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Assessment of Proximate and Physico-Chemical Potentials of Crude Kernel Oil Extracts of *Canarium schweinfurthii* Engl.

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ABSTRACT

The finite, depleting and unsustainable nature of fossil fuels remained a global concern. This had continued to stir up an urgent need to consider cheaper renewable and sustainable alternative. Consequently, the assay of proximate and physico-chemical potentials of crude kernel oil extracts of *Canarium schweinfurthii* Engl. was conducted. This was intended to evaluate the nutritional and some of the inherent biodiesel properties. The procedure according to Association of Official and Analytical Chemist (AOAC) were deployed to analyze the proximate, physico-chemical and fatty acids contents of the crude kernel oil extracted of the test plant. It was found that the oil sample of the test plant had 9.25±0.05% (moisture content), 6.10±0.09% (crude fiber), 23.62±0.02% (crude protein), 44.35±0.04% (crude lipid), 10.35±0.04% (ash) and 6.33±0.03% (carbohydrate). The physico – chemical assay of the oil revealed promising biodiesel properties with relative density (0.966±0.01 g/cm³), refractive index (1.465±0.05 at 30°C), calorific value (38.93±0.13MJ/kg), viscosity value (150.1±0.70 mm²/s), saponification value (220.30±0.98 mgKOH/g), peroxide value (4.26 ± 0.08meq/Kg), acid value (2.49±0.04 mgKOH/g), iodine value (64.70±0.10 g/100g) and cetane number (56.52±0.68). Furthermore, 14-methyl Pentadecanoic acid, methyl ester (C₁₇H₃₄O₂), 13,16-Octadecanoic acid, methyl ester (C₁₉H₃₄O₂) and Heptacosanoic acid, methyl ester (C₂₈H₅₆O₂) were the assayed fatty acids content of crude kernel oil extract of *C. schweinfurthii*. These had relative percentage abundance (RPA) of 25.80±0.04%, 67.60±0.30% and 6.60±0.03%. The findings clearly elucidated the biodiesel potential of the kernel oil sample of *C. schweinfurthii* and consequently recommended its incorporation. In this regard, it became imperative for concerted afforestation efforts that would guarantee its sustainable utilization.

Keywords: *Canarium schweinfurthii* Engl, Biodiesel, proximate, physico-chemical, fatty acids crude kernel oil extracts

Introduction

The escalating demands for energy consequent upon pressure resulting from increased human population, industrialization and economic activities, against the backdrop of finite, depleting

nonrenewable fossil fuel reserves has remained a challenge globally to teaming economies (Odjobo and Umar, 2019). Consequently, the quest for cheaper, sustainable and eco-friendly options has

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continued to gain global recognition. Also, mitigation of global warming and associated greenhouse emissions imply reduction in continued reliance on fossil fuels. The term biodiesel connotes type of diesel from biological sources (bio-based), also described as an alternative fuel for diesel engines. It's wide range of advantages include non-acidic, biodegradability environmental friendliness and higher energy efficiencies (Igbum *et al.*, 2012).

They are technically known as long C-C chained methyl esters, with high cetane numbers (CN), with other measurable and desirable properties similar to fossil-diesel fuels (Atabani *et al.*, 2012), developed as alternative to fossilized diesel, derived from lipids and oil-based plant and animal substrates. The competitive demand for these raw materials as food by man and livestock might pose a major setback. Consequently, the imperativeness for cheap, non-edible and less competitive organics as useful alternative biodiesel substrates (Umaru and Aberuagba, 2012).

This invariably informed the need for cheap plant materials derived from many feedstocks which could blend with diesel (Wang *et al.*, 2014). Such substrates include waste food oils, by-products of refined oil and fat from plant and animal origins etc. Many workers have shown attempts to evaluate the biodiesel potentials of different plants materials. *Jatropha curcas* (Thamizhselvi *et al.*, 2015); *Ceiba pentandra* (Montcho *et al.*, 2018); *Hura crepitans* (Adewuyi *et al.*, 2014); *Balanite aegyptiaca* (Ogala *et al.*, 2018) have shown some favorable outcomes.

