Assessment of Biodiesel Fuel Potentials of Seed Crude Oil Extracts of Balanites aegyptiaca (L.) Del

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ABSTRACTS: Study on assessment of biodiesel fuel potentials of seed crude oil extracts of Balanites aegyptiaca (L.) Del was carried out. Standard methods of the Association of Official and Analytical Chemist (AOAC) were adopted to evaluate the proximate, physico-chemical properties and fatty acid compositions of crude seed oil extracts of the test plant. The proximate constituents of the crude seed oil extract gave crude protein (22.09%), crude fat (56.75%), moisture content (1.35%), ash (4.70%), crude fiber (12.75%) and carbohydrate (23.6%). The crude oil physicochemical properties included saponification value (216.439mgKOH/g), peroxide value (4.84meq/kg), acid value (2.18mgKOH/g), iodine value (77.08g/100g), viscosity value (150.3@30°C) and cetane number (54.08), refractive index (1.487 @30°C), relative density (0.949g/cm³) while calorific value was 39.03(MJ/kg). The fatty acids composition of crude kernel oil extract of B. aegyptiaca indicated the presence of four (4) fatty acids, with relative percentage abundance (RPA) in the order of 67.17% (9,12-Octadecanoic acid (C18:C9,12) >16.22% (Pentadecanoic acid (C15:H14:0) >11.8% (Hepacosenoic acid (C17:H14:0)) > 4.72% (Oleic acid(C18:H14:0)). These properties conferred relative prospects on the crude oil of the test plant as a suitable potential biodiesel substrate and consequently, large scale afforestation efforts be renewed, to guarantee ready availability of the raw materials.

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The fossil fuels namely coal, natural gas and oil, remain the predominant global energy consumed in the world today (Yunus and Zuru, 2017). These sources are finite, expecting to be exhausted in the near future. The utilization of the nonrenewable energy is powered by rising human population and industrialization. This enhances carbon emissions, engenders environmental and human health concerns, as well as promoting ozone layer depletion and climate change (Banik et al., 2018). Consequent upon the aforementioned, attention is being directed to renewable energy resources in anticipation to the exhaustibility of fossil fuel reserves and the growing environmental concerns (Sreedhar and Yandapalli, 2016). Biodiesels are bio-based diesels, described as the best alternative fuels for diesel engines, are environmentally friendly, biodegradable, with higher energy efficiencies, and essentially non acidic (Igbunmet et al., 2012). Also known as methyl esters, they have higher cetane numbers (CN) which is the measure of diesel quality, with other characteristics similar to fossil-based diesel fuels. Conventionally, biodiesel is produced by trans-esterification of triglyceride feedstock such as vegetable oil, animal fat and used cooking oil. The resulting triglyceride is treated with methanol or other short chain alcohols with a catalyst. Homogeneous base catalysts are mostly used in industrial biodiesel production because trans-esterification reaction proceeds with fast rate under mild reaction conditions. However, separation of the catalyst and purification of the products require large amount of water (Jain and Sharma, 2014). The use of edible vegetable oil seeds for biodiesel production is strongly discouraged, owing to the tendency for rising cost due to competition for these edible substrates. In this regard, it becomes imperative for cheap, inedible biomass that meet all criteria for consideration as useful alternative biodiesel feedstock(Umaru and Aberuagba, 2012). Such substrates include waste food oils, by products of vegetable oil refining, vegetable oils or animal fats etc. Different studies have reported attempts to evaluate

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the biodiesel potentials of oil – rich seeds. Umaru and Aberuagba, (2012), studied the characteristics of Jatropha curcas oil seeds for biodiesel production. Odjobo and Umaru (2019), investigated the biodiesel fuel potential of Canarium schweinfurthii Seed and Pulp Oils in order to determine the fuel quality parameters of the biodiesel produced. The potentials of Hura crepitans seed oil as an alternative feedstock for biodiesel fuel have also been evaluated (Adewuyi et al., 2014). The use of seed oil of Balanites aegyptiaca as biodiesel feedstock in Nigeria is still at the infancy, as paucity of literatures accounted for this (Jauro and Adams, 2011; Gutti et al., 2012). This study therefore investigated the biochemical, constituents of Balanites aegyptiaca seed oil as a potential feedstock for biodiesel production.

