

Introduction and Basic Concepts

1.1 Introduction

Biodiesel is an alternative fuel for diesel engines that is produced by chemically reacting a vegetable oil or animal fat with an alcohol such as methanol. The reaction requires a catalyst, usually a strong base, such as sodium or potassium hydroxide, and produces new chemical compounds called methyl esters. It is these esters that have come to be known as biodiesel because its primary feedstock is a vegetable oil or animal fat, biodiesel is generally considered to be renewable. Since the carbon in the oil or fat originated mostly from carbon dioxide in the air, biodiesel is considered to contribute much less to global warming than fossil fuels. Diesel engines operated on biodiesel have lower emissions of carbon monoxide, unburned hydrocarbons, particulate matter, and air toxins than when operated on petroleum-based diesel fuel^[1].

Energy is a crucial factor for humanity to continue the economic growth and maintain high standard of living. It is anticipated that the world will need 50% more energy in 2030 than today, of which 45% will be accounted for by China and India^[2]. Declining reserves of fossil fuels beside recognition that climate change is stemmed by growing carbon dioxide emissions has generated the interest in promoting Biofuels as one of the leading renewable energy sources. The sustainable production of Biofuels is a valuable tool in stemming climate change, boosting local economies, particularly in lesser-developed parts of the world, and enhancing energy security for all. The 2009 United Nations climate change conference, commonly known as the Copenhagen Summit, underscored how renewable

and clean fuels sustainably created from bioenergy feedstocks can reduce greenhouse gas emissions (GHGs), improve food security, stimulate economic development and reduce global poverty. The forecast world biodiesel production of 16.4 billion liter's is projected to result in a reduction of GHG emissions of 35.9 million tons. The combined biofuels GHG emission reduction is 123.5 million tone's, an average reduction of about 57% compared to the emissions that would have occurred from the production and use of equivalent quantities of petroleum fuels. This is almost equal to the national GHG emissions of Belgium (131.3 million tons) or Greece (131.8 million tons).^[3]

1.2 Biofuels Blends

Blends of biodiesel and conventional hydrocarbon-based diesel are products most commonly distributed for use in the retail diesel fuel marketplace. Much of the world uses a system known as the "B" factor to state the amount of biodiesel in any fuel mix:^[4]

- 100% biodiesel is referred to as B100.
- 20% biodiesel, 80% petrodiesel is labeled B20.
- 5% biodiesel, 95% petrodiesel is labeled B5.
- 2% biodiesel, 98% petrodiesel is labeled B2

Blends of 20% biodiesel and lower can be used in diesel equipment with no, or only minor modifications,^[5] although certain manufacturers do not extend warranty coverage if equipment is damaged by these blends. The B6 to B20 blends are covered by the ASTM D7467 specification.^[6] Biodiesel can also be used in its pure form (B100), but may require certain

engine modifications to avoid maintenance and performance problems. ^[7]

Blending B100 with petroleum diesel may be accomplished by:

- Mixing in tanks at manufacturing point prior to delivery to tanker truck
- Splash mixing in the tanker truck (adding specific percentages of biodiesel and petroleum diesel).
- In-line mixing, two components arrive at tanker truck simultaneously.
- Metered pump mixing, petroleum diesel and biodiesel meters are set to X total volume, transfer pump pulls from two points and mix is complete on leaving pump.

1.3 Applications Biofuels

Biodiesel can be used in pure form (B100) or may be blended with petroleum diesel at any concentration in most injection pump diesel engines. New extreme high-pressure (29,000 psi) common rail engines have strict factory limits of B5 or B20, depending on manufacturer. Biodiesel has different solvent properties than petrodiesel, and will degrade natural rubber gaskets and hoses in vehicles (mostly vehicles manufactured before 1992), although these tend to wear out naturally and most likely will have already been replaced with FKM, which is nonreactive to biodiesel. Biodiesel has been known to break down deposits of residue in the fuel lines where petrodiesel has been used.^[8] As a result, fuel filters may become clogged with particulates if a quick transition to pure biodiesel is made. Therefore, it is recommended to change the fuel filters on engines and heaters shortly after first switching to a biodiesel blend.^[9]

Biodiesel has promising lubricating properties and cetane ratings compared to low sulfur diesel fuels. Depending on the engine; this might include high

pressure injection pumps, pump injectors (also called unit injectors) and fuel injectors.

1.4 Properties of Biofuels

The calorific value of biodiesel is about 37.27 MJ/kg. This is 9% lower than regular Number 2 petrodiesel.^[12] A variation in biodiesel energy density is more dependent on the feedstock used than the production process. Still, these variations are less than for petrodiesel^[9]. It has been claimed biodiesel gives better lubricity and more complete combustion thus increasing the engine energy output and partially compensating for the higher energy density of petrodiesel.

The color of biodiesel ranges from golden and dark brown, depending on the production method. It is slightly miscible with water, has a high boiling point and low vapor pressure. The flash point of biodiesel (>130 °C, >266 °F) is significantly higher than that of petroleum diesel (64 °C, 147 °F) or gasoline (-45 °C, -52 °F). Biodiesel has a density of ~ 0.88 g/cm³, higher than petrodiesel (~ 0.85 g/cm³).

Biodiesel contains virtually no sulfur^[12]. And it is often used as an additive to Ultra-Low Sulfur Diesel (ULSD) fuel to aid with lubrication, as the sulfur compounds in petrodiesel provide much of the lubricity.

1.4.1 Fuel Efficiency

The power output of biodiesel depends on its: blend, quality, and load conditions under which the fuel is burnt. The thermal efficiency for example of B100 as compared to B20 will vary due to the BTU content of the various blends. Thermal efficiency of a fuel is based in part on fuel characteristics such as: viscosity, specific density, and flash point; these characteristics will

change as the blends as well as the quality of biodiesel varies. The American Society for Testing and Materials has set standards in order to judge the quality of a given fuel sample ^[12].

Regarding brake thermal efficiency one study found that B40 was superior to traditional counterpart at higher compression ratios (this higher brake thermal efficiency was recorded at compression ratios of 21:1. It was noted that as the compression ratios increased the efficiency of all fuel types as well as blends being tested increased; though it was found that a blend of B40 was the most economical at a compression ratio of 21:1 over all other blends. The study implied that this increase in efficiency was due to fuel density, viscosity, and heating values of the fuels.

1.4.2 Combustion

Fuel systems on the modern diesel engine were not designed to accommodate biodiesel. Traditional direct injection fuel systems operate at roughly 3,000 psi at the injector tip while the modern common rail fuel system operates upwards of 30,000 PSI at the injector tip. Components are designed to operate at a great temperature range, from below freezing to over 1,000 degrees Fahrenheit. Diesel fuels is expected to burn efficiently and produce as few emissions as possible. As emission standards are being introduced to diesel engines the need to control harmful emissions is being designed into the parameters of diesel engine fuel systems. The traditional inline injection system is more forgiving to poorer quality fuels as opposed to the common rail fuel system. The higher pressures and tighter tolerances of the common rail system allows for greater control over atomization and injection timing. This control of atomization as well as combustion allows

for greater efficiency of modern diesel engines as well as greater control over emissions. Components within a diesel fuel system interact with the fuel in a way to ensure efficient operation of the fuel system and so the engine. If a fuel is introduced to a system-that has specific parameters of operation-and you vary those parameters by an out of specification fuel you may compromise the integrity of the overall fuel system. Some of these parameters such as spray pattern and atomization are directly related to injection timing.^[13]