Canarium schweinfurthii Engl. is a forest tree species which belongs to the Burseraceae family. It grows mostly in the equatorial forest regions of East, west and Central Africa (Orwa *et al.*, 2009). Locally, it is otherwise known as black date "ube okpoko" and "Atili" in Igbo and Hausa respectively (Odjobo and Umaru, 2019). It is endemic, with commercial quantities found in the central and southern Plateau, as well as in the north

central and south-eastern Nigeria, state of Nigeria and is also produced in similar quantities in other state of northern and south-eastern Nigeria. It produces its fruits in the rainy season, usually between the months of April and September (Kochar, 1981). The fruits have both nutritional and pharmaceutical use. The fruit is made of three parts: flesh, nut and kernel. The pulp is rich with protein, crude fat (23%), crude fiber, carbohydrate, ash and fat-soluble vitamins such as A, D, E, and K (Edou *et al.*, 2012).

The use of seed oil of *Canarium schweinfurthii* as biodiesel feedstock in Nigeria is still at the infancy, coupled with paucity of published works in this regard (Magashi and Abayeh, 2017; Odjobo and Umaru, 2019). The focus of this study therefore was to evaluate the biochemical properties of *C. schweinfurthii* kernel oil as a potential substrate for alternative diesel fuel.

Materials and Methods

Sourcing and Preparation of Kernel of Canarium schweinfurthii

The kernels of *Canarium schweinfurthii* were sourced from Toro - Bauchi State, collected in sterilized polythene bags and thereafter taken to Federal College of Forestry, Jos-Plateau, for identification (voucher number of FHJ 308).

Extraction of Crude Kernel Oil of Canarium schweinfurthii

The crude kernel oil extract of *Canarium schweinfurthii* was extracted, using modified procedure of Ejilah *et al.* (2012). It involved air – drying the nuts for 10days in the chemistry lab, FCFJ, followed by sorting, mechanically decorticated, toasting (MLambo *et al.*, 2011) and extracted by traditional method (Abu-Al-Futuh, 1989). It was decanted and dried, as described in Figure 1. The oil obtained was analysed for proximate and some potential biodiesel properties.

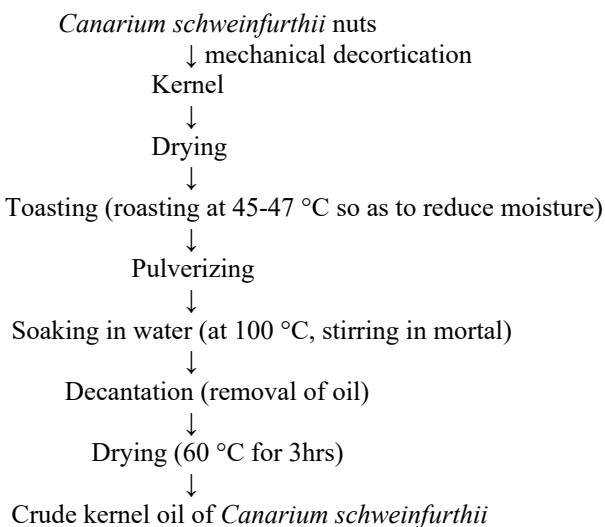


Figure 1: Flow chart of production Crude kernel oil of *Canarium schweinfurthii*

Proximate content Assay of Crude kernel oil of *Canarium schweinfurthii*

The proximate content Assay of extracted kernel oil of *C. schweinfurthii* was done following the procedure of AOAC (2008) at the National Research Institute for Chemical Technology (NARICT), Basawa Zaria, Kaduna State, northern Nigeria.

Physico-chemical and Potential Biodiesel Properties of Crude kernel oil of *C. schweinfurthii*

The physico-chemical composition analysis of extracted crude kernel oil of *C. schweinfurthii* were performed following the procedure of the American Society of Testing Material (ASTM, 1993; 2014). The acid value was tested by dissolving 2.0g 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). Titration of the mixture with 0.1M NaOH aqueous solution, followed constant shaking to faint pink color (Umaru and Aberuagba, 2012). Relative density, viscosity (using Clandon Viscometer, model: VT-03 Viscometer). The specific gravity (using specific gravity bottle), saponification value, peroxide and

iodine value based on description of Umaru and Aberuagba (2012).

