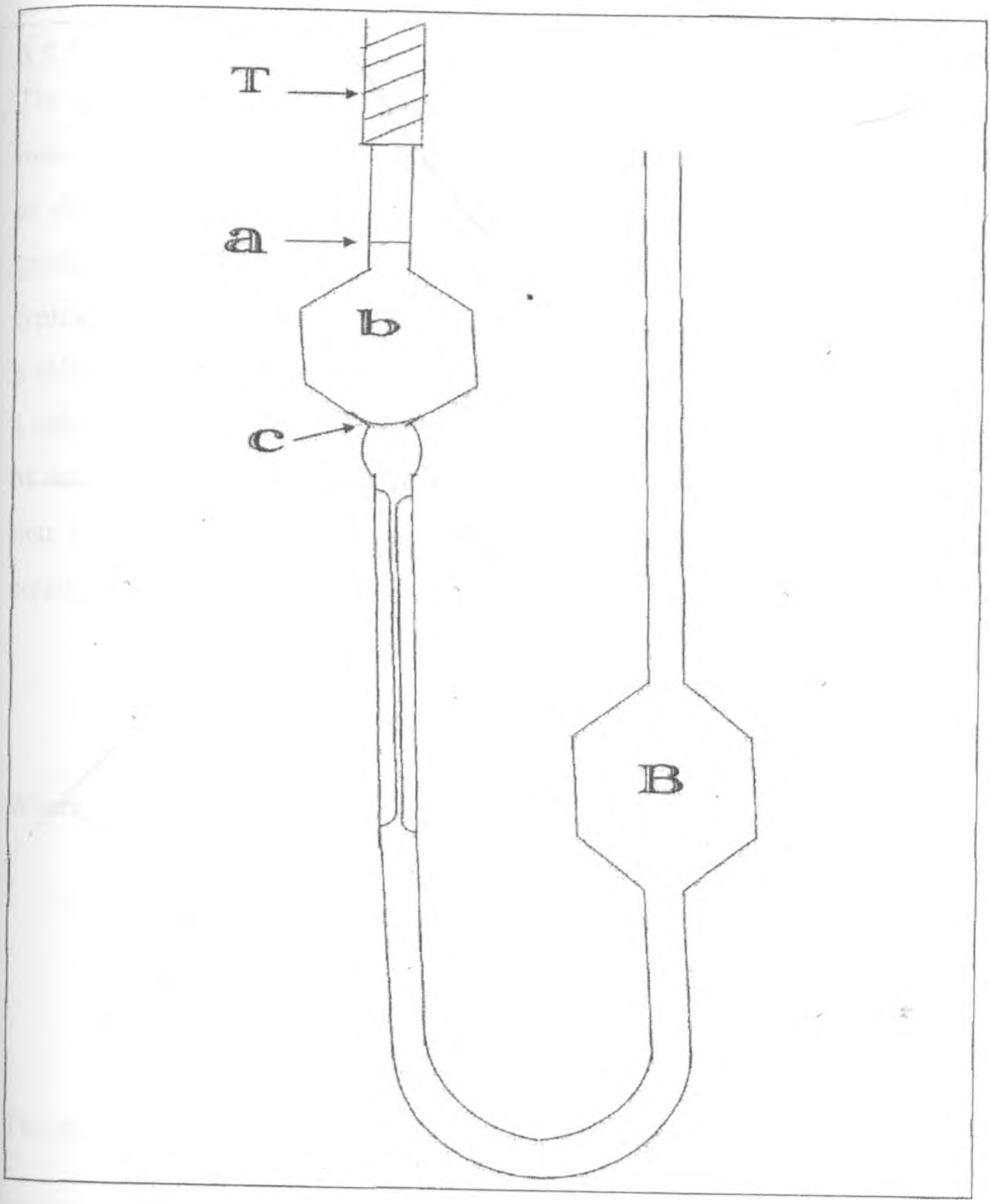


Fig. 3.1: Ostwald Viscometer

Diagram courtesy of Kimilu 2007

3.5.3 Acid value

The acid value (or "neutralization number" or "acid number" or "acidity") refers to the mass of potassium hydroxide (KOH) in milligrams that is required to neutralize one gram of chemical substance. The acid number is a measure of the amount of carboxylic acid groups in a chemical compound, such as a fatty acid, or in a mixture of compounds. In a typical procedure, a known amount of sample dissolved in organic solvent is titrated with a solution of potassium hydroxide with known concentration and with phenolphthalein as a color indicator. In a sample of biodiesel the acid number is used to quantify the amount of acid present. It is the quantity of base, expressed in milligrams of potassium hydroxide that is required to neutralize the acidic constituents in 1 g of sample. The following equation was used to calculate the acid number (acid value);

$$AN = (V_{eq} - b_{eq})N\frac{56.1}{W_{oil}} \tag{3.3}$$

Where

V_{eq} = amount of KOH (ml) consumed by the oil sample at the equivalent point

b_{eq} = amount of KOH consumed by the blank sample

N = concentration of KOH

W_{oil} = mass of the oil sample used

The molecular mass of KOH is 56.1

The molarity concentration (N) of KOH was calculated using the following relationship;

$$N = \frac{1000W_{KHP}}{204.23V_{eq}} \tag{3.4}$$

Where;

W_{KHP} = amount (g) of potassium hydrogen phthalate (KHP) in 50 ml of KHP standard solution

V_{eq} = amount of KOH (ml) consumed by 50 ml KHP standard solution at the equivalent point

The molecular weight of KHP is 204.23.

Procedure

The concentration N of KOH was determined as follows;

- 0.1% of KOH was prepared by dissolving 1gm KOH in one liter of distilled water in a 1 liter volumetric flask.
- 0.01M of KHP was prepared by dissolving 0.5106 g of KHP in 250ml of distilled water in a 250ml volumetric flask.
- 50ml of 0.01M KHP was titrated against 0.1% KOH using phenolphthalein indicator. The titration was repeated three times and the average volume used, V_{eq} calculated
- W_{KHP} was calculated by dividing the mass used to make 250ml of KHP by four.

The Acid Number was determined as follows;

- A clean and dry conical flask was weighed.
- 1ml of the oil sample was pipetted into the conical flask and reweighed and the weight recorded.
- The mass of the oil was determined by subtracting the mass of the empty flask.
- 10ml of isopropyl (propan-2-ol) was pippeted into the flask containing the oil sample.
- 2 drops of phenolphthalein indicator were added into the mixture of the oil and the alcohol.
- The mixture was then titrated against 0.1% KOH while constantly swirling the flask. The end point was reached when the colour of the mixture turned pink, this colour was supposed to persist for 15 seconds.
- The above procedures were repeated for the blank sample where only the isopropyl alcohol was titrated.

3.5.4 Calorific Value (Heating value)

The heating value or calorific value of a substance, usually a fuel or food, is the amount of heat released during the combustion of a specified amount of it. The calorific value is a characteristic for each substance. It is measured in units of energy per unit of the substance. Heating value is commonly determined by use of a bomb calorimeter.

The procedures for determining the calorific value using a bomb calorimeter are as described below (Kimilu 2007).

- The empty capsule was weighed using a optical beam balance and its mass recorded.
- The capsule was then filled with oil and reweighed. The mass of the oil was determined by subtracting the mass of the empty capsule.
- 1700ml of water was measured and put into the cooling jacket of the calorimeter.
- The capsule with the oil was put on the crucible and placed in the firing apparatus of the calorimeter.
- The bomb calorimeter was then assembled, charged with oxygen up to 25atms and the stirrer turned on.
- The temperature readings were taken at intervals of one minute for five minutes to make sure that the temperatures of the bomb were stable and then the bomb was fired.
- Temperatures were taken at intervals of half a minute for the entire range of the temperature rise and at one minute interval for five minutes after temperatures started to drop.

Calculations

The energy transferred to the cooling water was calculated using the relation;

$$\text{Energy (cal/g)} = 2335 \times \Delta T / \text{mass of capsule and oil} \qquad (3.4)$$

Where

ΔT = (maximum temperature attained) – (temperature at firing)

2335 is the energy due to the calorimeter

Energy contributed by combustion of capsule was calculated as:

$$\text{Capsule energy (cal/g)} = \text{capsule mass (g)} \times \text{energy due to capsule} \qquad (3.5)$$

The capsule energy was subtracted from the energy transferred to cooling water bath and the net energy contributed by combustion of oil determined.

The energy content was converted from cal/g and expressed as MJ/Kg using the conversion factor below;

1 calorie = 4.184 joules

3.5.5 Iodine Value

It measures the amount of iodine required to saturate the olefinic bonds. The iodine value is an indicator of the unsaturation of the fuel, which has been linked with formation of engine deposits and problems in storing the fuel.

Procedures

i. The weight of 0.5ml of the oil sample was weighed accurately into a 250 ml Erlenmeyer flask
ii. 20ml of carbon tetrachloride was added into the flask.
iii. 25.0 ml of Wijs reagent was pipetted into the fuel, carbon tetrachloride mixture. The flask was stoppered, the contents mixed by swirling and store in a dark place at room temperature for thirty minutes.
iv. At the end of 30 minutes, 10 ml of 30% potassium iodide solution was added to the sample solution followed by 100 ml of purified water.
v. The contents were immediately titrated with standard 0.1M sodium thiosulfate solution until the yellow color almost disappeared.
vi. 1 ml of 1% starch indicator solution was added and titration was continued with vigorous swirling to disappearance of the blue starch-iodine color.
vii. The above procedures were repeated for the blank where the flask contained all the chemicals except the oil sample.

Calculation

The Iodine value was calculated using the expression below;

$$\text{Iodine Value} = \frac{(\text{Blank Titer (ml)} - \text{Sample Titer (ml)}) \times (1.269)}{\text{Weight of Sample (g)}} \qquad (3.6)$$

3.5.6 Blend preparation

Blends between biodiesel from Jatropha (Jatropha Methyl Esters) and biodiesel from Croton (Croton Methyl Esters) were prepared and thereafter the above was blended with commercial diesel. Blends were also prepared between Croton Methyl Esters and Jatropha methyl esters with commercial diesel. The results are summarized in the table 3.1 below;

Table 3.1: Blends of neat JME and CME, their mixtures at different proportions with diesel.

CASE OF 75% J.M.E AND 25% C.M.E
Blends with Commercial Diesel
B5
B10
B20
CASE OF 50% J.M.E AND 50% C.M.E
Blends with Commercial Diesel

B5
B10
B20
CASE OF 25% J.M.E AND 75% C.M.E

Blends with Commercial Diesel
B5
B10
B20
CROTON BLENDS WITH DIESEL
Blends with Commercial Diesel
B5
B10
B20
JATROPHA BLENDS WITH DIESEL
B5
B10
B20

3.6 ENGINE TESTS AND INSTRUMENTATION

The engine used in this study is a Ford six cylinder turbo charged diesel engine rated at 86 Bhp, at 2250 RPM. The engine is coupled to a G-type Froude dynamometer for measuring the engine output over the entire range of operation. The loads were applied by regulating the amount of water going into the dynamometer with load increments in steps of 1lb. The engine's fuel system is fitted with two filters; primary and secondary filters to ensure that any suspended particles present in the fuel do not reach the injector pump because they can cause blockage. The fuel flow in the fuel system was facilitated by a fuel pump, to achieve fuel flow under pressure.

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

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

3.6.1 Engine performance testing

The engine performance testing procedures used in this study are as described by Kimilu (2007). Preliminary engine familiarization tests were done using DF2 fuel. The results indicated that normal engine runs could be achieved for speeds of up to 2000 RPM. After conducting full load test at varying speeds, 1500 RPM showed good repeatability and hence the study was carried out at this speed.

The engine was warmed up to the recommended operating temperature of cooling water of 125 to 130°F by running the engine on DF2 fuel at idle speed until the cooling water in the header tank attained the above temperature. The engine was then run at a constant speed of 1500 RPM and load varied in increments of 1 Lb starting with an initial load of

1 Lb. The increment of the load was continued until the running of the engine become erratic and the speed started to fluctuate (maximum load was 7 Lb). For each load the rate of fuel consumption and temperatures of the exhaust gas were recorded. This procedure was repeated for all the test fuels under study and the results obtained used to calculate the following parameters;

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

3.6.2 Rotational Speed

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

3.6.3 Measuring of fuel consumption

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

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

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

3.6.4 Determination of brake horse power

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

$$B.H.P = \frac{WN}{K} \qquad (3.7)$$

Where:

W = Net weight lifted by the dynamometer in pound (Lb)
N = Dynamometer shaft speed in RPM
K = Dynamometer constant

Dynamometer constant, K = 200

3.6.5 Determination of Brake Specific Fuel Consumption

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

$$BSFC = \frac{M \times 3600}{T \times BHP} \qquad (3.8)$$

Where:

M = mass of fuel
T = time in seconds used to consume mass of fuel M

3.6.6 Determination of thermal efficiency

Thermal efficiency is the relationship between actual heat energy stored within the fuel and power produced in the engine (indicated horsepower). The thermal efficiency Figure indicates the amount of potential energy contained in the fuel that is actually used by the engine to produce power. It therefore expresses power output of the engine as a percentage of the power obtained from chemical energy supplied of the fuel supplied.

It is calculated using the formula below;

$$TE = \frac{BHP \times 100}{P_{in}} \tag{3.9}$$

Where:

TE = Thermal efficiency, %

P_{in} = Power input

$$\text{Power input} = \frac{\text{Energy input}}{\text{Time, } t}$$

Energy input = Mass × Calorific value of fuel

3.7 FATTY ACID METHYL ESTERS DETERMINATION IN B100 BIODIESEL FROM *CROTON MEGALOCARPUS* BY GAS CHROMATOGRAPHY

The fatty acid methyl esters analysis was carried out with a splitless injection into an analytical column with a polar stationary phase and an FID detector. In order to determine the retention times of the fatty acid methyl esters in croton biodiesel, fatty acid methyl ester standards were run. Table 3.2 below provides an overview of all the instrument conditions.

Table 3.2: GC instrument conditions

Inlet temperature	250°C
Column flow	1 mL/min
Injection volume	1.0μL
Oven program initial temperature:	210°C
Hold time	13.0 min
Ramp 1:	20°C/min
Oven program final temperature	275°C
Hold time	18 min
Equilibration time	0.0 min
FID temperature	250°C
Air flow	45 ml/min
H2 flow	450 ml/min
Run time	35 min
Carrier gas	Helium

3.7.1 Gas Chromatography sample preparation

The procedure described below resulted into 10.0 ml of an n-heptane solution (in vial 'B') that contained about 50 micrograms of biodiesel in each 1.0ml of solution. Only 1.0 microliter (1.0 μL) of the solution was injected into the GC.

- 2.0 ml of pure n-heptane was added to a small screw cap vial and labeled (vial 'A'). 0.20 ml of deionized water was added to the n-heptane in vial 'A' and shaken.
- 0.10 ml biodiesel was added to vial 'A' and shaken. The water phase turned cloudy white and settled at the bottom. The contents were left to separate.
- 9.9 ml of n-heptane was put into a clean, dry vial and lebeled (vial 'B'). 0.1 ml was carefully withdrawn from the top phase (heptane phase) from vial 'A' and added to the 9.9 ml of heptane in vial 'B' to make a total volume of 10.0 ml. The contents were well shaken to achieve a homogenous mixture.
- 1μL of solution was withdrawn from vial 'B' and injected into the GC.

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 PROCESS OPTIMIZATION FOR BIODIESEL PRODUCTION FROM CRUDE OILS

To achieve maximum conversion of biodiesel, four influencing factors were investigated; effect of catalyst concentration, effect of methanol/oil molar ratio, effect of reaction temperature and effect of reaction time.

4.1.1 Effect of catalyst concentration

Since the purpose was to a certain whether the amount of KOH determined from titration was the optimum amount, this value was set as the reference amount. It is important to take into account the correct amount of catalyst used in the transesterification process, not only because it determines the reaction rate, but also because it can cause hydrolysis and saponification (Pedro et al., 2006).

Experimental results showed changes in transesterification process with varied catalyst concentration. As the KOH concentration increased, the conversion of triglyceride increased thus indicating an increase in methyl esters yield. At low concentration of KOH incomplete conversion of triglycerides into the methyl esters was observed as indicated by the wash test method. Biodiesel could not separate from the wash water instead a white emulsion was formed. However, a good separation was achieved when the KOH concentration reached 1.5 wt% for Jatropha oil and 0.75 wt% for Croton oil. Similarly in high concentrations of KOH poor separation was noted. This effect can be attributed to the fact that addition of excess alkaline catalyst caused more triglycerides' participation in the saponification reaction with KOH, resulting in the production of more amount of soap and reduction of the methyl ester yield. Titration results had shown that 1.6wt% of KOH was required for Jatropha oil while 0.8% KOH was required for croton oil to transesterify one liter of oil. The difference in the amount of KOH required was due to the difference in the acid value of the two oils, Jatropha oil had an acid value of 9.585 mg KOH/g oil, while Croton oil had acid value of 2.765 mg KOH/g oil.

4.1.2 Effect of methanol/oil molar ratio

The effect of the amount of methanol required for transesterification was conducted with different ratio of methanol to oil. The optimized catalyst concentration as obtained in the above section was adopted. The volumes of methanol/liter oil investigated were 120, 140, 160, 180, 200, 220 and 240 ml. After obtaining biodiesel from a given volume of methanol per liter of oil, wash test was performed and good biodiesel conversion was obtained at a methanol amount of 200ml per liter of oil for both croton and jatropha oils, Figure 4.1 below gives the summary of the results. With further increase in the methanol to oil amount above 200 ml, a very poor conversion on the biodiesel was observed during the wash test method, separation between biodiesel and glycerin became more difficult due to increased solubility of glycerin.

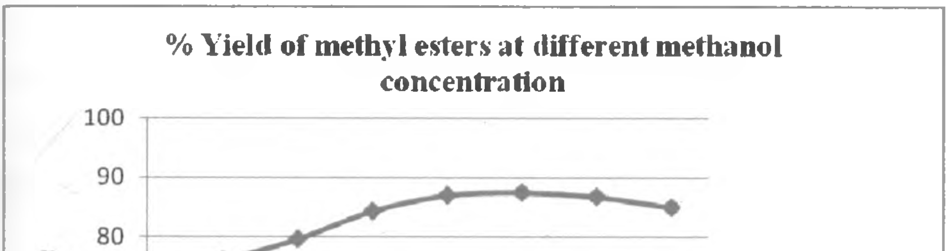


Figure 4.1: effect of methanol concentrateion on the % yield of biodiesel.

4.1.3 Effect of reaction temperature

To study the effect of reaction temperature on methyl esters' formation, the transesterification reaction was carried out under the optimal conditions obtained in the previous section (i.e. 200 ml of methanol, 1.5 wt% and 0.75 wt% KOH for Jatropha and Croton oil respectively and reaction time of one hour). The experiments were conducted at the following temperatures; 40 °C, 50 °C, 60 °C, 70 °C and 80 °C

Experimental results showed that the transesterification reaction could proceed within the temperature range studied but the reaction time to complete the reaction varied significantly with reaction temperature. It took a very short time to obtain separation at temperature 70 °C and 80 °C. However, the conversion was poor as showed by the wash test method and the percentage yield was low after 60 minutes, Figure 4.2 below. Good conversion was achieved at 60 °C reaction temperatures. Poor conversion at high temperatures could be attributed to the fact that there was increased methanol evaporation, hence very little was left behind to take part in reaction. Eevera et al., (2009) reported that higher temperature accelerates the side saponification reaction of triglycerides and this could also be a factor that contributed to poor conversion.

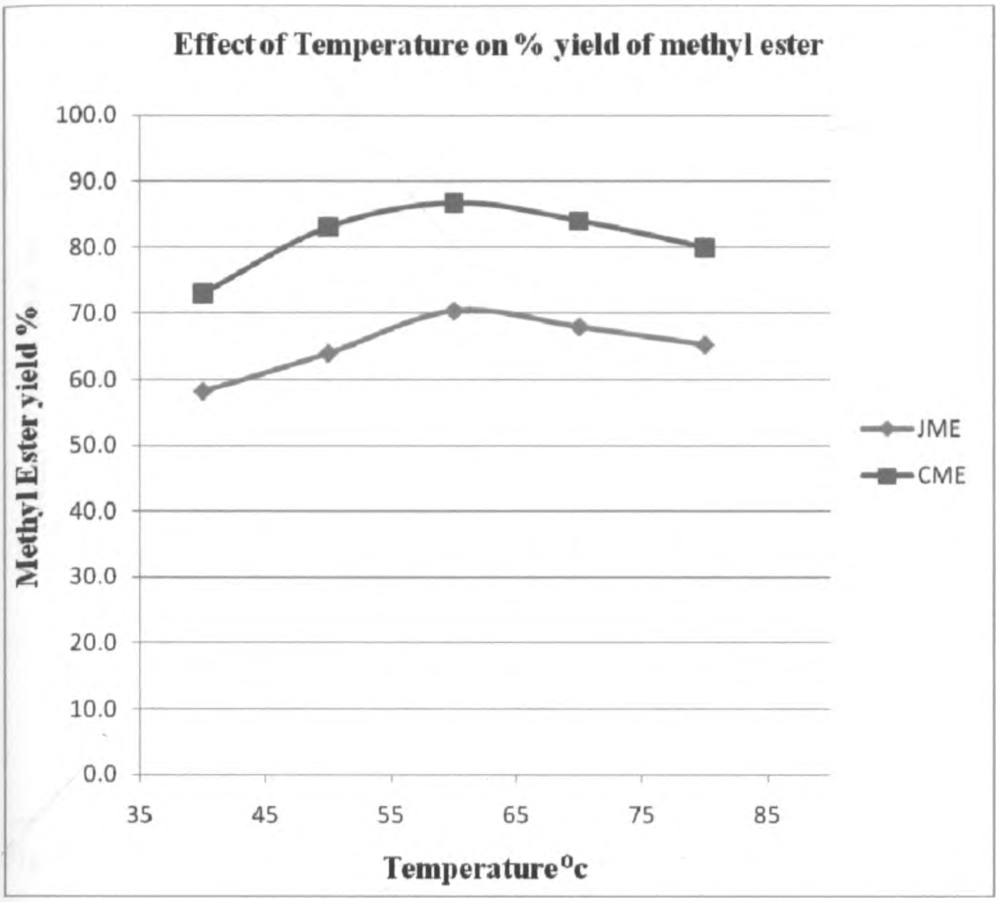


Figure 4.2: Effect of temperature on the % yield of biodiesel.

4.1.4 Effect of reaction time

The changes in biodiesel conversion with reaction time during the transesterification of the oils were observed when the samples collected after every 15 min were subjected to wash test method. In this experiment, glycerol started to separate within 15 min, however the wash test confirmed incomplete conversion. Biodiesel could not separate from the wash water and the white emulsion persisted. The ester content increased with reaction time from 15 min onwards and reached a maximum at a reaction time of 60 min at 60°C. The results from Figure 4.3 below indicate that an extension of the reaction time from 60 to 90 min had no significant effect on the conversion of triglycerides. Eevera et al., (2009) from their study reported that an extension in reaction time leads to a reduction in the product yield because longer reaction times enhanced the hydrolysis of esters (reverse reaction of transesterification), enhancing the saponification process.