One study found that during atomization biodiesel and its blends produced droplets that were greater in diameter than the droplets produced by traditional petrodiesel. The smaller droplets were attributed to the lower viscosity and surface tension of traditional petrol. It was found that droplets at the periphery of the spray pattern were larger in diameter than the droplets at the center this was attributed to the faster pressure drop at the edge of the spray pattern; there was a proportional relationship between the droplet size and the distance from the injector tip. It was found that B100 had the greatest spray penetration, this was attributed to the greater density of B100.^[14] Having a greater droplet size can lead to; inefficiencies in the combustion, increased emissions, and decreased horse power. In another study it was found that there is a short injection delay when injecting biodiesel. This injection delay was attributed to the greater viscosity of Biodiesel. It was noted that the higher viscosity and the greater cetane rating of biodiesel over traditional petrodiesel lead to poor atomization, as well as mixture penetration with air during the ignition delay period.^[14] Another study noted that this ignition delay may aid in a decrease of NOx emission.^[1]

1.4.3 Emissions

Emissions are inherent to the combustion of diesel fuels that are regulated by the U.S. Environmental Protection Agency (E.P.A.). As these emissions are a byproduct of the combustion process in order to ensure E.P.A. compliance a fuel system must be capable of controlling the combustion of fuels as well as the mitigation of emissions. There are a number of new technologies that are becoming phased in order to control the production of diesel emissions. The exhaust gas recirculation system, E.G.R., and the diesel particulate filter, D.P.F., are both designed to mitigate the production of harmful emissions.^[17]

While studying the effect of biodiesel on a D.P.F. it was found that though the presence of sodium and potassium carbonates aided in the catalytic conversion of ash, as the diesel particulates are catalyzed, they may congregate inside the D.P.F. and so interfere with the clearances of the filter. This may cause the filter to clog and interfere with the regeneration process.^[18] In a study on the impact of E.G.R. rates with blends of jathropa biodiesel it was showed that there was a decrease in fuel efficiency and torque output due to the use of biodiesel on a diesel engine designed with an E.G.R. system. It was found that CO and CO₂ emissions increased with an increase in exhaust gas recirculation but NO_x levels decreased. The opacity level of the jathropa blends was in an acceptable range, where traditional diesel was out of acceptable standards. It was shown that a decrease in Nox emissions could be obtained with an E.G.R. system. This study showed an advantage over traditional diesel within a certain operating range of the E.G.R. system.^[19]

1.4.4 Material compatibility

Plastics: High density polyethylene (HDPE) is compatible but polyvinyl chloride (PVC) is slowly degraded. Polystyrene is dissolved on contact with biodiesel.

Metals: Biodiesel (like methanol) has an effect on copper-based materials (e.g. brass), and it also affects zinc, tin, lead, and cast iron. Stainless steels (316 and 304) and aluminum are unaffected.

Rubber: Biodiesel also affects types of natural rubbers found in some older engine components. Studies have also found that fluorinated elastomers (FKM) cured with peroxide and base-metal oxides can be degraded when biodiesel loses its stability caused by oxidation. Commonly used synthetic rubbers FKM- GBL-S and FKM- GF-S found in modern vehicles were found to handle biodiesel in all conditions.

1.5 Current research

There is ongoing research into finding more suitable crops and improving oil yield. Other sources are possible including human fecal matter, with Ghana building its first "fecal sludge-fed biodiesel plant." Using the current yields, vast amounts of land and fresh water would be needed to produce enough oil to completely replace fossil fuel usage. It would require twice the land area of the US to be devoted to soybean production, or two-thirds to be devoted to rapeseed production, to meet current US heating and transportation needs.

Specially bred mustard varieties can produce reasonably high oil yields and are very useful in crop rotation with cereals, and have the added

benefit that the meal leftover after the oil has been pressed out can act as an effective and biodegradable pesticide^[20].

The NFESC, with Santa Barbara-based Biodiesel Industries is working to develop biodiesel technologies for the US navy and military, one of the largest diesel fuel users in the world.

A group of Spanish developers working for a company called Ecofasa announced a new biofuel made from trash. The fuel is created from general urban waste which is treated by bacteria to produce fatty acids, which can be used to make biodiesel.

Another approach that does not require the use of chemical for the production involves the use of genetically modified microbes^[21].

1.5.1 Biodiesel from Algal

From 1978 to 1996, the U.S. NREL experimented with using algae as a biodiesel source in the "Aquatic Species Program"^[22]. A self-published article by Michael Briggs, at the UNH Biodiesel Group, offers estimates for the realistic replacement of all vehicular fuel with biodiesel by utilizing algae that have a natural oil content greater than 50%, which Briggs suggests can be grown on algae ponds at wastewater treatment plants.^[23] This oil-rich algae can then be extracted from the system and processed into biodiesel, with the dried remainder further reprocessed to create ethanol.^[24]

The production of algae to harvest oil for biodiesel has not yet been undertaken on a commercial scale, but feasibility studies have been conducted to arrive at the above yield estimate. In addition to its projected high yield, algaculture — unlike crop-based biofuels — does not entail a decrease in food production, since it requires neither farmland nor fresh

water. Many companies are pursuing algae bio-reactors for various purposes, including scaling up biodiesel production to commercial levels.^[25]

Rodrigo E. Teixeira from the University of Alabama in Huntsville demonstrated the extraction of biodiesel lipids from wet algae using a simple and economical reaction in ionic liquids.^[26]

1.5.2 Biodiesel from Pongamia

Millettia pinnata, also known as the Pongam Oil tree or Pongamia, is a leguminous, oilseed-bearing tree that has been identified as a candidate for non-edible vegetable oil production.

Pongamia plantations for biodiesel production have a two-fold environmental benefit. The trees both store carbon and produce fuel oil. Pongamia grows on marginal land not fit for food crops and does not require nitrate fertilizers. The oil producing tree has the highest yield of oil producing plant (approximately 40% by weight of the seed is oil) while growing in malnourished soils with high levels of salt. It is becoming a main focus in a number of biodiesel research organizations. The main advantages of Pongamia are a higher recovery and quality of oil than other crops and no direct competition with food crops. However, growth on marginal land can lead to lower oil yields which could cause competition with food crops for better soil^[27].

1.5.3 Biodiesel from Jatropha

Several groups in various sectors are conducting research on *Jatropha curcas*, a poisonous shrub-like tree that produces seeds considered by many to be a viable source of biodiesel feedstock oil.^[28] Much of this research focuses on improving the overall per acre oil yield of *Jatropha* through advancements in genetics, soil science, and horticultural practices.^[29]

SG Biofuels, a San Diego-based *Jatropha* developer, has used molecular breeding and biotechnology to produce elite hybrid seeds of *Jatropha* that show significant yield improvements over first generation varieties. SG Biofuels also claims that additional benefits have arisen from such strains, including improved flowering synchronicity, higher resistance to pests and disease, and increased cold weather tolerance.^[30]

Plant Research International, a department of the Wageningen University and Research Centre in the Netherlands, maintains an ongoing *Jatropha* Evaluation Project (JEP) that examines the feasibility of large scale *Jatropha* cultivation through field and laboratory experiments.^[31]

The Center for Sustainable Energy Farming (CFSEF) is a Los Angeles-based non-profit research organization dedicated to *Jatropha* research in the areas of plant science, agronomy, and horticulture. Successful exploration of these disciplines is projected to increase *Jatropha* farm production yields by 200-300% in the next ten years.^[32]

1.5.4 Biodiesel from Fungi

A group at the Russian Academy of Sciences in Moscow published a paper in September 2008, stating that they had isolated large amounts of lipids from single-celled fungi and turned it into biodiesel in an

economically efficient manner. More research on this fungal species; *Cunninghamella japonica*, and others, is likely to appear in the near future.^[33]

