***ADDIS ABABA UNIVERSITY SCHOOL OF GRADUATE STUDIES
ENVIRONMENTAL SCIENCE PROGRAM***

*Moringa stenopetala seed oil as a potential feedstock for
Biodiesel production in Ethiopia*

*Thesis Submitted to School of Graduate Studies, Addis Ababa University, in Partial
Fulfillment of the Requirements for the Attainment of the Degree of Masters of
Science in Environmental Science*

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ACRONYMS

AOCS	American Oil Chemists Society
ASABE	American Society of Agricultural and Biological Engineers
ASTM	American Society for Testing Materials
AV	Acid Value
B100	100% Biodiesel
B$_{20}$MME	20% Moringa Methyl Ester + 80% Petrol Diesel
B$_{20}$ME	20% Mixture of Moringa Ester + 80% Petrol Diesel
BuOH	Buthanol
CN	Cetane number
CEN	European Committee for Standardization
DIN	German standard
EN	European Standard
EPE	Ethiopian Petroleum Enterprise
EtOH	Ethanol
FAME	Fatty acid methyl ester
FFA	Free fatty acids
GC	Gas Chromatography
GJ/T	Giga joules per metric ton
h	hour
ha	hectare
IV	Iodine Value
MME	Moringa Methyl Ester
ME	Mixture of Moringa Ester
MeOH	Methanol
MJ/KG	Mega Joule per Killogram
ULSD	Ultra Low Sulphur Diesel

ABSTRACT

In this work, Moringa stenopetala seed oil is evaluated for the first time as potential feedstock for Biodiesel. Transesterification of M.stenopetala seeds oil was carried out with methanol, ethanol and mixture of methanol & ethanol (ME) in 3:3 molar ratios and using KOH as a catalyst. The esters were characterized by various methods to evaluate their densities, viscosities, water & ash content, iodine values, acid numbers, cloud & pour points, gross heat of combustion and fatty acid composition to use it in diesel engines. The experimental results show that M.stenopetala seeds contain 45% of oil. The oil was found to contain high level of mono-unsaturated fatty acids (78%), while the saturated fatty acid amount to 22%. The dominant fatty acid is oleic (76%). When methanol and ethanol used in 3:3 molar ratio (ME), the amount of ethyl ester formed was 30% that of methyl ester. The most conspicuous property of biodiesels derived from M. stenopetala oil is the low kinematic viscosity of $3mm^2/s$ for mixed ester (ME) and $3.2mm^2/s$ for methyl ester at 40^oC, which is among the lowest reported for a biodiesel fuel. The physicochemical properties of mixed ester ME (3:3) was better than that of pure M.stenopetala methyl ester. Therefore, the best choice to use as a fuel would be the mixture of Moringa ester (ME). Their blending with conventional diesel (B_{20}) also studied. All of the determined physicochemical properties of M.stenopetala oil methyl ester and mixture of ester were found to comply with both the American ASTM D6751 and the European standard EN 14214. Biodiesel derived from M.stenopetala oils is an acceptable substitute for petrodiesel when compared to biodiesel fuels from other vegetable oils. Therefore, the major physicochemical properties of M.stenopetala seed oil make it an attractive alternative application to the existing feedstocks for biodiesel production in Ethiopia.

__Key words__: M.stenopetala seed oil, Biodiesel, Transesterification, Methyl ester, Mixture of ester, Fuel properties, Blend.

1 INTRODUCTION

1.1 Background and justification

Energy affects all aspects of development - social, economic, and environmental-including livelihoods, access to water, agricultural productivity, health, education and gender related issues. None of the Millennium Development Goals can be met without major improvement in the quality and quantity of energy services in the country (Ethiopia). Ethiopia imports its entire petroleum fuel requirement and the demand for petroleum fuel is rising rapidly due to a growing economy and expanding infrastructure. The annual consumption of petroleum fuels amounts to more than 1.1 million tones, which is equivalent to 5.4 % of total final energy consumption. In the second quarter of 2007/08 petroleum imports exceeded export earrings by 30% [National Bank of Ethiopia. June 2008). A decade ago, Ethiopia's expenditure on fuel was 1.5 billion birr. In recent years, a fuel import has shown a sharp increase. In the 2006-2007 fiscal year ending June 2007 the country imported 1.8 million tons of petroleum products valued at eight billion birr. According to the Ethiopian Petroleum Enterprise (EPE), the sole importer of petroleum, the cost would increase to 11 billion birr in the current fiscal year (2007-2008). (Kaleyesus Bekele, August2007).

Clean energy for today's economic development is crucial to assure a sustainable development in the country. Thus, looking for alternative sources of energy is of vital importance .Among the alternatives source of energy, biodiesel is the important one. Since one of the ways in which processes can be made greener is to use renewable resources to replace nonrenewable starting materials. Biodiesel fuels are derived from renewable biological resources and potentially inexhaustible source of energy for use in diesel engines. Oilseed crops such as soybean, canola, and sunflower are particularly useful for producing Biodiesel fuel. (Peterson, 1991,   Mittelbach et al.1990) Biodiesel production from conventional sources (soybean, rapeseed, sunflower, palm, etc.) increasingly has placed strain on food production, price and availability (Torrey, 2007). Therefore, the search for additional regional biodiesel feedstocks is an important objective. Some recent examples, studies of biodiesel from less common or unconventional oils include *M.olifera* (Rashid, U et al, 2008), tobacco (Usta, 2005), Pongamia (Karmee and Chadha, 2005), Jatropha (Foidl et al.,

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1996) and rubber seed (Ikwuagwu et al., 2000; Ramadhas et al., 2005) oils. In Ethiopia, the gross available potential land for production of feedstock for biodiesel is estimated about 23,305,890 hectares (High level African bio fuel seminar, Aug2007).

With the recent high and volatile prices of oil, the country has been forced to develop innovative policies to mitigate the impact of these high prices on its economies. The most effective policy in this respect is the diversification of energy supply sources in the transport sector, Biodiesel appear to offer the best opportunities. The development of Biodiesel in Ethiopia can bring about multiple benefits that include :(High-level biofuel seminar in Africa, 2007)

> Increased energy supply security through diversification and progressive substitution of oil; reduced national oil importation bill;

> Increased agricultural productivity through the use of agricultural residues and waste in productive processes;

> Increased employment opportunities in associated sectors i.e. agriculture, industry, infrastructure and research in both rural and urban areas;

> Uptake of clean cooking technologies using ethanol gel fuels and vegetable oil stoves; Reduced emission of pollutants, including greenhouse gases, thus providing both local and global environmental benefit

In order for Biofuels to significantly contribute to Ethiopia's energy needs and also take advantage of potential international trade opportunities, Biofuels need to be produced on large scales and require appropriate technologies and supporting policies. (High level Biofuel seminar in Africa, 2007). Therefore, this study uses *Moringa stenopetala* seeds oil for biodiesel production in laboratory scale.

The Moringaceae is a single-genus family of oilseed trees with 14 known species (Rashied ,U et al, 2008). *Moringa stenopetala* is often referred to as the African Moringa Tree because it is native only to Ethiopia and northern Kenya. Though it does grow in many other parts of the old- and new-world tropics, it is not as widely known as its close relative, *Moringa oleifera.* Many parts of

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the plant have been used in medicinal preparations. Whole plants have been used as living hedges, fences, and windbreaks. The wood is very soft; useful for paper but makes low-grade firewood and poor charcoal. The oil content of the seeds is 44.9 %(*S. Lalas et.al, 2003*). The crushed seeds are used as a coagulant similar to the chemical alum. In Ethiopia, *Moringa stenopetala* grows wild in elevations between 1000 and 1800 m, but it will grow as high as 2200m and as low as 300m (herbarium source) in Ethiopia. The potential growing areas are fall in a rainfall range from 300-1400 mm per year with soil reaction of p^H 6-7(Mayer (1990). It does not require fertile soils, in Sudan it performs well on marginal land and poor soils. (Dechasa Jiru, 1995)

M. stenopetala are widely present in southern Ethiopia and locally called shiferaw or aleko. The species is found to grow in Keffa, Gamo Gofa, Bale, Sidamo, Borana and Debub Omo zones, and in Konso and Dherashe especial weredas. In the Arba Minch and Wollayta areas, the local people cook the leaves of the *M. stenopetala* tree and eat them with their traditional *kurkufa* (a cereal dish made with maize and sorghom*)* (Yalemthehay. Mekonnen , 1999). In contrast, the people of Konso use the tree not only for food but also as a medicine and they cultivate it in large areas around their villages. (Jahn, 1986) as reported in Mayer (1990). To the authors' best knowledge, studies on *M.stenopetala* seed oil as the feedstock for biodiesel production was never conducted.

1.2 *Statement of the problem*

Reliable access to transport fuels concerns all countries. But for poor, oil importing countries such as Ethiopia it becomes an even more critical development and security issue. Ethiopia must therefore exploit all possible alternatives to mitigate its dependence on petroleum imports. Diesel is the most important transport fuel in Ethiopia as practically all the commercial freight and public transport runs on it. Substitution of petroleum diesel by biodiesel will improve access and security of supply. (Ministry of Mines and Energy, march 2007). Ethiopia imports all of its petroleum product requirements. The volume of petroleum import has been growing at a rate of 5 percent per year for the past ten years and reached 1.37 million tons in 2004/05. In the same period the import bill was grown at a much faster rate of 17 percent per year and reached 669 million US$ in 2004/05. The petroleum import bill has grown by 115% in just a year (2003/04 to 2004/05). This rapid growth in the import bill has contributed to the widening of the trade gap. In 2004/05 petroleum

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imports consumed 82 percent of total export earnings. Diesel constitutes 55% of the total petroleum import volume and 56% of the petroleum import bill (National Bank of Ethiopia, October 2006). In the second quarter of 2007/08 petroleum imports exceeded export earrings by 30%. (National Bank of Ethiopia, June 2008)

Most people living in Ethiopia have, until now, been unable to satisfy their household energy requirements with modern energy sources (kerosene, electricity, gas). In rural areas they use only biomass (wood, dung or agricultural waste) for cooking, baking and heating. The biomass energy consumption is estimated about 94% of the total. The low agricultural production is a consequence of deforestation, erosion and desertification. The area exposed to desertification in Ethiopia is estimated to be about 70% of the total land area. The major cause of this is the increase in population, which has resulted in an increase in biomass fuel consumption for household energy, land clearance for agricultural activities and biomass demand for construction materials. Due to these reasons, the remaining biomass stock is under threat leaving the soil open to erosion and the people even more challenged to feed themselves. Hence the average rate of erosion has been estimated 400 tones ha/annum. In addition, this distraction of vegetation means the loss of genetic resources of both plants and animals. In addition to that women and children faced long distance traveling for fuel wood collection and indoor pollution. (High level biofuel seminar in Africa, 2007)

On the other hand petroleum products which are used mainly at urban household center are entirely an imported commodity. Demand for these products is rising rapidly increasing due to in scarcity of fuel wood and the change of life style of the people. The rise in demand is accompanied by a much faster growth in the import bill because of rising petroleum prices and products. Supply security of petroleum fuels is essential to ensure continuous economic growth. Reduction of the petroleum import bill will enable the government to allocate more of its foreign exchange earnings to other development investments and expenditures.

In Ethiopia the gross available potential land for production of feedstock for biodiesel is estimated about 23,305,890 hectares and the total irrigable land for sugarcane production for ethanol

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production is about 700,000 hectares. Thus, Ethiopia has a potential to produce 1 billion liters of ethanol within available suitable land(the Minister of Mines and Energy, Augest2007).This amount of ethanol are excess enough for gasoline blending and can be used in transesterification process of *Moringa stenopetala* oil as a substitute in part of methanol in biodiesel production.

Therefore, this laboratory scale study helps for the development of clean, new, renewable energies and locally available, particularly biodiesel extraction from *M.stenopetala*, as an alternative solution to hydrocarbons, in response to the rise in oil prices which has adverse effects on the economies of the country. By extracting crude oil from *Moringa stenopetala* in large scale, Ethiopia will also save its foreign expenditure, create job opportunities, establish local industrial base, increase its economic growth and create clean environment. With that Ethiopia will be in a position to use biodiesel for energy use in the future from *M.stenopetala* seeds oil.

1.3   *Objectives.*

1.3.1   *The General Objective of this study is*

➢ To evaluate *M.stenopetala* seed oil as a potential raw material for biodiesel production in laboratory scale

1.3.2 *The specific Objectives are*

➢ To determine the oil content of *Moringa stenopetala* seeds

➢ To synthesize *M.stenopetala seed* oil esters using methanol, ethanol and mixture of methanol/ethanol in 3:3 molar ratios.

➢ To determine the fatty acid composition of *Moringa stenopetala* oils

➢ To measure the viscosity, density, cloud point, pour point, copper strip corrosion, heat of combustion, carbon and ash content, water content, iodine number and acid value of Moringa esters by following the standard methods in order to evaluate its use in diesel engines.

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1.4 Significance of the study

➢ to secure our fuel supplies as well as to reduce its petroleum import bill through the development of an indigenous fuel production

➢ Utilizing renewable energies will benefit the country from Clean Development Mechanism (CDM).

➢ The biodiesel production from *M.stenopetala* will build an agriculture based industry with potential for development of agri-businesses and agro-industries.

➢ to use biodiesel for household energy, electricity generation, running agricultural machineries etc

➢ to reduce emission of pollutants, including greenhouse gases, thus providing both local and global environmental benefit

➢ Development of biodiesel from *M.stenopetala* seed oils will contribute to soil and water conservation.

➢ A biodiesel program from *M.stenopetala* can help close the trade gap by reducing imported petroleum and also by increasing exports.

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2   LITERATURE REVIEW

2.1   Introduction-what is biodiesel?

According to the US Standard Specification for Biodiesel (ASTM 6751), biodiesel is defined as a fuel comprised of mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats. In this context, it can be used in diesel engines and heating systems (Mittelbach et al., 1983; Staat and Vallet, 1994). Biodiesel is an ecologically friendly fuel because it has a lower emission profile than petrodiesel and decreases the greenhouse gas emissions from combustion ignition engines (McCormick and Alleman, 2005). In addition, biodiesel is safer to handle (flash point above 110 °C), contains little or no sulfur or carcinogenic polyaromatic components, and decreases soot emission considerably, which is very advantageous in environmentally sensitive areas (Schuchardt et al., 1998; Knothe, 2005). Furthermore, biodiesel is a suitable outlet for the vegetable oil industry requiring little or no changes in current diesel engines when used in blends and also increases engine life due to its superior lubricity over petrodiesel (Knothe, 2005b; Ramos and Wilhelm, 2005). Usage of biodiesel will allow a balance to be sought between agriculture, economic development and the environment.

