

# **Chapter one**

## **1. Introduction and literature review**

### **1.1 Introduction**

#### **1.1.1 Renewable energy**

Renewable energy comes from natural sources (Malkivia and Pyh, 2002). Most renewable energy comes either directly or indirectly from the Sun. Solar energy is used for different purposes. In home solar energy is used to generate electricity, it is also used for commercial and industrial purposes (Malkivia and Pyh, 2002). The advantage of using renewable resources is that they are distributed over a wide geographical area, ensuring that developing regions have access to electricity generation at a stable cost for the long-term future. The sun's heat also drives the winds, whose energy, is captured with wind turbines. Then, the winds and the sun's heat cause water to evaporate. When this water vapor turns into rain or snow and flows downhill into rivers or streams, its energy can be captured using hydroelectric power (Tieten and Lewise, 2000). Renewable energy sources covered different locations, these resources are renewed through natural processes (Booth, 1998).

##### **1.1.1.1 Solar energy**

Solar Energy has many applications, the solar energy falling on the earth's continents is more than 200 times the total annual commercial energy currently being used by humans (Nada and Alrikabi, 2014). The government started solar power adoption with subsidies. A consumer who installs a solar panel array on a house can sell surplus energy to local utilities. The solar panel cost, reduced to 50%, which would make solar powered electricity cost comparable with other types of fuel, is possible within the next decade (Nada and Alrikabi, 2014). Solar Energy can be classified as two types. Passive solar and active solar.

Passive solar energy is making direct and indirect use of thermal energies from the sun. Indirect use of energy is possible only in buildings (or) structures.

A southern exposure of a building guarantees the maximum exposure of the sun's rays. Special metal leaf covering over windows and roofs can block out the sun during the summer months. Special thermal solar collectors can circulate water through the collection unit that collect the sun's thermal energy for the purpose of heating the water for use (Nada and Alrikabi, 2014).

Active Solar Energy is the use of the sun's electromagnetic radiation in generating electrical energy. Generally semiconductor silicon boron solar chips are used for this. The problem of these chips is one that they have low efficiency ratio and can only be used in supplying Energy needs of small devices (i.e. calculators, watches, radio etc.) (Nada and Alrikabi, 2014).

The main source of energy which applicable in Sudan for rural suburbs is solar energy, and Northern State has been considered as one of the best parts of the Sudan for exploiting solar energy (Asim, 2016).

Solar energy applications can be divided into two main categories: solar thermal application and photovoltaic technologies (PV). Solar thermal is a technology where the heat from solar energy is harnessed for heating purposes, while photovoltaic is a technology where arrays of cells which contain solar photovoltaic material convert the solar radiation into direct, current, electricity. PV technologies, it is seem to be like one of the solar energy technologies, in Northern State (Sudan) and provided a baseline research on the specific applications to assess the appropriateness of these technologies, and to find out the elements of sustainability within the introduced technologies (Asim, 2016).

### **1.1.1.2 Wind energy**

Wind, ultimately driven by atmospheric air, is just another way of collecting Energy. Sun also heats the atmosphere, which produces wind. It works on cloudy

days and rainy season also. In recent years, the growth of capacity to generate electricity from wind energy has been extremely rapid, to the degree that wind energy reduces the need for electricity generation using other sources of energy, it can reduce the adverse environmental impacts of those sources, such as production of atmospheric and water pollution, including greenhouse gases; production of nuclear wastes; degradation of landscapes due to mining activity; and damming of rivers (Wolsink, 2000). The location of wind turbines is a very important factor, which influences the performance of the machine. The windmills are generally located at the top of a tower to heights approximately 30 m. To avoid turbulence from one turbine affecting the wind flow at others it is located at 5-15 times blades diameter. Windmills are working both in horizontal axis and vertical axis. The basic mechanics of the two systems are similar (Wolsink, 2000). Wind passing over the blades is converted in to mechanical power, which is fed through transmission to an electrical generator. Wind turbines will not work in winds below 13 km an hour. They work best where the wind speed averages 22 km an hour. The majority of wind turbines produced at the present time are horizontal axis turbine with three blades, 15-30 m diameter, producing 50-350 Kwatt of Electricity. Wind energy produces no air or water pollution, involves no toxic or hazardous substances, and poses no threat to public safety (Wolsink, 2000).

Generation of electricity by wind energy has the potential to reduce environmental impacts, because unlike generators that use fossil fuel, it does not result in the generation of atmospheric contaminants or thermal pollution, and it has been attractive to many governments, organizations, and individuals. But others have focused on adverse environmental impacts of wind-energy facilities, which include visual and other impacts on humans; and effects on Wind power is a relatively mature technology. It competes with other energy sources in terms of price, environmental effects and usability. With the exception of hydro power, wind power

is closer to commercial profitability than any of the other renewable sources, though improved project economy is a vital challenge for wind power (Reiche and Bechnerger, 2004). Wind energy is widely applicable because wind resources are available in most countries. Among the renewable energy technologies, wind energy is relatively mature and many countries have resolved cost and technology challenges (Wolsink, 2000).

Wind is clean, free, indigenous and inexhaustible. Wind turbines do not need any type of fuel, so there are no environmental risks or degradation from the exploration, extraction, transport, shipment, processing or disposal of fuel. Not only is generation produced with zero emissions of carbon dioxide (during the operational phase) but it also does not release toxic pollutants (for example mercury) or conventional air pollutants (for example smog-forming nitrogen dioxide and acid rain-forming sulphur dioxide) (Suaad, 2013). Wind energy projects must be located in accordance with the *Planning Act*, the regional plans, and the municipal plans. The regional plans provide general locations for wind projects and guidelines for integrating wind turbines with other land-uses. The municipal plans can include targets and desires related to wind energy and provide a more detailed basis for turbine location, number, height and appearance (Suaad, 2013). Wind energy is a clean and environmentally friendly technology that produces electricity. Its renewable character and the fact it does not pollute during the operational phase makes it one of the most promising energy systems for reducing environmental problems at both global and local levels (Suaad, 2013).

Wind energy plants are considered a green power technology because it has only minor impacts on the environment. Wind energy plants produce no air pollutants or greenhouse gases (Suaad, 2013).

Wind energy is an ideal renewable energy because:

- It is a pollution-free, infinitely sustainable form of energy

- It doesn't require fuel
- It doesn't create greenhouse gases
- It doesn't produce toxic or radioactive waste

Any means of energy production impacts the environment in some way, and wind energy is no different. Like every other energy technology, wind power plants do have some effects on the environment. Wind turbines cause virtually no emissions during their operation and very little during their manufacture, installation, maintenance and removal. Compared to the environmental impact of traditional energy sources, the environmental impact of wind power is relatively minor (Suaad, 2013).

Wind farms are often built on land that has already been impacted by land clearing. The vegetation clearing and ground disturbance required for wind farms is minimal compared to coal mines and coal-fired power stations (Suaad, 2013). If wind farms are decommissioned, the landscape can be returned to its previous condition (Suaad, 2013).

The major challenge to using wind as a source of power is that the wind is intermittent and it does not always blow when electricity is needed. Wind energy cannot be stored (unless batteries are used); and not all winds can be harnessed to meet the timing of electricity demands (Suaad, 2013).

Wind-energy projects can have a range of economic and fiscal impacts, both positive and negative. Some of those impacts are experienced at the national or regional level; these involve, and for example, tax credits and other monetary incentives to encourage wind-energy production, as well as effects of wind energy on regional energy pricing (Suaad, 2013).

### **1.1.1.3 Biomass energy**

Bioenergy is beginning to gain importance in the global fight to prevent climate change. Biomass is the most important source for energy production

supplied by agriculture. Effective harnessing of bio-energy can energize entire rural milieu in a country like India where nature offers various types of biomass. This energy is also available in the form of biodegradable waste, which is the rejected component of available biomass (Popular Mechanics Magazine, 2005).

Biomass energy refers to fuels made from plants and animal wastes. The Biomass resource is, organic matter in which the energy of sunlight is stored in chemical bonds. When the bonds between carbon, hydrogen and oxygen molecules are broken by digestion, combustion (or) decomposition these substances release stored energy. Biomass energy is generated when organic matter is converted to energy. In alcohol fermentation, the starch in organic matter is converted to sugar by heating. This sugar is then fermented and finally ethanol is distilled and then blended with another fuel. An aerobic digestion converts biomass, especially waste product such as municipal solid waste and market waste. In this process, bacteria breakdown the organic material in the absence of oxygen and produce methane and carbon dioxide. Bioconversion is a nonpolluting, environmentally feasible and cost effective process (Time Magazine, 2005). The effluent and digester residues are rich in nitrogen and phosphorus, which can be recycled back to the soil as a fertilizer (Venkataraman and Elango, 2005). This method can derive 70% of the energy. The biomass is mixed with water and stored in an airtight tank. The organic wastes (Municipal Solid Waste) are collected separately and dried by natural method and shredded to the maximum particle size of 2–4 mm. This was stored in a plastic container at room temperature and used during all anaerobic digestion treatment. Domestic sewage was collected from a college campus before disposal. It was used in all anaerobic digestion experiment for diluting the feedstock to achieve the required total solids concentration for the present investigation. Experiments were carried out in 5 lit. Capacity batch type reactor operating in semi continuous mode with daily feeding. The digester was operated at room temperature at a constant hydraulic retention time

of 25 days with different organic loading rate. To start with, the digester was initiated by charging with 2.75 lit. of feed stocks (2%) along with 2 lit. of feed sludge. The digester was maintained anaerobic ally and stabilization was to take place for two weeks. During this stabilization period, pH was maintained in the range of 6.5 to 7.5 by adding sodium hydroxide. The pH and gas production were measured every day. It was found that the maximum biogas production is 0.36m<sup>3</sup>/kg of VS added/day at the optimum organic loading rate of 2.9 kg (Venkataraman and Elango, 2005).

#### **1.1.1.4 Hydro-electrical energy**

When climate change, global air temperature will increase, considerable regional impacts on the availability of water resources will occur (Schaepli *et al.*, 2007), which affect water users, water suppliers and water management structures. Hydropower has a large world's total electric energy generation in 2008 (Schaepli *et al.*, 2007) following the fossil energy resources carbon, mineral oil and natural gas. In regions with high precipitation rates and steep elevation gradients, like the European Alps, hydropower represents the main electric energy supply. Alpine countries such as Austria and Switzerland supply over the half of their electric energy mix with hydropower. In Austria, 62% of the internal gross electricity supply was produced by hydropower for the year 2009 and in Switzerland 56.5% for the year 2011 (Schaepli *et al.*, 2007). Moreover, recent significant worldwide increases in hydropower capacity are projected, whereby, the capacity growth in 2008 was second only to wind power (Schaepli *et al.*, 2007). The future development of hydroelectric power generation and its sensitivity to climate change is a relevant and prevailing issue (Schaepli *et al.*, 2007). Hydropower effect by climate change and the source of hydropower type. Whereas accumulation hydropower production is rather robust to climate variability due to the possibility of adaptation in storage management strategy, runoff-river power plants are directly affected by climate change impacts on runoff in its quantity and seasonality. Regarding reservoir power

plants, production strategies can be modified by taking advantage of the reservoir storage volume and adapting them to climate change effects and possible future changes in electricity demand. However, adaptation is only possible to a certain degree, because they will also be affected by changes in the mean annual runoff and only have limited elasticity in their management plans due to a seasonal runoff shift. Hydropower as a renewable and sustainable electric energy provider is closely linked to the hydrological situation of a certain region. Hydroelectric power generation depends largely on the regional catchment-based water balance and reacts sensitively to changes of the hydrological cycle in respect to water quantity and seasonality. Seasonal and quantitative changes in precipitation and evapotranspiration lead to inter-annual changes in runoff and hydrological storage, e.g., soil water content, snow cover and glaciers as well as their mean annual amount. Moreover, hydrological periodicities of low-flows and floods as well as the snow and ice storage, especially in mountainous areas, play an important role for runoff generation. When climate change conditions diverse changes of the mentioned water balance components are expected for the European Alps in the next decades, which are considered by several recent studies (Beniston *et al.*, 2011; Blöschl *et al.*, 2011; Klein *et al.*, 2011; Dobler *et al.*, 2010; Weber *et al.*, 2010; Weber *et al.*, 2009; Weingartner *et al.*, 2007; Horton *et al.*, 2006; Beniston, 2005; Zierl and Bugmann, 2005; Beniston, 2003; Viviroli *et al.*, 2003; Arnell, 1999). The hydrological changes can be expected to consist of are considerable changes in seasonal precipitation patterns indicating an increase in winter and a decrease in summer precipitation, a general increase of mean annual evapotranspiration, a decrease in mean annual runoff and seasonal changes of runoff regimes as well as a decrease of the snow and ice storage. Regarding runoff regimes, a future decrease in snow storage and therefore also in snow-melt leads to an increasing pluvial character until 2060 for the whole Upper Danube basin (Horton *et al.*, 2006).



The future start of the snowmelt period will be earlier in the year leading to a shift of the hydrological regime and of the seasonal runoff peak. Only in the glaciated alpine head-watersheds, changes of the ice storage play a considerable role (Weber *et al.*, 2010). As analyzed in various mountainous catchments, the latter undergo a transition from an ice-melt dominated runoff regime in the past to a more snow-melt dominated regime in the future with a significant shift of the runoff peak from summer to spring (Weber *et al.*, 2010; Weber *et al.*, 2009; Horton *et al.*, 2006; Huss *et al.*, 2010; Braun *et al.*, 2000).

