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Investigation of biodiesel fuel potential of Canarium Schweinfurthii Seed and Pulp Oils

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--ABSTRACT--
The This study reports on biofuel potential of canarium schweinfurthii seeds (CNSSO) and its pulp (CNSPO) oils. These were compared with fossil-based diesel. The physicochemical characterization of the crude oils was also conducted and compared to biodiesel produced; The oil yield of CNSSO and CNSPO are: 30.72% and 80.4% respectively using n-hexane as solvent. CNSSO and CNSPO were shown to have a very high acid value at 130.15 mg KOH/g oil and 101.54 mg KOH/g oil as compared to the biodiesel produced from seed 1.422mg KOH/g oil CNSME and pulp 0.842 mg KOH/g oil CNSPME. The CNSPO has the highest FAMES conversion of 89.48%, while CNSSO was 77.94% when trans-esterified using NaOH catalyst and oil-methanol ratio of 1:6 in two minutes of reaction time. The fuel and physicochemical properties of the seed oil biodiesel and that of pulp have shown great similarities and when compared to ASTM standard, the fuel properties both showed close compatibility hence suitable for diesel engine.
KEYWORDS; - *Canarium Schweinfurthii**,** FAMES, Trans-esterification, biofuel, physicochemical properties*

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I. INTRODUCTION

The increasing demands on energy and depleting fossils reserves has made research on alternative fuels continue to gain worldwide attention. Moreover, the increasing global warming and other environmental hazards have forced almost all countries to reduce their dependence on fossil fuels [1]. Biodiesel is currently the most common alternative fuel being developed and used as a replacement for petroleum-based diesel. It can be defined as a mixture of mono-alkyl esters of long chain fatty acids (FA) derived from renewable lipids such as vegetable oils and animal fats when reacted with an alcohol (methanol or ethanol) in the presence or absence of a catalyst [2,3,4]. Biodiesel is biodegradable, non-toxic, renewable, and has low emissions of CO, SO2, particulates and hydrocarbons (HC) as compared to fossil diesel [4]. The use of vegetable oils (edible and non-edible) plays an important role in biodiesel production. However, availability of these raw materials varies. This necessitates the search for new low-cost agricultural crops [5,6]. Currently one of the main concerns of biodiesel research area is to identify, characterize and perform engine performance analyses on biodiesels derived from many new feedstocks as well as their blends with diesel [7]. Globally, there are more than 350 oil-bearing crops identified for biodiesel production [3]. Black date "Atili" also known as "*Canarium schweinfurthii bursaraceae*" is found in the kingdom plantae, because it is made up of multicellular and non-motile organism and its leaves also contain chlorophyll. It possesses vascular bundles placing it in the sub-kingdom tracheophyta. It falls under the super division spermatophyte seed plants because it is a higher gymnosperm. The embryo bears two cotyledons which places it in the class magnoliopsiodae dicotyledons. It also belongs to the sub-class rosidae because of its polypetalous corolla [8]. In Nigeria, the fruit of the perennial tree plant is called "ube okpoko" in Igbo and "Atili" in Hausa. The fruit is commonly found in large quantities in Pankshin area, Plateau state of Nigeria and is also produced in similar quantities in other state of northern and south-eastern Nigeria, The fruit yields fats and oil [8]. The plant produces its fruits in the rainy season, usually between the months of April and September. The flowers grow in clusters at the end of the twigs and are small and dark green in colour, the fruit which are of two varieties – long spirals and short round in shape develop from the flowers [9].

The purpose of this work was to produce biodiesel from ''black dates'' *canarium schweinfurthii* seeds and its pulp and study the fuel quality parameters of the produced biodiesel (FAME) from each as well as the physicochemical properties as they compare to fossil diesel using ASTM standards. Important fuel properties such as density, viscosity, oxidation stability, calorific value, as well as cold flow properties i.e. cloud point and pour point were measured and compared with ASTM D6751 standards. In this study, biodiesel production was based on Transesterification process using alkaline NaOH catalyst. The success of this study could yield promising and massive new raw material for biodiesel production on a large scale.

II. MATERIAL AND METHOD

Sample collection

Canarium schweinfurthii fresh and well ripe fruits were purchased from local market in Mangu area of Jos Plateau State, Nigeria. The fruits were sampled by random sampling techniques. The freshly harvested fruits were collected in polyethene bags; the separation of the pulp with the seed was done manually. After the separation, the pulp is pounded into smaller particles and then dried. The fruit was identified in the Herbarium of Department of Biological Sciences, Ahmadu Bello University Zaria, Nigeria.