Chemically the oils/fats consist of triglyceride molecules of three long chain fatty acids that are ester bonded to a single glycerol molecule. These fatty acids differ by the length of carbon chains, the number, orientation and position of double bonds in these chains. Because different fatty acids have different physical and chemical properties, the fatty acid profile is probably the most important parameter influencing the corresponding properties of a vegetable oil or animal fat. Thus, biodiesel refers to lower alkyl esters of long chain fatty acids, which are synthesized either by transesterification with lower alcohols or by esterification of fatty acids.(Srivastava A, Prasad R. ,2000)

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Biodiesel can be produced from a variety of renewable lipid sources (Schuchardt et al., 1998; Knothe and Van Gerpen, 2005), including soybeans, canola, palm, peanut, physic nut (*Jatropha curcas*), cotton and sunflower oils. However, some of these oil sources are commodities whose prices are strongly dependent on the international market. Moreover, the food industry imposes a direct competition for this feedstock and this may be critical for a world whose population is increasing exponentially. For these and other reasons, non-edible oil sources are preferable for biodiesel production, particularly those requiring low agronomic demand for cultivation, a reasonable plant cycle, favorable geographic adaptability, high oil content and a low cost for cultivation and harvesting. (Domingos, A.K. et al., 2007)

2.2   Production of biodiesel

2.2.1   Transesterification process

The plant oils usually contain free fatty acids, phospholipids, sterols, water, and odorants and other impurities. Because of these, the oil can not be used as fuel directly. To overcome these problems the oil requires slight chemical modification mainly transesterification. Transesterification is the key and foremost important step to produce the cleaner and environmentally safe fuel from vegetable oils. Biodiesel is the monoalkyl esters of long chain fatty acids derived from renewable feed stocks, such as vegetable oil or animal fats, for use in compression ignition engine. Biodiesel, which is considered as a possible substitute of conventional diesel fuel is commonly, composed of fatty acid methyl esters that can be prepared from triglycerides in vegetable oils by transesterification with methanol. The resulting biodiesel is quite similar to conventional diesel fuel in its main characteristics. (Srivastava A, Prasad R., 2000)

Transesterification or alcoholysis is the displacement of alcohol from an ester by another alcohol in a process similar to hydrolysis, except that alcohol is used instead of water [Srivastava A, Prasad R., 2000]. This process has been widely used to reduce the high viscosity of triglycerides. The general reaction is shown below

Catalyst

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Vegetable oil + Methanol $\longrightarrow$ Biodiesel + Glycerol

$$RCOOR^1 + R^2OH \underset{\text{Catalyst}}{\rightleftharpoons} RCOOR^2 + R'OH$$

Ester   Alcohol   Ester   Alcohol

- Triglyceride + R'OH $\rightleftharpoons$ Diglyceride + $RCOOR^1$

Diglyceride + R'OH $\rightleftharpoons$ Monoglyceride + RCOOR'

Monoglyceride + R'OH $\rightleftharpoons$ Glycerol + $RCOOR^1$
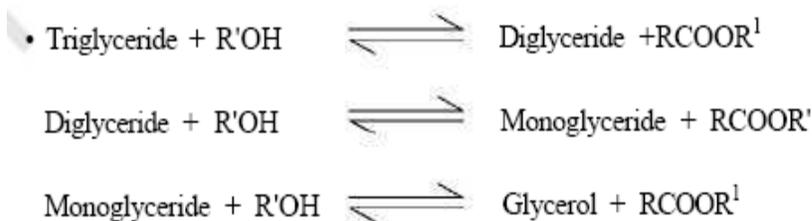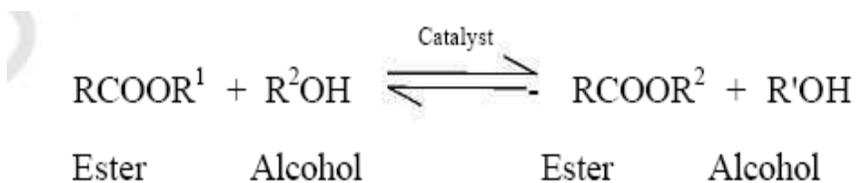
Equation 1. Transesterification reaction of vegetable oil with alcohol to esters and glycerol (Freedman, 1986)

In this reaction (equation 1), triglycerides, as the main components of vegetable oils, react with an alcohol to produce fatty acid mono-alkyl esters and glycerol. Alcohols are primary and secondary monohydric aliphatic alcohols having 1-8 carbon atoms (Sprules and Price, 1950). Among the alcohols that can be used in the transesterification process are methanol, ethanol, propanol and butanol. Methanol and ethanol are used most frequently, especially methanol because of its low cost and its physical and chemical advantages (polar and shortest chain alcohol). It can quickly react with triglycerides and NaOH is easily dissolved in it. In this case, the reaction is referred to as methanolysis. The stoichometry of methanolysis reaction requires 3 mol of methanol and 1 mol of triglyceride to give 3 mol of fatty acid methyl ester and 1 mol of glycerol. This reaction, in turn, consists of three consecutive reversible reactions with intermediate formation of diglycerides and monoglycerides. After the reaction, the glycerol is separated by settling or centrifuging and the layer obtained is purified to be used in its traditional applications (the pharmaceutical, cosmetics and food industries) or in its recently developed applications (animal feed, carbon feedstock in fermentations, polymers, surfactants, intermediates and lubricants) (Claude, 1999). The biodiesel

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phase is also purified before being used as diesel fuel. The high viscosity component, glycerol, is removed and hence the product has low viscosity like the fossil fuels. The mixture of these mono-alkyl esters can hence be used as a substitute for fossil fuels (Ma and Hanna, 1999)

After transesterification of triglycerides, the products are a mixture of esters, glycerol, alcohol, catalyst and tri-, di- and monoglycerides. Obtaining pure esters was not easy, since there were impurities in the esters, such as di- and monoglycerides (Ma and Hanna, 1999). The monoglycerides caused turbidity (crystals) in the mixture of esters. This problem was very obvious, especially for transesterification of animal fats such as beef tallow. The impurities raised the cloud and pour points. On the other hand, there are a large proportion of saturated fatty acid esters in beef tallow esters (almost 50% w/w). This portion makes the cloud and pour points higher than that of vegetable oil esters. However, the saturated components have other value-added applications in foods, detergents and cosmetics. The co-product, glycerol, needs to be recovered because of its value as an industrial chemical. Glycerol is separated by gravitational settling or centrifuging. (Ma and Hanna, 1999). The transesterification process can be done in a number of ways such as using an alkali catalyst, acid catalyst, biocatalyst or heterogeneous catalyst.
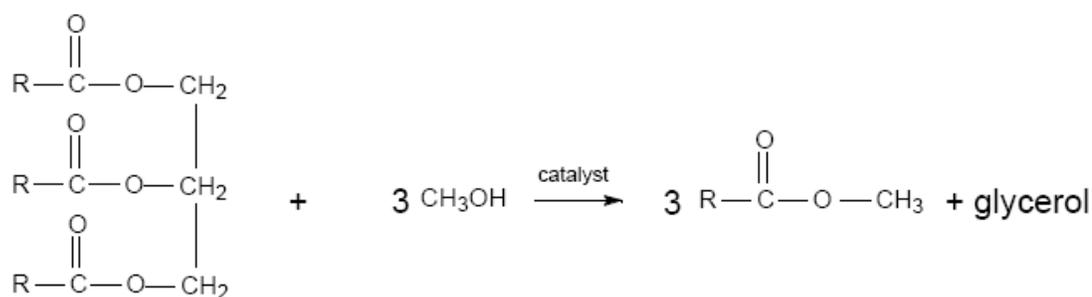
R is typically 16 or 18 carbons and may contain one to three carbon-carbon double bonds.

Equation 2. Transesterification reaction

2.2.1.1   *Transesterification using basic catalyst*

Generally, this reaction is catalyzed by a basic or an acid catalyst. In the alkali or basic process sodium hydroxide (NaOH) or potassium hydroxide (KOH) is used as a catalyst along with methanol

or ethanol. Initially, during the process, alcoxy is formed by reaction of the catalyst with alcohol and the alcoxy is then reacted with any vegetable oil to form biodiesel and glycerol. Glycerol being denser settles at the bottom and biodiesel can be decanted. This process is the most efficient and least corrosive of all the processes and the reaction rate is reasonably high even at a low temperature of 60 ℃. There may be risk of free acid or water contamination and soap formation is likely to take place which makes the separation process difficult (Ma and Hanna, 1999; Fukuda et al., 2001; Barnwal and Sharma, 2005).

Most studies of the basic-catalysed transesterification of vegetable oils involve the calculations of the triglyceride conversion rate, the changes in product composition during reaction or some of the quality parameters of biodiesel (Feuge and Gros, 1949; Freedman et al., 1984, 1986; Schwab et al., 1987; Peterson et al., 1991; Ali et al., 1995; Chang et al., 1996; Mittelbach, 1996; Boocock et al., 1998; Noureddini et al., 1998; Vicente et al., 1998; Darnoko and Cheryan, 2000). All of these aspects are related to the biodiesel purity, which means the methyl ester concentration in the biodiesel phase. Even though the biodiesel yield after the post-treatment stage is another relevant aspect of the process, it is considered less in the literature (Fro ̈hlich and Rice, 1995; Fro ̈hlich et al., 2000; Vicenteet al., 2004). The biodiesel yield could decrease due to the previously mentioned undesirable side-reactions like triglyceride saponification and free fatty acid neutralization and also to dissolution of the methyl ester in the glycerol phase. (Ma and Hanna, 1999)

For an alkali-catalyzed transesterification, the glycerides and alcohol must be substantially anhydrous (Wright et al., 1944) because water makes the reaction partially change to saponification, which produces soap. The soap lowers the yield of esters and renders the separation of ester and glycerol and the water washing difficult. Low free fatty acid content in triglycerides is required for alkali-catalyzed transesterification.

2.2.1.2 *Transesterification using acidic catalyst*

The second conventional way of producing biodiesel is using an acid catalyst instead of a base. Any mineral acid can be used to catalyze the process; the most commonly used acids are sulfuric acid and sulfonic acid. Although yield is high, the acids, being corrosive, may cause damage to the

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equipment and the reaction rate was also observed to be low and needs very high temperature and pressure. Freedman *et al.* investigated the transesterification of soybean oil with methanol using 1 wt % concentrated sulfuric acid (based on oil). They found that at 65°C and a molar ratio of 30:1 methanol to oil, it took 69 h to obtain more than 90% oil conversion of methyl esters. (Freedman et al., 1984, Schwab et al., 1987). If more water and free fatty acids are in the triglycerides, acid catalyzed transesterification can be used (Keim, 1945).

2.2.1.3 *Transesterification using biocatalyst*

It has been recently found that enzymes such as lipase can be used to catalyze transesterification process by immobilizing them in a suitable support. The advantage of immobilization is that the enzyme can be reused without separation. Also, the operating temperature of the process is low (50 °C) compared to other techniques. Disadvantages include inhibition effects which were observed when methanol was used and the fact that enzymes are expensive (Nelson et al., 1996; Shimada et al., 2002).

Because of the high energy cost of the conventional chemical process and additional purification step of glycerol, application of lipase in the biodiesel industry has become more attractive (Selmi and Thomas, 1998). In several studies transesterification of vegetable oils and animal fats with primary and secondary alcohols and straight- and branched-chain alcohols in solvent or solvent-free medium using lipases as catalysts has been reported (Mittelbach,1990; Nelson et al., 1996; Selmi and Thomas, 1998; Shimada et al., 1999). Because of the toxicity and flammability of organic solvents, and product recovery without further organic solvent evaporation, lipase-catalyzed transesterification in a solvent-free medium is important in industrial applications (Selmi and Thomas, 1998).

Alcoholysis of tallow with primary and secondary alcohols in solvent was investigated using lipase from Candida antarctica (SP435) by Nelson et al. (1996) who reported that the lipase of C. antarctica was most efficient for transesterifing triglycerides with secondary alcohols to give branched alkyl esters and methanolysis of oils occurred in a mixture with hexane even though three molar equivalents of methanol was present. Shimada et al. (1999) investigated methanolysis

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of vegetable oil (a mixture of soyabean and rapeseed oils) by enzymatic transesterification reaction. They reported that immobilized C. antarctica lipase was most effective for the methanolysis among lipases tested but it was inactivated in the mixture containing more than 1.5 molar equivalents of methanol in oil. Shimada et al. (1999) conducted the reaction by adding methanol stepwise to avoid lipase inactivation and converted 98.4% of the oil to its corresponding methyl esters (ME) at 30 °c after 48 h total reaction time.(Ma and Hanna, 1999)

2.2.1.4   *Transesterification using heterogeneous catalyst*

Heterogeneous catalysts such as amorphous zirconia, titanium-, aluminum-, and potassium-doped zirconias have also become popular for catalyzing the transesterification of vegetable oils. It has been reported that the conversion to methyl ester reaches 87% with the potassium-loaded alumina catalyst, when a mixture with a molar ratio of methanol to oil of 15:1 is refluxed for a reaction time of 7 h (Xie et al., 2006). Besides these, there have been several other reports on heterogeneous catalysts (Gryglewicz, 1999; Jitputti et al., 2006). However, the catalytic activities of most of them are not much greater than that of a homogeneous catalyst such as KOH. Furthermore, there is little information regarding their catalytic durability. Research is still in progress in order to solve the problem encountered in this process such as exhaustion of catalyst and to achieve higher conversions (Furuta et al., 2006).

Of all the methods mentioned above for production of biodiesel, only the alkali process is carried out in an industrial scale. It is cost effective and highly efficient. But problems arise in the downstream operations including separation of catalyst and unreacted methanol from biodiesel. The removal of the catalyst involves many complications and biodiesel requires repeated washing for attaining the necessary purity. The production of biodiesel using a biocatalyst eliminates the disadvantages of the alkali process by producing product of very high purity with less or no downstream operations (Fukuda et al., 2001). Haas (1997) also patented this method of production of biodiesel using a biocatalyst. However, the process has not yet been implemented in an industrial scale due to certain constraints like enzyme inhibition by methanol, exhaustion of enzyme activity and high cost of enzymes. (Ma and Hanna, 1999).

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2.2.2 Factors affecting transesterification process

2.2.2.1 The mechanism and kinetics

Transesterification consists of a number of consecutive, reversible reactions (Schwab et al., 1987; Freedman et al., 1986). The triglyceride is converted stepwise to diglyceride, monoglyceride and finally glycerol .A mole of ester is liberated at each step. The reactions are reversible, although the equilibrium lies towards the production of fatty acid esters and glycerol.(.(Ma and Hanna, 1999)

The reaction mechanism for alkali-catalyzed transesterification was formulated as three steps (Eckey, 1956). The first step is an attack on the carbonyl carbon atom of the triglyceride molecule by the anion of the alcohol (methoxide ion) to form a tetrahedral intermediate. In the second step, the tetrahedral intermediate reacts with an alcohol (methanol) to regenerate the anion of the alcohol (methoxide ion). In the last step, rearrangement of the tetrahedral intermediate results in the formation of a fatty acid ester and a diglyceride. When NaOH, KOH, K_2CO_3 or other similar catalysts were mixed with alcohol, the actual catalyst, alkoxide group is formed (Sridharan and Mathai, 1974). A small amount of water, generated in the reaction, may cause soap formation during transesterification. The mechanism of alkali-catalyzed transesterification is shown below.