The recent discovery of a variant of the fungus *Gliocladium roseum* points toward the production of so-called myco-diesel from cellulose. This organism was recently discovered in the rainforests of northern Patagonia and has the unique capability of converting cellulose into medium length hydrocarbons typically found in diesel fuel.^[33]

1.5.5 Biodiesel from used coffee grounds

Researchers at the University of Nevada, Reno, have successfully produced biodiesel from oil derived from used coffee grounds. Their analysis of the used grounds showed 10% to 15% oil content (by weight). Once the oil was extracted, it underwent conventional processing into biodiesel. It is estimated that finished biodiesel could be produced for about one US dollar per gallon. Further, it was reported that "the technique is not difficult" and that "there is so much coffee around that several hundred million gallons of biodiesel could potentially be made annually." However, even if all the coffee grounds in the world were used to make fuel, the amount produced would be less than 1 percent of the diesel used in the United States annually. "It won't solve the world's energy problem," Dr. Misra said of his work.^[34]

1.5.6 Exotic sources

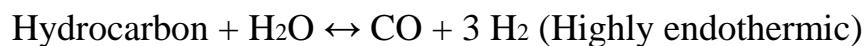
Recently, alligator fat was identified as a source to produce biodiesel. Every year, about 15 million pounds of alligator fat are disposed of in landfills as a waste byproduct of the alligator meat and skin industry. Studies

have shown that biodiesel produced from alligator fat is similar in composition to biodiesel created from soybeans, and is cheaper to refine since it is primarily a waste product.^[35]

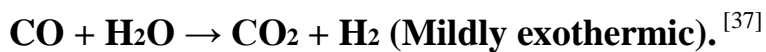
1.5.7 Biodiesel to hydrogen-cell power

A microreactor has been developed to convert biodiesel into hydrogen steam to power fuel cells.^[36]

Steam reforming, also known as fossil fuel reforming is a process which produces hydrogen gas from hydrocarbon fuels, most notably biodiesel due to its efficiency. Reformer is the processing device in which water vapour reacts with the liquid fuel under high temperature and pressure. Under temperatures ranging from 700 – 1100 °C, a nickel-based catalyst enables the production of carbon monoxide and hydrogen:



Furthermore, a higher yield of hydrogen gas can be harnessed by further oxidizing carbon monoxide to produce more hydrogen and carbon dioxide:



1.6 Acacia Senegal tree botanical classification

Family: *Leguminosae*.

Subfamily: *Mimosoideae*.

Genus: *Acacia*.

Species: *Senegal*.

English name: Gum Arabic, three thorned *Acacia*.

Arabic name: Hashab.^[38]

1.6.1 Description

Shrub to small tree 2-12 m. Bark yellow to light brown or grey, rough,

fissuring or flaking. Young branchlets gray, yellow or brown, pubescent to glabrous, with horizontal slit-like lenticels. Stipules not spinescent. Prickles at nodes, in threes 2 lateral pointing upward or forward and one central pointing downward or backward, falcate, dark brown with a grey base, 4-7 mm long. Leaves 1-6 cm long. Flowers white or cream, sessile. Calyx pubescent, 2 x 0.7mm, 5-6 lobed, creamy or pinkish. Stamens glandular, 4-7 mm long. Ovary glabrous 0.7 mm long; style 4.5 mm long, stipe 0.2 mm long. Pods pale brown to straw-colour, membranous, pubescent, flat, straight, oblong, 3-14 cm long, 1-3.3 cm wide. Seeds orbicular 8-12 mm diam, yellow or pale brown, compressed, areole central, crescent-shape, 1.5-6 x 2.5-5 mm; funicle 7.5 mm long. Seeds lie vertically on pods. Flowering November–February; fruiting January–April^[39].

1.6.2 General distribution

If found in Central Sudan, a continuous belt from east to west, though more successful on the western sand plains of Kordofan and Darfur. Widespread in Tropical Africa.

1.6.3 Uses

Acacia seeds does not have any noticeable use in Sudan, Some of them shall may be consumed by animals and the gestate part is wasted

1.6.4 Biology

A. senegal is presumably insect pollinated. Flowering starts from June to July in Sudan, December to January in South Africa, February to March in Pakistan, and August to December in India. Fruits ripen in January in Burkina Faso, July-September in Kenya, August in Pakistan, October in South Africa, and November-December in southern and central Niger. The

wind shakes seeds from the dehiscent pods, and sheet wash and grazing animals may extend the seed dispersal range.

1.6.5 Products

Food: The seeds are dried and preserved for human consumption as a vegetable. The dried seed is the main component of panchkut, a delicacy in Jodhpur, India, also containing fruits of *Capparis decidua*, *Cucumis sativa* and *Prosopis cinerearia*.

Fodder: Leaves and pods are browsed by sheep, goats and camels. Crude protein values are 20% for leaves, 22% for green pods, and 20% for dry pods (expressed as a percentage of dry matter).

Apiculture: Bees seek the nectar from the flowers. Honey amber in colour, with a mild aroma and granulates rapidly.

Fuel: An excellent fuelwood-sometimes the only wood species to survive in dry areas. The calorific value is estimated at 3000 kcal/kg. Wood yields of 120-190 cubic metres per hectare, with annual increments of 0.5-1.0 cubic metres per hectare have been recorded. The dense wood also yields charcoal.

Fibre: The long, flexible surface roots yield a strong fibre used for cordage, ropes and fishing nets.

Timber: The heartwood is almost black and takes polish well. It is used for making carts and Persian wheels, sugar cane crushers, agricultural implements, horse girths and tool handles.

Gum or resin: Gum arabic exudes from the duct of the inner bark; it is tapped in the hot season (May-June) when the trees are stressed. Tapping begins when trees are 4-5 years old. It commences after leaf fall and ceases during the colder months of the dry season. Gum nodules form in 3-8 weeks,

exuding from the former broken abscission scars. Care should be taken to keep the gum clean. Annual yields stand at 188-2856 g for young trees and 379-6754 g for older trees (7-15 years). Gum production is excellent on poor soils and higher in stressed trees. Essential oil: Seeds contain fat (khakhan), which is used both for medicine and for soap making.

Medicine: Roots are used to treat dysentery, gonorrhoea and nodular leprosy

1.6.6 Tree management

Weeding should be immediate in the season following planting and for the following 2 growing seasons. Protection of young trees from livestock browsing is essential. Seedlings are rather slow growing with initial annual increments of 30- 40 cm. For firewood production, trees can be cut on a rotation of 20 years using coppice with standards, lopping up to 50% of the lower crown in rainy season.

1.6.7 Germplasm management

Seed should be harvested before pods have dried for easy collection and to avoid insect attack. Seed is easily extracted by hand. Freshly extracted seed should immediately be dusted with an insecticide. There are 10,000-30,000 seeds/kg. Seed storage behaviour is orthodox; 5% germination following 51 years open storage at room temperature; viability can be maintained for 6 years with air-dried seeds stored at room temperature; viability can be maintained for several years in hermetic storage at 10 deg. C with 4.5-9% mc.

1.6.8 Pests and diseases

The buffalo treehopper (*Stictocephala bubalus*) may destroy seed crops. Spiders (*Cyclops* sp.) can smother young growing apices. Larval stage

of Coleoptera (bruchids), Lepidoptera, and Hymenoptera damage the seed. Locusts (*Acridium melanorhodon*) can defoliate vast areas overnight. *A. senegal* is also attacked by the fungi *Cladosporium herbarium*, *Fusarium* sp., *Ravenelia acaciae-senegalae* and *R. acaciocola*.^[41]

1.6.9 Chemistry

A. Senegal contains hentriacontane, a solid, long-chain alkane hydrocarbon. The leave also contain the psychoactive alkaloid dimethyltryptamine.^[42]

1.7 Objective of this study

This study aim to

- Extract oil from the seeds of A. senegal var singal by solvent extraction.
- Examine the physical chemical characteristics of the extracted oil .
- Convert the extracted A.senegal seed oil into biofuel by transesterification reaction
- Test the produced biofuel through spectroscopic analysis namely IR and GC-MS.