MATERIALS AND METHODS
The preliminary seed preparations and extractions was carried out in the chemistry laboratory of Federal College of Forestry, Jos. While analysis was done in National Research Institute for Chemical Technology (NARICT), Zaria Kaduna State, Nigeria.

Source of and Preparation of Seeds: The kernels of the test plant, Balanites aegyptiaca otherwise known as desert date, sourced from Toro - Bauchi State, were collected in sterilized polythene bags and identified in the Herbarium of the Federal College of Forestry, Jos (FCFJ), Plateau State, Nigeria.

Oil extraction: The modified methods of Ejilah et al. (2012), were adopted for the oil extraction processes. The nuts were air- dried in the chemistry lab, FCFJ, for 15 days. Dried nuts were sorted by removing damaged nuts which were believed to lower quality of oil (Sandulachi et al., 2019). One kilogram of the Nuts were mechanically decorticated to remove the kernels. The extracted kernels were further air-dried for 10 days. The kernels were weighed using weighing balance, pulverized using mortar and pestle followed by toasting at temperature between 45-47°C, so as to reduce moisture and ease extraction (MLambo et al., 2011). The kernel oil was extracted by traditional methods as described by Abu-Al-Futuh (1989), involving pouring of the pulverized toasted materials into hot water (floatation), followed by decantation and drying(Figure 1). The oil obtained was analyzed for proximate and some potential biodiesel properties.

Physical and Chemical Potential Biodiesel Property: The biodiesel properties of extracted oil of Balanites aegyptiaca were done in accordance with the American Society of Testing Material (ASTM, 1993)
methods. This to determine the kinetic, density viscosity (using Clandon Viscometer, model: VT-03 Viscometer), the specific gravity (using specific gravity bottle) as described Umaru and Aberuagba, (2012), saponification value, peroxide and iodine value (Pearson and Paraquit, 2006; Umaru and Aberuagba, 2012). The Acid value was tested by dissolving 2.0g of each of the oil samples separately in 50cm3 of mixed neutral solvent(25cm3 dimethyl ether with 25cm3 of ethanol carefully neutralized with 0.1M NaOH, using 1% phenolphthalein solution). The mixture was titrated with 0.1M NaOH aqueous solution with constant shaking to achieve a faint pink color (Umaru and Aberuagba, 2012).

**Fatty acids composition:** Gas chromatography and Mass Spectrometry (GC-MS) of model: QP2010 and HP5973 respectively, (NARICT), were used to determine the fatty acids composition of the oil sample of the *B. aegyptiaca* with as described by (Rizvi, 2009).

**Some measurable quantities:** The refractive index (1) determined using the Perkins mathematical formula reported by Babatunde and Bello (2016) (Eq. 1).

\[
RI = 1.45765 + 0.0001164 \times IV
\]

Where; RI = Refractive Index; IV = iodine value

The cetane number of the methyl esters content of the oil was calculated based on Krisnangkura (1986), as described by Adewuyi et al (2014), using the formula (Eq. 2) below

\[
CN = 46.3 + \frac{54.58}{SV} - (0.225 \times IV)
\]

Where SV = Saponification value; IV = iodine value

The calorific value was determined based on Batel et al (1980), as described by Adewuyi et al (2014), using the formula (Eq. 3) below

\[
CV = \frac{47,643-4.1871-38.31S}{3} (in \text{ KJ/kg})
\]

Where 1 = iodine value; S = Saponification value;