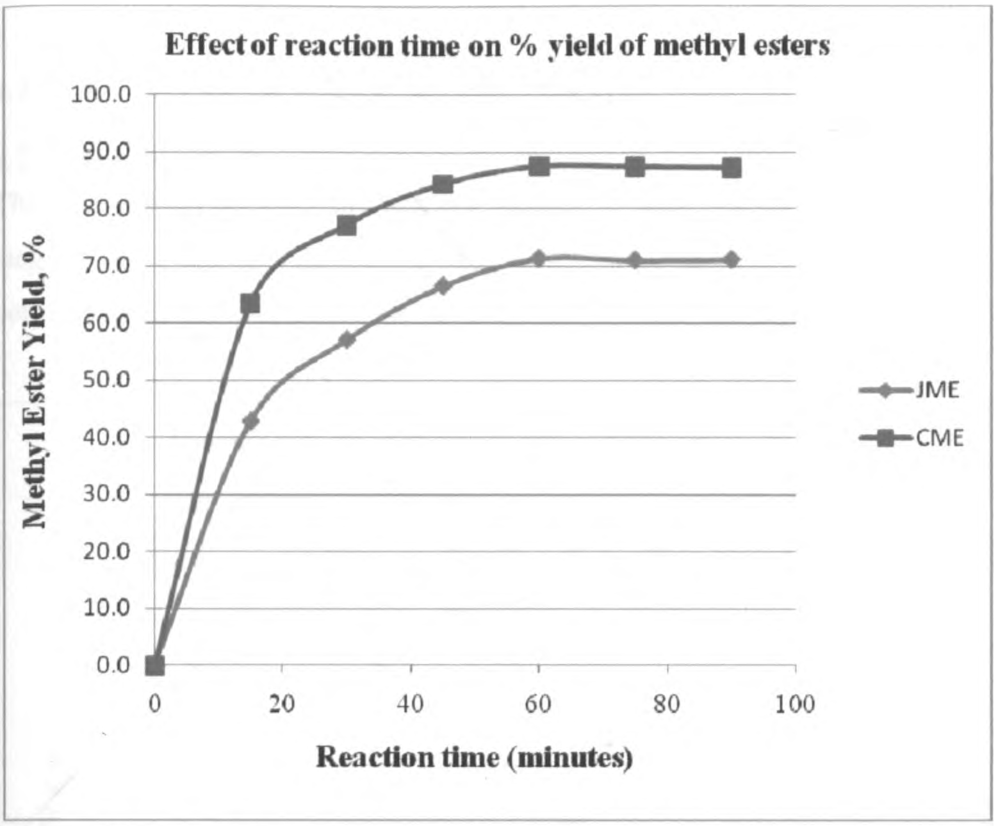


Figure 4.3: Effect of reaction time on the % yield of biodiesel

Table 4.1: Parameter optimization of biodiesel yield

Time (min)	% Biodiesel Yield		Temperature ^{0}C	% Biodiesel Yield		Amount of Methanol (ml)	% Biodiesel Yield	
	JME	CME		JME	CME		Croton	Jatropha
0	0.0	0.0	40	58.2	73.0	120	76.0	53.4
15	42.8	63.4	50	64.0	83.0	140	79.6	58.1
30	57.1	77.1	60	70.4	86.7	160	84.3	61.2
45	66.5	84.4	70	68.0	84.0	180	87.0	68.8
60	71.3	87.5	80	65.3	80.0	200	87.5	71.0
75	71.0	87.4				220	86.8	70.3
90	71.1	87.2				240	85.0	67.6

4.2 FUEL PHYSICOCHEMICAL PROPERTIES

4.2.1 Specific gravity

The relationship between the specific gravity of neat oils of *Jatropha curcas*, *Croton megalocarpus* and their resultant methyl esters with temperature is as shown in Figure 4.4 below. The values as measured at different temperatures are given in appendix (I)

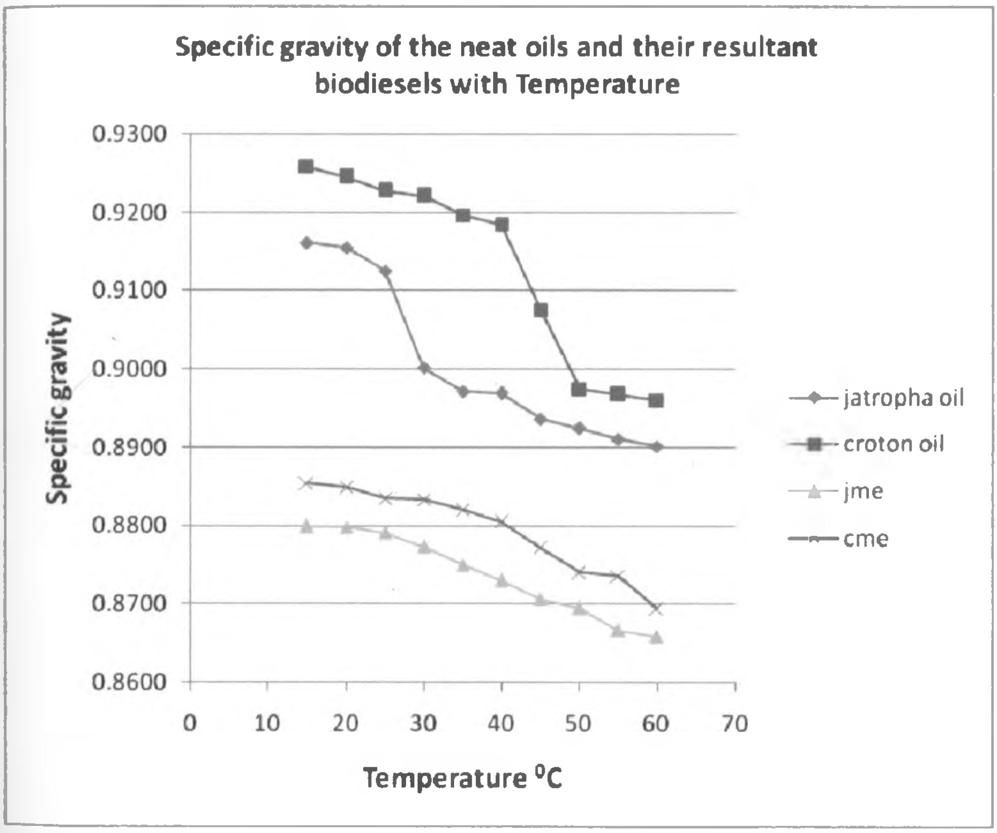


Fig 4.4: Variation of Specific gravity with temperature of *Jatropha curcas* oil, *Croton megalocarpus* oil and their resultant methyl esters.

From Figure 4.4, it is observed that specific gravity of the biodiesel is temperature dependent property and it decreased as temperatures increased from 15 °C to 60 °C. *Croton megalocarpus* oil had high specific gravity at all test temperatures than *Jatropha curcas* oil. Similarly CME gave high specific gravity values at all test temperature than JME, hence confirming that the physical properties of biodiesel are highly dependent on the properties of virgin oil. Fatty acid composition of the two virgin oils could be a major factor that brought the difference in the specific gravity. After converting the oils to methyl esters the specific gravity decreased by 4.37% and 3.96% at 15°C for *Croton megalocarpus* and *Jatropha curcas respectively*. 15°C was chosen because this is the temperature at which ASTM reference is made.

Upon blending with DF2, the specific gravity of CME and JME decreased significantly as shown in Figures 4.5 and 4.6 respectively at all test temperatures. However the measured specific gravity increased with increase in the percentage of biodiesel in a given blend, Figures 4.5 and 4.6

[1]

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[1] The specific gravity was determined in triplicate and the average value was plotted against temperature. The standard deviation of the three entries was determined and is presented in appendix I.

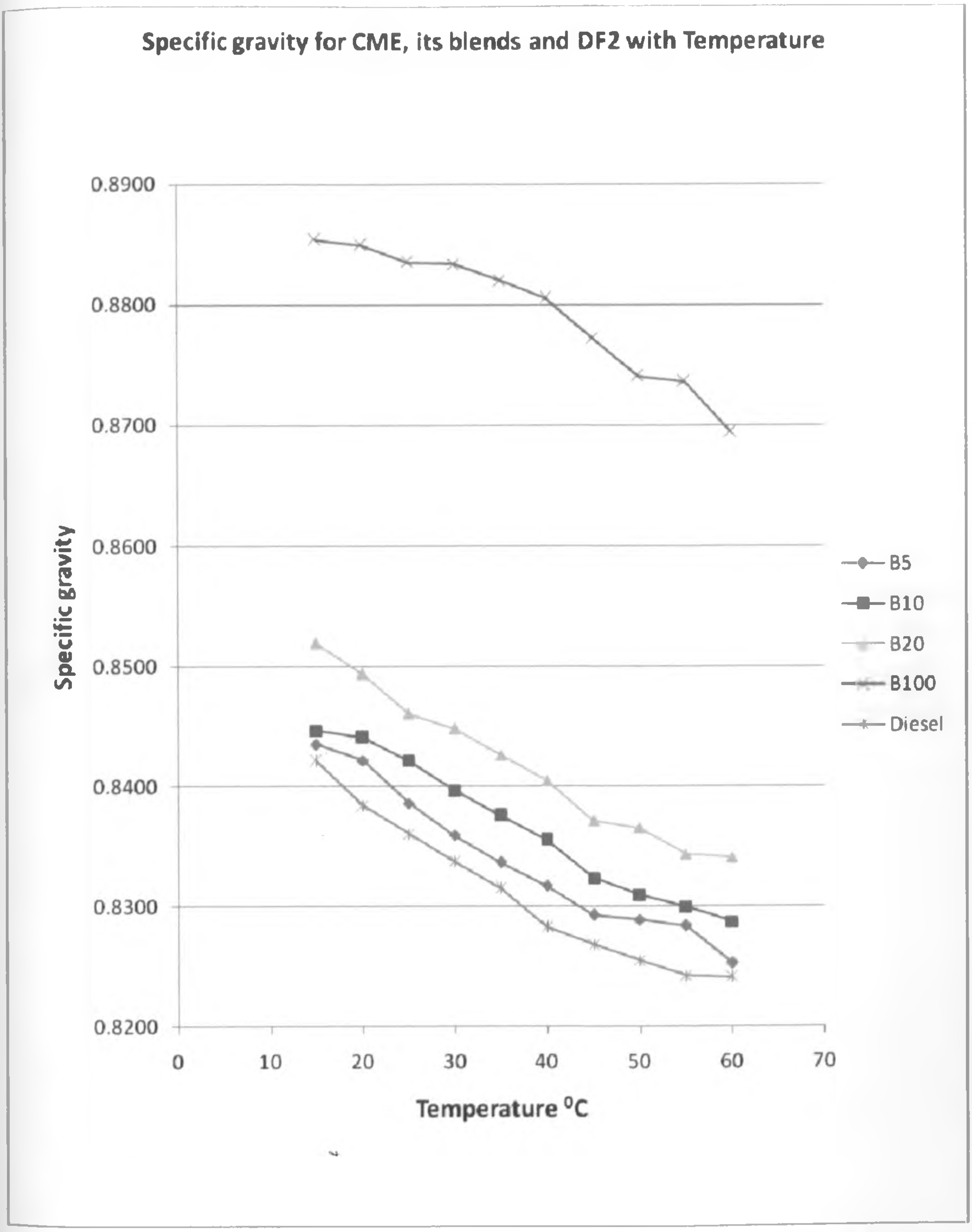

Fig. 4.5: Variation of specific gravity with temperature of CME, its blends with DF2 and DF2

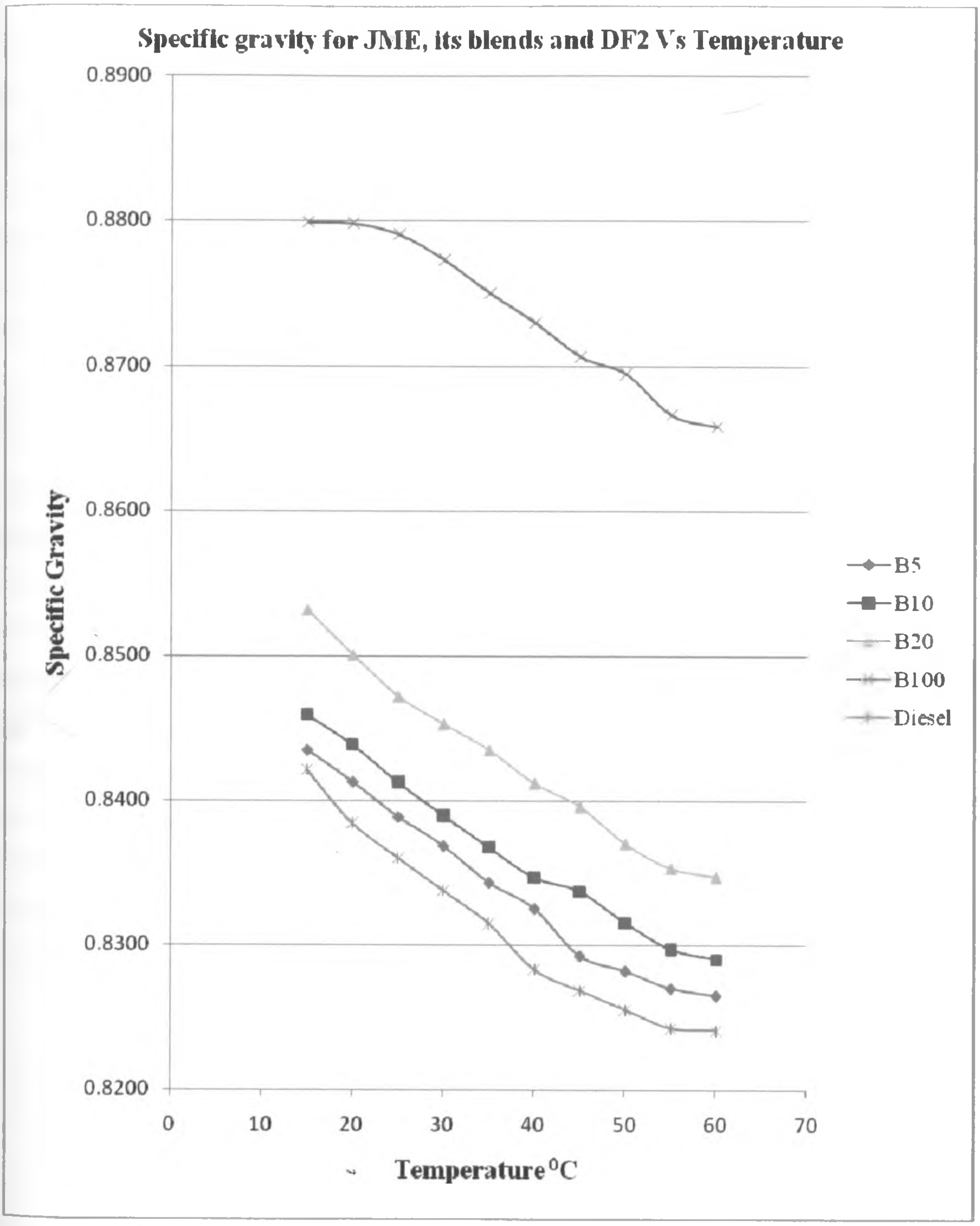

Fig. 4.6: Variation of specific gravity with temperature for JME, its blends with DF2 and DF2.

The specified range of specific gravity of DF2 by Kenya Bureau of Standards (KEBS) standard KS1309-1 is 0.820 and 0.870 at 20°C. From Figures 4.5 and 4.6 above it is observed that all biodiesel blends gave results that are within this specified range at all test temperatures. However, neat CME (B100) and JME (B100) could only attain the highest range after being preheated to 60°C and 45°C respectively. On the other hand neat *Jatropha curcas* and *Croton megalocarpus* oil gave values that were far above the specified upper limit range of 0.870 at all test temperatures (Figure 4.4).

4.2.2 Kinematic Viscosity

The values of kinematic viscosities determined at different temperatures are shown in Appendix 2. The relationship between the viscosity of neat *Jatropha curcas* and *Croton megalocarpus* oil and their resultant methyl esters are shown in Figure 4.7 below.

From Figure 4.7, it can be observed that the kinematic viscosity for both neat oils and neat methyl esters (B100) decreased as temperatures increased from 15°C to 60°C. After transesterification the oils to their corresponding methyl esters the kinematic viscosity decreased by 70.38% and 63.27% at 15°C for *Croton megalocarpus* and *Jatropha curcas* respectively. American Society for Testing and Material (ASTM) specifies the standard kinematic viscosity of biodiesel at 40 °C as 1.9 – 6.0 cSt (ASTM D6751). When JME and CME were blended with DF2, the kinematic viscosity decreased significantly (Figures 4.8 and 4.9 below) as the viscosity of the resultant fuel blend assumed the properties of DF2 because it was used in high proportion.

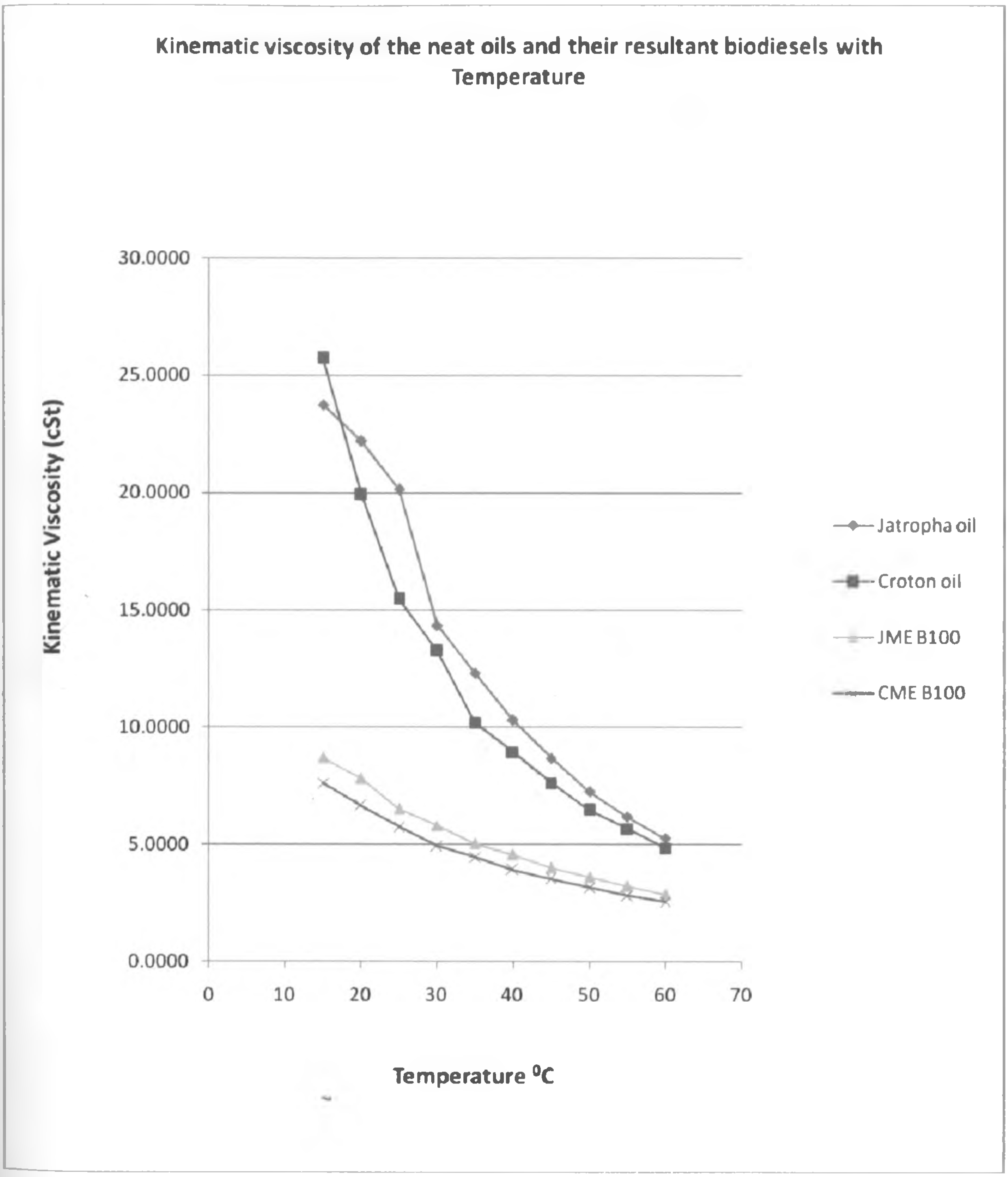

Fig 4.7: Variation of kinematic viscosity with temperature of *Jatropha curcas* oil, *Croton megalocarpus* oil and their methyl ester.

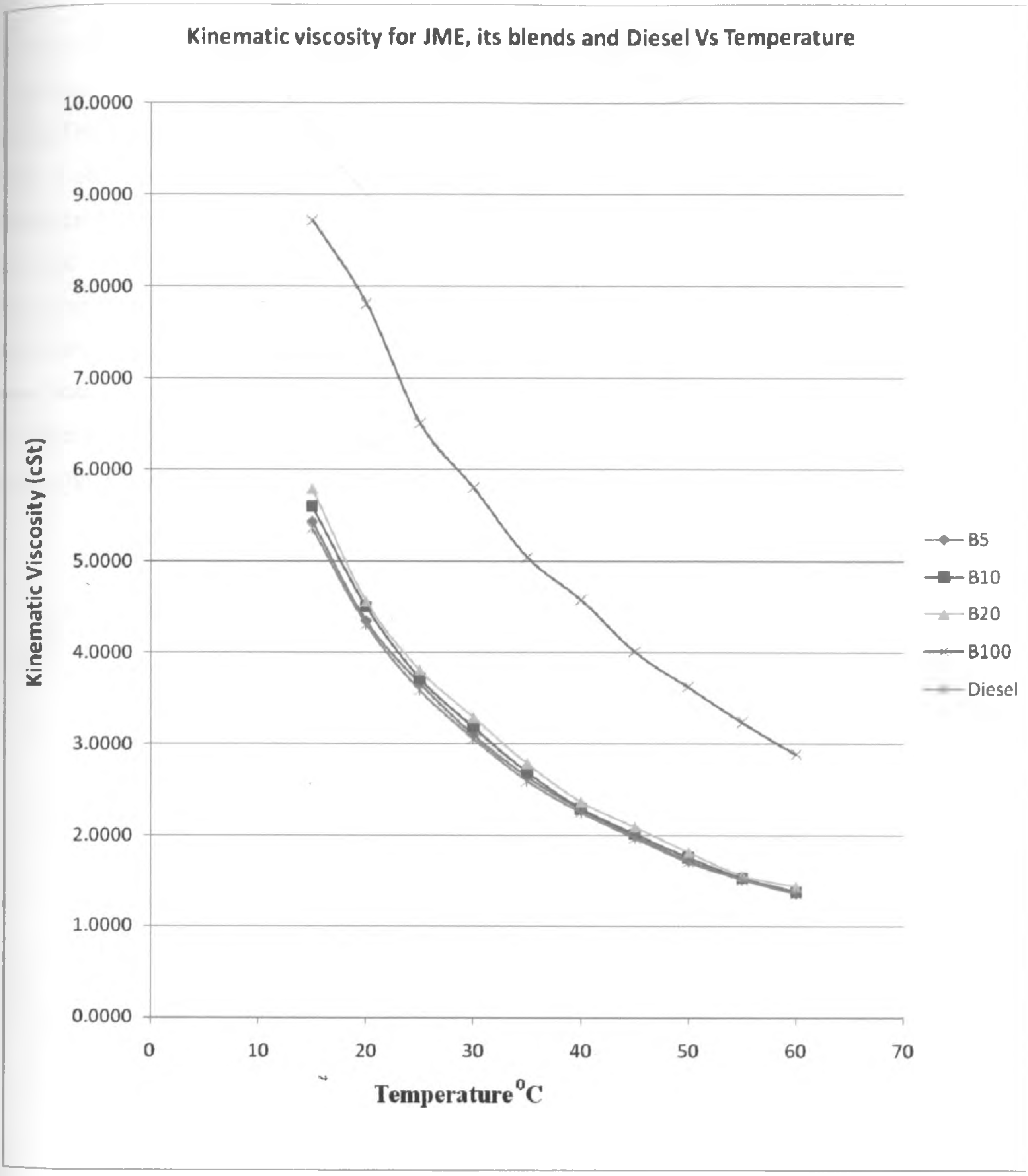

Fig. 4.8: Variation of mean kinematic viscosity with temperature for JME, its blends and DF2.

The viscosity specification for DF2 and biodiesel by KEBS KS 1309-1 (Specification for diesel fuels – part 1: Automotive gas oil) is 1.6 – 5.5 cSt (Appendix V) and that for ASTM D975 (standards for biodiesel) is 1.9 – 6.0 cSt at 40°C. Thus from Figures 4.8 and 4.6 it is observed that both neat JME and CME and their blends met this specifications. These results therefore indicate that when JME and CME fuels are heated to temperatures above 40°C, they produce normal engine performance.