Regarding research on future impacts on hydropower, most existing studies analyse the future development of the water cycle in terms of runoff and project changes to the future hydroelectric power generation. Various studies show a mean annual decline of runoff as well as seasonal runoff changes for different regions of the European Alps thus forecasting a future reduction of the mean annual hydroelectric power generation (Schaefli *et al.*, 2007; Blöschl *et al.*, 2011; Stanzel and Nachtnebel, 2010; Kuhn and Olefs, 2007; Lehner *et al.*, 2005, Piot, 2005). Besides for the European Alps, studies on climate change impacts on hydropower were carried out also for other regions of the world. For example, regarding the western U.S., several studies (Madani and Lund, 2010; Payne *et al.*, 2004; Vicuna and Dracup, 2007; Christensen *et al.*, 2004) came to similar findings in their respective region, showing a future decline in mean annual hydroelectric power generation and a seasonal shift due to changes of the hydrological regime. Regarding the European Alps, Schaefli *et al.* (2007) showed a decline in runoff and subsequent hydroelectric power generation for the time period 2070–2099 in a single highly glaciated catchment of a reservoir power plant in Switzerland which was mainly triggered by a decrease in precipitation, glacier retreat and an increase in evapotranspiration. Further, Stanzel and Nachtnebel (Stanzel and Nachtnebel, 2010) estimated the changes of the water balance and attributed hydroelectric power generation for the entire Austrian

territory using hydrological model outputs resulting in a decrease of 6 to 15% depending on the climate scenario for the time period 2025 to 2075. Due to climate change impacts on seasonal water availability and runoff regimes, an increase in hydroelectric power generation was observed in the winter, whereas a decrease could be found in the summer. Another recently published Austrian study (Blöschl *et al.*, 2011) confirms the shift from summer to winter production, but shows only small mean annual changes until 2050. Nonetheless, most of the studies do not directly model the changes of hydropower under altered climate conditions but rather try to assign it to altered runoff conditions (Blöschl *et al.*, 2011).

### **1.1.2 Biodiesel**

Interest in biodiesel is continuing to increase around the whole world. This is motivated primarily by concerns about greenhouse gas (GHG) emissions and global climate change, as well as the desire for renewable/sustainable energy sources, and an interest in developing domestic and more secure fuel supplies. Biodiesel is simple to use in compression ignition diesel engines with few or no modifications. Biodiesel is a renewable diesel replacement fuel that is manufactured from domestically produced oils or animal fats (Zhang *et al.*, 2003). To manufacture biodiesel, these fats and oils are chemically reacted with a short chain alcohol (such as methanol) and a catalyst to produce biodiesel and a glycerin co-product. Biodiesel can be used alone or blended with petroleum diesel in any proportion (Zhang *et al.*, 2003). Biodiesel can be legally blended with petroleum diesel in any percentage (Blanco-Canqui and Lal, 2007). Biodiesel has been registered with the U.S. EPA as a fuel and a fuel additive. Biodiesel is a fuel designed as a blend stock for use in blending with petroleum diesel fuel. It is not intended for use with gasoline. Biodiesel has been proven to reduce the emissions of hydrocarbons, carbon monoxide and particulates when used alone or with blends that include petroleum diesel. Biodiesel has excellent lubricity properties and is typically low in sulfur content, thus meeting

the needs of the EPA and new generation fuels (Blanco-Canqui and Lal, 2007). Biodiesel also could be defined as a fuel that contains mono-alkyl esters of long chain fatty acids derived from vegetable oils or animal fats (Vicente *et al.*, 2007). It showed similarity to physico-chemical properties of conventional fossil fuel (Pasqualino *et al.*, 2006).

Vegetable oils showed limitation as fuel in diesel engines due to two major reasons (high viscosity and poor volatility). Converting of biodiesel is a good solution to reduce the viscosity of vegetable oils (Paugazhabadivu and Jeyachandran, 2005). More than 350 crops have been studied, only sunflower, safflower, soybean, cotton seed, rapeseed, and peanut oils are considered as potential alternative fuels for diesel engines (Demirbas, 2007).

Sunflower is an important crop for biodiesel production (Niotou *et al.*, 2008). The higher cost of solid vegetable oil effects on the production cost of biodiesel (Hubera *et al.*, 2007). The pervious studies showed that biodiesel could be obtained by transesterification procedure (Aranda *et al.*, 2007) for the higher content of fatty acids and water (Piyanuch and Sasiwimol, 2009). Today researches use heterogeneous catalysts to decrease the processing costs (Trakarnpruk and Porntangjitlikit, 2008).

### **1.1.3 Baobab seed (*Adansonia digitata* L.)**

*Adansonia digitata* Fig 1.1 belongs to Bombacaceae family, the bombax or kapok family. African baobab also known as dead rat tree, Ethiopian sour gourd, Judas's bag, lemonade tree, monkey bread tree, monkey tamarind, Senegal calabash, and upside down tree, there are 8 species of *Adansonia* genus. *Adansonia digitata* a curious shaped, medium sized, deciduous tree (Ernest, 2012). Native to tropical Africa, baobab trees are bizarre in appearance with grotesquely swollen trunks the tree is usually massive, with a barrel like trunks. That may reach a diameter of 9 meter; few trees are tall as 25 meter (Kamatou and Vermaak, 2011). Baobab

generally produce leaves during the rainy season and shed their foliage during the dry season to reduce moisture loss, the tree produces large white flowers these hang down on long stalks. Fruit of the baobab Fig 1.2 large gourd like with velvety skin also hang down by long stalks. Leaves and fruits Fig 1.3 are eaten, commonly used as medicine (Kamatou and Vermaak, 2011). Phytochemical investigation revealed the presence of flavonoids, phytosterols, amino acids, fatty acids, vitamins and minerals. It is used in scurvy related diseases, laxative purpose. anti-diabetic, anti-diarrhoeal, anti- trypanosomal activities up to 21 meter in height and spreading branches, bark – smooth grayish, often with purplish tinge (or) brown, leaves digitate, leaflets 3 in young plants 5(or) 7 in older plants. 5 cm×12.5cm obviate oblong (or) lanceolate; flowers solitary, one of the longest lived trees of the world. It can tolerate well high temperature up to 40-42C. The tender roots, tubers, twigs, fruits, seeds, leaves and flowers are all edible and they are common ingredients in traditional dishes in rural areas in Africa (Ernest, 2012).



**Figure (1.1): *Adansonia digitata***



**Figure (1.2) Baobab pulp**



**Figure (1.3): Baobab seeds**

### 1.1.3.1 Scientific classification of *Adansonia digitata*

Botanical name :	<i>Adansonia digitata</i>
Family :	Bombacaceae
Kingdom :	Plantae
Subkingdom :	Viridiplantae
Infra kingdom :	Streptophyta
Division :	Tacheophyta
Sub-division :	Spermatophyte
Infradivision :	Angiosperm
Class :	Magnoliopsida
Super order :	Rosanae
Order :	Malvaless
Genus :	Adansonia
Species :	<i>Adansonia digitata</i> - baobab ( <a href="http://www.theplantlist.org/tpl1.1/record/kew-2621135">www.theplantlist.org/tpl1.1/record/kew-2621135</a> )

### **1.1.3.2 Distribution and habitat**

Baobab found in areas of south Africa, Botswana, Namibia, Mozambique and other tropical African countries where suitable habitat occurs. It grows in various parts of India chiefly in Bombay, Anthra, Bihar, utter Pradesh, Gujarat, Coromandel Coast and Ceylon. *Adansonia* is regarded as the “Queen of all carbon storage trees” (Nadkarni, 2009).

In Sudan the natural distribution of baobabs are in the southern part of the country. They thrive on sandy and rocky soils, from the short-grass savannah to the deciduous savannah woodlands. They are also common on mountain slopes such as the Jebel ed Dair in central Sudan, in the Nuba Mountains. In the eastern foothills of Jebel Marra, baobabs are known to occur Along wadis and in depressions, where water collects during rainy seasons, baobabs are found even in the very dry Northern parts of Darfur and Kordofan (Gebauer *et al.*, 2016).

### **1.1.3.3 Uses**

*Adansonia digitata* is one of the largest and long lived trees in the world. It is evident that the baobab is a nutritional, medicinal resource. It is a tree that can provide food, water, shelter and relief from sickness. Every part of the plant reported to be useful (Donaties *et al.*, 2011). The baobab fruit pulp which is primarily used as drinks and licked in raw form has been reported to provide both soluble and insoluble fibres which constitute about 50grams/100grams of the pulp (Adekunie *et al.*, 2013). The global demand for baobab has increased dramatically as more sectors such as cosmetic industry and used in pharmaceutical industry due to its fatty acid content known to have beneficial effects when applied on the skin (Donaties *et al.*, 2011). Baobab fruit pulp has been approved by statutory bodies for use in certain nutritional products. It is certain that commercialization of baobab products (seed oil. Fruit pulp) has increased especially after the FDA, EU have recognized the fruit pulp as a

food supplement. Numerous studies on the biological activities of baobab have been conducted with promising results (Donaties *et al.*, 2011). Including anti-inflammatory, analgesic, anti-pyretic, antioxidant, anti-viral activity and anti-diarrhea (Donaties *et al.*, 2011).

## **1.2 Literature review**

### **1.2.1 Biodiesel blend**

Biodiesel is simple to use in compression ignition diesel engines with few or no modifications. In addition, it can be blended at any level with petroleum diesel to create a biodiesel-diesel blend. In recent years, several countries have embarked on legislative and/or regulatory pathways that encourage the increased use of biodiesel fuel as a diesel fuel alternative.

Biodiesel, a promising oxygenated fuel generated from natural and renewable sources, is a fuel comprised of mono alkyl esters of long-chain fatty acids derived from renewable feed stocks. It is increasingly being examined as a potential substitute for conventional high-pollutant petroleum fuels because it is a biodegradable, non-toxic, and it relatively clean-burning fuel. Biodiesel can reduce some of the exhaust emissions compared to petroleum-based diesel when burned, whether used in pure form or blended with petroleum diesel. These reductions depend on the type of biofuel and its percentage in blends with petroleum diesel fuel (Ghazali *et al.*, 2015). Furthermore, it does not contribute to a net rise in the level of carbon dioxide in the atmosphere and minimizes the intensity of the greenhouse effect (Rodrigues *et al.*, 2012). Biodiesel is also better than diesel in terms of aromatic content and biodegradability (Kumar and Chauhan, 2013).

A high oil yield of any feedstock is necessary for ensuring a large production scale at cheap prices (Lam *et al.*, 2009). Biodiesel can be utilized neat or as a blend with

diesel fuel to reduce exhaust gas emissions (Atabani *et al.*, 2012). The high viscosity can lead to larger droplet size, poor vaporization and narrow injection spray angle.

The fuel density is also an important parameter, as fuel injection systems measure fuel by volume and thus the engine output power is influenced by changes in density due to the different injected fuel masses (Imtenan *et al.*, 2014). On the other hand, the energy content of the fuel has a direct influence on the engine power output and the usage of fuel with a lower energy content causes lower engine speed and power (Devaraj *et al.*, 2015). Furthermore, many researchers have focused on diesel-biodiesel blends which are considered as a viable fuel at low blending ratios (Moon *et al.*, 2010). At present, concern about environmental regulations has been the major reason to look for alternative fuels. The use of blended biodiesel-diesel fuel has presented a promising alternative in the world which is limited to low blending ratio (up to 20%).

Fuel additives are the most viable option introduced to improve fuel and blend properties Tables 1.1 and 1.2 at high blending ratio. However the utilization of these additives is restricted by their economic feasibility, toxicity and the properties of blended fuels (Qi *et al.*, 2011; Rakopoulos *et al.*, 2014; Rashedul *et al.*, 2014).



**Table (1.1): ASTM D 6751-15C Biodiesel Specification**

<b>Property</b>	<b>Test method</b>	<b>Specification</b>
Sulfur, % mass	ASTM D 5453	Max. 0.0015 <sup>a</sup> Max. 0.050 <sup>b</sup>
Cold soak filterability	ASTM D 7501	max. 200 seconds
Monoglyceride % mass	ASTM D 6584	max. 0.4
Ca and Mg (ppm)	EN 14538	max. 5
Flash point, C	ASTM D 93	min. 93
Water and sediment, % volume	ASTM D 2709	max. 0.050 % volume
Kinematic viscosity (40 C)	ASTM D 445	1.9 – 6.0 mm <sup>2</sup>
Sulfate ash, % mass	ASTM D 874	max. 0.02
Copper strip corrosion	ASTM D 130	max. No. 3
Cetane number	ASTM D 613	47 min
Cloud point, C	ASTM D 2500	Report <sup>a</sup>
Carbon residue, % mass	ASTM D 4530	max. 0.05
Acid number, mg KOH/g	ASTM D 664	max. 0.5
Free glycerin, % mass	ASTM D 6584	max. 0.02
Total glycerin, % mass	ASTM D 6584	max. 0.24
Phosphorus, ppm	ASTM D 4951	max. 10
Distillation temperature, 90 % recovered, C	ASTM D 1160	max. 360
Sodium and Potassium combined, ppm	EN 14538	max. 5
Oxidative stability, hours	EN 15751	min. 3

a/ S 15 grade. b/ S500 grade

**Table (1.2): ASTM D 7467 Blend specification Table**

Property	Test Method	Grade		
		B6 to B20 S15	B6 to B20 S500 <sup>A</sup>	B6 to B20 S5000 <sup>B</sup>
Acid Number, mg KOH/g, max	D664	0.3	0.3	0.3
Viscosity, mm <sup>2</sup> /s at 40°C	D445	1.9-4.1 <sup>C</sup>	1.9-4.1 <sup>C</sup>	1.9- 4.1 <sup>C</sup>
Flash Point, C, min	D93	52 <sup>D</sup>	52 <sup>D</sup>	52 <sup>D</sup>
Cloud Point, C, max or LTFT/CFPP, °C, max	D2500, D4539, D6371	E	E	E
Sulfur Content, (µg/g)	D5453	15	...	...
mass %, max	D2622	...	0.05	...
mass %, max	D129	...	...	0.50
Distillation Temperature, C, 90% vol recovered, max	D86	343	343	343
Ramsbottom Carbon Residue on 10% bottoms, mass %, max	D524	0.35	0.35	0.35
Cetane Number, min	D613 <sup>F</sup>	40 <sup>G</sup>	40 <sup>G</sup>	40 <sup>G</sup>
(1) Cetane index, min.	D976-80 <sup>H</sup>			
(2) Aromaticity, %vol, max	D1319-03 <sup>H</sup>	35	35	.....
Ash Content, mass%, max	D482	0.01	0.01	0.01
Water and Sediment, volume%, max	D2709	0.05	0.05	0.05
Copper Corrosion	D130	No. 3	No. 3	No. 3
Biodiesel Content, % (V/V)	D7371	6. - 20.	6. - 20.	6. - 20.

