THE POTENTIAL OF *Telfairia pedata* FOR LIQUID BIOFUEL AND SOAP PRODUCTION

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I56/22815/2011

A Thesis Submitted in Partial Fulfillment of the Requirements for the Award of the Degree of Master of Science (Chemistry) in the School of Pure and Applied Sciences, Kenyatta University

NOVEMBER, 2016

DECLARATION

This is my original work and has not been presented for a degree in any other university or for any other award.

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DEDICATION

To my daughter Rehema Suzan Gathoni, sister Joice and mum Julia.

ACKNOWLEDGEMENT

This thesis work was carried out under close supervision of Prof. Caroline L. Thoruwa and Prof. Thomas F. N. Thoruwa. I am indebted to them for their invaluable supervision and useful comments during the period of the study.

Support accorded in all ways by academic and technical staff of Department of Chemistry and Energy Engineering is gratefully acknowledged.

It is with sincere gratitude that I appreciate the assistance of Timothy Mugambi and his team, Kenya Pipeline Company and all the Kenya Bureau of Standards laboratory staff that supported me during the fuel and soap analysis.

This study was funded by NACOSTI of whom I highly acknowledge.

Finally, most sincere gratitude to my relatives, colleagues and close friends for all forms of support accorded during the entire study time.

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LIST OF ABBREVIATIONS AND ACRONYM

AOCS	American Oil Chemists' Society
ASTM	American Society for Testing and Materials
AV	Acid value
B10	Blends of 10% biodiesel in 90% diesel fuel
B100	Blends of 100% biodiesel in 0% diesel fuel
B100	Blends of 100% biodiesel in 0% kerosene fuel
B20	Blends of 20% biodiesel in 80% diesel fuel
B20	Blends of 20% biodiesel in 80% kerosene fuel
B5	Blends of 5% biodiesel in 95% diesel fuel
B50	Blends of 50% biodiesel in 50% diesel fuel
B50	Blends of 50% biodiesel in 50% kerosene fuel
B70	Blends of 70% biodiesel in 30% diesel fuel
B70	Blends of 70% biodiesel in 30% kerosene fuel
BK	Biodiesel Kerosene blend
CC	Coconut
CCI	Calculated cetane index
CI	Cetane index
CNME	*Cocos nucifera* methyl ester
CO	Carbon moxide
DF	Pure diesel fuel
FAME	Fatty Acid Methyl Esters
FBP	Final boiling point
FCA	Free Caustic Alkali
g/min	Grams per minute
GC	Gas Chromatography
IBP	Initial boiling point
IV	Iodine Value
KEBS	Kenya Bureau of Standards
KF	Pure kerosene fuel
KOH	Potassium Hydroxide
KPC	Kenya pipeline company
ME	Methyl ester
MIE	Matter insoluble in Ethanol
MS	Mass spectroscopy
NaOH	Sodium Hydroxide
NDIR	Non dispersive infrared
PV	Photovoltaic
SFME	Sunfower methyl ester
SV	Saponification value
TFM	Total fatty matter
TP	*Telfairia pedata*
TPME	*Telfairia pedata* methyl ester
WBT	Water boiling test

ABSTRACT

About two billion people around the world have no access to modern energy. More than 84% of Kenya population use kerosene for cooking and lighting therefore it is necessary to search for suitable alternatives to liquid and cooking fuels. In this study, oil extracted from *Telfairia pedata* Hook (Oyster nut) was transesterified in methanol using sodium hydroxide catalyst. Methyl ester obtained was characterized by GC-MS and further tested for fuel properties relative to conventional diesel fuels (automotive diesel and kerosene). The results identified linoleate, hexadecanoate and octadecanoate as the fatty acid esters in the methyl ester. The ester viscosity at (40^o C) was in the range of 4.22±1.9 mm^2/s for *Telfairia pedata* compared to 4.188 mm^2/s for automotive diesel fuels. The flash point of the ester was much higher (127^oC) than referenced diesel fuels (74^oC) and they are within the European standard EN-14214 for biodiesel of $>100^oC$. The density of *Telfairia pedata* ester was 0.8752 $g/cm^3$of which was higher than 0.8621 g/cm^3 automotive diesel and 0.7884 g/cm^3kerosene respectively. The esters were further blended with automotive diesel in ranges of 5-70% on volume ratio. Blends of 20% biodiesel in 80% petroleum diesel demonstrated the most ideal properties with viscosity and density very close to that of pure petroleum diesel. The esters were further tested in a multi-wick stove following standard water boiling test (WBT) and their performance in terms of time to boil, heat transfer efficiency, power output and specific fuel consumption .The esters burnt with odorless and non pungent smell with mean thermal transfer efficiency of 45±0.5% compared to 50±0.5% thermal transfer efficiency of petroleum kerosene fuel. However, the ester demonstrated fire power of 1136±7.4W which was 19.2% much lower compared to that of kerosene fuel. *Telfairia pedata*ester showed fuel properties very close to automotive diesel and thus could be used in diesel appliances without any modifications. Coconut esters on the other hand showed properties close to kerosene and gave stove performance characteristics almost similar to kerosene making it most favorable as bio-kerosene. An emission test was conducted to demonstrate suitability of the methyl esters (biodiesel) in reduction of CO emission in liquid fuel cooking stoves. The test system consisted of a stove platform an exhaust hood and a gas analyzer fitted with a non-dispersive infrared spectrometer system. All fuels emitted carbon monoxide; however *T. pedata* biodiesel fuel registered 53% less CO emission compared to kerosene fuel. Physiochemical analysis of extracted seed oil was carried out in order to justify its usefulness in soap industry. The following values were obtained for the various parameters measured; saponification 230.0±4.5 mg KOH/g, iodine value 109±1.0g I_2/100g, acid value 1.0±0.1 mg KOH/g. The analytical values obtained were significant in favor of the utilization of the *Telfairia pedata* for soap production. The lather volume and total fatty matter were 25ml and 6.5% lower than that of coconut respectively. Coconut soap showed better results for soap making due to its abundant lauric acid present compared to *T. pedata* (lather volume 640 cm^3 and 625 cm^3 respectively) however the blends of the two showed better results than *T. pedata* oil (Total Fatty Matter, 81.6% and 80.6% respectively).

CHAPTER ONE

INTRODUCTION

1.1 Background

Currently the world is coming to grips with the development of two looming potential disasters in global warming and oil rising prices. Worldwide 2 billion people, 27% of the world's population, had no electricity in the year 2000 (Ernest, Anil and Ishani, 2008). More than 99% of these people live in developing countries and 80% live in rural areas. In the absence of vigorous new policies in the energy sector, 1.4 billion people will still lack access to modern energy sources by 2030 (Schweres, 2004). More than 84% of Kenyans' population use kerosene for cooking and lighting (EAN, 2000). Use of kerosene for lighting and cooking is associated with health and safety problems leading to respiratory tract diseases. Fires resulting from kerosene stove incidents in urban slum dwelling have been rising claiming lives and leaving hundreds of thousands homeless (Ma and Hannah, 1999b). Kenya's fuel consumption stood at 1.4 and 3.3 million liters of petrol and fossil diesel, respectively per day in 2006, with an average growth rate of 2.8% per year. Projections indicate that Kenya will require 2.5 and 2.7 million liters of petrol and fossil diesel, respectively per day by 2030 (Owino, 2004).

Vision 2030 aims to transform Kenya to a globally competitive and prosperous nation with a high quality of life to all its citizens in a clean and secure environment (National Renewable Energy Laboratory, 2009). At the national level, producing more bio-fuels will generate new industries, technologies, jobs and markets. The world and the country should open up its eyes to the fact that fossil fuels will not be there forever and it is time

to move on to the other alternatives fuels. Plants are an alternative source of bio-fuels which will help reduce the environmentally related health problems and also provide employment opportunities (Norton, 2004). Kenya has the potential to produce oil from local oil crops which are well adapted to the harsh agro-ecological zones which constitute about 80% of the total landmass (Kalua, 2008).

Soaps and detergent are essential to personal and public health. Through their ability to loosen and remove soil from a surface, they contribute to good personal hygiene, reduce the presence of germs that cause infectious diseases, extend the useful life of clothes, tableware, linens, and surfaces and furnishing (Childers, 2000).

The general characteristic of soap is certain greasiness to the touch, ready solubility in water, with formation of viscid solutions which on agitation yield a tenacious froth or lather (Donkor, 1997). When soap is dissolved in water it breaks dirt away from surfaces. Through the ages soap has been used to cleanse, cure sores, dye hair, a skin ointment, and suppository in children suffering from constipation and also forms basis of many pills (Tafadzwa*et al*.,2012). The potential of plant oils for biodiesel and soap production can contribute towards the realization of the country's vision, to reduce pollution, global warming, provide alternative fuel, create job opportunities and improve the economy.

1.2 Definition of Biodiesel

Biodiesel is a monoalkyl esters of long chain fatty acids and a non-petroleum based fuel consisting of alkyl esters derived from trans-esterification of triglycerides or by esterification of free fatty acids with low molecular weight alcohol (Knothe, 2000).

Soap is a salt of a combination of oils or fats (triglycerides)with sodium hydroxide (lye) or potassium hydroxide in a process known as saponification (Tafadzwa *et al*., 2012).

1.3 Alternative Energy World

Biomass fuel with charcoal and wood fuel accounting for more than 68% of the nation consumption has dominated the energy sector in Kenya (Kalua, 2008). The largest government investment is petroleum which provides 22% while 10% of the total energy needs is accounted for by hydro power and geothermal projects.Hydro power however raises worries which stems from the perennial droughts that often lead to power outages (National Renewable Energy Laboratory, 2009). Half of ordinary Kenyans live on less than a dollar a day thus solar power which could provide another viable source of energy, remains way too expensive for them. Thus, the use of solar energy cannot be emphasized at this time(Schweres, 2004). Arrays of large turbines, known as wind farms are becoming an increasingly important source of renewable energy and are used by many countries as part of a strategy to reduce their reliance on fossil fuels (Robertson, 1996). Renewable energy will thus take the agricultural path opting for bio-fuel. The selection of an appropriate crop or mix of crops for the production of feedstock oil and the location of biodiesel production units are critical factors in developing a sustainable production system (Laichena, 1989). Key considerations

should ensure that the expansion of the sector does not lead to further deforestation. The crop of choice should not compete for water resources or land used to grow food crops and sustain wildlife resources, otherwise development goals of biodiesel production will be lost. The use of already existing food based products like soybeans and maize particularly in a continent like Africa where there is a dire need for food is unreasonable.

1.4 The Process of Making Biodiesel

Various ways have been considered in the processing of biodiesel from oils of animal and vegetable origin. The essence of any method is to reduce the high viscosity of the oils. Thermal cracking (pyrolysis), blending with diesel fuel (Schwab, Bayby and Freedman, 1987) and transesterification (Fungrai and Milfod, 1999). Three basics routes of transesterification to ester production from oils and fats are; Direct acid catalysed esterification of the oil with methanol, Conversion of oil to fatty acids and then to alkyl esters with acid catalysis and the most commonly used base catalyzed transesterification of the oil with alcohol (Leonard, 2012). The last method has been reported to be the most practical because of the physical characteristics of the fatty acid esters (biodiesel) produced are very close to those of diesel fuels. The process is also relatively simple and most economical for several reasons; low temperature and pressure required for processing and high conversion (98%) with minimal side reactions and reaction time (Fukuda *et al.,* 2001). The lower alkyl esters can be burned directly in unmodified diesel engines and common wick stove with very low deposit formation (Mittelbach and Tritthaet, 1988). Several types of vegetable oils with diversified

composition of fatty acids may be used for preparation of biodiesel. Coconut, sunflower, soya beans, rapeseed and palm oil are the most studied. However, there is no technical restriction to the use of other types of vegetable oils. Methanol is a preferred alcohol because of the simultaneous separation of glycerol (Demirbas, 2000).

1.5 History of Biodiesel

Transesterification of vegetable oil and fats was conducted as early as 1853 by E. Duffy and J. Patrick that was four decades before the first diesel engine became functional in 1993, running on peanut oil.Rudolf Diesel demonstrated his engine by running it on peanut oil while Henry Ford expected his model to run on ethanol a corn product (Shay, 1993). Eventually, in both cases, petroleum entered the picture and proved to be the most logical fuel source based on supply, price and efficiency. This resulted to a near elimination of the biomass fuel production infrastructure. The present environmental impact concerns and a decreasing oil deposits have made biomass fuels such as biodiesel a growing alternative (Hatcher, 2004).

1.6 Current Situation on Biodiesel

Energy insecurity has reduced a nation’s dependence on oil and substituted with use of locally available renewable sources. Development of biodiesel in Kenya from locally grown plants has received high level government attention as a result of the continued increases in the cost of fossil fuels and the increased environmental awareness regarding over reliance on wood fuel in Kenyan homes. This attention resulted in the formation of the National Biodiesel Committee under the Ministry of Energy provided by the Energy

Act 2006, (Kalua, 2008). The committee is composed of: government officials, stakeholders in research Institutions, both in private sector and non- government organization. Its interest is to deliberate on the framework of policy issues such as; subsidies, blending mandate and tax mandate. The committee has put much emphasis on promotion of *Jatropha curcus* oil for sustainable biodiesel production, in the country, claiming benefits of energy security, climate change mitigation and rural development (Tomomastu and Swallow, 2007).

Clean, secure environment, industrialization, healthy citizens and creation of jobs has been highly emphasized by the government. This has increased national funds towards science and technology for continued research and innovations (National Research Council, 2000). While this is going on, researchers in universities and other institutions are engaged in laboratory research on appropriate technical aspects of production and analysis of biodiesel fuel which formed the bases for the choice of this research project.

1.7 Soap Making Process

Soap is a salt of a combination of oils or fats (triglycerides) with sodium hydroxide (lye) or potassium hydroxide in a process known as saponification (Tafadzwa *et al*., 2012).Different ways have been considered to process soap from oils of vegetable and animal origin. The essence of any method is to ensure complete saponification reaction for a safe bar soap. During saponification reaction of glycerides with alkalis sodium hydroxide is used for solid or bar soaps and

potassium hydroxide is used for liquid soaps. These are characteristically different from soaps made from divalent metals such as calcium, magnesium, Aluminium or Iron (Shoge, 2011). Among the most practiced are; hot process or Kettle process, Cold process (Donkor, 1997), and Rebatch process (Mittelbach*et al*.,1996). Cold process is the most commonly used because it involves making soap from the scratch resulting in a natural and quality soap (Donkor, 1997). A wide variety of oils available today has made it inexpensive, good quality; health related benefits and safer environment on soaps made (Shoge, 2011). Several types of vegetable oils may be used for soap preparation; coconut, palm and olive oil are the most studied. Considering the type of lye, sodium hydroxide is better as it results into a softer soap (Childers, 2000).

1.8 Alternative Cleaning Power

Bar soap used for laundry and by extension toiletry are by far one of the most used consumer commodity in Kenya and the whole of Africa. It is only second to cooking oil, salt and onions (Robertson, 2002). The world in general, about 43 million of the population use soap and 2% use alternatives; lemon juice, baking soda and sugar scrub for exfoliating the skin, white vinegar for cleaning glasses, windows and a fabric softener. Use of microfiber a disposable and a source of bleached cotton has also been used as an alternative but it is not environmentally friendly because it is plastic

(Mittelbach *et al*., 1996). Soaps and detergents found in the home can be grouped into four categories; personal cleansing, laundry, dishwashing and household cleaning. Within each category are different product types formulated with ingredients selected to perform a broad cleaning functions as well as to deliver properties specific to that product (Shoge, 2011). Soap from vegetable oils do not harm the environment and is biodegradable (Viorica *et al.,* 2011). Assessment of the oil properties of *Telfairia pedata* for soap production will be studied in this work.

1.9 Current Situation on Soaps

Many communities in different part of the world have been involved in small-scale soap making as a means of generating income for their families (Vivian*et al*., 2014). One of the industries that require expansion is the small scale soap making which does not require high level of technology and large capital (Milwidsky and Gabriel 1994). Devolution of funds has come along with small scale soap making industries which ensures equitable distribution of income as the industries can be planted even in the remotest part of the country (Chatterjee and Pakrashi, 1994). Apart from providing cheaper soaps for domestic use, they also serve as training grounds for local entrepreneurs in decision making and management (Alam, 2011). The knowledge and experience gained has been transferred to medium and large scale industries and has also provided opportunities for utilization of locally available raw materials (Alam, 2011).This will assist the government to achieve its goals in industrializing the rural areas as outlined in the Kenya growth and development strategy (Session paper No.10 of 2012 on vision 2030). Palm, coconut, and Neem are the most commonly used oil

plants in Kenya for soap preparation since they are easily available (Shoge, 2011). Work on chemical properties of soap using *T.pedata* seed oil has not been published, therefore the purpose of this work is to use its oil as a cheap source of fatty material in laundry soap preparation.

1.10 History of Soap

Romans sources claim that the origin of the soap dates back to at least 600BC when the Phoenicians prepared it from goat's tallow and wood ash. Soap was used widely throughout the Roman Empire primary as a medicine (Childers, 2000; Ellis, 2007). Mention of soap as a cleanser does not appear until the second century A.D. By the eighth century, soap was common in France, Italy and Spain but it was rarely used in the rest of Europe until as late as the 17th Century. In 1823, Eugene-Michel, put the soap forming process into a concrete chemical terms. The soap production starting from triglycerides and alkalis is accomplished for more than 2000 years. Until the early 1900's, much of the soap used was made at homes (Ellis, 2007). Successful soap making today is a result of much better understanding of chemistry, experience and a wider variety of ingredients to choose from (Shoge, 2011).

1.11 Statement of the Problem

Kenya is an energy intensive country. The high and steadily growing use of conventional fossil fuel energy is less and less compatible with the notion of sustainable development that promotes durable, safe and environmentally friendly sources of energy. Vision 2030 aim at a clean, safe environment, soap from vegetable oils is

biodegradable. A strong rise in the use of renewable energy and organic products is thus inevitable. Vegetable oil may provide such an alternative.

1.12 Justification

Kenya, like most other developing countries continues to import petroleum products which account for over 40% of foreign exchange and 52% cosmetic products imports. Out of the total petroleum imports, 60% goes to diesel fuel oil (MPND, 2005). This coupled with diminishing automotive fossil fuel resources, as witnessed by escalating oil prices and environmental problems associated with use of conventional fossil fuel, drives the country to slowly shift from dependence on petroleum diesel fuel to biodiesel alternative (Knott, 2007). Homemade soaps are of high quality, healthy and environmentally friendly because the oils and fats used are biodegradable (Viorica *et al*., 2011). Biodiesel and soap industry will create employment and reduce poverty for the rural poor families which constitute 80% women and youth. In implementing its energy policies, the government also hopes to protect the environment. Biodiesel is a clean burning and biodegradable fuel compared to petroleum diesel (Bowman *et al*., 2006).

Use of biodiesel will reduce green house gas emissions, monitor environmental degradation and improve general population health. Extraction of vegetable oils from which biodiesel and soap is processed produces a dry high protein meal by-product, which if correctly processed is a most valuable stock feed or organic fertilizer (Brady *et al*., 2000). In addition, the glycerin a core product of transesterification has both

medicinal and industrial application such as soap and cosmetics (Chalmers and Bathe, 1978).

1.13 General objectives

To develop biodiesel and soap from *Telfairia pedata* oil and to determine their potential for domestic use.

1.14 Hypothesis

i. Oil from*Telfairia pedata* will produce biodiesel and soap that meets the ASTM standards and KEBs standards respectively.

ii. Biodiesel produced from *Telfairiapedata* does not produce carbon monoxide emission when burnt

1.15 Specific Objectives

The specific objectives of this project were to:

i. Determine the physical and chemical properties of the oil extracted from *T.pedata*nuts.

ii. Determine the chemical composition ofbiodiesel prepared from *T. pedata*oil using GC-MS.

iii. Investigate the potential of *T.pedata* methyl esters (biodiesel) and *T. pedata*-kerosene blends as fuel for cooking via the standard water boiling tests.

iv. Investigate the CO emissions of *T.pedata* methyl ester (biodiesel) and *T. pedata* biodiesel-kerosene blends during the standard water boiling tests.

v. Investigate the physical and chemical properties of the soap made from *T.pedata* and compare it with soap from Coconut oil using Kenya Bureau of Standards (KEBS);

CHAPTER TWO

LITERATURE REVIEW

2.1 Plants under Study

2.1.1 *Telfairia pedata (sm.ex sims) Hook*

Telfairia pedata is in the family *curcubitacea.* It is native to mainlands which are Tanzania, Isles of Zanzibar, Pemba and Mozambique and cultivated in Central, East and Southern Africa from Rwanda. It is commonly known as "Mukwini" by Meru community and "Mkwema" by Wachagga in Tanzania (FAO, 1988). Itis an oil nut plant found in lowland coastal and river line forests at elevations of up to 1100 m, in areas with mean annual rainfall of 1000 mm or 2000 mm (Figure 2.1). Well drained medium loam soils provide excellent growth conditions. It is a drought resistance plant; seeds last for eight years and the plant life cycle are 20 years (Okoli, 2007).

It is a perennial plant, does not suffer seasonal climatic changes and is drought resistant, with low susceptibility to disease and pest attack;Apart from grasshoppers and termites, there are few pests and diseases which infest the plant. The tendrils forms part of rich agro forestry system of Mt. Meru and Mt. Kilimanjaro in Tanzania (Figure 2.2). Its agro forestry system is a good carbon dioxide sink with low maintenance (Goodchild, 1967). In its third year, it produces 10 to 30 fruits and in each fruit there are 70 to 150 seeds. In Tanzania a good plantation can reach an annual seed yield of 3 to 7 tons per hectare. Oil content has been reported to be high between 60-66% (w/w) oil. The fatty acids present include; Oleic acid, Linolenic acid, Linoleic acid, Palmitic acid and stearic acid (FAO. 1988). The oil is used as medicine for stomach troubles and rheumatism in East Africa

and the Wachagga of Tanzania use the seeds as tonic after child birth. After extraction the press cake makes valuable feed for livestock being rich in proteins (Okoli, 1988)**.**

The plant is propagated by seed (Figure 2.3). Seeds are often planted directly along the drip line of large trees. Vegetative propagation is effective using layering and cuttings which are easily obtained by pruning and when the fruit ripen, they split gradually (Okoli, 1988). Natural population is eroding the plant. No germ plasm collection is known to exist. (FAO, 1988).However, some work on production and characterization of biodiesel from fluted pumpkin (*Telfairia occidentalis* Hook F) seed oil has been done (Ossai *et al.*, 2011).

Figure 2.1 *Telfairia pedata* plant

Figure 2.2 *Telfairia pedata* fruit

Figure 2.3 *Telfairia pedata* nuts

2.1.2 *Cocos nucifera* L. (Coconut)

Coconut belongs to family Palmae. It is referred to as *Nazi* in Kiswahili. Its present day distribution extends over most of the highlands and the coastal tropics (Child, 1974). Main coconut producing areas are Central and Southern America, West and East Africa, phillipines and West Indies (Satyabalan, 1982). In Kenya, coconut palm tree (Figure 2.4) is a versatile plant of the coastal people from which many products are made including: copra, toddy (mnazi), leaves (makuti), brooms, coconut shell, shell charcoal, baskets, fresh coconut tree "tree of life" and it has great significance in terms of food, shelter and employment (Harrie*et al*., 2004). The coconut tree tolerates poor sandy soils with saline water and survives frequent cyclones. The tree bears a bunch of fruit (Figure 2.5) each month and requires minimum maintenance. The estimate yield is about 149 million nuts per year in Kenya (Laichena, 1989).Dried fresh (the white endosperm) of the nut, is the commercial product that enters the world trade. The content is between 65% and 72% oil with a high content of lauric acid (44%) and the oil has both edible and industrial uses (Pryde, 1979).

Major Industrial uses are soap and cosmetic manufacture, production of plasticizers, synthetic resin and rubber (Erhan, 2005). Coconut meal or cake which is left over after the oil has been extracted contains about 18-25% protein and is thus mostly used for animal feed (piggery, poultry and cattle), making cookies or manufacture of organicfertilizers (Thampan, 1981).

Figure 2.4 Coconut palm tree

Figure 2.5 Fresh Coconut copra

2.2 Biodiesel

Biodiesel is described as ‘carbon neutral’, that is a fuel that producesno net output of carbon in form of carbon dioxide (Kemp, 2006).It is the only alternative fuel that meets all the petroleum diesel requirements because it contains oxygen therefore resulting to reduced emissions. Example; B20 reduces air toxics by 20% to 40% while B100 reduces air toxics by 40% to 60%. Toxics which causes acid rains like sulfur oxides are completely eliminated by use of biodiesel to power motor industry (Kemps, 2006). Biodiesel gives better lubricity and more complete combustion. The engine energy output is increased and partially compensating for the higher energy density of petrol diesel. It is the most valuable form of renewable energy, environmentally friendly, ideal for heavily polluted cities and can be used directly in any existing unmodified diesel engine (Knothe, 2006).