Materials and Methods

2.1 Materials

2.1.1 Sample origin

The sample was collected by the forestry authority at ELobaiyed during the season 2014. It was 2kg of seeds light brown in and colour, free from any extraneous matter.

2.1.2 Preparation of the sample

The sample was converted into course powder and kept in self sealing bags till further use.

2.2 Methods

2.2.1 Oil extraction

One Thousand gram of A. Senegal seeds were ground and oil was extracted by n-hexane in a soxholet extraction. N-hexane was removed from the oil using rotary evaporator.

2.2.2 Determination of oil percentage.

The weight of oil extracted from 10 g of seeds powders was measured to determine the lipid content. Result was expressed as the percentage of oil in the Dry matter of Seed powders.

2.2.3 Determination of the Acacia seed oil density

The weight of a 50 ml density bottle was accurate, determined. The density bottle was filled with oil and weight, the weight of the oil was found (m) and the density (ρ) was calculated as:

$$\rho = \frac{m}{v}$$

Where ρ is the density, m is the mass of the oil, and v is its volume

2.2.4 Determination of the Acacia seed oil colour

It was essential that the determination be carried out in subdued ambient light, i.e., not facing a window or in direct sunlight. The prepared sample was poured into a cell which was clean and dry and was pre warmed so that no solid matter separates from the sample during the determination.

The cell containing the sample was placed within the black metal heath gamest the side of the liephlening cabinet holding the colour racks. The colour was then immediately determined, initially by using the colour racks in the ratio of 10 yellow to 1 red. Then was corrected until an accurate colour match was obtained.

2.2.5 Determination of the Acacia seed oil Moisture content.

A 5.0g of well mixed sample were weighed into a tared beaker that has been dried and cooled previously in a dessicator. The sample was heated on a hot plate, rotating the beaker gently by hand to avoid spattering that may result from rapid ebullition of moisture; the end was judged by the cessation of the rising bubbles of steam as well as the absence of foam.

When the end point has been reached the sample was heated momentarily to the point of mistrusts smoking. The beaker with its contents was cooled to room temperature in dessicator and weighed.

Calculation:-

$$\text{Moisture and volatile matter \%} = \frac{\text{loss - in - mass , g}}{\text{mass - of - sample , g}} \times 100 \%$$

2.2.6 Determination of the Acacia seed oil refractive index

The refractometer prisms were cleaned, dried and several drops of the sample were placed on the lower prism. The prisms were closed and tightened firmly with the screwhead and then it was let until the sample

came to the temperature of the instrument 40°C. The instrument was adjusted and lighted and the most distinct reading was obtained and the refractive index was determined. Three readings were taken and the average refractive index was calculated.

2.2.7 Determination of the Acacia seed oil saponification value.

The test solution was prepared by adding 0.5ml of the bromophenol blue indicator solution (reagent-3) to each 100ml of the aqueous acetone solution (reagent-1) and titrated with 0.01N HCl (reagent 2) or 0.01n NaOH (reagent 4) till the test solution was yellow in colour.

A 40g of the oil to be tested were weighed into a test tube (apparatus-1) which has been rinsed well with the test sample solution. One ml of water was added to the test sample, warmed in water bath and shaken vigorously.

A 50 ml of the test solution were added warmed and well shaken and the content were allowed separating to two distinct layers. The upper one coloured green blue.

A 0.01N HCl was slowly added from a micro burette, warming, shaking and addition of HCl were repeated till the yellow colour of the upper layer remained permanent, the total volume of the acid was recorded and soap was calculated as sodium.

$$\text{ppm soap as sodium} = \frac{mL_s - mL_b \times N \times 304}{\text{mass of sample, g}} \cdot 4$$

Where:-

mL_s= volume, mL HCl obtained in procedure -4

mL_b= volume, mL HCl obtained in procedure -5

N=normality of HCl

2.2.8 Determination of the Acacia seed oil free fatty acids

A 7.05g of the sample were accurately weighed in Erlenmeyer flask. A 75 ml of hot neutralized alcohol and 2 drops of indicator were added. The contents of the flask were then titrated with standard sodium hydroxide solution with vigorous shaking till permanent pink colour remained apparent for 30 seconds, then the acid value was calculated.

$$\text{Free fatty acids} = \frac{\text{mL, of, alkali} \times N \times 28.2}{\text{mass, of, sample, g}}$$

2.2.9 Determination of the Acacia seed oil peroxide value:

A 5.0g of the sample were accurately weighed into 250 ml Erlenmeyer flask and solutions of 3:2 acetic acid/chlorotorm (30 ml) were added and stopered with a glass stopper and swirled to dissolve the sample. A 5ml of saturated potassium iodide was added and allowed to stand for 1 minute with occasional shaking and 30 ml of distilled water were added. Then the content of the flask were titrated with 0.1N sodium thiosulphate with constant agitation.

2.2.10Determination of the Acacia seed oil Iodine Value

Was calculated by the following equation

$$IV = 8555.559 \times RI - 12425.928$$

IV= Iodine Value

RI= Refractive index

(This model is taken from the American specification works in the laboratories Savola)

2.2.11 Determination of the Acacia seed oil Ester value

Was calculated as the difference between the valuet of saponification and the value of free fatty acids

Ester value = saponification – FFA

2.3 Biodiesel production

Alkaline-catalysed transesterification is the most widely used process for biodiesel production because it is very fast and yields large amount of biodiesel. However, to use alkaline catalysts, the free fatty acid (FFA) level should be below a desired limit (ranging from less than 0.5% to less than 3%). Most of non-edible oils have high FFA values. Therefore, transesterification with alkali based catalyst yield a considerable amount of soap which are emulsifiers that make the separation of glycerol and ester phases very difficult. Acid-catalysed esterification was found to be a good solution to this problem. However the reaction rate was considerably less, requiring lengthy reaction periods. Therefore, the best approach to produce biodiesel from non-edible oils with high FFA values is the acid-catalysed esterification process followed by Alkaline-catalysed transesterification process.

2.4. Testing of biodiesel.

2.4.1 Infra red analysis of biodiesel

The sample was loaded directly in the KBr windows ,introduced into the FT IR and scanned at $4000-400\text{ cm}^{-1}$ at resolution intervals of 4.000 cm^{-1} using NICOLET (370 DTGS). The IR spectrum was recorded.

2.4.2 Gas chromatography-mass spectrometric analysis for biodiesel

Cas Chromatography/ Mass Spectrometry (GC/MS) for liquid Products, the liquid product was analyzed on a Shimadzu Gas Chromatograph, GC-17A linked to a Q P 5000 Mass Spectrometry detector. The gas chromatograph contained a Restek Rxi-5 ms column of length and inner diameter of 30 m and 0.25 mm, respectively, with the stationary

phase being 5% phenyl. The carrier gas was helium, with a 1 ml/min continuous flow rate. A "Class-5000" application software controlled the instrumentation system on the computer. The column oven starting temperature was set at 40°C with a hold time of 4 minutes, then ramped to 220°C at a heating rate of 4°C/min, with a hold time of 10 minutes. Lastly, the oven temperature was brought to 320°C at a rate of 5°C/min with a final hold of 5 minutes. The NIST 107 and 21 libraries were used to identify the compounds. A split ratio of 30:1 was used. This split ratio is explained as follows:

30 parts of sample is thrown out while 1 part is allowed to enter the system from the total quantity injected. Twenty mg of sample of biodiesel were mixed with one ml of Dichloromethane (DCM) solvent. One μL of the solution was brought to the GC/MS after the column in the machine was automatically cleaned with Dichloromethane (DCM).