Oxidation Stability, hours, min	EN 15751	6	6	6
Lubricity, HFRR at 60°C, micron (µm), max	D6079	520 <sup>I</sup>	520 <sup>I</sup>	520 <sup>I</sup>

<sup>A</sup> Under United States of America regulations, if Grades B6-20 S500 are sold for tax exempt purposes then, at, or beyond terminal storage tanks, they are required by 26 CFR Part 48 to contain the dye Solvent Red 164 at a concentration spectrally equivalent to 3.9 lb per thousand barrels of the solid dye standard Solvent Red 164, or the tax must be collected.

<sup>B</sup> Under United States of America regulations, Grades B6-20 S5000 are required by 40 CFR part 80 to contain a sufficient amount of the dye Solvent Red 164 so its presence is visually apparent. At or beyond terminal storage tanks, they are required by 26 CFR Part 48 to contain the dye Solvent Red 164 at a concentration spectrally equivalent to 3.9 lb per thousand barrels of the solid dye standard Solvent Red 26.

<sup>C</sup> If Grade No. 1-D or blends of Grade No. 1-D and Grade No. 2-D diesel fuel are used, the minimum viscosity shall be 1.3 mm<sup>2</sup>/s.

<sup>D</sup> If Grade No. 1-D or blends of Grade No. 1-D and Grade No. 2-D diesel fuel are used, or a cloud point of less than -12C is specified, the minimum flash point shall be 38C.

<sup>E</sup> It is unrealistic to specify low temperature properties that will ensure satisfactory operation at all ambient conditions. In general, cloud point (or wax appearance point) Low Temperature Flow Test, and Cold Filter Plugging Point Test may be useful to estimate vehicle low temperature operability limits but their use with B6 to B20 has not been validated.

<sup>F</sup> Calculated cetane index approximation, Test Method D4737, is not applicable to biodiesel blends.

<sup>G</sup> Low ambient temperatures, as well as engine operation at high altitudes, may require the use of fuels with higher cetane ratings. If the diesel fuel is qualified under Table 1 of Specification D975 for cetane, it is not necessary to measure the cetane number of the blend. This is because the cetane number of the individual blend components will be at least 40, so the resulting blend will also be at least 40 cetane number.

<sup>H</sup> These test methods are specified in 40 CFR Part 80.

<sup>I</sup> If the diesel fuel is qualified under Table 1 of Specification D975 for lubricity, it is not necessary to measure the lubricity of the blend. This is because the lubricity of the individual blend components will be less than 520 micron (µm) so the resulting blend will also be less than 520 (µm).

## 1.2.1.1 Physicochemical properties of oil, biodiesel and blends

### 1.2.1.1.1 Kinematic viscosity

The viscosity is important for the estimation of optimum storage, handling, and operational conditions. Thus, the accurate determination of viscosity

is essential to many product specifications. So it is mandatory to determine the viscosity of vegetable oil especially when it will be used as fuel (Stephen, 2013).

#### **1.2.1.1.2 Density**

Density is a fundamental physical property that can be used in conjunction with other properties to characterize both the light and heavy fractions of petroleum and petroleum products. Determination of the density or relative density of petroleum and its products is necessary for the conversion of measured volumes to volumes at the standard temperature of 15°C (Stephen, 2013).

#### **1.2.1.1.3 Cloud point and pour point**

These are basic tests for fuels in winter and cold countries that can keep you running in cold weather (Stephen, 2013).

*Cloud point* is the temperature of a liquid sample when the smallest observable cluster of wax crystals first appears upon cooling under prescribed conditions. The color of the sample should be 3.5 and lower.

*Pour point* is the lowest temperature at which movement of the test specimen is observed under prescribed conditions of test.

#### **1.2.1.1.4 Acid number**

The acid number is used to determine the level of free fatty acids in oil or processing acids that may be present in the biodiesel or diesel fuel oil when produced, or those which form upon aging. Biodiesel blends with a high acid number have been shown to increase fueling system deposits and may increase the likelihood for corrosion (Stephen, 2013).

#### **1.2.1.1.5 Iodine number**

Is a degree of unsaturated bonds of fats and oils . If the iodine number is high that is the indicator of more C=C in the oil which will affect the engines performance (Stephen, 2013).

#### **1.2.1.1.6 Saponification number**

It expresses the amount of base that will react with 1 g of sample, this then gives an estimation of the amount of acid present in the oil sample, higher SV mean higher acid numbers and higher possibility of soap formation (Stephen, 2013).

#### **1.2.1.1.7 Calorific value**

This test method is especially useful for estimating the heat of combustion of burner and diesel fuels for which it is not usually critical to obtain very precise heat determinations (Stephen, 2013).

#### **1.2.1.1.8 Water content**

A Knowledge of water content of the oil or any raw materials is important in manufacturing, purchase or transfer for taking more precaution also it will help to determine the product quality and performance. Presence of water in the engines will causes corrosion for the internal parts (Stephen, 2013).

#### **1.2.1.1.9 Cetane number**

Cetane number is a measure of the ignition quality of the biodiesel fuel and influences combustion roughness (Stephen, 2013). The cetane number requirements depend on engine design, size, nature of speed and load variations, and on starting and atmospheric conditions. Increase in cetane number over values actually required does not materially improve engine performance (Stephen, 2013). Accordingly, the cetane number specified should be as low as possible to ensure maximum fuel availability (Stephen, 2013).

#### **1.2.1.1.10 Flash point**

The lowest temperature corrected to a barometric pressure of 101.3 kPa (760 mm Hg), at which application of an ignition source causes the vapors of a specimen of the biodiesel and blends sample to ignite under specified conditions of test. This test is important parameter for transporting, shipping and storing to provide the perfect condition for the cargo (Stephen, 2013).

#### **1.2.1.1.11 Copper Strip Corrosion**

The copper strip corrosion test is designed to assess the relative degree of corrosivity of biodiesel and blends in petroleum products (Stephen, 2013).

### **1.2.2 Oil extraction techniques**

There is a variety methods used for extraction of plant oil, with each method exhibiting certain advantages as determining the biological and physiochemical properties of the extracted oil. Oils are extracted only from the parts of seeds, fruits, kernels or germs.

#### **1.2.2.1 Mechanical pressing extraction**

The extraction of oil from seeds is accomplished by mechanical pressing which is the best technology with low cost compared to the other methods. Mechanical extraction of the oil is accomplished by exerting sufficient force on confined seed. Under this condition pressure is high enough to rupture the force oil from the seed to escape. Extraction is accomplished by compressing the material in container that has small perforations (Sukhdev *et al.*, 2008).

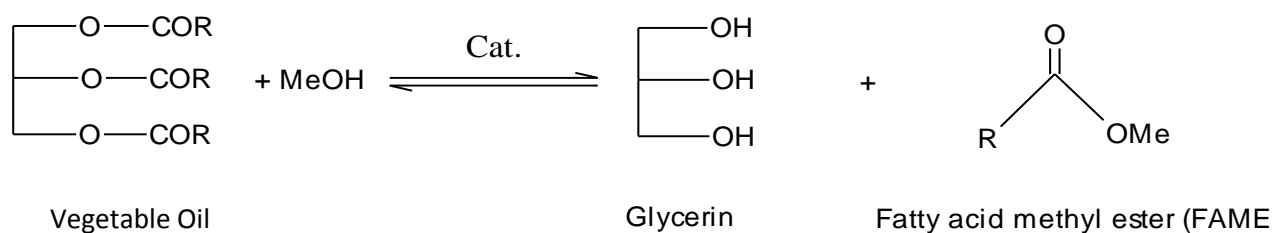
#### **1.2.2.2 Soxhlet extraction**

The plant seed which may contain many benefit compounds is extracted by using the Soxhlet extractor. The round-bottom distillation flask initially contained

an extraction solvent and it heated up. As the solvent vapour goes up to condenser, it condenses and accumulates inside the extractor (William, 2007).

### 1.2.3 Transesterification methods of Biodiesel production

Transesterification process Fig (1.4) is a conventional and the most common method for biodiesel production. In transesterification reaction homogeneous catalysts (alkali or acid) or heterogeneous catalysts can be used. The catalysts split the oil into glycerin and biodiesel and they could make production easier and faster (Barnard *et al.*, 2007).



**Figure (1.4): Biodiesel production via transesterification reaction**

In this method, fatty acid alkyl esters are produced by the reaction of triglycerides with an alcohol, especially ethanol or methanol, in the presence of alkali, acid or enzyme catalyst etc.

The sodium hydroxide or potassium hydroxide, which is dissolved in alcohol, is generally used as catalyst in transesterification reaction (Dube *et al.*, 2007). The products of the reaction are fatty acid methyl esters (FAMES), which is the biodiesel, and glycerin (Vicente *et al.*, 2004). Ethanol can be also used as alcohol instead of methanol. If ethanol is used, fatty acid ethyl ester (FAEE) is produced as product (Hanh *et al.*, 2009). Methyl ester rather than ethyl ester production was preferred, because methyl esters are the predominant product of commerce, and methanol is considerably cheaper than ethanol (Zhou and Boocock, 2003).

However, methanol usage has an important disadvantage, it is petroleum based produced.

Whereas ethanol can be produced from agricultural renewable resources, thereby attaining total independence from petroleum-based alcohols (Saifuddin and Chua, 2004). Ethanol is also preferred mostly in ethanol producing countries. Propanol and butanol have been also used as alcohols in biodiesel production (Encinar *et al.*, 2007).

Alkali-catalyzed transesterification proceeds much time faster than that catalyzed by an acid and it is the one most used commercially (Dube *et al.*, 2007; Singh *et al.*, 2006). The most commonly used alkali catalysts are NaOH, CH<sub>3</sub>ONa, and KOH (Vicente *et al.*, 2004). Potassium hydroxide (KOH) and sodium hydroxide (NaOH) flakes are inexpensive, easy to handle in transportation and storage, and are preferred by small producers. Alkyl oxide solutions of sodium methoxide or potassium methoxide in methanol, which are now commercially available, are the preferred catalysts for large continuous-flow production processes (Singh *et al.*, 2006).

For acid-catalyzed systems, sulfuric acid has been the most investigated catalyst, but other acids, such as HCl, BF<sub>3</sub>, H<sub>3</sub>PO<sub>4</sub>, and organic sulfonic acids, have also been used (Lotero *et al.*, 2005). But in alkali catalyzed method, glycerides and alcohol must be substantially anhydrous, otherwise it leads to saponification (Helwani *et al.*, 2009). Due to saponification the catalytic efficiency decreases, the separation of glycerol becomes difficult and it also causes gel formation (Helwani *et al.*, 2009). In homogeneous catalyzed reactions, separation of catalyst from the reaction mixture is hard and expensive. With this purpose, large amount of water is used to separate catalyst and product (Vyas *et al.*, 2010).

On the other hand, undesired by-product formation such as glycerin can be seen, the reaction lasts very long and energy consumption may be very high. Thus, researchers have focused on development of new biodiesel production methods and the



optimization of the processes (Sharma *et al.*, 2008). Hence, various processes such as supercritical process, microwave assisted method and ultrasound assisted method have been recently developed.

Alternative energy stimulants or non-classical energies have been used for many years to increase the reaction rate and to enhance the yield of particular reaction products (Nuechter *et al.*, 2000).

#### **1.2.4 Fatty acid profile of biodiesel**

Biodiesel is an alternative fuel consisting of alkyl esters of free fatty acids from vegetable oils or animals fats. The higher amounts of fatty acid compositions in the oils used as feedstock can influence quality of the biodiesel (Palligarnai and Vasudevan, 2008). In, commercial processors an acid-catalyzed esterification reactor is used to process excess free fatty acids prior to base-catalyzed transesterification (Palligarnai and Vasudevan, 2008).

The biodiesel that made by alkali-catalyzed (e.g., NaOH, KOH) transesterification with methanol has a short reaction time (Palligarnai and Vasudevan, 2008). The properties of a biodiesel fuel are influence by (component fatty esters include ignition quality, heat of combustion, cold flow, oxidative stability, viscosity and lubricity) (Gerhard, 2005).

#### **1.2.5 Gas emission and environmental effects**

Global warming, in fact is increase average of earth temperature around surface, the scientists research present during 100 years ago, the average of temperature near earth surface had increase (IEA, 2010). International group has announced in report about climate changes (IPCC) that is valid reference in field of climate changes and global warming effects "further of temperature increase that observed in the middle of 20 century, is due to greenhouse gases that human has produced" (IEA, 2010). The average of earth surface temperature has increase

between 1.1 to 6.4C. Scientist believes even if the amount of greenhouse gases (GHG) of the Earth's atmosphere remain stable, effects of it will be endure until end of third millennium (IEA, 2010). Furthermore, other things are effected into the global warming, there are melting of ice and the rising of sea level (Anomohanran, 2011; Joseph *et al.*, 2011). Many researchers studied the global environmental stability (Pragya *et al.*, 2012), they observed that, the change in the condition of earth climate influence to potential impact on agricultural production as it relates to the issues of soil and water effects (Kumar *et al.*, 2001). In urban areas, the electrical energy was conventionally provided using fossil fuels resources which can be conserved (Annette *et al.*, 2012).

Recently, energy is very important, it plays major roles in different human needs like water pumps, transport, light and other applications such as business, industry, commerce, and public services, such as modern healthcare, education, and communication, are highly dependent on access to energy services (Ellene *et al.*, 2010).

The lack of energy services are effected directly to many poverty indicators, such as infant mortality, illiteracy, and life expectancy (Demirbas, 2008).

### **1.2.6 Previous studies about biodiesel**

Research and development in the field of biofuels, in general, and biodiesel in particular are not new endeavours (Bala, 2005). However, they gained momentum in the last couple of decades due to the increasing economic concerns and environmental awareness about the use of petroleum derived fossil fuels (Bala, 2005).