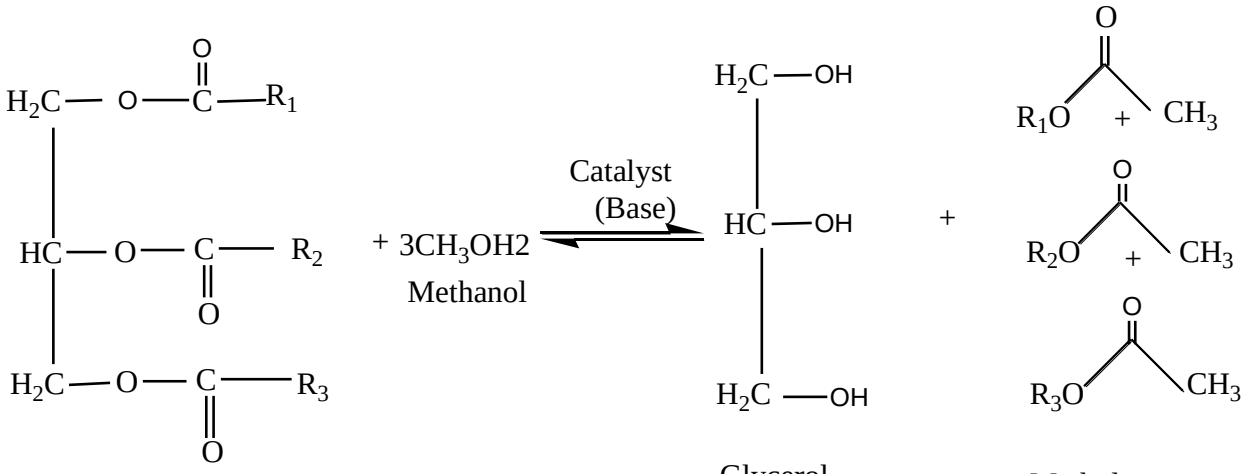
More energy is available in the fuel than is used to grow the crop, press the seeds, process the oil seeds to biodiesel and distribute the product, this is a positive energy balance. Several countries have active biodiesel programmes. Such countries also have given legislative support and have drawn up national policies on biodiesel development. The wide variety of motives for action taken can observe: increase of energy supply, reduction of dependence on fossil energy, reduction of harmful local acting emissions, protection of soil by biodegradable products and reduction of health hazards by using non toxic produce. In 1991, the European community (EC) proposed tax reduction for the use of bio-fuels including biodiesel. Today 21 countries worldwide produce biodiesel (Kemps, 2006).In the event of a motor crash, biodiesel is safer than fossil

diesel since its flash point >130^{o}C which is (2.3- 3.3 times) higher than kerosene. Flash point for kerosene (45.5) and automotive diesel fuel (74.0), pure biodiesel (B100) fuels from *Jatropha curcas* L. recorded >100^{o}C (Wagutu *et al.,* 2010).

According to the University of Minnesota in 2006, the production and use of soybean biodiesel decreases lifecycle greenhouse gas emissions by 41% over regular diesel (Knott,2007).

2.3 Transesterification of Vegetable Oil

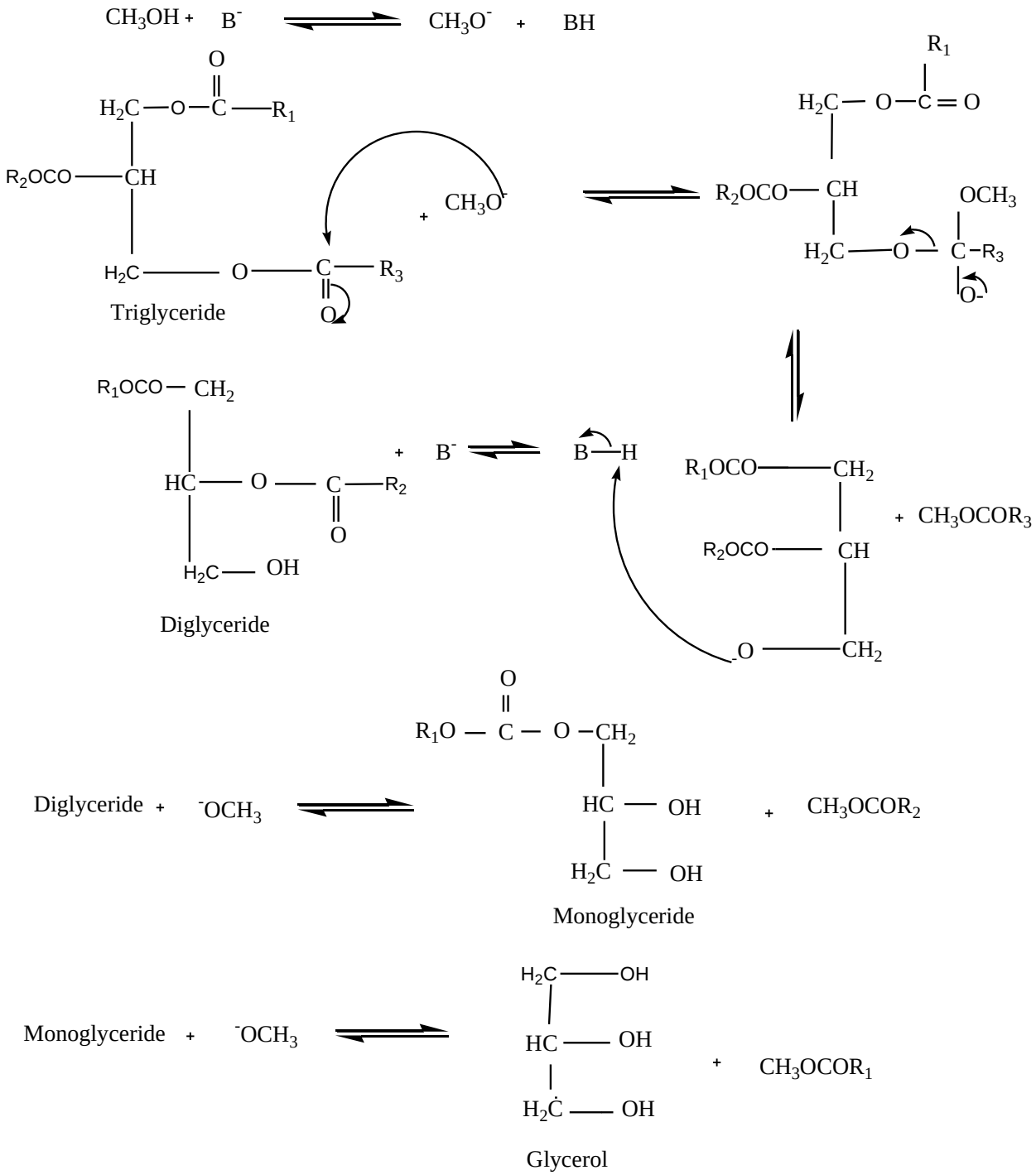
Transesterification describes important class of organic reactions where an ester is transformed into another through interchange of alkoxy moiety. Triglycerides reacts with an alcohol in presence of a strong acid or base catalyst producing a mixture of fatty acid alkyl esters (biodiesel) and glycerol, Scheme 1 (Fukuda *et al*.,2001).



Scheme 1; Transesterification reaction

The overall equation is a sequence of three consecutive and reversible reactions, in which diglycerides and monoglycerides are formed as intermediate (Freedman *et al*., 1986). The proposed mechanism for the reaction is shown in the **Scheme 2:** Several aspects, including the type of catalyst, alcohol to vegetable oil molar ratio, temperature, water content and free fatty acids have been singled out to have an influence on the course of transesterification (Meher*et al*., 2006).

Alkaline catalyses are preferred because of less corrosive nature and the fact that the reaction proceeds much faster than in acid catalyzed reaction (Oliveira *et al*., 2000). Metal hydroxides (KOH and NaOH) are used often because they are cheaper than metal alkoxides (Schuchardt *et al.*, 1997).



Scheme 2: Transesterification of oil with methanol to esters and glycerol

KEY
B^- = Base catalyst
R = alkyl group

2.4Fuel Combustion

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

2.5 Properties of Biodiesel

The American Society for Testing and materials (ASTM) has developed specifications for biodiesel fuels, AST D6751 (**Table 2.1**)

Table 2.1; Fuel parameters, methods and limits

	Property	Standard procedure	Limits
1	**Flash point**	**ASTM D93**	**130^{o}C min**
2	**Water content**	**ASTM D95**	**0.050% vol., max.**
3	**Distillation temperatures**	**ASTM 86**	**360^{o}C max.**
4	**Copper corrosion**	**ASTM D130**	**No. 3 max.**
5	**Cetane index**	**ASTM D 4737**	**47 min**
6	**Color**	**ASTM D1500**	**0.5-0.8 units**
7	**Density**	**ASTM D1289**	**1000g/cm^{3} max.**
8	**Kinematic viscosity at 40^{o}C**	**ASTM D445**	**1.9-6.0 min^{2}/sec**
9	**Smoke point**	**ASTM D1322**	**6mm min**

Source: (ASTM biodiesel fuels D6751) (Knothe, 2006)

These specifications were created in a way that allows biodiesel to be made from various feedstocks using a variety of processes so long as the finished esters comply with the specifications.

2.5.1 Analytical Properties

2.5.1.1 Gas Chromatography (GC) Analysis

The sample mixture is separated mainly by the boiling point and the structure (polarity) of the individual compounds (Mittelbach *et al*., 1996). The structure of component and their boiling points are the major factors determining the retention time (Van Gerpen *et al*., 2004). Usually, larger molecules have longer retention times in GC. When a material eluting from the column at a certain retention time is detected, this is shown by a peak in the chromatogragm. The intergrated value of the peak amplitude over time is proportional to the amount of material causing them (Lencher *et al*., 1997). This constitutes the usefulness of GC in quantifying the amounts of components in a mixture. Compound of a specific nature can be expected to elute. They are therefore very useful in establishing the nature of the compounds in a mixture (Mittelbach *et al*., 1996).

Unfortunately the method only detects if a compound is eluting, not its identity or structure. The identity or structure is established through the use of hyphenated method. The most common method is combination with mass spectrometry (GC-MS). The spectra in MS record how much a compound is broken up into fragments by beam of electrons energy. The way a compound splits into fragments is characteristic of its structure (Van Gerpen *et al*., 2004).

2.6Biodiesel Blends

Blends of biodiesel with automotive diesel fuel and Kerosene is a representation of a common utilization of biodiesel. In the United States, B20 is recognized as an alternative diesel fuel under criteria of the Energy Policy Act (EPACT). In France, biodiesel is utilized as a lower-level blend with conventional diesel fuel (Knothe, 2000). The blends are made in volumetric percentages and designated as BX where X is the percentage of biodiesel in the blend. For example, B10 has 10% biodiesel and 90% convectional diesel, therefore, B100 is pure biodiesel while B0 is pure automotive diesel or pure Kerosene (Knothe, 2005).

2.7Water Boiling Test (WBT)

WBT is a rough simulation of a cooking process that is intended to help fuel analyst understandhow well heat energy is transferred from the cooking fuel to the cooking pot (VITA, 1985). Biodiesel fuels developed are tested against kerosene fuel in common capillary fed wick stove. Each fuel boils one liter of water in three phases; high power phase, (cold start), high power phase (hot start) and low power simmering phase, intended to mimic the most common cooking tasks: boiling and simmering. The test is carried out to investigate the potential of fatty esters developed in domestic cooking as alternative to kerosene.

2.8Emissions

This is the determination of the amount of CO emitted by the given fuel and the blends. The test system consists of a stove platform and an exhaust hood which draw gases

upwards where they are detected by a probe connected to the gas emission analyzer fitted with a non-dispersive infrared spectrometer (Edwards, 2004). The amount of the carbon monoxide is registered after every five minutes in parts per million.

2.9 Soap

2.10 Chemical properties of soap

Kenya Bureau of Standards (KEBs) has developed spefications for soap, KS: 81 (Table 2.2)

Table 2.2; Soap parameters, methods and limits (KS, 2007)

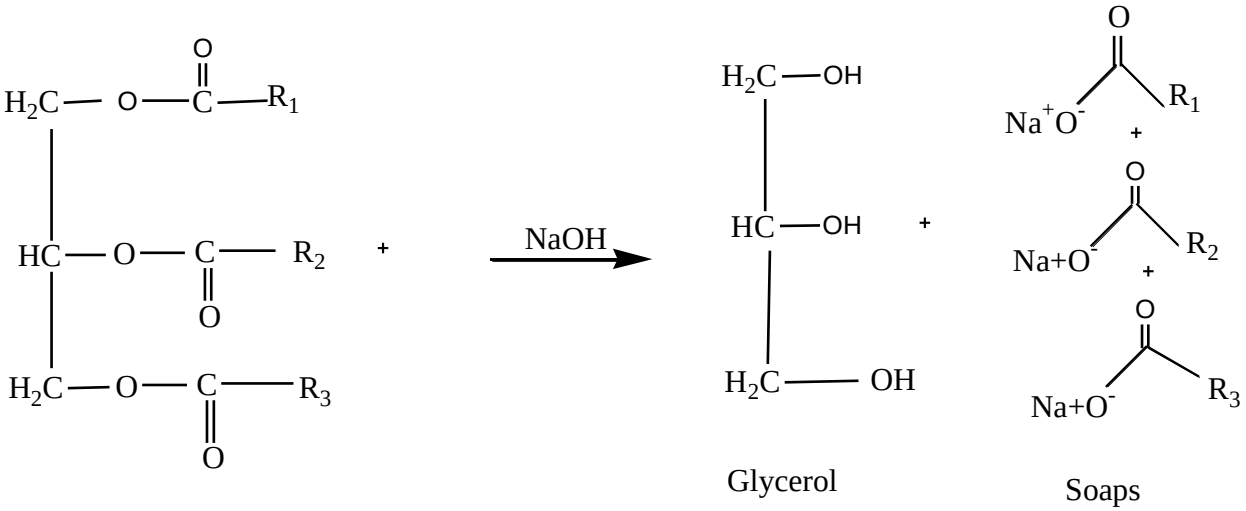
Test parameters	Test Methods	Limits	
		Minimum	**Maximum**
Total Fatty Matter (TFM) in (%)	TES/04/TM/09	70	85
Free Caustic Alkali (FCA)in (g)	TES/04/TM/08	0.0429	
Matter Insoluble in Ethanol (MIE) in (g)	TES/04/TM/04	0.03	0.5
Lathering in (cm^3)	TES/04/TM/05	150	700

Vegetable oils are more readily absorbed by the skin while animal oils have been found to clog pores and aggravate certain skin conditions. Vegetable oil soaps are chemically superior and can be of higher quality than soaps made with animal fats (Wamukonye, 1995). Natural ingredients; natural oil and glycerin, are rarely used in commercially manufactured soap, if used at all is sparingly. Phosphates are non biodegradable, when phosphate detergents are used, disposal of the waste water is a problem. The breakdown of the phosphorus complexes in detergent wastewater creates freely available phosphates; these contribute to the oversupply of phosphates in the waterways and

cause an imbalance of the aquatic ecosystem which causes growth of algal blooms which are toxic to aquatic life (Viorica *et al*., 2011).

Handmade soap retains extra glycerin. It is one of the best lubricants that attract moisture to the skin (Shay,1993). Glycerol and fatty acids are widely used as raw material in cosmetics, soap production, synthetic detergents and grease removers (Serri, *et al.,* 2008). Almost any fatty substance can be employed in soap-making, but the choice is naturally restricted by the price of the fat and also the quality of the soap desired (Shay, 1993).

The soap production starting from triglycerides and alkalis has been accomplished for more than 2000 years (Childers, 2000). Soap making ingredients are locally available (Ellis, 2007). Top quality handmade soaps are devoid of artificial colors, fragrances and preservatives that can cause allergies, irritation and cancer (Taiwo *et al*., 2008). Nowadays, researchers have used sodium hydroxide - catalyzed hydrolysis of esters which has advantages of the reaction being one way rather than reversible and the product are easier to separate and also produce softer soaps (Pinto and Lancas, 2006), scheme 3. Lye (sodium hydroxide) contains one sodium ion and one hydroxide ion. The sodium ion does not take part in the reaction but only the hydroxide ion. When the acid and the base are mixed together, the triglycerides release the single glycerol molecule which enables the fatty acids to combine with hydroxide ions to form soap (Wamukonye, 1995).



Scheme 3: Saponification reaction process

CHAPTER THREE

MATERIALS AND METHODS

3.1 Collection and Preparation of Plant materials

Telfairia pedata seeds were bought from Chuka market in Tharaka Nithi County (Eastern Kenya) and they were identity and confirmed at Kenya National Herbarium, Nairobi, reference number NMK/BOT/CTX/1/2.

Coconuts were purchased from Mombasa, Kongowea Market (Coastal Kenya).

Decortications was done manually while the seed kernels of *T. pedata* were then washed carefully and thoroughly to remove foreign matter using de-ionized water. They were dried under the sun for three days, ground using a Warring blender. Coconuts (*C.nucifera*) were de-haired, cut into two halves and the copra removed using special coconut grater locally known as "Mbuzi". The grated copra was spread on a tray and sun dried to remove water.

3.2 Determination of Moisture Content

Five hundred grams of the cleaned seed samples of *Telfairia pedata* were weighed and dried in an oven at 110^{o}C for 7 hours. The seeds were then removed from the oven and allowed to cool in a desiccator for 30 minutes. Weights of the cooled sample were then used to calculate the moisture content from Equation 3.1. The procedure was repeated three times and average weights used in the calculation (AOCs, 1997a);

$$Moisture\ \ \% \ = \frac{Sample\ weight\ before\ drying - Sample\ weight\ after\ drying}{Sample\ weight\ before\ drying} \times 100 \qquad 3.1$$

3.3 Oil Extraction

Oil was extracted from the two samples by solvent extraction method. The ground dry seeds materials were refluxed with n-hexane in a soxhlet extractor for 4 hours. After exhaustive extraction of each sample, the oil-hexane miscella was transferred to a rotary vacuum evaporator (model R300B) with temperature of water bath set at 40^{o}C to remove n-hexane. The oil was then treated with 10% (v/w) anhydrous sodium sulfate to remove traces of water. Dry oil was weighed, bottled and stored in a deep freezer waiting transesterification process (Warra *et al*., 2011).

3.4 Determination of Physical and Chemical Parameters of Oil

The physical properties; Viscosity was determined using viscometer, density by hydrometers at room temperature and refractive index using a refractometer. Acid values, Saponification values, Calorific value and iodine numbers were analyzed according to American Oil Chemist Standard (AOCS, 1997a; AOCS, 1997b) at thechemistry laboratory at Kenyatta University, Kenya.

3.4.1 Iodine Value (IV)

Exactly 2g of dried oil sample was weighed using a balance into a 250ml Erlenmeyer flask and 10ml of carbon tetrachloride added to dissolve the oil. In another flask, 10 ml of carbon tetrachloride was pipette out and added into each flask. The flasks were then stoppard and the contents mixed by swirling slowly. The mixtures were stored in a dark place at 25±5^{o}C for 30 minutes (AOCS, 1997a). At the end of 30 minutes, 15 ml of 10%w/v potassium iodide solution and 100 ml of distilled water were added to each

solution and titrated immediately with 0.1 N sodium thiosulfate solutions until the yellow color almost disappeared. Approximately 1 ml of starch indicator solution was then added and titration continued drop wise with vigorous swirling to enable disappearance of the blue starch-iodine color. The blank was titrated in the same manner. The average titer obtained from triplicate of experiments per sample was designated; titration= a ml and that of the blank as titration =b ml. Iodine value was calculated from Equation 3.2 (AOCS, 1997a);

$$\text{IV} = \frac{\text{b} - \text{a} \ \times \text{N} \ \ \text{sodium thiosulfate} \ \times 12.69}{\text{Sample weight in grams}} \quad [3.2]$$

Where; IV= iodine value, N= normality of sodium thiosulfate and 12.69= number of grams of iodine in 0.1 M ICl (Wijs solution).

Iodine value of the mixture in methyl esters (biodiesel) was also calculated from GC-MS results using Equation 3.3 for comparison;

$$IV_{mixture} = \quad 100 \times \frac{(A_f \times 253.81 \times db)}{MW_f} \qquad [3.3]$$

Where;

IV= is iodine value, A_f is the amount in % of fatty composition in the mixture (GC-MS), db= is the number of double bonds, $MW_{f\,=}$ is molecular weight of the fatty components as shown by MS spectra and 253.81 = the atomic weight of two iodine atoms that are theoretically added to one double bond.

3.4.2 Saponification Value (SV)

A mass of 2g of oil sample was weighed in a conical flask. Exactly 25 ml of ethanolic potassium hydroxide (0.5 M in 95% ethanol) was added. To the flask, a reflux condenser was attached and the sample heated for one hour in a hot plate magnetic stirrer while stirring gently. Phenolphthalein indicator was added to the sample, while still hot, then titrated with 0.5 M HCl. Average volume obtained from triplicate of average volume obtained recorded as titer = a ml. Blanks were run at the same time and average volume obtained recorded as titer = b ml. Saponification value was calculated from Equation 3.4 (Van Gerpen *et al.*, 2004);

$$SV = \frac{b - a \times 28.05}{Sampleweightingrams} [3.4]$$

Where; SV= Saponification value and 28.05= grams KOH in 0.5 M KOH solution.

3.4.3 Acid Value (AV)

The acid value is defined as the amount of milligrams of KOH required to neutralize the free acidity in 1g of the oil sample. A volume of 50 ml diethylether was mixed with 25 ml ethanol (95%) and 1 ml phenolphthalein solution. Exactly 2g of oil sample was dissolved in the mixture and titrated with 0.1 M NaOH while shaking constantly until a pink color persisted for at least 15 seconds. Triplicate of experiment were performed and average volume used in the calculation by Equation 3.5. (AOCS, 1997b);

$$AV = \frac{Titrevolume \times 4.0}{Sampleweightingrams} \qquad 3.5$$

Where; Av= acid value, Titre Volume = volume of NaOH used to neutralize the oil sample and 4.0 = number of grams of NaOH in 0.1 M NaOH solution.

3.4.4 Calorific Value

The gross calorific value was determined using a bomb calorimeter model (CAB 101) made in Germany. Approximately 0.846 g fuel sample was weighed in a bomb crucible. The bomb cup was placed on its stand provided with the outfit. Firing nickel wire piece was stretched between the electrodes of the bomb (ASTM, 1998a). A wicking cotton thread, 9 cm long was tied to the stretched wire and the end dipped inside the sample in the crucible. The crucible then was placed on the support ring (figure 3.1) and 3.0×10^{6} N/m^2 of 3 oxygen gas. Calorific can was filled with distilled water until a weight of 3 kg (water plus the can) was obtained to submerge the bomb completely. The bomb was placed on the three supports in the calorimeter vessel and checked for leakage (confirmed by absence of bubbles). Cover of the water jacket with thermometer completeness tested by firing circuit test plug.

The temperature of the calorimeter vessel was allowed to stabilize and the initial temperature taken $\pm0.001^{o}C$, the fire switch was then pressed for 2 seconds to ignite the sample. Satisfactory firing was confirmed by failure of the switch (Muthengia *et al.,* 2005). The final temperature of the apparatus was taken after 10 minutes $\pm0.001^{o}C$. Readings were taken after sequential 3 minutes until the reading was found to be within a range of $\pm0.002^{o}C$. The final temperature was recorded. Rise in temperature was calculated as a difference from initial to final temperature reading. Each sample was tested three times and the average values of weight of sample and temperature rise taken for the final determination of total heat release from the sample. The gross heat released was calculated from (Equation 3.6) (Muthengia *et al*., 2005)

$$H = \frac{Cv\Delta T - 0.01260}{M} \quad 3.6$$

Where;

H= Calorific value, Cv= Heat capacity of apparatus (10.380 J/^{o} C) and 0.12600 J = Constant heat gain.