There was no significant difference in the viscosity of the biodiesel blends after CME and JME were blended with DF2 to make (B5, B10 and B20) blends. Similarly these values were close to those of DF2 (Figure 4.8 and 4.9), hence blends up to 20% biodiesel and 80% diesel can give engine performance similar to those of DF2 that may not require major engine modifications

[2]

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[2] The kinematic viscosity measurements were done in triplicate the average value was determined and plotted against the test temperature. The standard deviation of the three entries was determined and is presented in appendix I

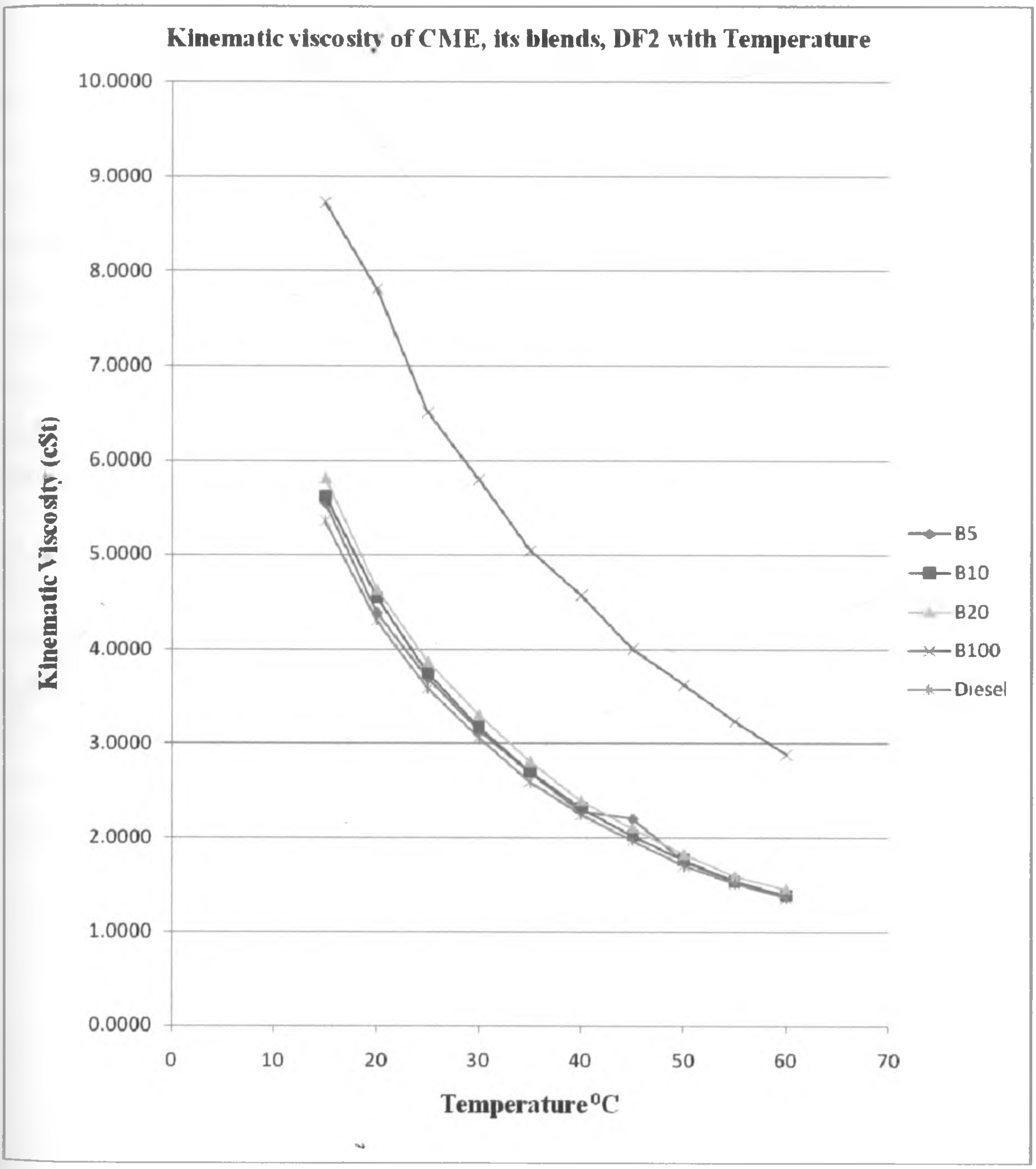

Fig. 4.9: Variation of mean kinematic viscosity with temperature for CME, its blends and DF2.

4.2.3 Acid value

The acid values of the fuel samples determined are shown in Table 4.2. The acid values for unprocessed oils were high above the limit set by ASTM D975, with neat *Jatropha curcas* oil giving the highest acid value of 9.585 mgKOH/g oil as compared to other fuel samples. This may be due to presence of free fatty acids. This value was higher than that reported by Kimilu (2007) and Munavu (1982) who reported values of 0.8939 and 3.52 mgKOH/g respectively. The acid values for B100 samples as determined were 96.37% (JME) and 87.96% (CME) lower than that of neat *Jatropha curcas* and *Croton megalocarpus* oils respectively, Table 4.1. According to ASTM D975, the maximum limit for acid number is 0.8mgKOH/g. From table 4.1 all measured samples gave acid values that were within this range

4.2.4 Iodine value

The iodine values of the fuel samples are shown in Table 4.2 below. The measured iodine values for all the fuel samples were found to be within the allowed maximum limits of 115gI_2/100g oil and 120gI_2/100g oil as per ASTM D6751 and EN 14214 respectively except for neat *Croton megalocarpus* oil which gave a high iodine value of 133.849gI_2/100g oil. The iodine value for *Croton megalocarpus* obtained is almost similar to that reported by Munavu and Odhiambo (1984) of 133gI_2/100g oil.

[3]

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[3] The acid value, iodine value and the calorific value measurements were done in duplicate; table 4.2 presents the average value.

Table 4.2: The iodine values, acid values and calorific values for neat oils, neat B100 and their blends with DF2

Sample	Acid Value (mgKOH/g oil)	Iodine Value (mg I_2/g oil)	Calorific Value (MJ/Kg)
Jatropha oil	9.585	102.426	35.777
Croton oil	2.765	133.849	36.41
CME BLENDS			
B5	0.112	3.384	40.333
B10	0.116	20.737	39.777
B20	0.237	25.984	39.507
B100	0.333	111.038	34.833
JME BLENDS			
B5	0.119	20.068	40.968
B10	0.12	23.449	39.673
B20	0.216	26.857	39.488
B100	0.348	88.83	35.32
DF2	0	0	41.907

4.2.5 Calorific value (Heating value)

The calorific value for neat *Jatropha curcas* and *Croton megalocarpus* oils and their blends with DF2 are shown in Table 4.2. The calorific values of JME (B100) and CME (B100) blends obtained were 35.320 MJ/Kg and 34.833 MJ/Kg respectively. The values are 15.72% and 16.88% respectively lower than that of conventional diesel fuel. The calorific value for JME (B100) is lower than that reported by Kimilu (2007) and Jefferson et al., (2009). The calorific value of neat J*atropha curcas* oil was high but that of *Croton megalocarpus* oil was lower than that reported by Munavu and Odhiambo (1984) of 31.50 and 37.60 MJ/Kg respectively (Appendix VI). From the results it is observed that the calorific value is a function of the percentage of methyl esters blended with diesel, it decreased as the methyl ester percentage increased. The slight difference can be attributed to difference in sources of the plant seeds, the age of the oil as well as analytical methods used.

4.3 EFFECT OF BLENDING METHYL ESTERS ON THE PHYSICOCHEMICAL PROPERTIES OF METHYL ESTERS

The other major objective of this research project was to study the effect of blending JME and CME (different proportions) on the physicochemical properties of biodiesel and to compare the results to those of pure JME and CME biofuels. Biodiesel mixtures consisting of *Jatropha curcas methyl esters* (JME) and *Croton megalocarpus methyl esters* (CME) were prepared in the following proportions; 25%JME and 75%CME, 50%JME and 50%CME and 75% JME and 25%CME. The physicochemical properties studied included;

- Specific gravity
- Kinematic viscosity
- Acid value
- Iodine value
- Calorific (Heating) value

4.3.1 Specific gravity

The measured specific gravities are presented in appendix (I). Figures 4.10 to 4.13 give the relationship of the effect of temperature on the measured specific gravities of biodiesel consisting of a mixture of JME and CME, neat methyl esters of jatropha and croton and their blends with diesel for comparison. The effect of temperature change was investigated by heating the biodiesels. The specific gravities of neat biodiesel as well as their blends was analyzed at preheated temperature ranging from 15°C to 60°C with an increment of 5°C to simulate engine performance.

The results as presented in Figure 4.10 shows that the specific gravities of B5 blends were close and almost similar to that of diesel oil at all test temperatures. JME50% and CME50% B5 blends gave higher values at temperatures below 40°C as compared to other blends.

Biodiesel blends containing 10% and 20% methyl esters had specific gravity values higher than those of diesel though comparable (Figures 4.11 and 4.12) below. However, the specific gravities of neat methyl esters were significantly higher than that of diesel but decreased remarkably with increasing temperature, Figure 4.13. Since DF2 was present in high percentage in all blends, (B5, B10, B20) the results fuel blends adopted the diesel properties

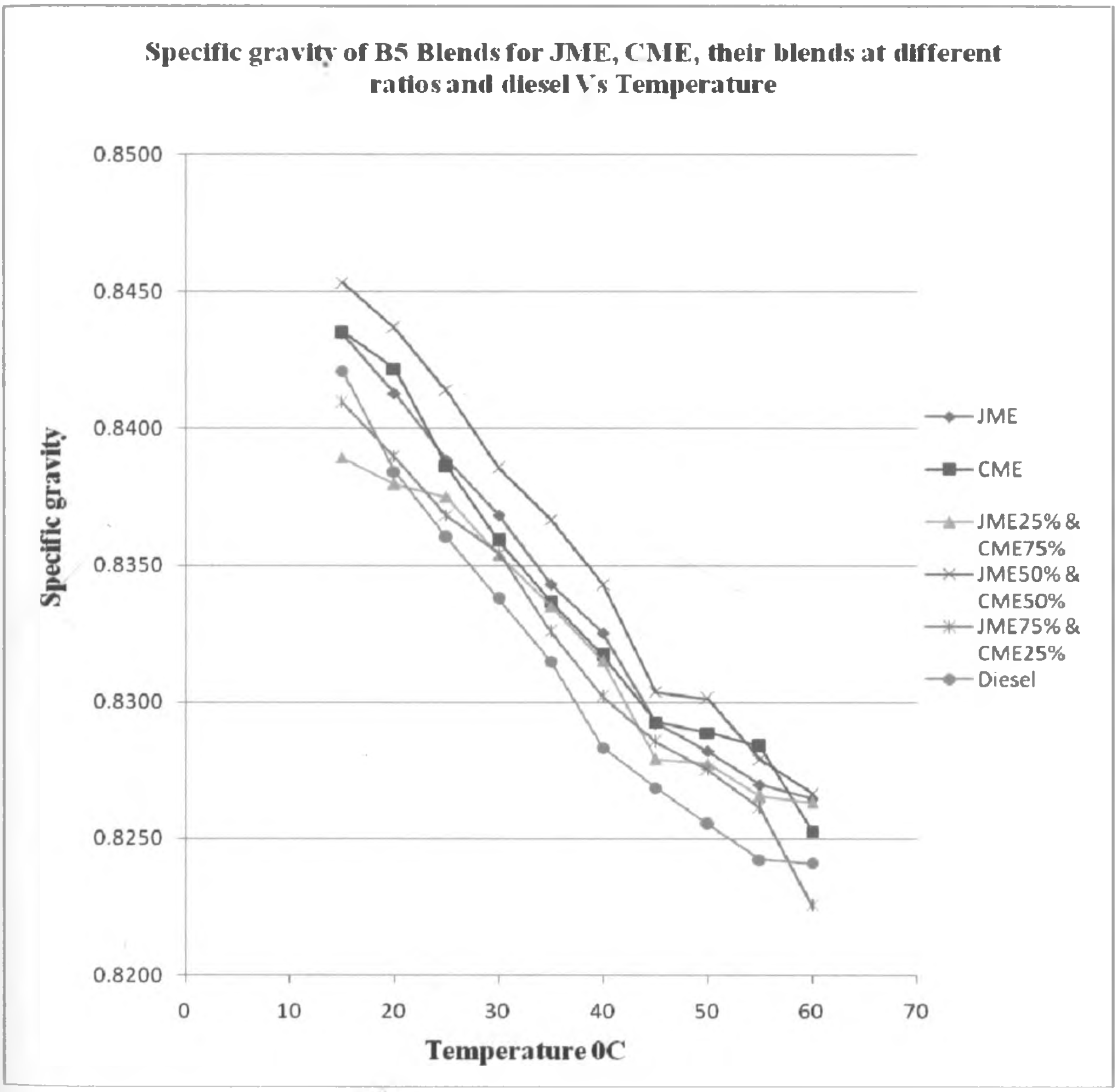

Fig. 4.10: Variation of specific gravity with temperature for the B5 blends of JME, CME, their blends at different ratios and DF2.

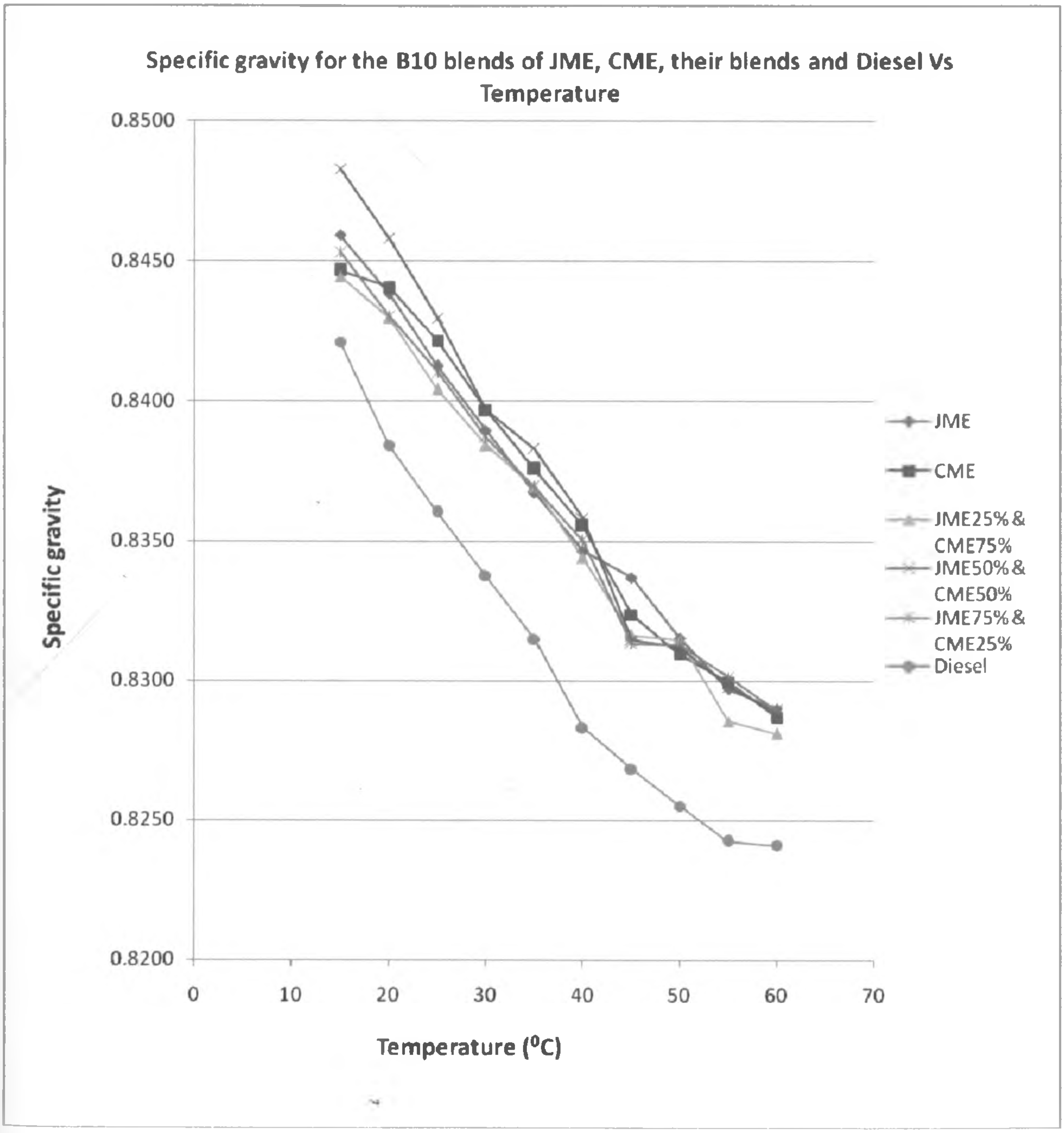

Fig. 4.11: Variation of mean specific gravity with temperature for the B10 blends of JME, CME, their blends at different ratios and DF2.

From Figures 4.10 to 4.13 it can be noted that the specific gravity values of B5, B10, B20 and B100 blends for CME75% & JME25%, CME50% & 50%JME and CME25% & 75%JME are similar and in the same range as those of pure *jatropha* and *croton* methyl esters, there was no significant difference. However, their variation as compared to those of diesel is high at higher biodiesel blends with diesel (B10 and B20).

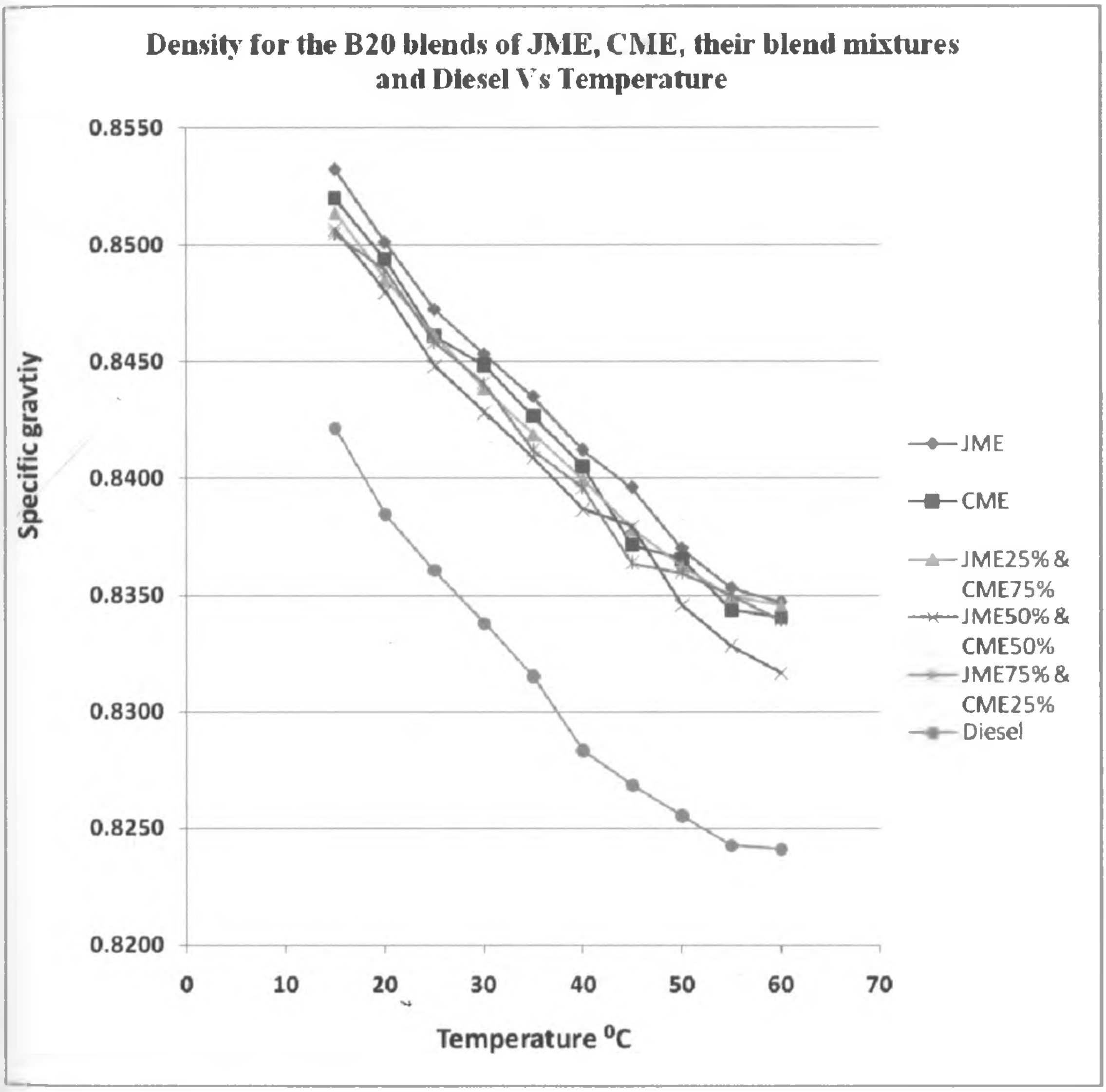

Fig. 4.12: Variation of specific gravity with temperature for the B20 blends of JME, CME, their blends at different ratios and DF2

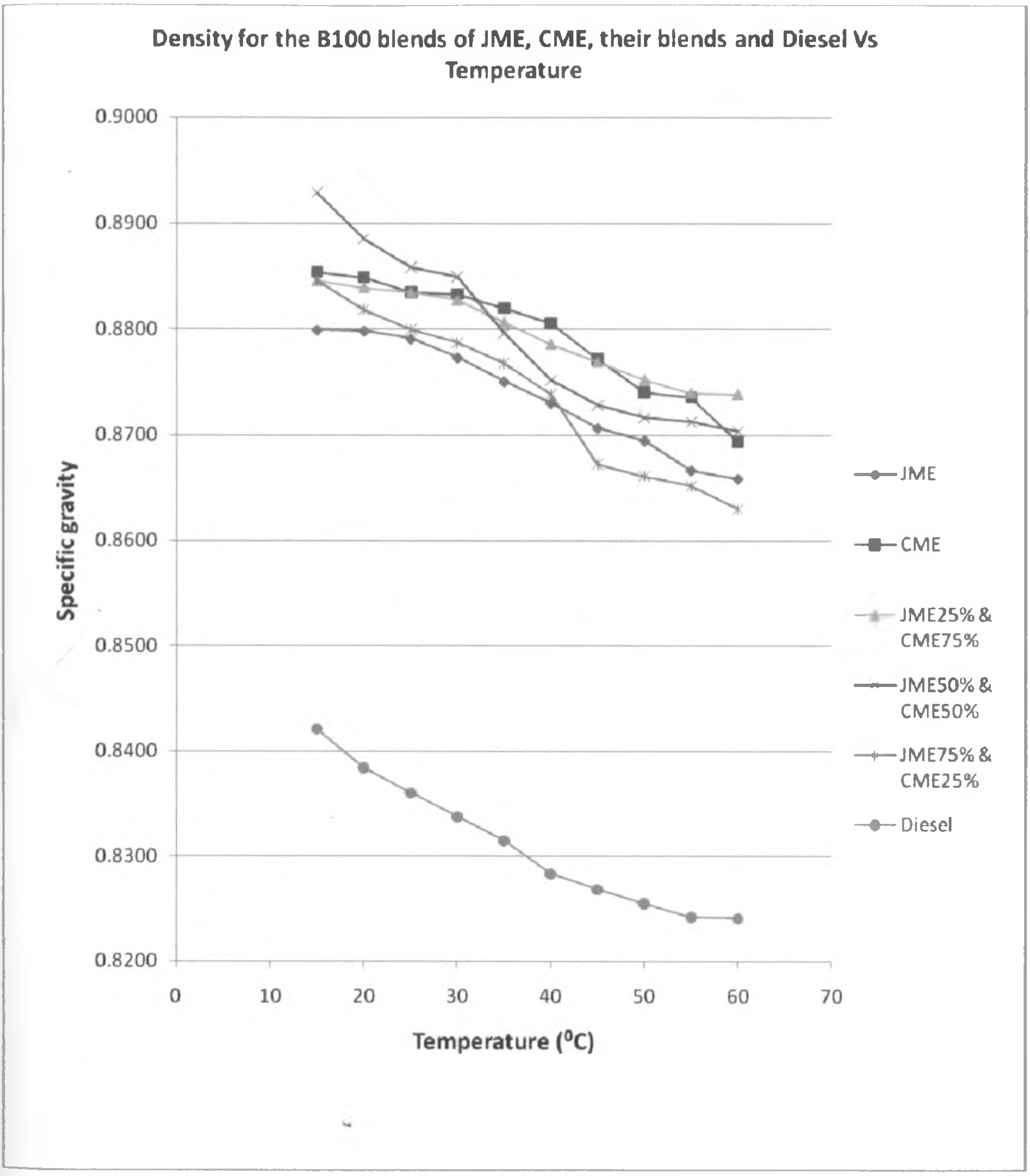

Fig. 4.13: Variation of mean specific gravity with temperature for the B100 blends of JME, CME, their blends at different ratios and DF2

4.3.2 Kinematic viscosity

The measured kinematic viscosities are presented in appendix (II). From the properties of the blends shown in appendix (II), it can be observed that neat biodiesel (JME and CME) and their blends at different ratios have high kinematic viscosity compared to diesel. Blending with diesel up to B20 reduced the viscosity comparable to that of diesel and made it suitable to be used in the diesel engine without major engine modifications.