Fatty acids content assay of crude kernel oil of *Canarium schweinfurthii*

The fatty acids content assay of the crude kernel oil extract of the *C. schweinfurthii* was carried out using modified procedure of Rizvi (2009), using Gas chromatography and Mass Spectrometry (GC-MS) of model: QP2010 and HP5973 respectively. This was carried out at the National Research Institute for Chemical Technology (NARICT), Zaria - Kaduna State.

Some Measurable Biodiesel Properties

Some important biodiesel properties such as cetane number (CN), calorific value (CV) and refractive index (RI) were determined using reference formulae as follow

The cetane number (CN) of the methyl esters content of the oil was calculated based on Krisnangkura (1986), as described by Adewuyi *et al.* (2014), using the formula (1) below

$$CN = 46.3 + \frac{5458}{SV} - (0.225 \times IV) \dots\dots (1)$$

Where SV = Saponification value; IV = iodine value

The calorific value (CV) was determined based on Batel *et al.* (1980), as described by Adewuyi *et al.* (2014), using the formula (2) below: -

$$CV = 47,643 - 4.187 I - 38.315 (in \text{Kj/kg}) \dots\dots (2)$$

Where I = iodine value; S = Saponification value

The refractive index (RI) determined using the Perkins formula (3) reported by Babatunde and Bello (2016).

$$RI = 1.45765 + 0.0001164 IV \dots\dots (3)$$

Where RI = Refractive Index; IV = iodine value

Results

The results on proximate content assay of the crude kernel oil extracts of the test plant indicated 9.25±

0.05%, 6.10±0.09%, 23.62±0.02%, 44.35±0.04%, 10.35±0.04% and 6.33±0.03% for moisture content, crude fiber, crude protein, crude lipid, ash and carbohydrate respectively (Table 1).

The average values of physico-chemical content of crude kernel oil extract of the test plant revealed that relative density, saponification value, peroxide value, and acid value were 0.966±0.01 g/cm³, 220.3±0.98 mg KOH/g, 4.26±0.08 meq/Kg and 2.49±0.04 mgKOH/g respectively. While the, iodine and viscosity stood at 64.70±0.10 g/100g and 150.1±0.70 mm²/s respectively (Table 2).

Cetane Number, Calorific Value, Refractive Index and Fatty Acids

The mathematically evaluated indicated 56.52 ± 0.68, 38.93 ± 0.13 MJ/kg and 1.4652 (@ 25°C) for cetane number (CN), calorific value (CV) and refractive index (RI) respectively.

14-methylpentadecanoic acid, methyl ester (C₁₇H₃₄O₂), 13,16-Octadecanoic acid, methyl ester

(C₁₉H₃₄O₂) and Heptacosanoic acid, methyl ester (C₂₈H₅₆O₂) were the fatty acids of crude kernel oil extract of *C. schweinfurthii* assayed. These fatty acids had relative percentage abundance (RPA) of 25.80±0.04% (C₁₇H₃₄O₂), 67.60±0.30% (C₁₉H₃₄O₂) and 6.60±0.03% (C₂₈H₅₆O₂).

Table 1: The proximate analysis of crude Kernel oil *Canarium schweinfurthii*

Proximate composition (%)	<i>Canarium schweinfurthii</i>
Moisture	9.25±0.05
Crude fibre	6.10±0.09
Crude protein	23.62±0.02
Crude lipid	44.35±0.04
Ash	10.35±0.04
Carbohydrate	6.33±0.03
Mean values ± standard deviation for n = 3	

Table 2: Comparative average physico-chemical composition of Crude Kernel oil extracts of *Canarium schweinfurthii*