Biodiesel is, gradually, becoming a vital issue due to the graving use fossil fuels and the urgent need to decrease the amounts of greenhouse gas emissions (Delshad *et al.*, 2010). Thus, energy concerns, growing environmental awareness and economic considerations are the major driving forces behind the worldwide direction towards

producing biofuel from bioresources (Ramayah *et al.*, 2012). Biodiesel is a better alternative compared to conventional diesel fuel (Cacciatore *et al.*, 2012). Bioenergy industry develop the economic in rural areas (Radics *et al.*, 2015). The majority of US farmers would use biodiesel if the prices were comparable to conventional diesel (Lahmann, 2005), whereas the American public agree that using biofuels is a good idea (Wegener and Kelly, 2008). According to Eurobarometer, in 2010 more than 70% of Europeans agreed that biodiesel should at least be encouraged, adding that they are even more optimistic about more sustainable biofuels (Gaskell *et al.*, 2010). Amigun *et al.*, (2011) reported that biodiesel production and its supply chain may be affected by personal, social, and institutional factors and beliefs within different communities in South Africa.

### **1.2.7 FTIR Infrared spectroscopy**

FT-IR is being employed as a modern analytical technique for detecting the conversion of biodiesel because it is a fast and easy detection method. Raw oils and the methyl esters are noted as fairly strong absorbers in the infrared region of the electromagnetic spectrum ( $1750\text{--}1760\text{ cm}^{-1}$ ). The wavelength of the carbonyl peak is a sign at ( $\sim 1744\text{ cm}^{-1}$ ) to monitor the progress of the reaction. Lin-vien *et al.*, (1991) studied this method to be effective in a known system but noted its limitation because it is not specific for the end product and there could be a number of interferences. This method is however, being used because spectral resolution is not needed for more specific analysis. They pointed out that the peak typical of the methyl ester ( $\text{OCH}_3$ ) at  $1436\text{ cm}^{-1}$  is very narrow and moves along the raw oil peak. These characteristics were noted to make the peak unattractive for monitoring the progress of the biodiesel reaction (Lin-vien *et al.*, 1991). However, they observed the peak measurement to give a direct indication of the attachment of the alkyl group of the alcohol with the fatty acids of the triglycerides but the peak is not influenced by the alkyl group ( $-\text{CH}_3$ ) (Lewis *et al.*, 2004). Ivanoiu and others performed a

comparative study on biodiesel synthesis from different vegetable oils and used infrared spectroscopy using KBr plates in the range of 4000-400  $\text{cm}^{-1}$ .

The ester carbonyl group stretching vibration at 1740  $\text{cm}^{-1}$  is shown by strong bands, esteric –COC vibration at 1171 and 1207  $\text{cm}^{-1}$  reveals medium intensity bands, and the presence of the  $(\text{CH}_2)_n$  group vibration band is seen at 724  $\text{cm}^{-1}$ . They observed the absence of a broad band at the 2500-3300  $\text{cm}^{-1}$  region which confirms the low moisture and free fatty acid content of the sample (Ivanoiu *et al.*, 2011).

### **1.2.8 Gas Chromatography (GC)**

Gas chromatography (GC), is a common type of chromatography used in analytical chemistry for separating and analyzing compounds that can be vaporized without decomposition. Typical uses of GC include testing the purity of a particular substance, or separating the different components of a mixture (the relative amounts of such components can also be determined). In some situations, GC may help in identifying a compound. In preparative chromatography, GC can be used to isolate pure compounds (Pavia *et al.*, 2006; Robert and Eugene, 2004).

In gas chromatography, the mobile phase (or "moving phase") is a carrier gas, usually an inert gas such as helium or an unreactive gas such as nitrogen. The stationary phase is a microscopic layer of liquid or polymer on an inert solid support, inside a piece of glass or metal tubing called a column (a homage to the fractionating column used in distillation). The instrument used to perform gas chromatography is called a gas chromatograph (or "aerograph", "gas separator").

The gaseous compounds being analyzed interact with the walls of the column, which is coated with a stationary phase. This causes each compound to elute at a different time, known as the retention time of the compound. The comparison of retention times is what gives GC its analytical usefulness (Pavia *et al.*, 2006).

Gas chromatography is in principle similar to column chromatography (as well as other forms of chromatography, such as HPLC, TLC), but has several notable differences. Firstly, the process of separating the compounds in a mixture is carried out between a liquid stationary phase and a gas mobile phase, whereas in column chromatography the stationary phase is a solid and the mobile phase is a liquid. (Hence the full name of the procedure is "Gas–liquid chromatography", referring to the mobile and stationary phases, respectively.) Secondly, the column through which the gas phase passes is located in an oven where the temperature of the gas can be controlled, whereas column chromatography (typically) has no such temperature control. Thirdly, the concentration of a compound in the gas phase is solely a function of the vapor pressure of the gas (Pavia *et al.*, 2006).

Gas chromatography is also similar to fractional distillation, since both processes separate the components of a mixture primarily based on boiling point (or vapor pressure) differences. However, fractional distillation is typically used to separate components of a mixture on a large scale, whereas GC can be used on a much smaller scale (i.e. micro scale) (Pavia *et al.*, 2006).

Gas chromatography is also sometimes known as vapor-phase chromatography (VPC), or gas–liquid partition chromatography (GLPC). These alternative names, as well as their respective abbreviations, are frequently used in scientific literature. Strictly speaking, GLPC is the most correct terminology, and is thus preferred by many authors (Robert and Eugene, 2004).

### **1.2.9 Atomic absorption spectroscopy (AAS)**

In AAS the absorption of resonant radiation by ground state atoms of the analyte is used as the analytical signal. Accordingly, a source delivering the resonant radiation of the analyte is required as well as an atom reservoir into which the analyte is introduced and atomized. The absorption of resonance radiation is highly selective

as well as very sensitive and thus, AAS became a powerful method of analysis, which is now used for trace elemental determinations in most analytical laboratories for a wide variety of applications (Settle, 1997).

Atomic absorption spectroscopy (AAS) is a spectroanalytical procedure for the quantitative determination of chemical elements employing the absorption of optical radiation (light) by free atoms in the gaseous state. In analytical chemistry the technique is used for determining the concentration of a particular element (the analyte) in a sample to be analyzed. AAS can be used to determine over 70 different elements in solution or directly in solid samples employed in pharmacology, biophysics and toxicology research (Settle, 1997).

Atomic absorption spectrometry was first used as an analytical technique, and the underlying principles were established in the second half of the 19<sup>th</sup> century by Robert Wilhelm Bunsen and Gustav Robert Kirchhoff, both professors at the University of Heidelberg, Germany (Settle, 1997).

The modern form of Atomic absorption spectroscopy (AAS) was largely developed during the 1950s by a team of Australian chemists. They were led by Sir Alan Walsh at the CSIRO (Commonwealth Scientific and Industrial Research Organization), Division of Chemical Physics, in Melbourne, Australia (Welz and Sperling, 1999).

A primary source is used which emits the element-specific radiation. Originally continuous sources were used and the primary radiation required was isolated with a high-resolution spectrometer (McCarthy *et al.*, 2012). However, owing to the low radiant densities of these sources, detector noise limitations were encountered or the spectral bandwidth was too large to obtain a sufficiently high sensitivity (McCarthy *et al.*, 2012). Indeed, as the width of atomic spectral lines at atmospheric pressure is of the order of 2 pm, one would need for a spectral line with  $\lambda = 400$  nm a practical

resolving power of 200000 in order to obtain primary radiation that was as narrow as the absorption profile. This is absolutely necessary to realize the full sensitivity and power of detection of AAS (McCarthy *et al.*, 2012).

Therefore, it is generally more attractive to use a source which emits possibly only a few and usually narrow atomic spectral lines. Then low-cost monochromators can be used to isolate the radiation. Accordingly, it was very soon found that using sources for which the physical widths of the emitted analyte lines are low is more attractive (Hergenroder and Niemax, 1988). This is necessary so as to obtain high absorbance. Indeed, when the bandwidth of the primary radiation is low with respect to the absorption profile of the line, a higher absorption results from a specific amount of analyte as compared with that for a broad primary signal. Primary radiation where narrow atomic lines are emitted is obtained with low-pressure discharges as realized in hollow cathode lamps (HCL) or low-pressure rf discharges (Hergenroder and Niemax, 1988).

Recently, however, the availability of narrowband and tunable laser sources, such as the diode lasers, has opened up new perspectives. Here only the analytical line is present and the use of a monochromator is superfluous. When tuning is applied the absorption profile can be scanned, which allows the dynamic range to be increased, as measurements are taken in the side-wings of the lines as well as at their maxima. Also, correction for non-element specific background absorption then becomes very easy, and switching from one element to another becomes feasible, certainly when several diode lasers are provided (Hergenroder and Niemax, 1988). The restriction, however, still lies in the laser sources due to the limited spectral range that can be covered at this moment and which only goes down to the green. However, a recent breakthrough reaching down to the 400 nm range has been achieved, which should increase the prospects of this approach (Hergenroder and Niemax, 1988).

In the present commercially available instrumentation, virtually always only line sources are used as primary sources, which generally leads to a high analytical sensitivity and power of detection as well as to a high dynamic range within which the Lambert–Beer law (Hergenroder and Niemax, 1988). Commercially available diode AAS systems already exist. A linear relationship between the absorption and the concentration can only apply when all radiation passing to the detector is absorbed to the same extent by the analyte atoms (the ideal case) (Hergenroder and Niemax, 1988). In a real case, the calibration curve displaying the relationship between the concentration and the absorption bends off towards the concentration axis, as a result of the presence of non-absorbed radiation. For a primary source emitting narrow lines (line widths being below 1/5 of those of the absorption lines) non-absorbed radiation mainly consists of contributions from non-absorbed lines of the cathode material or of the filler-gas that fall within the spectral bandwidth of the monochromator (Hergenroder and Niemax, 1988). Furthermore, at high concentrations a decrease in dissociation gives rise to lower absorbance and suppression in ionization leads to higher absorbance. Thus the calibration curve starts to bend towards the concentration axis and towards the absorption axis, respectively (Hergenroder and Niemax, 1988).

In AAS the analyte must be present in the atomic vapor state (Ng *et al.*, 1988). Therefore, the use of an atomizer is required. Both flames and furnaces are used and the appropriate methodologies are known as flames AAS and graphite furnace AAS, respectively (Ng *et al.*, 1988). The shape of the atomizer with respect to obtaining the highest possible atomic vapor cloud density is still an important field of research. To this aim, attempts can be made to increase the efficiency of the sample introduction device as well as to increase the residence time of the atomic vapor in the atomizer or to prevent a diffusion of the analyte out of the absorption volume



(Ng *et al.*, 1988). In order to achieve these aims, special methods of atomization have been developed, which are based on volatile compounds formation, as is done with the hydride technique (Ng *et al.*, 1988). AAS is generally used for the analysis of liquids and thus solids must first be brought into solution. Therefore, wet chemical decomposition methods are of use, but involve all the care that is normally required in trace analysis to prevent element losses or contamination and the according systematic errors. For direct solids analysis a few approaches also exist (Ng *et al.*, 1988).

### **1.2.10 Research objective**

- To study the chemical compositions of Baobab seeds.
- To extract Baobab oil using the technique which ensures a high yield.
- To convert oil to biodiesel by transesterification reaction.
- To blend the produced biodiesel with conventional diesel and ethanol in different portions.
- To study the effect of diesel-biodiesel and diesel-biodiesel-ethanol blends on physicochemical properties of Baobab biodiesel and compare these properties with ASTM standard.
- To examine the gases emission for blends in diesel engine.

## Chapter Two

### 2. Materials and Methods

#### 2.1 Materials

Dried seeds of baobab were collected (April, 2016), from research center of medicinal and aromatic plants in Khartoum, Sudan. Identification and authentication were performed and voucher specimens have been deposited in the herbarium of Medicinal and Aromatic Plant and Traditional Medicine Research Institute (MAPTMRI).

##### 2.1.1 Sample treatment

Samples were cleaned to remove dirt, sun-dried for three days and finally ground in an electric mill and stored in room temperature.



**Figure (2.1): Baobab seed cake**



**Figure (2.2): Electrical mill**

## **2.2 Methods**

### **2.2.1 Chemical extraction (Soxhlet extraction method)**

n-Hexane was used to extract oil from 1000 g of baobab seeds at 60°C for 8 hours. The remaining solvent was dried using rotatory evaporator.



**Figure (2.3): Soxhlet system**



**Figure (2.4): Rotary evaporator**

## **2.2.2 Proximate analysis of baobab seeds**

The moisture content, ash, crude fiber, crude protein, and fat contents were analyzed by AOAC methods

### **2.2.2.1 Determination of moisture content**

The moisture content determined by selecting two grams and added into a pre-dried aluminum dish, with a lid then placed in a temperature controlled oven at  $103\text{C} \pm 2$  overnight (about 8 hours). The moisture content was calculated as percentage of the original weight of the sample using the formula below (AOAC, 2008):

$$\text{Moisture content (\%)} = \frac{W_1 - W_2}{W_3} \times 100$$

Where:  $W_1$  = weight of dish + lid,  $W_2$  = weight of dish +lid + sample, and  $W_3$  = weight of dish +lid + sample after drying.

### **2.2.2.2 Determination of ash content**

Ash content was measured by weighting two grams and placed in muffle furnace at 600°C for 6hours. The sample was transferred to cooling room and then weighted and calculated using the formula below (AOAC, 2008):

$$\text{Ash content (\%)} = \frac{W_1 - W_2}{\text{Weight of sample}} \times 100$$

Where:  $W_1$ = weight of crucible with ash,  $W_2$ = weight of empty crucible.

### **2.2.2.3 Determination of crude fiber**

Crude fiber was measured by weighting two grams of fat free meals was treated successively with a boiling solution of  $H_2SO_4$  and KOH. The residue was separated by filtration, washed, dried, weighed and ashed at 500°C. The loss of the weight resulting from ashing corresponded the crude fiber in the sample (AOAC, 2008).

### **2.2.2.4 Determination of protein content**

Protein content was determined by using 0.2 g of defatted sample and weighed accurately into a micro-kjeldahl flask, 0.4g of catalyst mixture and 3.5 ml of concentrated sulphuric acid were added, the flask was then placed into the kjeldahl digestion unit for about 2 hours until a colorless digest solution was obtained. The flask was left to cool to room temperature. 20 ml of 40% sodium hydroxide solution were added to the digested solution and the mixture was heated.