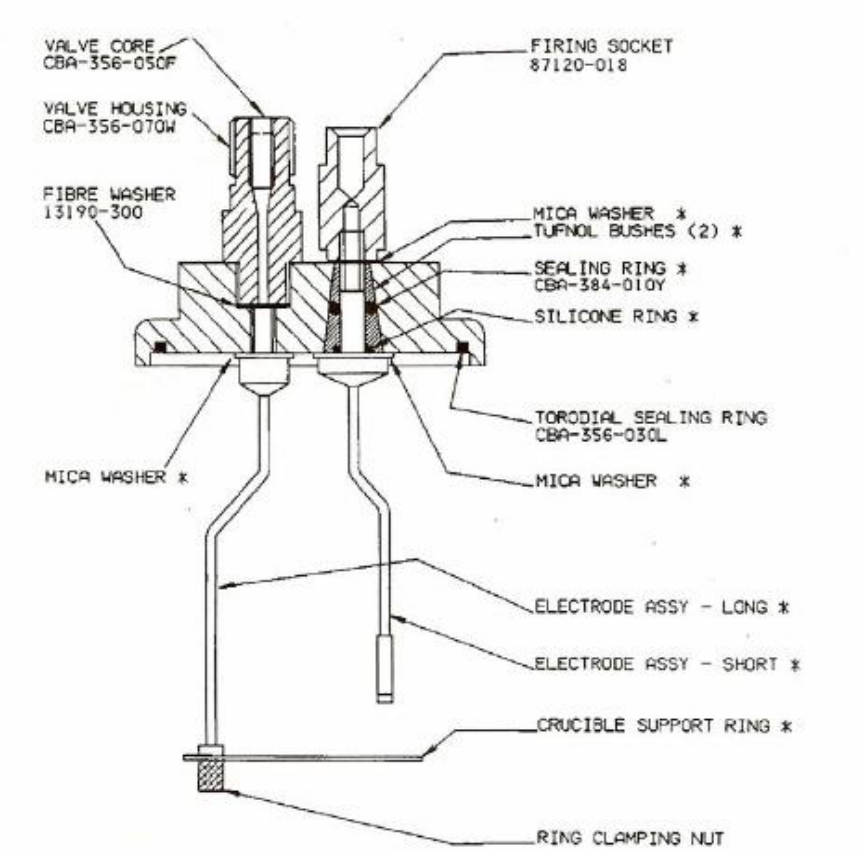


Figure 3.1 Bomb calorimeter electrode assemblies

3.5 Soap Preparation

3.5.1 Determination of Lye and the Amount of Water

The amount of lye in the recipe depends on the mass of the fat or oil (Childers, 2000);

Mass of lye =Mass of fat or oil x Sodium factor [3.7]

About 162.05 g of water was poured into a beaker; 69.45 g of NaOH (lye) was added to the glass bowl containing water slowly and stirred well with a wooden spoon (hands well protected with plastic gloves). About 500 g of *T. pedata* oil was heated at 55^{o}C in a 1000ml glass beaker into which the water/lye mixture was added. The content was stirred with a wooden spoon for 30 minutes, a honey like consistency substance 'trace' was formed as an indication of a chemical reaction for the formation of soap. At this stage stirring was stopped and the mixture poured into a plastic mould, covered with a towel and kept undisturbed for 48 hours. The mold was then unwrapped, soap removed and kept wrapped in a towel on a wooden rack for 2 weeks for it to age (Child, 1974; Childers, 2000).

A similar procedure was used in preparation of *C. nucifera* soap.

3.5.2 Preparation of Soap from a Blend of *T.pedata* oil and *C. nucifera* oil

The procedure from the (section 3.5.1) was followed with 300 g of *T. pedata* oil, 200 g *C. nucifera* oil, 85.3 g of lye and 198.7 g of water (Child, 1974; Childers, 2000).

3.6 Determination of the Physical and Chemical Properties of *T.pedata,* Coconut, and Blend Soaps

Physiochemical properties for the three types of soap; *T. pedata* oil soap, *T. pedata* oil/*C. nucifera* oil soap blend and *C. nucifera* oil soap were determined and their results compared to KEBs stardands. These properties include: total fatty matter, total free alkali, matter insoluble in ethanol and lathering according to (KEBS) Kenya Bureau of Standards (KS 81, 2005; EAS 186, 2000). The physicochemical properties of soaps and

complete saponification determine their quality, efficiency and their cleansing properties (Vivian *et al.*, 2014)

3.6.1 Total Fatty Matter (TFM)

Total Fatty Matter (TFM) was determined according to (KS 81, 2005). About five grams of 2-3 mm grated soap noodles sample was weighed into a glass beaker and dissolved in 100 ml hot water (40^{o}C). The solution was then transferred to a separating funnel while washing down the glass beaker containing the soap solution with 50 ml hot water (40^{o}C) and the washing added to the separator. 3 drops of methyl orange indicator and 25 ml of 4N hydrochloric acid were added to the separator.

A pink color appeared and an excess of 5 ml of hydrochloric acid was added. The content in the separator was allowed to cool for 30 minutes at room temperature then 100 ml petroleum ether, boiling range 40-60^{o}C (the solvent carrier liquid) was added. Vigorous shaking the separator and releasing the pressure was repeated 3 times.

The content was then allowed to stand until there was a clear separation of two layers an aqueous and organic layer. The aqueous layer was transferred into a 250 ml beaker labeled (A) and the organic layer in a beaker labeled (B). The aqueous layer from beaker (A) was returned into the separator and extraction was repeated with 100 ml light petroleum ether. The content was allowed to settle and the aqueous layer was separated from the organic layer. The two organic layers were mixed in the separator washed with the distilled water until the washing was neutral to methyl orange. The extract was filtered through a filter paper, covered with anhydrous sodium sulfate into a

dry pre-weighed flask. The separator and the filter paper were then washed with 50 ml petroleum ether each and the washing transferred to the petroleum ether solution which was then evaporated off in a vacuum rotor vapor. The soap content was heated in the oven at 103^{o}C for one hour and then transferred into desiccators, allowed to cool for 30 minutes and weighed.

The total fatty matter in the sample was calculated from average weights obtained from triplicate of experiments as a percentage by equation 3.8;

$$\frac{M_1}{M_2} \times 100 \qquad [3.8]$$

Where: M_1 =Mass in g of the dried soap

M_2= Mass in g of test portion

3.6.2 Lather Volume

Five grams of 2-3 mm diameter noodles of soap from each sample to be tested was weighed and added to the blender jar with 100 ml water with 300ppm calcium water hardness. The blender was run for exactly 60 seconds and the content was poured into a 1000 ml measuring cylinder and the total volume in the cylinder was taken (EAS 186, 2000).

3.6.3 Total Free Alkali (TFA)

TFA was tested according to, (KS 81, 2005, EAS 186, 2000). Five grams of soap sample was weighed into a 250 ml conical flask on a heating plate and to it 100 ml ethanol solution was added. The flask was fitted into a reflux condenser and gently

heated until the soap content completely dissolved. Exactly 3.0 ml 1 N sulfuric acid solution was added and gently boiled for 10 minutes then allowed to cool to an ambient temperature. The content in the flask was then titrated against 0.1 N ethanol potassium hydroxide solutions in the presence of 3 drops of phenolphthalein indicator. Total free alkali content expressed as the percentage by mass of sodium hydroxide was calculated from the average of volume obtained from triplicate of experiments as percentage by equation 3.9;

$$\text{Total free alkali content}(\text{m m \%}) = 0.04 \times \frac{V_0T_0 - V_1T_1}{M} \times 100 \quad [3.9]$$

Where; m=mass of the test portion V_0= volume in ml of the sulfuric acid solution used the determination (check), V_1=volume in ml of potassium hydroxide solution used in the titer, T_0= exact normality of sulfuric acid solution used, T_1= exact normality of potassium hydroxide solution.

3.6.4. Matter Insoluble in Ethanol (MIE)

MIE was determined according to (KS: 81, 2005, ISO 673, 1981). Five grams of the soap was weighed into a 250 ml conical flask, 100 ml freshly boiled ethanol was added into the flask and refluxed under gentle heat for 30 minutes swirling in order to avoid any material adhering to the bottom of the flask. After all the content in the flask dissolved it was transferred to a sintered glass crucible that was dried in the drying oven for 103^{o}C for one hour, allowed to cool in a desiccators to room temperature and weighed to the nearest 0.001 g.

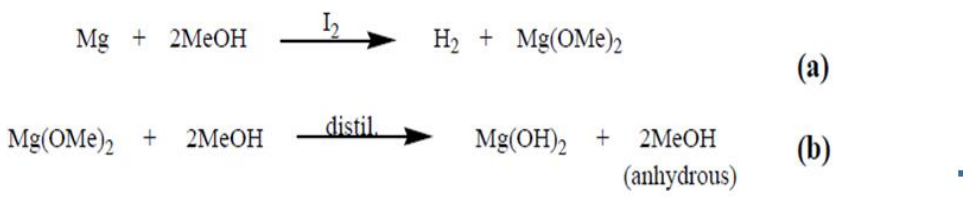
The content in the crucible was filtered using a vacuum pump; the flask was washed off using 50 ml hot ethanol near to its boiling point and filtered off the insoluble material to the crucible. The residue in the crucible was washed with 25 ml for three times with hot ethanol until all the alcohol soluble were removed. The crucible with the residue was placed in the oven at 103^{o}C for one hour, removed and placed in desiccators for it to cool completely to room temperature and weighed. The operation of drying in the oven, cooling in the desiccators and weighing was repeated 3 times until the difference in mass between 2 successive weighing was less than 0.001g. Matter insoluble content was expressed as percentage by weight was calculated from the average of volume obtained from triplicate of experiments as percentage by equation 3.10;

$$\text{Matter insoluble in Ethanol (m m \%)} = \frac{W_1}{W_0} \times 100 \qquad [3.10]$$

Where; W_0= Weight in grams of the matter insoluble in alcohol, W_1=Weight in grams of the material taken for test.

3.7 Preparation of Methyl Esters (Biodiesel)

One gram of fresh oil was dissolved in 10 ml of isopropyl alcohol to make vegetable oil solution which was then titrated with 0.025 M NaOH. The pH of oil solution was checked with a pH meter after every milliliter of NaOH solution titrated. Titration was stopped when the pH rose to 8-9.The volume of NaOH solution used for pH to reach 8-9 was recorded and weight of NaOH required for neutralizing 1000 ml of oil calculated. This amount plus 3.5 g NaOH to catalyse the reaction was the required amount for 1000 ml of oil (De-Filippis *et al.*, 1995);



Scheme 4: Dehydration of methanol

Methanol was initially dried by Lund and Bjerrum method using magnesium turnings in a reaction catalyzed by iodine (Scheme 4) (De-Filippis *et al*., 1995).A dry round-bottomed flask of 2 liters capacity was fitted with a double surfaced condenser and a calcium chloride guard tube. Exactly 5 g of dry magnesium turnings and 0.5 g of iodine was placed in the flask followed by 75 ml of commercial grade methanol. The mixture was heated gently until all the iodine disappeared. A further 0.5 g of iodine was added to achieve lively evolution of hydrogen. Heating was continued until all the magnesium was converted into magnesium methanoate (the contents of the flask turned milky), (Scheme 4a). A further 900 ml of the commercial methanol was then distilled off directly in a bottle and stored over type 3A molecular sieves.

3.7.1 Synthesis of Methyl Esters (Biodiesel)

For each sample of the oil, 1000 ml was reacted with a solution of predetermined amount of NaOH in 300 ml methanol (30.0% by volume of oil) in a 2 liters conical flask. A magnet rod was placed inside the flask which was then fitted with a double surfaced reflux condenser. The contents of the flask were heated in a hot plate magnetic stirrer (Stuart SB 160) with temperature set at 70^{o}C and magnetic revolutions at 700 rpm. The mixture was stirred and refluxed for 4 hours. The solution was then left to

cool to room temperature and emptied in a 2 liters capacity separating funnel and left to stand for 12-24 hours (Ma and Hanna, 1999a). The mixture separated into two layers, the bottom glycerol layer was drained and the crude ester layer left in the separating funnel. The ester was purified by washing gently with warm water at 45^{o}C and then draining the water from the bottom of the separating funnel. Rinsing was done repeatedly until the discarded wash water reached pH level of 6-7 and no soap bubbles appeared. The ester was then dried using 10% (w/v) anhydrous Na_2SO_4 and stored in a freezer waiting fuel properties analysis.

Ester conversion from the oil was tested in methanol; based on the fact that methyl esters are quite soluble in methanol while triglyceride has a very low solubility. Exactly 27 ml of methanol was well shaken with 3 ml of the ester sample at room temperature. Absence of oily material settling at the bottom of a test tube after 20 minutes indicated complete conversion of the oil into methyl esters (Chisholm and Hopkins, 1964).

3.8 Purification of the Glycerol

The glycerol was heated at 65^{0}C in a beaker for 1 hour to remove the excess methanol and then strained using cotton wool through a filter funnel to remove any impurities into a beaker (David *et al*., 2006).

3.9 Fuel Property Measurement

Physiochemical parameter determined for the oils were also done for the methyl esters and there results compared. Fuel properties were tested using procedures ideal for conventional automotive fuels. The properties tested include, fatty acid composition, water content, copper corrosion, ASTM color, kinematic viscosity, ash content, density, flash point, distillation temperatures, cetane index and refractive index.

3.9.1 Determination of Water Content of Methyl Esters

Water content was determined according to ASTM D95 procedure (ASTM, 1999a). Exactly 100 ml of test ester sample was measured in to a graduated measuring cylinder and transferred to a glass still. The ester material adhering to the cylinder was rinsed with 50 ml petroleum ether, boiling range 80-110^{o}C (the solvent carrier liquid) and then two more times with 25 ml portions of the solvent. Glass beads were added to reduce bumping during boiling. The condenser tube and receiver were well cleaned and dried to ensure free drainage of water into the bottom of the receiver. A loose cotton plug was inserted at the top of the condenser to prevent atmospheric moisture condensing inside it. The components of the apparatus were assembled (Figure 3.2) and cold water circulated through the jacket of the condenser. Heat was applied to the still using a heating mantle, adjusting the rate of boiling so that it condenses at the rate of 2-5 drops per second. Distillation was continued until no water was visible in any part of the apparatus except in the receiver with the volume remaining constant for 5 minutes.

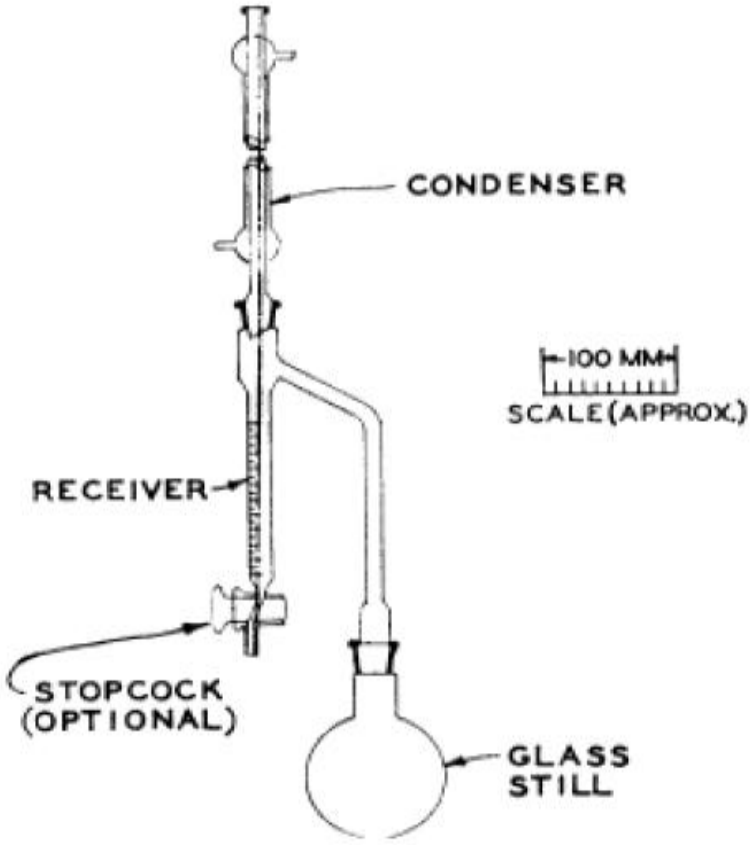


Figure 3.2 Typical assembly for water content determination

When the evolution of water was complete, the receiver and the content were allowed to cool to room temperature. Drops of water adhering to the sides were dislodged with a glass rod and transferred to the water layer. The volume of the water was read to the nearest scale division and recorded as a percentage of the total volume of sample. A solvent blank was established by distilling 100 ml of petroleum ether in the same procedure. The blank was determined to the nearest scale division and used to correct the volume of water in the receiver.

The water in the sample was calculated from average volume obtained from triplicate of experiments as a percent by equation 3.11(AOCs, 1997a);

$$\text{Water (v v \%)} = \frac{\text{Volume in water trap} - \text{Volume in solvent blank}}{\text{Volume in test sample}} \times 100 \quad [3.11]$$

3.9.2 Determination of Copper Corrosion of Methyl Ester

Copper corrosion was determined following the ASTM D130 procedures, (ASTM, 1994). Copper strips (99.9% purity) each measuring 12.5 mm thick and 75 mm long were used. Surface blemishes by oxidation from all six sides of the strip were removed using 65 µm silicon carbide paper and the metal dust from the strip cleaned by rubbing vigorously with clean pads of absorbent cotton until a fresh pad remained unsoiled. Exactly 30 ml of ester sample, free of any suspended or unstrained water, was placed into a clean, dry 25 mm by 150 mm test tube. The polished copper strip was slid into the sample tube. The tube was then Stoppard with a vented cork and placed in a test bomb (Figure3.3). The bomb was then immersed in a water bath maintained at 100±^{o}C. After 3 hours ±5 minutes (for diesel fuels and esters) and 2 hours for (kerosene), the content of the test tube were removed and put into a 150 ml beaker. Immediately the strip was removed and immersed in isooctane (wash solvent). The strip was removed from wash solvent and dried with quantitative filter paper (by blotting), then inspected for evidences of tarnishing or corrosion by comparison with the copper strip corrosion standards Appendix 1. Each sample was tested 3 times under the same test conditions.

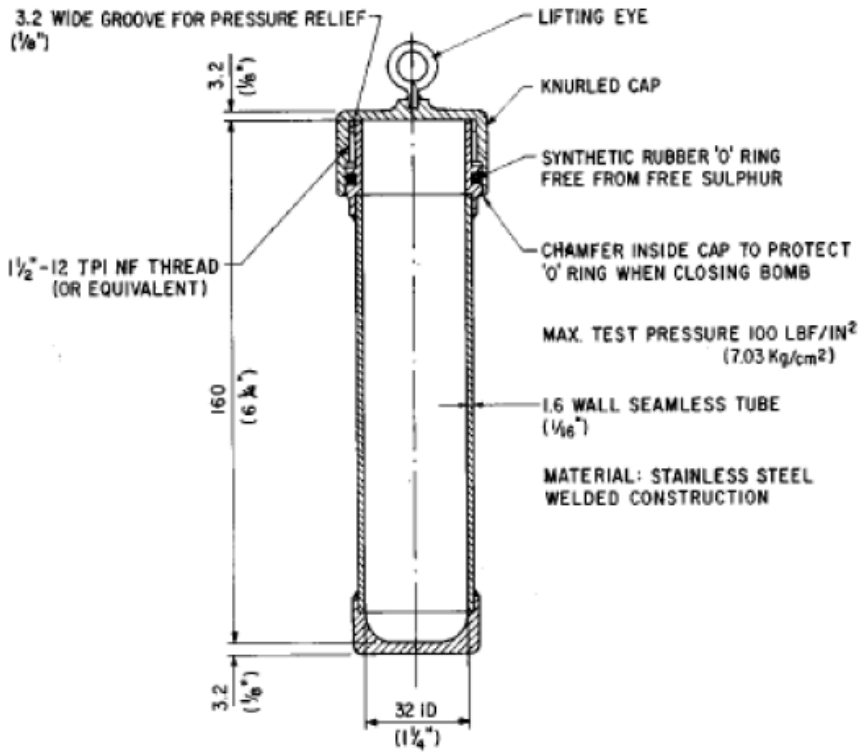


Figure 3.3; Copper strip corrosion test bomb

3.9.3 Determination of Color of Methyl Ester

ASTM color of the ester was determined following ASTM D1500 procedure (ASTM 1998a). Lovibond colorimeter, consisting of light source, glass color standards, sample container housing with cover and viewing piece was used in this test. The glass sample container was filled to a depth of 50 mm with deionized water and placed in the compartment of the colorimeter through the standard glass was observed. The sample in its container was placed in the other compartment. The two containers were then covered to exclude all the exterior light. The light source was switched on and the color of sample compared with that of the standard glass containing deionized water. The test

was repeated 3 times for every fuel sample, average value was reported as the ASTM color value.

3.9.4 Determination of Kinematic Viscosity at 40^{o}C of Methyl Ester

ASTM D 445 procedures were followed in the determination of viscometer with a narrower capillary tube was selected for each sample figure 3.4. Viscometers holders were used to mount the calibrated glass capillary with the test sample to the sample mark and allowed to remain in the bath for 30 minutes to reach the test temperature

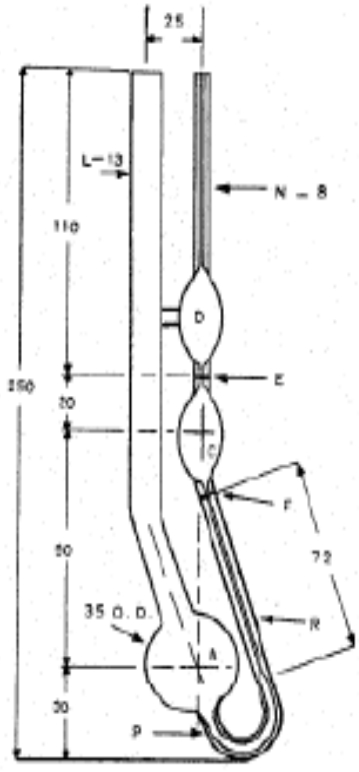


Figure 3.4; Cannon-Fenske viscometer tubes

The volume of the sample was adjusted to the mark after temperature equilibrium was reached. Pressure was applied to adjust the head level of the sample to a position in the capillary arm of the instrument about 7 mm above the first timing mark. With the sample flowing freely, the time required for the meniscus to pass from the first to the second timing mark was taken in seconds. The procedure was repeated three times for each sample to make three measurements of flow time. The measurements were recorded and the average used in the calculation of the kinematic viscosity from the measured flow time and viscometer constant (Equation 3.12);

$V = C \times t$ [3.12]

Where; v=Kinematic viscosity (mm^2/s), C= calibration constant of the viscometer ($(mm^2/s)/s$) and t= time in seconds**.**

3.9.5 Ash Content Determination

ASTM D482 procedure was followed in the determination of ash content of the methyl esters developed by (ASTM, 2000a). Platinum crucibles 200 ml capacity were preconditioned by heating to 800^oC for 10 minutes in an electric muffles furnace and then cooled to room temperature in a desiccators (without desiccating agent). The crucibles were then weighed, ±0.1 mg. The samples were mixed thoroughly before weighing to distribute catalyst fines and other particulate material throughout the sample. Satisfactory mixing was achieved by 10 minutes shaking using a mechanical shaker. Exactly 100 g of each fuel sample was weighed into a crucible, using a top-loading balance. Each crucible was carefully heated with a Bunsen burner until the contents ignited on introduction of a flame using a burning splint. The sample was left

to burn leaving only a carbonaceous residue when the burning ceased. The residue was transferred to a muffle furnace and heated at 772±25^{o}C until all carbonaceous material disappeared. The furnace was then switched off and crucible left to cool. The crucibles were then transferred to desiccators for further cooling to room temperature. The contents were weighed ±0.1 mg. The crucible was reheated at 775^{o}C for 20-30 minutes then cooled in desiccators and reweighed again. This was repeated until consecutive weights differed by ≤0.5 mg. The mass of the ash was calculated from average of triplicate of experiments as a % of the original samples (Equation 3.13)

$$\text{Ash}\% \ \frac{w \times 100}{W} \quad 3.13$$

Where w= mass of the ash in grams and W= mass of the sample in grams

3.9.6 Density Measurement

The test method, ASTM D1298 was used in determination of densities using glass hydrometers (ASTM, 1999b). The hydrometer cylinder, thermometer and test sample were brought to a constant temperature of 20^{o} C in a water bath. The sample was then transferred to a clean temperature stabilized hydrometer cylinder without splashing to avoid the formation of air bubbles. Mercury in the thermometer with a range -1 to +38^{o}C was inserted and the test sample stirred in a combination of vertical and rotational motions to ensure uniform temperature and density throughout the liquid sample. The temperature of the sample was recorded ±0.1^{o}C and a hydrometer ranging 600-1100 g/cm^{3} lowered into the liquid. Hydrometer was released when in a position of equilibrium, taking care to avoid wetting the stem above the level at which it floats freely (Figure 3.5). The hydrometer was allowed to come to rest and all the bubbles to

come to the surface at least after 5 minutes. The scale reading was made to the nearest one –fifth of a full scale division. The test was repeated 3 times for each sample and the average value recorded as density.