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Pre-step: $OH^- + R'OH \rightleftharpoons R'O^- + H_2O$ or

$NaOR' \rightleftharpoons R'O^- + Na^+$

Step 1.
$$ROOCR_1 + {^-}OR' \rightleftharpoons R_1-\overset{\overset{\displaystyle OR}{|}}{\underset{\underset{\displaystyle OR'}{|}}{C}}-O^-$$

Step 2.
$$R_1-\overset{\overset{\displaystyle OR}{|}}{\underset{\underset{\displaystyle OR'}{|}}{C}}-O^- + HOR' \rightleftharpoons R_1-\overset{\overset{\displaystyle ROH^+}{|}}{\underset{\underset{\displaystyle OR'}{|}}{C}}-O^- + {^-}OR'$$

Step 3.
$$R_1-\overset{\overset{\displaystyle ROH^+}{|}}{\underset{\underset{\displaystyle OR'}{|}}{C}}-O^- \rightleftharpoons R_1COOR' + HOR$$

Where R-OH diglyceride, R_1 long chain alkyl group, and R' short alkyl group
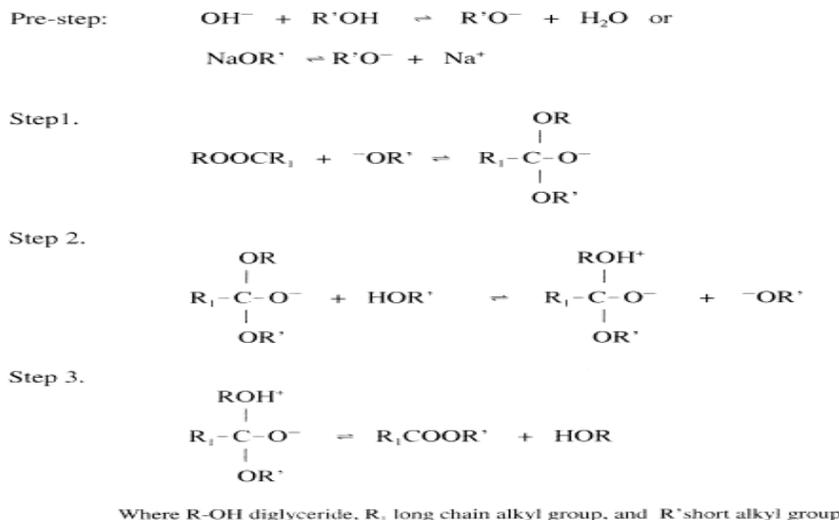
Figure 1.The mechanism of alkali-catalyzed transesterification of triglycerides with alcohol (Sridharan and Mathai, 1974; Eckey, 1956)

2.2.2.2 The effects of moisture and free fatty acids

The effects of moisture (water) and free fatty acids Wright et al. (1944) noted that the starting materials used for alkali-catalyzed transesterification of glycerides must meet certain specifications. The glyceride should have an acid value less than 1 and all materials should be substantially anhydrous. If the acid value was greater than 1, more NaOH was required to neutralize the free fatty acids. Water also caused soap formation, which consumed the catalyst and reduced catalyst efficiency. The resulting soaps caused an increase in viscosity, formation of gels and made the separation of glycerol difficult and therefore, water content should be less than 0.3%. Bradshaw and Meuly (1944) and Feuge and Grose (1949) also stressed the importance of oils being dry and free (<0.5%) of free fatty acids. Freedman et al. (1984) stated that ester yields were significantly reduced if the reactants did not meet these requirements. Sodium hydroxide or sodium methoxide reacted with moisture and carbon dioxide in the air, which diminished their effectiveness. The effects of free fatty acids and water on transesterification of beef tallow with methanol were investigated (Ma et al., 1998a). The results showed that the water content of beef tallow should be kept below 0.06% w/w and free fatty acid content of beef tallow should be kept below 0.5%, w/w in order to get the best conversion. Water content was a more critical variable in the

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transesterification process than were free fatty acids. The maximum content of free fatty acids confirmed the research results of Bradshaw and Meuly (1944) and Feuge and Grose (1949).

2.2.2.3   *The effect of molar ratio*

One of the most important variables affecting the yield of ester is the molar ratio of alcohol to triglyceride. The stoichiometric ratio for transesterification requires three moles of alcohol and one mole of glyceride to yield three moles of fatty acid ester and one mole of glycerol. The molar ratio is associated with the type of catalyst used. An acid catalyzed reaction needed a 30:1 ratio of BuOH to soybean oil, while an alkali-catalyzed reaction required only a 6:1 ratio to achieve the same ester yield for a given reaction time (Freedman et al., 1986).

Bradshaw and Meuly (1944) stated that the practical range of molar ratio was from 3.3 to 5.25:1 methanol to vegetable oil. The ratio of 4.8:1 was used in some examples, with a yield of 97-98%, depending upon the quality of the oils. If a three step transesterification process was used, the ratio was reduced to 3.3:1. Methanol present in amounts of above 1.75 equivalents tended to prevent the gravity separation of the glycerol, thus adding more cost to the process.

Higher molar ratios result in greater ester conversion in a shorter time. In the ethanolysis of peanut oil, a 6:1 molar ratio liberated significantly more glycerine than did a 3:1 molar ratio (Feuge and Grose, 1949). Rapeseed oil was methanolyzed using 1% NaOH or KOH (Nye and Southwell, 1983).They found that the molar ratio of 6:1 of methanol to oil gave the best conversion. When a large amount of free fatty acids was present in the oil, a molar ratio as high as 15:1 was needed under acid catalysis (Sprules and Price, 1950). Freedman et al. (1984) studied the effect of molar ratio (from 1:1 to 6:1) on ester conversion with vegetable oils. Soybean, sunflower, peanut and cottonseed oils behaved similarly and achieved highest conversions (93-98%) at a 6:1 molar ratio. Tanaka et al. (1981), in his novel two-step transesterification of oils and fats such as tallow, coconut oil and palm oil, used 6:1-30:1 molar ratios with alkali catalysis to achieve a conversion of 99.5%. (Ma and Hanna, 1999). A molar ratio of 6:1 was used for beef tallow transesterification with methanol (Ali, 1995; Zhang 1994).Zhang reported 80% by tallow weight of esters was recovered in the laboratory.

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2.2.2.4   The effect of catalyst

Catalysts are classified as alkali, acid, or enzyme. Alkali-catalyzed transesterification is much faster than acid-catalyzed (Freedman et al., 1984). However if a glyceride has a higher free fatty acid content and more water, acid-catalyzed transesterification is suitable (Sprules and Price, 1950; Freedman et al., 1984). The acids could be sulfuric acid, phosphoric acid, hydrochloric acid or organic sulfonic acid. Alkalis include sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide, sodium amide, sodium hydride, and potassium amide and potassium hydride. (Sprules and Price, 1950). Sodium methoxide was more effective than sodium hydroxide (Freedman et al., 1984; Hartman, 1956) because of the hydroxide group is responsible for the formation of soaps by the side-reaction of saponification of the triglycerides and they contain only a minor amount of the hydroxide group as impurity and due to the assumption that a small amount of water was produced upon mixing NaOH and MeOH. The opposite result was observed by Ma et al. (1998a). NaOH and NaOCH$_3$ reached their maximum activities at 0.3 and 0.5% w/w of beef tallow, respectively. Sodium hydroxide was also chosen to catalyze the transesterification because it is cheaper. Ester conversions at the 6:1 ratio for 1% NaOH and 0.5% NaOCH$_3$ were almost the same after 60 min (Freedman et al., 1984). Sodium hydroxide, however, is cheaper and is used widely in large-scale processing. The transesterification of soybean oil with methanol, ethanol and butanol, using 1% concentrated sulfuric acid, was unsatisfactory when the molar ratios were 6:1 and 20:1 (Freedman et al., 1984). A 30:1 ratio resulted in a high conversion to methyl ester. More recently, an immobilized lipase was employed to catalyze the methanolysis of corn oil in flowing supercritical carbon dioxide with an ester conversion of >98% (Jackson and King, 1996).

2.2.2.5   The effect of reaction time

The conversion rate increases with reaction time. Freedman et al. (1984) transesterified peanut, cottonseed, sunflower and soybean oils under the condition of methanol to oil ratio of 6:1, 0.5% sodium methoxide catalyst and 60°C. An approximate yield of 80% was observed after 1 min for soybean and sunflower oils. After 1 h, the conversions were almost the same for all four oils (93-98%). Ma et al. (1998a) studied the effect of reaction time on transesterification of beef tallow with methanol. The reaction was very slow during the first minute due to the mixing and dispersion of

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methanol into beef tallow. From one to five min, the reaction proceeded very fast. The apparent yield of beef tallow methyl esters surged from 1 to 38. The production of beef tallow slowed down and reached the maximum value at about 15 min. The di- and monoglycerides increased at the beginning and then decreased. At the end, the amount of monoglycerides was higher than that of diglycerides. (Ma and Hanna, 1999).

2.2.2.6   *The effect of reaction temperature*

Transesterification can occur at different temperatures, depending on the oil used. In methanolysis of castor oil to methyl ricinoleate, the reaction proceeded most satisfactorily at 20-35°C with a molar ratio of 6:1-12:1 and 0.005-0.35% (by weight of oil) of NaOH catalyst (Smith, 1949). For the transesterification of refined soybean oil with methanol (6:1) using 1% NaOH, three different temperatures were used (Freedman et al., 1984). After 0.1 h, ester yields were 94, 87 and 64% for 60, 45 and 32°C, respectively. After 1 h, ester formation was identical for the 60 and 45°C runs and only slightly lower for the 32°C run. Temperature clearly influenced the reaction rate and yield of esters. (Ma and Hanna, 1999).

2.3   *Parameters which define the fuel quality of biodiesels*

2.3.1   *Cetane Number*

Cetane number is a measure of the self-ignition quality of the fuel. 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. No. 2 diesel fuel usually has a cetane rating between 45 and 50 while vegetable oil is 35 to 45. Biodiesel is usually 50 to 60. The ignition quality affects engine performance, cold starting, warm up and engine combustion roughness. Cetane rating is related to the volatility of the fuel where more volatile fuels have higher ratings. A high cetane fuel also may lead to incomplete combustion and smoke if the fuel ignites too soon by not allowing enough time for the fuel to mix with air for complete combustion. Fuels with low Cetane Numbers will result in difficult starting, noise and exhaust smoke. In general, diesel engines will operate better on fuels with Cetane Numbers above 50. Cetane numbers measure the ignition of diesel, much like octane numbers measure the ignition

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of gasoline. These numbers represent the measure of a fuel's willingness to ignite. Biodiesel has a higher cetane number than that of diesel, largely because of its higher oxygen content (Jackson MA, King JW, 1996). It is important to note that biodiesel's cetane number can vary widely, based on differences in fatty acid composition of the feedstock oil and the saturation level of the fatty acids (Saka S, Kusdiana D, 2001).

2.3.2   *Acid Number*

 Acid number (value) 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. (National Renewable Energy Laboratory, Colorado, USA, September 2001)

Acid number is a measure of acids in the fuel. These acids emanate from two sources: (i) acids utilized in the production of the biodiesel that are not completely removed in the production process; and (ii) degradation by oxidation. For biodiesel blends the acid number will change as a result of the normal oxidation process over time. Once purchased, biodiesel fuel blends that will not be utilized immediately should be monitored for changes in acid number as an indicator of fuel degradation. (Engine manufacturers association, 2006)

2.3.3   *Cloud Point*

Cloud point is the temperature at which oil starts to solidify is known as the cloud point. While operating an engine at temperatures below oil's cloud point, heating will be necessary in order to avoid waxing of the fuel. Small crystals of fuel begin to form in the liquid causing haziness as the sample is cooled. It is an indicator of the utility of petroleum oil for some applications. In the case of biodiesel, the haze is made up of crystallized fuel molecules, specifically crystallized stearic and/or palmitic methyl esters (Knothe and Dunn, 2001). Using a product below its cloud point may reduce the lubricating properties, and may plug filters. For biodiesel, the settled material may not cause lubrication problems, but the remaining liquid may have lower properties relative to the fully mixed fuel. The pour point and cloud point are both higher for biodiesel fuel than for

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gasoline-based diesel, indicating that biodiesel will tend to gel at higher temperatures than diesel, causing engine problems. (Lee et al, 1996, Heraud, A., 1992)

2.3.4   Viscosity

Viscosity refers to the thickness of the oil (flow properties), and is determined by measuring the amount of time taken for a given measure of oil to pass through an orifice of a specified size. Viscosity affects injector lubrication and fuel atomization. Fuels with low viscosity may not provide sufficient lubrication for the precision fit of fuel injection pumps, resulting in leakage or increased wear. Fuel atomization is also affected by fuel viscosity. Diesel fuels with high viscosity tend to form larger droplets on injection, which can cause poor combustion, increased exhaust smoke and emissions. The viscosity of biodiesel and biodiesel blends also increases more rapidly than diesel as temperature is decreased. Certain impurities also tend to significantly increase the viscosity of biodiesel (Allen et al, 1999).

2.3.5   Calorific Value or Heat of Combustion

Heating Value or Heat of Combustion is the amount of heating energy released by the combustion of a unit value of fuels. One of the most important determinants of heating value is moisture content. Air-dried biomass typically has about 15-20% moisture, whereas the moisture content for oven-dried biomass is negligible. Moisture content in coals varies in the range 2-30%. However, the bulk density (and hence energy density) of most biomass feed stocks is generally low, even after densification – between about 10 and 40% of the bulk density of most fossil fuels. Liquid biofuels however have bulk densities comparable to those for fossil fuels. The energy content of biodiesel and diesel is 37MJ/Kg and 45MJ/Kg respectively. (Weast et al, 1985–1986; Freedman et al, 1989).

2.3.6   Melting Point or Pouring Point

Melt or pour point refers to the temperature at which the oil in solid form starts to melt or pour. In cases where the temperatures fall below the melt point, the entire fuel system, including all fuel lines and fuel tank will need to be heated (Lee et al, 1996, Heraud, A., 1992).

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2.3.7 Flash Point (FP)

The flash point temperature of diesel fuel is the minimum temperature at which the fuel will ignite (flash) on application of an ignition source. Flash point varies inversely with the fuel's volatility. Minimum flash point temperatures (standard) are required for proper safety and handling of diesel fuel. Biodiesel and diesel have a common *boiling point*, but biodiesel has a higher *flash point* because biodiesel has a high number of FAMEs, which are generally not volatile. Thus, biodiesel is safer to handle at higher temperatures than diesel (National Renewable Energy Laboratory, Colorado, USA, 2001).

2.3.8 Total Fatty Acids

Total Fatty Acid is the analysis of the amount of fatty acids present in the biodiesel. It is an indication of the conversion efficiency of the original feedstock. Gas Chromatographic Analysis of Fatty Acids indicates the composition of each of the biodiesels. The largest fraction of fatty acids for each of the biodiesels is a potential indication of the rest of the properties. The methyl esters follow some patterns. The soy, canola, and two yellow grease ME are mostly oleic and linoleic acid (C18, one and two double carbon bonds), while the two largest components of the lard, edible tallow, and inedible tallow ME are oleic and palmitic acid (C18, one C:C bond, and C16, saturated). Free glycerin and total glycerin (by the Christina Planc method) is a good indicator as to the cleanup of the fuel, or of the degree of completion during the reaction. As such, it should remain in the specifications for biodiesel. (Neff et al , 2000 , Warne et al , 2001).

2.3.9 Iodine Value of Oils and Fatty Acids

Iodine value is 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. The Iodine value is determined by measuring the number of double bonds in the mixture of fatty acid chains in the fuel by introducing iodine into 100 grams of the sample under test and measuring how many grams of that iodine are absorbed. Iodine absorption occurs at double bond positions – thus a higher Iodine number indicates a higher quantity of double bonds in the sample, greater potential to polymerize

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and hence lesser stability. One can hence see that the process of transesterification (conversion of plant oil in to biodiesel) reduces the iodine value to a small extent. (National Renewable Energy Laboratory, Colorado, USA, September 2001)

2.3.10 *Ash content*

Ash content measures the amount of ash left after a sample is burned. The presence of ash may indicate undesirable impurities or contaminants. As such, it provides one measure of the suitability of a product for a given application. The maximum acceptable value for diesel meeting D 975 requirements is 0.01%, which should be easily met with most of the biodiesels. Ash content for bio-fuels is typically lower than for most coals, and sulphur content is much lower than for many fossil fuels. Unlike coal ash, which may contain toxic metals and other trace contaminants, biomass ash may be used as a soil amendment to help replenish nutrients removed by harvest (National Renewable Energy Laboratory, Colorado, USA, September 2001).

2.3.11 *Water and Sediment*

Fuel should be clear in appearance and free of water and sediment. The presence of these materials generally indicates poor fuel handling practices. Water and sediment can shorten filter life or plug fuel filters, which can lead to engine fuel starvation. In addition, water can promote fuel corrosion and microbial growth. The level of water specified is within the solubility level of water in fuel and, as such, does not represent free water. Limits are established to allow measured results to be compared to a maximum level acceptable for proper engine operation (Engine manufacturers association)

2.3.12 *Copper Strip Corrosion*

The copper strip corrosion test indicates potential compatibility problems with fuel system components made of copper alloys such as brass and bronze. The limit specified is the same as that for petroleum diesel fuel. (Engine manufacturers association)

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2.3.13 Carbon Residue

The Carbon residue test is intended to provide some indication of the extent of carbon residue that results from the combustion of a fuel. The limit specified is the same as that for petroleum diesel fuel (Engine manufacturers association).