Results and discussion

3.1A.senagal seed oil

3.1.1 Results and discussion

Table 1:Test of physical and chemical properties of oil from A.senagal seeds.

Test	Value
Density (g/cm ³)	0.915
Refractive Index (40°C)	1.4628
Colour (Red / Yellow)	1.5/29.04
Moisture	0.8%
Free Fatty Acid	3.8%
Saponification (ml/g)	848.4
Peroxide Value(ml/g)	6
Iodine Value (ml/g)	89.144
Ester Value(ml/g)	844.6

Table 2 comparison between Specification of Acacia seeds oil

And groundnut oil and sunflower oil

Tests	Specification of the oil obtained from A.Senegal Seed	Specification of the oil sunflower	Specification of the oil groundnut
Density(g/cm ³)	0.915	0.918-0.923	0.912-0.920
Refractive Index(40°C)	1.4628	1.461-1.469	1.460-1.465
Colour (Red/Yellow)	1.5/29.04	1-9\10-70	1-9\10-70
Moisture parentage	0.8%	0-10	0-10
Free Fatty Acid Parentage	3.8	0.2-3	0.2-3
Saponification (ml/g)	848.4	188-194	188-194
Peroxide Value (ml/g)	6	1-15	1-15
Iodine Value (ml/g)	89.144	110-143	80-106
Ester Value (ml/g)	844.6	100	100

3.1.2 Discussion

The density found in the range of edible oils (Sunflower oil and groundnuts oil). The refractive index compared with the results of the groundnuts oil for Standardization Sudanese found it resembled exactly. Colour sample found a good percentage of edible oils. Comparing the free fatty acids the Standardization for each of the Sudanese groundnuts oil and sunflower found it very high so it cannot be used for eating or food as oil only after treatment. Possible to turn into biofuels from non-treatments. This is result is good to complete the process of esterification of biofuels. The saponification Very high compared with the Standardization of the Sudanese edible oils (Sunflower oil and groundnuts oil), with that being the esterification process in one easy. Quantity less than the quantity of both sunflower oil and groundnuts oil in Standardization of the Sudanese edible oils, less peroxide value means that reducing the oxidation process sample this easy the esterification process for oil. The iodine value found in the range of edible oils (Sunflower oil and groundnuts oil). The ester value very high compared with the Standardization of the Sudanese edible oils (Sunflower oil and groundnuts oil), easy the esterifyeable , good for biofuels.

3.2 Biodiesel:

3.2.1 Analysis of the biodiesel:

3.2.1.1 IR analysis

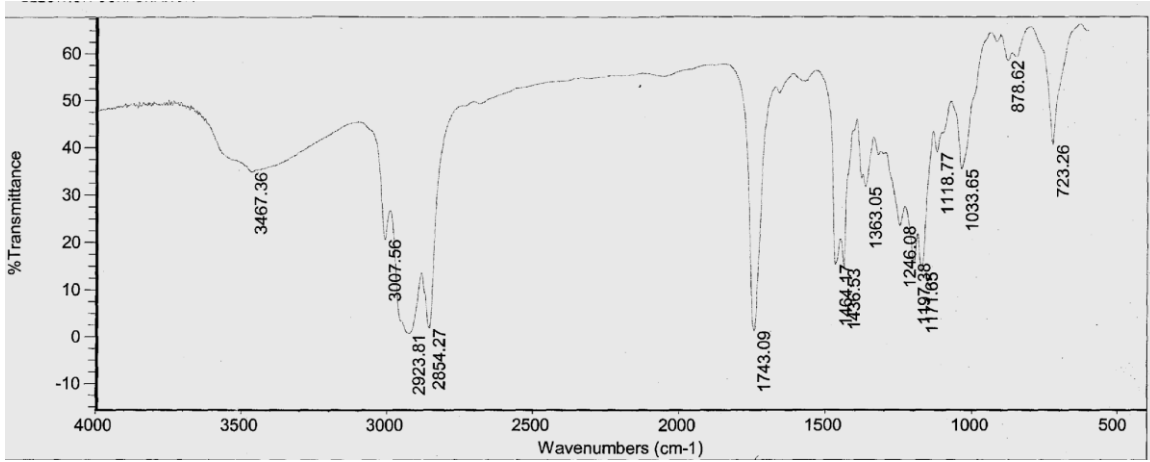


Fig.1: FT-IR spectrum of the biodiesel before treatment

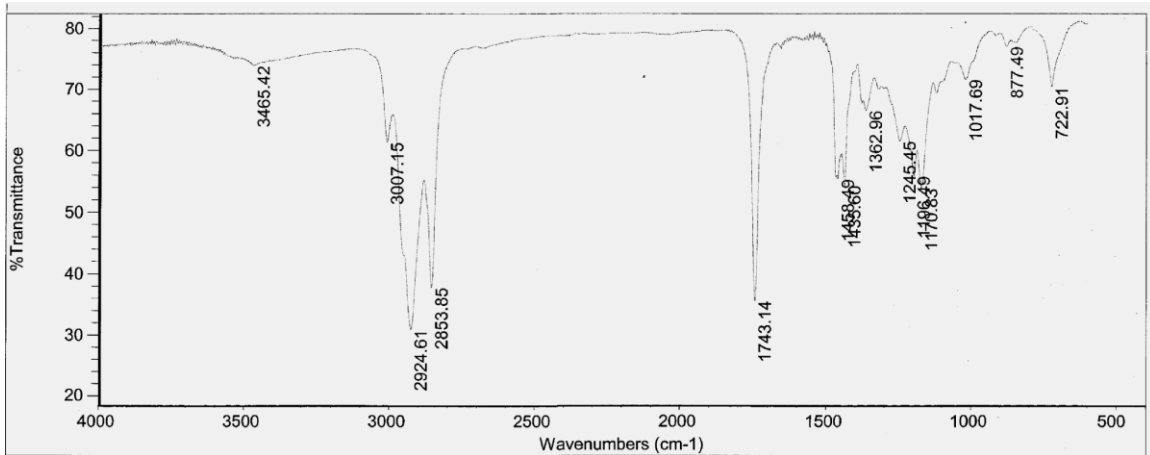


Fig.2: FT-IR spectrum of the biodiesel obtained from A. senegal seeds oil.

3.2.2.2 Result GC-MS analysis the biodiesel:

Table3.3: Components of biodiesel indentified by GC-MS

NO	NAME	FORMULA	MW	RT	AREA	AREA%
1	Hexadecanoic acid	C ₁₆ H ₃₂ O ₂	256	29.64	7252000	12.19
2	9,12-Octadecadienoic acid	C ₁₈ H ₃₂ O ₂	280	32.83	19030000	31.99
3	9-Octadecenoic acid	C ₁₈ H ₃₄ O ₂	282	32.94	32330000	54.35
4	Octadecanoic acid	C ₁₈ H ₃₆ O ₂	284	33.40	760834	1.279
5	9,12-Octadecadienyl chloride, (Z,Z)-	C ₁₈ H ₃₁ ClO	298	34.86	74292	0.1249
6	Eicosanoic acid	C ₂₀ H ₄₀ O ₂	312	36.81	34035	0.0572