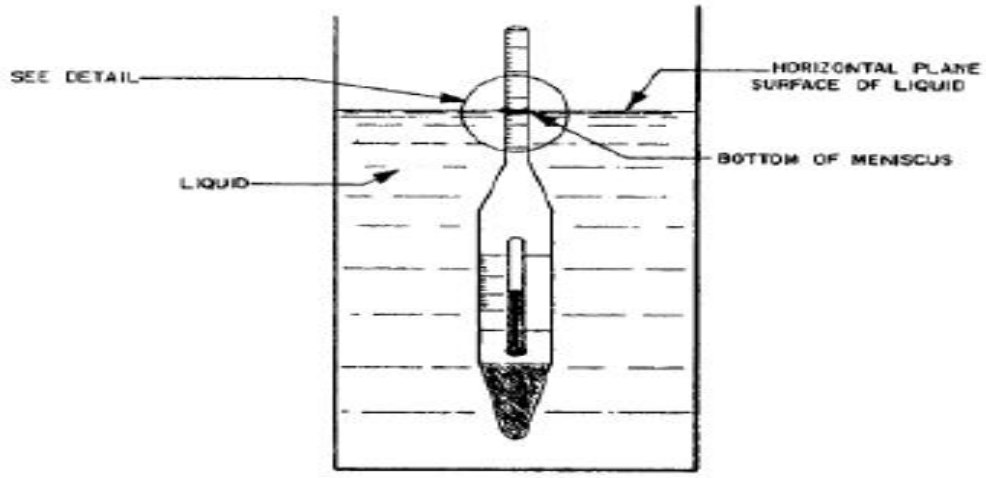
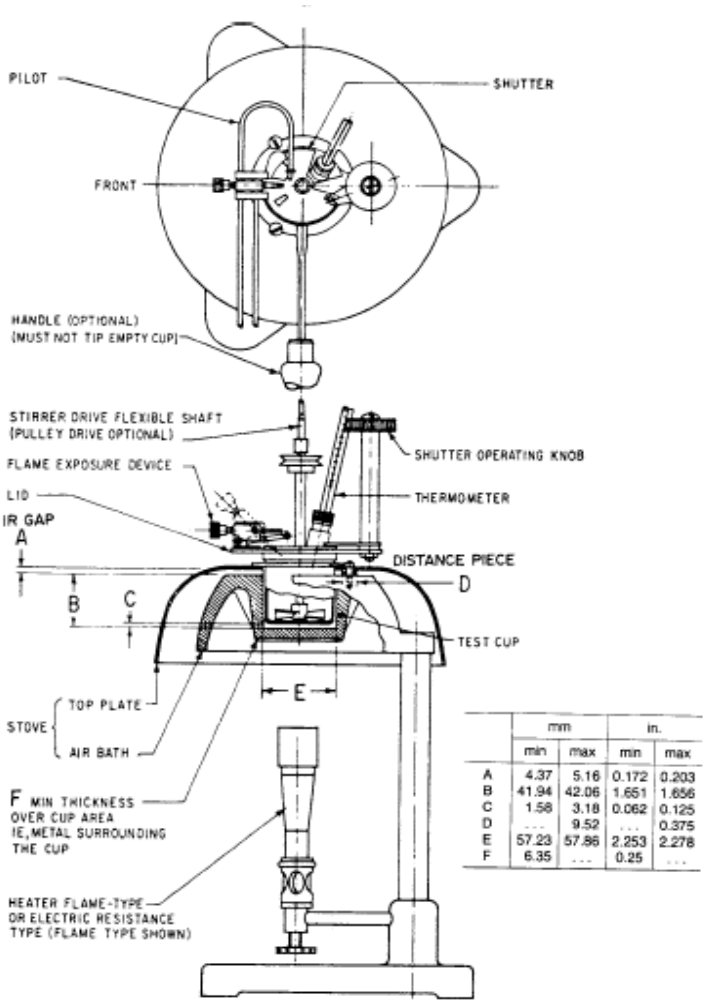


Figure 3.5; Hydrometer for measuring density

3.9.7 Determination of Flash-Point of Methyl Ester (ASTM-D93)

The test method ASTM D93, using automated Pensky-Martens closed-cup apparatus (Koehler K 16200) was followed (ASTM, 1999c). The fuel sample was filled to the mark inside of the test cup. Temperature of the sample was set at 18^{o}C below the expected minimum flash point (100^{o}C for esters).The cup was then covered and the assembly placed into the apparatus. The locking device was properly engaged and the temperature measuring device inserted into a holder. The test flame was lit, and adjusted to a diameter of 3.2-4.8 mm. Heat was applied and controlled to increase at a rate of 5-6^{o}C per minute. The stirring device was at 100 rpm, stirring in a downward direction.



	mm		in.	
	min	max	min	max
A	4.37	5.16	0.172	0.203
B	41.94	42.06	1.651	1.656
C	1.58	3.18	0.062	0.125
D	...	9.52	...	0.375
E	57.23	57.86	2.253	2.278
F	6.35	...	0.25	...

Figure 3.6 Pensky –Martens closed flash tester

When the temperature of the test sample reached 23±5^{o}C below the expected flash point (100^{o}C for esters), the ignition source was directed into the test cap at regular intervals of 5 minutes with simultaneous interrupted of the stirring until a flash was detected. The reading on the temperature measuring device at the time of flash detection was recorded as the observed flash point. Each fuel was tested 3 times and the average reported as the flash point of the test sample. The test method, ASTM D86 was followed to distill the fuels at various temperatures in a laboratory batch distillation unit, Model ADU-4

(figure D) (ASTM, 2000b). The test sample was precisely measured to 100 ml mark of measuring cylinder and then transferred as completely as practical to a distillation flask of 125 ml capacity ensuring that none of the liquid went into the vapor tube of the flask, a few boiling chips were added to overcome bumping. Mercury thermometer in the range 0-400^{o}C provided with a snug-fitting cork was fitted in the neck of the flask such that the bulb was centered in the neck and the lower end of the capillary leveled with the highest point on the bottom of the inner wall of the vapor tube.

The flask vapor tube provided with a snug fitting rubber was fitted tightly into the condenser tube. The flask support board was the raised gently to fit tightly against the bottom of the flask. The measuring cylinder that had been used to measure the sample was placed in a temperature controlled bath under the lower end of the condenser tube without rinsing. The end of the condenser tube was centered tube was centered in the measuring cylinder extending a distance of at least 25 mm but not below the 100 ml mark. To reduce evaporative loss of the distillate, the cylinder was covered with a piece of blotting paper. The drip tip of the condenser was kept away from the wall of the cylinder and heat applied gently. Initial boiling point (IBP) was taken to be the temperature at which the first drop of the condensate hit the bottom of the receiving cylinder. After the IBP, systematic observation of temperature reading and volume of condensate recovered in the receiver cylinder were made recorded ±0.5 ml, respectively.

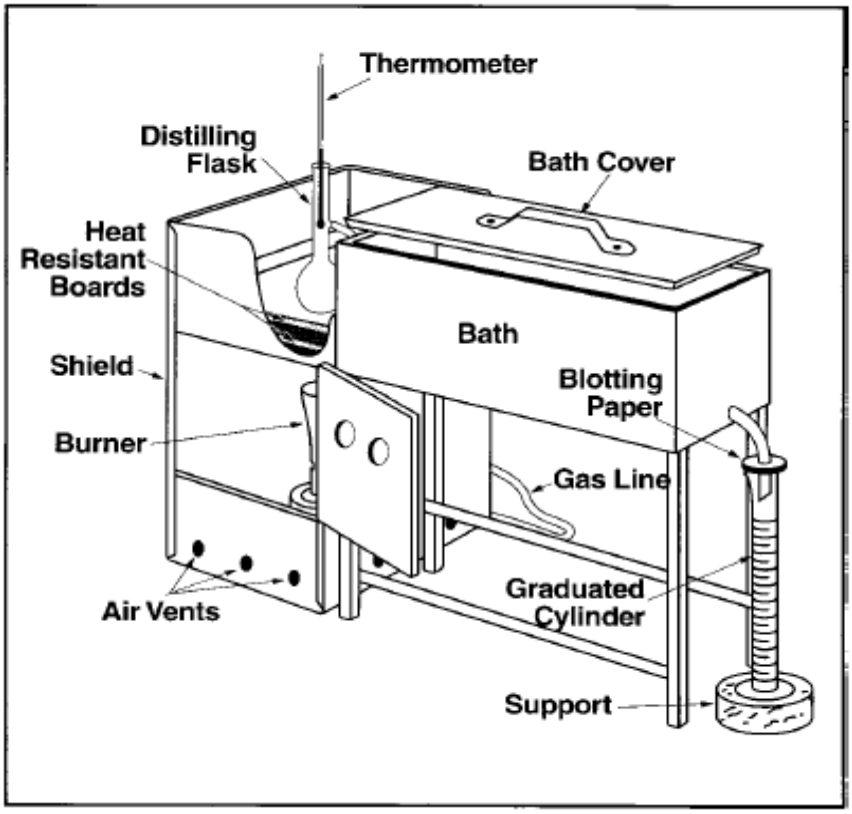


Figure 3.7; Distillation apparatus for ASTM D86

When the residue liquid in the flask was approximately 5 ml, heating was reduced and the final boiling point (FBP) recorded after 5 minutes. Heating was discontinued and distillate allowed to drain into the receiving cylinder to allow determination of total volume recovered. After the flask had cooled its contents was poured in a 5 ml measuring cylinder to determine the percent residue and loss. Triplicate of experiments were performed per sample and average volumes and temperatures determined.

3.9.8 Calculated Cetane Index (CCI)

The calculated cetane index was determined following ASTM D 4737 procedures which incorporates density at 15^{o}C and distillation temperatures from ASTM D86

(ASTM,1997b). For variable equation (Equation 15) was used to estimate the cetane index of distillate fuels. Density of each fuel was determined at 15^{o}C as described in test method at D1298, recovery temperatures of the fuel at 10%, 50% and 90% was recorded as described in test method D86. CCI was calculated as a correlation in SI units between the density and 10%, 50% and 90% recovery temperature of the fuel as follows.

$CCI=45.2+(0.0892)(T_{10N})+[0.131+(0.901)(B)]+[0.0523-0.420)(B)][T_{90N}]+[0.00049][(T_{10N})^2-(T_{90N})^2]+(107)(B)+(60)(B)^2$

Where; CCI=Calculated Cetane Index by four variable equation,

$B= [e^{(-3.5)(DN)}]-1$, where DN= (density at 15^{o}C-0.85)

$T_{10N=}T_{10}$-215, where T_{10}=10% recovered temperature determined by test method D86,

$T_{50N}=T_{50}$-260, where T_{50}=50% recovered temperature determined by test method D86,

$T_{90N}=T_{90}$-310, where T_{90}=90% recovered temperature determined by test method D86.

3.9.9 Determination of Smoke Point

Kerosene was burned in a smoke point lamp according to ASTM D1322 and the maximum flame obtainable without smoke was measured. Apiece of dried wick was soaked in 20 ml of the fuel and placed in a wick tube of a clean dry candle at 25±0.1^{o}C, ensuring that the candle air vent was free from fuel. The wick was trimmed of frayed ends horizontally using scissors so that 6 mm projects from the end of the candle. The candle was lithe and the flame adjusted to approximately 10 mm high and the candle allowed to burn for 5 minutes. The candle was raised until the smoky tail appeared, then the candle was lowered slowly through the stages of flame appearance. Triplicate observations were done to get a precise reading of the scale.

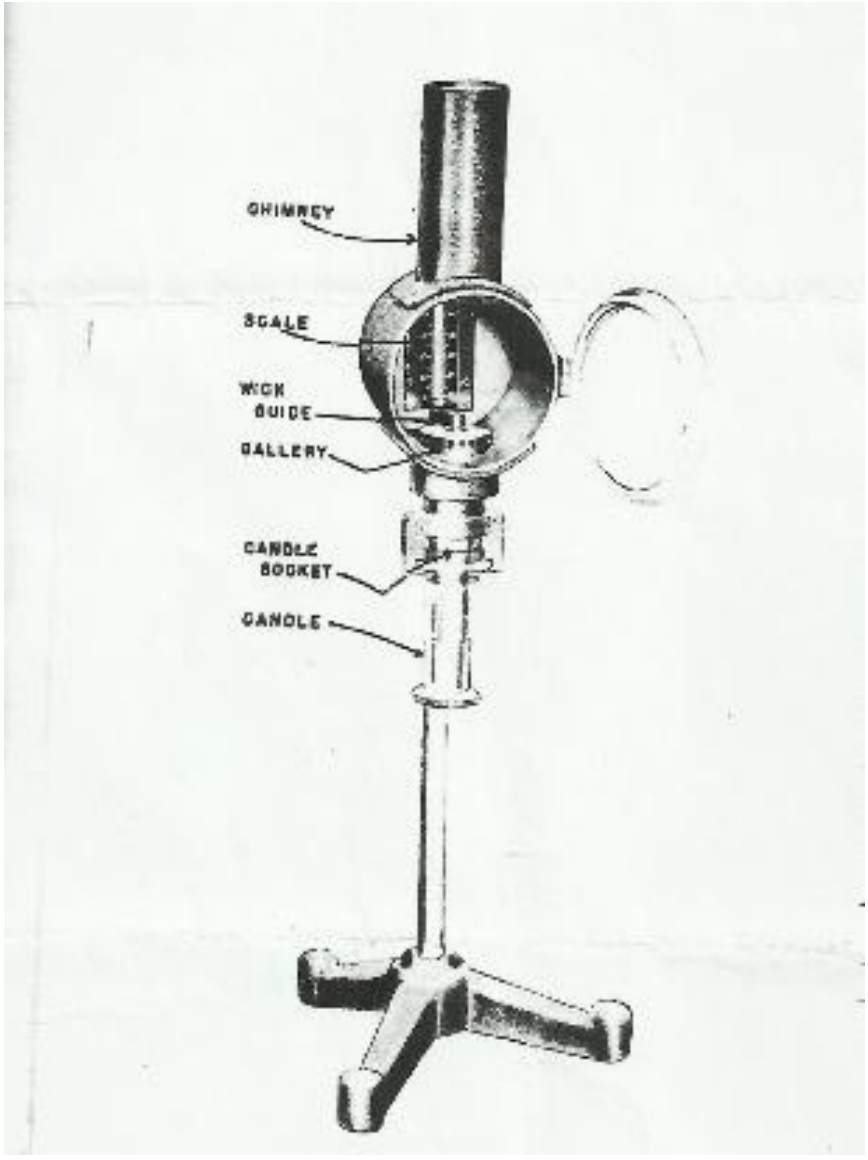


Figure 3.8; Smoke point lamp

3.9.10 Determination of Refractive Index

Abbe type of refractive thermometer (RFM 330 - England) was used with its temperature controlled to within 25±0.1^{o}C through a thermostatically controlled water bath and motor driven pump to drive water through the instrument (Ufuk *et al.*, 2008). Two drops of moisture free sample were transferred onto the prism of the refract meter. The prism was then closed and tightened firmly with the screw head. The sample was allowed to stand for 4 minutes so as to come to the temperature of the instrument. The instrument and the light source were adjusted to avoid parallax interference, the test button was then pressed and scale pointer for refractive index read accurately and recorded. Each sample was tested three times and average reported as the refractive index of the test sample.

3.9.11 Blending of Biodiesel Fuels with Automotive Diesel Fuel

Blends of B5, B10, B20, B50 and B70 biodiesel fuels of *Telfairia pedata* and *Coco nucifera* L. with automotive diesel fuel were prepared in 1000ml lots, on a volumetric basis measured by graduated measuring cylinders. The fuels were manually swirled for 10 minutes to obtain a homogenous mixture. The biodiesel and the stock fuels have different colors, therefore, the uniform color of the blended fuel was used as an indication of thorough mixing. Samples of the blends were analyzed for fuel parameters in comparison with pure biodiesel and unblended automotive diesel.

3.9.12 Water Boiling Test (WBT)

Stove performance indicators were tested by determining the quantity of water that was tuned to water vapor by a given quantity of fuel within a given duration of time, in a Standard Water Boiling Test (WBT) Version 3.0 (Bailis *et al.*, 2007). The test compared the ester fuels against kerosene fuel. A multi wick (8) kerosene stove weighing 825.5g, with fuel tank capacity of 1.25 g was used for each fuel tested shown in (Figure 3.9).

Figure 3.9; Wheel brand multi wick stove and pot

Aluminium pot (Big Wheel Brand model 62of weight 315.15 g and capacity of 3.5 liters, measuring 20 cm internal diameter and 10.5 cm depth was used for each fuel. The stove was fitted with wicks of length 20 cm, diameter 10 mm, the stove weight was determined to ±1 g using Adan AFB-4100L electronic balance. The stove tank was

filled with 504.1 g of the test fuel and the total weight of stove plus fuel determined to ±1 g, 30 minutes duration was allowed for the new wicks to draw the fuel. During high power (cold start), 1001 g of cold water was weighed and poured into the pot. The ambient air and initial water temperatures were recorded. The water was heated to boiling with a temperature changes being recorded after every minute using a Brannan mercury thermometer (Bailis *et al.,* 2007). Fire was put off after boiling and the weight of water evaporated and the mass of the fuel consumed determined. For each fuel triplicates of experiments were performed and mean values recorded.

High power (hot start) followed immediately after the first test while stove was still hot. Time taken and fuel consumed to boil 1001 g of cold water was recorded. Low power (simmering) phase followed immediately after the second test while the stove and the water in the pot were still hot. The boiled water remaining after the second phase was returned for simmering lasting for 45 minutes. The fire was controlled by varying the wick height keeping the water temperature 2-3^{o}C below the boiling point. Fire was put out after 45 minutes and water vaporized and the fuel consumed determined. This test was repeated three times for each fuel sample.

3.9.13 Calculation of the Stove Performance Indicators

Calculations were performed based on the water boiling revised calculation procedure (Bailis *et al.,* 2007).

3.9.13.1 Thermal Transfer Efficiency

This is the ratio of the work done by heating and evaporating water to the energy consumed by burning the fuel. It is calculated using Equation 15 (Bailis *et al*., 2007);

$$h_c = \frac{4.186 \times M_1 \times \Delta T \ + (2260 \times M_2}{m \times Cv} \qquad [3.14]$$

Where; hc= thermal transfer efficiency, M_1= the mass (g) of water in the pot, 4.186J/g ^{o} C= the specific heat capacity of water, change in T = change in water temperature in ºC, M_2= mass (g) of water evaporated from the pot, 2260J/g= the latent heat of evaporation of water, m= the mass in (g) of fuel consumed during test phase of the test, C_v= the calorific value of the fuel sample (J/g).

3.9.13.2 Burning Rate (R_C)

This is the measure of the rate of fuel consumption while bringing water to a boil. It was calculated by dividing the equivalent fuel consumed by the time of the test in minutes (Bailis *et al.*, 2007);

$$\mathrm{R_c} = \frac{\mathrm{m}}{\mathrm{t}} \qquad [3.15]$$

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

3.9.13.3 Specific Fuel Consumption (SC_c)

This is defined for any number of cooking tasks and should be considered “the fuel required to produce a unit output” whether the output is boiled water, cooked beans or loaves of bread (Smith, 1993);

$$SC_c = \frac{\mathrm{m}}{\mathrm{M_1}} \qquad 3.16$$

Where m=the mass (g) of fuel consumed during test phase of the test, M_1= the mass (g) of water in pot.

3.9.13.4 Fire Power (FPc)

This is the ratio of the fuel energy consumed by the stove per unit time. It gives the average power output of the stove (in watts) during the test face (Bailis *et al*., 2007);

$$\mathrm{FPc} = \frac{\mathbf{m \times Cv}}{\mathbf{60 \times t}} \qquad [3.17]$$

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

3.9.13.5 Evaporation Rate (W_c)

This is the measure of the rate of water loss through evaporation during the test (Bailis *et al* 2007);

$$W_c = \frac{M_2}{t} \qquad 3.18$$

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

3.10 Emissions

In each WBT conducted for the three samples of fuels, carbon monoxide emissions were monitored, recorded and summed up for each phase of the WBT. The test system consisted of a stove platform and an exhaust hood Figure (3.10 and 3.11) which drew gases upwards where they were detected by a probe connected to the gas emission

analyzer fitted with a non-dispersive infrared spectrometer (NDIR) system Model KANE 455 (UK).

The amount of the carbon monoxide was registered after every five minutes difference in parts per million. Total emissions were calculated using the following equation (Zhang, 2000);

$$\frac{CO_{CS} + CO_{HS}}{2} + CO_{simmering} \quad 3.19$$

Averaging the two high power phase's; cold start (CS) and hot start (HS) accounts for the fact that a stove may sometimes be used before cooling completely from previous use.

Figure 3.10 Exhaust hood and the connected probe

Figure 3.11 Non-dispersive infrared spectrometer

CHAPTER FOUR

RESULTS AND DISCUSSION

4.1 Oil Extraction

The ratio of mass of oil to the dry seed kernels extracted was used to determine the oil yields. Coconut yielded 42.0%, *T. pedata* yielded 62.48%, that is 3.52% lower than the reported 66% (FAO, 1988), as shown in the table 4.1.

Table 4.1 Oil yields and moisture content (±standard deviation)

Seed sample	Average weight of kernel (g)	Average weight of oil (g)	Average moisture (%)	Oil recovered (%)	Appearance
Telfairia pedata	491.3±2	307.5±0.5	0.5±0.1	62.48±0.5	Lime yellow
Cocos nucifera	922.38±1.0	379.0±0.3	12.4±1.1	42.0±0.2	colorless

4.2 Yields of Methyl Esters (Biodiesel) from Crude Oils

T. pedata yielded 80% while *C. nucifera* yielded 75% of methyl esters which was 18% lower than the 93% reported by (Wagutu *et al.*, 2010). The difference from 100%, yield was attributed to lose due to the saponification of the free fatty acids present in the oil (Knothe, 2005).

4.3 Analysis of Oils and Methyl Esters

4.3.1 GC-MS analysis

The percent of methyl ester composition obtained from the analysis of the biodiesel fuels and peak areas are shown in Table 4.2 alongside their literature values from other records. Representative GC peaks characteristic for coconut and *T. pedata* are shown in Figure 4.1 and 4.2 respectively. In all the samples the solvent and the derivertizing

agents used for preparing the sample were the first materials to elute from the GC. These are shown by very small low intensity peaks within the chromatogram. The sample components eluted at retention times depending on their structure (polarity) and the boiling point (Mittelbach *et al*., 1996). Larger molecules took a longer retention time in the GC. For example, from *T. pedata* methyl ester chromatogram figure 4.2, unsaturated methyl 9 (Z), 12 (Z)-octadecadienoate (C18:2) had retention time 25.031 minutes while methyl hexadecanoate (C16:0) in the same mixture eluted after 23.419 minutes. Fatty acid identities from the library search are shown in appendices III and IV.

Table 4.2; Ester composition of the biodiesel fuels

Biodiesel	Fatty acids	Fatty Acids Ester	Retention Time (min)	% composition obtained	Literature Values in (%)
T. *pedata* ME	Linoleic acid	Methyl linoleate (C18:2)	25.031	53.66	44.33
	Palmitic acid	Methyl hexadecanoate (16:0)	23.419	32.03	35.00
	Stearic acid	Methyl octadecanoate C18:0)	25.255	10.31	14.04
	Total			95.99	93.34
Coconut ME	Lauric acid	Methyl dodecanoate (C12:0)	18.917	33.17	30.02
	Myristic acid	Methyl tetradecanoate (C14:0)	21.202	16.23	16.00
	Palmitic acid	Methyl hexadecanoate (C16:0)	23.419	42.88	44.00
	Stearic acid	Methyl octadecanoate (C18:0)	25.255	6.30	3.00
	Oleic acid	Methyl 9(E)-octadecenoate (C18:1)	24.964	1.13	5.00
	Linoleic	Methyl 9(Z), 12(Z)-octadecadienoate (C18:2)	25.031	0.66	2.20
	Total			99.91	96.24

ME- Methyl Ester * (Chisholm, 1964, Munavu and Odhiambo, 1984,Okoli, 1988) Umer *et al.,* 2010.