The ammonia evolved was trapped into 10 ml of 2% boric acid solution, then titrated against 0.02 N hydrochloric acid using universal indicator. The total nitrogen and protein were calculated using the following formula (AOAC, 2008):

$$\text{Crude nitrogen (\%)} = \frac{\text{Volume of HCl} \times N \times 14 \times 100}{\text{Weight of sample} \times 1000}$$

$$\text{Crude nitrogen (\%)} = \text{Nitrogen (\%)} \times 6.25$$

Where: Nitrogen (%) = crude nitrogen, Protein (%) = crude protein, and N = normality of HCl.

14 = equivalent weight of nitrogen.

### 2.2.2.5 Determination of fat content

Fat content was assessed using two grams of samples which were extracted with hexane for 8 hours using Soxhlet apparatus. The solvent was evaporated and the remaining crude fat was determined using the following formula (AOAC, 2008):

$$\text{Fat (\%)} = \frac{W_2 - W_1}{\text{Weight of sample}} \times 100$$

Where:  $W_1$  = weight of empty flask,  $W_2$  = weight of flask with oil

### 2.2.3 Elemental Analysis

Accurately 2g of dry ashed sample and 5 ml of HCl 20% was added, a clear solution was obtained, the digest was allowed to cool and then standard solution prepared (Pearson and Dawson, 1981).



**Figure (2.5): Atomic Absorption Spectrometer**

## 2.2.4 Physicochemical characteristics of Baobab oil

ASTM (American Society for Testing and Materials) and Standard methods for the analysis of oils, fats and derivatives.

**Table (2.1): ASTM test methods and instrument of Baobab biodiesel and blends**

Test	Method	Instrument	Instrument Model
Density at 15°C (g/cm <sup>3</sup> )	ASTM D4052	Densitometer	DMA4500
Kinematic viscosity at 40C (cSt)	ASTM D445	Viscometer	LAUDA_A100
Calorific value (MJ kg <sup>-1</sup> )	calculation	Calculation	Calculation
Total Acid Number (mgKOH/g)	ASTM D974	Si analytic	484Titro plus
Cloud point (C)	ASTM D2500	Cloud and pour test cabinet	P592
Pour point (C)	ASTM D97	Cloud and pour test cabinet	P592
Flash point (C)	ASTM D93	STANHOPE-SETA	UK- 43-100-2
Copper Strip Corrosion (3 Hours at 100C)	ASTM D130	STANHOPE-SETA	15157-0T
Water Content (wt%)	AOCS Ca 2e-84	MITSUBISHI	Moisture meter CA-21

### 2.2.4.1 Oil content (%)

The total oil content of seeds was determined according to AOAC (2008). 5g of finely ground samples were accurately weighted in an empty thimble and was then plugged with a piece of cotton, n. hexane was poured into a pre-weighed round

bottomed flask. The Soxhlet apparatus was assembled and the sample was extracted for 8 hours using steam bath. After carefully dismantling the apparatus. The solvent was evaporated to dryness using a rotator evaporator. The oil content was calculated as percentage according to the following equation.

$$\text{Oil content \%} = \frac{\text{weight of oil extracted}}{\text{weight of sample}} \times 100$$

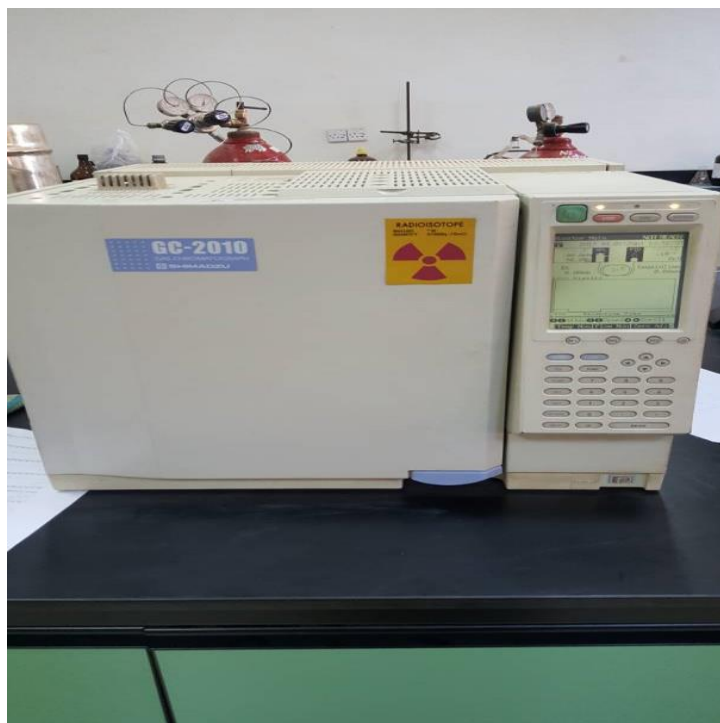
#### **2.2.4.2 Color**

Samples of oils were filtered through filter paper immediately before testing. An appropriate cell was filled with oil and placed in the tintometer near-by the window for light. The instrument was switched on and looked through the eye piece. The light yellow colour was observed (Pearson and Dawson, 1981).

#### **2.2.4.3 Free fatty acid**

The oil sample was mixed before weighing. Then the designated sample size weighed into an oil-sample bottle or Erlenmeyer flask; amount of hot, neutralized alcohol and 2 mL of indicator was added with vigorous shaking, the titration was made with alkali, permanent pink color was appearance of the same intensity as that of the neutralized alcohol before adding the sample. The color was persists for 30 s (ASTM, 2011). Fatty acid content of Baobab oil and biodiesel was determined using GC-2010 gas chromatograph Fig (2.6) (SHIMADZU). Capillary column DB-1 (30m×0.25mm×0.25mm). The detector temperature was programmed at 300°C with flow rate of 30.0 ml/min. The injection mode was split, the temperature was set at 250C, nitrogen and air were used as the carrier gas. The identification of the peaks Characteristic and Composition of Baobab seed Oil achieved by retention times by means of comparing them with authentic standards analyzed under the same conditions.





**Figure (2.6): Gas Chromatography**

#### **2.2.4.4 Density at 15C (g/cm<sup>3</sup>)**

A small volume (approximately 0.7 ml) of liquid sample was introduced into an oscillating sample tube and the changed in oscillating frequency caused by the change in the mass of the tube was used in conjunction with calibration data to determine the density of the sample (ASTM, 2002).



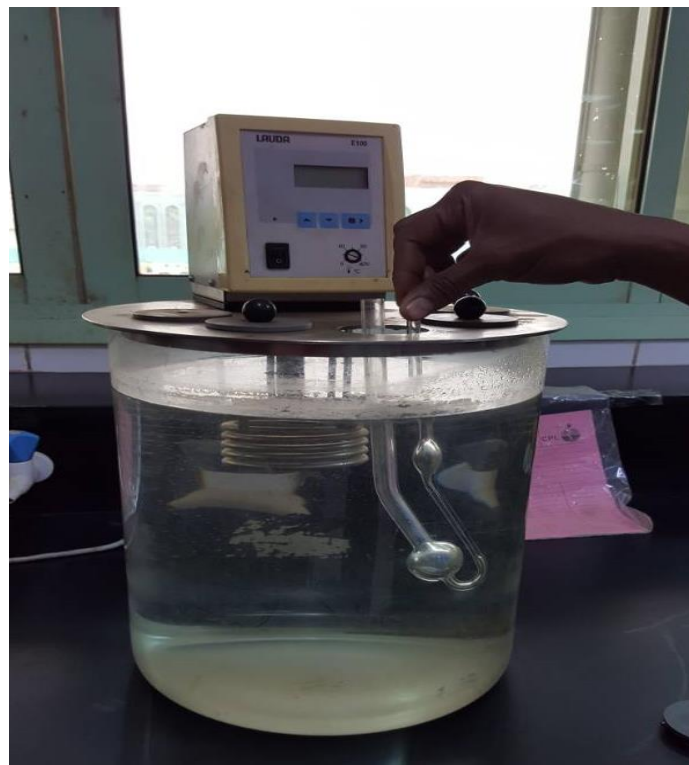
**Figure (2.7): Density meter**

#### **2.2.4.5 S.G (specific gravity)**

The sample was brought to a specified temperature and a test portion was transferred to a hydrometer cylinder that had been brought to approximately the same temperature. The appropriate hydrometer, also at a similar temperature, was lowered into the test portion and allowed to settle. After temperature equilibrium had been reached, the hydrometer scale was recorded, and the temperature of the test portion was taken (ASTM, 2002).

#### **2.2.4.6 Kinematic viscosity at 40C(cSt)**

The time was measured for a fixed volume of liquid to flow under gravity through the capillary of a calibrated viscometer Fig 2.8 under a reproducible driving head and at a closely controlled and known temperature. The kinematic viscosity was the product of the measured flow time and the calibration constant of the viscometer (ASTM, 2004).



**Figure (2.8): Viscometer**

#### **2.2.4.7 Calorific value (MJ kg<sup>-1</sup>)**

Adiabatic bomb calorimeter was used in the experiment. The effective heat capacity of the calorimeter was determined using benzoic acid of a certified calorific value of 26.4698 MJ/kg under standard conditions. About 1 ml of distilled water was pipetted into the bomb. An accurately weighed sample of the order of 0.5 g was introduced into the oil cup and placed in the bomb. A length of fine cotton thread was suspended in the sample from a nickel-chromium wire in order to act as a source of ignition. The bomb was assembled and charged with oxygen at 35 atmospheres. The initial temperature of the calorimeter was adjusted to about 275°K below ambient temperature to minimize heat losses. After about five minutes of natural heat transfer to the jacket water, the firing circuit was closed, and the temperature of the jacket water recorded until it was found to fall for a period of about five minutes. The temperature rise was noted and the net calorific value was calculated using the equation below. The experiment was carried out in triplicate allowing a difference of about 0.28 MJ/Kg between the values obtained (Shoemaker *et al.*, 1996).

#### **Calculation:**

Calorific value (cal/g) = (water equivalent (g) + water quantity of inner cylinder) × raised temperature (C) – calory correction /quantity of sample (g)

#### **2.2.4.8 Cloud point (C)**

The sample was brought to be tested to a temperature at least 14C above the expected cloud point. Any moisture presented was removed by a method such as filtration through dry lintless filter paper until the oil was perfectly clear, but made such filtration at a temperature of at least 14C above the approximate cloud point. The sample was poured into the test jar to the level mark. The test jar was closed tightly by the cork carrying the test thermometer (ASTM- D 2500-02, 2004).

### 2.2.4.9 Pour point (C)

The sample was cooled after preliminary heating at a specified rate and examined at intervals of 3C for flow characteristics. The lowest temperature at which movement of the specimen was observed and recorded as the pour point (ASTM D 97-04, 2004).



**Figure (2.9): Cloud point and pour point tester**

### 2.2.4.10 Acid value ( $\text{mg KOH g}^{-1}$ )

The sample was dissolved in a mixture of toluene and propan-2-ol containing a small amount of water and titrated potentiometrically with alcoholic potassium hydroxide using a glass indicating electrode and a reference electrode or a combination electrode. The meter readings were plotted manually or automatically against the respective volumes of titrating solution and the end points are taken only

at well-defined inflections in the resulting curve. When no definite inflections were obtained and for used oils, end points were taken at meter readings corresponding to those found for aqueous acidic and basic buffer solutions (ASTM- D 664–04, 2004).

#### **2.2.4.11 Iodine Value ( $\text{mg g}^{-1}$ )**

Approximately, 0.2 grams of oil was accurately weighed and placed in a dry and clean flask especially for the test. A 10 ml of chloroform was used for dissolving the oil. A 25 ml of pyridine sulphate dibromide solutions was added and finally 20 ml of KI (0.1N) were added to the contents of the flask. The flask was then stoppered and the mixture was allowed to stand for 10 minutes in a dark place. The stopper and the side of the flask were rinsed with enough amount of distilled water, the contents of the flask were then shaken and titrated against 0.1N sodium thiosulphate solution using starch liquid as an indicator. A blank determination was carried out simultaneously (Paquot and Hautfenne, 1987).

#### **Calculation;**

$$\text{Iodine value (IV)} = \frac{(b-a) \times 0.01269 \times 100}{S}$$

S

Where;

b: Volume (ml) of sodium thiosulphate in blank solution

a: Volume (ml) of sodium thiosulphate in test active solution

S: Weight (gm) of the oil sample

0.01269: Iodine factor.

#### **2.2.4.12 Peroxide Value ( $\text{mEq kg}^{-1}$ )**

One gram of the oil was accurately weighed into 250 ml conical flask. Thirty ml of a mixture of glacial acetic acid and chloroform (3:2) were added and the solution was swirled gently to dissolve the oil. A 0.5 ml of 0.1N KI was added to the flask, and then the contents of the flask were left to stand for one minute before

adding 30 ml of distilled water. After a while, the contents were titrated with 0.01N sodium thiosulphate until the yellow colour almost disappeared. A 0.5 ml of 1% starch solution was added, and the titration continued with vigorous shaking until the blue colour completely disappeared. The number of ml of 0.01N sodium thiosulphate required (a) were recorded. The same process was repeated for blanks. The number of ml of 0.01N sodium thiosulphate required by the blank (B) was recorded (Paquot and Hautfenne, 1987).

**Calculation;**

$$\text{Peroxide value (PV) of the oil} = \frac{(b-a) \times N \times 100}{S}$$

Where;

b: Reading of blank (ml).

a: Reading of oil (ml).

S: Original weight of oil sample (gm).

**2.2.4.13 Saponification Value (mg/KOH g<sup>-1</sup>)**

The sample was melted and filtered through filter paper to remove any impurities and last traces of moisture. The dry sample weighed about 1.5 to 2g into 250 ml Erlenmeyer flask. A 25 ml of the alcoholic potassium hydroxide solution was pipetted into the flask. The sample flask and blank flask were connected with air condenser, then were kept in water bath to boiling within one hour. A 10 ml of hot ethyl alcohol neutral to phenolphthalein were washed down the inside of the condenser when the flask and condenser have cooled.

The excess of potassium hydroxide was titrated with hydrochloride acid using about 1.0 ml of phenolphthalein as indicator (Paquot and Hautfenne, 1987).

**Calculation:**

$$\text{Saponification value} = \frac{56.1 - (B - S)N}{W}$$

Where;

B = Volume in ml of standard hydrochloric acid required for the blank.