2.3.14 Distillation (boiling point range)

Distillation is a method for determining the full range of volatility characteristics of a hydrocarbon liquid by progressively boiling off a sample under controlled heating. Different methods are available for distillation: atmospheric, vacuum, and simulated. Biodiesel is fundamentally different than petroleum based diesel, and it is especially evident with distillation. Biodiesel has a fairly homogenous consistency of straight chain hydrocarbons, all with 16 to 18 carbons. Consequently it exhibits a boiling point rather than a distillation curve. (Engine manufacturers association)

The degree of saturation of the fatty acids attached to the glycerol backbone determines the boiling point of the triglyceride. Generally, the FAMEs, which are mainly comprised of carbon chain lengths from 16 to 18, have boiling points in the range of 330–357 oC; thus the specification value of 360 oC is easily achieved (Azam et al., 2005).

2.4 The role of petroleum fuels in the Ethiopian energy sector

In Ethiopia biomass energy meets ninety-five percent of the national energy demand. The largest share of the energy supplied is then consumed for domestic uses. Petroleum products and electricity supply only 4% and 1% of the national energy demand respectively. In terms of gross supply the contribution of petroleum fuels and electricity is therefore relatively insignificant. However, petroleum fuels and electricity supply practically all the critical applications of a modern economy including transport and communication, trade and industry, and social services. (Ministry of mines and energy, march 2007)

The modern transport sector including road, rail, air and sea, is exclusively dependent on petroleum fuels; small and large industries depend on petroleum fuels for thermal and mechanical applications; urban households depend on petroleum for domestic cooking while rural

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households depend on it for lighting. Without transport fuels markets and trade, including exports, cannot function and development and growth will be impossible. (Ministry of mines and energy, march 2007)

According to the data obtained from Ethiopian Petroleum Enterprise, 452,629 metric tons of petroleum products were imported in the first quarter of 2007/08, which showed 17.7 percent and 16.6 percent increase over the previous quarter and the corresponding period of last year. Quarterly increment in volume was observed in all products, namely, Regular Gasoline (26.4 percent), Jet Fuel (32.6 percent), Fuel Oil (5.1 percent) and Gas Oil (12.5 percent). .Gas oil imports accounted for about 55 percent of the total volume of petroleum imports during the review quarter. (National bank of Ethiopia,www.nbe.gov.et ,2007)
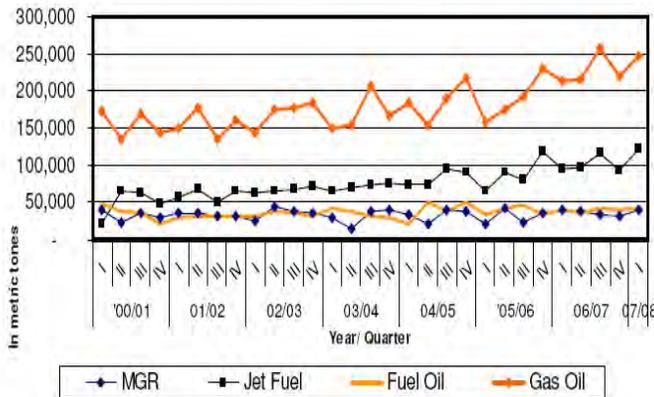
Figure 2 Trends in the volume of petroleum products imported from 2000/01-2007/08

Oil import bill during the review quarter amounted to Birr 2.61 billion, which was 29 and 30 percent higher than the level in the previous quarter and the same period of last fiscal year, respectively, as the value of all types of petroleum products increased.(National bank of Ethiopia, 2007)

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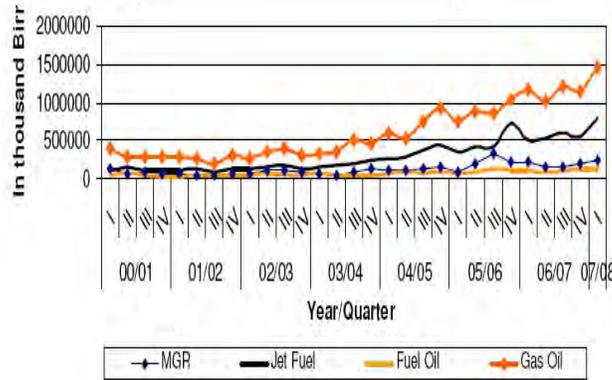
Figure 3 Trends in the value of imported petroleum products from 2000/01-2007/08

2.4.1 Biodiesel and Ethiopia's strategy for improving access to transport services

Improving access to transport services is a key to the transformation of a subsistence economy to a modern market economy. In realization of this, the Ethiopian government is implementing an ambitious program of transport infrastructure development. Infrastructure is, however, only part of the solution for improving transport services. Access to transport technologies and energy must also be enhanced for the country to fully benefit from its expanding transport infrastructure.

Diesel is the most important transport fuel in Ethiopia as practically all the commercial freight and public transport runs on it. Substitution of petroleum diesel by biodiesel will improve access and security of supply. (Ministry of Mines and Energy, march 2007)

2.5 MORINGA STENOPETALA - THE MIRACLE TREE

2.5.1 Taxonomy and Distribution

Moringa stenopetala belongs to family Moringaceae that is represented only by a single genus Moringa. The genus is represented by 14 species to which *Moringa stenopetala* belongs. Northeast

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tropical Africa is a center of endemism plus diversity to the genus (Mark, 1998). The taxonomic position of the family is not clear. It has some features similar to those of Brassicaceae and Capparidaceae but the seed structure does not agree with either of the above families. Pollen studies have not provided any other suggestions and recent molecular studies have pointed to a relationship with the Carricaceae. These indicate that the taxonomic position of the family is not yet settled and is open for further studies. Its seed physiology is also not yet studied in the country (Edwards et al., 2000).

Moringa stenopetala is a tree 6-10m tall; trunk: more or less 60cm in diameter at breast height; crown: strongly branched sometimes with several branches; thick at base; bark: white to pale gray or silvery, smooth; wood: soft; Leaves: up to 55cm long; Inflorescence: pubescent, dense many flowered panicles ca. 60cm long (Edwards et al., 2000).

The species is known by different vernacular names such as Shiferaw (Am), Aleko, Aluko, Halako (GG), Kallanki (Ben), Telahu (Tse), Haleko, Shelchada (Kon), Haleko (Bur), Haleko (Dh) and Cabbage Tree (Eng).(Ethiopian tree foundation fund, 2004)

The Genus follows the distribution pathway from Rajasthan to south West Africa (Africa, Madagascar and parts of Asia, including Arabia and India) (Mark, 1998). The habitat where the genus occur in Ethiopia as summarized from the herbarium sheets of the National herbarium includes: rocky areas along rivers, dry scrub land, Acacia-Commiphora woodland, water courses with some evergreens, Open Acacia-Commiphora bush land on grey alluvial soil and in cultivation around village. *Moringa Stenopetala* is cultivated in terraced fields, gardens and small towns. The species is found to grow in Keffa, Gamo Gofa, Bale, Sidamo, Borana and Debub Omo zones, and in Konso and Dherashe especial weredas. (Ethiopian tree foundation fund, 2004).

The National herbarium has few collections of Moringaceae. The overall collections were represented by 5 species of which the larger part is *Moringa stenopetala*. Many of the collections were from Gamo Gofa. There are small seed collections of Moringa species in the Institute of Biodiversity Conservation and Research from Gamo Gofa. However, the viability of these seeds is

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not yet tested. There is no information documented on *Moringa stenopetala* localities in the eastern and northern parts of Ethiopia. It is not clear whether this is due to lack of exploration to the area or really absence of the species in the area.(Ethiopian tree foundation fund, 2004).

Figure 4.*M.stenopetala* leaves for market   *M.stenopetala* leaves for cooking

2.5.2 Origin and Uses

Moringa stenopetala is often referred to as the African Moringa Tree because it is native only to southern Ethiopia and northern Kenya. Though it grows in many other parts of the tropics, it is not as widely known as its close relative, *Moringa oleifera* but often considered generally more desirable than *M. oleifera* (Mark, 1998).

It is reported that the edible parts are exceptionally nutritious (Rams, 1994). The leaves are one of the best vegetable foods that can be found in the locality. All parts of the tree except the wood are edible, providing a highly nutritious food for both humans and animals. The flowers are a good nectar source for honey; can be eaten or used to make a tea and the seeds are rich oil sources,44.9%,(*S. Lalas et.al, 2003*) for cooking and lubricant uses. Many parts of the plant have been used in medicinal preparations. The wood is very soft; useful for paper but makes low-grade firewood and poor charcoal (*S. Lalas et.al, 2003*). Attracting attention in recent decades is the use of the dried, crushed seeds as a coagulant (Jahn, 1984). Even very muddy water can be cleared

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when crushed seeds are added. Solid matter and some bacteria will coagulate and then sink to the bottom of a container. The cleaned water can then be poured off and boiled. Use 100 milligrams (about 1 to 1 ½ seeds) of crushed seed to clean 1 liter of muddy water (Gupta and Chaudhuri, 1992).

2.5.3 Cultivation and Harvesting

It has been reported that *Moringa stenopetala* grows wild in elevations between 1,000 and 1,800 m (Mark, 1998) but it will grow as high as 2200m and as low as 300m (herbarium source) in Ethiopia. However, communication with the local people showed that currently this species is known in wild in localized areas in Debub Omo around Turmi. Otherwise it is known as cultivated plant in most places. Studies show that light frosts will do it no harm and freezes, though, may cause it to die back to ground level, where new sprouts may be produced. Full sun is normal, though partial shade is tolerated. It is resistant to dry weather. Optimum light for germination of all Moringa species is half shade.(Ethiopian tree foundation fund, 2004).

Seeds should be planted about 2 cm deep in soil that is moist but not too wet. Sprouting occurs normally in 1-2 weeks. It can be allowed to grow for shade (6-15 m), or kept low (about 1-1.5 m) for easier harvesting. Moringa stenopetala quickly produces a large gray trunk and leaves covered with glistening nectars. It quickly sends out new growth from the trunk when cut, or from the ground when frozen. Living fences can be continually cut back to a few feet. It is an extremely fast-growing tree and continued to grow during the exceptionally long dry season (Ethiopian tree foundation fund, 2004).

Very young whole plants, young leaves and even older leaflets and flowers can be harvested for food. The slender young pods are picked for use like green beans. Seeds of older pods may be shelled from the pods and cooked like green peas. The older flowering branches can be pruned repeatedly to stimulate production of new branch shoots as additional sources of leaves. Moringa is resistant to most pests, though root rot can occur if the soil is too wet. (Ethiopian tree foundation fund, 2004).

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2.5.4   Cooking and Nutrition

It was reported that Moringa foliage and fruit pods are rich sources of calcium and iron, and good sources of vitamins A, B, and C (when raw) and of protein (including goodly amounts of the sulfur-containing amino acids, methionine and cystine) (Rams, 1994). Both young and older leaves are edible, though older ones are milder and tender. They can be cooked in soups or boiled. Young pods may be also cooked. Immature seeds are often cooked and eaten as a fresh vegetable, while mature seeds can be dried and roasted. The flowers can be cooked or oven-dried and steeped as tea. Dried leaves can be stored as future soup or sauce supplements. Blossoms are edible; they taste like radish. Browning seeds from mature pods that are mashed and placed in boiling water causes an excellent cooking or lubricating oil to float to the surface. The oil preserves well although become rancid with age. Its roots are used as a flavoring and in poultices; and edible oil can be extracted from its seeds. The green pods and surrounding white material can be removed from larger pods and cooked in various ways. (Ethiopian tree foundation fund, 2004).

It is reported that *M. stenopetala* had larger and more appealing in appearance and more palatable leaves, more drought resistance, and larger seeds as compared to the widely known Indian Moringa. (Ethiopian tree foundation fund, 2004).

2.5.5   Socioeconomic Values

It is reported that in some parts of Africa there are folk beliefs that Moringa trees planted on graves keep away hyenas and its branches guard against witchcraft. For this reason many families plant Moringa species on and around the graves of their relatives. I believe this way of thought, therefore, has a great contribution to the conservation of the species. In some parts of southern Ethiopia, especially among the konso people, the abundance of Moringa species in the garden or on farmland indicates the social status of the owner among the society. The one with many Moringa tree in the garden or on farmland has a higher social status and also considered rich. In Konso if a man wants to get married and asks a girl to be his wife then the first question that the parents of the would be wife ask to know is how many Moringa trees he has in his garden or farmland. They thought that if the husband has many Moringa trees in his garden or farmland then their daughter

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will have no problem to feed her babies even when drought happens. For this reason konso people especially young men are encouraged to plant Moringa in their garden as well as on their farmlands. This teaches us that culture by itself has a great role in conservation and sustainable utilization of locally important tree species. (Ethiopian tree foundation fund, 2004).

M. stenopetala is planted together with fruit trees in the cropped fields in Konso. Sometimes the trees are also used to provide partial shade for crops like sorghum in the southern Ethiopia. Whole plants have been used as hedges and fences. *M. stenopetala* can also be planted as a windbreak. As soon as the upper branches of the tree grew broader, the tree can be pruned to stimulate more profuse growth of their lower branches, thus thickening the hedge. Vegetables cultivated behind it profited from this protection. The species can also be grown as an ornamental tree in private gardens and home compounds. (Ethiopian tree foundation fund, 2004).

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3 MATERIALS AND METHODS

3.1 Materials

The *Moringa stenopetala* seed used in this process was purchased from Podo PLC, Addis Ababa. Number 2 diesel was obtained from Ethiopian petroleum enterprise, Addis Ababa. All the chemicals were analytical grade and obtained from chemistry department. Laboratory work was undertaken in Addis Ababa University, chemistry department and in Ethiopian petroleum enterprise.

3.2 Methods

3.2.1 Experimental Setup and Procedure

The operations studied in the experimental work were:

- ➢ Extraction of oils
- ➢ Transesterification
- ➢ Phase separation
- ➢ Washing, purification and biodiesel yield
- ➢ Characterization of *M.stenopetala* derived biodiesels using different parameters

In this study ethanol, methanol and mixtures of methanol/ ethanol in 3:3 molar ratio in presence of a catalyst (KOH) were used. After the reaction was completed, the reaction products separated into two layers; the ester product formed on the upper layer and the by-product glycerin formed in the lower layer. The residual catalyst and unreacted excess alcohol were distributed between the two phases. After separation of the phases, the catalyst and alcohol were washed from the ester with water.

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3.2.1.1 Determination of moisture content of the seeds

30g of the crushed cleaned *M.stenopetala* seed was weighed and dried in an oven at 105oc for 24hrs and the weight was taken. After 24 hours, the sample was removed from the oven and placed in the desiccator for 30 minutes to cool. It was then removed and re-weighed. The percentage moisture in the seed was calculated from the formula:

Moisture content = 100(W_1- W_2)/ (W1 - Wc) %......................................Equation 3

Where W_1 = Original weight of the sample before drying;

W_2 = Weight of the sample after drying.

Wc = weight of empty crucible

3.2.1.2 Extraction of M. stenopetala seeds oil

350g of crushed *M. stenopetala* seeds were placed in the thimble and 1.5L of normal hexane was poured in to the round bottom flask .The apparatus was heated at 60oC and allowed for 6hrs continuous extraction using soxhlet apparatus. The solvent was removed at 65oC under vacuum using a rotary evaporator to obtain crude *M. stenopetala* oil and the percentage of oil extracted was determined using equation (4).The procedure was repeated in triplicate and recorded.

Seed oil content = (W_o/W_s) 100 %...Equation 4

Where Wo = weight of oil extracted

Ws = weight of the sample

Figure 5. *M.stenopetala seeds*   *Crushed M.stenopetala seeds*

3.2.1.3 Transesterification of M.stenopetala oil

3.2.1.3.1 Transesterification with methanol

For the synthesis of methyl ester, a two-stage process was chosen as it removes the majority of the mono-, di-, and tri-glycerides in the first stage and those remaining could be taken out in the second stage (Lang et al.,2001a), resulting in a more purified product. The amount of *M.stenopetala* oil used in the reaction was 300 g. A 6:1 molar ratio of methanol to oil was used in order to utilize 100% stoichiometric excess of methanol (Lang et al., 2001a). Therefore, 68 g of methanol is used for the entire procedure, and 34g is used per stage. The amount of potassium hydroxide used was 1.0 wt. %(3g) of the vegetable oil.