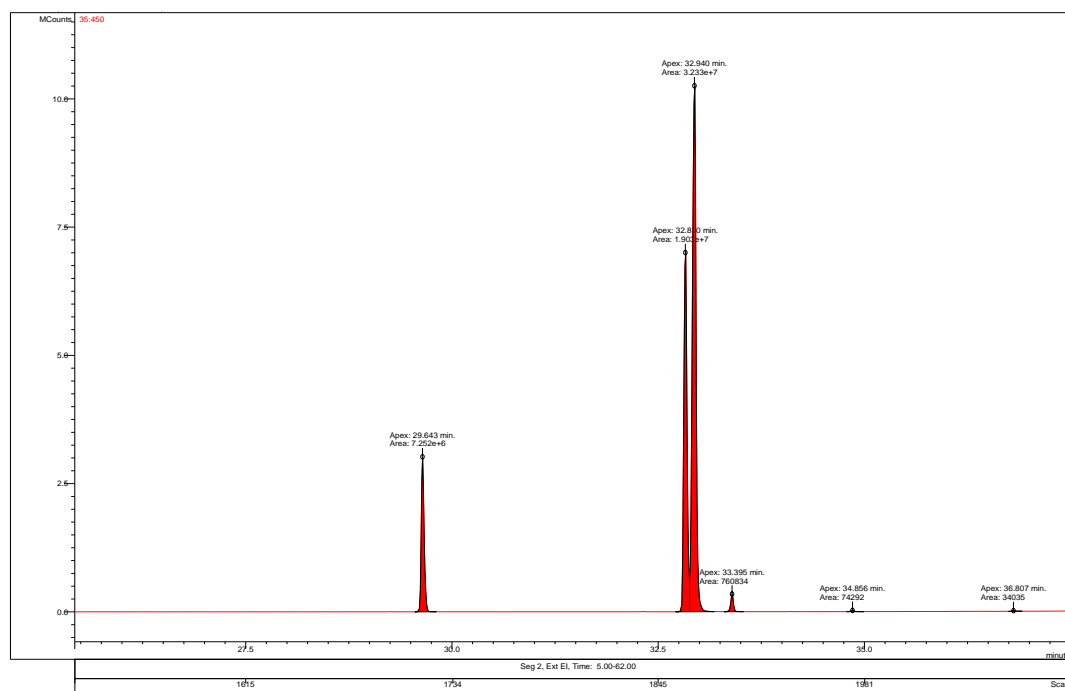


Fig.3 chromatogram of biodiesel showing the major components

RT:29.64

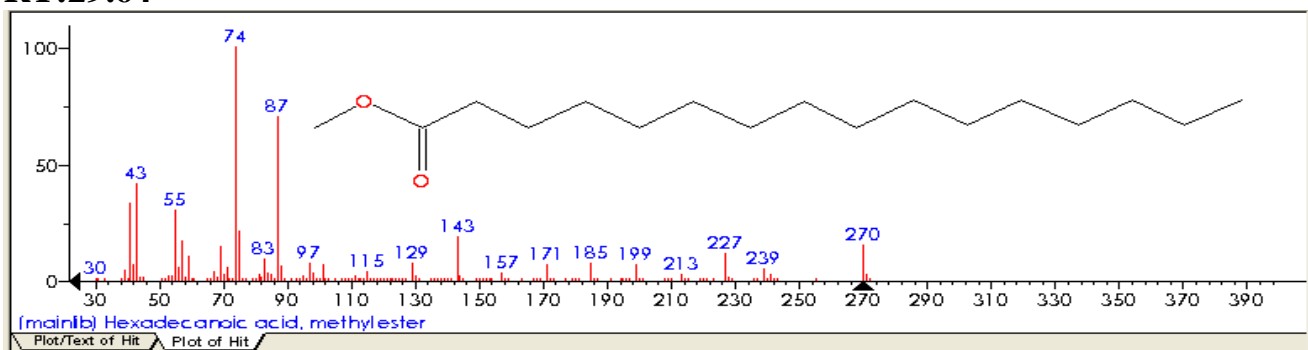


Fig.4 MS spectrum of Hexadecanoic acid

RT: 32.83

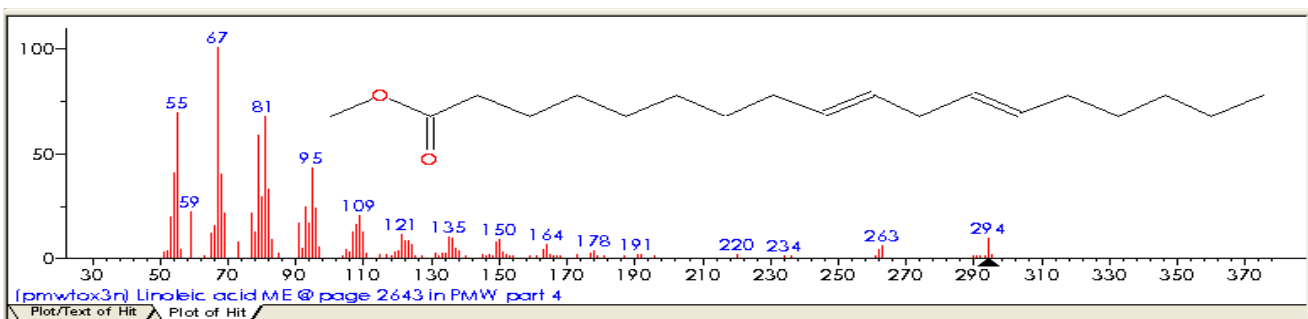


Fig.5 MS spectrum of 9, 12-Octadecadienoic acid

RT: 32.94

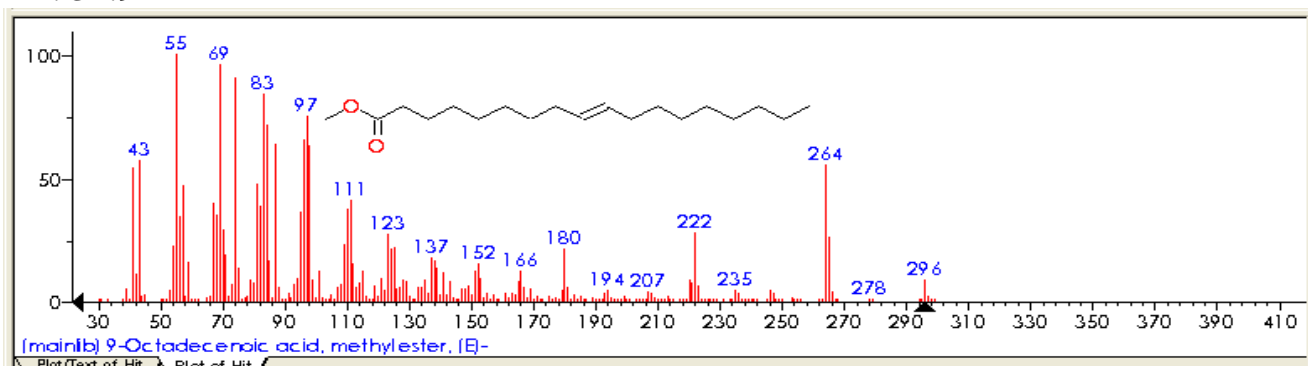


Fig.6 MS spectrum of 9-Octadecenoic acid

RT:33.40

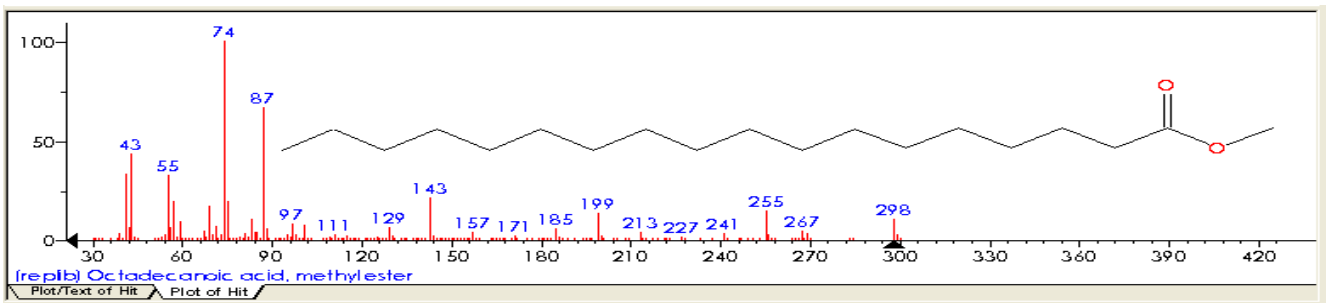


Fig.7 MS spectrum of Octadecanoic acid

RT:34.86

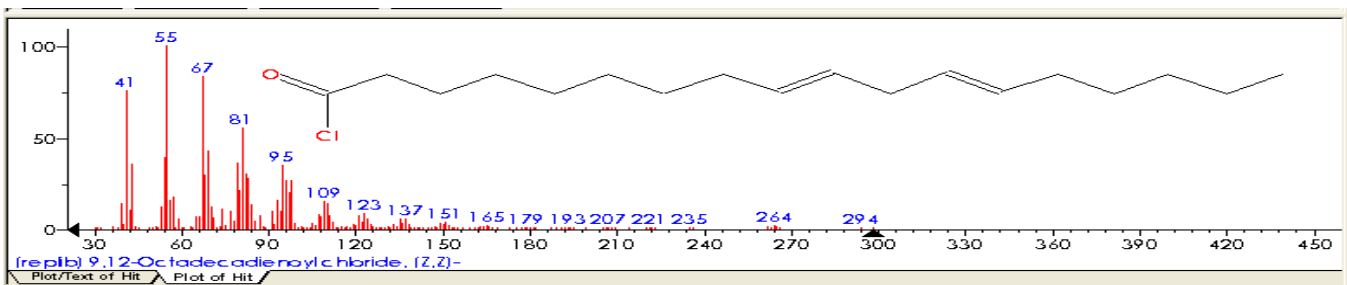


Fig.8 MS spectrum of 9, 12-Octadecadienoyl chloride, (Z,Z)-

RT:36.81

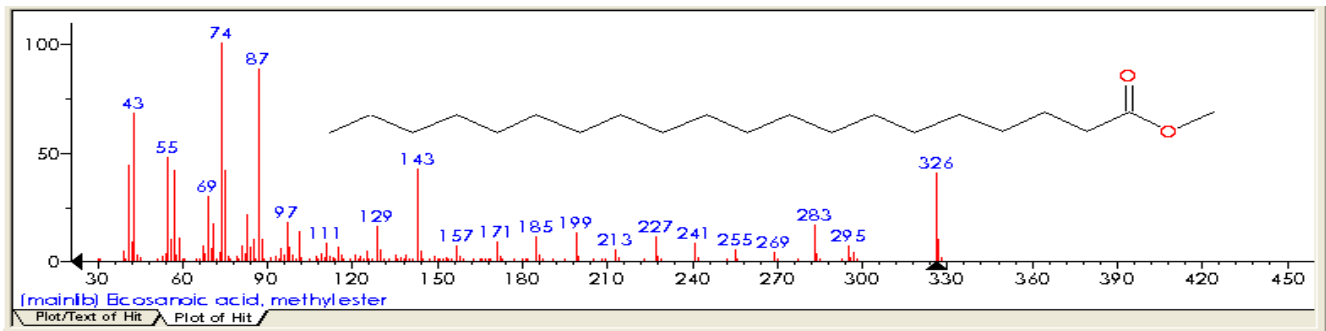


Fig.9 MS spectrum of Eicosanoic acid

3.3.2 Discussion

3.3.2.1 IR analysis

IR were obtained from two results IR. The first pre-treatment by CaSO₄ (granules) found it peaks OH and tow after treatment of the Moisture on peak of (OH).

In the results IR first, According to the scan, saturated (-C-H) stretching peaks were found at 2923.81, 2854.27 cm^{-1} respectively .bending peak of Methylene group (-C-H₂ -) at 1436.53 cm^{-1} ; bending peak of Methyl group (-CH₃) at 1363.05 cm^{-1} ,a peak of (C=O) at 1743.09 cm^{-1} and a(C-O) peak at 1197.38 cm^{-1} , these peaks indicate presence of esters. Also there is a peak 723.26 cm^{-1} which indicates the long chain structure furthermore, it is noticed that there is a medium broad peak of (O-H) at 3467.36 cm^{-1} (Due to moisture) and C=C absorption at 3007.56 cm^{-1} . In the results IR seconds: According to the scan, saturated (-C-H) stretching peaks were found at 2924.61, 2853.85 cm^{-1} respectively .bending peak of Methylene group (-C-H₂ -) at 1435.60 cm^{-1} ; bending peak of Methyl group (-CH₃) at 1362.96 cm^{-1} ,a peak of (C=O) at 1743.14 cm^{-1} and a(C-O) peak at 1196.49 cm^{-1} , these peaks indicate presence of esters. Finally, C=C absorption at 3007.15 cm^{-1} .

3.3.2.2 GC/MS analysis

The GC/MS explain expected acids in the sample and the percentage shown in the table 3.3 which is Hexadecanoic acid, 9, 12-Octadecadienoic acid, 9-Octadecenoic acid, Octadecanoic acid , 9, 12-Octadecadienoyl chloride, (Z,Z)-, Eicosanoic acid. A higher ratio acid was 9-Octadecenoic acid and the least Eicosanoic acid. The all transfer to methyl ester shown in Fig 3.4, 3.5, 3.6, 3.7, 3.8, 3.9.