Parameter	<i>Canarium schweinfurthii</i> ¹	Reference ²
Relative density(g/cm ³)	0.966± 0.01	0.86-0.90(g/cm ³) (EN rec)
Refractive index (@ 30°C)	1.465±0.05	
Saponification value (mg KOH/g)	220.30±0.98	
Peroxide value (meq/Kg)	4.26±0.08	
Acid value (mgKOH/g)	2.49± 0.04	0.60(EN rec)
Iodine value (g/100g)	64.70±0.10	120(g/100g) (EN rec)
Viscosity value (mm ² /s)	150.1±0.70	
Cetane number	56.52±0.68	51(EN rec)
Calorific value (MJ/kg)	38.93±0.13	35.00(EN rec)
Colour	Light yellow	
Oil class	Non-drying	

¹ (Present study), ²(Adewuyi *et al.*, 2014), Mean values ± standard deviation for n = 3

Table 3: Fatty Acid Composition of Crude Kernel oil extracts of *Canarium schweinfurthii*

S/ N	Retention Time (tR) min	Compound	Molecular formula	HIT Quality (%)	Percentage composition
1	18.77	14methyl Pentadecanoic acid, methyl ester	C ₁₇ H ₃₄ O ₂	92	25.80±0.04
2	20.49	13, 16-Octadecanoic acid, methyl ester (E,E)	C ₁₉ H ₃₄ O ₂	90	67.60±0.30
3	20.69	Hepta cosanoic acid, methyl ester	C ₂₈ H ₅₆ O ₂	87	6.60±0.03
Three compounds			TOTAL		100
Mean values ± standard deviation for n = 3					

Discussion

The proximate analysis of crude kernel oil Canarium schweinfurthii

The proportion of percentage ash, lipid and crude protein contents of the non-esterified crude kernel oil extract of *Canarium schweinfurthii* implied high mineral content (Hassan *et al.*, 2011). These values compared favorably with the percentage crude protein obtained for *B. aegyptiaca*, lower than the value reported by Oderinde *et al.* (2009), but higher than that indicated by *Hura crepitans* oil extracts, which were non-esterified as well. *C. schweinfurthii* gave a relatively higher % moisture content than non-esterified *Cyperus esculentus* and *Hura crepitans*, however its lipid content provides a rich potential resource for biodiesel production (Hassan *et al.*, 2011). Ayoade *et al.* (2017), reported a relatively lower ash, crude lipid and crude protein contents for non-esterified crude kernel oil. Maduelosi and Angaye (2015). Reported 26.09, 0.78, 19.28, 30.56, 3.14 and 20.03 as values for percentage moisture content, crude fiber, crude protein, crude lipids ash and carbohydrate of non-esterified. However, the high crude lipid makes it the choice substrate for biofuel and other industrial products.

Biodiesel properties Crude kernel oil of Canarium schweinfurthii

Canarium schweinfurthii recorded a relative density value (0.966±0.01 g/cm³) favourably compared with 0.896-0.898 g/cm³ (*Cyperus esculentus*), 0.929 g/cm³ (*Hura crepitans*) and 0.86-0.90 g/cm³ (EN) reported by Sidohoude *et al.* (2018, 2019) and Adewuyi *et al.* (2014) respectively. This figure is not significantly different from the Automation Gas Oil (AGO) limit of 0.96 g/cm³ indicated by Igbum *et al.* (2013) as well as the standard ASTM (0.875-0.900) and EN14214 (0.86-0.900) range as reported by Odjobo and Umar (2019), showing good potential for biodiesel production.

The refractive index (RI) of 1.465±0.05(@ 30°C) recorded from the oil extract of *C. schweinfurthii* oil, similar to 1.46 (*Cyperus esculentus*) and 1.472 (*Hura Crepitans*) indicated by Adel *et al.* (2015) and Sidohoude *et al.* (2019) respectively. Comparatively, Manji *et al.* (2013), reported an RI (1.478) from non - esterified oil extract of *B. aegyptiaca*, suggesting these oils as potential biodiesel resources. The refractive index had been thought to form the basis of relating the ratio of the velocity of light in vacuum to the velocity of light in a medium (Oderinde *et al.*, 2009). This, they described as determining the saturation. Japir *et al.* (2017), established that the RI decreases