In the first stage, 1.5 g of KOH is added to 34g of methanol and stirred until the catalyst was completely dissolved. *M.stenopetala* oil (300 g) was placed in an Erlenmeyer flask equipped with a magnetic stirrer and thermometer and the methanol/KOH solution was added to the oil. This mixture was stirred for 30 min at 25 ^{0}C, and then poured into a separatory funnel. After about an hour separation has occurred, and the glycerol was removed from the separatory funnel as a dark brown colored liquid from the bottom of the flask. Another 1.5g of KOH is added to 34g of methanol, and stirred until the KOH dissolved. This was then added to the *M.stenopetala* methyl ester obtained from the first stage, and was again stirred for 30 min. afterwards; the mixture was added to a separatory funnel and allowed to separate overnight.

3.2.1.3.2 Transesterification with ethanol

Ethyl ester of *M.stenopetala* oil was prepared in a similar way as methyl esters. The transesterification was carried out at 70 ^{o}C and 25 ^{o}C for 2 h with vigorous agitation in order to achieve full conversion. In order to avoid the emulsion after the transesterification reaction, 0.1% aqueous tannic acid was used as a washing solution to remove catalyst. (Kulkarni et al, 2006).

3.2.1.3.3 Transesterification with mixture of methanol and ethanol in 3:3 molar ratios

A mixture of methanol and ethanol in 3:3 molar ratios was used for the transesterification reaction, keeping the molar ratio of oil to alcohol 1:6. The reaction was carried out in a batch type of reactor. 100g of *M.stenopetala* oil was placed in a dry Erlenmeyer flask equipped with a magnetic stirrer and thermometer. In another dry Erlenmeyer flask 1.0 g of potassium hydroxide was mixed with mixture of methanol and ethanol (11.25g of methanol and 15.5g of ethanol).This mixture was then added to the oil and stirred vigorously for 50 min at room temperature. The mixtures was poured to separatory funnel and allowed to separate overnight. The ester layer was washed 3–4 times with 0.1% tannic acid solution to reduce emulsification. ((Kulkarni et al, 2006).

Figure 6. Transesterification of *M.stenopetala* oil

3.2.1.4 Phase separation

After complete esterification (as evident from GC), the reaction was stopped and the reaction mixture was allowed to stand overnight while phase separations has occurred. The ester phase was then decanted from the equilibrium mixture.

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Figure 7. *During phase separation*   *Purification stage*   *Purified Moringa biodiesel*

3.2.1.5 Washing and purification

When Biodiesel was first made it was quite caustic with a pH of between 8.0 and 9.0.Washing with water neutralized the product. Traces of methanol along with the catalyst were washed with hot water (55°C) and ethanol with 0.1% tannic acid solution. Since Biodiesel has a lower specific gravity than water, the water was sinking to the bottom and the Biodiesel was remaining over the water. The remaining methanol/ ethanol was removed with the help of a Rota-Evaporator (R-114, Buchi, = Switzerland) from the ester. After about 30 min the entire methanol/ethanol has boiled off. A layer of sodium sulfate crystals was added to a vacuum filtration funnel, and the ester was filtered through it to remove any traces of water present. The dried *M.stenopetala* methyl/ethyl ester was then bottled and kept for characterization studies.

3.2.1.6 Biodiesel yield

The biodiesel yield (% wt) after the post-treatment stage, relative to the amount of *M.stenopetala* oil poured into the reactor, was calculated from the methyl/ethyl ester and vegetable oil weights. (Vicente, G., 2006)

Biodiesel yield = (mass of methyl-ethyl ester) X100...Equation 5

                               (mass of oil)

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3.2.1.7 *Characterization of the extracted oil and biodiesel fuels*

To determine the suitability for use in diesel engines, methyl/ethyl esters were then characterized by determining their diesel properties following the standard methods. Using standard procedures as listed in Table 1, physical and chemical properties such as density, viscosity, heat of combustion, cloud and pour points, copper strip corrosion, water and sediment content, ash content, ASTM color, flash point, acid value, and iodine value were determined and compared with ASTM standards and number 2 diesel.

The fatty acid compositions of the methyl/ethyl esters are measured by gas chromatography using a GC (GC 1000DPC) equipped with a DB-FFAP column and flame ionization detector. The viscosities of the esters were determined at 40 ᵒc using Cannon-Fenske glass capillary viscometer tube in SETA KV-8 viscometer bath and the specific gravity were determined at 15ᵒc using Hydrometer. The experiments were performed thrice to obtain the viscosity data. The heats of combustion of the methyl/ethyl esters were measured using an Oxygen Bomb Calorimeter. In order to ensure complete combustion after firing, approximately 50 wt. % benzoic acid powder was mixed with the sample liquids. The saponification value of *M.stenopetala* oil was determined according to Sonntag (1982). Flame Atomic Absorption Spectrophotometer (FAAS) determined alkali and alkaline earth metals, BUCK SCIENTIFIC MODEL 210 VGP, East Norwalk, USA. 1g of the sample was extracted by conc. 10ml of HNO_3 and 3ml of 30% of H_2O_2.

The flash point was determined using Pensky-Martens closed cup tester and corrected to atmospheric pressure (760mmHg) using the equation (6)

Corrected flash point =C + 0.033(760 − P)...**Equation 6**

    Where, C = observed flash point

        P = ambient barometric pressure

Distillation of boiling point range was carried out according to ASTM D86 and corrected temperature readings to 760mmHg pressure using the equation (7 and 8)

Cc =0.00012(760–P) (273 + tc)..Equation 7

Where tc = the observed temperature reading, oc

Cc = corrections to be added algebraically to the observed readings

P = barometric pressure prevailing at the time and location of the test, mmHg

Then, corrected temperature (oc) = tc + Cc..Equation 8

The cetane index (ASTM D 976) was calculated from density and distillation data using equation (9)

Cetane index = 454.74 –1641.416D + 774.74D² – 0.554B + 97.803(LogB) ²......Equation 9

Where, D =Density at 15oC, g/ml

B = corrected mid boiling point in oC

Table 1. Standard Methods

Fuel Properties	Standard method
Specific gravity	ASTM D1298
viscosity	ASTM D445
Cloud point	ASTM D2500
Pour point	ASTM D97
Flash point	ASTM D93
Distillation of boiling point range	ASTM D86
Fatty acid composition	AOCS Ca5a-40
ASTM color	ASTM D1500
Copper strip corrosion	ASTM D130
Ash content	ASTM D482
Acid value	ASTM D974
Iodine value	AOCS Cd 1c-85
Water content	ASTM D95
Conradson Carbon residue using 10% distillation residue	ASTM D189
Heat of combustion	ASTM D240
Cetane index	ASEM D976

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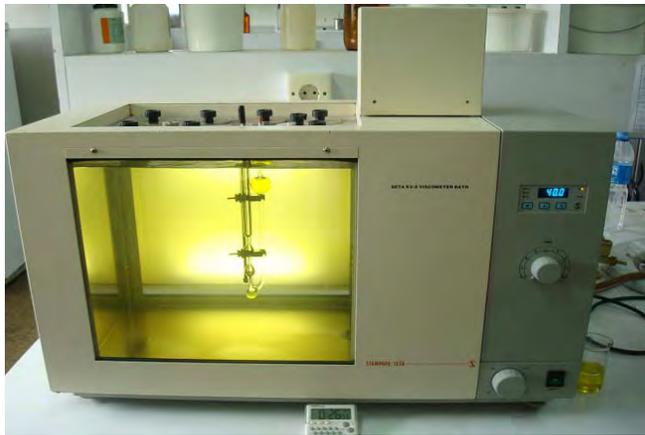
Cannon-Fenske glass capillary viscometer

Petroleum products distillation apparatus
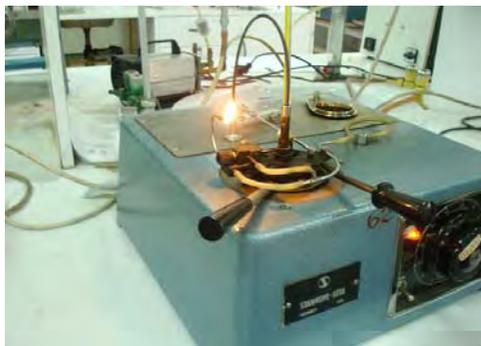
Pensky-Martens closed cup tester

ash content determination

Hydrometer

The Peltier device apparatus

Figure 8. Photos of different instruments

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4   RESULT AND DISCUSSION

4.1   Moringa stenopetala seed oil

The oil from *M.stenopetala* seeds from Ethiopia was extracted using n-hexane as a solvent by soxhlet apparatus. The extracted oils were liquid at room temperature. The oils were pale yellow liquids at ambient temperature with characteristic unique odor and palatability.

4.1.1   Oil content, saponification value and Moisture content of M.stenopetala seeds

The yield of oil was found to be 45.3% that is in agreement with previous literature, 44.9, (*S. Lalas et al, 2003*). The high oil yield allows the possibility of economical exploitation which results in lower operation costs compared to some other oilseeds, such as soybeans and cottonseeds, which have average oil contents of only 20% and 14%, respectively. Lower operation costs result from higher oil percentage mainly due to less capacity needed for the extruder and oilseed press. *(Schinas P. et al, 2008).*The moisture content of the *M.stenopetala* seeds was 5%. The saponification value of *M.stenopetala* oil was 178.23 mg of soap (as potassium oleate)/g of oil which is in agreement with the previous literature, 177.24 mg KOH/g. (*S. Lalas et al, 2003*).

4.1.2   Fatty acid composition of M.stenopetala oil

The fatty acid composition of *M.stenopetala* seed oil is shown in the Table 2. The oil was found to contain high level of unsaturated fatty acid (78%) with one double bond, while the saturated fatty acid amount to 22%. The dominant fatty acid is oleic(76%) and the oil belongs to the oleic acid category.(Sonntag ,1982).These results agree well with those reported for *M.stenopetala* samples collected in Kenya (*Lalas et.al, 2003*) .

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Table 2 .Fatty acid profile of *Moringa stenopetala* seeds oil

Fatty acid	Systemic name	Formula	Structure	Amount (wt %)
Palmatic	Hexadecanoic	$C_{16}H_{32}O_2$	16:0	6.1
Oleic	cis-9-Octadecenoic	$C_{18}H_{34}O_2$	18:1	76.0
Stearic	Octadecanoic	$C_{18}H_{36}O_2$	18:0	7.5
Arachdic	Eicosanoic	$C_{20}H_{40}O_2$	20:0	3.8
Arachideic	eicosenoic	$C_{20}H_{38}O_2$	20:1	1.7
Behenic	Docosanoic	$C_{22}H_{44}O_2$	22:0	4.4
others	-	-	-	0.5

The fatty acid composition of *M.stenopetala* in comparison to the fatty acid profiles of *M.olifera*, sunflower, soybean, rapeseed and palm oils is shown in table 3. It is indicated that *M.stenopetala* oil has higher saturation than soy bean, sunflower and rapeseed oils, but lower saturation than palm oil. It is important also to remark that, the absence of polyunsaturated fatty acids (*C18:2 & C18:3)* in *M.stenopetala* oil in comparison to that of soybean ,sunflower & rapeseed oil, may provide advantages in terms of the oxidative stability of *M.stenopetala* oil. The fatty acid composition of *M. stenopetala* oil was similar to that of the *M.olifera* and there was a marked difference in the percentage composition of C18:0, C18:1 and C22:0. Another interesting fact is the high content of behenic (docosanoic) acid in *M. stenopetala* oil. The oil possesses significant resistance to oxidative degradation due to its content of behenic acid (Lalas et al, 2003).

Table 3. Fatty acid composition (%) of the oils of *M. stenopetala*, Soybean, *M.olifera*, Sunflower, Rapeseed and palm

Fatty acid	*M.stenopetala*	soybean[1]	*M.olifera[1]*	Sunflower[1]	Rapeseed[1]	Palm[1]
C16:0	6.1	11	6.5	6.4	3.6	44.1
C18:0	7.5	4	6.0	4.5	1.5	4.4
C18:1	76.0	23.4	72.2	24.9	61.6	39.0

[1] U. Rashid et al,2008

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C18:2	–	53.2	1.0	63.8	21.7	10.6
C18:3	–	7.8	-	<1(trace)	9.6	0.3
C20:0	3.8	-	4.0	-	-	0.2
C20:1	1.7	-	2.0	-	1.4	-
C22:0	4.4	-	7.1	-	-	-

In summary, the fatty ester profile of *M. stenopetala* oil different from those of soybean, sunflower, rapeseed and palm oils, but with minor quantitative difference with *M.olifera* oil which is also influencing the corresponding properties of esters. Another important point would be *M.stenopetala* seeds will not compete with food supply as soybean and sunflower do if used for biodiesel.

4.2 Biodiesel yield of M. stenopetala using different alcohols

4.2.1 Biodiesel yield of M.stenopetala methyl ester

A two-stage process was chosen for the synthesis of *M.stenopetala* methyl ester as it removes the majority of the mono-, di-, and tri-glycerides in the first stage and those remaining could be taken out in the second stage (Lang et al.,2001a), resulting in a more purified product. This facilitated the reaction to nearly complete conversion in the second step. (X.lang et al, 2001a). It has been reported that in a commonly used single-stage process, a period of 1h is required to achieve 98% conversion of rapeseed oil to methyl esters at 25°C (Peterson et al ,1991). This longer period was due to the fact that vegetable oil transesterification with alkanols is a reversible chemical reaction. Also, since the by product, glycerol, was less volatile than the alkanols, the reaction equilibrium can not be shifted to high product yield during one stage process by simple distillation. Therefore, a two stage process would work better than a one stage process. (X.lang et al, 2001a). In order to estimate the biodiesel yield after the reaction and separation stages, the methyl ester weight yield,

relative to the initial amount of vegetable oil, was worked out. The yield of Moringa methyl ester relative to the initial amount of *M.stenopetala* oil was 95-97.6%.

4.2.2 Biodiesel yield of M.stenopetala ethyl ester

When ethanol was used in 6:1 ethanol-to-oil molar ratio and 1% of KOH as a catalyst at both 70°C and 25°C, no phase separation was observed after 2 h reaction time. This might be due to the catalyst type. It has been reported that KOH was less effective than methoxide (CH_3ONa) as a catalyst for ethyl ester synthesis from vegetable oils. This is because ethanol(p^{Ka} = 15.9) and other primary alcohols are some what weaker acids compared to water (p^{Ka} = 15.7), while methanol(p^{Ka} = 15.5) is a slightly stronger acid .Therefore, the reaction of KOH with methanol may favors the formation of methoxide ion, the reactivity between KOH and other alcohol to form respective alkoxide anion would be very low . Although KOH is an excellent base catalyst for methyl esters, it becomes less effective for ethyl esters. (X.lang et al, 2001b). However, when small amount of NaCl powders was added to mixture of ethanol, KOH and *M.stenopetala* oil, phase separation had occurred. But the biodiesel yield was significantly very low (< 50%). This was due to the formation of emulsions when washed with tannic acid solution.

Although methyl and ethyl esters are good lubricity additives, their preparation methods have their own advantages and disadvantages. The formation of ethyl esters is environmentally attractive because unlike methanol, ethanol is produced from renewable resources and is not toxic as methanol. Also, ethanol has better solvent properties than methanol for solubility of oil. However, formation of emulsion after the transesterification reaction makes ethanolysis more complicated and impractical (Meher et al., 2006b). Due to yield loss, *M. stenopetala* ethyl ester was not produced for all characterization tests.