**RESULTS AND DISCUSSION**

The proximate composition analysis of the crude kernel oil of *Balanites aegyptiaca* gave 1.35% moisture, 4.70% Ash, 56.75% crude lipid, 22.09% protein, 12.75% crude fibre and 2.6% carbohydrate (Figure 2). The relatively lower % moisture content of *Balanites aegyptiaca* is an indication of a reasonable longer shelf life of *Balanite* oil over *Canarium schweinfurthii* (Adewale et al, 2009; Jauro and Adams, 2011). The high content of % ash, %lipid and %crude protein oil extracts is an indication high proportion of minerals as reported by Ibok et al (2008) and Hassan et al., (2011). The % crude protein obtained for *B. aegyptiaca* is closely similar to the value reported by Oderinde et al (2009) from *Hura crepitans* oil extracts (Figure 2). Arora and Tak (2013), reported a range of 26.0-26.8% from *Balanites roxburghii* oil extract. The high protein constituent of the oil provides a good source of protein supplement in both human and animal diets (Hassan et al., 2011). *B. aegyptiaca* oil extract has more % crude fiber than *H. crepitans* (12.75 >6.70%). This suggests its use as ingredient for animal feeds (Oderinde et al., 2009). The oil showed a very low content of carbohydrate compared to *H. crepitans*. This high carbohydrate content and crude fiber suggests the suitability of compounding the latter in animal feed, while the former could reduce the risk of coronary heart diseases, hypertension and breast cancer and diabetes.

**Biochemical composition and Biodiesel Properties of Balanites aegyptiaca:** The average biochemical composition *Balanites aegyptiaca* revealed that the crude kernel oil had 0.949g/cm³, 216.4mg KOH/g and 2.18mgKOH/g as relative density, saponification and acid values respectively. While the peroxide, iodine and viscosity values were 4.84(meq/Kg), 77.08g/100g and 150.3mm²/s respectively. The crude kernel oil gave Light yellow Colour at room temperature and a non-drying oil class due to its iodine value(77.08 g/100g) (Figure 2).The cetane number and refractive index determined were 54.18 and 1.487(@ 30°C), while the calorific value was 39.03 MJ/kg (Figure 2). The relative density of the *B. aegyptiaca* oil extract (0.949 g/cm³) compared favourably with 0.950 g/cm³.
Assessment of Biodiesel Fuel Potentials of Seed Crude Oil….