S = Volume in ml of standard hydrochloric acid required for the sample.

N = Normality of standard hydrochloric acid.

W = Weight in gm of the oil/fat taken for the test.

**2.2.4.14 Carbohydrates**

Accurately (0.5g) of samples was extracted with ether-ethanol mixture. the crushed material was refluxed in Soxhelt's apparatus for 30 minutes, then filtered and centrifuged. To supernatant sodium hydroxide and sulphuric acid were added, after centrifuge the clear supernatant was collected.

A number of aliquots (1ml) was taken separately in test tubes, 1ml of reagent G was added to each test-tube and then they were heated in a boiling water-bath for 10 minutes. Test-tubes were cooled to room temperature, 1ml of sulphuric acid was added to each test-tube to develop the blue coloration. The total volume of each test-tube was made up to 10 ml with distilled water. The O.D values of the coloured solutions were then measured through 620nm wavelength in a colorimeter against blank (Paquot and Hautfenne, 1987).

**2.2.4.15 Free Fatty Acid Treatment**

2% concentrated Sulphuric acid in 100 ml of methanol were added to 500 ml of hot crude baobab oil. The mixture was kept at 55°C for two hours with continuous stirring at 3000 rpm. The mixture was transferred to a separating funnel and allowed to settle for 24 hours. The lower layer of glycerol, sulfuric acid and unreacted methanol was separated from the upper layer of treated oil. The oil was

washed three times with warm distilled water at 40 °C to remove impurities and soap (Kombe *et al.*, 2007).

#### **2.2.4.16 Transesterification Reaction**

500 ml of oil were placed into a 1 L beaker and heated up to 60°C, 100 ml of fresh methanolic potassium hydroxide were added under stirring at 3000 rpm for two hours. The mixture was transferred to a separating funnel and kept for 24 hours. Then the lower, glycerol layer was drained and the upper biodiesel layer was washed, three times, with warm distilled water to remove soap, methanol and remaining glycerol (Okullo *et al.*, 2006).

#### **2.2.4.17 Identification of baobab methyl ester**

The conversion of baobab oils to biodiesel was investigated using Fourier transform infrared spectroscopy (FTIR). Fig 2.10 Thermo Nicolet iS5 FT-IR spectrophotometer (Germany), equipped with a ZnSe crystal attenuated total reflectance (ATR) cell was used to obtain the IR spectra in the mid region 400 to 700 cm<sup>-1</sup> with 24 scans (Mahamuni *et al.*, 2017).



**Figure (2.10): FTIR spectrophotometer**



#### 2.4.4.18 Engine and Gas Emissions Test

2L-T Toyota multi-cylinder diesel engine model and KANE AUTOMOTIVE 1985 exhaust gas analyzer were used to measure Carbon Di oxide CO<sub>2</sub>, Nitrogen mono oxide NO and other Nitrogen Oxides NO<sub>x</sub>. The engine test and gas analyzer are shown in Figs 2.11 and Fig. 2.12, Table 2.2 shows the specifications of the engine. The engine was firstly operated with fossil diesel for few minutes to warm up. The engine was tested with three speeds 1000 rpm, 1500 rpm and 2000 rpm without load conditions. The test was started with fossil diesel followed by B20 blend. The gas analyzer was connected to exhaust to measure the concentrations of gases emitted, all results were recorded after 30 second from engine operation. Same procedure was applied for B20E20 and B20E30 fuel blends. The experiment repeated twice for each blend at the three speeds. Finally the engine was flushed with fossil diesel.

**Table (2.2): Diesel engine specification**

<b>Item</b>	<b>Value</b>
Engine model	2L- T Toyota 1985
Engine type	4-cylinder diesel engine
Displacement	2.4 L
Cylinder bore and strok	92 mm
Colling system	Radiator
Compression ratio	20:1



**Figure (2.11): Diesel engine**



**Figure (2.12): Gas analyzer connect to exhaust**

## Chapter Three

### 3. Results and Discussion

#### 3.1 Proximate composition of *Adansonia digitata* seeds

Table (3.1) shows the proximate compositions of *Adansonia digitata* seeds.

The seeds contained  $3.5 \pm 0.1$ ,  $4.49 \pm 0.05$ ,  $14.3 \pm 0.05$ ,  $20.42 \pm 0.04$ ,  $12.97 \pm 0.015$ ,  $44.32 \pm 0.25\%$  and  $363.024 \pm 0.51$  K Cal/100g of moisture, ash, lipids, fiber, protein, carbohydrates and total energy respectively.

The moisture content  $3.5 \pm 0.1\%$  was lower to that obtained by Magdi (2004), also moisture content was less comparable to that reported by Salisu *et al.*, (2015) and also, it less than that reported by Nkafamiya *et al.*, (2007). Moisture content is variable even in the same variety depending upon the locality and other environmental factors. Low moisture content is a good indicator for long shelf life which is very useful in storage of food.

Ash content was  $4.49 \pm 0.05\%$ , was more than reported by Magdi (2004)  $3.8 \pm 0.1\%$  and less to that reported by Salisu *et al.*, (2015) who reported that ash content  $7.29 \pm 0.08\%$ . Also, ash content value was less than that obtained by Nkafamiya *et al.*, (2007) which it was  $5.01 \pm 0.07\%$ .

The lipid content was  $14.3 \pm 0.05\%$ , was more than reported by Nkafamiya *et al.*, (2007) was  $12.72 \pm 0.01\%$ , but it is less to that made by Salisu *et al.*, (2015) who reported a lipid content value  $20.45 \pm 0.05\%$ .

The fiber content of *Adansonia digitata* seeds was  $20.42 \pm 0.04\%$ . It was more than reported by Magdi (2004) was  $16.2 \pm 0.9\%$ , also it more than both reported by Salisu *et al.*, (2015) and Nkafamiya *et al.*, (2007) they reported a fiber content  $12.15 \pm 0.05\%$  and  $6.71 \pm 0.03\%$  respectively.

**Table (3.1): Proximate composition of *Adansonia digitata* seeds**

Constituents	Percentage of each Composition %
Moisture	3.5 ± 0.1
Ash	4.49 ± 0.05
Crude lipids	14.3 ± 0.05
Crude fiber	20.42 ± 0.04
Crude protein	12.97 ± 0.01
Carbohydrate	44.32 ± 0.25
Total energy (K Cal/100g)	363.024 ± 0.51

The protein content was  $12.97 \pm 0.01\%$  was less than those reported by Magdi (2004), Salisu *et al.*, (2015) and Nkafamiya *et al.*, (2007) reported a protein content  $18.4 \pm 0.5$ ,  $29.79 \pm 0.03\%$  and  $21.75 \pm 0.12\%$  respectively.

The carbohydrate content was  $44.32 \pm 0.25\%$ . It is more than that reported by Salisu *et al.*, (2015) who reported a carbohydrate of  $25.91 \pm 0.54\%$ , but it less than those reported by Magdi (2004) and Nkafamiya *et al.*, (2007). This shows that the carbohydrate in the baobab seed do not vary much with variation in geographical location.

The total energy of *Adansonia digitata* seeds was  $363.024 \pm 0.51$  K Cal/100g are similar comparable to total energy of *Adansonia digitata* seeds was  $363.8 \pm 9.7$  K Cal/100g obtained by Magdi (2004). The variation in values may be due to method of analysis and species and climatic conditions. However the results showed that seeds could serve as an animal feed nutrient because of it's relatively high carbohydrate, fat, minerals, protein content and good source of energy.

### 3.2 Minerals composition of *Adansonia digitata* seeds

Table (3.2) shows the minerals composition of *Adansonia digitata* seeds. The seeds contained 90.29, 9.61, 7.00, 0.268 and 0.227 ppm of potassium, Calcium, Phosphorus, Zinc and Iron respectively. Trace elements constitute essential part of any balanced diet and required for normal growth, potassium showed the highest concentration (90.29 ppm) comparable to other detected minerals, iron showed the lowest concentration (0.227 ppm). The lower concentration of seeds heavy metals iron (Fe) and zinc (Zn) is an indication of little or no toxicity. In general the low concentrations were within the safety limit. The minerals composition of *Adansonia digitata* seeds were less comparable to both studies made by Magdi (2004) and Nasreldin *et al.*, (2016). The average range of concentrations of the elements detected compares very well in most cases with other works, however, there were a number of disparities (Chadare *et al.*, 2009) associated to soil type, geographical location of baobab, probable genetic effect, sample quality, analytical method employed and this is significant for mineral element data base of Baobab seeds (Isaac *et al.*, 2013).

**Table (3.2): Minerals composition of *Adansonia digitata* seeds**

Minerals	Concentration (ppm)
K	90.29
Ca	9.61
P	7.00
Zn	0.268
Fe	0.227

Iron and zinc are responsible for energy release in the cells and contributes to proper functioning of many antioxidants. Iron together with other major nutrients (Ca, Mg,

K etc.) are need for red blood cell formation in order to release energy in muscles, in other words zinc is very necessary for the body, in various ways, including manufacturing of DNA, wound healing, maintaining strong immune system for fighting infections (Isaac *et al.*, 2013).

### **3.3 Physicochemical characterization of *Adansonia digitata* seeds oil**

Table (3.3) shows the oil content and physicochemical characterization of *Adansonia digitata*. The oil extract has a yellow colour.

The oil content of *Adansonia digitata* seed was 21.5%, it was less than that reported by Nkafamiya *et al.*, (2007) and Aliyu *et al.*, (2015) who reported an oil content of  $45.00 \pm 003\%$  and  $29.33 \pm 0.01\%$  respectively.

Free fatty acids were 3.8% which is more than 1.9635% reported by Alia (2016).

The density at 15C was  $0.9154 \text{ g/cm}^3$  more than that reported by Alia (2016) and Hagir (2017) which were  $0.881 \text{ g/cm}^3$  and  $0.768 \text{ g/cm}^3$  respectively. The specific gravity obtained was 0.9163%, it is lower than that reported by Zahrau *et al.*, (2014) who reported a specific gravity of 0.937% and higher than the result obtained by Magdi (2004) and Alia (2016) which were  $0.9 \pm 0.0\%$  and 0.781% respectively. Kinematic viscosity at 40C was found to be 33.69% which is similar to the  $33.72 \pm 1.17\%$  reported by Salisu *et al.*, (2015).

The calorific value was 43.797 MJ/ kg is roughly similar to the 45.97 reported by Aiman *et al.*, (2017) for *Sterculia setigera* and higher than that reported by Mangas for *et al.*, (2012) and Giwa *et al.*, (2010) which were 32.8 for *Sterculia striata* and 39.37 MJ/kg respectively.

Cloud point of *Adansonia digitata* oil was +9C, it less comparable to the +19C reported by Aiman *et al.*, (2017).

Pour point of *Adansonia digitata* was -3C which was much lower than that the +15C reported by Aiman *et al.*, (2017).

**Table (3.3): Physicochemical characterization of the oil extract**

Parameters	Values
Oil content (%)	21.5
Colour	Light yellow
Physical state at room temperature	Liquid
Free fatty acid (%)	3.8
Density at 15C (g/cm <sup>3</sup> )	0.9154
S.G (specific gravity)	0.9163
Kinematic viscosity at 40C(cSt)	33.69
Calorific value (MJ kg <sup>-1</sup> )	43.797
Cloud point (C)	+9
Pour point (C)	-3
Acid value (mg KOH g <sup>-1</sup> )	1.7
Iodine Value (mg g <sup>-1</sup> )	54
Peroxide Value (mEq kg <sup>-1</sup> )	7.60
Saponification Value (mg/KOH g <sup>-1</sup> )	275.05

Acid value of *Adansonia digitata* seeds was 1.7 mg KOH g<sup>-1</sup> more than those reported by Aliyu *et al.*, (2015) and Nkafamiya *et al.*, (2007), they reported acid values of  $0.47 \pm 0.01$ ,  $0.33 \pm 0.03$  mg KOH g<sup>-1</sup> respectively, but less than that reported by Salisu *et al.*, (2015) and Alia (2016) which were  $2.75 \pm 0.14$ , 3.927 mg KOH g<sup>-1</sup> respectively.

Iodine value was 54 mg g<sup>-1</sup> less comparable to those reported by Magdi (2004), Nkafamiya *et al.*, (2007), reported an iodine values of  $88.0 \pm 4.1$ ,  $87.9 \pm 0.02$ , mg g<sup>-1</sup> respectively, but it higher more than that reported by Aliyu *et al.*, (2015) and Alia

(2016) which were  $23.03 \pm 0.07$ ,  $1 \text{ mg g}^{-1}$  respectively. They showed similarities to those reported by Salisu *et al.*, (2015) and Zahrau *et al.*, (2014).

Peroxide value of *Adansonia digitata* seeds was found  $7.60 \text{ mEq kg}^{-1}$  which was higher than the result obtained by Salisu *et al.*, (2015), Nkafamiya *et al.*, (2007) and Alia (2016) which were  $6.02 \pm 0.48$ ,  $4.5 \pm 0.06$ ,  $1.42 \text{ mEq kg}^{-1}$  respectively. The saponification value was  $275.05 \text{ mg/KOH g}^{-1}$  which is similar to that reported by Magdi (2004), Salisu *et al.*, (2015), Nkafamiya *et al.*, (2007), Aliyu *et al.*, (2015) and Zahrau *et al.*, (2014), but less than that reported by Alia (2016) which was  $338.4925 \text{ mg/KOH g}^{-1}$ .

### **3.4 Fatty acid composition of Baobab seed oil**

Table (3.4) shows free fatty acid composition of *Adansonia digitata* seed oil. The major fatty acid obtained is palmitic acid which comprises 28.25%, followed by oleic (14.33%) and linoleic (14.25%). The baobab seeds oils contained high proportions of palmitic acid as saturated fatty acid, oleic acid as mono unsaturated acid and Linoleic acid as poly unsaturated acid as well as that order for saturated, mono-poly unsaturated obtained by Osman (2004) who reported that the baobab seed oil is an excellent source of saturated, mono-and polyunsaturated fatty acids. Polyunsaturated fatty acid plays an important role in modulating human metabolism. Therefore, the high linoleic acid content is of nutritive significance because of the ability of some unsaturated vegetable oils to reduce cholesterol levels (Al-Qarawi *et al.*, 2003). The saturated fatty acids composition was 57.4%, 27.61% mono unsaturated fatty acids and 14.43% poly unsaturated acids. The values are higher comparable to that determined by Magdi (2004) who reported that the oil is composed of, approximately, 31.7% saturated fatty acids, and less comparable to monounsaturated and polyunsaturated fatty acids reported which is 37%, 31.7% respectively.