4.2.3   Biodiesel yield of mixture of M.stenopetala esters in 3:3 molar ratio of methanol and ethanol

The purpose of using mixture of methanol and ethanol is to take the advantage of better solubility of oil in ethanol than methanol and better reactivity of methoxide ion than ethoxide to attain the desired equilibrium. Also, mixed esters may act as a better lubricity additive than pure methyl esters (Kulkarni et al, 2006). Another advantage of using mixture of methanol and ethanol is, if part

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of the methanol is replaced by ethanol, and then there would be less dependency on the synthetic sources for methanol especially for Ethiopia who has a potential to produce 1 billion liters of ethanol within available suitable land. (Minister of Mines and Energy, August2007)

Fig 9. shows the GC of methyl, ethyl and mixture of esters. It is observed from fig 9c that, when mixture of methanol and ethanol were used, ethyl esters also formed along methyl esters. The fatty acid composition is presented in table 4.
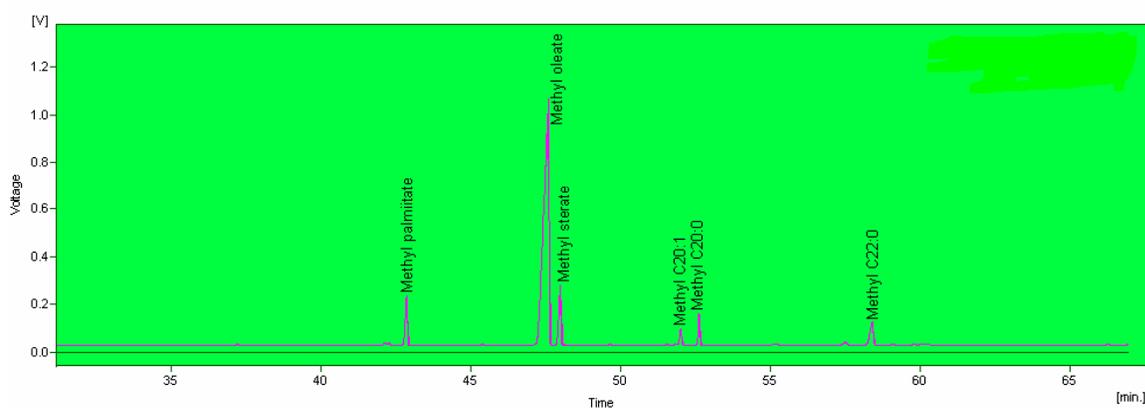
Fig 9a. GC spectra of *Moringa stenopetala* methyl ester showing the presence of different fatty acids.
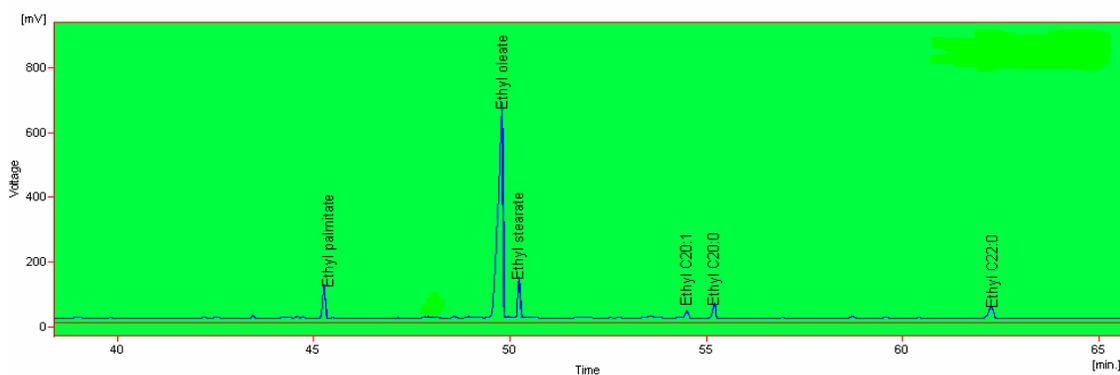
Figure 9b GC spectra of *M.stenopetala* ethyl ester

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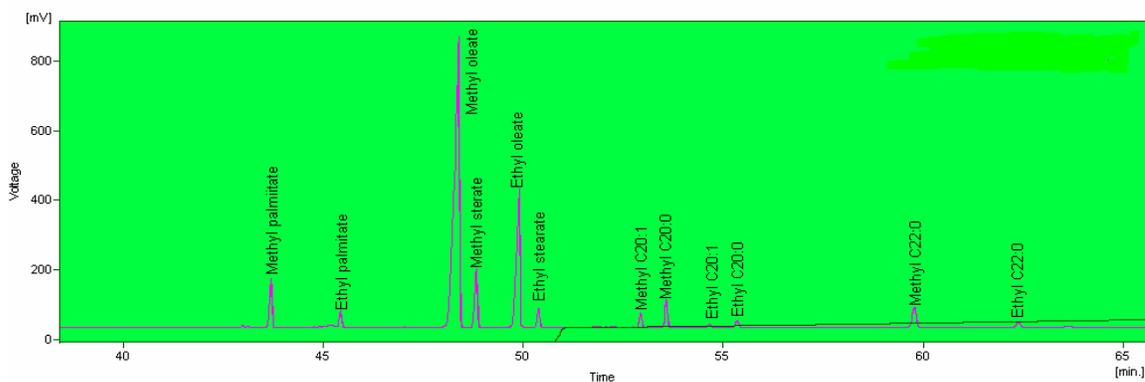
Fig. 9c GC spectra of *Moringa stenopetala* mixture of methyl ethyl ester (ME) with 3:3 Molar ratio of methanol and ethanol

In the case of mixture of esters the formation of ethyl esters was 30% that of the methyl esters (fig 9 and table 4). Even though the molar ratio of methanol to ethanol was 3:3 the formation of ethyl esters was much lower than the methyl esters. The reason for this is slow reaction rate of ethanol compared to methanol. (Kulkarni et al, 2006).The slower reaction rate of ethanol when compared with methanol can be explained by the reaction mechanisms of alkaline catalyzed transesterification. As Kulkarni et al, (2006) explains in case of the KOH catalyzed transesterification, when triglyceride molecule is reacted with the monohydroxy alcohol, the active catalyst species is alkoxide anion, which is formed by the reaction between potassium hydroxide and alcohol (Sridharan and Mathai, 1974). In case of methanol, CH_3O^-, methoxide and in case of ethanol, $C_2H_5O^-$, ethoxide anions are formed. This is a preliminary step in alkaline catalyzed transesterification

$$OH^- + R'OH \longleftrightarrow R'O^- + H_2O.............................Equation\ 10$$

The alkoxide anions formed in the preliminary step attacks the carbonyl carbon atom of the triglyceride molecule to form tetrahedral intermediate in the first step of the reaction. This is a rate determining step of transesterfication reaction. Therefore, the rate of the alkaline catalyzed transesterfication reaction is determined by the reactivity of the alkoxide anion. Reactivity of methoxide is more than the ethoxide anion. The reason for this is, as the length of the carbon chain

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increases, nucleophilicity of the alkoxide anion decreases leading to a decrease in the reactivity of alkoxide anion (Sridharan and Mathai, 1974). This causes the slower reaction rate of ethanol than methanol and ultimately less amount of ethyl esters were formed compared to methyl ester when mixture of methanol/ethanol was used for transesterification of *M.stenopetala* oil. Even though the formation of ethyl esters was slow, the overall rate of formation of esters was fast. The fast rate of formation of esters was due to the better solubility of oil in a mixture of alcohols. *M.stenopetala* oil which is non-polar is more soluble in ethanol than methanol due to low polarity of ethanol (0.654) than methanol (0.762) (Zakaria et al., 2004). Hence, when a mixture of methanol and ethanol was used, ethanol contributed for better solubility of oil. As the solubility of oil in mixture of alcohols was more there was less mass transfer limitations involved in the reaction mixture and ultimately the formation of esters was fast. (Kulkarni et al, 2006). The yield of mixtures of Moringa esters relative to the initial amount of *M.stenopetala* oil was 92- 94%.

Table 4 Fatty Acid composition of *M.stenopetala* methyl ester, ethyl ester and Mixtures of ester in 3:3 molar ratios of ethanol & methanol, in (%wt)

Fatty acid	Ester			
	MME[*]	EE[**]	ME²(3:3)	% formation of Ethyl Ester to that of Methyl Ester in mixures of Esters
C16:0(Methyl)	6.2		4.7	
C16:0(Ethyl)		6.4	1.4	29.8%
C18:0 (Methyl)	7.7		5.8	
C18:0 (Ethyl)		7.7	1.8	31%
C18:1 (Methyl)	76.0		58.2	
C18:1 (Ethyl)		76.2	18.0	30.9%
C20:0(Methyl)	3.9		3.0	
C20:0(Ethyl)		3.8	0.9	30%
C20:1(Methyl)	1.8		1.4	
C20:1(Ethyl)		1.7	0.4	28.6%
C22:0(Methyl)	4.5		3.4	
C22:0(Ethyl)		4.2	1.0	29.4
				Average = 30%
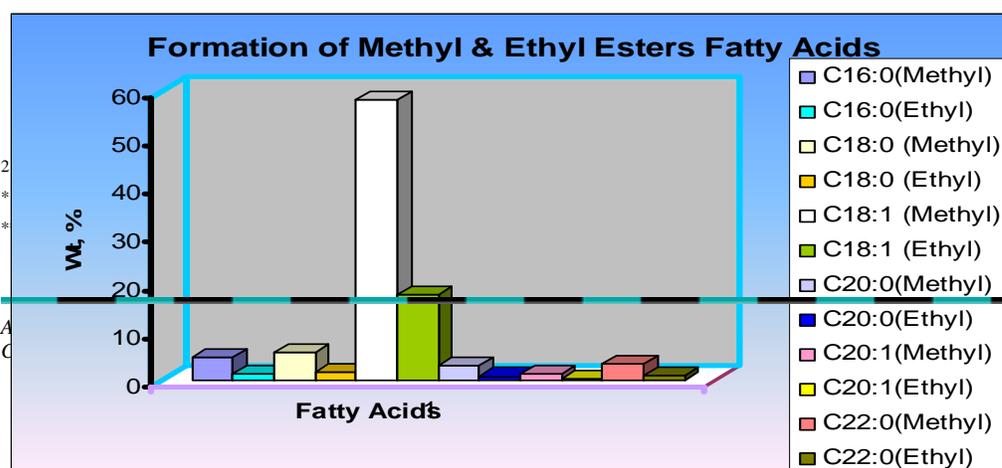
Figure 10. Formations of methyl and ethyl esters fatty acids in a mixture of methanol and ethanol in   3:3 molar ratios.

4.3   *Physicochemical properties (characterization) of M.stenopetala esters*

The *M.stenopetala* esters were characterized by following the standard ASTM methods to evaluate their densities, viscosities, acid numbers, cloud & pour points, ash & carbon content, iodine value, gross heat of combustion, cetane number, flash point, boiling point distribution and water content to determine its suitability for use in diesel engines.

4.3.1   *Density (ASTM D 1298) of M.stenopetala oil and esters*

The densities of *M.stenopetala* oil, the biodiesel esters and their blending with 80% of conventional diesel (B20MME &B2OME) at 15oC are presented in Fig.11 and compared with number two diesel. Density is an important quantity for diesel fuel injection systems (P. Schinas et al, 2008). The density of Moringa oil, Moringa methyl ester and mixture of esters at 15oC were 0.8493, 0.8482 & 0.8435g/ml respectively. The density of #2-diesel fuel at 15oC from our experiment was 0.8587g/ml where as the densities of B20MME & B20ME were 0.8552 and 0.8539g/ml respectively. The densities of the esters are lower than both Moringa oil and #2 diesels. The densities of the mixtures of ester are lower than methyl ester. The densities of both B20 are lower than # 2 diesels but higher than their respective esters. According to Clark (1988), low relative density is indicator of good ignition properties of fuels.

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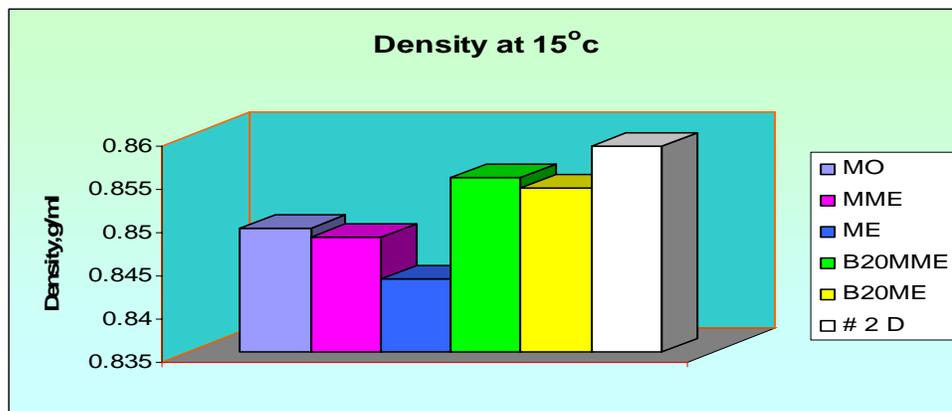
Figure 11. Densities of M.stenopetala oil(MO), No. 2 diesel (# 2 D), Moringa methyl ester (MME), mixtures of Moringa Esters (ME) and their blending (B$_{20}$MME & B$_{20}$ME)

4.3.2 Kinematic Viscosity of M.stenopetala oil and esters

Viscosity is the most important property of biodiesel since it affects the operation of fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel. High viscosity leads to poorer atomization of the fuel spray and less accurate operation of the fuel injectors (Demirbas A, 2008). The kinematic viscosity of *M.stenopetala* oils and its esters at 40°C are given in table 5 and compared with *J.curcus* methyl ester, palm oil methyl ester and castor oil methyl ester. The kinematic viscosities were determined according to the standard procedure of ASTM D 445.The kinematic viscosity of *M.stenopetala* oil was 9.4mm^2/s.   After transesterification the viscosity of the esters was significantly reduced. The viscosities of methyl and mixture of *M.stenopetala* esters were 3.2 and 3.067mm^2 /s respectively .The kinematic viscosities of the mixture of esters are slightly lower than that of methyl esters. This might be due to their density differences as the relation ship between density and viscosity of vegetable oil methyl ester were given in the literature. There are high regressions between density and viscosity values of vegetable oil methyl esters. An increase in density from 0.860 to 0.885 gm/ml for vegetable oil methyl esters or biodiesel increases the viscosity from 3.59 to 4.63mm^2/s and the increases are highly regular. (Bala BK, 2005). The kinematic viscosity of both *M.stenopetala* esters is significantly lower than those of the methyl ester of *J.curcus*, palm and castor bean oils as shown in the table 5.