Figures 4.14 to 4.17 gives the relationship of the effect of temperature on the measured kinematic viscosities of biodiesel consisting a mixture of JME and CME at different ratios, neat methyl esters of jatropha and croton and their blends with diesel. From the results it can be observed that at temperatures above 40°C the kinematic viscosity of the three blends (B5, B10 and B20) varied very slightly with increase in temperature.

Literature review, show that heating biodiesel makes its spray characteristics more like those of diesel oil, which is the direct result of viscosity reduction. Therefore, the effect of temperature change was investigated by heating the biodiesels. The viscosities of neat biodiesel as well as the blends were analyzed at preheated temperature in the range of 15 °C to 60°C with an increment of 5°C to simulate engine performance.

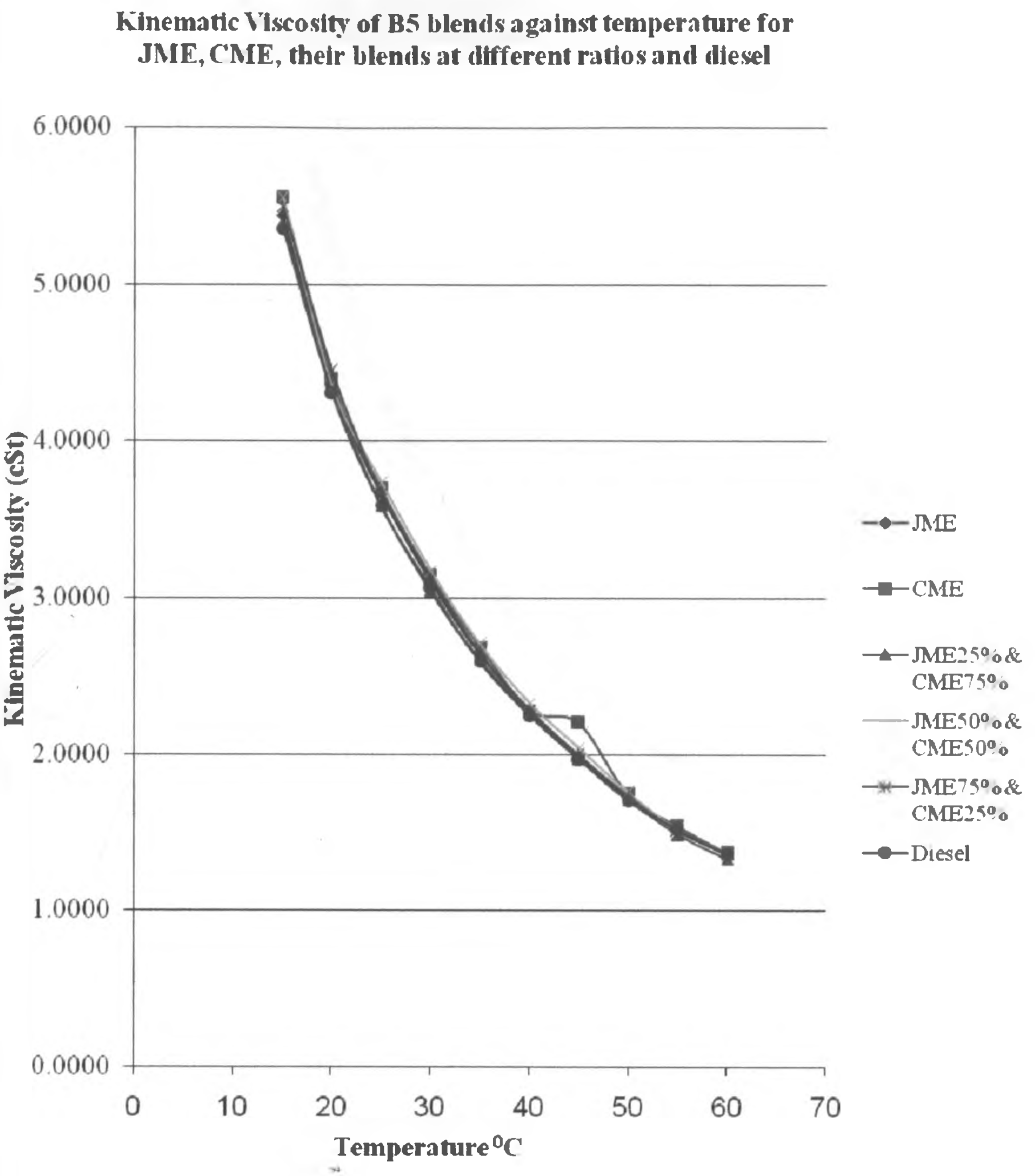

Fig. 4.14: Variation of mean kinematic viscosity with temperature for the B5 blends of JME, CME, their blends at different ratios and DF2.

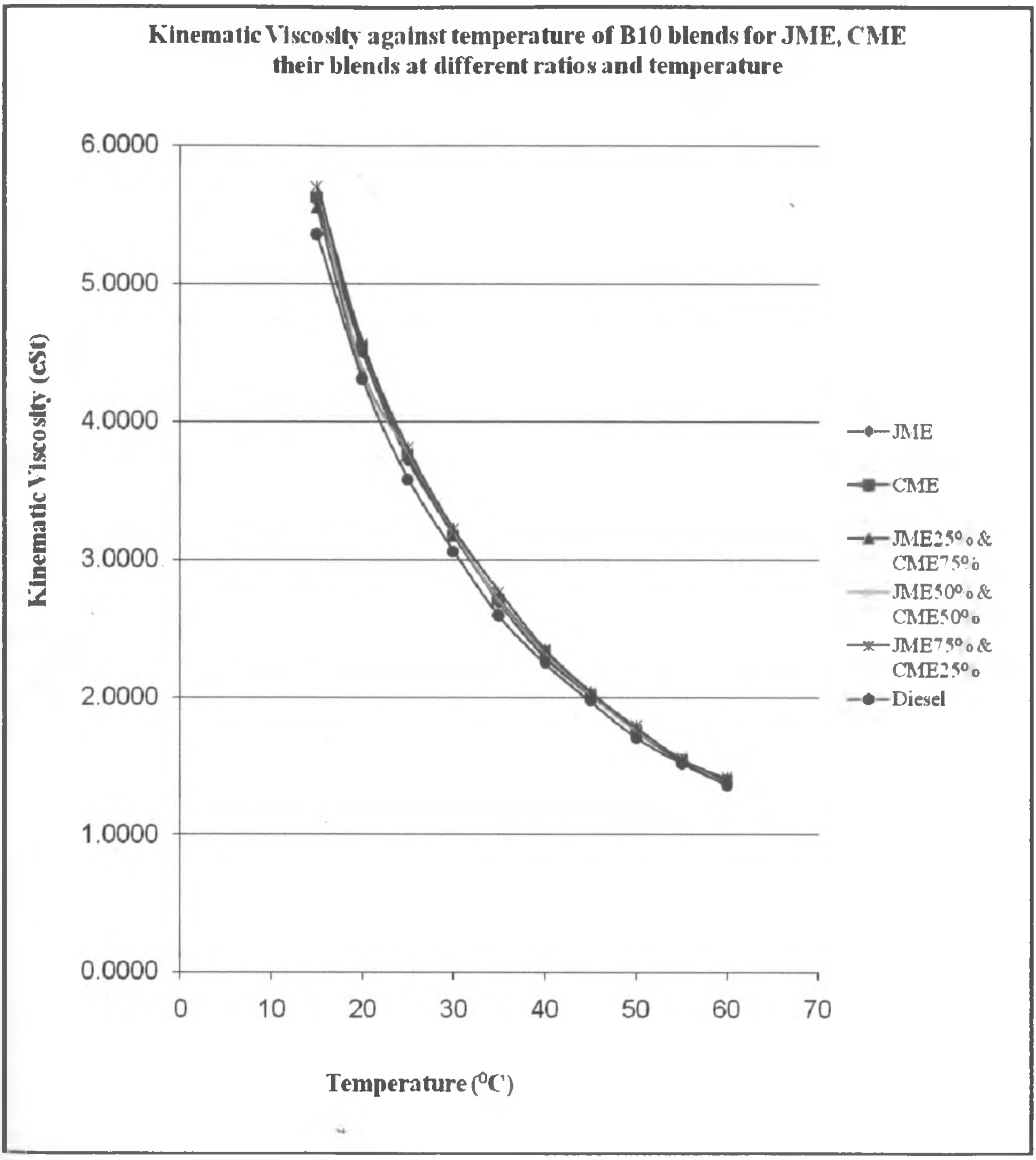

Fig. 4.15: Variation of mean kinematic viscosity with temperature for the B10 blends of JME, CME, their blends at different ratios and DF2

The results as presented in Figures 4.14 and 4.15 shows that the kinematic viscosity of B5 and B10 blends are close to that of diesel oil at all measured temperatures. On the other hand biodiesel blends containing 20% methyl esters had viscosity almost similar to diesel oil at temperatures over 35°C. However, the viscosity of neat biodiesel oil was higher than that of diesel but decreased remarkably with increasing temperature and it became close to diesel oil at temperatures above 40°C.

From Figures 4.14 to 4.16 it can be noted that the kinematic viscosity values of B5, B10 and B20 blends for JME25% & CME75%, CME50% & 50%JME and CME50% & 50%JME are similar to those of unmixed biodiesel, there is no significant difference. However, from Figure 4.17 the difference is distinct for B100. Neat biodiesel mixtures gave kinematic viscosities that were less than those of isolated JME and CME at all test temperatures. Thus this gives an explanation that there exist differences in physical properties of neat isolated methyl esters from those of a mixture of methyl esters in their neat form.
[4]

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[4] Both the specific gravity and kinematic viscosity measurements were done in triplicate, the average value was plotted against the test temperature. Standard deviation of the three measurements was determined and is presented in the appendix

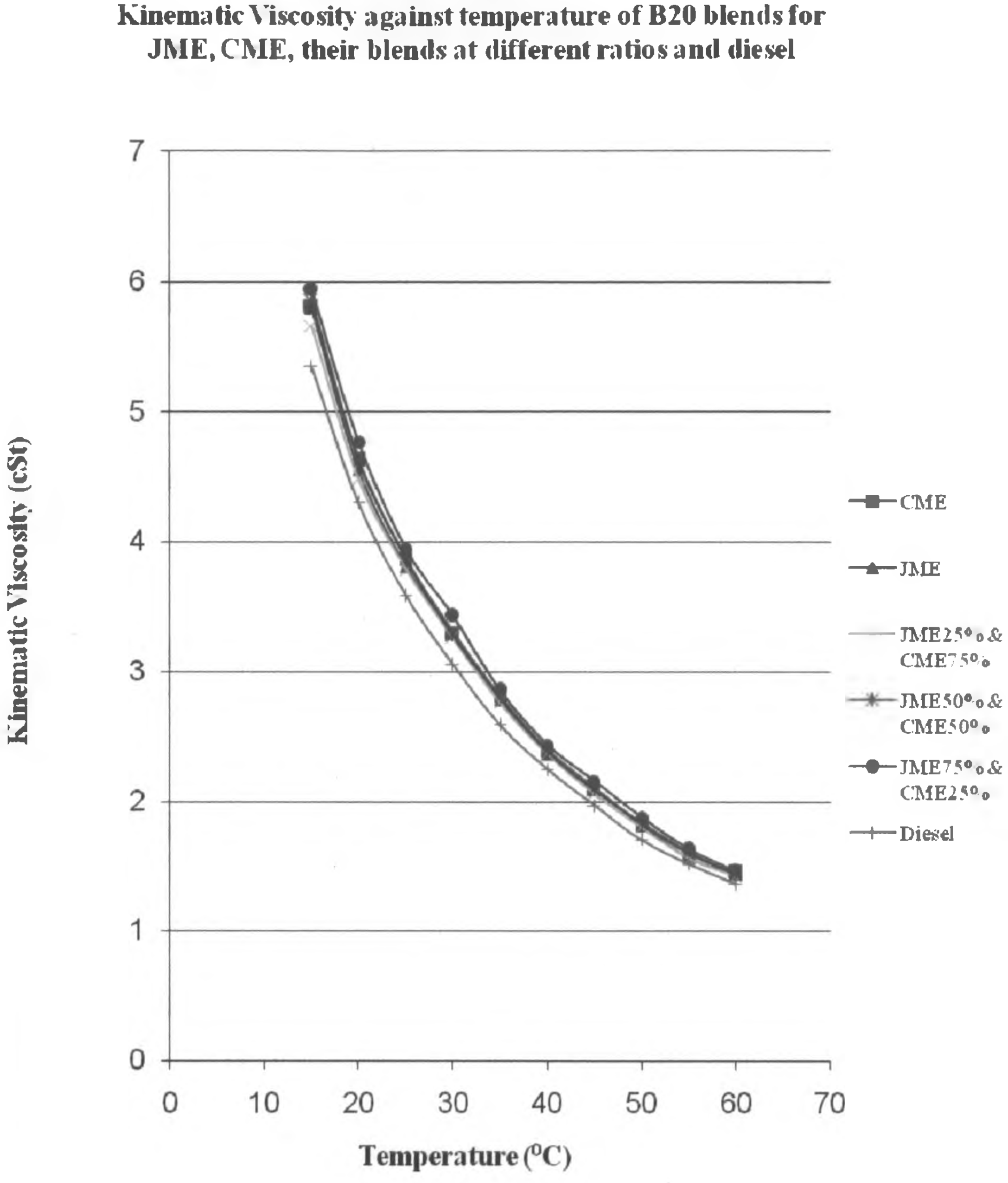

Fig. 4.16: Variation of kinematic viscosity with temperature for the B20 blends of JME, CME, their blends at different ratios and DF2

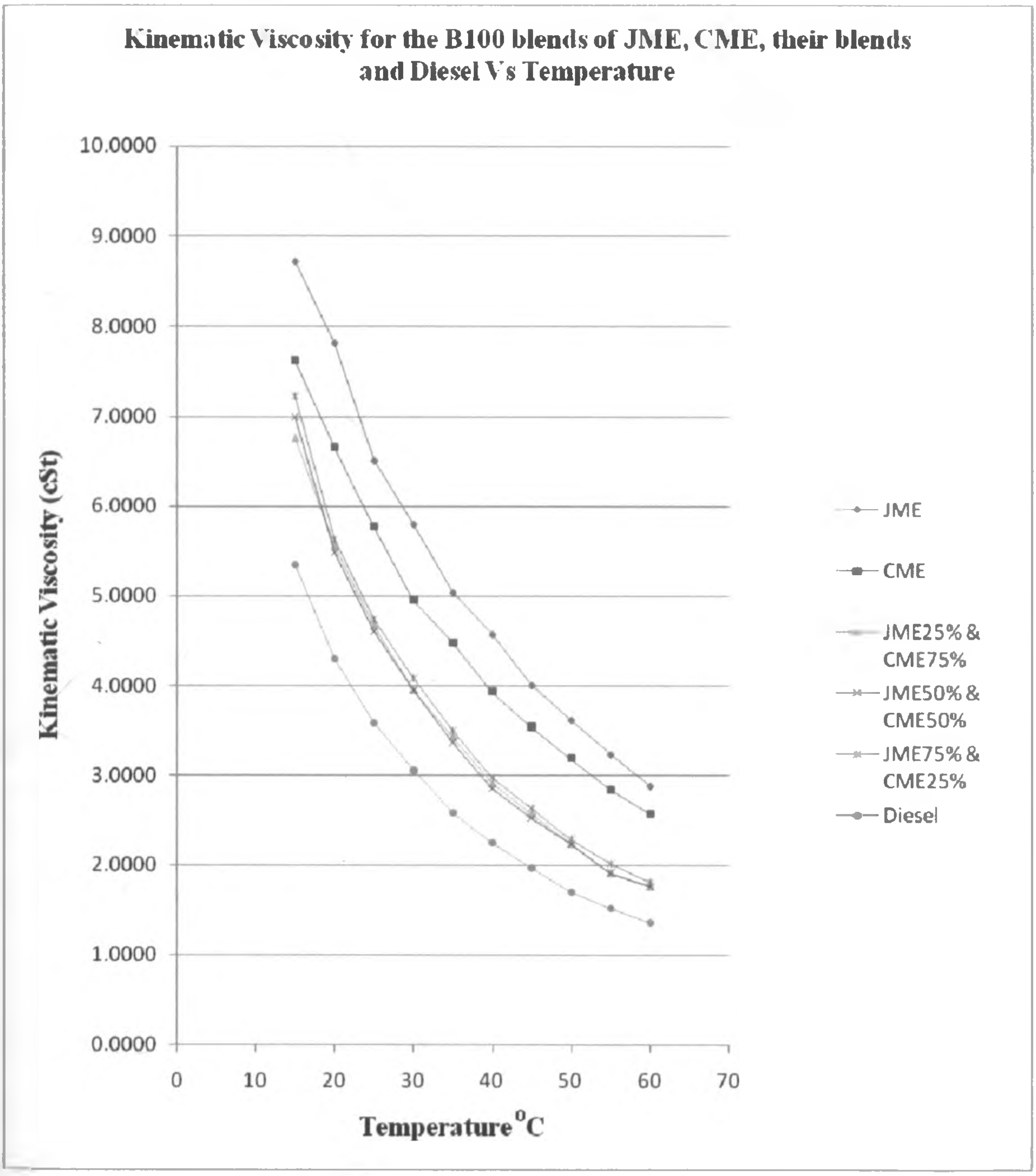

Fig. 4.17: Variation of mean kinematic viscosity with temperature for the B100 blends of JME, CME, their blends at different ratios and DF2

4.3.3 Acid value

The acid values of the fuels are summarized in Table 4.3. The results obtained were all within the maximum allowed limit of 0.8mgKOH/g as per ASTM D 975 with B100 blends giving high values as compared to other blends. A relationship can be generated between the acid number and percentage of biodiesel in a given blend, the higher the biodiesel percentage the higher the acid value.

Table 4.3: The iodine values, acid values and calorific values for neat B100 blend mixtures and their blends with DF2

Sample	**Acid Value (mgKOH/g oil)**	**Iodine Value (mg I_2/g oil)**	**Calorific Value (Mj/Kg)**
Case of 25%JME 75% &CME Blends			
B5	0.113	17.333	40.757
B10	0.113	27.495	39.978
B20	0.222	27.27	39.582
B100	0.352	111.614	35.41
Case of 50%JME & 50%CME Blends			
B5	0.115	21.503	39.454
B10	0.235	16.714	39.387
B20	0.24	27.05	38.663
B100	0.34	109.488	35.367
Case of 75%JME 25% & CME Blends			
B5	0.119	10.833	38.812
B10	0.123	10.575	37.473
B20	0.243	24.84	37.505
B100	0.34	98.465	35.291

4.3.4 Iodine Value

The measured iodine values are summarized in Table 4.3. All values obtained were within the maximum allowed limits of 115gI_2/100g oil and 120gI_2/100g oil as per ASTM D6751 and EN 14214 respectively. The blends with high croton methyl ester percentage gave high iodine values (especially the higher blends except B5).[5]

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[5] Acid value, iodine value and calorific value measurements were done in duplicate, table 4.3 presents the average values.

4.3.5 Calorific Value

The measured calorific values are also shown in Table 4.3. The values obtained shows dependency on the percentage of methyl ester contained in a given blend, the higher the methyl ester composition, the lower the calorific value. Since biodiesel has lower energy content compared to commercial diesel, blends with higher percentage of methyl esters are expected to have low calorific value. Blends with high jatropha methyl ester percentage gave low calorific values as compared to blends with high croton methyl ester percentage.

4.4 DETERMINATION OF PHYSICOCHEMICAL PROPERTIES OF CROTON B100

CME B100 was analyzed for kinematic viscosity, acid value and cloud point using American Standards for Testing and Material (ASTM). The neat CME was sampled from the first batch of biodiesel produced whereas samples for the laboratory test were taken from the last batch of biodiesel produced. The results obtained by ASTM methods are summarized in the table 4.3 below and are compared to those obtained using laboratory methods.

Table 4.4: Physicochemical properties using ASTM methods

Property analyzed	ASTM method	*Value obtained	Value obtained from the lab
Kinematic Viscosity @ 40°C	D445	3.8006	3.9297
Acid value	D974	0.275	0.333
Cloud point	D2500	8 °C	Not determined

* US laboratory (WMU)

Before analyzing using ASTM methods, the neat CME was subjected to high vacuum distillation to remove any traces of unreacted mono glyceride, di glyceride and triglyceride to enhance purity of the biodiesel. From the results, the differences between the values of the respective properties investigated were comparable even though the laboratory methods used gave slightly high values. Kinematic viscosity was 3.4% higher while acid value was 17% higher. Both kinematic viscosity value and acid value obtained are within the allowed limits as stipulated by the standard methods used (ASTM D445 and ASTM D974). The results thus show the reproducibility of the method used to produce croton biodiesel by transeterification.

4.5 IDENTIFICATION OF FATTY ACID METHYL ESTERS FROM CROTON BIODIESEL

Gas chromatographic analyses were carried out for the identification of fatty acid methyl esters produced from *Croton megalocarpus* oil. The identification of fatty acid methyl esters was based on comparing the retention times of the peaks from the sample (CME B100) and the standards. The results are presented in Figures 4.18 to 4.21 and Table 4.4.

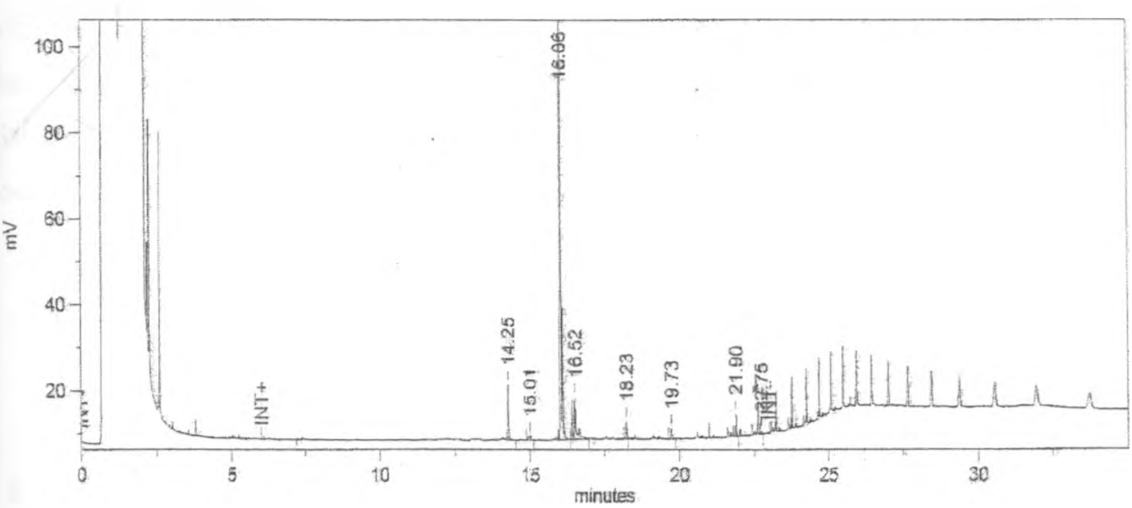

Fig. 4.18: GC spectrum for B100 CME before high vacuum distillation

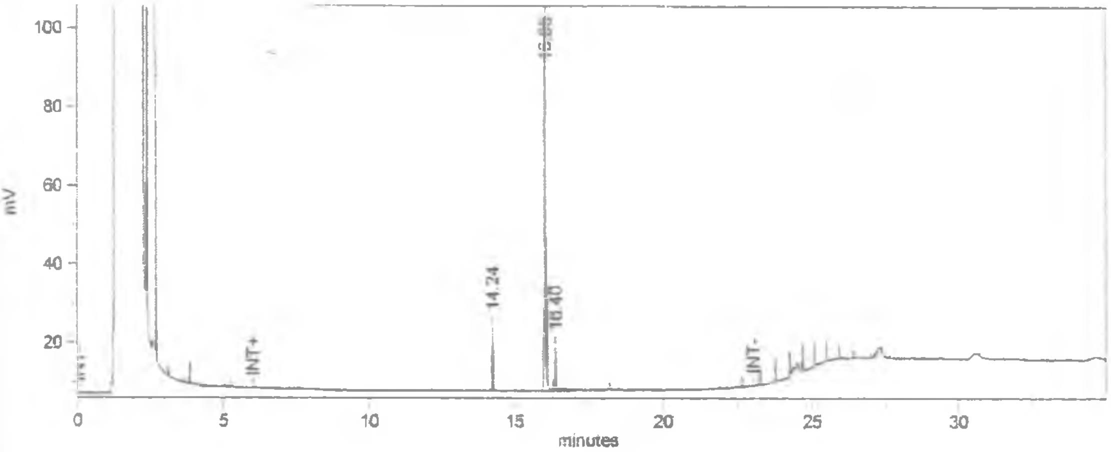

Fig. 4.19: GC spectrum for B100 CME after high vacuum distillation

From the chromatograms of B100 CME it can be observed that before high vacuum distillation there were peaks above 18 min which could be as a result of contamination with unconverted mono-glycerides, di-glycerides and triglycerides (Fig. 4.18). Most of these peaks however disappeared after the B100 CME was subjected to high vacuum distillation leaving only three peaks. Evidently, peaks that appeared at retention times above 18 minutes were eliminated (Fig. 4.19) by the high vacuum distillation process.