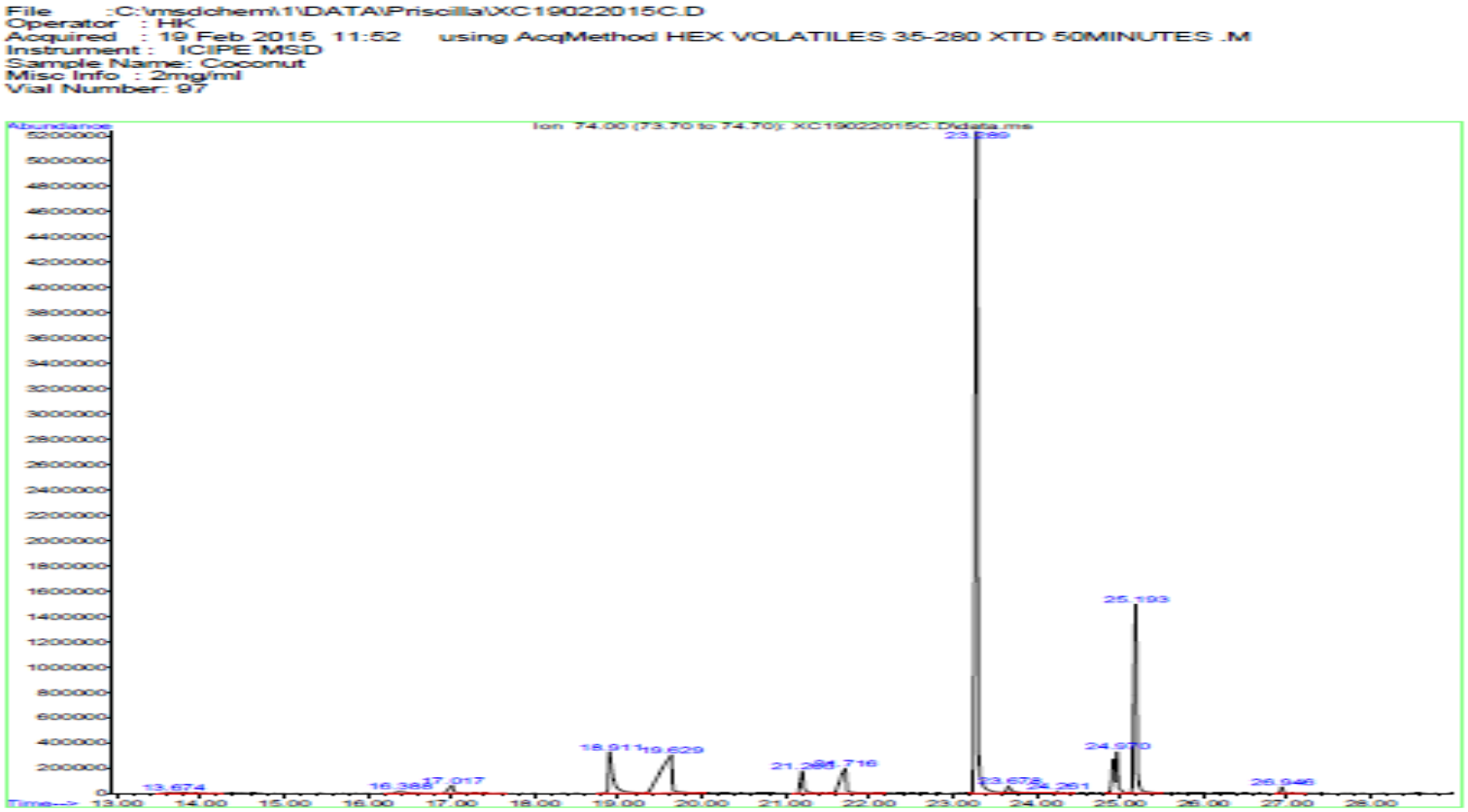


Figure 4.1 GC trace of fatty acid methyl esters derived from C. *nucifera*

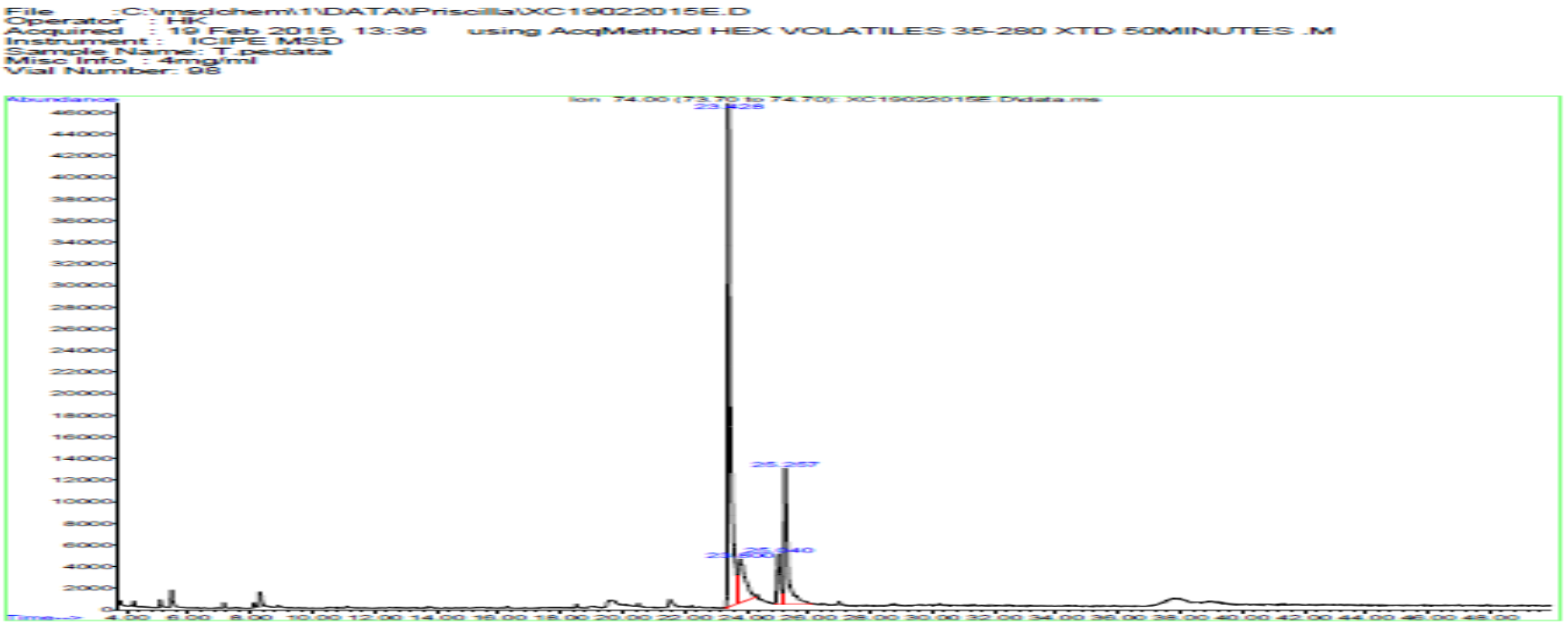


Figure 4.2 GC trace of fatty acid methyl esters derived from *T. pedata*

The main fatty acid ester identified in *T. pedata* biodiesel are methyl 9(*Z),* 12(*Z)*-octadecadienoate (C18:2), which is unsaturated component, methyl hexadecanoate (C16:0), and methyl octadecanoate (C18:0). Coconut ester also recorded six component in the mixture; the major being methyl hexadecanoate (C16:0), (42.80%) methyl dodecanoate (C12:0), (33.17%) all saturated components. Among the minor components was methyl 9(Z) 12(Z)-octadecanoate.

4.3.2 Physiochemical Properties

The oils and esters properties: iodine value, acid value, density, viscosity, saponification value, refractive index, calorific value from the two plants oils and their corresponding methyl esters are listed in the table 4.3**.**

Table 4.3; Chemical properties of the oils and their methyl esters

Sample	Density at 20^{o}C (g/cm^{3})	Viscosity 40^{o}C (mm^{2}/s)	Iodine value-wij's (mg/g)	Acid Value (mg/g)	Saponification Value (mg/g)	Calorific Value (MJ/kg)	Refractive Index at 25^{o}C
T.*Pedata* oil	0.9102±0.5	28.3±1.9	109±1	1.0±0.1	230.6±4.5	37.45±0.3	1.4654
TPME	0.875±2.5	4.22±1.9	112.3±2.0	0.5±0.1	195.3±2.3	39.25±0.5	1.4542
Coconut oil	0.9121±1.3	20.0±0.1	2.7±3.9	1.02±0.2	261.56±0.8	34.6±7.1	1.4516
CNME	0.8561±0.8	2.71±0.6	2.4±1.2	0.3±0.1	273.2±0.3	34.8±0.02	1.4312
Kerosene	0.788±0.003	2.4±0.01	-	-	-	43.6±0.7	1.4421
Auto Motive diesel	0.848	4.188±4	<20	<0.01	-	42.5±0.4	1.4712

KEY
TPME- *T. pedata* Methyl Ester
CNME- *C. nucifera* Methyl Ester

The limitation for acid value for biodiesel by ASTM standards is a maximum of 0.8 mg KOH/g. The acid value of the TPME and CNME has met the ASTM requirements as

shown in table 4.3, which is 0.5 and 0.3 mg KOH/g, respectively. The use of iodine value is rendered redundant when oxidative stability is described by indices of allylic positions and bis-allylic to double bonds are especially susceptible to oxidation. For example the bis-allylic position in linoleic acid which was identified as the unsaturated fatty acids in *T. pedata* biodiesel but not in coconut methyl ester is more prone to auto-oxidation than the allylic positions.

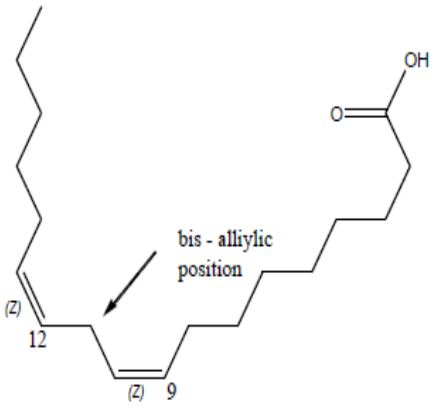


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Figure 4.3; Structure of linoleic acid

The relative rates of oxidation given in the literature are one (1) for oleates (methyl, ethyl esters), 41 for linoleates and 98 for linolenates (Lencher *et al.*, 1997). A major drawback of the iodine value is that it does not distinguish these differences. Storage conditions are factors that should be considered when defining the susceptibility of unsaturated fuels for oxidation (Leung *et al.*, 2006). Based on the experimental results in table 4.3, above the iodine values of methyl esters are almost identical to that of the parent oils. Calculated iodine value by the GC-MS chromatograms are higher than the Wij's solution method because equation 4.3 assumes full iodonization and also treats all the double bonds as being equally reactive to oxidation (Knothe, 2002). The

saponification value (SV) is an indicator of the molecular weight of the biodiesel and increases with decreasing molecular weight (Knothe, 2002). *T. pedata* oil and methyl ester indicated 230.6 and 195.3, respectively in table 4.3. This indicates lower molecular weights given their high composition of short chain fatty acid (C16), 79.59%. On transesterification, the saponification value (sv) of *T. pedata* esters decreased from that of parent oils, while that of Coconut ester increased. The increase can be explained by the fact that the process removes the heavier glycerol molecules from the oil thus reducing the average molecular weight of the resulting methyl ester. Thus the table 4.3 indicates that *T. pedata* methyl ester has the highest molecular weight than *C. nucifera* esters.

4.4 Fuel Properties

The fuel properties of the two synthesized biodiesel compared with kerosene and automotive diesel fuels are shown at table 4.4. Further comparisons were made with biodiesel from one of the most studied biodiesel feedstock: sunflower oil. All the data reported here are means of triplicate determination with an accuracy of ± 0.05.

Table 4.4; Fuel properties of methyl esters and diesel fuels

Test	Description	Automotive diesel	Kerosene	TPME	CNME
	Appearance	clear	clear	Lemon yellow	clear
D1298	Density at 20^{o}C (g/ml)	0.848	0.7884	0.8752	0.8714
	Density at 15^{o}C (g/ml)	0.8621	0.7890	0.8794	0.8682
D445	Viscosity at 40^{o}C (MJ/kg)	4.16±0.04	2.35±0.5	4.22±0.3	2.71±0.04
D93	Flash Point (^{o}C)	74±3.0	45.5±6.1	127.5±1.3	106.5±0.7
D4738	Cetane number	49.2±1.5	42.67±1.5	55.46±0.7	41.53±1.9
D130	Copper corrosion	1b	1a	1b	1b
D95	Water content (%)	<0.05	<0.05	<0.05	<0.05
D1500	Color ASTM	1.40	0.01	0.50	0.10
D86					
	IBP%	192.0±3.3	157.2±2.0	228.0±3.5	118.5±6.1
	10	239.0±2.8	170.0±1.3	319.2±2.8	245.0±2.1
	20	263.0±1.9	176.0±0.5	321.9±1.4	253.0±2.1
	30	278.5±0.4	181.5±0.8	323.0±3.9	259.1±11
	40	290.0±0.4	187±1.2	326.5±2.1	265.5±7
	50	301.0±1.8	194.0±1.6	340.5±1.6	271.0±1.8
	60	313.0±2.3	201.0±1.1	343.5±2.5	275.5±0.1
	70	326.0±9.3	209.0±0.6	364.0±4.6	279.5±0.7
	80	340.0±11.3	219.0±11	369.5±2.8	290±0.7
	90	358.0±7.1	231.0±6.9	371.5±0.7	299.5±10
	95	371.0±5.9	240.0±6.3	373.5±0.3	321.5±8.1
	FBP	385.0±4.5	261.0±1.9	375.0±0.6	335.0±1.4
	Recovery at 365^{o}C (ml)	92.0±0.6	92.25±2.5	95.0±0.2	88.95±0.6
	Total volume (ml)	98.0±0.07	99.0±0.4	97.8±0.2	99.5±1.8
	Residue (ml)	1.0	1.0	*	0.25±1.2
	Loss (ml)	1.0±0.05	1.0±0.06	0.2±0.01	0.25±0.5

1a-light orange, almost the same with the polished strip, 1b-Dark orange, TPME = *Telfairia pedata* methyl esters, CNME=Coco nucifera methyl esters, IBP- initial boiling point, FBP- Final boiling point, *Decomposed

Kinematic viscosity of biodiesel samples was determined at 40^{o}C (ASTM D445) as prescribed per the standard. The data obtained is used to determine the flow ability. The viscosity of biodiesel was found to be slightly greater than of diesel fuels but much lower than that of parent vegetable oils table 4.3. Viscosity difference of parent oil and biodiesel could thus form a basis for an analytical procedure applied to determining the conversion of vegetable oil to methyl ester (Knott, 2007).

On the basis of literature, table 4.4, the ester viscosity has a direct relationship with some chemical characteristics of the lipids, such as the degree of unsaturation, the position of the double bond and the chain length of the fatty acids that constitute the triacylglycerides from which the esters are derived (Knothe, 2005). From table.4.4, the double bond reduces the kinematic viscosity even more with increase in the number of the double bonds in the chain. This is seen with *T. pedata* methyl ester which has the higher degree of unsaturation 85.5 % of C18:2, recording viscosity slightly lower than coconut methyl ester whose degree of unsaturation is 5%.

The main factor that seemed to influence the viscosity of the investigated biodiesel fuels is the chain lengths of the constituent esters. This explains the lower kinematic viscosity for coconut methyl ester (2.71 mm^2/s) which compared closely to that of kerosene (2.35 mm^2/s), as a result from a high content 90%, of short chain (C6-C14) methyl esters. Methyl esters of *T. pedata* constitutes mostly of C16-C18 esters giving viscosity much higher than coconut at 4.22 mm^2/s which compared well to automotive fuel, 4.2 mm^2/s.

Distillation characteristics of the methyl esters (biodiesel) along with the two referenced diesel fuels (kerosene and automotive diesel) are shown in the Figure 4.4.

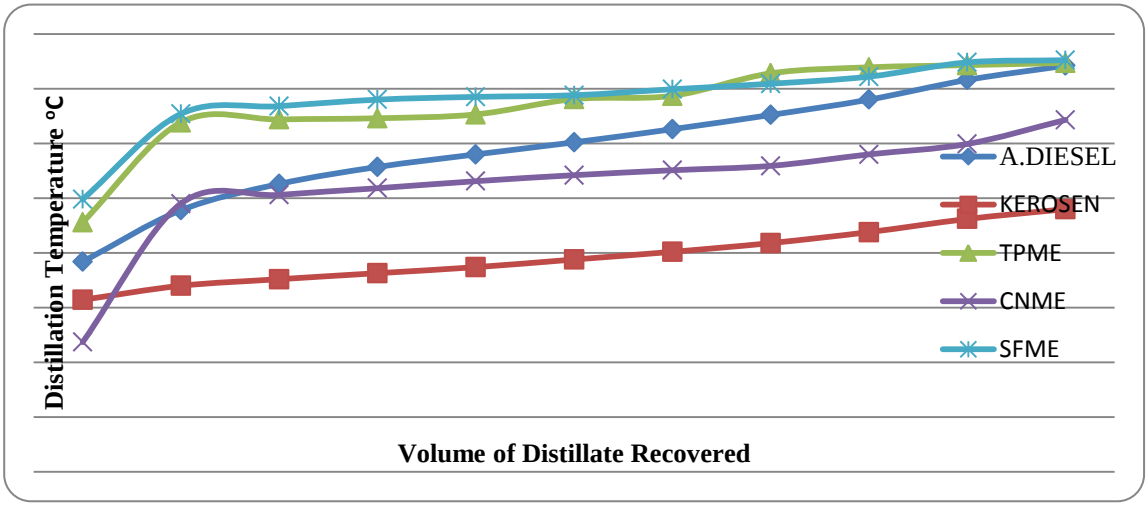

Figure 4.4; Distillation profiles for methyl esters and diesel fuels

The curves show *T. pedata* biodiesel as being less volatile than the referenced fuel (CNME) after the initial boiling point (IBP), (228.0^{o}C), (118.5^{0}C),respectively, Coconut methyl ester had the lowest IBP, this could be attributed to presence of many individual fatty esters of different chain length, C6-C18, and a wide range of boiling point in the coconut. Kerosene was the most highly volatile with a final boiling point of 261^{o}C (Wagutu *et al*., 2010).

4.5 Biodiesel Blends with Automotive Diesel Fuel

The unsaturation of the pure biodiesel (B100) may affect the fuel stability under poor storage. As seen in figure 4.2, a pure biodiesel has a narrow range of boiling points which may be caused by different weather especially winter; therefore blending of the biodiesel with diesel fuels may improve these conditions. Comparisons of fuel

properties of automotive diesel with blends of *T. pedata* and *C. nucifera* biodiesel in ranges of (5-70) % biodiesel in the mixture are shown in table 4.5 and 4.6, respectively. Blends of TPME and CNME seemed ideal for the improvement of the heating value of the fuel from 39.25 and 34.8 MJ/kg to be between 41 and 42 MJ/kg, respectively. The blends in this range also showed viscosity within the same range (4.2 mm^2/s) as pure automotive diesel between 5-20% biodiesel in the mixture; therefore *T. pedata* methyl esters is a viable fuel for motor engine and also for domestic use especially cooking.

Table 4.5; Blends of TPME with Automotive diesel (DF100)

Test	Description	DF(B0)	B5	B10	B20	B50	B70	B100
Appearance		clear	clear	clear Lemon yellow	clear Lemon yellow	Lemon Yellow	Lemon yellow	Lemon yellow
Iodine value (Wijs)		<20	15.5±0.9	21.3±0.4	37.5±1.5	56±2.1	73±1.0	112.3±1.3
Calorific value (MJ/kg)		43.5±0.4	42.5±0.3	41.8±0.2	41.6±4.5	41.6±3.4	40.2±0.6	39.3±2.8
Acid value (mg/g)		<0.01	0.05	0.07	0.09	0.5	0.8	1.0
Refractive index (oC)		1.4719	1.4682	1.4678	1.4655	1.4602	1.4514	1.4542
D93	Flash point (C)	73.5±3.0	74.0±0.4	80.5±2.9	85.2±3.0	89.5±4.5	104.1±6.1	127.5±1.3
D1298	Density at 20 ^{o}C (g/ml)	0.8480	0.8490	0.8510	0.8510	0.8689	0.8718	0.8752
	Density at 15^{o}C (g/ml)	0.8621	0.8575	0.8578	0.8587	0.8693	0.8828	0.8843
D445	Viscosity at 40^{o}C (mm2/s)	4.188±4.0	4.188±3.2	4.189±3.1	4.190±5.0	4.191±2	4.192±0.5	4.22±1.9
D95	Water content (%)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05±0.2
D130	Copper corrosion	1b	1b	1b	1b	1b	1b	1b
D4738	Cetane Number	49.2±0.6	51.2±1.2	52.3±0.2	53.2±1.7	53.3±3.0	53.7±0.4	54.3±1.5
D86	% volume recovered		Distillation (^{o}C)					
	IBP	193.0±2.3	191.0±2.2	187.5±2.5	185.0±4.5	162.0±5.5	148.5±3.2	116.0±6.7
	10%	240.0±2.5	242.0±1.4	244.0±1.4	262.0±3.0	289.0±1.9	297.0±1.6	319.0±0.6

Table 4.5 continues to page 74

Table 4.5 continues from page 73

			)±1.9	265.5±3.5	267.0±1.9	269.0±3.1	312.0±4.9	321.0±0.6
	30%	280.5±0.3	281.5±0.3	291.0±1.5	292.0±1.9	300.0±1.1	311.0±4.8	323.0±0.6
Test	**Description**	**DF(B0)**	**B5**	**B10**	**B20**	**B50**	**B70**	**B100**
	40%	290.0±0.5	292.0±2.1	294.0±2.1	297.5±3.1	310±0.5	320.0±8.1	326.0±1.9
	50%	300.0±1.6	302.0±1.8	304.0±2.1	309.0±1.4	333.5±3.2	334.0±5.3	340.0±3.0
	60%	312.0±2.2	314.5±2.1	316.0±1.5	322.0±4.5	336.51±1.8	340.0±4.5	362.5±7.5
	70%	325.0±9.1	327.0±1.4	329.0±1.4	335.0±1.1	346.0±1.4	348.0±1.3	364.0±0.5
	80%	340.0±11.2	343.5±4.9	347.5±0.4	350.0±0.8	354.0±4.6	355.0±1.5	365.5±10
	90%	357.0±7.0	359.0±3.2	360.0±0.1	360.5±1.4	360.5±2.8	365.0±1.4	370.0±0.9
	95%	370.0±4.6	371.5±5.3	371.5±4.0	372.0±0.5	372.5±3.1	372.0±1.7	373.0±5.4
	FBP	386.0±5.8	385.0±4	380.0±6.7	378.0±2.8	376.5±3.7	374.0±5.2	375.5±1.5
	Recovery at 365^{o}C(ml)	92.0±0.5	93.0±0.1	93.0±0.1	93.0±0.5	93.0±0.5	95.0±0.2	95.5±0.2
	Total volume (ml)	98.0±0.7	99.0±0.1	99.0±0.1	98.0±0.2	98.0±0.2	98.0±0.5	98.5±0.4
	Residue (ml)	1.0	0.5	0.5	1.0	1.0	1.0	0.5
	Loss (ml)	1.0	0.5	0.5	1.0	1.0	1.0	0.5

Table 4.6 Blends of CNME with automotive diesel (DF100)

Test	Description	DF(B0)	B5	B10	B20	B50	B70	B100
Appearance		clear	clear	clear	clear	clear	Clear	clear
Iodine value (Wij,s)		<20.0	0.942±0.5	1.06±1.5	1.33±0.5	1.503±1.5	1.82±0.4	2.4±1.2
Acid value (mg/g)	<0.01	0.02	0.031	0.052	0.112	0.18	0.3±0.1	
Calorific value (MJ/kg)	42.5±0.4	42.3±1.6	41.1±0.2	39.5±1.4	37.0±0.5	36.5±0.5	34.8±0.02	
Refractive Index (^{o}C)		1.4719	1.4671	1.4582	1.4492	1.4403	1.4383	1.4309
D93	Flash point ^{o}C	74±3.0	79±0.4	83.0±1.1	87.5±0.7	92.5±1.5	101.0±1.2	106.5±0.7
D1298	Density (20 ^{o}C)	0.848	0.8496	0.8502	0.853	0.8696	0.8701	0.8714
	Density (15 ^{o}C)	0.8621	0.8512	0.8593	0.8599	0.8602	0.867	0.8682
D445	Viscosity (40 ^{o}C)	4.16±0.04	4.157±0.3	3.91±0.5	3.8±1.3	3.25±2.0	2.95±0.4	2.71±0.6
D95	Water content (%)	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
D130	Copper corrosion	1b	1b	1b	1b	1b	1b	1b
D4738	Cetane Number	49.2±0.6	48.0±0.5	46.5±1.3	44.57±4.9	43.0±0.5	42.5±3.2	41.53±1.2
D86	Distillation (^{o}C)							

Table 4.6 continues to page 76

Table 4.6 continues from page 77

	IBP	192.0±3.3	191.5±1.1	187.0±1.4	185.0±3.5	162.0±3.8	148.0±3.8	118.5±6
Test	**% volume recovered**	**DF(B0)**	**B5**	**B10**	**B20**	**B50**	**B70**	**B100**
	10	239.0±2.8	240.0±1.8	240.5±1.5	241.5±7	242.5±1.7	243.5±3.2	245.593.9
	20	263.0±1.9	262.0±1.8	263.0±4.0	260.0±1.2	258.0±0.5	256.0±2.3	254.0±2.1
	30	278.5±0.4	277.7±1.5	276.0±5.2	275.5±0.5	273.0±3.9	272.5±1.2	260.5±12
	40	290.0±0.4	289.0±2.8	286.0±2.4	284.5±3.5	275.0±0.5	268.5±4.9	266.5±11
	50	301.0±1.8	300.0±7.1	298±4.9	290.0±2.1	282.0±2.9	277.0±2.0	271.0±1.8
	60	313.0±2.3	312.0±11	310.0±2.8	308.0±0.7	290.0±14	280.5±3.4	275.5±0.1
	70	326.0±9.3	325.0±1.3	323.5±10	319.0±1.1	302.0±3.9	295.5±2.0	280.5±0.7
	80	340.0±11.3	339.0±13	337.0±7.9	328.5±1.2	299.5±2.1	291.0±5.0	290.5±10
	90	358.0±7.1	356.0±0.7	353.0±2.8	349.0±1.3	320.0±2.2	305.0±1.6	299.5±8.1
	95	371.0±5.9	367±1.4	369.5±3.1	362.0±1.4	354.0±4.7	325.5±1.8	321.0±8.4
	FBP	385.0±4.5	380.5±1.1	375.0±1.7	370.5±1.5	359.5±5.5	330.093.9	335.0±1.4
	Recovery at 365 ^{0}C (ml)	92.0±0.5	93.0±0.2	94.0±0.5	93.0±0.8	95.0±0.3	96.0±0.5	95.5
	Total volume (ml)	98.0±0.2	98.0±0.2	98.0±0.2	98.0±0.5	98.0±0.1	98.0±0.5	98.5±0.5
	Residue (ml)	1.0	0.5	1.0	0.5	1.0	1.0	1.5
	Loss (ml)	1.0	1.5	1.0	1.5	1.0	1.0	0.5

4.6 Water Boiling Tests (WBT)

Water Boiling Test was conducted according to (Zhang, 1998) to demonstrate suitability of the methyl esters as alternative or supplementary fuel to kerosene in domestic cooking applications. All the biodiesel fuels were tested in a Chinese common capillary – fed wick stove. The fuels burnt with a transparent blue flame producing a characteristic sweet smell for methyl esters with some faint grey- white carbon matter deposited at the bottom of the cooking pot. Kerosene on the other hand produced a strong smell and a thicker deeper grey carbon matter was deposited at the bottom of the cooking pot. The mean values of parameters obtained at the end of three phases are presented in tables 4.7 and 4.8, respectively.