1470

The refractive index of 1.487 (@30°C) recorded from crude oil extract of B. aegyptiaca oil was close to 1.36, 1.466 and 1.471 observed for Hura crepitans (Ottih et al., 2015), Jatropha curcas (Umaru and Aberuagba, 2012) and Manji, et al. (2013), indicated a refractive index (RI) value of 1.478 from non-esterified oil extract of B. aegyptiaca. These findings thus suggested the oil from these seeds as potential bio diesel resources. According to Oderinde et al (2009), the refractive index describes the ratio of the velocity of light in vacuum to the velocity of light in a medium. It indicates the level of saturation of the oil as well as loss of unsaturation. The RI reduces with reduction in double bond (unsaturation). Japir et al (2017), pointed that high refractive index of oils is attributable to the high number of carbon atoms in their fatty acid composition. Acid values (AV) of 2.18mgKOH/g obtained for non-esterified oil extract of B. aegyptiaca was higher than 0.995 mg KOH/g reported from esterified study by Jauro and Adams (2011). Other workers reported 7.09 mg KOH/g and 36.2 mg KOH/g AVs for non-esterified crude oils of H. crepitans (Ottih et al, 2015) and J curcas (Umaru and Aberuagba, 2012). According to Ezilah, et al. (2012), the acid value indicates the extent of decomposition of the constituent glycereids by lipase activities. The acid value of the oil determines its, edibility, shelf life as well as industrial applications. Low AV oils (<4.0 mg KOH/g) (Nwe et al., 2019), are edible to human and livestock, stable over a long period of time and protect against rancidity (long shelf life) (Summonu et al., 2017). High AV value renders the oil inedible, but useful for production of paints, liquid soap and shampoos (Aremu et al., 2006a). Very low acid value is an indication of a good biodiesel potential (Umaru and Aberuagba, 2012). The peroxide value (PV) of oils 4.84 meq/Kg was obtained for non-esterified oil extract of B. aegyptiaca. 2.0 meq/Kg and 20.0 meq/Kg were reported for Jatropha curcas (Umaru and Aberuagba, 2012) and Hura crepitans (Ottih et al., 2015), while Jauro and Adams (2011) indicated a PV of 8.0 meq/Kg from esterified Balanites aegyptiaca oil extract. Manji et al. (2013), observed that a low PV indicated oil stability against oxidative degradation. They further remarked that rancidity commences when the peroxide value reaches 20 - 40 meq/kg (Charles and Guy, 1991). This has been viewed to result in polymerization of the esters and the formation of the gums and sediments, which clog the filters of the engines (Clark et al., 1984; Montcho et al., 2018).The iodine value (IV) of 77.08 g/100g of crude oils extract of B. aegyptiaca was higher than 42.28 g/100g reported for esterified sample by Jauro and Adams (2011). However, higher values (105.0 g/100g and 149.6 g/100g) were obtained from non-esterified oils of Jatropha curcas (Umaru and Aberuagba, 2012) and H. crepitans (Ottih et al., 2015). According to Jauro and Adams (2011), oil classification is based on its iodine value (IV). Thus IV of < 100 g/100g, between 100-130 g/100g and > 130 g/100g are considered non-drying, drying and semi-drying respectively. Consequently, the IV (77.08 g/100g) of the test crude oil of B. aegyptiaca renders the oil a non-drying. Higher IV also implies higher propensity for rancidity by oxidation (Ouilly et al., 2017). The low iodine value of the oil is highly advantageous because the oil would be stable to polymerization and/or oxidation. The lower IV authenticates seed oils for biodiesel production (Nwe et al. 2019). The saponification value (SV) of 216.43mgKOH/g obtained from crude oil extract of B. aegyptiaca oil compares favorably with 220.19 mg KOH/g and 190.0 mg KOH/g from non-esterified oil extracts of Hura crepitans (Ottih et al 2015) and Jatropha curcas.
(Umaru and Aberuagba, 2012) respectively. However, esterified oil extract of *B. aegyptiaca* gave a relatively lower SV 134.6 mg KOH/g (*B. aegyptiaca* (Jauro and Adams, 2011). According to Ejilah et al. (2012), The SV provides an index of the average molecular mass of fatty acids present in seed oil. The higher SV implies higher of molecular mass fatty acids. Oil extracts ranging from 130 to 193 mg KOH/g (Jauro and Adams, 2011), 210–213 mg KOH/g (Nwe et al., 2019), 220.19mgKOH/g (Otth et al, 2015), etc, were considered suitable for use in biodiesel production. This is because higher saponification had been thought to improve the lubrication property of the oil, reduces engine wear, extend the operational life and efficiency of diesel fuel pumps and injectors (Ejilah et al. 2012). In their opinion, Ottih et al (2015), suggested that oils with saponification value of 220.18 mg KOH/g could be good for soap making, paint driers and production of shaving cream. (Mater, 2012). The viscosity values (VV) of the crude oil extracts of *B. aegyptiaca* of 150.3 mm²/s was higher than values of 5.91 mm²/s (*H. crepitans*), 34.42 mm²/s (esterified *B. aegyptiaca*) and 40.0 mm²/s (non-esterified *Jatropha curcas*), reported by Ottih et al (2015), Jauro and Adams (2011) and Umaru and Aberuagba (2012) respectively. Meher et al. (2006), opined that viscosity reflects the operation of fuel injection from the diesel injector, flow in fuel pumps, and pipelines especially at low temperatures. Azuaga et al (2018), affirmed that viscosity of oil extracts depends on the nature of the constituent triglycerides, as well as their chemical properties. They explained that the oil viscosity and density increase and decrease respectively, with saturation unsaturation polymeric triglyceride chains. Viscosity also depends on sheer stress and temperature. Sheer stress does not have much effect on the storage of oils which are used for edible purposes but the temperature does affect it.