Biodiesel production (Alkaline-catalysed Transesterification process)

The oil was heated to 130^{o}C in a beaker, placed on a hot plate, then 1% (m/m oil) of Methanol NaOH (Sodium methoxide) was added (ratio 6:1) to the oil. And the mixture stirred by a magnetic stirrer. The mixture (methanolic NaOH + Oil) was left for 5minutes and poured into a separating funnel then allowed to stand for 24 hours. After which the lower layer (containing glycerine unreacted methanol, unreacted NaOH, trace of water and salts) from biodiesel. The top layer in the separatory funnel is biodiesel. It was washed by adding, 35 mL of tap water to the separatory funnel. Swirled gently for about 1 minute to dissolve the methanol, glycerin, sodium hydroxide, and any soap. Then drained the biodiesel layer (top) into a clean, dry beaker.

Determination of FAME

To determine the FA compositions of ME, a biodiesel sample (1 μL) was injected into a gas chromatography (Shidmadzu, GC-MSQP2010plus) equipped with a Mass Spectrometer (MS) detector and a Rtx 5MS capillary column of 30 m × 0.25 μm × 0.25 mm. An initial temperature of 60 °C was maintained for 0 min, which was then increased at 10 °C per min to 180 °C maintained for 2 min and finally 15 °C per min to reach 280 °C. The column was maintained at the final temperature for another 4 min. The oven, injector and the interface temperatures were set at 60, 250 and 250°C respectively. The carrier gas was helium with the column flow rate at 1.10 mL/min at a 50:1 split ratio (Linear velocity 24.2 cm/sec).

Analysis of fuel properties

In this study, the physical and chemical properties of CNSSO, CNSPO and the FAMEs were determined. Moreover, Table 1 shows a summary of the equipment and test methods used in this study to analyse properties according to the ASTM D 6751 standard.

Table 1 Experiment specifications and instrumentation

Property	Equipment	ASTM D6751
Viscosity $mm2s^{-1}$ @ 40^{o}C	SVM 3000[a]	D7042/D445
Flash Point	Pensky-martens flash point-automatic NPM440[b]	D 93
Oxidative stability @110^{o}C	873 Rancimat [c]	D 675
Cloud and Pour point	Cloud and Pour point tester-automatic NTE450[b]	D 2500 and D 97
Density gm^{-1} @40^{o}C	SVM 3000[a]	D 1298
Carbon Residue	Conradson Carbon Residue Apparatus	D 189
Caloric value	C2000 basic calorimeter[d]	N/S
Refractive index@24.8^{o}C	RM 40 Refractometere[e]	N/S
Cetane number	Cetane Method Test Engine Assembly	D 613

*Manufacturer: a: Anton Paar (UK), b: Normalab (France), c: Metrohm (Switzerland), d: and IKA (UK), e: Mettler Toledo (Switzerland) *N/S ≡ not specified in ASTM D6751 test methods.*

III. RESULTS VIEW

Properties of crude oils (CNSSO and CNSPO) in Comperism to biodiesel fuel (CNSME and CNSPME)

Table 2 shows the properties of CNSSO and CNSPO in comparison with those of the biodiesel produced. Having considered the data presented in Tables 2, it can be seen that the viscosity was successfully reduced from 82.1 to 3.85 mm2/s-1 CNSME and 4.40 CNSPME respectively compared to ASTM D6751 and EN1214 standards. ., The refractive index was reduced from 1.4637 to 1.4434 and 1.4539 for CNSME and CNSPME respectively, density at 40 °C was from 0.97 to 0.90 gm-1 for CNSME and 0.97 to 0.88 gm-1 for CNSPME. The values are within the required limit (ASTM D6751 and EN14214). However, the viscosities obtained (CNSME and CNSPME) were still higher than the limit specified by both the ASTM D 6751 and EN 14214 standards. This might be attributed to the high viscosities of the parent oil. The same was observed by (Sanford et al.,2009) for castor methyl ester as the kinematic viscosity of castor methyl ester was 15.25 mm2/s-1 compared to 251.2 mm2/s-1 for the crude oil. The cloud and pour points of CNSME and CNSPME were measured and the values obtained are 6 °C and -5oC respectively. Moreover, the oxidation stability of CNSME (5.39 h), CNSPME (5.51h) meets both the ASTM D6751 and EN 14214 standards of 3 and 6 h, respectively. As seen, CNSSO and CNSPO were shown to have a very high acid value at 130.15 mg KOH/g oil and 101.54

mg KOH/g oil as compared to 1.422mg KOH/g oil CNSME and 0.842 mg KOH/g oil CNSPME. Higher acid value can cause fuel system deposits and reduces the lifelong of fuel pump (Ong H et al, 2011). Calorific value of fuel increase with chain length of molecule (Knothe G.,2005). The highest calorific value belongs to fossil diesel (45.8 MJ/kg). The calorific value of CNSME is 39.69 MJ/kg, CNSPME 37.698 MJ/kg the lower calorific value as compared to fossil diesel is due to the higher oxygen content of the biofuels (SahooL P. et al, 2009 and Diesel Fuel tech Review.2007).