4.6.1 Phase 1 – High Power (Cold Start)

Stove performances were affected by various fuel properties. Fuel is drawn up through the wick fibers to the combustion chamber by capillarity. Viscosity of the fuel affected the fuels availability to the chamber. Coconut methyl ester had very close properties to kerosene; viscosity (2.7 and 2.4 mm^2/s respectively) table 4.3, time to boil, of the CNME and kerosene (18.5 and 12 minutes respectively) and the rates of burning (2.3 and 2.1 respectively). TPME had a viscosity of $4.22mm^2/s$ and took a longer time 26.5 minutes to boil 1000 g of water table 4.7.The fuels heating value and viscosity also affected the specific fuel consumption and firepower. Short time to boil and less fuel consumption were attributed by low viscosity and high energy content for kerosene fuel. The thermal transfer efficiency for kerosene and CNME was found to be closer 50% and 48 %. Kerosene fuel took the least time to boil the water 12 minutes,

consuming more than 50% less than the mass of the fuel TPME consumed to bring the equal volume of water to boil. This gave the fuel the highest power output (1.406kW) followed by CNME (1.356kW) and TPME had the least with (1.139 kW).

Table 4.7; Mean stove performance indicators high power (cold start) phase

High power (cold Start)	**Units**	***T.pedata* ME**	**Coconut ME**	**Kerosene**
Time to boil	Min	26.5±0.5	18.5±0.6	12.0±0.1
Fuel consumed	G	53.1±0.5	43.01±0.6	26.23±0.5
Burning rate	g/min	2.0±1.0	2.3±1.3	2.1±0.5
Thermal transfer efficiency	%	45±1.0	48±0.6	50±0.6
Specific fuel consumption	g/L	53.0±0.5	43.0±0.5	26.2±0.5
Evaporation rate	g/min	5.36±0.17	5.86±0.03	7.11±0.18
Fire power	Watts	1139±13	1356±7	1406±10

4.6.2 Phase 2-High Power Hot Start

Slightly lesser time (2-3 minutes) was required to boil water in high power hot start phase table 4.8, than in cold start for the T. *pedata* ME, coconut ME, and Kerosene. This gave a small increase in the power output (4-6%) during this phase. This would be explained by the fact that the fuel in the stove tank would be in a slightly higher temperature than room temperature. This increases the flash point and decreases the viscosity, thus increasing the fuel mobility by capillarity and increasing the ease of burning. Heat transfer efficiency remained more or less the same as cold start. Possibly because the metallic stove body conducts heat fast such that within five minutes the body would be at room temperature. Burning rate remained relatively the same as in phase 1.

Table 4.8; Mean stove performance indicators high power (hot start) phase

High power (Hot start)	Units	*T. pedata* ME	Coconut ME	Kerosene
Time to boil	min	22.5±0.6	16.5±0.6	10.0±0.6
Fuel consumption	g	44.52±0.4	38.52±0.2	23.14±0.4
Burning time	g/min	1.98±1.2	2.3±1.2	2.3±1.2
Thermal transfer efficiency	%	45%±0.3	47%±0.6	53%±0.6
Specific fuel consumption	g/L	44.5±1.0	38.5±0.9	23.1±0.6
Evaporation	g/min	6.2±0.1	6.3±0.19	6.9±0.23
Firepower	Watts	1229±14	1362±8	1682±12

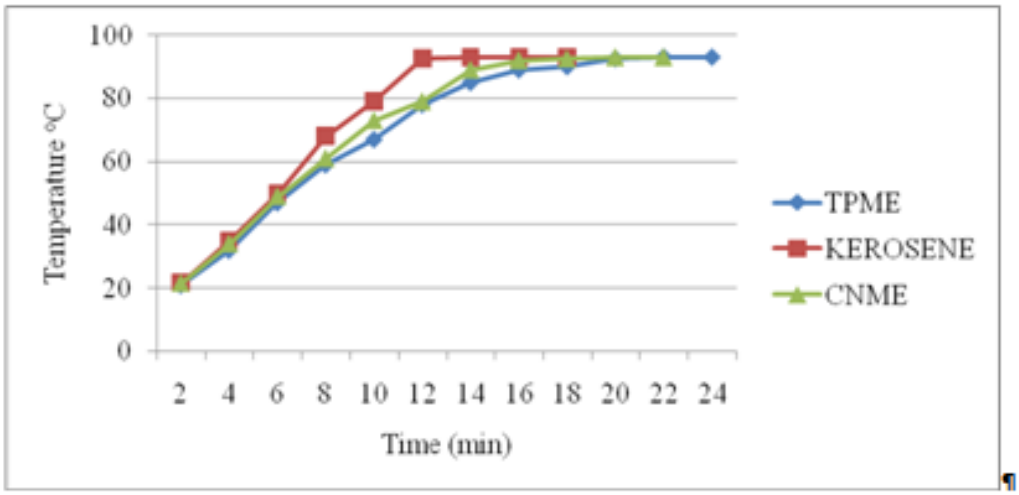

Figure 4.7; Water boiling during high power hot start

4.6.3 Phase 3- Low Power Hot Start

This phase was intended to maintain water at a high temperature with minimal power output from the stove and the boiling temperature was (3-4^{o}C) below the boiling point. The fire power was ranged between (1205-1299W), which shows a closer relationship table 4.9.The thermal efficiency for the fuels remained relatively the same (40-43%). The rate of burning remained within the same range for all the fuels (1.7 – 2.2 g/min).

Specific consumption during this phase seemed to be only a factor of calorific value of the fuel. Thus kerosene consumed the least mass of fuel 80.3 g to maintain the water for 45 minutes while TPME with the lowest heating value consumed 111.8 g mass of fuel to simmer. Thus Kerosene seems to be the best of the three fuels in terms of time taking and fuel consumption.

Table 4.9; Mean stove performance indicators low power (simmering) phase

Low power (hot start)	Units	Coconut ME	*T. pedata* ME	Kerosene
Time to boil	Min	45	45	45
Fuel consumed	g	89.6±0.2	100.2±0.2	74.7±0.2
Burning time	g/min	1.9	2.2	1.7
Thermal transfer efficiency	%	40±1.0	42±2.9	43±0.9
Specific fuel consumption	g/L	103.1±1.4	111.8±2.0	80.3±1.2
Evaporation rate	g/min	11.6±0.16	10.9±0.2	11.5±0.03
Firepower	Watts	1235±7.4	1299±6.8	1205±2.6

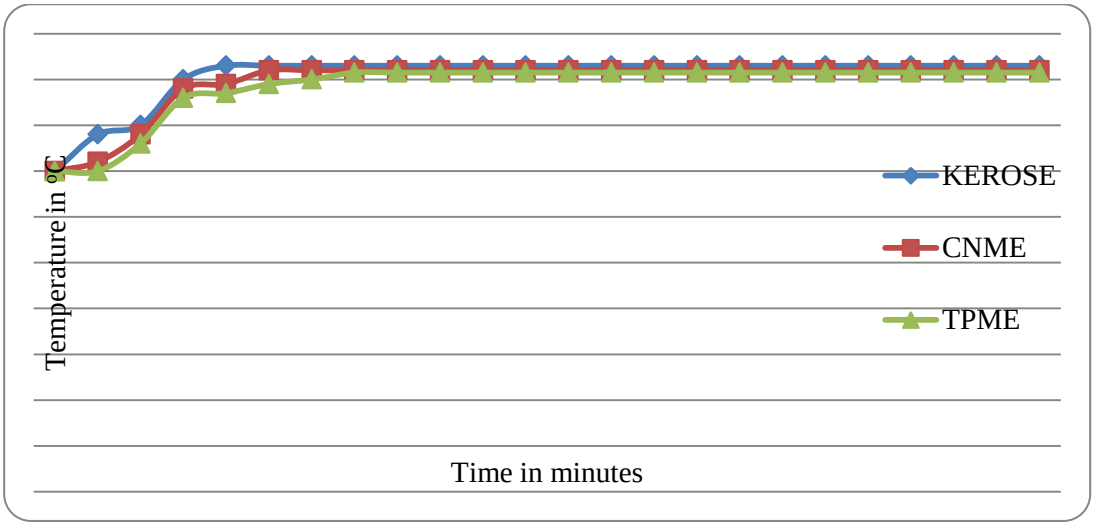

Figure 4.8; Water boiling during simmering

Figure 4.7and 4.8 represents water temperature profiles for boiling and simmering performance tests, respectively. In both phases the change in water temperature with

time seemed constant for each of the three fuels. However, CNME was found to be closer to kerosene than TPME.

4.7 Biodiesel Blends with Kerosene Fuel

The high unsaturation of the pure biodiesel (B100) may affect the capillary action of the fuel in the stove tank during cooking and therefore the time to boil increases as well as the fuel consumed as shown in table 4.8, therefore blending the biodiesel with the kerosene may improve this condition. Comparisons of fuel properties of kerosene with blends of B20, B50 and B70 TPME biodiesel are shown in the table 4.10**.**

Table 4.10; Blends of TPME with kerosene (KF 100)

TEST	**Description**	**B0**	**B20**	**B50**	**B70**	**B100**
Appearance		clear	Clear	Clear lemon yellow	Lemon yellow	Lemon yellow
D1298	Density at 20^0C (g/ml)	0.788	0.7995	0.8318	0.8687	0.8752
	Density at 15^0C (g/ml)	0.798	0.8025	0.8325	0.8502	0.8794
D445	Viscosity at 40^0C (mm^2/s)	2.35±0.5	3.12±1.2	3.67±0.4	3.86±1.4	4.22±1.2
D93	Flash point (^{0}C)	45.5±6.1	73.0±0.1	97.5±5.1	100.3±1.1	127.5±0.2
D95	Water content (%)	<0.05	<0.05	<0.05	<0.05	<0.05
D1322	Smoke point (mm)	30±0.5	29.2±0.3	28.9±0.5	28.6±0.2	28.5±0.2
D86	% volume of distillate		Distillation ^{o}C			
	IBP	157.2±3.0	155.5±1.1	192.6±1.2	196.5±2.1	228.0±2.5
Table 4.10 continues to page 81		1.	172.0±1.2	244.6±0.5	260.5±1.8	319.2±1.3

Table 4.10 continues from page 80

	20%	176.0±1.1	177.5±2.3	248.9±0.6	285.4±0.6	321.9±8.2
	30%	181.5±0.4	183.0±0.8	252.3±1.3	287.6±1.7	323.0±1.5
	40%	187.7±1.5	185.5±2.3	257.1±2.3	291.8±0.6	326.5±1.5
	50%	194.0±0.3	192.0±0.9	267.3±08	303.9±0.2	340.0±4.5
	60%	201.0±0.1	203.5±0.4	272.3±0.7	307.0±1.3	343.5±2.3
	70%	209.0±6.5	213.5±0.6	286.5±4.1	325.2±1.2	364.2±2.5
	80%	219.0±1.7	225.0±0.9	294.3±6.1	331.9±2.5	369.5±0.3
	90%	231.0±3.4	240±4.5	301.3±4.1	336.8±2.6	371.5±3.1
	95%	240.0±0.6	252.0±0.5	306.8±1.5	340.0±2.0	373.2±3.2
	FBP	261.5±1.2	270.5±0.7	318.4±0.8	346.0±0.5	375.9±3.4
	Recovered 365	99.0±0.4	98.5±2.7	98.0±5.5	98.5±3.8	97.8±4.2
	Residue	1.0±1.0	0.5±0.1	0.5±1.0	0.5±1.0	1.0±0.5
	Loss	1.0±0.01	1.0±0.01	0.15±0.1	0.2±0.1	0.2±0.01

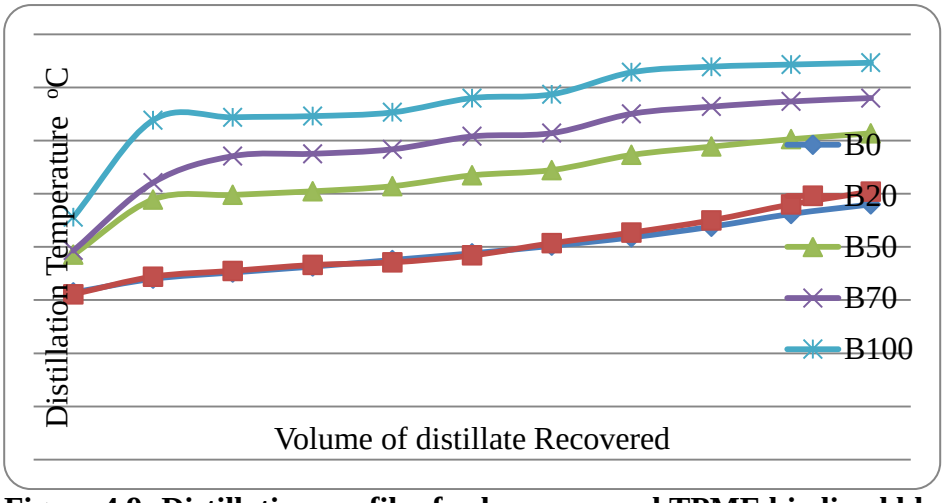

Figure 4.9; Distillation profiles for kerosene and TPME biodiesel blends

Figure 4.9 the curves show that B0 and B20 overlaps meaning that the fuels are very volatile as compared to other blends after the initial boiling point (IBP). B100 was the

least volatile, the higher the volume of kerosene in the blend, the higher the volatility and the lower the final boiling point (FBP).

4.7.1 Water Boiling Tests for Blends of TPME with Kerosene Fuel

Blends of TPME at the volumes of, B20, B50 and B70 were tested to investigate the CO emission compared to pure biodiesel (B100) and pure kerosene (B0).

Table 4.11; Mean stove performance indicators high power (cold start) phase

High power test (cold start)	units	B0	B20	B50	B70	B100
Time to boil	min	12.0±1.3	16.5±0.1	18.3±0.6	22.5±0.5	26.5±0.5
Fuel consumed	g/m	26.3±0.6	40.5±2.5	43.3±0.5	48.5±1.5	53.2±0.3
Specific fuel consumption	g/liter	2.1±1.6	2.45±3.4	2.38±1.6	2.2±0.8	2.02±2.3
Thermal efficiency	%	50±0.5	49.5±2.5	48±1.5	46.5±2.1	45±0.5
Evaporation rate	g/m	7.11±6.8	6.25±0.3	5.78±5.0	5.56±1.1	5.35±1.3
Firepower	watts	1406±10	1390±5.8	1365±6.5	1263±7.8	1136±7.4

The viscosity of the fuels was improved by adding respective volumes of kerosene, from table 4.11 the time to boil reduced with the increased kerosene percentage. The low viscosity and high energy content for kerosene blend biodiesel resulted in less fuel consumption and a short time to boil. Viscosity of the biodiesel can be reduced by kerosene because its diluency (Signh *et al*., 2010).

Table 4.12; Mean stove performance indicators, high power (hot start) phase

High power test (Hot start)	Units	B0	B20	B50	B70	B100
Time to boil	min	10.0±1.2	14.5±0.5	16.0±0.5	19.5±1.7	22.3±1.5
Fuel consumed	g	23.14±1.6	35.5±3.7	38.54±4.1	41.53±0.5	44.5±1.5
Burning rate	g/m	2.3±3.4	2.4±0.5	2.3±2.6	2.1±3.1	1.98±0.4
Thermal transfer efficiency	%	53±0.6	48±4.5	47±1.5	46±6.0	45±2.4
Specific fuel consumption	g/liter	23.1±4.1	26.5±0.5	38.5±6.1	41.5±1.0	44.5±3.6
Evaporation rate	g/m	6.9±3.1	6.8±2.0	6.3±1.5	6.25±0.8	6.2±0.7
Firepower	watts	1233±9.7	1230±10	1226±3.8	1231±6	1229±12

Slightly lesser time was required to boil the water as can be seen in table 4.12 as compared to table 4.11. As mentioned earlier in table 4.9, at this phase the fuel in the stove tank was in a slightly higher temperature than room temperature and therefore the flash point was increased and the viscosity lowered, thus increasing the ease of burning due to the increased fuel mobility by capillary action.

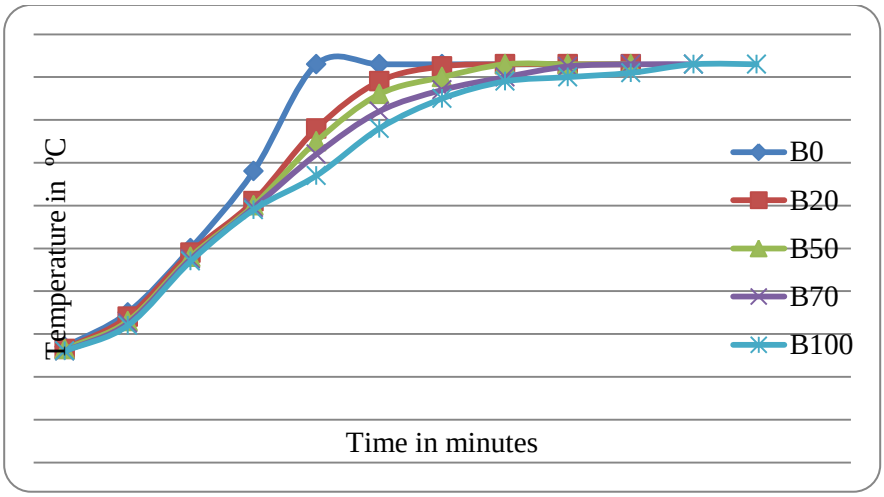

Figure 4.10; Water Boiling During Hot Start Phase for Kerosene

Table 4.1; Mean stove performance indicators low power (hot start) phase

Low power test (hot start)	Units	B0	B20	B50	B70	B100
Time to boil	min	45	45	45	45	45
Fuel consumed	g	74.7±0.6	85.0±3.5	89.5±2.9	94.75±1.9	100.5±1.2
Burning rate	g/m	1.7±0.2	1.9±0.5	1.9±1.8	2.05±2.9	2.2±1.5
Thermal efficiency	%	43±2.8	42±3.1	41.5±2.5	41±1.9	40±2.4
Specific fuel consumption	g/liter	80.3±1.1	92.3±0.7	102.5±0.2	106.5±0.5	110.5±0.2
Evaporation rate	g/m	11.5±0.2	11.5±1.4	11.6±1.8	11.25±1.6	10.9±11.2
Firepower	watts	1205±8.1	1215±6.9	1239±10	1256±9.1	1270±11

The power is required to keep the water at simmering (3-4 ^{0}C) below the boiling temperature as the parameters tend to improve with the addition of higher volumes of kerosene.

4.8 Emission Results

Stove emission tests was conducted to demonstrate suitability of the methyl esters (biodiesel) for safe domestic cooking in Kenya (Zhang, 2000). In each WBT conducted for the three samples of fuels, carbon monoxide emissions measured via gas emission analyzer model KANE 455/010E (U K.

Kerosene fuel grade 1-K contains 0.04% sulfur by weight; it was used for this experiment as a control (ASTM, 2000a).The monitoring system consisted of a stove platform and an exhaust hood which drew gases upwards where they were detected by a probe connected to the gas emission analyzer, fitted with a non-dispersive infrared

spectrometer (NDIR) system (Zhang, 2000) as shown Fig 3.11. The mean values in grams per minute were presented in table 4.14.

Table 4.14; Carbon monoxide emissions across the three phases for the three fuel samples

FUEL	cold start(g/min)	hot start(g/min)	simmer(g/min)
Kerosene	0.0860±0.02	0.0824±0.02	0.0783±0.02
TPME	0.0393±0.01	0.0381±0.01	0.0362±0.01
CNME	0.0442±0.01	0.0398±0.01	0.0376±0.01

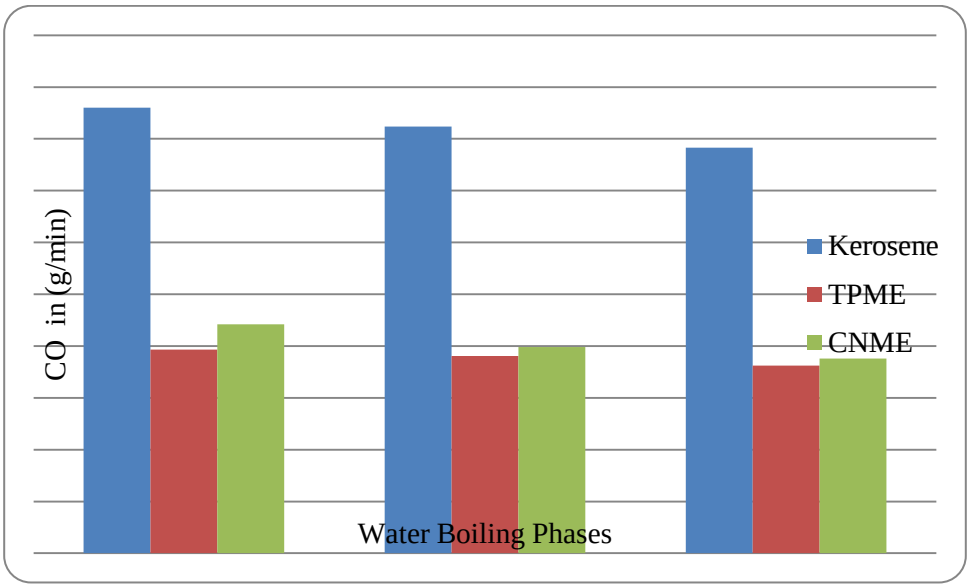

Figure 4.12; CO emission profile- all phases; cold, hot and simmering

Kerosene had the highest CO emission while TPME emitted the least amount in all the phases as shown above in the above graphs. However, the difference in emission for TPME and CNME was minimal; where in cold start, hot start and simmering the differences were 0.0049, 0.0017 and 0.0014 g/min respectively. Carbon monoxide was formed when the fuel and the air are not completely burned.

Considering the fact that a stove may sometimes be used before cooling completely from previous use, averaging the two phases; hot and cold power phases were done and recorded in the table 4.15.

Table 4.15; Total CO emissions for simmering phase and overall phases

FUEL	Total CO emitted in Simmering (g/min)	Average Total CO emitted for all phases (g/min)
Kerosene	0.0783±0.02	0.0822±0.03
TPME	0.0376±0.01	0.0378±0.02
CNME	0.0362±0.02	0.045±0.02

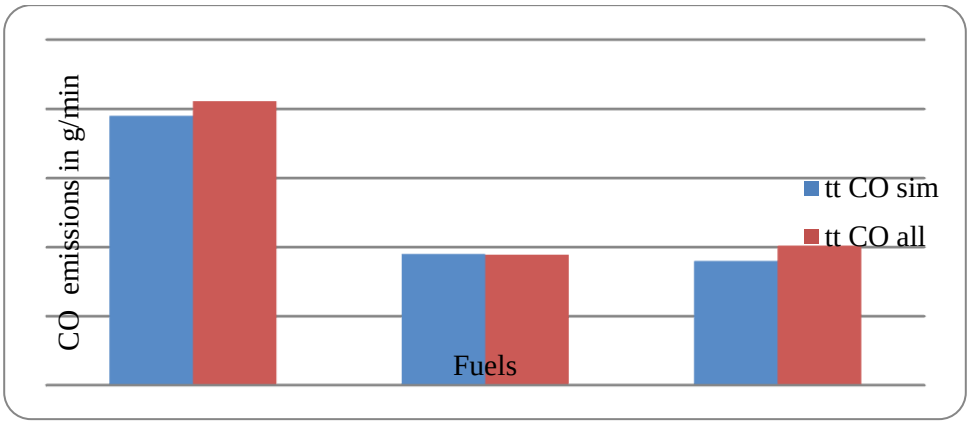

Figure 4.13; Average carbon monoxide emitted during simmering and all phases

KEY
tt CO sim= Total CO for simmering phase
tt CO all= Average total CO for all water boiling tests phases

All the fuels registered CO emissions as could be observed on the grey matter deposited at the bottom of the cooking pot. Kerosene fuel recorded the highest emission 54% difference. Total CO emissions for TPME and CNME for the simmer phase and over the entire WBT were not significantly different as can be seen on the tables 4.14 and figure 4.13; 0.0014 g/min difference for total CO emitted on simmer phase and 0.0047

g/min for total CO emitted in all phases. Still on the same tables, the CO emissions increased with increased burning rate. The total CO emitted over all phases was highest for kerosene, CNME and TPME was the lowest. This can be accounted by the other hydrocarbons present in the kerosene (Owino, 2004) and the soapy matter formed in the biodiesels (Meher *et al.,* 2006). However, all the fuels attained the World Health Organization standards for unvented stoves, heaters and fuel-based lamps of carbon monoxide emission of no more than 0.16g/min (WHO, 2010).