with reduction in unsaturation. They further explained RI increases with C-C of the oils. Acid values (AV) of 2.49 ± 0.04 mg KOH/g recorded from the oil extract of *C. schweinfurthii* was less than values from other non-esterified viz: 7.23-10.78 mgKOH/g (*Cyperus esculentus*) and 4.81 mgKOH/g (*H. crepitans*), but greater than 0.60 mgKOH/g (EN) indicated by Adel *et al.* (2015), Sidohoude *et al.* (2019) and Adewuyi *et al.* (2014) respectively. Other workers reported 7.09 and 36.2 mgKOH/g AVs for non-esterified crude oils extracts of *H. crepitans* (Ottih *et al.*, 2015) and *J. curcas* (Umaru and Aberuagba, 2012). The acid value (AV) had been thought to reflect the degree of decomposition of glycerides by lipase activities (Ejilah *et al.*, 2012). It determines the edibility, shelf life and extent of industrial applications. Oils with Low AVs (< 4.0 mg KOH/g) are edible to human and livestock, stable over a long period of time and protect against rancidity (long shelf life) (Sunmonu *et al.*, 2017; Nwe *et al.*, 2019). According to Umaru and Aberuagba (2012), oils with very low AVs reflect good biodiesel potential. However, those with high AVs indicate inedibility, but could find useful applications in paints, liquid soap and shampoos productions (Aremu *et al.*, 2006a).

The peroxide value (PV) of 4.26 ± 0.08 meq/kg from the kernel crude oil extract of *C. schweinfurthii* was higher than 0.79-1.52 meq/kg (*Cyperus esculentus*) and 28.02 meq/kg (*Hura crepitans*) reported by Adel *et al.* (2015) and Sidohoude *et al.* (2019) respectively. Low PVs have been reported to confer stability against microbial metabolism of oils (Manji *et al.*, 2013). In their opinion, posited that rancidity commences at a high range 20 - 40 meq/kg (Charles and Guy, 1991). This was explained (Clark *et al.*, 1984) to promote esters polymerization in addition to gum and sediments precipitation, which clog filters of automobile engines (Montcho *et al.*, 2018).

The iodine value (IV) of 64.70 ± 0.10 g/100g of crude oils extract of the test plant gave lower

values than those of other non-esterified sources such as *Cyperus esculentus* (71.82-72.94 g/100g), *Hura crepitans* (123.21 g/100g) and EN standard value (120g/100g) documented by Adel *et al.* (2015), Sidohoude *et al.* (2019) and Adewuyi *et al.* (2014) respectively. Oil classification depends on its IVs (Jauro and Adams, 2011). Oil extracts with IVs < 100 g/100g, between 100-130 g/100g and > 130 g/100g are considered non-drying, drying and semi-drying respectively.

Consequently, the test kernel oil extract with IVs of 64.79 g/100g is classified non-drying. Higher IVs also suggest higher tendency for rancidity by oxidation (Ouilly *et al.*, 2017). Thus, low IV of the test oils is highly advantageous, suggesting its stability to polymerization and/or oxidation agents. Low IVs consequently imply suitability for biodiesel (Nwe *et al.*, 2019).

The saponification value (SV) of 220.30 ± 0.98 mg KOH/g recorded in this study oil was slightly higher than 198.98-201.24 mg KOH/g (*Cyperus esculentus*) and 210.29 mg KOH/g (*Hura crepitans*) described by Adel *et al.* (2015) and Sidohoude *et al.* (2019). Similarly, 220.19 mg KOH/g and 190.0 mg KOH/g had been reported from non-esterified oil extracts of *Hura crepitans* (Ottih *et al.*, 2015) and *Jatropha curcas* (Umaru and Aberuagba, 2012) respectively. The SV increases with molecular mass of fatty acids (Ejilah *et al.*, 2012), Oil extracts ranging from 130 to 193 meq/Kg (Jauro and Adams, 2011), 210–213 mg KOH/g (Nwe *et al.*, 2019), 220.19mgKOH/g (Ottih *et al.* 2015), etc, were found appropriate manufacturing of biodiesel. Higher SVs were opined to improve the lubrication property of the oils, reduce engine wear, prolong operational life and efficiency of diesel fuel pumps and injectors (Ejilah *et al.*, 2012). Ottih *et al.* (2015), also suggested oils with SV of 220.18mgKoH would also be appropriate manufacturing soaps, paint driers and shaving cream.