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Table 5.Viscosity @ 40°c with their corresponding standard deviation

Moringa oil	$9.4 \pm 0.013mm^2/s(cSt)$
Moringa methyl ester(MME)	$3.231 \pm 0.0006mm^2/s(cSt)$
Mixtures of Moringa esters(ME)	$3.067 \pm 0.0007mm^2/s(cSt)$
Jatropha methyl ester[3]	$3.75 \ mm^2/s(cSt)$
Palm methyl ester[3]	$13.91 \ mm^2/s(cSt)$
Castor bean methyl ester[3]	$10.94 \ mm^2/s(cSt)$
# 2 Diesel fuel	$3.7 \pm 0.001mm^2/s(cSt)$

It is interesting to note that the viscosities of both esters were lower than number two diesel fuel as shown in table 4 & fig.4. The viscosity of #2 diesel fuel was 3.7mm²/s .*M. stenopetala* esters appears to be a biodiesel fuel with one of the lowest viscosity ever reported for a biodiesel fuel. *M. stenopetala* esters thus meet the requirements of the ASTM D6751 biodiesel standards, which prescribe viscosity ranges of 1.9–6.0mm²/s (cst).
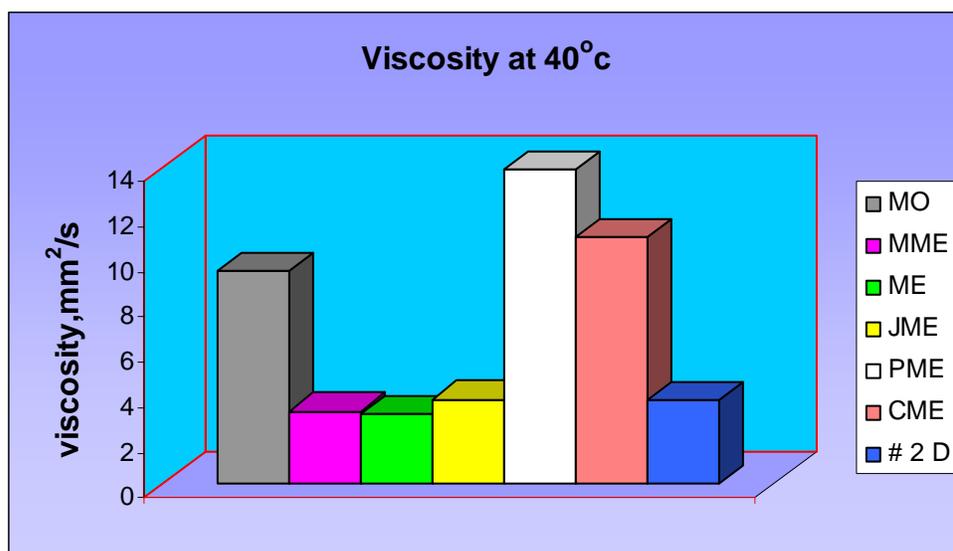
 Figure 12.   Viscosity of Moringa oil, methyl and mixtures of Moringa esters, Jatropha, palm, & castor methyl esters and No 2 diesel at 40°c

4.3.3 Acid number (AN) of M.stenopetala oil and esters

The acid numbers or acid value of *M.stenopetala* oils, mixtures of esters and methyl esters are presented in table 6. The acid value was determined according to ASTM D974.The titrated acidities

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[3] Mesifin kinfu, 2008

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of the *M .stenopetala* seed oil was 1.42mg KOH/g of oil .Based on the acid value, the free fatty acid content of *M.stenopetala* oil was 0.71%. Therefore, the oil does not need acid pretreatment for transesterification. The maximum acid value for alkaline transesterification is 2mg [KOH]/ g [oil] recommended by Canakci and Van Gerpen (2001b). High fuel acidity is associated with corrosion and engine deposits, particularly in the fuel injectors. It is known that FFA content higher than 3% decreases the transesterification yield, inhibiting the formation of methoxides by neutralization of part of the catalyst present, and producing soaps within the reaction medium. Soap formation would exacerbate the problem of phase separation at the stage of product recovery. (Keim, 1945; Mittelbach and Tritthart, 1988; Meneghetti et al., 2006a).

The suggested ASTM standard for biodiesel sets the maximum acid value of 0.8mg KOH/g of oil while the German standard DIN V 51606 sets it at 0.5mg KOH/g (knothe et al, 1997). The acid value of moringa methyl ester and mixtures of Moringa esters were 0.126 and 0.212mg KOH/g respectively. The result of esters shows that it is below the maximum value given for both standards. The acid number of the biodiesel is with in the ASTM specification, which indicates that this will not pose problem on the long-term performance of the engine (Kulkarni et al, 2006)

Table 6 Acid value of *M.stenopetala* oil and *M.stenopetala* esters

M.stenopetala oil	1.42mgKOH/g ± 0.007
Moringa methyl ester(MME)	0.126mgKOH/g ± 0.003
Mixtures of Moringa esters(ME)	0.212mgKOH/g ± 0.004

4.3.4 *Boiling point (Distillation) distributions of M.stenopetala esters.*

Distillation was carried out by simple (atmospheric) distillation using ASTM D 86. The boiling point distributions of Moringa methyl esters, mixtures of Moringa esters, commercial #2 diesel fuel and their corresponding B$_{20}$ blending are shown in fig13. The initial boiling point of MME, ME, B$_{20}$MME, B$_{20}$ME & No.2 diesel was 306, 320, 192,195 & 186°C respectively. 50% of number two commercial diesel fuel was recovered at temperatures lower than the initial boiling point of both

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esters. This shows that number two diesel are highly volatile compared to the esters of Moringa oil but the boiling point (95% off) of # 2 diesel fuel was quite higher than to those of all the esters. Mixtures of Moringa esters are relatively less volatile than methyl ester of Moringa oil at all temperatures. Influences on the vapor pressure (volatility) properties of esters were related to fatty acid composition of the esters. In both esters after 95% recovery, the esters were releasing smoky fume substances indicating that the esters were decomposed. How ever, 98% are recovered in case of # 2 diesels and their blending with 20% of Moringa biodiesels. The remaining 2% were non-volatile residues.
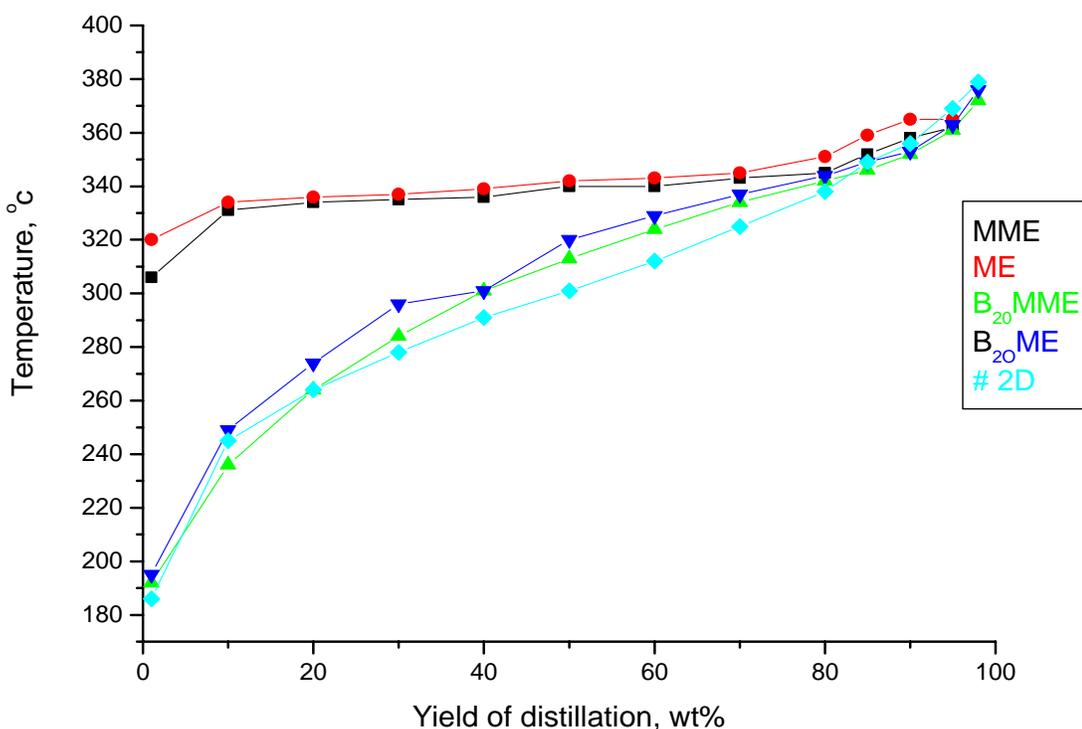
Figure 13. Distillation curves of Moringa methyl esters, mixtures of Moringa esters, their blending with 80% of No.2 diesel, and number two diesel

The table below shows the distillation range of biodiesel (methyl and mixtures of esters), B_{20}MME, B_{20}ME and No 2 diesel. From the table it can be clearly seen that No. 2 diesel was more broad range of distillation than Moringa esters indicating that No. 2 diesel contains more mixtures.

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Table 7 Distillation range of MME, ME, B₂₀MME, B₂₀ME & No.2 diesel

Distillation range (ºc)	MME	ME	B₂₀ MME	B₂₀ME	# 2 Diesel fuel
	306-362	320-365	192-372	195-376	186-379

4.3.5 *The Conradson Carbon residue of M.stenopetala esters*

One crucial parameter for the quality of biodiesel is the Conradson carbon residue, which is very low for both esters and also meets the existing ASTM D189 and German standard (DIN V 51606, 1994), which is less than 0.3%, measured from 10% distillation residue. It corresponds to 0.03% using 100% of the original sample. The Conradson carbon residue of *M.stenopetala* esters was determined from 10% distillation residue (the residue left over after 90% of it recovered by distillation) using standard method, ASTM D189. The Conradson carbon residue of *M.stenopetala* methyl ester and mixtures of esters were 0.075 and 0.0778% respectively. The Conradson carbon residue of #2 diesels was 0.092%. The Conradson carbon residue is relatively applicable to non-volatile biodiesel products that partially decomposed on distillation at atmospheric pressure. Both esters are relatively more volatile than #2 diesels on 10% distillation residue.
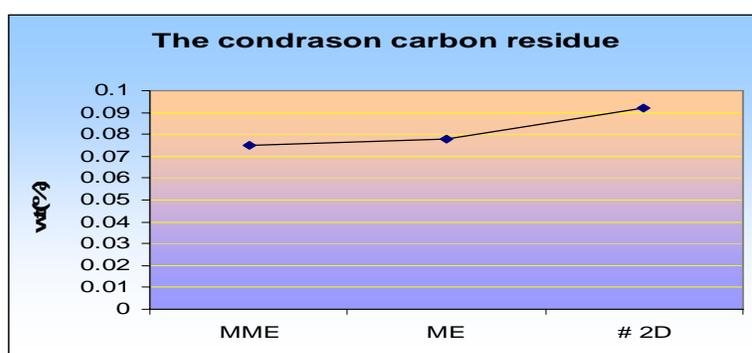
Figure 14 the Conradson carbon residue of MME, ME & No 2 diesel.

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4.3.6 *Cloud and Pour point of M.stenopetala esters (ASTM D2500 & ASTM D97)*

The cloud and pour point of both esters were the same and equal to 15°C & 12 °C respectively. These results are higher when compared to Jatropha oil derived biodiesel but less than for palm oil biodiesel, which also contains even higher amounts of saturated fatty acids, and *M.olifera* oil derived biodiesel (table8). The key fatty acids limiting the cold flow quality of biodiesel are palmatic (16:0) and stearic acids (18:0) as their melting point of the fatty acid esters are higher. The saturated fatty acid compounds had significantly higher melting points than unsaturated fatty acid compounds (Knothe et al, 2005). The relatively high content of C22:0(behenic acid), which possesses an even higher melting point than C16:0 or C18:0 contributes to the high cold flow properties of *M.stenopetala* oils. The reason is that the cold flow properties of biodiesel are determined by the amounts of higher-melting components (usually the saturated esters) and not their nature. (Rashid, U. et al.2008). If the oil is refined and winterized the cloud point may decreases as reported by Bol (2004) that the cloud point results of refined and unrefined soyethyl ester was -9 & 15°C respectively.

Polyunsaturated fatty acids improve cold flow properties but are most susceptible to oxidation (Knothe et al, 2005). In this respect biodiesel from *M.stenopetala* oil are less susceptible to oxidation. But when 80% of # 2 diesels blended with 20% of both esters (Moringa biodiesels) the cloud and pour point were +4 °C and -5 °C respectively. The pour and cloud point significantly decreased which allows to use B$_{20}$ almost in all Ethiopian geographies. The cloud and pour point limit is not specified on the ASTM standards. It is determined by local climate that, it should be below the monthly tenth percentile minimum ambient temperature of the region (ASTM[1], 2002)

Table 8. The cloud & pour point of MME, ME, B20MME, B20ME & No.2 diesel

	Cloud point(°C)	Pour point(°C)
MME	15	12
ME	15	12
B$_{20}$MME	4	-5
B$_{20}$ME	4	-5

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M.olifera oil methyl ester[4]	18	17
Palm oil methyl ester[5]	20	-
Jatropha oil methyl ester[5]	0	-
# 2 Diesel	0	<-8

4.3.7 *Cetane number (CN) of M.stenopetala esters*

The CN is one of the prime indicators of the quality of diesel fuel. It relates to the ignition delay time of a fuel upon injection into the combustion chamber. The CN is a measure of ignition quality of diesel fuels and high CN implies short ignition delay. The longer the fatty acid carbon chains and the more saturated the molecules, the higher the CN (Demirbas A. 2008).

The cetane number of *M. stenopetala* methyl esters and mixtures of esters were determined to be 58 and 60 respectively. The cetane number was calculated from density (at 15°C) and corrected middle distillates temperature (°C) of their respective esters using equation 9. The cetane numbers of methyl oleate, methyl palmitate and methyl stearate are 59.3, 85.9 and 101, respectively, (Knothe et al., 2003). The cetane number of mixtures of Moringa esters is greater than Moringa methyl esters. This is probably due to the density of esters. According to Clark (1988) low relative density is indicator of good ignition properties of fuels. The densities of mixtures of Moringa esters lower than Moringa methyl esters. The CN of B$_{20}$MME, B$_{20}$ME & No 2 diesel were 53.6, 54.5 and 50°C respectively.

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[4] Data fromU. Rashid et al,2008

[5] Data from Mesfin kinfu,2008

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M. stenopetala-derived biodiesel easily meets the minimum cetane number requirements in both the ASTM D6751 and EN 14214 biodiesel standards, which are a minimum of 47 and 51, respectively as shown in the table 7.

Table 9 Calculated Cetane index of MME, ME, B20MME, B20ME & No.2 diesel

	MME	ME	B20MME	B20ME	No.2 D	ASTM Limit	EN 14214
CN	58	60	53.6	54.5	50	Min 47	Min 51

4.3.8 *Water content of M.stenopetala esters*

Fuel contaminated with water can cause engine corrosion or may cause a reversion of fatty acid methyl esters to fatty acids, which can lead to filter plugging [Schinas P, et al, 2008]. In the biodiesel production process, water contamination of biodiesel plays a significant role in both the quantity control of the feedstock and the end product. Biodiesel, although considered hydrophobic, can contain as much as 1500mg/l of dissolved water droplets. The presence of water in biodiesels reduces the caloric value, enhances corrosion, promotes growth of microorganisms and increases the probability that oxidation products are formed during long term storage. Additionally, water cleaves the ester bond of the FAMEs via hydrolytic degradation (A. Steinbach et al, 2008). Therefore, EN 14214 imposed a maximum content of 500 mg/l of water in biodiesel (Schinas P. et al, 2008). In this study, the produced methyl and mixtures of Moringa esters were routinely dried over anhydrous sodium sulphate. This technique was proved efficient enough and the water content of both Moringa methyl ester and mixtures of Moringa esters were almost zero.

4.3.9 *Flash point of M.stenopetala esters*

The flash point was determined after the sample was preheated to remove residual methanol and ethanol according to the standard method, ASTM D93. The flashpoint of *M.stenopetala* methyl

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ester and mixtures of Moringa esters were 185°C and 197 °C respectively. The flash point of mixtures of Moringa esters was significantly greater than Moringa methyl esters. This is due to the fact that mixtures of Moringa esters are less volatile than Moringa methyl esters. The flash points of both esters are far greater than that of the conventional # 2 diesel. The flash point of #2 diesel fuel was 78°C. The flash point of B20MME & B20ME were 82 & 85°C respectively. Hence, storing *M.stenopetala* derived biodiesel and its biodiesel-diesel blends are safe as compared to storing diesel alone. *M. stenopetala* esters thus meet the requirements of the ASTM D6751 biodiesel standards, which prescribe the minimum flash point of 130°C.
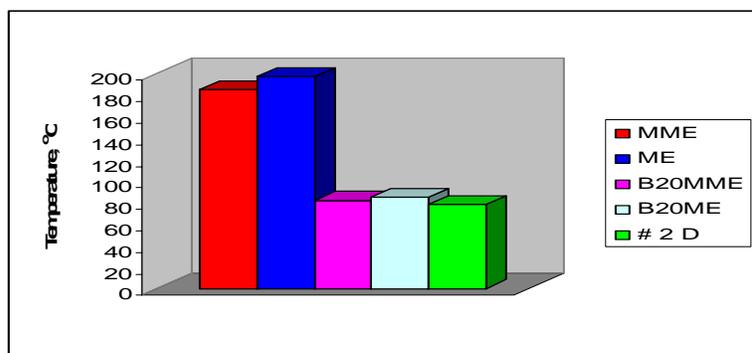
Figure 15 The flash point of No.2 Diesel fuel, methyl and mixtures of moringa esters oil and their blending with 80% of No.2 diesel (B20)

4.3.10 *Ash content of M.stenopetala esters*

The ash content was determined according to the standard ASTM D 482 method. The ash content of methyl and mixtures of Moringa esters were 0.0098 and 0.0067% respectively. It has been demonstrated that heating values are negatively related to ash content, with every 1% increase in ash concentration decreasing the heating value by 0.2 MJ/kg [Cassida KA. et al, 2005]. Furthermore, ashes and inorganic elements (e.g. alkali) produced during combustion may cause a number of serious problems to power plants through slagging, corrosion and fouling. Fouling is

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generally defined as the accumulation of unwanted materials on the surfaces of processing equipment leading to a decrease in the exchanger efficiency; slagging is related to the low melting point of deposits, which causes the formation of a glassy layer that must be removed (Monti A.et al, 2008). Finally, corrosion is caused by the interaction between deposits and metal surface of the exchanger, which involves extra costs in maintenance, whilst significantly decreasing the plant life span [Reumerman PJ. et al, 2002]. Importantly, the degree of fouling, slagging and corrosion is strictly dependent on ashes and minerals released during combustion, a process that substantially depend on biomass characteristics [Venturi P.et al, 2003). The ash content of moringa stenopetala biodiesel easily meets the requirements of the ASTM D6751 biodiesel standards, which prescribe a maximum of 0.01%.