3.3 Conclusion

- The oil of acacia non edible due to its fatty acids exceeds the range of the edible oils.
- Esterification value was very high compared with other oils.
- A.senegal seeds oil high Esterification value and high free fatty acid content compound to known edible oil. Hence it is more suitable for biofuel production.
- The transesterification reaction was clean yielding biofuel is high qualities.
- GC-MS analysis showed that the Biofuels product is methyl ester and free from other undesired products.

3.4 References

- 1-International Energy Agency (IEA). (2010). CO₂ emissions from fuel combustion Retrieved 29th ,8, 2014, from <http://www.iea.org/co2highlights/co2highlights.pdf>
- 2-Jain, S., & Sharma, M. P. (2010a). Biodiesel production from Jatropha curcas oil. *Renewable and Sustainable Energy Reviews*, 14,9, 3140-3147.
- 3-Jatropfuels. (2012). From feedstock cultivation to full market integration Retrieved 29th ,8, 2014, from <http://www.jatropfuels.com/161-0-Biofuels.html#Fuel%20characteristics%20and%20advantages>
- 4-Ahmad, A. L., Yasin, N. H. M., Derek, C. J. C., & Lim, J. K. (2011). Microalgae as a sustainable energy source for biodiesel production: A review. *Renewable and Sustainable Energy Reviews*, 15,1, 584-593.
- 5-"Biodiesel Basics - Biodiesel.org". biodiesel.org. 2012. <http://www.biodiesel.org/what-is-biodiesel/biodiesel-basics> Retrieved 2014-6-14
- 6- Deborah O'Connell, etc (2007) *Biofuels in Australia –issues and prospects* Australia ,Csiro7,10.64-67
- 7- "American Society for Testing and Materials". ASTM International. Retrieved 2014-02-13.
- 8-McCormick, R.L. (2006) Biodiesel Handling and Use Guide Third Edition <http://www.nrel.gov/vehiclesandfuels/npcf/pdfs/43672.pdf> " (Retrieved 2013-12-18.
- 9- "US EPA Biodiesel Factsheet"
Twenty<http://www.epa.gov/otaq/fuels/renewablefuels/documents/420f13048.pdf>. Retrieved 2014-05-10.
- 10 – M.A.Elsayed ,etc ,(2003)Carbon and Energy Balances for a Range of Biofuels ,Sheffield Hallam University, England.1,1,60-66