4.8.1; Emissions for the Kerosene and TPME Blends

Emission tests (Zhang, 2000) was conducted to demonstrate suitability of the kerosene-biodiesel blends as a safe fuel for domestic cooking and in reduction of CO emission thus global warming. In each WBT conducted for the three blends carbon monoxide emissions in grams /minute were monitored, recorded and summed up for each phase of WBT in table 4.16.

Table 4.16; CO emissions across the three phases for the three blends

Fuel blends	Cold start (g/min)	Hot start (g/min)	Simmer (g/min)
B0	0.0872±0.02	0.0835±0.02	0.0793±0.01
B20	0.0754±0.01	0.0725±0.03	0.0688±0.02
B50	0.0637±0.03	0.0615±0.02	0.0583±0.01
B70	0.0518±0.01	0.0505±0.01	0.0478±0.01
B100	0.0401±0.01	0.0395±0.02	0.0373±0.02

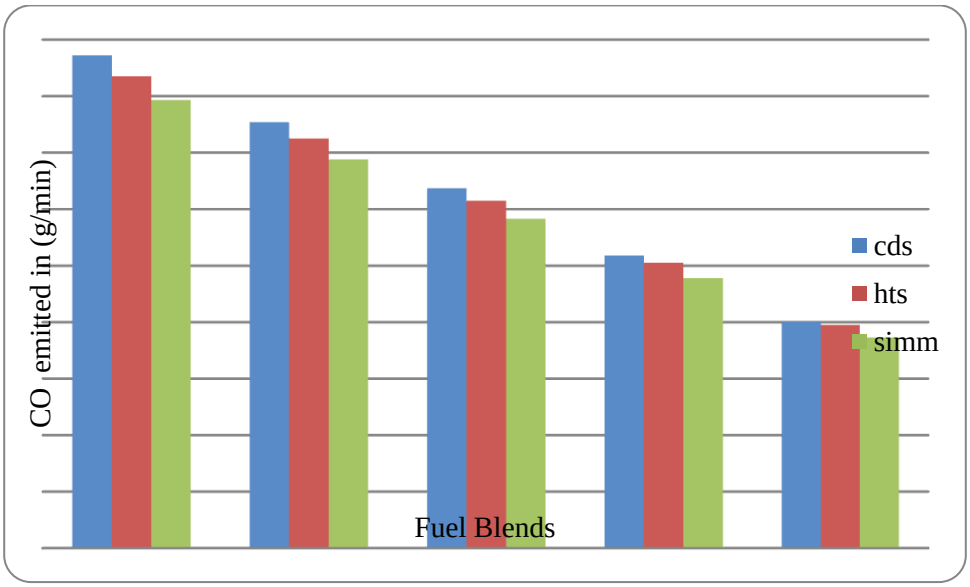

Figure 4.14; CO emission profile- all phases; cold, hot and simmering

KEY
cds= High power cold start phase
hts= High power hot start phase
simm= simmering phase

Carbon monoxide levels decreased with increased percentage biodiesel blends in all the phases.B0 (pure kerosene) has the highest emission in hot start; 0.0835g/min while B100 (pure T. *pedata* biodiesel fuel) has 0 .0395g/min, this was 53% less. In all the phases the trend is the same as illustrated in table 4.16 and figure 4.14. Considering the fact that a stove may sometimes be used before cooling completely from previous use, averaging the two phases; hot and cold power phases were done and recorded in the table 4.17**.**

Table 4.17; Mean CO Emission for simmering phase and overall phases(cold, hot and simmering)

Fuel blends	Mean CO-simmer phase (g/min)	Mean CO-All phases (g/min)
B0	0.0793±0.02	0.0833±0.01
B20	0.0678±0.01	0.0722±0.02
B50	0.0573±0.01	0.0694±0.02
B70	0.0468±0.01	0.0500±0.01
B100	0.0373±0.01	0.03896±0.01

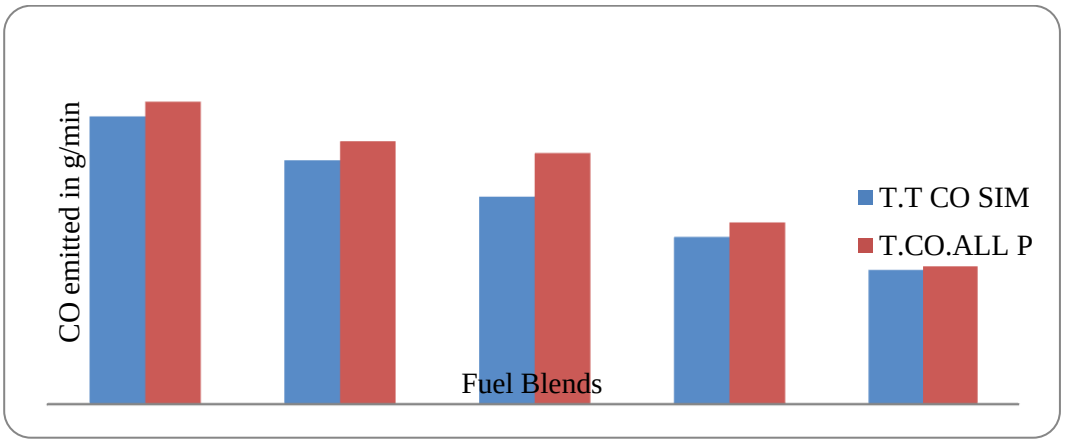

Figure 4.15; CO emission profile during simmering as average for all the phases (High Power cold, hot and simmering)

KEY
T.T CO SIM = Total CO emitted in simmering phase
T.CO. ALL P = CO emitted in all phases

Total CO emitted in all the three phases was summed up and the average emissions obtained as illustrated in table 4.17. B100 had the least emission; 0.0771 g/min, while B0 registered the highest amount 0.1607 g/min. However, all the emissions from the blends were within the WHO standards for unvented cooking appliances.

4.9 Preparation of T. *pedata*, C. *nucifera* Soaps

The experimental yields of the *T. pedata* oil soap was 582.5 g, *C. nucifera* oil soap was 597.37 g and *C. nucifera* oil/ *T. pedata* oil blend soap was 592.5g as shown on table 4.18, and the samples shown in figure 4.16..

Table 4.18; Types of soap prepared

Types of soap	Amounts in grams (g)
T. pedata	582.50
C. nucifera	597.35
T. pedata/C.nucifera blend	592.50

Figure 4.16 Coconut soap *T. pedata* soap Coconut/*T. pedata* soap

Coconut oil soap had the largest weight, 33.70% this was attributed by the higher short chain hydrocarbons present in Coconut oil therefore retains more water and increases yields (Browning, 2003) compared to *T. pedata* oil which weighed 32.86%. *T. pedata* oil/Coconut oil blend soap, 33.42% was also heavier than *T. pedata* oil soap. The soaps were creamy in color though no colorant was added. The color of the soaps was derived from the *T. pedata* oil and Coconut color itself. The blend soap felt harder compared to

the *T. pedata* soap and the pure coconut oil soap was hardest which was attributed to the low iodine value registered by the Coconut oil (Robertson, 2002). Vegetable oil with unsaturated carbon chains produces soft soaps (Norton, 2004), thus *T. pedata* soap felt softer.

Table 4.19; Chemical properties of Soap

Test parameters	**Test Methods**	***T. pedata* Oil Soap**	**Coconut Oil Soap**	***T. pedata*/ Coconut oil Blend Soap**	**House Reference Material**	**Limits**
Total Fatty Matter (TFM) in (%)	TES/04/TM/09	80.6±0.5	78.1±0.15	81.06±0.1	82.98±0.4	70% minimum.85 % maximum
Free Caustic Alkali (FCA)in (g)	TES/04/TM/08	-	-	-	0.009±0.1	Maximum 0.0429 g
Matter Insoluble in Ethanol (MIE) in (g)	TES/04/TM/04	0.042±0.2	0.044±0.1	0.043±0.1	0.037±0.1	0.03 g Minimum-0.5 g Maximum
Lathering in (cm^3)	TES/04/TM/05	625±5	640±5	630±5	650±5	150cm^3Minimum-700cm^3Maximum

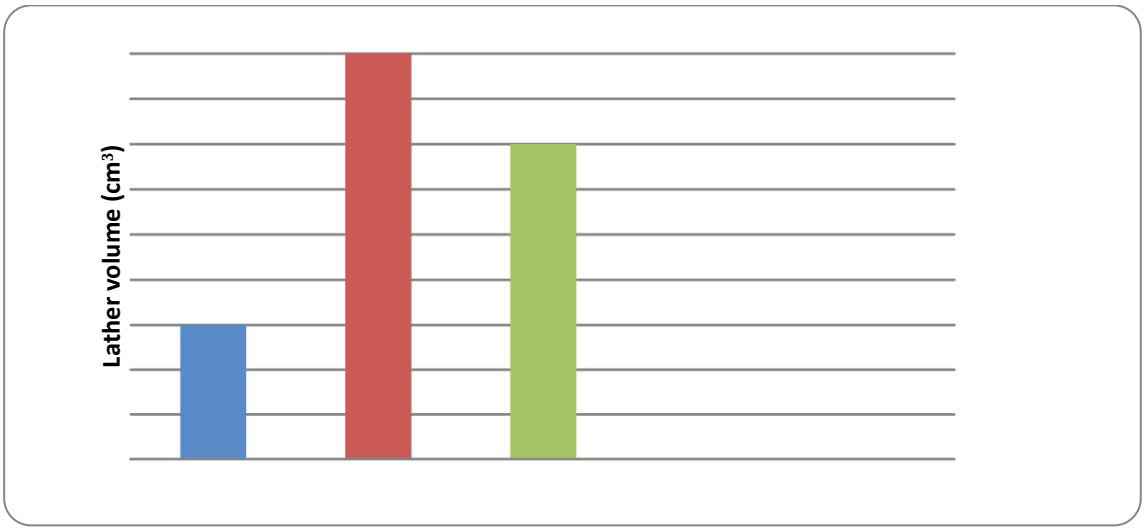

Figure 4.17; Lather profile for all soaps

KEY: TP OIL- *T. pedata* oil soap, CC OIL-Coconut oil soap, Blend- *T. pedata*/ Coconut oil soap

Total Fatty Matter (TFM) of all the soaps were less than the KEBS standard but within the range. Coconut oil has a higher saponification value and a smaller iodine value of which both properties play a significant role in the quality of the soap (Robertson, 2002, Browning, 2003). Soap with more than 0.0429% free caustic alkali as sodium hydroxide would irritate and burn the skin of the users and clothes wear out (Childers, 2000) Unconverted lye increases alkalinity and cause skin burning (Browning, 2003). However all the soaps were free of caustic alkali indicating satisfactory comparable effects. Coconut based soaps registered higher lather volume compared with the other soaps. This soap is very soluble and will lather easily even in sea water (Charlmers *et al*., 1978). Lathering is reduced by effect of super fatted handmade soap especially for the *T. pedata*. Coconut oils have low iodine value due to the presence of short chain saturated carbons; lauric, palmitic, oleic and stearate acids therefore retains more water within the soap hence higher lather volume (Browning, 2003;Vivian *et al.,* 2014).

However, all the soaps were within the KEBs range. The soap that produces a lather volume ≥ 150 ml in the hard water (tough conditions) would perform very well in any normal washing water which is usually < 300ppm hardness (Browning, 2003).

The total alkaline materials present in the finished soap; hydroxides, Sodium II oxide, carbonates and bicarbonates results from reaction of the hydroxides and the dissolved carbon dioxide in the ethanolic solution (Vivian *et al*., 2014). The five types of soaps registered absence of any free alkali whose results confers with the free caustic alkali indicating total lye conversion thus comparable satisfactory effects. Matter Insoluble in Ethanol is the portion which is insoluble in hot 95% ethanol which could have resulted from the extraction process of the oils. Each oil has a percentage of non saponifiable components that do not become soap themselves, but remain in the soap; non plant materials, vitamins and minerals that may nourish the skin (Robertson, 2002). All the three soaps were within the given KEBS standards as shown in Figure 4.16.

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

The investigations reported in the present work aimed at production of fatty acid methyl esters FAME (biodiesel fuel) and soap from *Telfairia pedata*. The work also evaluated the fuel parameters of the biodiesel in comparison with convectional diesel fuels; automotive diesel and kerosene in order to demonstrate suitability of the esters as substitutes or supplements for fossil diesel fuels. This was compared with the FAME of coconut and sunflower oils. The CO emissions of *Telfairia pedata* biodiesel and biodiesel/automotive diesel blends prepared were also analyzed to demonstrate their potential as alternative biofuel. The percentage yields for the *T. pedata* oil was 62.5% by solvent extraction. This indicates high oil content recovery suitable for economic exploitation. The yields for the refined methyl ester were 80% meaning minimal losses were encountered during production and refining processes.

GC analysis showed various types of fatty acids in the *T. pedata* vegetable oil ester which identified as stearic acid, palmitic acid and linoleic acid as the major fatty acids. The methyl esters identified and quantified by GC-MS in *T. pedata* oil were methyl 9(Z), 12(Z)-octadecanoate (linoleate) (53.66%), methyl hexadecanoate (palmitate) (32.03%), and methyl octadecanoate (stearate) (10.31%), while in *Cocos nucifera* were methyl dodecanoate, methyl tetradecanoate, methyl hexadecanoate and methyl octadecanoate.

Fuel parameters analysis showed that the heat of combustion of the *T. pedata* methyl esters was 39.25 MJ/kg less than that of automotive diesel 42.5 MJ/kg and kerosene 43.6MJ/kg. Analysis of volatility characteristics and viscosity showed closer results for *T. pedata* biodiesel (4.22mm^2/s) with automotive diesel (4.18mm^2/s) while Kerosene was more viscous (2.4mm^2/s). The flash point for *T.pedata*127 °C biodiesel fuels was higher than that of automotive and kerosene fuels 74 and 45.2 °C respectively and was within the European standards. High ignition temperature (flash point) for biodiesel allows fuel safety in handling with little risk of fire hazards. This is an important quality for user application since the majority targeted to use ester fuelled stoves are rural women and probably children. In general, biodiesel made from vegetable oils of *Telfairia pedata* showed close properties as shown in table 4.4 to automotive diesel fuel thus can be used as neat or blend fuels in motor vehicle diesel engines with little or no modifications of the engine and the fuel supply equipments.

Coconut methyl ester similarly showed compatibility with kerosene fuel. This could thus be used as alternative to kerosene for domestic cooking. Utilization of the ester as cooking fuel has varied ecological, economical and sociological benefits to the general population. Oil crop plantations would utilize marginal land in Kenya and control environmental degradation. Biodiesel fuels and soap production industry would create jobs for many youths and women raising their standard of living.

Fuel analysis of the methyl esters was carried out according to ASTM procedures for the analysis of fossil diesel fuels. The tests procedures for viscosity, density, copper corrosion, water content, flash point, distillation and ash content differs with automotive

diesel. Blends of 20% biodiesel in 80% automotive diesels gave the best fuel properties, giving the blend fuel both the good attributes of automotive fuel (high energy content, wide volatility range, low viscosity and low density). Blending could also reduce other problems associated with pure biodiesel such as oxidative instability (due to unsaturated components), emissions of nitrogen oxides, clogging of filters, and deposit formation in the injection systems and affinity to water.

Analysis of the results of water boiling tests for *Telfairia pedata* biodiesel fuel indicates that the fuel is able to burn effectively in a common wick stove. Variations within and between the factors of fuel performance for *Telfairia pedata* ester was minimal. The results of high power phase indicated that cooking with *Telfairia pedata* ester requires 50-100% more time to get the work when compared to kerosene. However, blending of the *Telfairia pedata* biodiesel with kerosene helped to reduce time for water boiling. Absence of strong smell and matter deposited at the bottom of the pot accrues the fuel better health benefits as compared to the smoke, particulate matter and complex mix of organic compounds produced by the burning of biomass fuels and kerosene. *T. pedata* gave mean CO emission of 0.03896 ±0.02 g/min, B20 (biodiesel/kerosene) 0.0722±0.01 g/min and kerosene 0.03896±0.01 g/min. This confirms that, blending the *T. pedata* biodiesel and kerosene, resulted to reduced CO emissions.

Soaps from the oils of *T. pedata*, Coconut, and blend registered total fatty matter that was 80.6%, 78.15% and 81.06% which is below the house reference material 82.98%, respectively. Saponification reaction was complete therefore there was no free alkali present in all the three soaps; *T. pedata* oil, Coconut oil and blend oil based soaps.

Coconut oil soap registered the highest lather volume by 640 cm^3 compared to *T. pedata*/coconut blend 630cm^3while *T. pedata* 625cm^3 had the lowest lather volume, however all the soaps met the KEBS standards. This research finding confirms that the alternative fuels and handmade soap will contribute greatly to attaining country's vision 2030.

5.2 Recommendations

The following areas of research can be carried out to enhance the quality of the results obtained in this study.

i. Further studies in detailed chemical characterization of exhaust emission among different engine. This would contribute to verification of the alternative fuel as far as greenhouse gases regulation and climate change are concerned.
ii. Further studies on lighting properties of biodiesel and its blends.
iii. Further study on the purification of biodiesel to meet EN 14214 standard, the problem could be solved if better reaction technologies are implemented that will reduce or eliminate soap and emulsification problems.
iv. Further studies on determination of herbal properties of the *T. pedata* oil for soap making and comparing it with commercial soaps.

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LISTS OF APPENDICES

Appendix I: ASTM Copper Strip Classification Specifications

Classification	Designation	Description
1	Slight tarnish	a. Light orange, almost the same as freshly polished strip
		b. Dark orange
2	Moderate tarnish	a. Claret red
		b. Lavender
		c. Multicolored with lavender blue or silver, or both overlaid on claret red
		d. Silvery
		e. Brassy or gold
3	Dark tarnish	a. Magenta overcast on brassy strip
		b. Multicolored with red and green showing (peacock) but no gray
4	Corrosion	a. Transparent black, dark grey, or brown with peacock green barely showing
		b. Graphite or lusterless black
		c. Glossy or jet black

Appendix II: Test Specimen Mass versus Ash Content

Expected ash, mass (%)	Test specimen, mass (g)	Ash mass (mg)
0.18	9	20
0.1	20	20
0.05	40	20
0.04	50	20
0.02	100	20
0.01	100	10
0.001	100	1

Appendix III *Telfairia pedata* Methyl Ester Mass Spectra

Library Searched : C:\Database\Adams2.L
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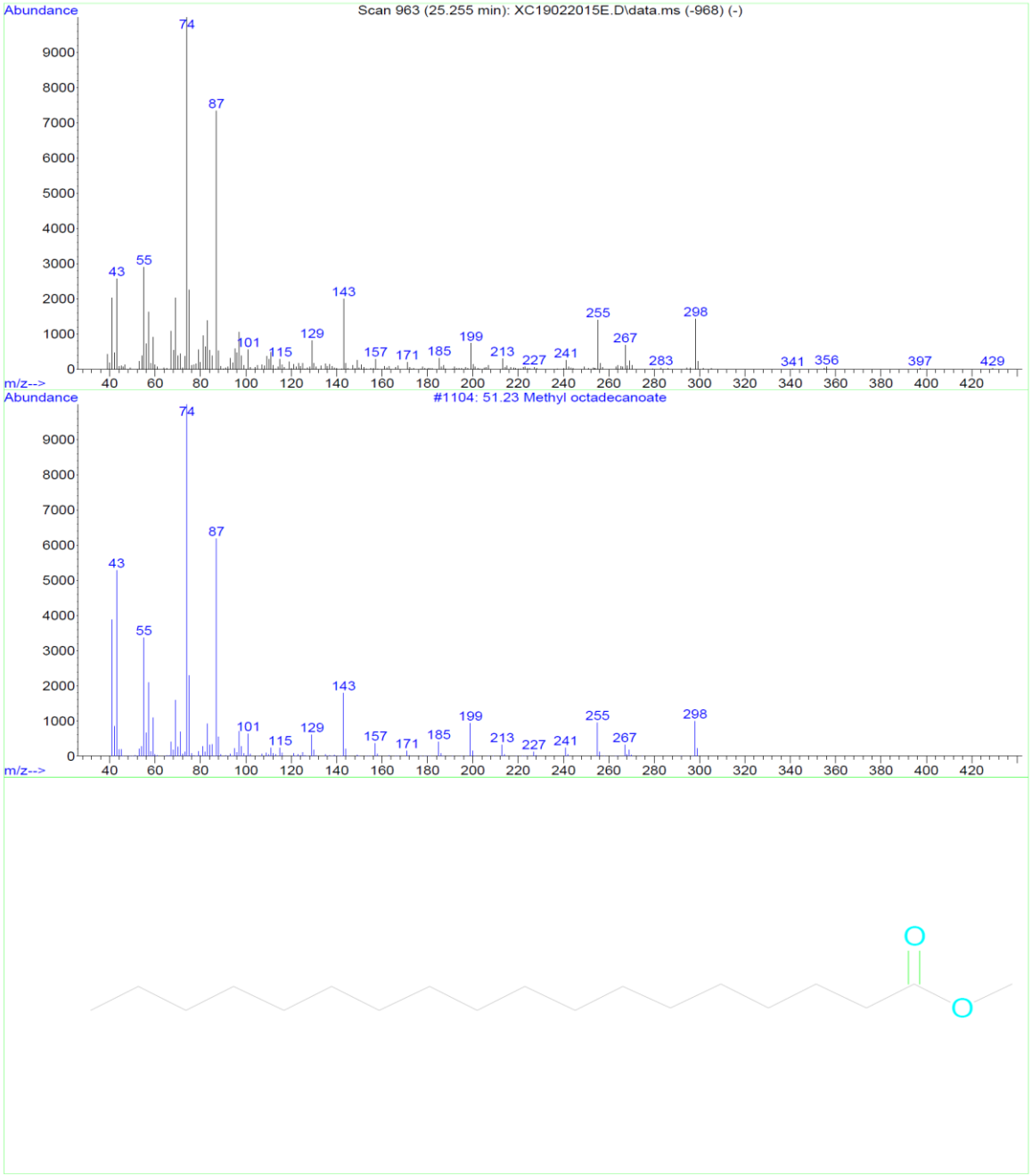
ID : 51.23 Methyl octadecanoate