4.3.11 *The Iodine Value (IV) of M.stenopetala esters*

The IV provides information as to the unsaturation degree of the oil, which directly affects its stability with regards to oxidation. The reason for autoxidation is the presence of double bonds in the chains of the fatty compounds. The autoxidation of unsaturated fatty compounds proceeds with different rates depending on the number and position of double bonds. The species formed during the oxidation process cause the fuel to eventually deteriorate. Small amounts of more highly unsaturated fatty compounds have a disproportionately strong effect (Knothe and Dunn, 2003). The iodine value of *M.stenopetala* oil was 69.21 g I_2/100 g of oil. The iodine value reported by *S. Lalas et al (2003*) was 65.8 g I_2/100 g of oil. In this regard, *M.stenopetala* oils are relatively stable to oxidation when compared to canola, sunflower, linseed and soybean oils (Table 8). In this sense, methyl esters obtained from sunflower oil, soy oil or canola seed oil cannot meet this specification because of their high proportion of unsaturated chains. However, if commercial production of *M.stenopetala* oil is desired, the iodine number will not be a constraint

The iodine value of the conventional fuel was approximately 10 (Peterson, 1997). Therefore, the biodiesls had significantly higher degree of unsaturation than diesel fuel. When heating unsaturated fatty acid, polymerization of glycerides will occur which lead to gum formation. The problem could be worse with the increase in the number of double bonds in the fatty acid chains. To ensure the quality of biodiesel as alternative fuel, it was proposed to limit the unsaturated fatty

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acids in biodiesel specifications, especially in the content of higher unsaturated fatty acids, like linolenic acid. (X.lang, 2001b). *M. stenopetala* oils thus easily meet the requirements of the EN 14214 biodiesel standards, which prescribe a maximum iodine value of 120g I$_2$/100g of oil.

Table 10 Iodine value of *M.stenopetala*, soybean, canola, linseed & sunflower oils.

IV	*M.stenopetala oil*	Soy bean oil	Canola oil	Sunflower	Linseed oil
69		136.4[6]	127[7]	129[8]	156.7[9]

4.3.12 *Alkali metals and alkaline earth metals in M.stenopetala esters*

The alkali and alkaline earth metals were determined by atomic absorption spectrophotometer. After esterification and subsequent treatment, alkali metals and alkaline earth metals may be present in biodiesel as unwanted residue. Because the presence of high amounts of alkaline metals in biodiesel may be linked with ash formation in the combustion engine (Demirbas A., 2008). Standard DIN EN 14214 permits a cumulative concentration of 5mg/kg for both the alkali metals sodium and potassium and also for the alkaline earth metals magnesium and calcium. (A. Steinbach et al, 2008). The potassium content of the produced Moringa methyl ester and mixtures of Moringa esters were 3.3 and 3.46mg/l respectively that indicates that the washing procedure used was efficient in catalyst removal. From table 9, the total alkali metals for Moringa methyl ester and mixtures of esters are 3.734 & 3.972mg/l respectively where as the total alkaline earth metals are 0.863 & 0.976mg/l respectively for Moringa methyl ester and mixtures of Moringa esters. The high amount of potassium in both esters results from due to KOH used as a catalyst in transesterification process.

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[6] Data from Ferrari et al. (2005)
[7] Data from S.l.dmytrshn et al, (2004)
[8] da ta from olivera S. et al, 2007

[9].data from demirbas A. 2008

Table 11Alkali metals and alkaline earth metals in *M.stenopetala* esters

	Sodium(Na)	Potassium(K)	Magnesium(Mg)	Calcium(Ca)
MME	0.434	3.30	0.018	0.845
ME	0.512	3.46	0.016	0.960

4.3.13 *Heat of combustion (Caloric value) of M.stenopetala esters*

The heat of combustion determined according to ASTM D240. The heat of combustion of *M.stenopetala* methyl ester and mixtures of Moringa esters were 38.23 & 39.5MJ/KG respectively. Heat of combustion measures the energy content of biodiesels that determines the suitability of these materials as alternative to diesel fuels (x.lang, 2001b). The heat content of diesel fuel approximately was approximately 45MJ/KG (Kulkarni et al, 2006).Mixtures of Moringa esters 12% less heat energy on a mass basis where as Moringa methyl ester 15% less heat energy than diesel fuel on a mass basis. According to Srivastava A, et al (2000) the caloric value of both soybean and palm oil methyl esters were 33.5MJ/KG. The caloric value of mixture of Moringa ester is greater than Moringa methyl ester.

In summary, the physicochemical characteristics of the biodiesels, namely; Density@15°c, Kinematic Viscosity @40°c, Flashpoint, Cloud Point, pour point, Cetane No., Acid No. ash and carbon content ,distillation, copper strip corrosion ,caloric value, ASTM color ,water content and Iodine Value were summarized and analyzed in comparison with the standards as depicted in (Table 10). It is clearly observed that *M. stenopetala* derived biodiesel well agree with all the standard specifications of ASTM D 6751. It also compromise with the European standard, EN 14214, except for density and viscosity result which were below the specifications.

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Table 12. Summary of the physicochemical characteristics (mean values) of *M.stenopetala* derived biodiesels in comparison with the standards of ASTM and EN

Fuel properties	Units	MME	ME	#2 Diesel	US ASTM D6751 Standard	EN 14214
Density@15°c	g/ml	0.8482	0.8435	0.8587	***	0.86-0.9
viscosity@40°c	mm²/s	3.2	3.067	3.7	1.9- 6	3.5- 5
Flash point	°c	185	197	78	Min 120	Min 130
Cetane number	-	58	60	50	Min 47	Min 51
Distillation@90% off by vacuum	°c	358	365	358	Max 360	**
Acid number	mgKOH/g	0.126	0.212	-	Max 0.8	Max 0.5

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Iodine value	g I$_2$/100g of oil	69	69	-	***	Max 120
Ash content	Wt, %	0.0098%	0.0067%	-	0.01	
Condrason carbon residue (10%)	Wt,%	0.075	0.0778	0.092	*	Max 0.3
Caloric value	MJ/KG	38.23	39.5	-	***	**
Water content	Wt, %	Nil	Nil	-	***	Max 500mg/l
Copper strip corrosion	Number	1b	1a	-	Max No3	**
ASTM color	Number	1.5	<1.5	-	Max No3	**
Cloud point	^{O}C	15	15	0	***	**
Pour point	^{O}C	12	12	<-8	***	**
Alkali metals	mg/l	3.734	3.972	-	***	5mg/KG
Alkaline earth metals	mg/l	0.863	0.976	-	***	5mg/KG

*** No standard in ASTM

** No standard in EN

- Not determined

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5 CONCLUSION and RECOMMENDATION

5.1 Conclusion

The aim of this study was to evaluate *M.stenopetala* seed oil as a potential raw material for biodiesel production. *M.stenopetala* oil was extracted and chemically converted via an alkaline transesterification reaction to fatty acid methyl ester and mixture of esters in the presence of KOH as a catalyst.

The experimental results are described as follows

> ➢ *M.stenopetala* seeds were found to be rich in oil, with an average yield of 45%, allowing the possibility of economical exploitation.

> ➢ *M.stenopetala* seed oil contains 78% of mono-unsaturated fatty acids and 22% of saturated fatty acid. The dominant fatty acid is oleic (76%).

> ➢ Biodiesel production in laboratory scale provided a yield of nearly 97.5 wt% for Moringa methyl ester, 94 wt % for mixture of Moringa ester and less than 50 wt % for Moringa ethyl ester.

> ➢ Using ethanol alone for transesterification process of *M.stenopetala* oil was not feasible for large-scale production.

> ➢ All of the determined parameters of *M.stenopetala* oil methyl ester and mixture of ester were found to comply with both the American ASTM D6751 and the European FAME standard EN 14214.

> ➢ The refining process of both esters (washing with warm distilled water in case of methyl ester and washing with 0.1% of tannic acid solution for mixture of ester) were proved effective in regard to reducing free glycerol content. In this study, the sufficient number of washing steps was determined to be three.

> ➢ The most conspicuous property of biodiesels derived from *M. stenopetala* oil is the low kinematic viscosity of 3- 3.2mm²/s, which is among the lowest reported for a biodiesel fuel.

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➤ The physicochemical properties of mixed ester ME (3:3) was better than that of pure *M.stenopetala* methyl ester. Therefore, the best choice to use as a fuel would be the mixture of Moringa ester (ME).

➤ Biodiesel derived from *M. stenopetala* oil is an acceptable substitute for petrodiesel when compared to biodiesel fuels derived from other vegetable oils.

➤ The major physicochemical properties of *M.stenopetala* seed oil make it an attractive alternative application of the existing feedstocks for biodiesel production in Ethiopia

5.2 Recommendations

➤ Further investigation of biodiesel originated from M.stenopetala seed oil can be widened by the examination of different catalyst types and the impact of M.stenopetala seed oil methyl ester and mixture of ester (ME) on the exhaust emissions in respect to other biodiesels.

➤ Full characterization of *M.stenopetala* seed oil should be conducted to identify the oil for human consumption

➤ Some anti-gelling additives may be needed to improve the cold flow quality of Moringa derived biodiesel in application of B_{100}

➤ Designing incentives to local people to plant and protect the tree as well as to harvest the seed

➤ On spot oil extraction and use of the residue for water treatment especially to remove hard water.

➤ Study should be conducted on the yield of *M.stenopetala* seed per tree.

➤ Detail studies regarding agronomic and environmental requirements are essential for feasibility analysis of *M.stenopetala* seeds.

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APPENDICES

Appendix A : Biodiesel Standards

This appendix contains the specifications of the following biodiesel standards:

Table A-1: ASTM D6751 (United States): Standard Specification for Biodiesel

Table A-2: EN 14214 (Europe): Automotive Fuels: FAME for Diesel Engines. Requirements and Test Methods.

The European standard EN 14214, which went into effect in 2003, supersedes the biodiesel standards in European countries that are members of the European Committee for Standardization (CEN). Therefore, no standards from individual European countries are given. CEN standards apply in the following member countries: Austria, Belgium, Cyprus, Czech Republic, Denmark, Finland, France, Estonia, Germany, Greece, Hungary, Iceland, Ireland, Italy, Latvia, Lithuania, Luxemburg, Malta, the Netherlands, Norway, Poland, Portugal, Slovakia, Slovenia, Spain, Sweden, Switzerland, and the United Kingdom. The European standard EN 590 for conventional diesel fuel contains a

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provision that conventional diesel fuel can contain up to 5% FAME meeting the standard EN 14214. In addition to the biodiesel standards, analytical standards have been developed in the United States and Europe for the purpose of including them as prescribed methods in biodiesel standards [23].

Table A-1: ASTM D6751 (United States): Standard Specification for Biodiesel

Biodiesel Standard ASTM D6751 (United States)

Property	Test method	Limits	Unit
Flash point (closed cup)	D 93	130.0 min	°C
Water and sediment	D 2709	0.050 max	% volume
Kinematic viscosity, 40°C	D 445	1.9–6.0	mm²/s
Sulfated ash	D 874	0.020 max	% mass
Sulfur	D 5453	0.0015 max or 0.05 max[a]	% mass
Copper strip corrosion	D 130	No. 3 max	
Cetane number	D 613	47 min	
Cloud point	D 2500	Report	°C
Carbon residue (100% sample)	D 4530	0.050 max	% mass
Acid number	D 664	0.80 max	mg KOH/g
Free glycerin	D 6584	0.020 max	% mass
Total glycerin	D 6584	0.240 max	% mass
Phosphorus content	D 4951	0.001 max	% mass
Distillation temperature, atmospheric equivalent temperature, 90% recovered	D 1160	360 max	C

[a]The limits are for Grade S15 and Grade S500 biodiesel, respectively. S15 and S500 refer to maximum sulfur specifications (ppm).

Source: The Biodiesel Handbook. *AOCS Press*,2005 [23}

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Table A-2: EN 14214 (Europe): Automotive Fuels: FAME for Diesel Engines. Requirements and Test Methods.

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Biodiesel Standard EN 14214 (Europe)

Property	Test method	Limits min	Limits max	Unit
Ester content	EN 14103	96.5		% (m/m)
Density; 15°C	EN ISO 3675 EN ISO 12185	860	900	kg/m³
Viscosity; 40°C	EN ISO 3104 ISO 3105	3.5	5.0	mm²/s
Flash point	EN ISO 3679	120		°C
Sulfur content	EN ISO 20846 EN ISO 20884		10.0	mg/kg
Carbon residue (10% dist. residue)	EN ISO 10370		0.30	% (m/m)
Cetane number	EN ISO 5165	51		
Sulfated ash	ISO 3987		0.02	% (m/m)
Water content	EN ISO 12937		500	mg/kg
Total contamination	EN 12662		24	mg/kg
Copper strip corrosion (3 hr, 50°C)	EN ISO 2160		1	
Oxidative stability, 110°C	EN 14112	6.0		hr
Acid value	EN 14104		0.50	mg KOH/g
Iodine value	EN 14111		120	g iodine/100 g
Linolenic acid content	EN 14103		12	% (m/m)
Content of FAME with ≥4 double bonds			1	% (m/m)
Methanol content	EN 14110		0.20	% (m/m)
Monoglyceride content	EN 14105		0.80	% (m/m)
Diglyceride content	EN 14105		0.20	% (m/m)
Triglyceride content	EN 14105		0.20	% (m/m)
Free glycerine	EN 14105, EN 14106		0.02	% (m/m)
Total glycerine	EN 14105		0.25	% (m/m)
Alkali metals (Na + K)	EN 14108, EN 14109		5.0	mg/kg
Earth alkali metals (Ca + Mg)	prEN 14538		5.0	mg/kg
Phosphorus content	EN 14107		10.0	mg/kg

Source: The Biodiesel Handbook. *AOCS Press*,2005 [23}

Appendix B: Biodiesel investment in Ethiopia- Area and Status

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No.	Company name	Area requested (ha)	Region	Origin Of the Company
1	Flora ECCO Power	15000	Oromia	Germany & Israel
2	Sun Biofuel	50000	SNNRS	England
3	LHBCHATZ	100000	Oromia	Israel
4	BECCO Company	3000	SNNRS	Ethiopia
5	Villar Energy Co.	100000	Afar & Oromia	Israel
6	RINA International Investment	80000	Oromia	–
7	Kenya Bioenergy Limited	100000	–	South Africa
8	Gento Consulting Ltd	100000	–	–
9	Global Trinity group	100000	–	USA
10	Ethan	10000	BGRS & SNNRS	Ethiopia
11	Beta	100	SNNRS	Ethiopia
12	Asossa Association of Biofuels	10000	BGRS	Ethiopia
13	FRI-EL-Green Power	30000	SNNRS	Italy
	Total	698,100		

Source M.Kinfu, 2008 [113]

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