Table 2: Physicochemical and Fuel properties of crude (CNSSO and CNSPO) oils in Comperism with biodiesel (CNSME and CNSPME).

Property	CNSPO	CNSSO	CNSME	CNSPME	ASTM D6751	EN 14214	DIESEL
Acid value mgKOH/g	101.54	130.15	1.422	0.842	< 0.3	-	0.35
Free fatty acid mgKOH/g	50.77	50.77	0.654	0.421	-	-	-
Saponification value mgKOH/g	216.05	216.05	56.86	61.98	-	-	-
Iodine value g/100g	64.84	64.84	48.68	52.38	-	-	-
Moisture content (%)	0.916	0.916	0.3	0.1	-	-	-
Refractive index@24.8^oC	1.4637	1.4637	1.4434	1.4539	N/A	N/A	-
Specific gravity@40^oC	0.916	0.916	0.856	0.89	0.82		0.88
Viscosity mm^2s^{-1} @40^oC	82.1	82.1	3.85	4.4	1.9-6.0	3.5-5.0	2.6
Density gm^{-1} @40^oC	0.97	0.97	0.90	0.88	0.875-0.900	0.86-0.900	0.85
Flash point ^oC	209.8	205.9	120	130	> 130	101	70
Pour point	N/D	N/D	-5^oC	-5^0c	-	-	-20oC
Cloud point	N/D	N/D	6^oC	6^oC	-	-	-
Oxidative stability @110	-	-	5.39h	5.51h	3h (min)	6h (min)	6h(min)
Calorific value MJ / kg	-	-	39.69	37.698	-	-	42
Cetane Number			46.56	44.58	47		46

N/D ≡ Not detected, N/A ≡ Not available

Fatty acid compositions of CNSSO, CNSPO, CNSSME and CNSPME

Table 3 shows the results of free fatty acid compositions of (CNSSO. CNSSME CNSPME and CNSPO). Based on the GCMS analysis, it was found that CNSME contained 18.21% saturated FAs and 1.78% unsaturated FAs. CNSPME contained 4.01% saturated FAs and 19.44% unsaturated FAs. It can be concluded that CNSPME is mainly dominated by unsaturated FAs, which is an indication for low oxidation stability, which can be delayed by addition of antioxidant (Shahabuddin M. et al, 2012). Therefore, it is necessary to supplement the CNSPME with conventional antioxidants such as propyl gallate (PrG) to make up for its low oxidation stability (Hajari et al., 2014).The oxidation stability of fuels is an important element which can help to determine the quality of fuel and it can also affect some of fuel physical and chemical properties such as density, viscosity and water content. While CNSME is dominated by saturated FAs and this may result in decrease in viscosity, because as the proportion of saturated fatty acids with longer carbon chain increases, it can lead to decrease viscosity (Ong H et al,2011). The difference in fatty acid profile in the crude oils and biodiesel is due to the derivatization that occurs during transesterification of the biodiesel produced as FAMEs content is high, due to derivatization. The crude oil contains quite low quantity of FFA (https://www.sciencedirect.com/topics/food-science/free-fatty-acids) while remaining fatty acids are present as triacylglyceride (TAG-bound). During trans-esterification reaction, all these fatty acids (FFA + TAG bound) gets converted to FAME in the biodiesel leading to high fatty acid profile as compared to the lower FFA content in the crude oil.

Table 3. FAME composition of biodiesel (CNSME and CNSPME) as compared to crude oil (CNSSO and CNSPO)

Fatty acids composition (as % methyl ester)	CNSPME	CNSME	CNSSO	CNSPO
C10:0	0.24	0.15	ND	ND
C12:0	ND	ND	ND	ND
C14:0	0.16	0.45	ND	ND
C16:0	4.19	1.51	30.85	11.26
C16:1	34.05	30.85	1.51	5.68
C18:0	14.02	3.56	17.42	26.89
C18:1	1.78	19.44	20.42	12.18
C20:0	8.30	0.56	2.47	1.87
C22:0	7.72	0.87	ND	ND
Total Saturated FA (%)	18.21	4.01	48.27	38.15

Total Monounsaturated FA (%)	1.78	19.44	20.42	12.18
Polyunsaturated FA (%)	N/D	N/D	N/D	N/D

N/D ≡ Not detected

IV. CONCLUSION

In this study, CNSME and CNSPME were produced and tested for various properties. They were found to have good potential to be used as a future energy source due to its significant calorific value, comparatively better cold flow properties and reasonable viscosity. Most parameters tested compared favorably with fossil diesel.

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