The viscosity values (VV) of the crude kernel oil extracts of *C. schweinfurthii* of 150.1 ± 0.70 mm²/s was higher than values of 23.91-24.43 mm²/s (*Cyperus esculentus*) reported by Sidohoude *et al.* (2018). Ottih *et al.* (2015) indicated a VV 40.0 mm²/s from crude oil extract of *Jatropha curcas*. The oil viscosity determines the operation of fuel injection of the diesel injector, flow in fuel pumps (Meher *et al.*, 2006), the nature of the inherent triglycerides (Azuaga *et al.*, 2018). They explained that the oil viscosity and density affect with saturation unsaturation polymeric triglyceride chains.

Cetane Number, Calorific Value and Fatty Acids Composition

The cetane number (CN) of 56.52 ± 0.68 was relatively comparable to 44.53 (*Hura crepitans*) and the EN standard value of 51.00 (Sidohoude *et al.*, 2019; Adewuyi *et al.*, 2014). However, Sidohoude *et al.* (2018), described a range of 59.01-60.47 for oil extract of *Cyperus esculentus*. Other relative values 47.8 (*Sclerocarya birrea*) and 52.85 (*Ceiba pentandra*) reported Ejilal *et al.* (2012) and Montcho *et al.* (2018) respectively. The CN defines the fuel's capacity to spark itself (Aligrot, 1994). The higher the CN, the faster the ignition time and the improve the burning quality (Haidara *et al.*, 1996; Montcho *et al.*, 2018). The CN of 56.52 is slightly above the range of 40-55 of petrol diesel recommended by ASTM D975 (Sidohoude *et al.*, 2018). Demirbas (2006), pointed out that fatty acids with longer C-C chain, with more saturated molecules are more prone to have higher CN and higher combustion efficiency (Ejilal, 2012).

According to Montcho *et al.* (2018), calorific value (CV) determines the energy released when one kilogram of fuel is burned. The CV of 38.93 ± 0.13 MJ/Kg obtained was slightly lower than 39.07 MJ/Kg (*H. crepitans*) and higher than the range of 36.36-37.452 MJ/Kg (*Cyperus esculentus*) and the EN recommended value of 35.00 MJ/Kg (Adewuyi *et al.*, 2014; Sidohoude

et al., 2018; Sidohoude *et al.*, 2019). This portends a good biodiesel potential.

The fatty acids constituent of extracted oils are affected by some other inherent oil characteristics such as cetane number, viscosity, oxidation stability, etc. (Sidohoude *et al.*, 2018). Unsaturated fatty acids content confers stability and durability to the oil. The Higher unsaturated (C-C) chain the lower CN of its biodiesel (Sidohoude *et al.*, 2018).

Conclusion and Recommendations

The study revealed the proximate constituent of crude kernel oil extract of the test plant, indicating reasonable energy content (crude protein and crude lipid) with relatively low ash, fiber and carbohydrate. The physico – chemical characteristics of the oil revealed comparative biodiesel content of relative density, refractive index, calorific value, viscosity value, saponification value, peroxide value, acid value, iodine value and cetane number. Furthermore, 14-methyl Pentadecanoic acid, methyl ester (C₁₇H₃₄O₂), 13,16-Octadecanoic acid, methyl ester (C₁₉ H₃₄O₂) and Heptacosanoic acid, methyl ester (C₂₈H₅₆O₂) were the fatty acids composition of crude kernel oil extract of *C. schweinfurthii*. The fatty acids had relative percentage abundance (RPA) ranging from $6.60 \pm 0.03\%$ to $67.60 \pm 0.30\%$. These observed properties of the crude oil extract of *C. schweinfurthii* clearly showed its biodiesel potentials. Consequently, an enhanced afforestation effort of the plant species would guarantee its sustainable utilization.

Conflict of interest

The authors declare no conflicts of interest in this study.

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