- 11- National Biodiesel Board (2005). "Energy Content" . Jefferson City, USA. p. 1.
<http://www.biodiesel.org/docs/ffs-basics/energy-content-final-oct-2005.pdf?sfvrsn=6>
 Retrieved 2014-7-24.
- 12-ASTM Standard D6751-12, (2003), "Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels," ASTM International, West Conshohocken, PA, 2003, DOI: 10.1520/C0033-03, astm.org "Generic biodiesel material safety data sheet (MSDS)" Retrieved 2014-03-15.
- 13-Mark Z. Jacobson,(2009) *Energy Resour. Technol.* **1**,31, 208-201 ;
- 14-Chen, P., Wang, W., Roberts, W. L., & Fang, T. (2013). Spray and atomization of diesel fuel and its alternatives from a single-hole injector using a common rail fuel injection system. *Fuel*, **10**, 3 850-861.
- 15- Hwang, J., Qi, D., Jung, Y., & Bae, C. (2014). Effect of injection parameters on the combustion and emission characteristics in a common-rail direct injection diesel engine fueled with waste cooking oil biodiesel. *Renewable Energy* ,**6**, 39-17
- 16- McCarthy, P. P., Rasul, M. G., & Moazzem, S. S. (2011). Analysis and comparison of performance and emissions of an internal combustion engine fuelled with petroleum diesel and different bio-diesels. *Fuel*, **90**,**6**, 2147-2157.
- 17-United States Environmental Protection Agency. (2014,). National Clean Diesel Campaign. Retrieved From the Environmental Protection Agency website:
<http://www.epa.gov/diesel/>[15-9-2014].
- 18-Hansen, B., Jensen, A., & Jensen, P. (2013). Performance of diesel particulate filter catalysts in the presence of biodiesel ash species. *Fuel*, **10**,**6**,234-240.
- 19-Gomaa, M. M., Alimin, A. J., & Kamarudin, K. A. (2011). The effect of EGR rates on NOX and smoke emissions of an IDI diesel engine fuelled with Jatropha biodiesel blends. *International Journal of Energy & Environment*, **2**,**3**, 477-490
- 20-Future Energies (2003). "PORT HUENEME, Calif: U.S. Navy to Produce its Own Biodiesel: Future Energie: Thefuture of energy.
http://www1.eere.energy.gov/bioenergy/pdfs/mustard_hybrids.pdf Retrieved22-8-2014

21- "Newsvine - Ecofasa turns waste to biodiesel using bacteria". Lele.newsvine.com. 2008

<http://lele.newsvine.com/news/2008/10/18/2014473-ecofasa-turns-waste-to-biodiesel-using-bacteria>. Retrieved 2014

22-John Sheehan, Terri Dunahay, John Benemann, Paul Roessler (1998). A look back at the U.S. Department of Energy's Aquatic Species Program: Biodiesel from Algae. Close-out Report. United States Department of Energy. Retrieved 2014

23-Michael Briggs (2004). "Widescale Biodiesel Production from Algae". UNH Biodiesel Group (University of New Hampshire). Archived from the original on March 24, 2006.

24-"Valcent Products Inc (2006). Develops "Clean Green" Vertical Bio-Reactor". *Valcent Products*. 99, 2, 340

25- "Technology: High Yield Carbon Recycling". GreenFuel Technologies Corporation.

http://en.wikipedia.org/wiki/GreenFuel_Technologies_Corporation#References

Retrieved 2014

26-R. E. Teixeira (2012). "Energy-efficient extraction of fuel and chemical feedstocks from algae". *Green Chemistry* 14 ,2.: 419–427. doi:10.1039/C2GC16225C

27-"Pongamia Factsheet

<http://www.cilr.uq.edu.au/UserImages/File/factsheets/Pongamia%20Binder1.pdf>.

Retrieved 2014

28- B.N. Divakara, H.D. Upadhyaya, S.P. Wani, C.L. Laxmipathi Gowda (2010). "Biology and genetic improvement of *Jatropha curcas* L.: A review". *Applied Energy* 87, 3, 732–742. doi:10.1016/j.apenergy.2009.07.013.

29- Biofuels Digest (2011). "Jatropha blooms again: SG Biofuels secures 250K acres for hybrids". Biofuels Digest. [http://www.biofuelsdigest.com/bdigest2011/05/16/jatropha-blooms-again-sg-biofuels-secures-250k-acres-for-hybrids//](http://www.biofuelsdigest.com/bdigest2011/05/16/jatropha-blooms-again-sg-biofuels-secures-250k-acres-for-hybrids/)

Retrieved.2014

- 30- SG Biofuels (2012). "Jmax Hybrid Seeds". SG Biofuels. <http://www.sgfuel.com/pages/hybrid-seeds-and-services/jMax-hybrid-seeds.php> Retrieved 31-8-2014 .
- 31-Plant Research International (2012). "JATROPT (Jatropha curcas): Applied and technical research into plant properties". Plant Research International. Retrieved 22-8-2014
- 32- Biodiesel Magazine (2011). "Energy Farming Methods Mature, Improve". Biodiesel Magazine. <http://www.biodieselmagazine.com/articles/7743/energy-farming-methods-mature-improve> Retrieved 23-8-2014
- 33-Sergeeva, Y. E.; Galanina, L. A.; Andrianova, D. A.; Feofilova, E. P. (2008). "Lipids of filamentous fungi as a material for producing biodiesel fuel". *Applied Biochemistry and Microbiology* 44 (5): 523.
- 34- Strobel, G.; Knighton, B.; Kluck, K.; Ren, Y.; Livinghouse, T.; Griffin, M.; Spakowicz, D.; Sears, J. (2008). "The production of myco-diesel hydrocarbons and their derivatives by the endophytic fungus *Gliocladium roseum* (NRRL 50072)". *Microbiology* 154 , **11**,: 3319–3328. doi:10.1099/mic.0.2008/022186-0. PMID 18957585.
- 35- Henry Fountain (2008). "Diesel made Simply From Coffee Grounds". *New York Times*. **10**, 17-19.
- 36-Irving, P. M.; Pickles, J. S. (2007) Operational Requirements for a Multi-fuel Processor that Generates Hydrogen from Bio- and Petroleum-Based Fuels for Both SOFC and PEM Fuel Cells. *ECS Transactions*, **5**, 665-671
- 37-Park, G.; Seo, D. J.; Park, S.; Yoon, Y.; Kim, C.; Yoon (2004), W. Development of microchannel methanol steam reformer. *Chem. Eng.* , **10,1**, 87-92
- 38-Xuan, J.; Leung, M. K. H.; Leung, D. Y. C.; Ni, (2009) M. A review of biomass-derived fuel processors for fuel cell systems. *Renewable and Sustainable Energy Reviews*, **13**, 1301-1313.

39-Elamin, H.M.,(1989) ,*Sudan Acacias*, the publishing Section Information Department ,Forest Research Institute ,Khartoum .

40--Elamin, H.M.,(1990) ,*Trees and shrubs of the Sudan* ,Ithaca press Exeter, Sudan.

41-Glicksman, M.,(1969) Gum technology in the food industry, Ithaca press ,New York.

42-Khalil, S.K.W. & Elkheir, Y.M. (1975). “Dimethyltryptamine from *the leaves of certain Acacia species of Northern Sudan.*” *Lloydia* 38, **3**:176-177