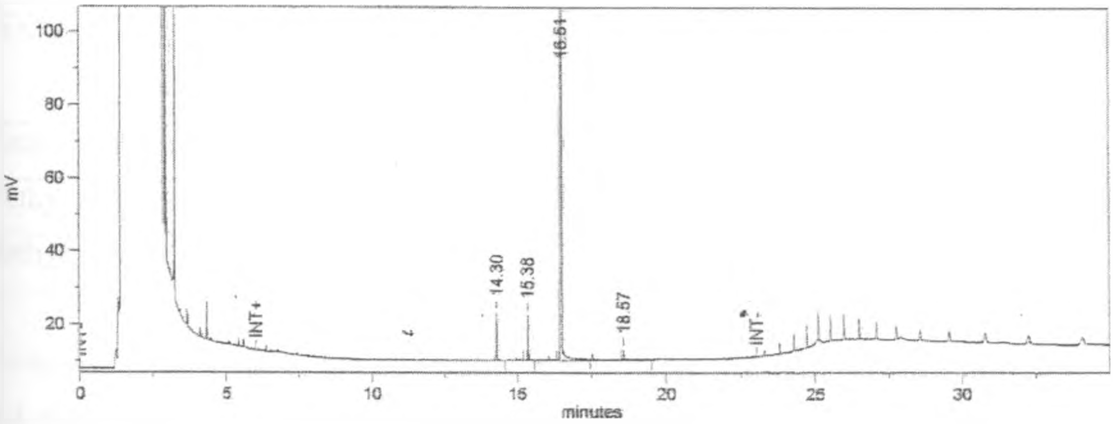

Fig. 4.20: GC spectrum for Methyl Stearate standard

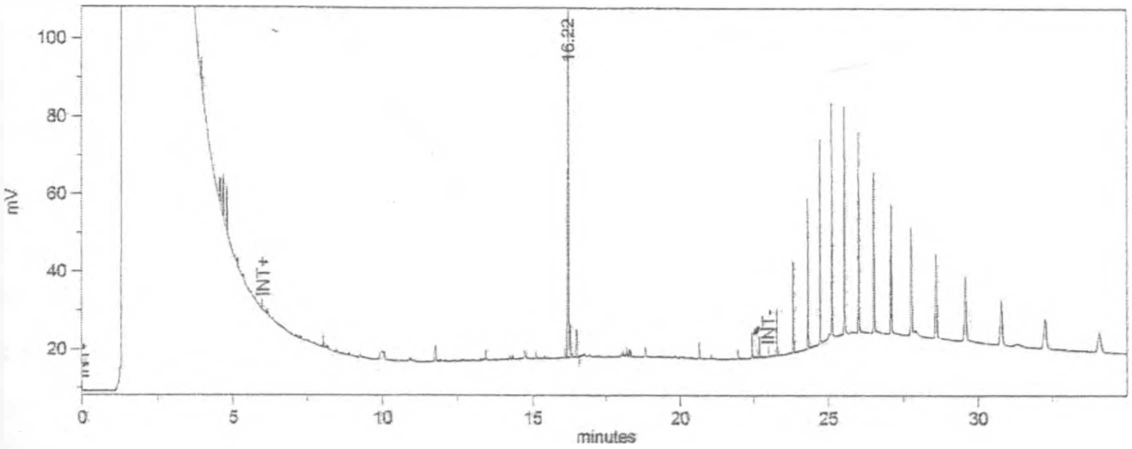

Fig 4.21: GC spectrum for Methyl Oleate standard

On the basis of the chromatogram of the biodiesel sample (Fig. 4.18 and Fig. 4.19) and that of the standards (Fig. 4.20 and 4.21) and the retention times, the main methyl ester components in the sample were identified. Relative fatty acid methyl ester compositions of *Croton megalocarpus* was found to be methyl oleate, methyl stearate and methyl palmitate.

Table 4.5: Retention time and cut time for methyl esters identified from CME (B100)

FAME	Carbon no.	Sample Retention time (mins)	Standard Retention time (mins)	Cut time (mins)
Methyl palmitate	16:0	14.24	14.20	14.15-14.30
Methyl oleate	18:1	16.05	16.22	16.00-16.25
Methyl stearate	18:0	16.40	16.51	16.38-16.60

These results show that croton oil consists of three major acids; palmitic acid, stearic acid and oleic acid. From the results obtained it can therefore be concluded that *Croton megalocarpus* oil has higher percentage of unsaturated fatty acids (oleic acid) and lower percentage of saturated fatty acids (stearic and palmitic acids) as shown by their peak intensities. The unsaturation levels of neat croton oil and CME (B100) as determined by iodine value was 133.849 mg I_2/g oil and 111.038 mg I_2/g oil respectively which is in good agreement with the fatty acid composition data obtained.

4.6 ENGINE PERFORMANCE TESTING

4.6.1 Brake Specific Fuel Consumption

The computed brake specific fuel consumption is presented in appendix (III). Values presented in the appendix are mean values of brake specific fuel consumption. Figures 4.22, 4.23 and 4.24 compares the brake specific fuel consumption of diesel and various fuels namely: JME and CME, mixture of JME and CME and diesel in various proportions at varying brake loads in the range of 5.595 to 39.165. It was observed that the specific fuel consumptions of the blends as well as diesel oil decreased with increasing load from 5.595 to 33.570 and tended to increase with further increase in brake horse power. The brake specific fuel consumptions were comparable for blends of up to B20.

The similarity of the brake specific fuel consumption results for methyl ester blends to those of diesel could be attributed to the combined effects of reduced fuel density, reduced viscosity and increased calorific (heating) value of the blends of up to 20% biodiesel and 80% diesel oil.

There was no significant difference observed on the brake specific fuel consumption between the blends of JME and CME with diesel from those of a mixture of JME and CME with diesel up to B20. All values obtained were comparable.

The difference in the brake specific fuel consumption between neat CME and diesel was clear and significant as shown in Fig. 4.25 below. At lower loads the difference was 2% at 5.595 kW but with increased load, the difference increased to 11.1% at 27.975 kW.

Other tests have shown that the efficiency of conversion of energy power is comparable for biodiesel and the petroleum-based diesel reference fuel. Therefore, the brake specific fuel consumption (BSFC), the parameter most often used by engine manufacturers to characterize fuel economy will be at least 12.5% higher for biodiesel (Van Garpen et al., 2004). Since BSFC measures how much fuel may be required to do a certain quantity of work it automatically implies that the smaller the BSFC, the more efficient the engine. This study has shown that operating the engine on diesel and its blends with up to 20% (B20) of the esters is more efficient than using neat (100%) methyl esters.

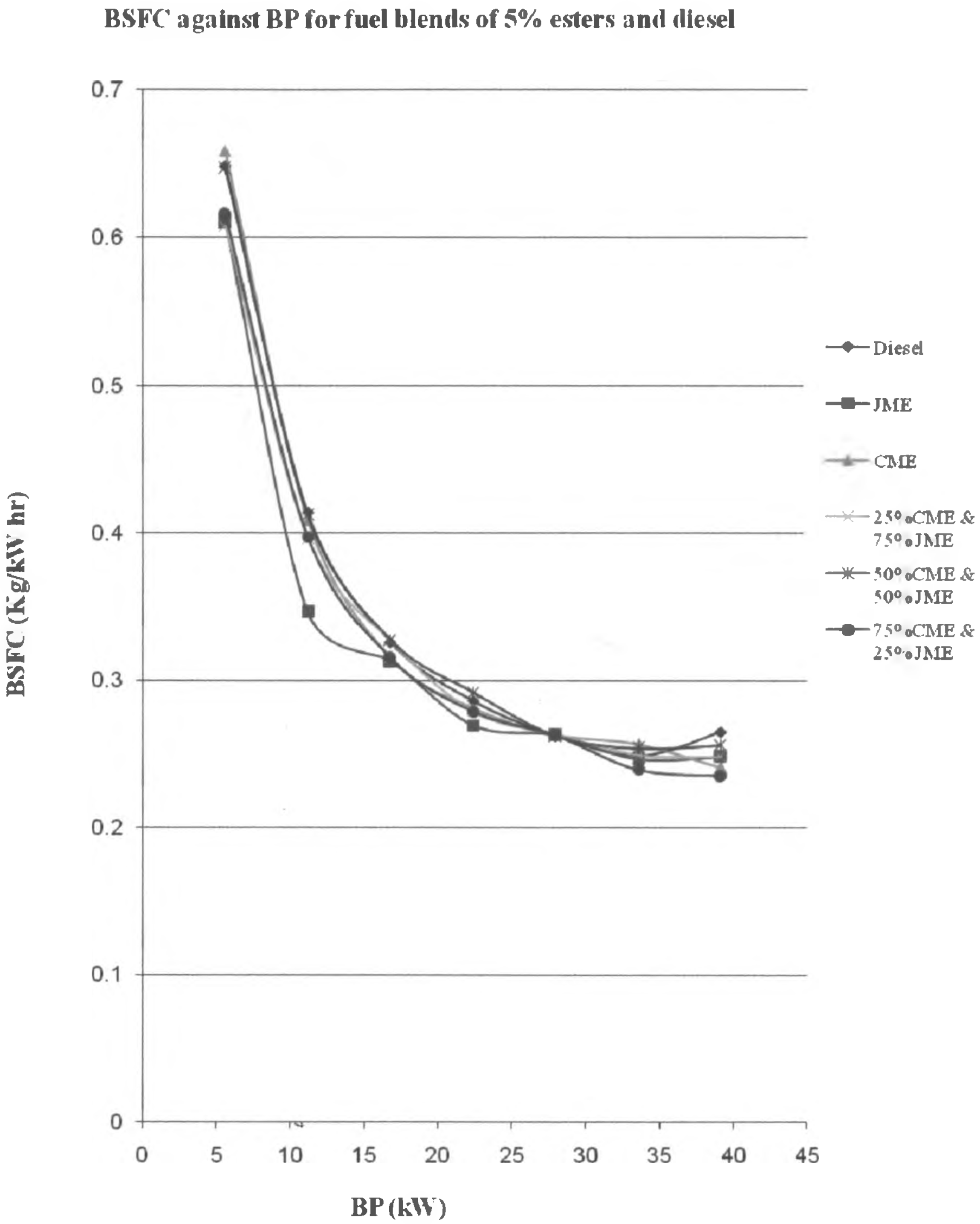

Fig. 4.22: Effect of brake power (BP) on the mean brake specific fuel consumption (BSFC) for B5 blends and diesel.

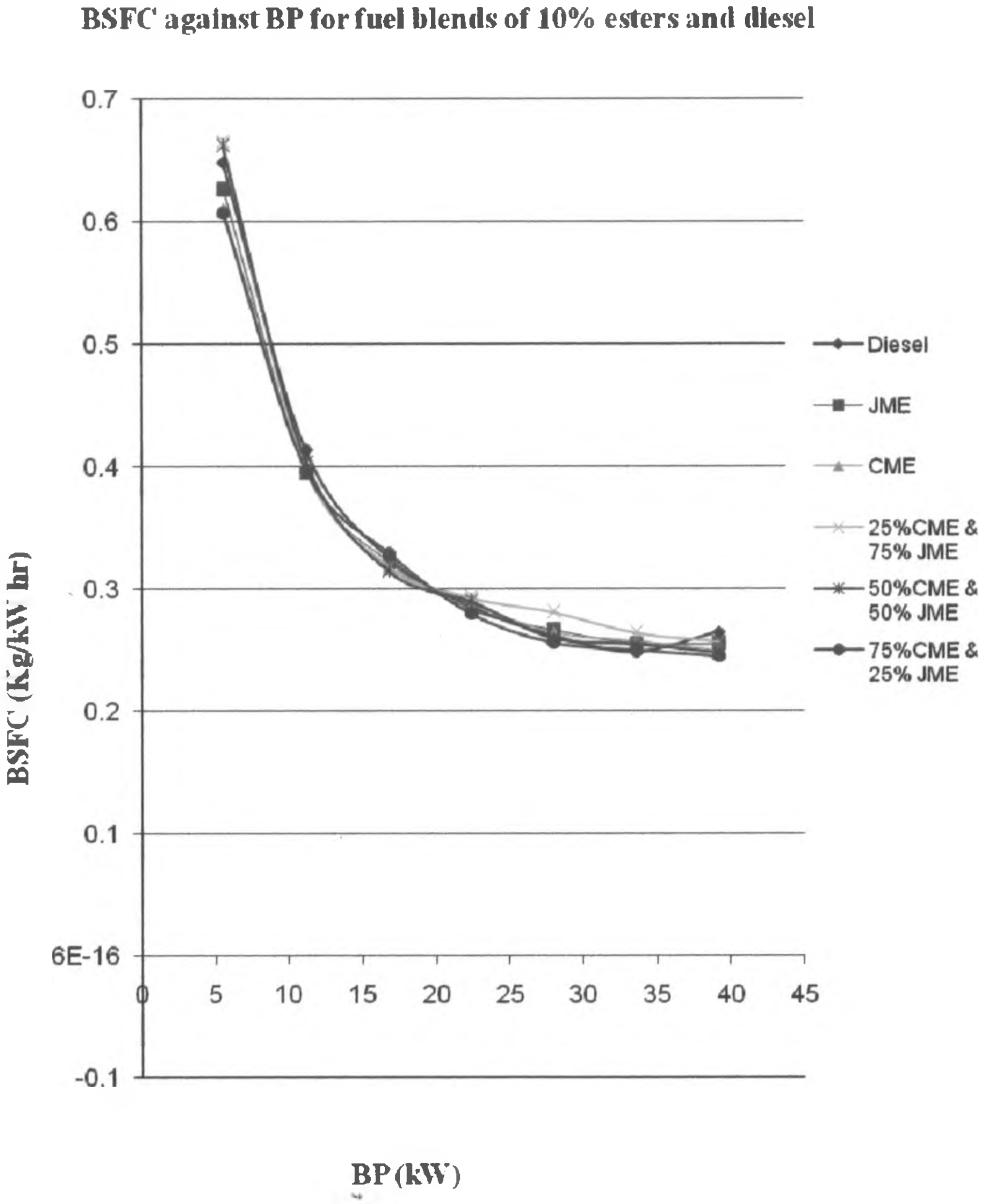

Fig. 4.23: Effect of brake power (BP) on the mean brake specific fuel consumption (BSFC) for B10 blends and diesel.

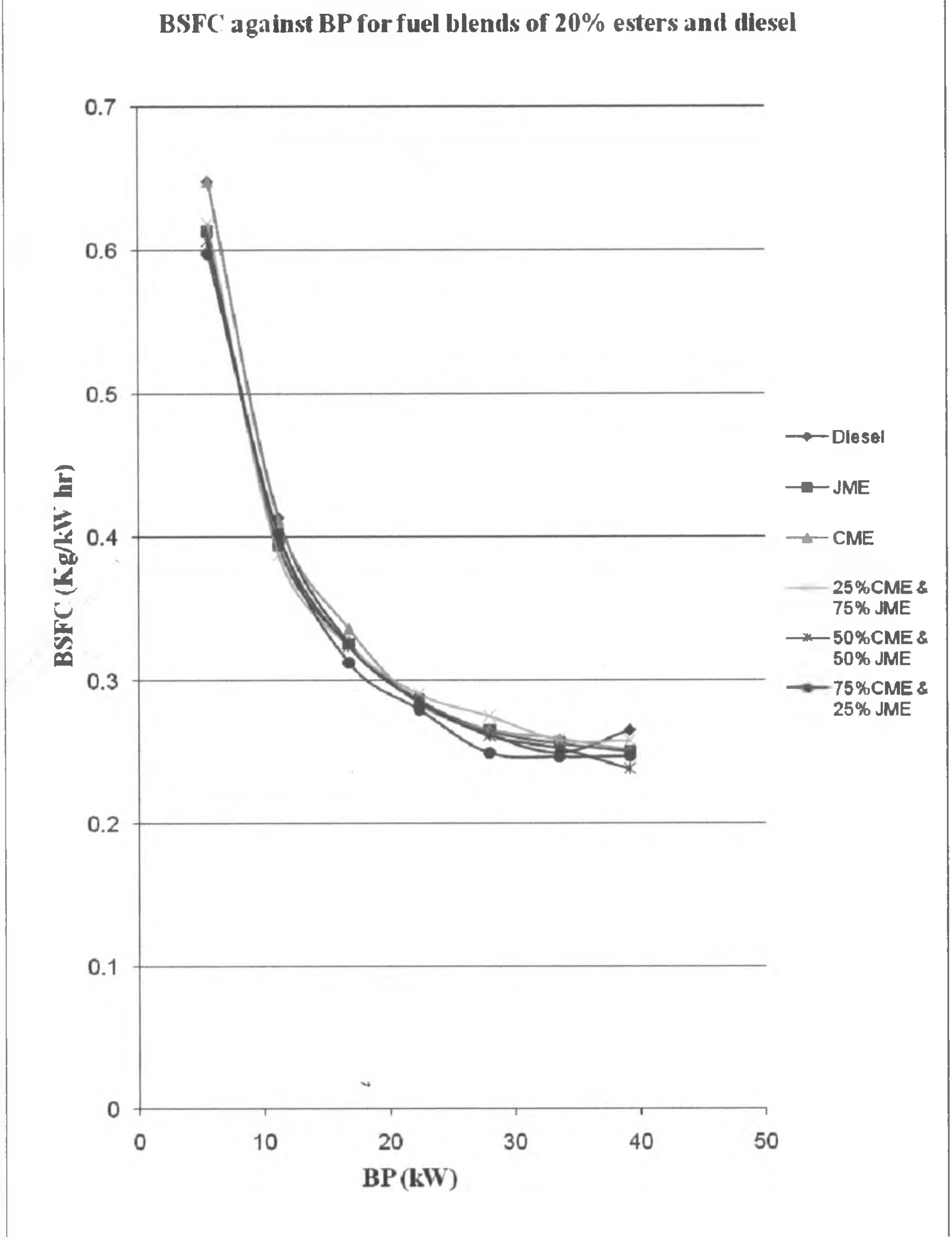

Fig. 4.24: Effect of brake power (BP) on the mean brake specific fuel consumption (BSFC) for B20 blends and diesel.

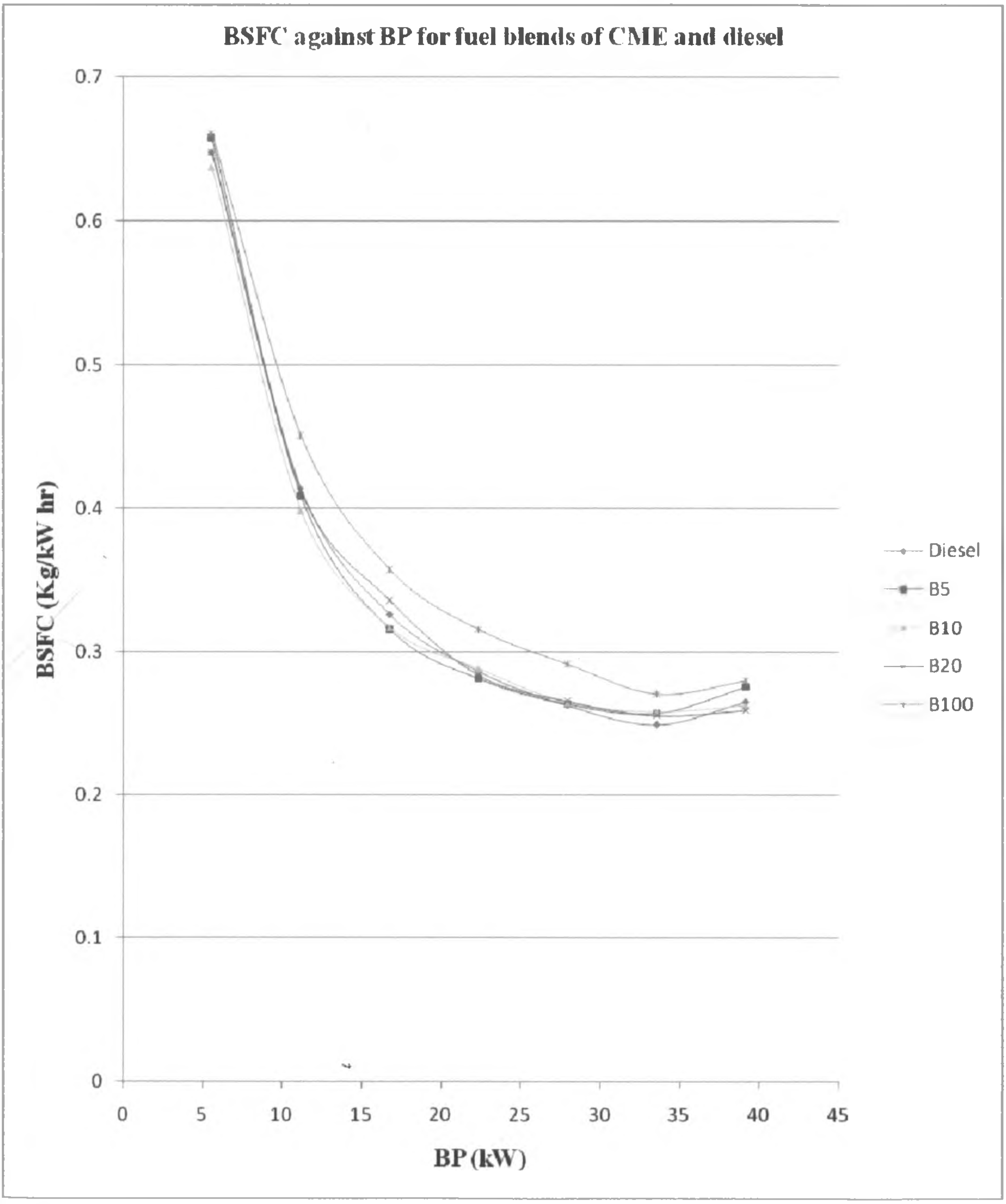

Fig. 4.25: Effect of brake power (BP) on the mean brake specific fuel consumption (BSFC) for CME blends and diesel.

4.6.2 Thermal Efficiency

The measured thermal efficiencies are presented in appendix (III). All values presented are mean average thermal efficiency values. The variation of brake thermal efficiency of the engine at different loads for various biodiesel blends of JME, CME and mixed esters at different ration are shown in Figures 4.26, 4.27 and 4.28 below and compared with the brake thermal efficiency obtained with diesel.

From the test results and from Figures 4.26, 4.27 and 4.28, it was initially observed that with increased brake power, the brake thermal efficiencies of neat CME, diesel and the blends increased and maximum thermal efficiencies were obtained at brake horse power of 33.570. However there was decrease in thermal efficiency with increase in brake power. There was a considerable increase in thermal efficiencies with the blends up to B20 compared to the thermal efficiency of diesel oil. The maximum values of thermal efficiencies with B5, B10 and B20 blends were observed as 36.87%, 37.41% and 37.99% respectively.

No significant difference in thermal efficiency was observed between the blends of JME and CME with diesel and the methyl ester mixtures of JME and CME. This can be due to the fact that since the physicochemical properties were similar, it was expected that the engine performance of the fuel sample must compare to each other.
[6]

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[6] Brake specific fuel consumption and thermal efficiency measurements were done in triplicate; the average value was plotted against the brake power. Standard deviation was determine and is presented in appendix III. Exhaust temperature measurements were only done in duplicate and the average value plotted against the brake power.