**Table (3.4): free fatty acid composition of *Adansonia digitata* seeds oil**

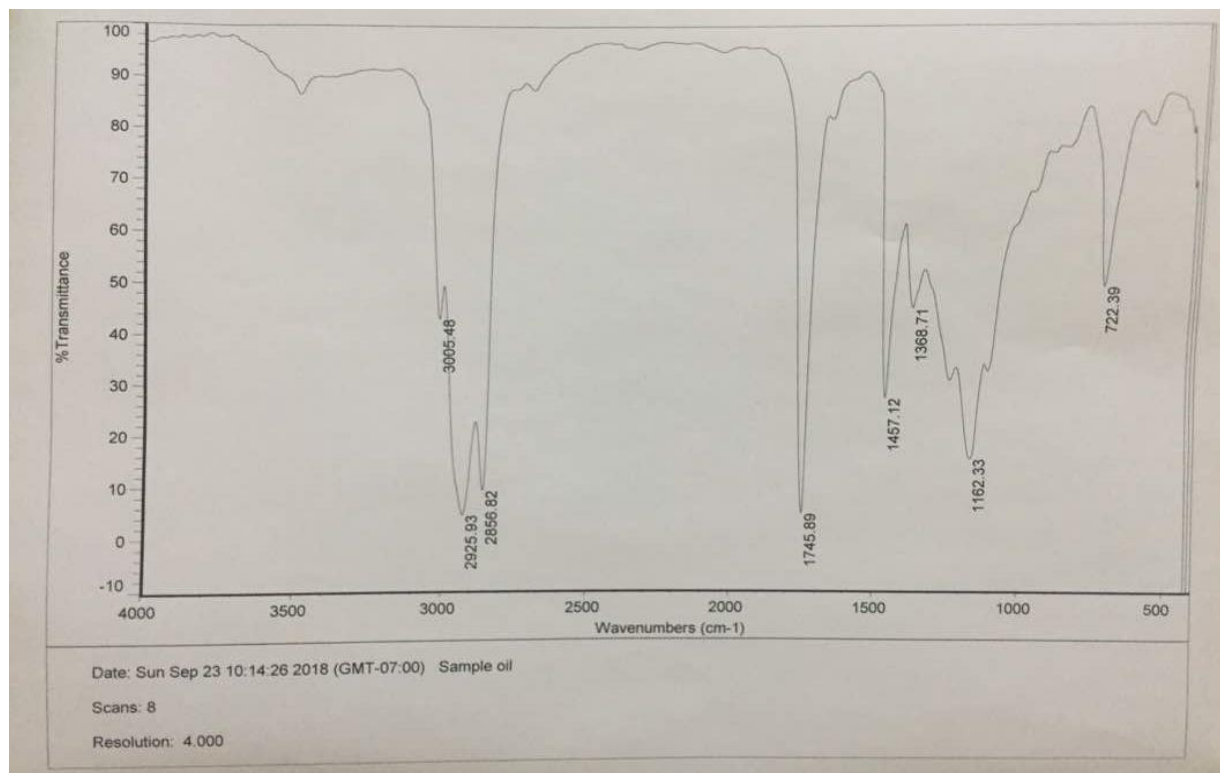
Free fatty acid	Formula	Structure	Area %
Palmitic acid	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	C16:0	28.25
Oleic acid	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	C18:1	14.33
Linoleic acid	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	C18:2	14.25
Palmitoleic acid	C <sub>16</sub> H <sub>30</sub> O <sub>2</sub>	C16:1	12.4
Stearic acid	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	C18:0	10.75
Heptadecanoic acid	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	C17:0	9.69
Myristic acid	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	C14:0	7.15
Arachidic acid	C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>	C20:0	1.2
cis-10-Heptadecenoic acid	C <sub>17</sub> H <sub>32</sub> O <sub>2</sub>	C17:1	0.58
Elaidic acid	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	C18:1	0.3
Linolelaidic acid	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	C18:2	0.18

The presence of high free fatty acid in fuel may cause corrosion of internal engine parts and thus affects the engine performance (Silitonga *et al.*, 2014). Also high free fatty acids in raw materials of biodiesel can cause soap formation and low yield of biodiesel and the separation of the methyl ester from glycerin will be difficult. The maximum limit of free fatty acid in crude oil should be less than 4% (Johanes and Hirata, 2008).

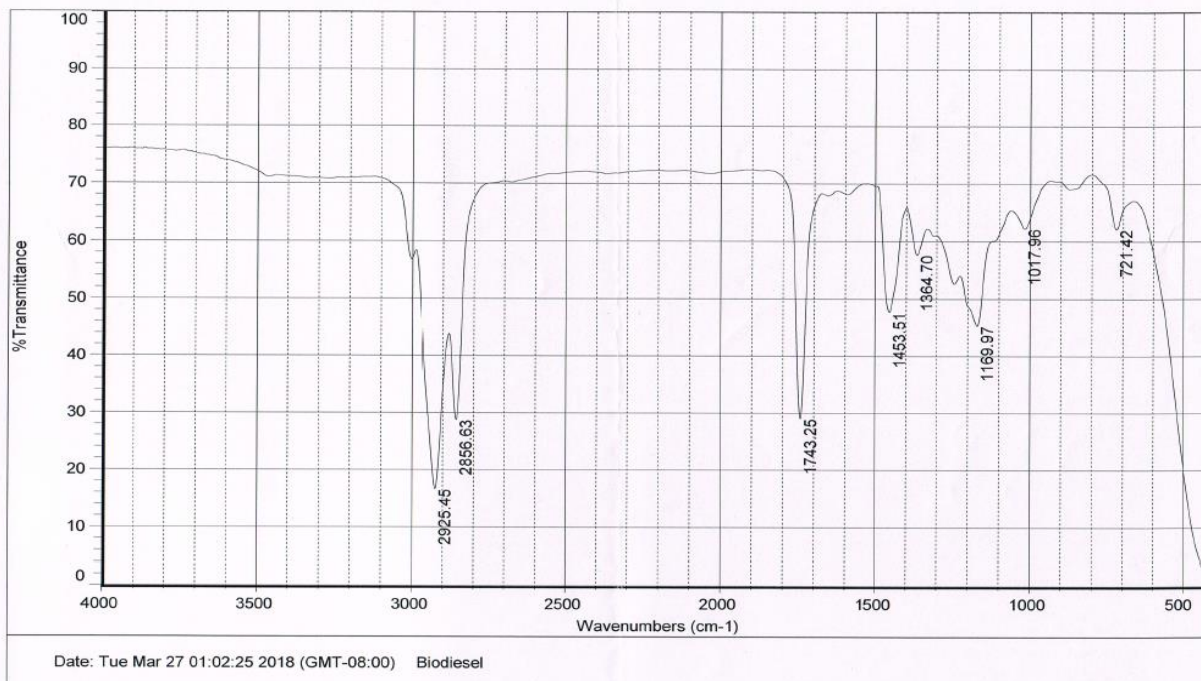
### **3.5 Fourier transform infrared spectroscopy (FTIR) of Baobab seed oil and its Baobab biodiesel**

Fig 3.1 and 3.2 show the FTIR of the oil and Biodiesel. The spectrums of Baobab oil shows absorbance peaks at, 2925.93 cm<sup>-1</sup>, 2856.62 cm<sup>-1</sup> which are similar to that obtained in Baobab biodiesel absorbance peaks 2925.45 cm<sup>-1</sup>, 2856.63 cm<sup>-1</sup> due to C-H stretching. Baobab oil absorbance at 1745.89 cm<sup>-1</sup> represent of C=O Carbonyl

group of esters was similar to that absorbance obtained in Baobab biodiesel 1743.25  $\text{cm}^{-1}$ .



**Figure (3.1): FTIR spectrum of baobab oil**



**Figure (3.2): FTIR spectrum of baobab biodiesel**

Furthermore, peaks at  $1368.71\text{ cm}^{-1}$  and  $1364.7\text{ cm}^{-1}$  can be attributed to the glycerol group  $\text{O}-\text{CH}_2$  (mono-, di- and triglycerides) of Baobab oil and Baobab biodiesel respectively. Also, absorbance at  $1162.33\text{ cm}^{-1}$  and  $1169.97\text{ cm}^{-1}$  of Baobab oil and Baobab biodiesel respectively, due to stretching of  $\text{O}-\text{CH}_3$  which indicates the conversion of oil to methyl ester due to C-O of esters in triglycerides. The range  $1500\text{-}900\text{ cm}^{-1}$  known as “fingerprint” region. The peak at  $1453.51\text{ cm}^{-1}$  correspond to the asymmetric stretching of  $-\text{CH}_3$  present in the biodiesel spectrum and should be absent in the refined oil spectrum, Baobab oil and Baobab biodiesel showed peaks at  $722.39\text{ cm}^{-1}$  and  $721.42\text{ cm}^{-1}$  respectively which represent aromatic C-H (Rabelo *et al.*, 2015).

### **3.6 Ester content of Baobab biodiesel**

Table (3.5) shows the ester content of *Baobab* biodiesel. The total ester content of biodiesel was found to be 98.40% of total components which indicate that the triglycerides were successfully converted to methyl ester to produce high purity biodiesel.

The obtained *Baobab* biodiesel presented 46.08% of palmitoleic fatty acid ester (as methyl ester) as the major constituent, followed by myristic acid methyl ester and lauric acid methyl ester with percentage of 19.47%, 12.2% respectively. Comparison with *Moringa* biodiesel mainly contents of Oleic, Palmitic, and seatric acid methyl esters with percentages of 81.6%, 5.2% and 4.0% respectively as reported by David *et al.*, (2015).

The saturated free fatty acid methyl ester (FAME) in Baobab biodiesel was found 50.8% which is slightly greater than percentage of unsaturated fatty acid methyl esters which is 47.53%.

In *Moringa* biodiesel the percentage of unsaturated fatty acid methyl esters is greater than percentage of saturated fatty acid methyl esters which is 83.0% and

17.0% respectively as reported by David *et al.*, (2015). Biodiesel feedstock largely depends on fatty acid composition (Bhave *et al.*, 2013; Atabani *et al.*, 2014).

**Table (3.5): Ester content of Baobab bio diesel**

No.	Name	Formula	Area %
1	Palmitoleic acid M.E	C <sub>16</sub> H <sub>30</sub> O <sub>2</sub>	46.0843
2	Myristic acid M.E	C <sub>14</sub> H <sub>28</sub> O <sub>2</sub>	19.4814
3	Lauric acid M.E	C <sub>12</sub> H <sub>24</sub> O <sub>2</sub>	12.2408
4	Cis- 10-Pentadecenoic acid M.E	C <sub>15</sub> H <sub>30</sub> O <sub>2</sub>	7.6434
5	Cis- 10-Heptadecenoic acid M.E	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	5.0237
6	Palmitic acid M.E	C <sub>16</sub> H <sub>32</sub> O <sub>2</sub>	2.3675
7	Heptadecenoic acid M.E	C <sub>17</sub> H <sub>34</sub> O <sub>2</sub>	2.0205
8	Arachidic acid M.E	C <sub>20</sub> H <sub>40</sub> O <sub>2</sub>	0.9883
9	Stearic acid M.E	C <sub>18</sub> H <sub>36</sub> O <sub>2</sub>	0.7314
10	Linolelaidic acid M.E	C <sub>18</sub> H <sub>32</sub> O <sub>2</sub>	0.6034
11	Cis-8,11,14-Eicostrienoic acid M.E	C <sub>20</sub> H <sub>32</sub> O <sub>2</sub>	0.4570
12	Capric acid M.E	C <sub>10</sub> H <sub>20</sub> O <sub>2</sub>	0.3740
13	Cis- 11- Eicosenoic acid M.E	C <sub>20</sub> H <sub>38</sub> O <sub>2</sub>	0.1470
14	Elaidic acid M.E	C <sub>18</sub> H <sub>34</sub> O <sub>2</sub>	0.1335
15	Caproic acid M.E	C <sub>6</sub> H <sub>12</sub> O <sub>2</sub>	0.1122

### 3.7 Physicochemical properties of baobab biodiesel and blends

The data presented in Table (3.6) shows the physicochemical characterization of *Adansonia digitata* biodiesel and blends.

The density of Biodiesel, B20 (biodiesel 20%, diesel 80%), B20E20 (Biodiesel 20%, ethanol 20%, diesel 60%) and B20E30 (Biodiesel 20%, ethanol 30%, diesel 50%)

was obtained at 0.8866, 0.8519, 0.8403 and 0.8864 g/cm<sup>3</sup> respectively which showed similarity to both studies reported by Buhari *et al.*, (2014) and Danbature *et al.*, (2016) which were 0.86 and 0.8553g/cm<sup>3</sup> respectively for the same plant.

**Table (3.6): Physicochemical properties of baobab biodiesel and blends**

Parameters	Value					
	Biodiesel	ASTM D 6751	B20	B20E20	B20E30	ASTM D7467
Density at 15C (g/cm <sup>3</sup> )	0.8866	-	0.8519	0.8403	0.8864	-
Kinematic viscosity in 40C (cSt)	5.8	1.9-6.0	3.6	3.4	2.7	1.9-4.1
Calorific value (MJ kg <sup>-1</sup> )	44.051	-	44.354	44.456	44.5	-
Total acid Number (mgKOH/g)	0.20	Max.5	0.16	0.14	0.13	Max 0.3
Cloud point (C)	+7	-	+12	+8	+8	-
Pour point (C)	+6	-	-6	-8	-12	-
Flash point (C)	80	Min.93	76.0	-	-	Max 52
Copper strip corrosion (3 Hours at 100C)	1b	Max No.3	1a	1a	1a	Max 3
Water content (wt%)	0.1	Max 0.05	0.05	0.056	0.048	Max 0.05

The Kinematic viscosity of Biodiesel, B20, B20E20 and B20E30 was obtained at 5.8, 3.6, 3.4 and 2.7 cSt respectively. The Kinematic viscosity value of Biodiesel was higher than that determined by Buhari *et al.*, (2014) and Danbature *et al.*, (2016) which were  $0.859 \pm 0.0349$  and 3.144 cSt respectively. The calorific value of Biodiesel, B20, B20E20 and B20E30 was obtained at 44.051, 44.354, 44.456 and 44.5 MJ kg<sup>-1</sup> respectively. The The calorific value was similar to that reported by Danbature *et al.*, (2016) which was 44.063 MJ kg<sup>-1</sup> for the same plant. Compared to

diesel fuel, lower calorific value and higher viscosity which influenced the combustion characteristics. Fuels with high kinematic viscosity tend to form larger droplets during injection which can consequently lead to poor combustion. Therefore, the uneven combustion characteristics of the produced biodiesel fuel reduced the engine life (Muralidharan *et al.*, 2011).