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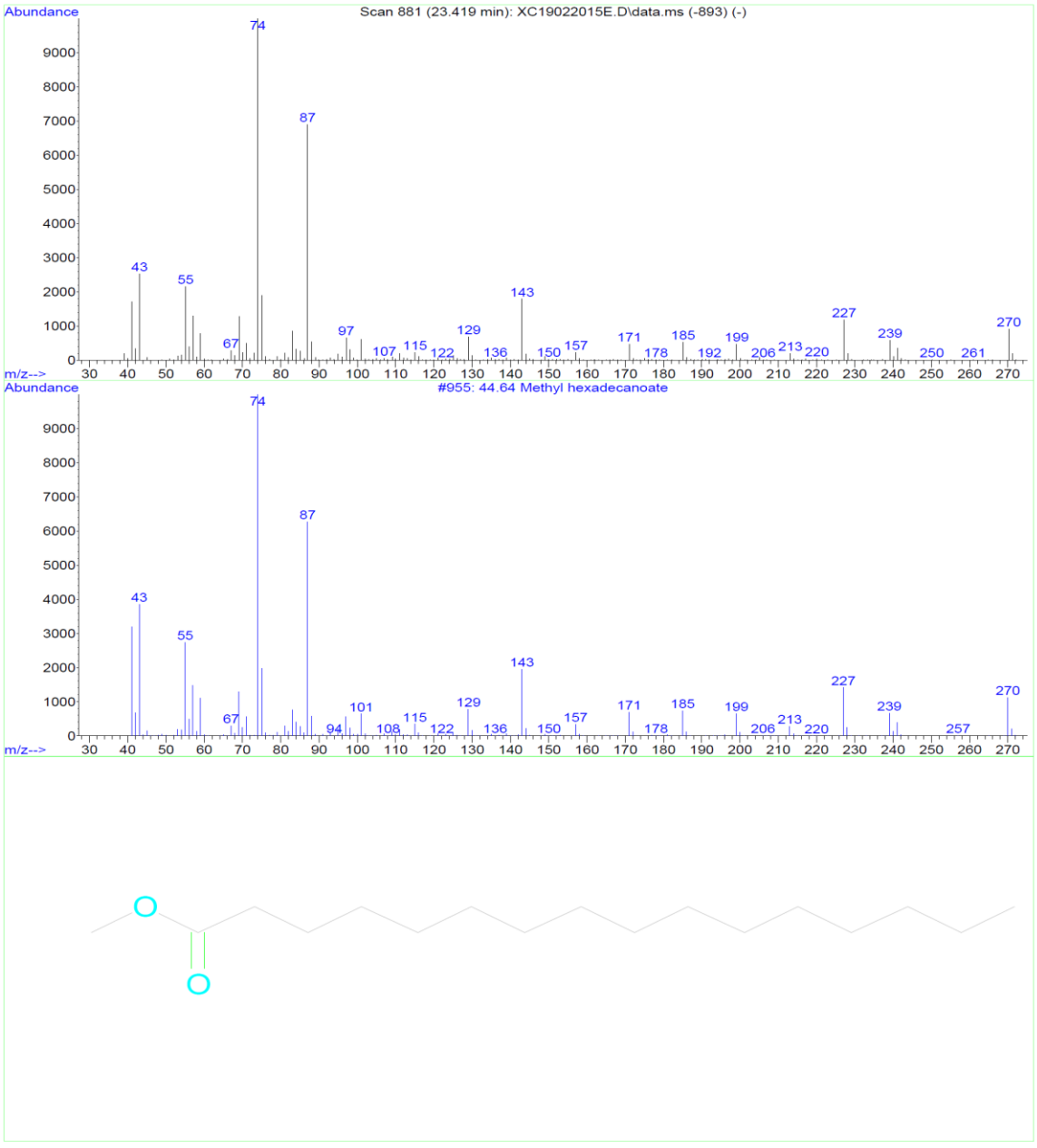
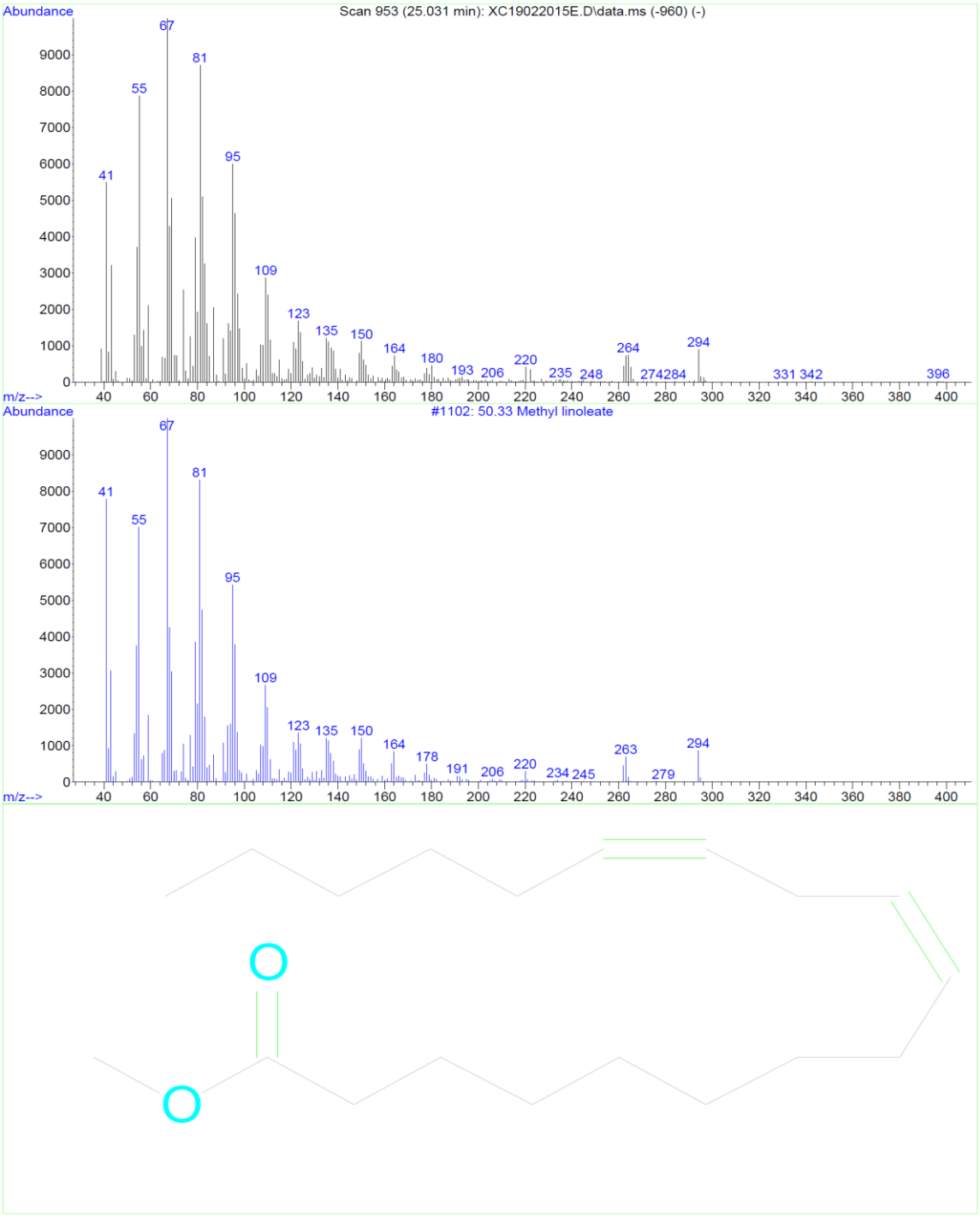


Library Searched : C:\Database\Adams2.L
Quality : 99
ID : 50.33 Methyl linoleate



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Sample : T.pedata
Misc : 4mg/ml
ALS Vial : 98 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : C:\msdchem\1\METHODS\default.m
Title :

Signal : EIC Ion 87.00 (86.70 to 87.70): XC19022015E.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	4.440	29	34	36	BV 2	4239	113693	5.83%	2.438%
2	4.534	36	38	54	VV	10973	453385	23.26%	9.720%
3	5.090	60	63	69	VV 2	1915	72048	3.70%	1.545%
4	7.143	150	154	166	PV	1251	44959	2.31%	0.964%
5	23.428	877	881	894	PV	30347	1948994	100.00%	41.785%
6	23.815	894	899	930	VV 4	5800	1204906	61.82%	25.832%
7	25.044	947	954	960	PV 2	3157	215947	11.08%	4.630%
8	25.259	960	963	987	VV 3	9004	590028	30.27%	12.650%

Appendix IV Coconut nucifera Methyl Ester Mass spectra

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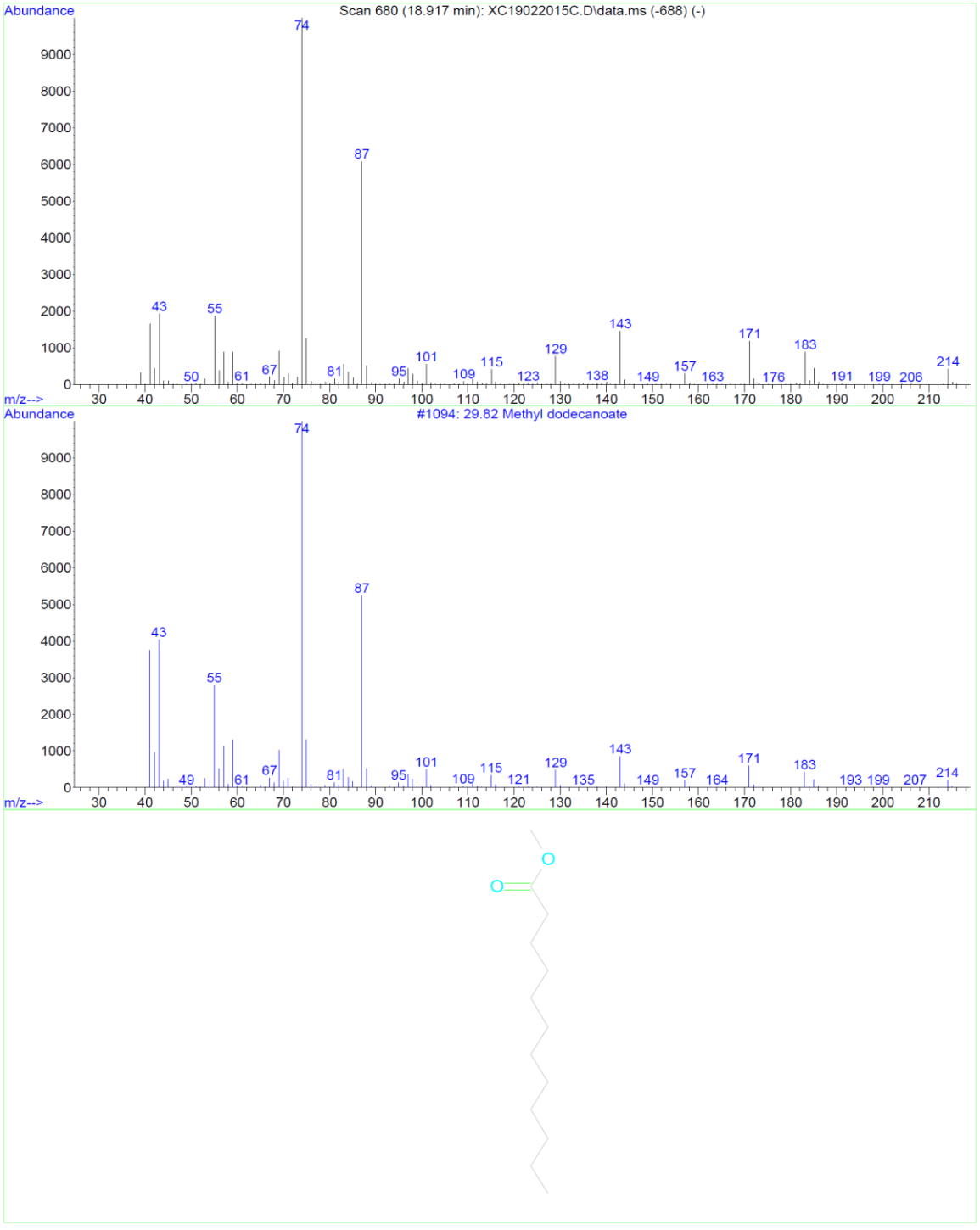

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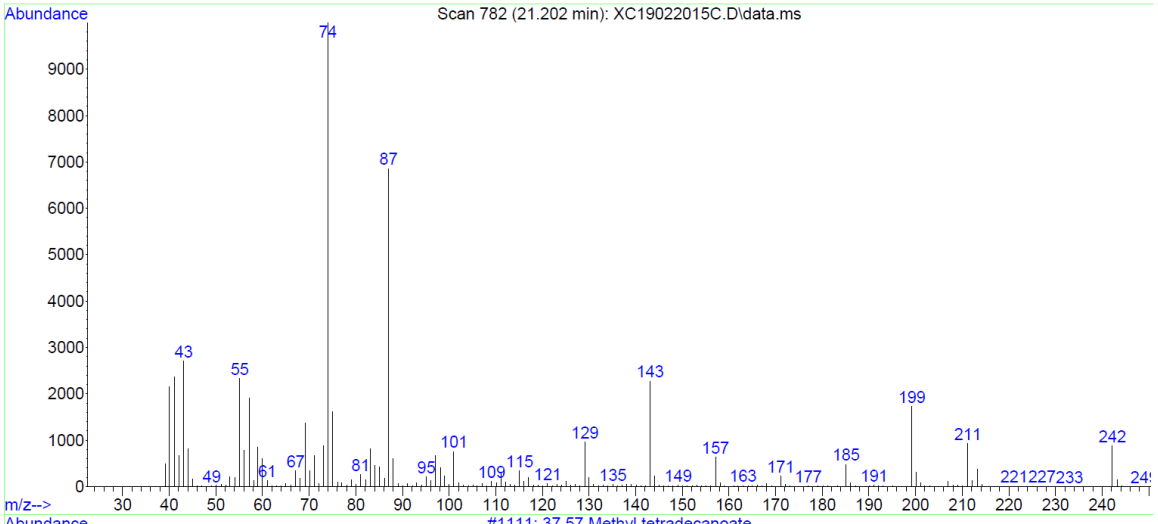

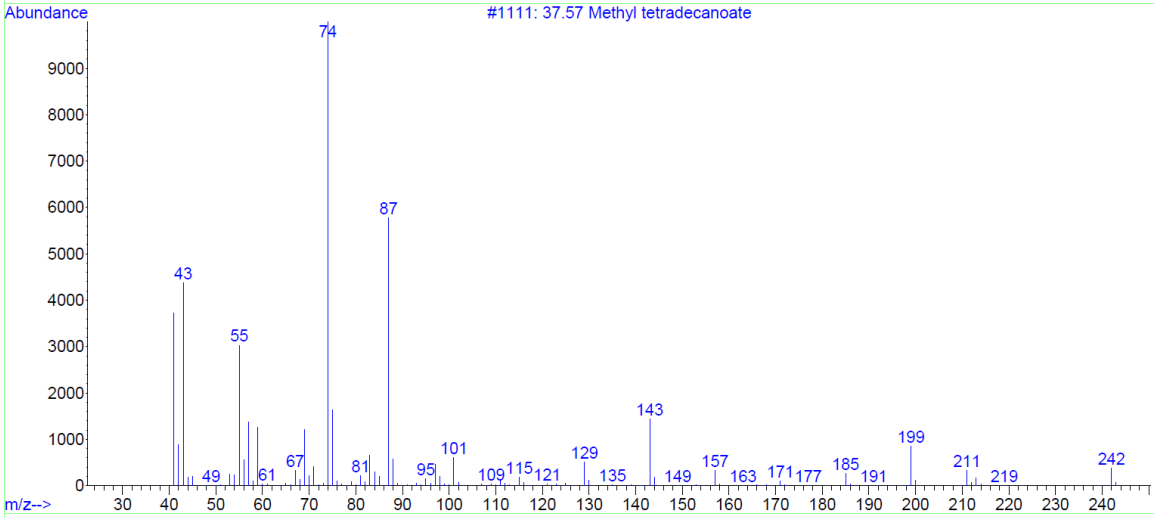

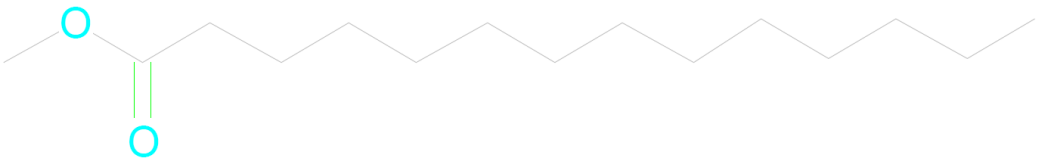

Library Searched : C:\Database\Adams2.L
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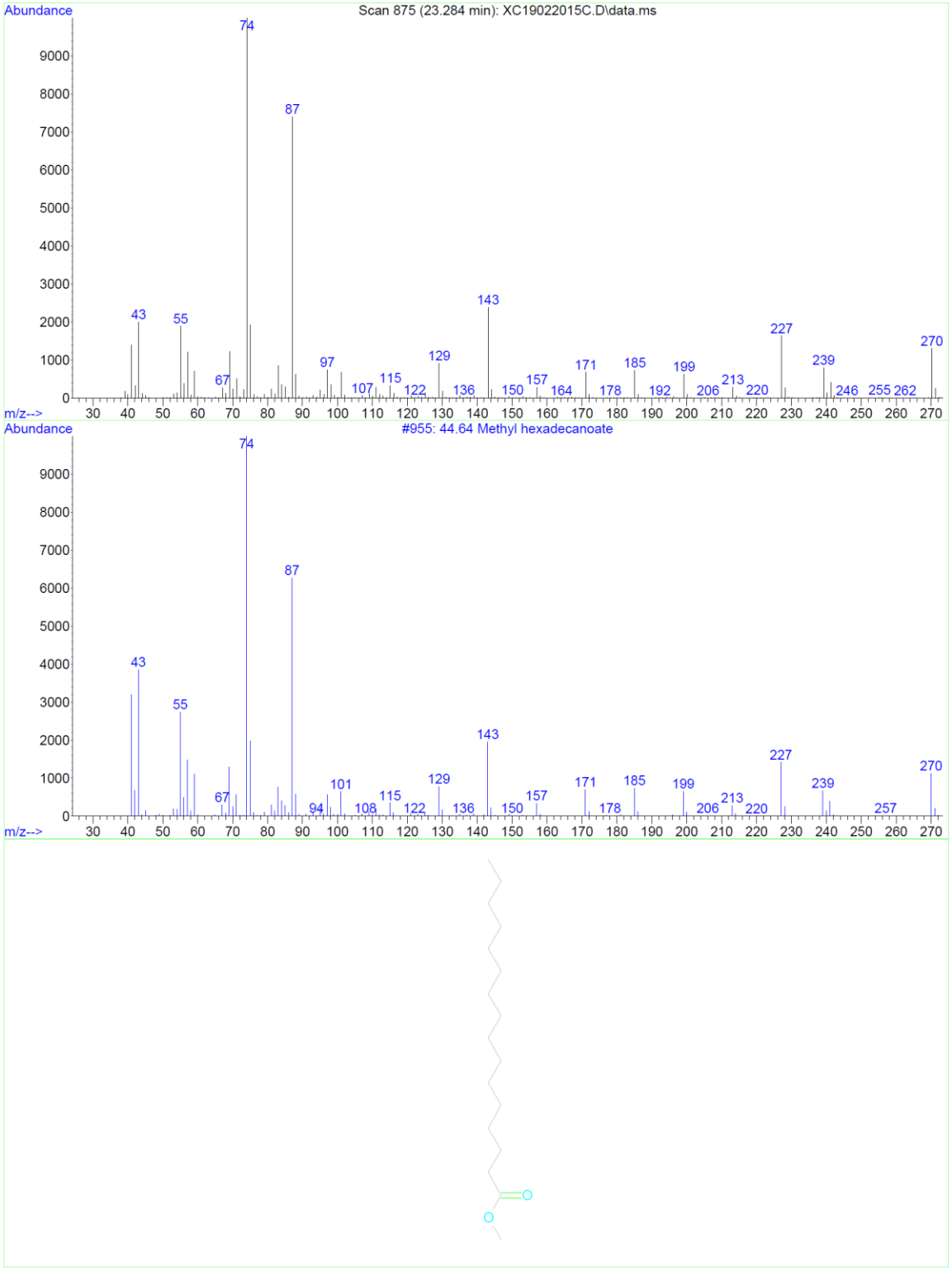

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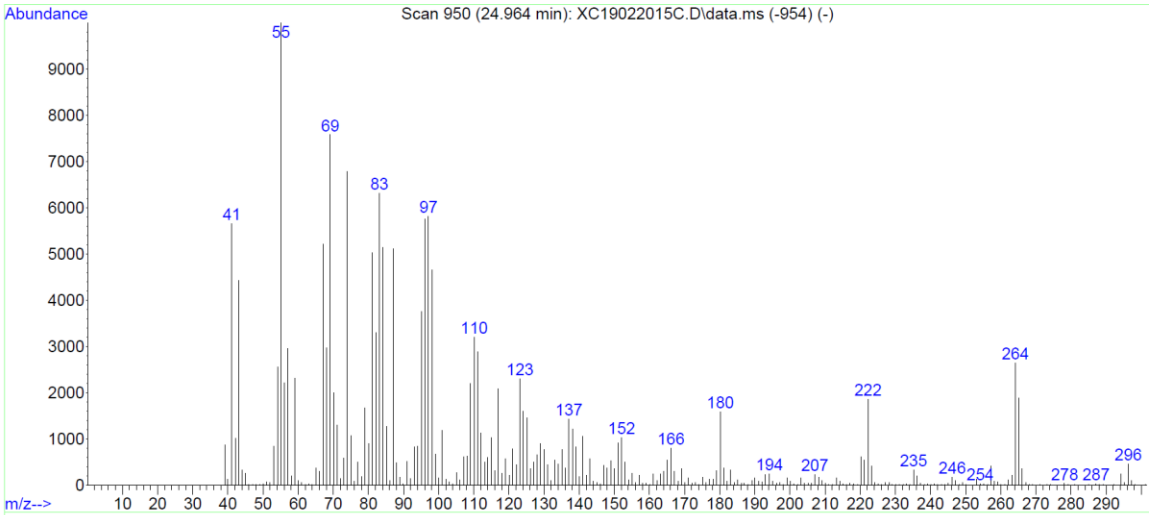

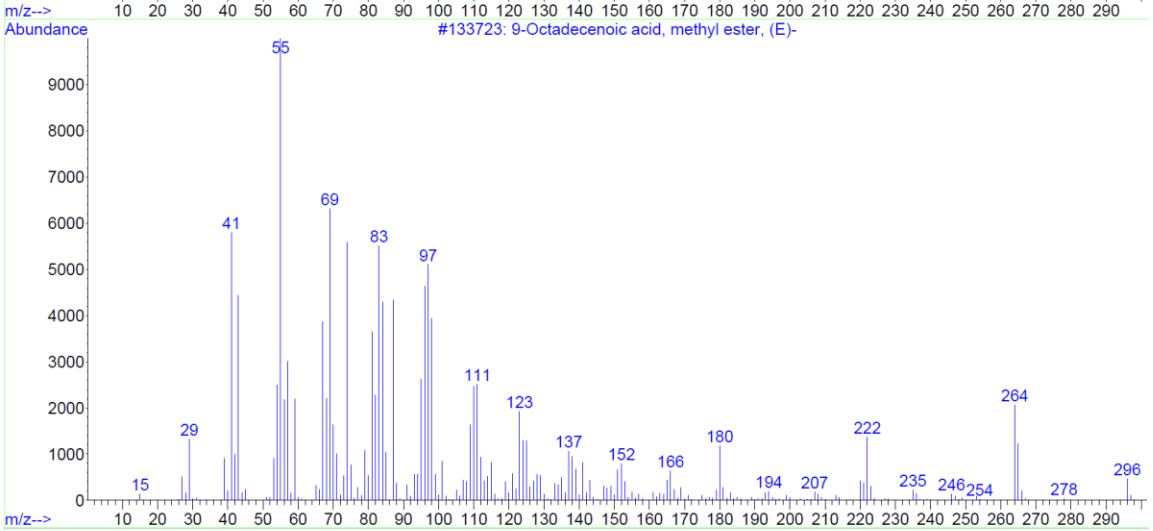

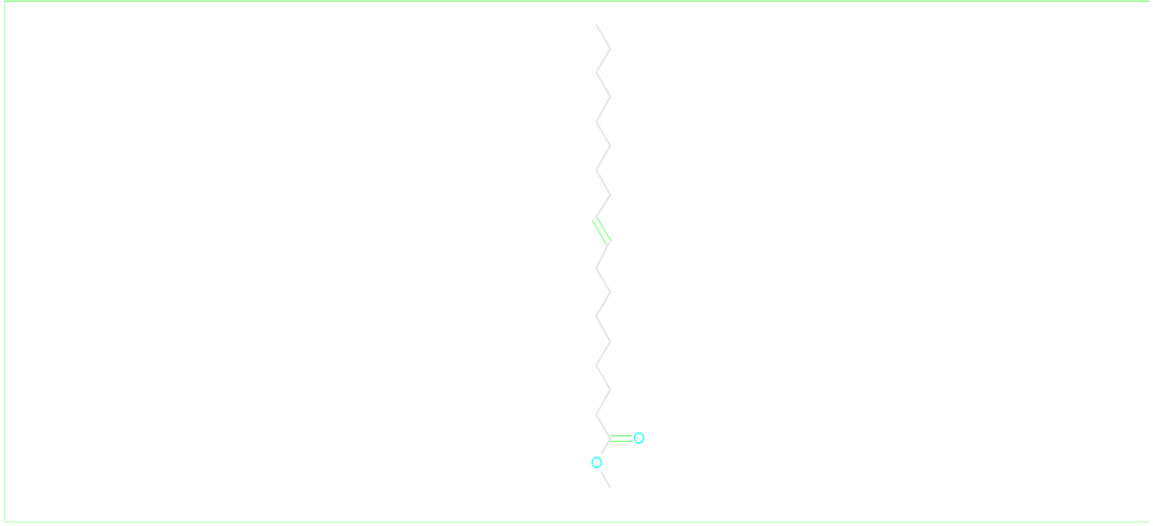

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Misc : 2mg/ml
ALS Vial : 97 Sample Multiplier: 1

Integration Parameters: autoint1.e
Integrator: ChemStation

Method : C:\msdchem\1\METHODS\default.m
Title :

Signal : EIC Ion 74.00 (73.70 to 74.70): XC19022015C.D\data.ms

peak #	R.T. min	first scan	max scan	last scan	PK TY	peak height	corr. area	corr. % max.	% of total
1	13.674	438	446	472	BV 7	7431	1353363	1.65%	0.692%
2	16.388	560	567	590	BV 2	15588	1506048	1.84%	0.770%
3	17.017	590	595	623	VV	60229	3153208	3.85%	1.613%
4	18.911	673	680	698	BV	302171	12847155	15.70%	6.571%
5	19.629	698	712	731	VV	308885	29189210	35.66%	14.929%
6	21.205	777	782	798	BV	156588	5039588	6.16%	2.578%
7	21.716	798	805	826	VV	196636	10370148	12.67%	5.304%
8	23.289	872	875	889	BV	4767555	81854571	100.00%	41.865%
9	23.678	889	893	916	VV 2	49486	3132305	3.83%	1.602%
10	24.261	916	919	927	VV 3	11794	309264	0.38%	0.158%
11	24.970	945	950	957	PV 2	280753	11337149	13.85%	5.798%
12	25.193	957	960	974	VV	1352695	34352418	41.97%	17.570%
13	26.946	1034	1038	1050	BV	43163	1075135	1.31%	0.550%

Sum of corrected areas: 195519563

default.m Wed Feb 25 12:05:56 2015