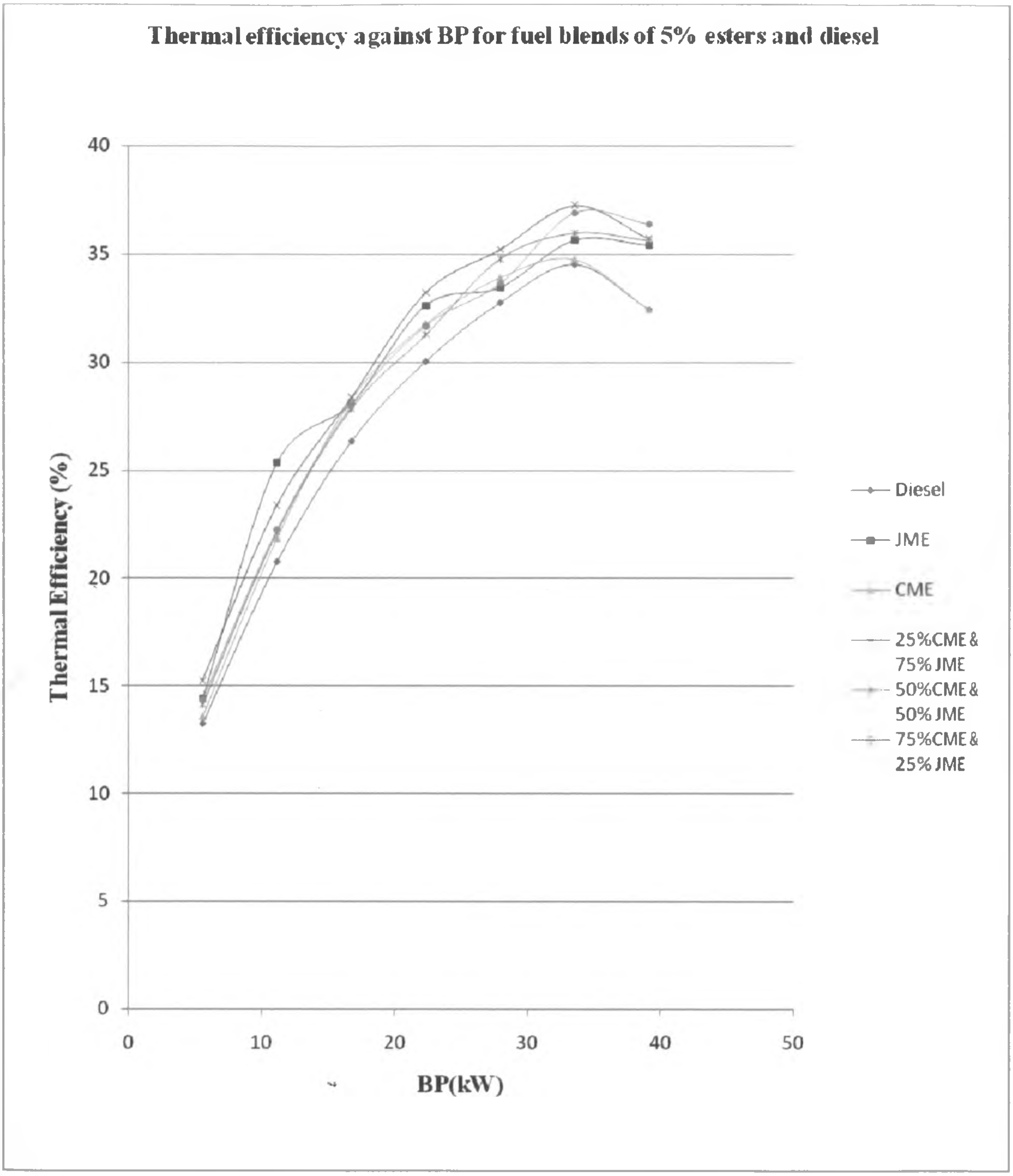

Fig. 4.26: Effect of brake power (BP) on the mean Thermal Efficiency (TE) for B5 blends and diesel

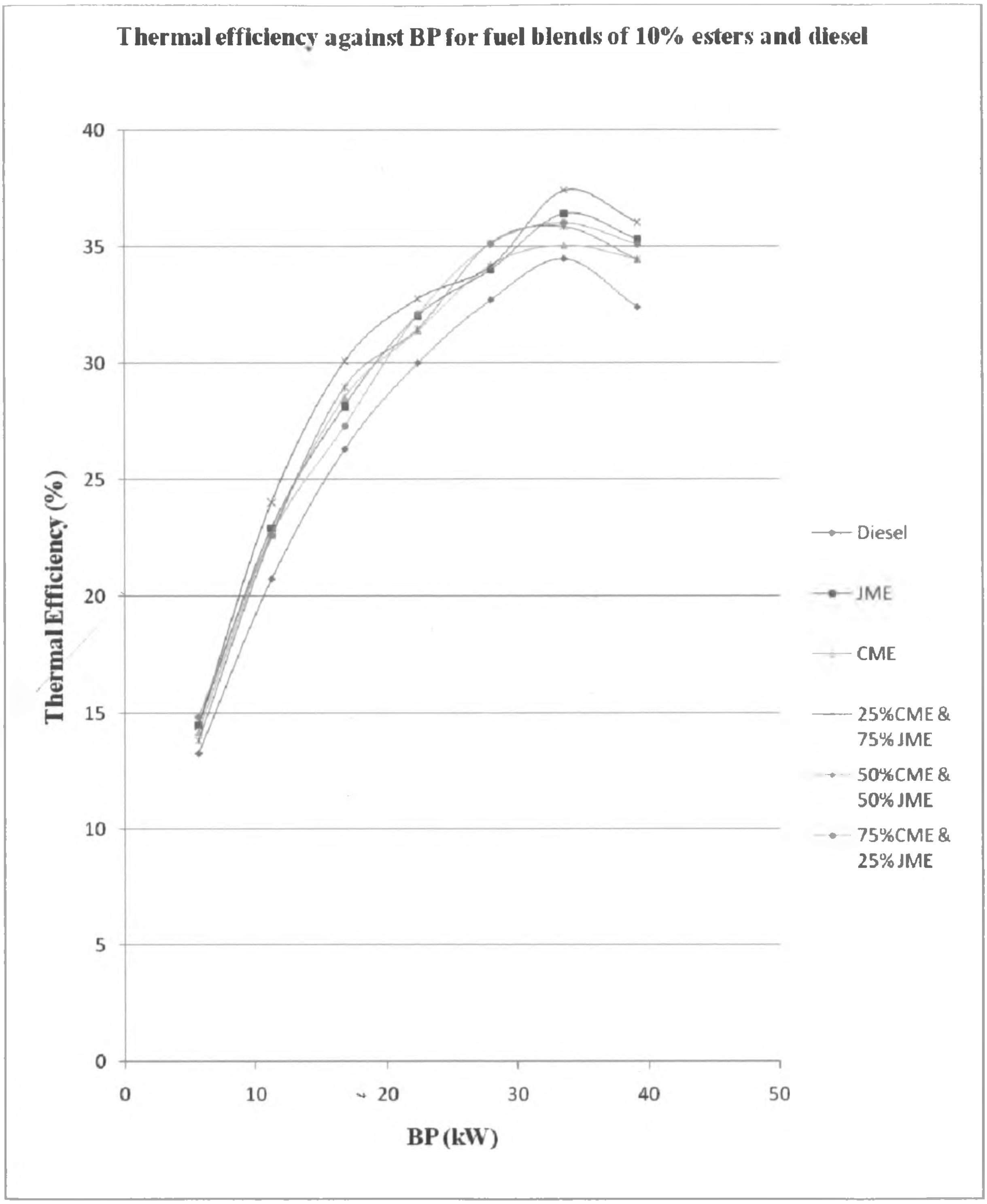

Fig. 4.27: Effect of brake power (BP) on the mean Thermal Efficiency (TE) for B10 blends and diesel

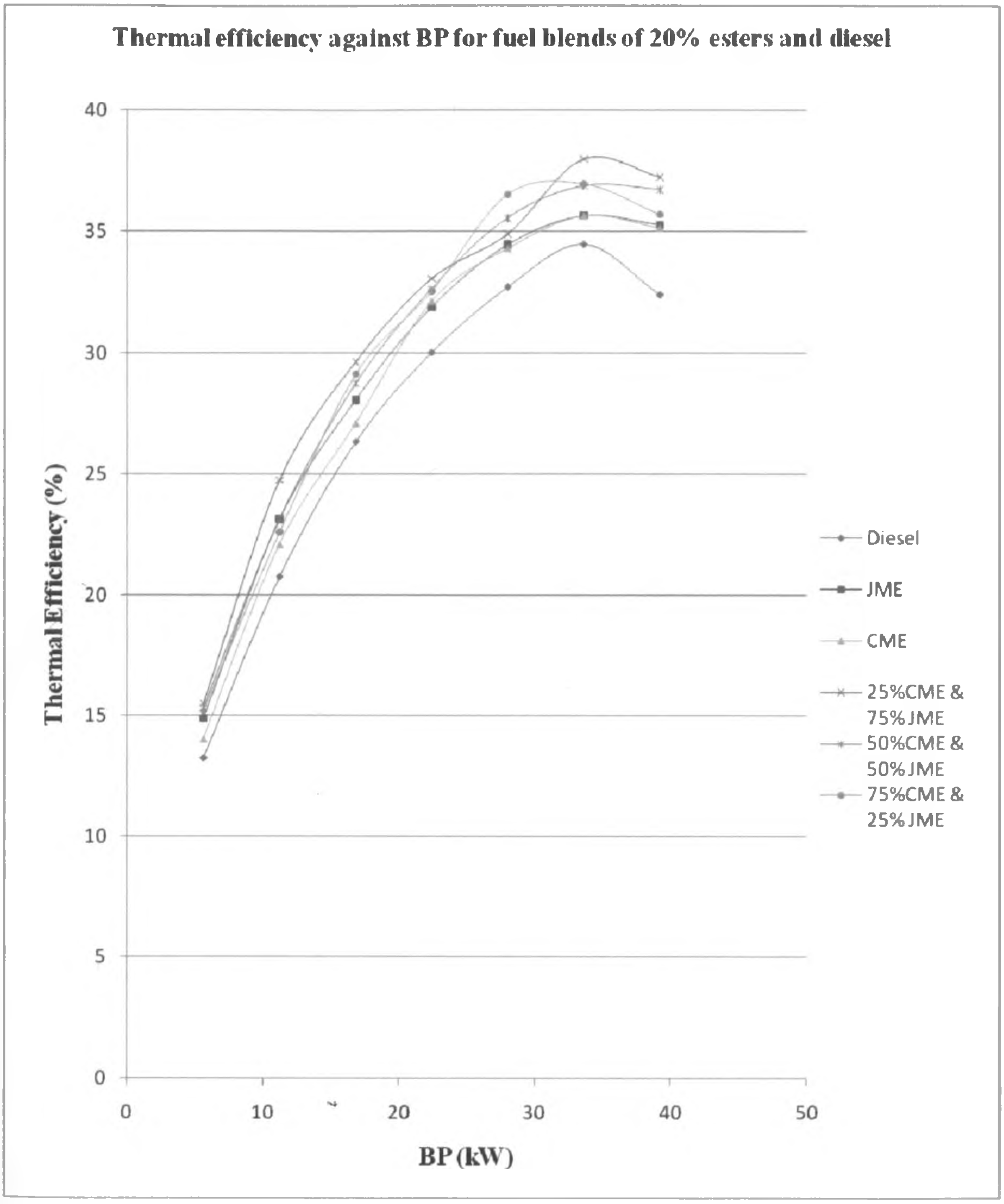

Fig. 4.28: Effect of brake power (BP) on the mean Thermal Efficiency (TE) for B20 blends and diesel

The drop in thermal efficiency with increase in proportion of vegetable oil or neat alkyl ester is always attributed to the poor combustion characteristics due to their high viscosity and poor volatility. The brake thermal efficiency refers to the relationship between actual heat energy stored within the fuel and the power produced in the engine (indicated power), (Pramanik 2003). The thermal efficiency values indicate the amount of potential energy contained in the fuel that is actually used by the engine to produce power.

Hence, in this study, the increase in brake thermal efficiency for neat biodiesel and its blends with diesel up to 20% biodiesel as compared to diesel fuel could be attributed to improved combustion of neat biodiesel and its blends in the engine. It could also be due to increased fuel flow by reducing internal pump leakage (in the case of damaged or old engine) because of high density and viscosity of biodiesel. The lower mass-based heating values of biodiesel and there blends required larger mass fuel flow to maintain constant energy input to the engine. High thermal efficiency implies more of the energy input in the biodiesel fuel and its blends with diesel was converted to work by the engine, thereby decreasing unburned fuel emissions as compared to commercial diesel.

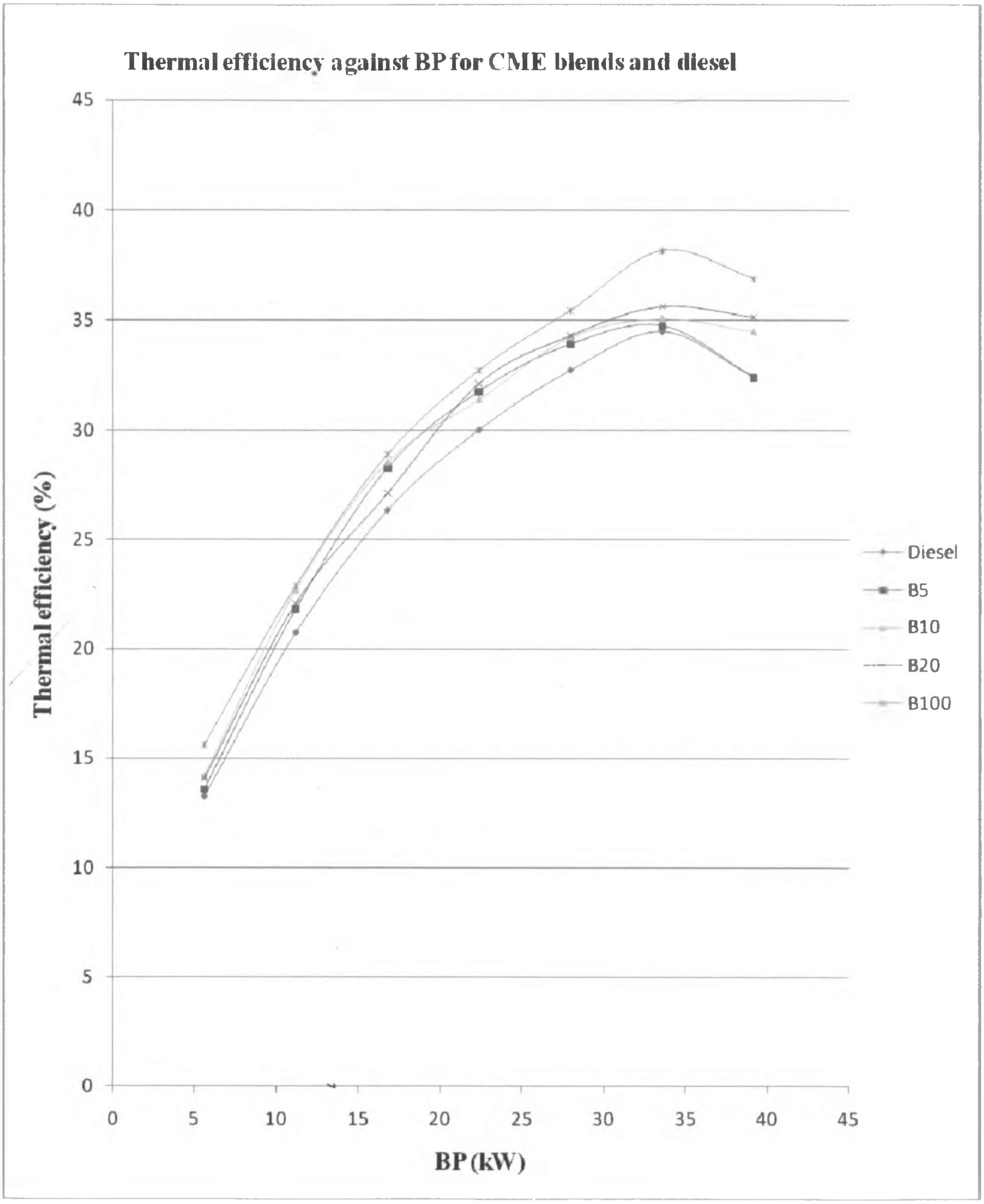

Fig. 4.29: Effect of brake power (BP) on the mean Brake Thermal Efficiency (BTE) for CME blends and diesel.

4.6.3 Exhaust gas temperature

The measured exhaust gas temperature as a function of bake power is presented in appendix (III). All values presented in the appendix table are mean average exhaust temperature values. Figures 4.30, 4.31 and 4.32 show the variation of exhaust gas temperature with load in the range of 5.595 to 39.165 brake power for diesel, neat CME and the various blends of JME, CME with DF2. The results show that the exhaust gas temperature increased with increase in brake power in all cases.

The highest value of exhaust gas temperature of 540°C was observed with the biodiesel blends, whereas the corresponding value with diesel was found to be 500°C. The maximum temperature recorded for CME B100 was 520°C. This could be attributed to the difference in viscosities between the neat biodiesel, its blends and diesel. High viscosity values of fuels results in slightly inferior combustion characteristics.

The exhaust temperature for all the biodiesel blends was observed to be close to that of diesel oil for the entire load range, there was no significant difference especially at lower values of brake powers.

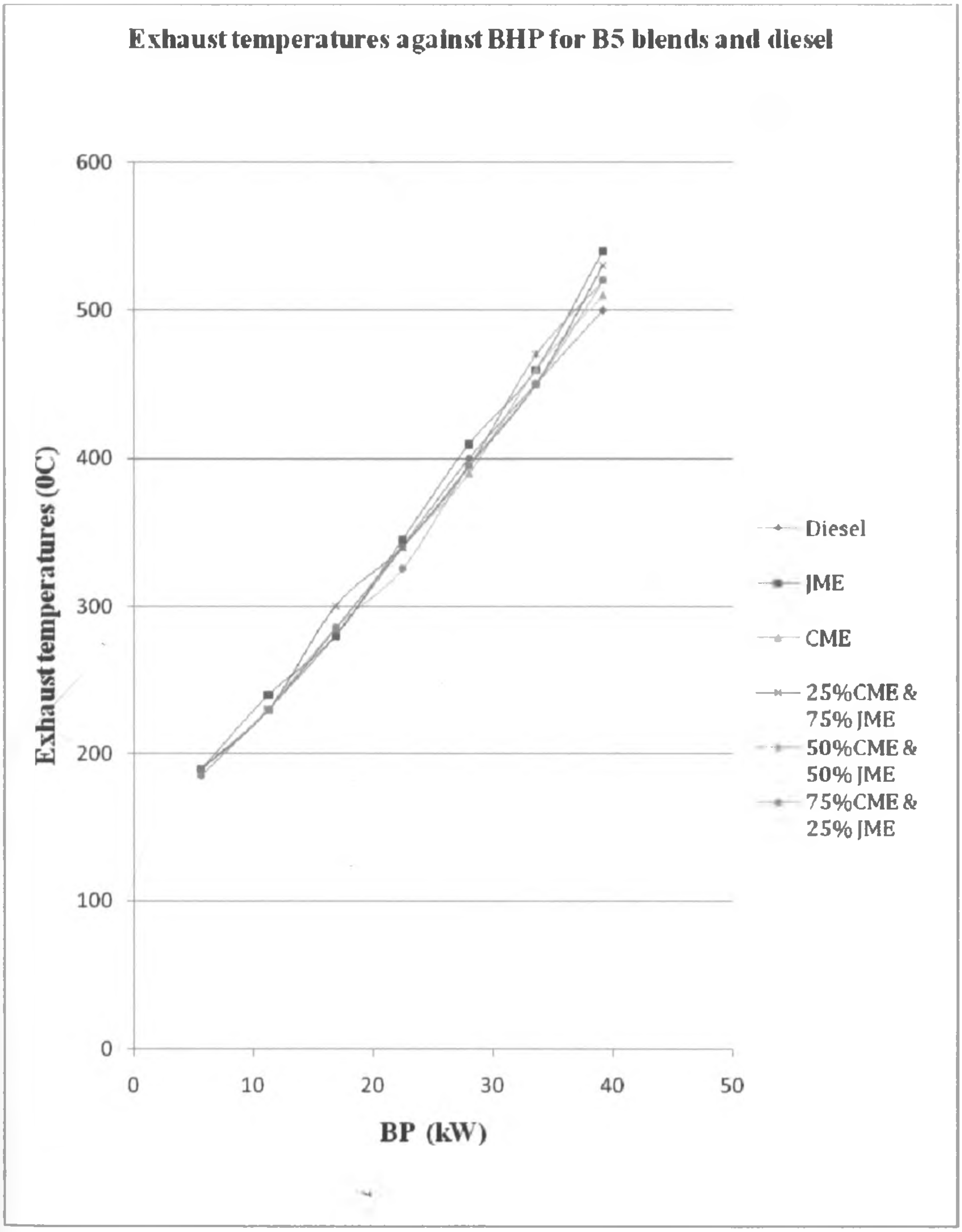

Fig. 4.30: Effect of brake power (BP) on exhaust temperatures for B5 blends and diesel.

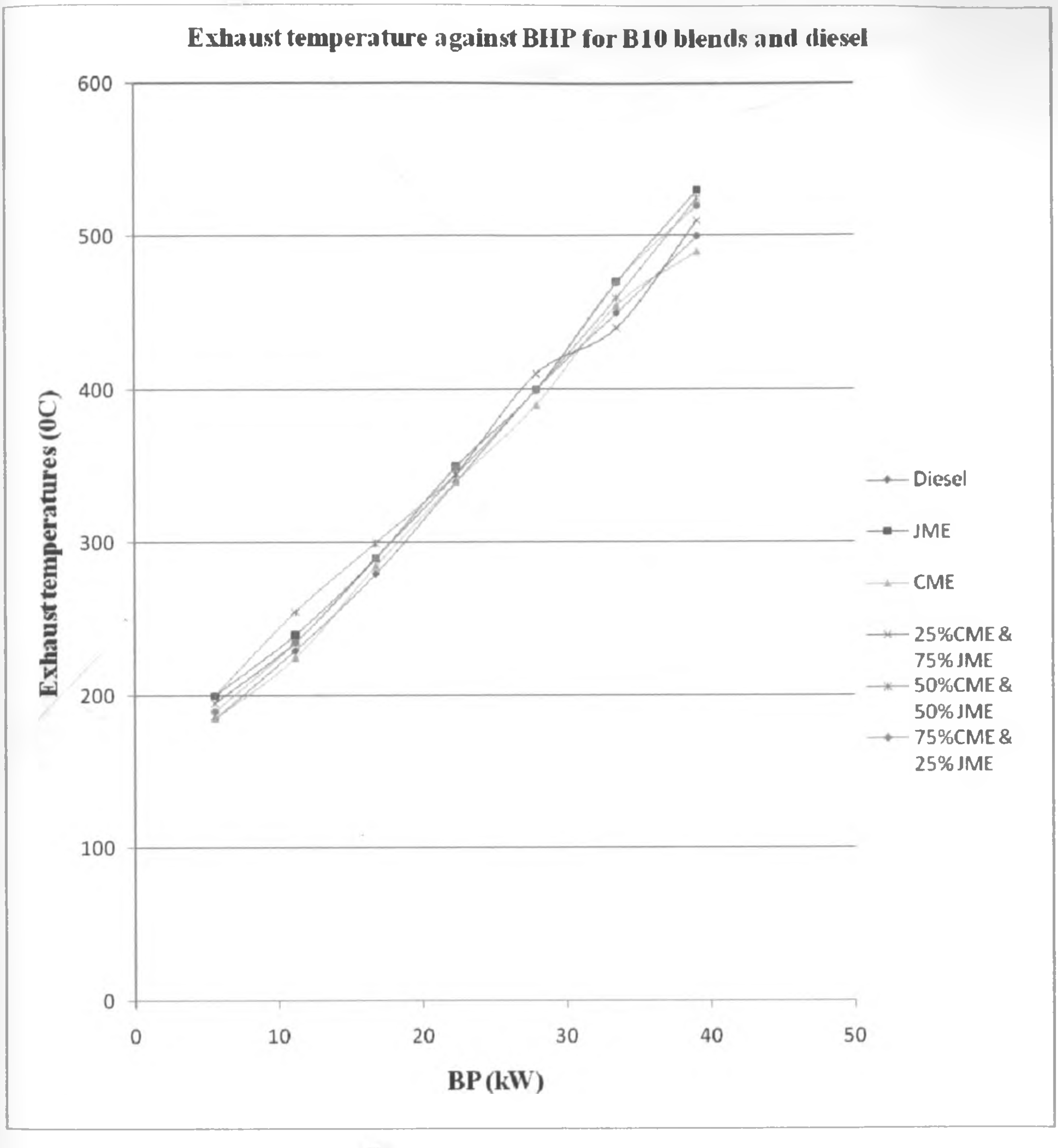

Fig. 4.31: Effect of brake power (BP) on exhaust temperatures for B10 blends and diesel.