The cloud point of Biodiesel, B20, B20E20 and B20E30 was obtained at 7, 12, 8 and 8°C respectively. The cloud point value was lower to that reported by Buhari *et al.*, (2014) who was reported that pour point was 10°C for the same plant and higher to that obtained by Danbature *et al.*, (2016) which was 6°C.

The pour point of Biodiesel, B20, B20E20 and B20E30 was obtained at -6, -6, -8 and -12°C respectively. The pour point value was higher comparable to that determined by Danbature *et al.*, (2016) which was -1.5°C, but it lower than that obtained by Buhari *et al.*, (2014) which was 10°C for the same plant. Fuel blends have the same pour point compared to biodiesel-diesel fuel blends. But biodiesel normally must be has a pour point higher than conventional diesel.

The flash point of Biodiesel and B20 obtained was at 80, 76°C respectively which was lower comparable to that determined by Danbature *et al.*, (2016) and Buhari *et al.*, (2014) which was 160, 170°C respectively.

Table 3.6 shows the physical and chemical properties of Biodiesel and blends in comparison with ASTM D 6751 for bio diesel and ASTM D 7467 for blends. B20 blend had successfully met all the requirements of ASTM D 7467. B20E20 and B20 E30 also met all the requirements of ASTM except flash point test which is not detected, for the high flammability of two blends due to alcohol content. However this will lead to serious problems in transporting and storage if temperature is not controlled. On another hand starting the engine with this two blends will be very fast compared with B20 and conventional diesel.

### 3.8 Gas emission of baobab biodiesel blends

Tables (3.7), (3.8), (3.9), (3.10) and (3.11) show gas emission of biodiesel-blends. The engine was set at a different speeds 1000, 1500 and 2000 rpm respectively. Due to the ethanol's low energy content, the power will decrease using the diesel-ethanol blended fuel.

Biodiesel used as blends in different portions to petroleum diesel showed that on combustion of biodiesel – petroleum diesel blends, the level of carbon di-oxide ( $\text{CO}_2$ ) were reduced significantly; whereas the amount of oxides of nitrogen ( $\text{NO}_x$ ) was increased, since biodiesel and alcohol were oxygenated, engines have more complete combustion than with ordinary diesel (Muralidharan *et al.*, 2011).

Mono-nitrogen oxides NO and  $\text{NO}_2$  nitric oxide and nitrogen dioxide are termed as  $\text{NO}_x$ . They are produced from the reaction of nitrogen and oxygen gases in the air during combustion at high temperatures (Kumar, 2012). The oxides of nitrogen ( $\text{NO}_x$ ) are precarious pollutant emissions, which are produced, when the fuel is burnt at high temperature causing dissociation of  $\text{N}_2$ , which ultimately leads to the formation of nitric acid. The  $\text{NO}_x$  is also responsible for weakening the ozone layer (Shahid and Jamal, 2011).  $\text{NO}_x$  emission from biodiesel increases or decreases depending on the engine family and testing procedures (Shahid and Jamal, 2011). The results presented in Tables (3.7) (3.8) (3.9) and (3.10) showed that  $\text{CO}_2$ , NO and  $\text{NO}_x$  emissions generally increases with speeds .when engine set at speed 1000 rpm the concentration of  $\text{CO}_2$  gas for diesel , B20, B20E20 and B20E30 was (2.0, 0.3, 1.2 and 1.0 %) respectively, at the speed 1500 rpm the  $\text{CO}_2$  concentration increased for each blend to give (2.1, 1.0, 2.0 and 1.8 %) respectively. at the greatest speed of 2000 rpm the concentration of  $\text{CO}_2$  reach up to (2.3, 1.6, 2.0 and 1.8 %) respectively. conventional diesel recorded the greatest emission of  $\text{CO}_2$  gas followed by B20E20, B20E30 and B20.

**Table (3.7): Gases emission of diesel**

Speed (rpm)	CO <sub>2</sub> (%)	NO (ppm)	NO <sub>x</sub> (ppm)
1000	2.0	56	58
1500	2.1	93	96
2000	2.3	122	128

**Table (3.8): Gases emission of B20**

Speed (rpm)	CO <sub>2</sub> (%)	NO (ppm)	NO <sub>x</sub> (ppm)
1000	0.3	35	35
1500	1.0	45	47
2000	1.6	55	57

**Table (3.9): Gases emission of B20E20**

Speed (rpm)	CO <sub>2</sub> (%)	NO (ppm)	NO <sub>x</sub> (ppm)
1000	1.2	75	79
1500	1.2	85	88
2000	2.0	119	124

**Table (3.10): Gases emission of B20E30**

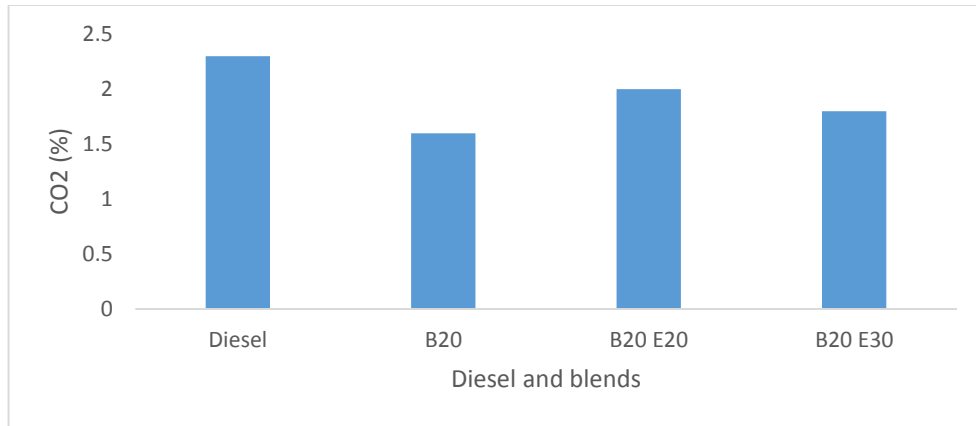
Speed (rpm)	CO <sub>2</sub> (%)	NO (ppm)	NO <sub>x</sub> (ppm)
1000	1.0	52	54
1500	1.2	70	78
2000	1.8	77	87

**Table (3.11): Gases emission for diesel and blends at 2000 (rpm)**

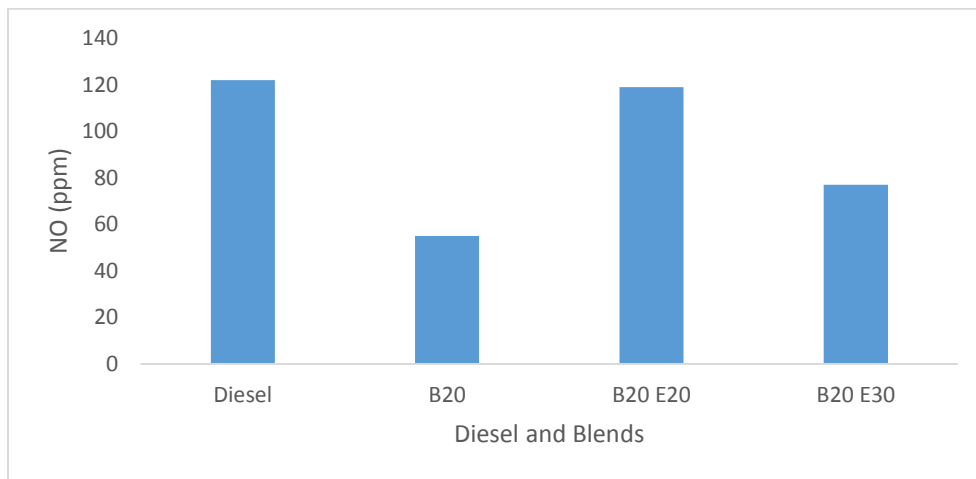
	CO <sub>2</sub> (%)	NO (ppm)	NO <sub>x</sub> (ppm)
<b>Diesel</b>	2.3	122	128
<b>B20</b>	1.6	55	57
<b>B20E20</b>	2.0	119	124
<b>B20E30</b>	1.8	77	87



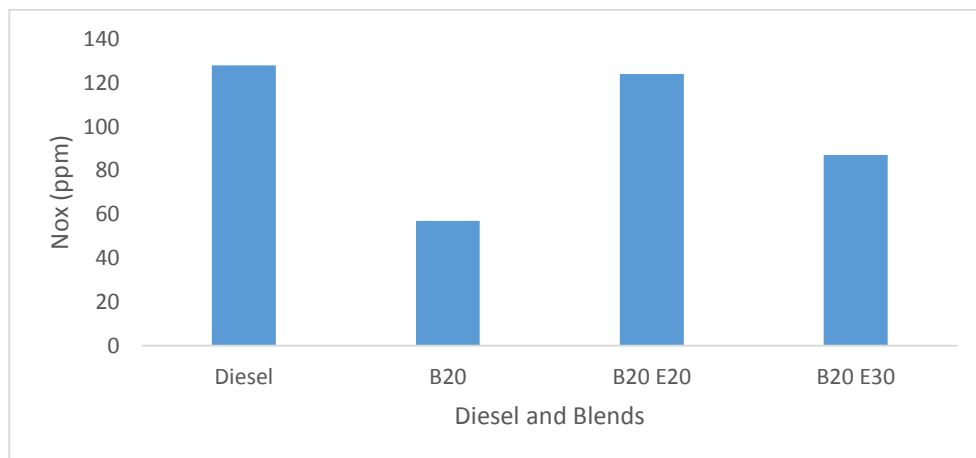
The detected concentrations of NO gas at first speed 1000 rpm for diesel, B20, B20E20 and B20E30 were (56, 35, 75 and 52 ppm respectively), at speed 1500 rpm NO concentration increased for all blends (93, 45, 85 and 70 ppm respectively) and at last speed of 2000 rpm the concentrations of NO gas reach up to (122, 55, 119 and 77 ppm respectively). The blend E20B20 recorded the highest concentration of NO gas at 1000 rpm, but at 1500 and 2000 rpm the concentration was lower than conventional diesel with small difference (less than 10 ppm) according to that diesel and B20E20 both have the greatest emissions of NO gas followed by B20E30 blend, while B20 has the lowest emission. NO<sub>x</sub> emissions from diesel and blends B20, B20E20 and B20E30 at 1000 rpm were (58, 35, 79, and 45 ppm respectively), at speed of 1500 rpm the obtained concentrations for NO<sub>x</sub> were (96, 47, 88 and 78 ppm respectively), at last speed 2000 rpm emissions increased to (128, 57, 124, and 87 ppm respectively). The blend B20 also recorded the lowest emission of NO<sub>x</sub> gases. Table (3.11) shows gas emissions for diesel and blends at speed of 2000 rpm. The emissions of CO<sub>2</sub>, NO and NO<sub>x</sub> reduced by 69.56% 45.0% and 44.5% respectively when B20 blend used over conventional diesel. Figures (3.3), (3.4) and (3.5) shows that B20 has lowest emissions for CO<sub>2</sub>, NO, NO<sub>x</sub> gases then B20E30 the emissions of the blend B20E20 was relatively high but still less than conventional diesel. Biodiesel contains about 8% less energy per gallon than petroleum diesel. For B20, this could mean a 1% to 2% difference, but most B20 users report no noticeable difference in performance or fuel economy. Greenhouse gas and air-quality benefits of biodiesel are roughly commensurate with the blend B20 (Shahid and Jamal, 2011).



**Figure (3.3): Diesel and Blends Vs CO<sub>2</sub> gas concentration at 2000rpm**



**Figure (3.4): Diesel and Blends Vs NO gas concentration at 2000rpm**



**Figure (3.5): Diesel and Blends Vs NO<sub>x</sub> gas concentration at 2000 rpm**

### 3.9 Conclusions

Biodiesel is an important new alternative fuel. It can be produced from many vegetable oils. In this research, biodiesel was produced from baobab seed oil (*Adansonia digitata*).

- The study investigated the oil rich baobab seed as a potential, alternative and second generation transport fuel for diesel engines. The study found a 21.5% oil yield using the n-hexane method.
- The seed of *Adansonia digitata* examined in this work have been shown to contain oil in reasonable levels.
- The crude oil was converted to biodiesel by an alkali catalyst transesterification reaction. Fatty acids were obtained. Important physicochemical fuel properties were measured under relevant ASTM standards.
- The produced biodiesel fuel was within the recommended standards of biodiesel fuel and can be used as fossil fuel substitute.
- The biodiesel -diesel blend and biodiesel -ethanol -diesel blends properties are within the acceptable range of ASTM standards.
- All blends showed lower gases emission than conventional diesel in engine test.
- The NO<sub>x</sub> emissions increased and fuel efficiency decreased with increasing percentages of biodiesel beyond B20.
- The ratio of NO<sub>x</sub> and CO<sub>2</sub> is important for both improving fuel efficiency and reducing exhaust emissions for field operations in crop production.

### **3.10 Recommendations**

- TGA and oxidative stability testes for biodiesel, diesel-biodiesel and diesel - biodiesel ethanol blend need to be investigated.
- Research on possibility of use of Baobab seeds in paper manufacture due to relatively high fiber content.
- Research on possibility of process remain seeds to serve animal nutrition due to its relatively high carbohydrate, fat, protein content and good source of energy.

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