**Fatty acids composition of crude kernel oil extract of *B aegyptiaca*: The analysis of fatty acids composition of crude kernel oil extract of *B aegyptiaca* revealed the presence Pentadecanoic acid (C15H30O2), 9,12-Octadecanoic acid (C19 H32O2), Heptacosanoic acid (C27H56O2) and Oleic acid(C18H32O2) (table 3). The relative percentage abundance (RPA) of these fatty acids were in the order of 67.17% (9,12- Octadecanoic acid (C19 H32O2)) > 16.22% (Pentadecanoic acid (C15H30O2)) > 11.89% (Heptacosanoic acid(C27H56O2)) > 4.72% (Oleic acid(C18H32O2)) (**Table 3**).

The cetane number obtained showed a higher value (54.18) than the minimum recommended standard value (EN 14214) of 51.00(Sidohounde et al, 2019).

Many workers have recorded relative values of cetane number (CN) based on the different origins. CN of 44.53, 47.80, and 52.85 are obtained from seed oils of *Hura crepitans* (Sidohounde et al., 2019). *Sclerocarya birrea* (Marula) (Ejilah et al., 2012) and *Ceiba pentandra* (Montcho et al., 2018). According to Montcho et al. (2018), the cetane index measures a fuel ability to ignite itself (Aligrot, 1994). The higher the cetane number, the shorter the ignition delay time and the better the combustion quality (Haidara et al., 1996). The cetane index of *Balanites aegyptiaca* is 54.18 (Table 2). This value was close to range of 40.0 – 55.0 of petrol diesel recommended by ASTM D975 (Sidohounde et al., 2018). According to Demirbas (2006), longer chain fatty acids with more saturated molecules are more likely to produce higher cetane numbers and higher combustion efficiency (Ejilah, 2012). According to Sidohounde et al. (2018), some properties of oil (viscosity, oxidation stability, cetane number, etc), affect the fatty acids composition of extracted crude oil. Unsaturated fatty acids content of confers stability and durability to the oil. Highly unsaturated oil and the length of the C- C chain could reduce the cetane number of its biodiesel (Sidohounde et al., 2018).

**Conclusion**: The study revealed the crude oil extract of *Balanites aegyptiaca* to give high crude protein (22.09%) and crude fat (56.75%), saponification value (216.43 mg KOH/g), peroxide value (4.84 meq/Kg), acid value (2.18 mg KOH/g), iodine value (77.08/g/100g), viscosity value (150.3 mm²/s), cetane number (54.08), and calorific value (39.03 MJ/kg). Fatty acids assayed were in the order of 67.17% (9, 12-Octadecanoic acid, C19 H32O2) > 16.22% (Pentadecanoic acid, C15H30O2) > 11.89% (Heptacosanoic acid, C27H56O2) > 4.72% (Oleic acid, C18H32O2) (**Table 3**).

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**Table 2**: Fatty Acid Composition of *Balanites aegyptiaca* Seed oil Extracts

| S/N | Retention Time (RT) min | Compound | formula | HIT | Quality (%) | Percentage composition |
|-----|------------------------|----------|---------|-----|-------------|------------------------|
| 1   | 18.78                  | Pentadecanoic acid, 14-methyl methyl ester | C15H30O2 | 92  | 16.22       |                        |
| 2   | 20.49                  | 9,12-Octadecanoic acid, methyl ester (E,E) | C19H32O2 | 93  | 67.17       |                        |
| 3   | 20.69                  | Heptacosanoic acid, methyl ester | C27H56O2 | 91  | 11.89       |                        |
| 4   | 21.17                  | Oleic acid | C18H32O2  | 90  | 4.72        | (Total) 100            |

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*CHOMINI, MS; DASPAN, AJ; KAMBAI, C; CHOMINI, AE; BASSEY, EA; FATOKE V; RABIU, AU*
Assessment of Biodiesel Fuel Potentials of Seed Crude Oil

(Heptacosanoic acid, C\textsubscript{28}H\textsubscript{56}O\textsubscript{2}) > 4.72 % (Oleic acid, C\textsubscript{18}H\textsubscript{34}O\textsubscript{2})

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