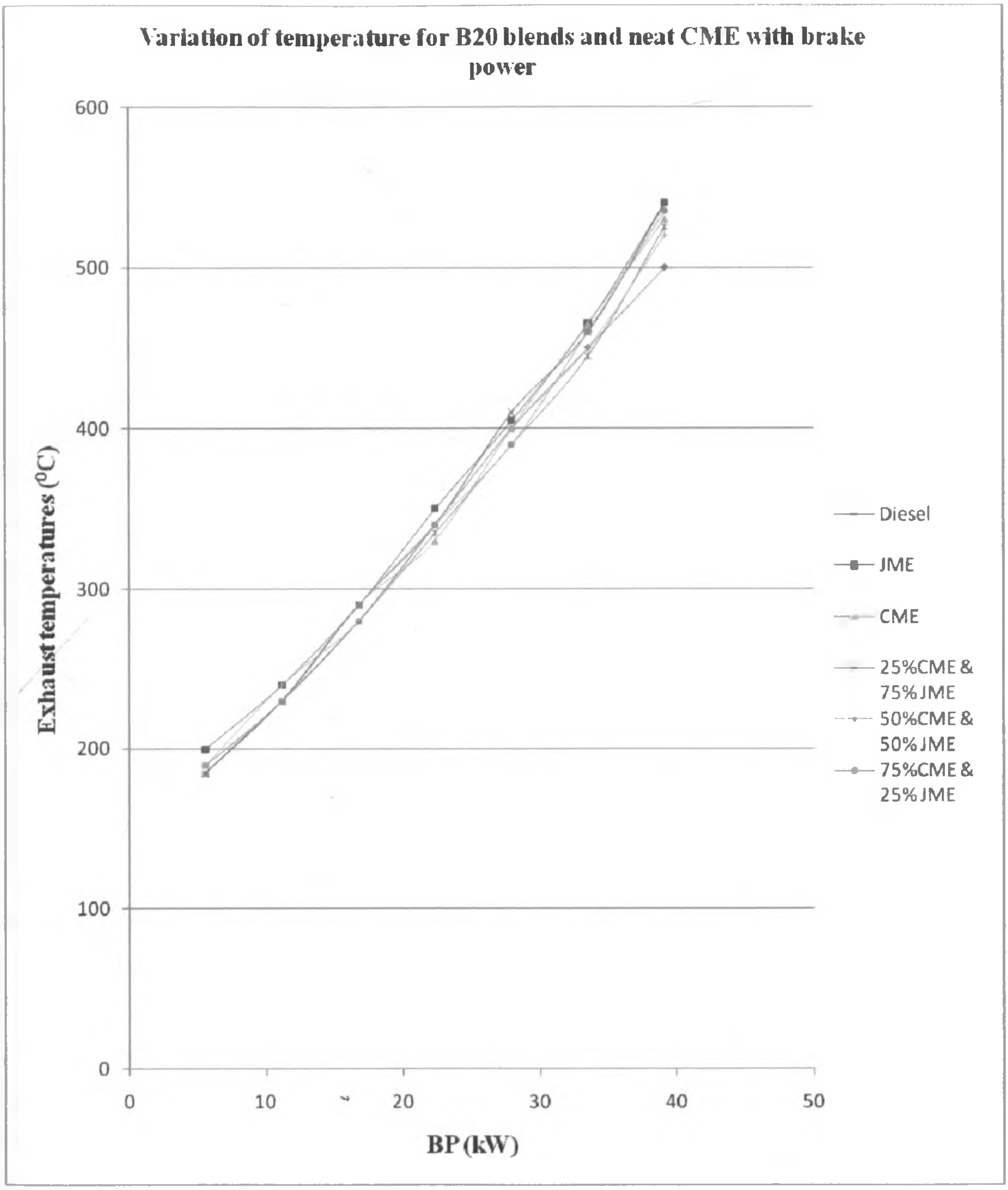

Fig. 4.32: Effect of brake power (BP) on exhaust temperatures for B20 blends, CME B100 and diesel.

CHAPTER FIVE
CONCLUSION AND RECOMMENDATIONS

The primary objective of this research project was to investigate the effect of blending *Jatropha curcas* methyl esters and *Croton megalocarpus* methyl esters on the physico-chemical biodiesel properties and the effect on engine performance. Identity of fatty acids composition in neat croton oil as well as fatty acid methyl esters composition in *croton megalocarpus* were also carried out. The vegetable oils were converted to equivalent esters through transeterification using base catalyst (potassium hydroxide). Biodiesel mixture containing 25%CME & 75%JME, 50%CME&50%JME and 75%CME & 25%JME was prepared. The physicochemical properties of these biodiesel mixtures plus those of the methyl esters from jatropha and croton were characterized e.g. specific gravity, kinematic viscosity, acid value, calorific value and iodine value and compared to those of diesel fuel.

Neat jatropha oil had a high acid value of 9.585mgKOH/g oil as compared to croton oil of 2.765mgKOH/g oil. On the other hand croton oil had high iodine value of 133.8mg I_2/g oil compared to that of jatropha oil of 102.4 mg I_2/g oil. These values however dropped after transesterification and decreased even further upon blending of biodiesel with commercial diesel fuel to fall within the allowed limits.

Higher specific gravity values as well as kinematic viscosity values were observed in the case of neat biodiesel as compared to diesel. Specific gravity was in the range of 4.3% to 5.7% higher at 15°C and kinematic viscosity was in the range of 21.3% to 50.9% higher at 40°C than diesel oil. Blending the biodiesel with diesel up to B20 reduced both specific gravity and kinematic viscosity significantly to compare to those of diesel at all test temperatures from 15°C to 60°C. Neat biodiesel gave low calorific values; the values were in the range of 13.1% to 15.8% lower than that of commercial diesel. The calorific value improved upon blending the methyl esters with commercial diesel with the increase proportional to the amount of methyl ester in the blend.

The parameters used in engine tests included; brake specific fuel consumption and brake thermal efficiency. There was no significant difference observed on the brake specific fuel consumption between the biodiesel blends up to B20 and those of commercial diesel.

However, the difference in the brake specific fuel consumption between neat CME and diesel was considered significant. At lower loads the difference was 2% at 5.595 kW but as the load was increased the difference also increased to a value of 11.1% at 27.975 kW. On the other hand there was a considerable increase in thermal efficiencies with neat biodiesel (CME B100) and the biodiesel blends up to B20 compared to the thermal efficiency of diesel oil.

Analysis of biodiesel from *croton megalocarpus* using gas chromatography identified it to contain three major methyl esters; methyl palmitate, methyl stearate and methyl oleate. These methyl esters reflect the kind of fatty acid contained in croton oil.

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

1. A mixture of two methyl esters in different ratios does not result in fuel with different physicochemical properties from that of the parent methyl ester.
2. Blends of biodiesel with diesel up 20% and neat CME (B100) gave both high brake thermal efficiency and brake specific fuel consumption than commercial DF2.
3. Biodiesel blends with commercial DF2 can be used in diesel engine without modification of the engine because most of the physicochemical properties were comparable except the calorific value.
4. *Croton megalocarpus* oil contains three major fatty acids; stearic acid, palmitic acid and oleic acid.

The following work is recommended for further study;

1. Engine performance testing using neat jatropha and croton biodiesel mixtures in different rations,
2. The long term durability of the engine performance using biodiesel as fuel.
1. Quantification of fatty acid methyl esters in croton biodiesel.

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APPENDICES

APPENDIX (I) Specific Gravities

(A) Neat oils and their resultant methyl esters

Temperature	Jatropha oil	Stdev	Croton Oil	Stdev	J.M.E	Stdev	C.M.E
15	0.91620	0.00256	0.92590	0.00316	0.87990	0.00301	0.88540
20	0.91560	0.00217	0.92460	0.00167	0.87980	0.00180	0.88490
25	0.91260	0.00266	0.92280	0.00247	0.87910	0.00252	0.88350
30	0.90020	0.00208	0.92220	0.00221	0.87730	0.00218	0.88340
35	0.89720	0.00261	0.91980	0.00073	0.87510	0.00123	0.88210
40	0.89700	0.00225	0.91860	0.00092	0.87300	0.00127	0.88060
45	0.89370	0.00681	0.90760	0.00807	0.87070	0.00776	0.87720
50	0.89250	0.00180	0.89750	0.00138	0.86950	0.00148	0.87410
55	0.89120	0.00280	0.89680	0.00428	0.86670	0.00392	0.87360
60	0.89020	0.00320	0.89610	0.00302	0.86590	0.00307	0.86940

(B) Neat methyl esters and their blends with DF2

C.M.E

Temperature	B5	Std Dev	B10	Std Dev	B20	Std Dev	B100	Std Dev
15	0.84350	0.00271	0.84470	0.00279	0.85190	0.00275	0.88540	0.00288
20	0.84220	0.00205	0.84410	0.00199	0.84940	0.00202	0.88490	0.00191
25	0.83860	0.00261	0.84220	0.00259	0.84600	0.00260	0.88350	0.00256
30	0.83590	0.00211	0.83970	0.00213	0.84480	0.00212	0.88340	0.00215
35	0.83370	0.00216	0.83760	0.00196	0.84260	0.00206	0.88210	0.00165
40	0.83170	0.00193	0.83550	0.00178	0.84050	0.00185	0.88060	0.00156
45	0.82930	0.00712	0.83240	0.00729	0.83710	0.00721	0.87720	0.00748
50	0.82890	0.00169	0.83100	0.00164	0.83650	0.00167	0.87410	0.00158
55	0.82840	0.00318	0.83000	0.00337	0.83430	0.00328	0.87360	0.00360
60	0.82530	0.00316	0.82870	0.00313	0.83400	0.00315	0.86940	0.00311

J.M.E Blends

Temperature	B5	Std Dev	B10	Std Dev	B20	Std Dev	B100	Std Dev
15	0.84350	0.00294	0.84590	0.00223	0.85800	0.00179	0.87990	0.00229
20	0.84130	0.00185	0.84390	0.00192	0.85500	0.00195	0.87980	0.00197
25	0.83890	0.00254	0.84130	0.00230	0.85100	0.00206	0.87910	0.00232
30	0.83680	0.00216	0.83900	0.00210	0.84700	0.00213	0.87730	0.00213
35	0.83430	0.00144	0.83670	0.00204	0.84500	0.00217	0.87510	0.00207
40	0.83250	0.00141	0.83470	0.00219	0.84300	0.00245	0.87300	0.00212
45	0.82920	0.00762	0.83370	0.00502	0.84000	0.00257	0.87070	0.00493
50	0.82820	0.00153	0.83150	0.00239	0.83700	0.00324	0.86950	0.00244
55	0.82700	0.00376	0.82970	0.00333	0.83300	0.00415	0.86670	0.00376
60	0.82650	0.00309	0.82900	0.00517	0.82900	0.00619	0.86590	0.00466

Case of 50%JME and 50% CME

Temperature	B5	Std Dev	B10	Std Dev	B20	Std Dev	B100	Std Dev
15	0.83890	0.00206	0.84450	0.00776	0.85140	0.00491	0.88460	0.00349
20	0.83800	0.00174	0.84300	0.00392	0.84850	0.00283	0.88400	0.00229
25	0.83750	0.00207	0.84040	0.00307	0.84610	0.00257	0.88350	0.00232
30	0.83540	0.00198	0.83840	0.00301	0.84380	0.00250	0.88280	0.00224
35	0.83350	0.00216	0.83690	0.00252	0.84190	0.00234	0.88070	0.00225
40	0.83150	0.00223	0.83440	0.00218	0.83990	0.00220	0.87860	0.00222
45	0.82790	0.00503	0.83160	0.00180	0.83780	0.00342	0.87690	0.00423
50	0.82770	0.00239	0.83150	0.00148	0.83620	0.00194	0.87530	0.00216
55	0.82660	0.00347	0.82860	0.00127	0.83490	0.00237	0.87400	0.00292
60	0.82630	0.00539	0.82810	0.00123	0.83460	0.00331	0.87390	0.00435

Case of 50%JME and 50% CME

Temperature	B10	Std Dev	B10	Std Dev	B20	Std Dev	B100	Std Dev
15	0.84530	0.00435	0.84830	0.00278	0.85060	0.00527	0.89290	0.00402
20	0.84370	0.00423	0.84580	0.00201	0.84800	0.00296	0.88860	0.00249
25	0.84140	0.00349	0.84300	0.00220	0.84480	0.00263	0.88580	0.00241
30	0.83860	0.00292	0.83970	0.00211	0.84280	0.00256	0.88500	0.00234
35	0.83670	0.00232	0.83830	0.00221	0.84090	0.00236	0.87960	0.00228
40	0.83430	0.00229	0.83580	0.00222	0.83860	0.00220	0.87520	0.00221
45	0.83040	0.00225	0.83150	0.00463	0.83790	0.00321	0.87280	0.00392
50	0.83610	0.00224	0.83120	0.00228	0.83460	0.00188	0.87170	0.00208
55	0.82790	0.00222	0.82980	0.00319	0.83280	0.00223	0.87130	0.00271
60	0.82670	0.00216	0.82890	0.00487	0.83170	0.00305	0.87040	0.00396

Case of JME75% & CME25%

Temperature	B10	Std Dev	B10	Std Dev	B20	Std Dev	B100	Std Dev
15	0.84090	0.00589	0.84530	0.00433	0.85040	0.00203	0.88460	0.00527
20	0.83900	0.00320	0.84310	0.00261	0.84890	0.00221	0.88190	0.00321
25	0.83680	0.00274	0.84110	0.00247	0.84580	0.00230	0.88000	0.00305
30	0.83550	0.00267	0.83870	0.00239	0.84400	0.00239	0.87870	0.00296
35	0.83260	0.00240	0.83690	0.00230	0.84120	0.00247	0.87680	0.00263
40	0.83020	0.00219	0.83500	0.00221	0.83960	0.00259	0.87390	0.00256
45	0.82850	0.00286	0.83130	0.00375	0.83640	0.00261	0.86730	0.00236
50	0.82750	0.00178	0.83130	0.00203	0.83590	0.00373	0.86610	0.00223
55	0.82610	0.00199	0.83020	0.00259	0.83500	0.00375	0.86510	0.00220
60	0.82260	0.00259	0.82890	0.00373	0.83390	0.00433	0.86300	0.00188

(C) Relationship of specific gravity between blends at different ratios of JME and CME

B5 Blends

Temperature	JME25% & CME75%	Std Dev	JME50% & CME50%	Std Dev	JME75% & CME25%	Std Dev	Diesel	Std Dev
15	0.83890	0.00118	0.84530	0.00114	0.84090	0.00112	0.84210	0.00468
20	0.83800	0.00113	0.84370	0.00077	0.83900	0.00060	0.83840	0.00434
25	0.83750	0.00142	0.84140	0.00080	0.83680	0.00050	0.83600	0.00317
30	0.83540	0.00135	0.83860	0.00078	0.83550	0.00049	0.83380	0.00222
35	0.83350	0.00151	0.83670	0.00079	0.83260	0.00043	0.83150	0.00210
40	0.83150	0.00157	0.83430	0.00079	0.83020	0.00040	0.82830	0.00203
45	0.82790	0.00283	0.83040	0.00173	0.82850	0.00118	0.82690	0.00200
50	0.82770	0.00149	0.83010	0.00083	0.82750	0.00050	0.82550	0.00198
55	0.82660	0.00196	0.82790	0.00119	0.82610	0.00081	0.82430	0.00198
60	0.82630	0.00287	0.82670	0.00184	0.82260	0.00132	0.82410	0.00179

B10 Blends

Temperature	JME25% & CME75%	Std Dev	JME50% & CME50%	Std Dev	JME75% & CME25%	Std Dev	Diesel	Std Dev
15	0.84450	0.00188	0.84830	0.00539	0.84530	0.00363	0.84210	0.00468
20	0.84300	0.00220	0.84580	0.00503	0.84310	0.00362	0.83840	0.00434
25	0.84040	0.00223	0.84300	0.00347	0.84110	0.00285	0.83600	0.00317
30	0.83840	0.00236	0.83970	0.00239	0.83870	0.00237	0.83380	0.00222
35	0.83690	0.00256	0.83830	0.00223	0.83690	0.00240	0.83150	0.00210
40	0.83440	0.00263	0.83580	0.00216	0.83500	0.00240	0.82830	0.00203
45	0.83160	0.00296	0.83150	0.00207	0.83130	0.00252	0.82690	0.00200
50	0.83150	0.00305	0.83120	0.00206	0.83130	0.00256	0.82550	0.00198
55	0.82860	0.00321	0.82980	0.00198	0.83020	0.00260	0.82430	0.00198
60	0.82810	0.00527	0.82890	0.00174	0.82890	0.00350	0.82410	0.00179

B20 Blends

Temperature	JME25% & CME75%	Std Dev	JME50% & CME50%	Std Dev	JME75% & CME25%	Std Dev	Diesel	Std Dev
15	0.85140	0.00433	0.85060	0.00213	0.85040	0.00415	0.84210	0.00468
20	0.84850	0.00261	0.84800	0.00213	0.84890	0.00370	0.83840	0.00434
25	0.84610	0.00247	0.84480	0.00214	0.84580	0.00330	0.83600	0.00317
30	0.84380	0.00239	0.84280	0.00219	0.84400	0.00233	0.83380	0.00222
35	0.84190	0.00230	0.84090	0.00261	0.84120	0.00228	0.83150	0.00210
40	0.83990	0.00221	0.83860	0.00273	0.83960	0.00219	0.82830	0.00203
45	0.83780	0.00375	0.83790	0.00316	0.83640	0.00216	0.82690	0.00200
50	0.83620	0.00203	0.83460	0.00321	0.83590	0.00210	0.82550	0.00198
55	0.83490	0.00259	0.83280	0.00351	0.83500	0.00209	0.82430	0.00198
60	0.83460	0.00373	0.83170	0.00359	0.83390	0.00193	0.82410	0.00179

B100 Blends

Temperature	JME25% & CME75%	Std Dev	JME50% & CME50%	Std Dev	JME75% & CME25%	Std Dev	Diesel	Std Dev
15	0.88460	0.00321	0.89290	0.00340	0.88460	0.00197	0.84210	0.00213
20	0.88400	0.00316	0.88860	0.00324	0.88190	0.00217	0.83840	0.00213
25	0.88350	0.00261	0.88580	0.00266	0.88000	0.00222	0.83600	0.00214
30	0.88280	0.00214	0.88500	0.00220	0.87870	0.00233	0.83380	0.00219
35	0.88070	0.00213	0.87960	0.00236	0.87680	0.00238	0.83150	0.00261
40	0.87860	0.00213	0.87520	0.00238	0.87390	0.00244	0.82830	0.00273
45	0.87690	0.00219	0.87280	0.00258	0.86730	0.00254	0.82690	0.00316
50	0.87530	0.00273	0.87170	0.00260	0.86610	0.00311	0.82550	0.00321
55	0.87400	0.00351	0.87130	0.00274	0.86510	0.00414	0.82430	0.00351
60	0.87390	0.00359	0.87040	0.00269	0.86300	0.00440	0.82410	0.00359

APPENDIX (II) Kinematic Viscosities

(A) Neat oil and their resultant methyl esters

Temperature	Jatropha	Std Dev	Croton	Std Dev	JME B100	Std Dev	CME B100	Std Dev
15	23.74840	0.00171	25.72000	0.00063	8.72270	0.00170	7.61740	0.00096
20	22.22460	0.00265	19.93500	0.00048	7.81530	0.00113	6.65520	0.00069
25	20.14390	0.00170	15.49530	0.00266	6.51380	0.00124	5.76770	0.00086
30	14.35100	0.00137	13.24700	0.00116	5.80270	0.00041	4.95350	0.00097
35	12.31570	0.00153	10.20200	0.00024	5.04470	0.00315	4.48100	0.00132
40	10.31890	0.00265	8.96190	0.00238	4.57990	0.00156	3.92970	0.00197
45	8.70900	0.00238	7.63070	0.00258	4.00890	0.00072	3.53890	0.00210
50	7.24760	0.00157	6.48470	0.00023	3.62380	0.00149	3.18790	0.00207
55	6.18420	0.00429	5.67560	0.00274	3.23940	0.00214	2.83780	0.00207
60	5.27800	0.00485	4.85790	0.00269	2.88850	0.00143	2.57340	0.00209

(B) Neat methyl esters and their blends

C.M.E Blends

Temperature	B5	Std Dev	B10	Std Dev	B20	Std Dev	B100	Std Dev
15	5.54760	0.00025	5.62360	0.00130	5.82120	0.00051	8.72270	0.00078
20	4.38840	0.00049	4.54720	0.00109	4.63450	0.00064	7.81530	0.00079
25	3.69320	0.00081	3.75020	0.00067	3.86980	0.00078	6.51380	0.00074
30	3.13840	0.00085	3.17110	0.00086	3.30450	0.00085	5.80270	0.00086
35	2.68670	0.00086	2.70360	0.00090	2.81410	0.00087	5.04470	0.00088
40	2.28230	0.00092	2.32210	0.00052	2.39880	0.00082	4.57990	0.00072
45	2.20060	0.00094	2.02120	0.00089	2.10600	0.00093	4.00890	0.00091
50	1.74490	0.00112	1.76450	0.00119	1.82550	0.00114	3.62380	0.00115
55	1.53810	0.00136	1.53660	0.00065	1.59240	0.00118	3.23940	0.00101
60	1.36830	0.00171	1.38850	0.00084	1.45540	0.00149	2.88850	0.00128

J.M.E Blends

Temperature	B5	Std Dev	B10	Std Dev	B20	Std Dev	B100	Std Dev
15	5.43360	0.00057	5.59630	0.00104	4.38600	0.00131	8.72270	0.00104
20	4.34510	0.00066	4.50030	0.00099	3.68700	0.00114	7.81530	0.00095
25	3.66360	0.00052	3.72000	0.00093	3.02300	0.00096	6.51380	0.00083
30	3.10020	0.00081	3.18590	0.00089	2.55200	0.00086	5.80270	0.00079
35	2.63680	0.00087	2.68990	0.00087	2.12600	0.00086	5.04470	0.00084
40	2.27870	0.00055	2.29300	0.00082	1.82000	0.00083	4.57990	0.00084
45	1.98910	0.00093	2.01600	0.00079	1.52800	0.00072	4.00890	0.00079
50	1.72310	0.00134	1.75740	0.00085	1.31100	0.00070	3.62380	0.00083
55	1.51850	0.00109	1.53400	0.00087	1.14000	0.00075	3.23940	0.00095
60	1.36130	0.00157	1.38640	0.00101	1.00900	0.00078	2.88850	0.00104

Case of 75%CME & 25%JME

Temperature	B5	Std Dev	B10	Std Dev	B20	Std Dev	B100	Std Dev
15	5.39560	0.00078	5.54760	0.00116	5.66160	0.00130	6.76350	0.00104
20	4.33070	0.00084	4.35230	0.00118	4.48950	0.00119	5.55770	0.00101
25	3.58800	0.00095	3.76880	0.00111	3.78730	0.00109	4.67400	0.00102
30	3.03760	0.00088	3.18460	0.00128	3.26490	0.00090	3.95350	0.00089
35	2.60370	0.00087	2.71420	0.00132	2.76100	0.00089	3.43410	0.00088
40	2.26210	0.00089	2.33050	0.00108	2.37030	0.00086	2.91310	0.00087
45	1.97190	0.00089	2.04070	0.00137	2.05730	0.00084	2.57950	0.00086
50	1.71380	0.00089	1.75250	0.00173	1.80210	0.00067	2.23420	0.00078
55	1.48490	0.00101	1.54070	0.00151	1.55930	0.00065	1.91110	0.00083
60	1.33310	0.00112	1.39100	0.00191	1.42170	0.00052	1.76070	0.00082

Case of 50%JME and 50% CME

Temperature	B5	Std Dev	B10	Std Dev	B20	Std Dev	B100	Std Dev
15	5.54760	0.00130	5.69960	0.00151	5.85160	0.00137	6.99150	0.00035
20	4.35230	0.00108	4.35230	0.00122	4.63890	0.00112	5.48550	0.00068
25	3.73920	0.00066	3.77430	0.00089	3.86290	0.00074	4.60530	0.00083
30	3.16940	0.00084	3.19580	0.00089	3.28010	0.00086	3.95350	0.00083
35	2.70360	0.00083	2.70050	0.00087	2.80540	0.00084	3.37170	0.00085
40	2.32570	0.00085	2.31860	0.00085	2.38460	0.00085	2.85360	0.00085
45	2.04070	0.00092	2.01830	0.00089	2.08940	0.00091	2.52220	0.00091
50	1.75740	0.00114	1.75410	0.00098	1.83370	0.00109	2.23420	0.00109
55	1.51850	0.00034	1.55980	0.00041	1.60890	0.00036	1.91110	0.00112
60	1.36580	0.00086	1.36730	0.00055	1.43420	0.00076	1.76070	0.00132

Case of JME75% & CME25%

Temperature	B5	Std Dev	B10	Std Dev	B20	Std Dev	B100	Std Dev
15	5.49440	0.00095	5.69960	0.00088	5.94280	0.00074	7.21950	0.00090
20	4.44610	0.00089	4.56310	0.00085	4.77460	0.00079	5.62990	0.00088
25	3.66710	0.00072	3.80450	0.00075	3.94680	0.00087	4.74280	0.00080
30	3.12660	0.00086	3.22210	0.00086	3.43300	0.00089	4.08530	0.00087
35	2.64740	0.00089	2.76920	0.00089	2.86160	0.00090	3.49660	0.00089
40	2.28170	0.00065	2.34830	0.00071	2.43750	0.00090	2.97250	0.00077
45	1.99200	0.00090	2.03610	0.00090	2.15700	0.00091	2.63680	0.00090
50	1.73290	0.00117	1.78360	0.00111	1.88000	0.00093	2.28870	0.00104
55	1.51080	0.00089	1.55050	0.00095	1.63210	0.00105	2.01440	0.00093
60	1.36480	0.00113	1.40860	0.00114	1.46440	0.00106	1.81100	0.00105

(C) Relationship between kinematic viscosity of blends at different ratios of JME and CME

B5 Blends

Temperature	JME25% & CME75%	Std Dev	JME50% & CME50%	Std Dev	JME75% & CME25%	Std Dev	Diesel	Std Dev
15	5.39560	0.00088	5.54760	0.00091	5.49440	0.00090	5.35310	0.00092
20	4.33070	0.00080	4.35230	0.00084	4.44610	0.00082	4.30470	0.00086
25	3.58800	0.00020	3.73920	0.00024	3.66710	0.00022	3.58460	0.00025
30	3.03760	0.00075	3.16940	0.00080	3.12660	0.00077	3.05940	0.00081
35	2.60370	0.00074	2.70360	0.00104	2.64740	0.00089	2.59120	0.00112
40	2.26210	0.00084	2.32570	0.00082	2.28170	0.00018	2.24720	0.00049
45	1.97190	0.00098	2.04070	0.00020	1.99200	0.00092	1.96960	0.00094
50	1.71380	0.00147	1.75740	0.00167	1.73290	0.00157	1.70400	0.00171
55	1.48490	0.00019	1.51850	0.00109	1.51080	0.00082	1.51850	0.00085
60	1.33310	0.00147	1.36580	0.00138	1.36480	0.00143	1.36130	0.00136

B10 Blends

Temperature	JME25% & CME75%	Std Dev	JME50% & CME50%	Std Dev	JME75% & CME25%	Std Dev	Diesel	Std Dev
15	5.54760	0.00136	5.69960	0.00129	5.69960	0.00138	5.35310	0.00092
20	4.35230	0.00085	4.35230	0.00089	4.56310	0.00109	4.30470	0.00086
25	3.76880	0.00171	3.77430	0.00186	3.80450	0.00167	3.58460	0.00025
30	3.18460	0.00094	3.19580	0.00029	3.22210	0.00020	3.05940	0.00081
35	2.71420	0.00049	2.70050	0.00079	2.76920	0.00082	2.59120	0.00112
40	2.33050	0.00112	2.31860	0.00134	2.34830	0.00104	2.24720	0.00049
45	2.04070	0.00081	2.01830	0.00085	2.03610	0.00080	1.96960	0.00094
50	1.75250	0.00025	1.75410	0.00028	1.78360	0.00024	1.70400	0.00171
55	1.54070	0.00086	1.55980	0.00089	1.55050	0.00084	1.51850	0.00085
60	1.39100	0.00092	1.36730	0.00094	1.40860	0.00091	1.36130	0.00136

B20 Blends

Temperature	JME25% & CME75%	Std Dev	JME50% & CME50%	Std Dev	JME75% & CME25%	Std Dev	Diesel	Std Dev
15	5.66160	0.00157	5.85160	0.00167	5.94280	0.00147	5.35310	0.00092
20	4.48950	0.00018	4.63890	0.00082	4.77460	0.00084	4.30470	0.00086
25	3.78730	0.00089	3.86290	0.00104	3.94680	0.00074	3.58460	0.00025
30	3.26490	0.00022	3.28010	0.00024	3.43300	0.00020	3.05940	0.00081
35	2.76100	0.00082	2.80540	0.00109	2.86160	0.00019	2.59120	0.00112
40	2.37030	0.00092	2.38460	0.00020	2.43750	0.00098	2.24720	0.00049
45	2.05730	0.00077	2.08940	0.00080	2.15700	0.00075	1.96960	0.00094
50	1.80210	0.00082	1.83370	0.00084	1.88000	0.00080	1.70400	0.00171
55	1.55930	0.00090	1.60890	0.00091	1.63210	0.00088	1.51850	0.00085
60	1.42170	0.00143	1.43420	0.00138	1.46440	0.00147	1.36130	0.00136

B100 Blends

Temperature	JME25% & CME75%	Std Dev	JME50% & CME50%	Std Dev	JME75% & CME25%	Std Dev	Diesel	Std Dev
15	6.76350	0.00147	6.99150	0.00164	7.21950	0.00157	5.35310	0.00092
20	5.55770	0.00059	5.48550	0.00034	5.62990	0.00083	4.30470	0.00086
25	4.67400	0.00074	4.60530	0.00100	4.74280	0.00089	3.58460	0.00025
30	3.95350	0.00020	3.95350	0.00023	4.08530	0.00022	3.05940	0.00081
35	3.43410	0.00089	3.37170	0.00084	3.49660	0.00064	2.59120	0.00112
40	2.91310	0.00065	2.85360	0.00093	2.97250	0.00059	2.24720	0.00049
45	2.57950	0.00075	2.52220	0.00079	2.63680	0.00077	1.96960	0.00094
50	2.23420	0.00080	2.23420	0.00084	2.28870	0.00082	1.70400	0.00171
55	1.91110	0.00088	1.91110	0.00091	2.01440	0.00090	1.51850	0.00085
60	1.76070	0.00147	1.76070	0.00139	1.81100	0.00143	1.36130	0.00136

Appendix (III): Engine Performance Tests

(A) Brake Specific Fuel Consumption

B5 Blends

BHP	Diesel	Std Dev	JME	Std Dev	CME	Std Dev	25%CME & 75% JME	Std Dev	50%CME & 50% JME	Std Dev	75%CME & 25% JME	Std Dev
5.5950	0.6481	0.0002	0.6095	0.0011	0.6580	0.0009	0.6077	0.0008	0.6463	0.0012	0.6152	0.0008
11.1900	0.4138	0.0005	0.3464	0.0014	0.4088	0.0005	0.3967	0.0007	0.4124	0.0010	0.3973	0.0009
16.7850	0.3260	0.0008	0.3129	0.0017	0.3156	0.0009	0.3269	0.0009	0.3274	0.0007	0.3155	0.0006
22.3800	0.2861	0.0009	0.2693	0.0013	0.2810	0.0012	0.2792	0.0009	0.2919	0.0005	0.2790	0.0009
27.9750	0.2624	0.0009	0.2627	0.0011	0.2632	0.0007	0.2634	0.0007	0.2624	0.0013	0.2627	0.0013
33.5700	0.2490	0.0009	0.2467	0.0007	0.2570	0.0008	0.2491	0.0009	0.2538	0.0010	0.2396	0.0011
39.1650	0.2650	0.0009	0.2483	0.0009	0.2753	0.0008	0.2599	0.0006	0.2563	0.0013	0.2430	0.0016

B10 Blends

BHP	Diesel	Std Dev	JME	Std Dev	CME	Std Dev	25%CME & 75% JME	Std Dev	50%CME & 50% JME	Std Dev	75%CME & 25% JME	Std Dev
5.5950	0.6481	0.0002	0.6258	0.0008	0.6375	0.0002	0.6646	0.0009	0.6615	0.0008	0.6077	0.0010
11.1900	0.4138	0.0005	0.3954	0.0007	0.3984	0.0005	0.3993	0.0009	0.4048	0.0008	0.3977	0.0010
16.7850	0.3260	0.0008	0.3219	0.0009	0.3169	0.0008	0.3192	0.0009	0.3152	0.0010	0.3294	0.0009
22.3800	0.2861	0.0009	0.2831	0.0009	0.2882	0.0009	0.2930	0.0009	0.2904	0.0008	0.2806	0.0009
27.9750	0.2624	0.0009	0.2666	0.0007	0.2643	0.0009	0.2812	0.0009	0.2598	0.0009	0.2563	0.0009
33.5700	0.2490	0.0009	0.2492	0.0009	0.2580	0.0009	0.2568	0.0010	0.2549	0.0009	0.2501	0.0008
39.1650	0.2650	0.0009	0.2569	0.0011	0.2624	0.0009	0.2665	0.0011	0.2653	0.0010	0.2566	0.0008

B20 Blends

BHP	Diesel	**Std Dev**	JME	**Std Dev**	CME	**Std Dev**	25%CME & 75% JME	**Std Dev**	50%CME & 50% JME	**Std Dev**	75%CME & 25% JME	**Std Dev**
5.5950	0.6481	0.0002	0.6132	0.0008	0.6481	0.0009	0.6185	0.0009	0.6069	0.0012	0.5981	0.0006
11.1900	0.4138	0.0005	0.3948	0.0008	0.4124	0.0008	0.3876	0.0007	0.4022	0.0010	0.4026	0.0007
16.7850	0.3260	0.0008	0.3253	0.0008	0.3360	0.0009	0.3240	0.0009	0.3240	0.0009	0.3123	0.0008
22.3800	0.2861	0.0009	0.2862	0.0008	0.2835	0.0011	0.2903	0.0012	0.2851	0.0008	0.2794	0.0008
27.9750	0.2624	0.0009	0.2649	0.0008	0.2655	0.0012	0.2750	0.0008	0.2618	0.0009	0.2489	0.0009
33.5700	0.2490	0.0009	0.2561	0.0008	0.2556	0.0015	0.2527	0.0008	0.2524	0.0008	0.2460	0.0008
39.1650	0.2650	0.0009	0.2588	0.0009	0.2592	0.0010	0.2578	0.0009	0.2534	0.0008	0.2547	0.0009

(B) Thermal Efficiency

B5 Blends

BHP	Diesel	**Std Dev**	JME	**Std Dev**	CME	**Std Dev**	25%CME & 75% JME	**Std Dev**	50%CME & 50% JME	**Std Dev**	75%CME & 25% JME	**Std Dev**
5.5950	13.2546	0.0009	14.4178	0.0011	13.5639	0.0009	15.2625	0.0008	14.1174	0.0009	14.3569	0.0008
11.1900	20.7602	0.0009	25.3646	0.0011	21.8346	0.0008	23.3830	0.0008	22.1267	0.0009	22.2328	0.0007
16.7850	26.3494	0.0009	28.0834	0.0014	28.2857	0.0008	28.3718	0.0009	27.8656	0.0010	27.9943	0.0009
22.3800	30.0224	0.0009	32.6256	0.0009	31.7594	0.0008	33.2262	0.0009	31.2551	0.0011	31.6610	0.0009
27.9750	32.7372	0.0009	33.4559	0.0010	33.9098	0.0008	35.2106	0.0009	34.7709	0.0013	33.6180	0.0007
33.5700	34.4938	0.0009	35.6244	0.0012	34.7369	0.0009	37.2296	0.0011	35.9508	0.0009	36.8700	0.0009
39.1650	32.4178	0.0009	35.3965	0.0010	32.4211	0.0008	35.6930	0.0012	35.6069	0.0008	36.3488	0.0012

B10 Blends

BHP	Diesel	**Std Dev**	JME	**Std Dev**	CME	**Std Dev**	25%CME & 75% JME	**Std Dev**	50%CME & 50% JME	**Std Dev**	75%CME & 25% JME	**Std Dev**
5.5950	13.2546	0.0009	14.4990	0.0010	14.1970	0.0009	14.4558	0.0008	13.8178	0.0010	14.8190	0.0008
11.1900	20.7602	0.0009	22.9497	0.0010	22.7152	0.0010	24.0617	0.0009	22.5803	0.0010	22.6439	0.0008
16.7850	26.3494	0.0009	28.1934	0.0011	28.5610	0.0011	30.1011	0.0009	29.0022	0.0012	27.3366	0.0009
22.3800	30.0224	0.0009	32.0524	0.0008	31.4004	0.0013	32.7853	0.0009	31.4776	0.0010	32.0925	0.0009
27.9750	32.7372	0.0009	34.0306	0.0009	34.2398	0.0007	34.1646	0.0009	35.1764	0.0010	35.1282	0.0009
33.5700	34.4938	0.0009	36.4110	0.0009	35.0749	0.0007	37.4080	0.0009	35.8521	0.0012	36.0092	0.0009
39.1650	32.4178	0.0009	35.3214	0.0010	34.4903	0.0008	36.0499	0.0009	34.4552	0.0010	35.0983	0.0009

B20 Blends

BHP	Diesel	**Std Dev**	JME	**Std Dev**	CME	**Std Dev**	25%CME & 75% JME	**Std Dev**	50%CME & 50% JME	**Std Dev**	75%CME & 25% JME	**Std Dev**
5.5950	13.2546	0.0009	14.8859	0.0009	14.0608	0.0010	15.5196	0.0008	15.3433	0.0009	15.2060	0.0009
11.1900	20.7602	0.0009	23.1234	0.0009	22.0955	0.0010	24.7636	0.0008	23.1529	0.0009	22.5901	0.0009
16.7850	26.3494	0.0009	28.0619	0.0009	27.1172	0.0011	29.6264	0.0009	28.7424	0.0009	29.1239	0.0010
22.3800	30.0224	0.0009	31.8906	0.0009	32.1389	0.0010	33.0675	0.0008	32.6635	0.0008	32.5503	0.0010
27.9750	32.7372	0.0009	34.4571	0.0009	34.3150	0.0010	34.9054	0.0010	35.5705	0.0010	36.5364	0.0012
33.5700	34.4938	0.0009	35.6456	0.0009	35.6541	0.0011	37.9920	0.0009	36.8877	0.0009	36.9674	0.0008
39.1650	32.4178	0.0009	35.2735	0.0009	35.1520	0.0008	37.2371	0.0009	36.7404	0.0009	35.7144	0.0008

(C) Exhaust temperatures (in ^{0}C)

B5 Blends

BHP	Diesel	JME	CME	25%CME & 75%JME	50%CME & 50%JME	75%CME & 25%JME
5.595	185	190	190	190	190	185
11.190	230	240	230	230	230	230
16.785	280	280	285	300	285	285
22.380	340	345	340	340	340	325
27.975	400	410	390	395	395	395
33.570	450	460	460	450	470	450
39.165	500	540	510	530	520	520

B10 Blends

BHP	Diesel	JME	CME	25%CME & 75%JME	50%CME & 50%JME	75%CME & 25%JME
5.595	185	200	185	195	200	190
11.190	230	240	225	235	255	235
16.785	280	290	285	290	300	290
22.380	340	350	340	345	345	350
27.975	400	400	390	410	400	400
33.570	450	470	455	440	460	470
39.165	500	530	490	510	525	520

B20 Blends

BHP	Diesel	JME	CME	25%CME & 75% JME	50%CME & 50% JME	75%CME & 25% JME	CME B100
5.595	185	200	185	185	190	190	190
11.190	230	240	230	230	230	230	240
16.785	280	290	290	290	280	290	280
22.380	340	350	330	340	335	340	340
27.975	400	405	400	410	390	390	400
33.570	450	465	465	460	445	460	450
39.165	500	540	530	540	525	535	520

APPENDIX (IV) Fatty acid and methyl ester properties

(A) Selected properties of some common fatty acids

Trivial name (Acronym)	**Molar mass**	**M.p (^{0}C)**	**B.p (^{0}C)**	**Cetane No.**	**Heat of Combustion (Kg-cal/mol) (25^{0}C)**
Caprylic acid (Octanoic acid); 8:1	144.22	16.5	239.3	32	
Capric acid (Decanoic acid); 10:0	172.27	31.5	270	47.5	1453.07
Lauric acid (Dodecanoic acid); 12:0	200.32	44	131	58.9	1763.25
Myristic acid (Tetradecanoic acid); 14:0	228.38	58	250.5	64.9	2073.91
Palmitic acid (Hexadecanoic acid); 16:0	256.43	63	350	72.6	2384.76
Stearic acid (Octadecanoic acid); 18:0	284.48	71	360d	85.3	2696.12
Oleic acid (9Z - Octadecanoic acid); 18:1	282.47	16	286	54.2	2657.4
Linoleic acid (9Z, 12Z - Octadecanoic acid); 18:2	280.45	-5	229-30	35	2695.4
Linolenic acid (9Z, 12Z, 15Z - Octadecanoic acid); 18:3	278.44	-11	230-2	33	2437.2
Erucic acid (13Z - Docosenoic acid); 22:1	338.58	33-4	265		2413.3

Source: Bagby et al., (1984)

(B) Selected properties of some common methyl esters

Trivial name (Acronym)	Molar mass	M.p (^{0}C)	B.p (^{0}C)	Cetane No.	Heat of Combustion (Kg-cal/mol) (25^{0}C)
Methyl caprylate (Methyl octanoate); 8:0	158.24		193	33.6	1313
Methyl caprate (Methyl decanoate); 10:0	186.3		224	47.7	1625
Methyl laurate (Methyl dodecanoate); 12:0	214.35	5	266	61.4	1940
Methyl myristate (Methyl tetradecanoate); 14:0	242.41	18.5	295	66.2	2254
Methyl palmitate (Methyl hexadecanoate); 16:0	270.46	30.5	415-8	74.5	2550
Methyl stearate (Methyl octadecanoate); 18:0	298.51	39.1	442-3	86.9	

Source: Bagby et al., (1984)

APPENDIX (V) Kenya Bureau of standards (KEBS) DF2 requirements

Serial No. Characteristics	Requirements
Kinematic Viscosity @40^0C (cSt)	Min - 1.6 Max - 5.5
Copper strip corrosion, 3 h at 100 ^{0}C,max	1
Distillation recovery at 365 0C, % (v/v)	Min - 90 End point 0C max, 400
Density @ 20 0C, g/ml	Min - 0.820 Max - 0.870
Flash point, Pensky Martens closed cup, 0C min.	60
ASTM, color max.	3.5
Cetane index (calculated) min	48
Cloud point, 0C	Report
Cold Filter Plugging Point, CFPP, 0C max	6
Cloud point - CFPP 0C	12
Sediment % (m/m) max	0.01
Water, (v/v) max	0.05
Ash, % (m/m) max	0.01
Sulfur content % (m/m)	0.5
Carbon residue conradson 10% residue, % (m/m) max	0.15
Neutralization value, stsrong acid no.; mg KOH/g	Nil
Total acid no.; mg KOH/g	0.5

APPENDIX (VI) Fatty acid composition of some conventional and non-conventional oil seeds

(a) Major fatty acids in Wight % of some non conventional oil seeds

Non-conventional oil seed	Fatty acid compositon (% by mass of methyl esters)						
	Palmitic (16:0)	stearic (18:0)	Oleic (18:1)	Linoleic (18:2)	Linolenic (18:3)	Arachidic (20:0)	>20:0
Acacia podalynifolia	11.90	2.30	17.70	65.00	65.00	1.30	
Alerites molucana	7.70	3.80	23.70	40.40	24.40		
Annona squamosa	14.90	5.10	45.50	32.60	32.60	1.50	
Azadirachta indica	20.80	19.70	35.60	20.10	20.10		
Balmnites aegyptiaca	20.90	19.70	25.70	32.40	32.40	1.00	
Bauhinia variegata	21.80	15.20	10.00	49.80	49.80	1.60	0.50
Caesalpenia decapetala	9.00	4.70	16.90	38.70	68.70	0.50	
Calodendrum capense	23.60	4.50	33.70	35.60	35.60	1.00	
Croton megalocarpus	5.40	4.00	9.00	78.10	1.20	25.50	
Erythrina abyssinica	14.50	4.10	50.20	21.10	21.10	2.30	5.70
Erythrina lysistemon	25.30	5.70	26.50	35.60	35.60	2.90	3.30
Passiflora edulis	10.10	2.30	15.70	71.10	71.10		

Source: Munavu and Odhiambo 1984

(b) **Major fatty acids in Wight % of some conventional oil seeds**

conventional oil seed	Fatty acid compositon (% by mass of methyl esters)						
	Palmitic (16:0)	stearic (18:0)	Oleic (18:1)	Linoleic (18:2)	Linolenic (18:3)	Arachidic (20:0)	>20:0
Sunflower (Kenya)	8.00	6.10	17.30	68.60			
Sunflower (USA)	6.40	4.20	23.90	61.40	3.00	1.00	
Soy bean	9.70	4.60	23.60	56.70	4.20	0.90	
Buffalo gourd	9.00	4.00	27.00	58.00		2.40	
Pea nut oil	8.30	3.10	56.00	26.00			4.20
Safflower	6.40	4.50	13.80	75.30			

Source: Munavu and Odhiambo 1984

PPENDIX (VII) Oil content for non-conventional oil seeds and their heating values (Calorific values)

oil seed	Heating Value (Kj/g)	Ratio (Relative to Diesel)
Afzelia cuanzensis	42.10	93.70
Annona squamosa	40.80	90.80
Areeasstrum romanzofianum	39.60	88.10
Azadirachta indica	40.10	89.20
Balmnites aegyptiaca	40.80	90.70
Bauhinia purpulea	39.90	88.70
Caesalpenia decapetala	41.50	92.40
Calodendrum capense	40.80	90.80
Citrullus vulgaris	39.40	87.50
Craibbia ellioti	39.60	88.10
Croton megalocarpus	37.60	83.60
Cucumis spp	40.30	89.70
Cuprerssus lusitanica	39.30	88.80
Erythrina abysinnica	39.20	87.30
Passiflora edulis	40.70	90.60
Sesamum indica	40.80	90.70
Sterulia africana	40.00	88.90
Jatropha curcas	31.50	91.35

Source: Munavu and Odhiambo 1984

APPENDIX (VIII) Water viscosity and density

Temperature	Density (g/ml)	Viscosity (cSt)
15	0.99919	1.1390
20	0.99823	1.0087
25	0.99713	0.8910
30	0.99567	0.8004
35	0.99408	0.7200
40	0.99224	0.6536
45	0.99022	0.5960
50	0.98807	0.5492
55	0.98565	0.5040
60	0.98324	0.4699

Source: Hand book of Chemisty by Lange N. A. Handbook Publishers, INC. Sandusky Ohio (1941)

APPENDIX (IX) Density, Viscosity and Iodine values of some non-conventional oil seeds

Oil seed	Density, g/ml (25 ^{0}C)	Kinematic viscosity (cSt)	Iodine value
Acacia podalynifolia	0.9250	54.3	116
Afzelia cuanzensis	0.9175	40.5	101
Annona squamosa	0.9190	55.4	84
Arecasstrum romanzofianum	0.8715	22.2	35
Azadirachta indica	0.8890	20.6	61
Balanites aegyptica	0.9050	43.6	79
Bauhinia purpurea	0.9495	24.6	105
Caesalpenia decacetala	0.9825	55.1	108
Calodendrum capense	0.8764	28.1	102
Craibbia ellioti	0.8900	29.6	148
Citrus sinsensis	0.9100	29.4	38
Croton megalocarpus	0.8756	29.7	133
Erythrina abyssinica	0.8565	23.6	66
Erythrina lystemon	0.9470	46.6	85
Jatropha curcas	0.9135	31.5	92
Macadamia ternifolia	0.9170	20.6	81
Passiflora edulis	0.9165	18.8	127
Sterculia africana	0.9210	18.8	118