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Production of biodiesel using novel *C. lepodita* oil in the presence of heterogeneous solid catalyst

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ABSTRACT

Present study was designed to produce biodiesel using *Cola lepidota* seed oil in the presence of clay catalyst. The extraction was done in petroleum ether and oil was characterized using Fourier Transform Infrared Spectrophotometer (FTIR) and scanning electron microscope (SEM) techniques. The biodiesel produced, was characterized for specific gravity, kinematic viscosity, American petroleum index (API) gravity, flash point, cloud point, aniline point and diesel index. The result from FTIR shows that there was C-N stretching aliphatic amine at 1072.46 cm^{-1}, CH_2X alkyl halides at 1226.77 cm^{-1}, C-C stretching (in ring) aromatics at 1442.80 cm^{-1}, N-O asymmetric stretching nitro compounds at 1527.67cm^{-1}, C=C stretching α, β unsaturated esters at 1712.85 cm^{-1}, C-C stretching aromatics at 2924.18 cm^{-1}, O-H stretch or free hydroxyl alcohols or phenols at 3610.86 cm^{-1}. The oil yield was 1.76%. The result revealed that the biodiesel showed the following properties; specific gravity (0.862 g/cm^3), viscosity (4.8mm^2/sec), API (30.24 ^oC), flash point (80 ^oC), cloud point (-2 ^oC), aniline point (68 ^oC) and diesel index (1.424). These values were within the recommended limits of American Standard for Testing Material (ASTM D6751). This study reveals that *C. lepidota* oil is a veritable precursor for biodiesel production and other industrial applications.

Capsule Summary: The potential of a novel agro-product (*C. lepidota* seeds oil) for biodiesel production in the presence of a heterogeneous clay catalyst was evaluated and biodiesel produced was characterized for fuel quality.

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INTRODUCTION

Cola lepidota is an edible wild fruit found in the humid west and central African forests (Ogbu and Umeokechukwu, 2014). In Nigeria, the fruit pulp is eaten by human and some wild animal (primate especially) because of their large nutritional value and tasty pulp (Ogbu et al., 2007). The economic importance of *Cola lepidota* fruit in African serves as a supplement for vitamins in diet. Recent findings have revealed that the fruit contains bioactive compounds such as polyphenols, alkaloids, saponine and anthraquinones, etc. which possess some medicinal potentials (Mohammed et al., 2011). *Cola lepidota* commonly called yellow monkey cola is identified by various names as achicha or ochiricha in Igbo speaking state and Ndiya in Efik as well as ibibios of Akwa-Ibom State, Nigeria. *Cola lepidota* tree is 18m high with a twisted trunk and lumps, the leaflet are up to 60cm long

Fig. 1: *Cola lepidota* seeds (upper) and *Cola lepidota* fruits (below) used for oil extraction

(Ogbu and Umeokechukwu, 2014). Biodiesel is a renewable, biodegradable fuel manufactured domestically from vegetable oils, animal fats or recycled restaurant grease (Angelo et al., 2005; Chung et al., 2019; Hoseini et al., 2019; Kpan and Krahl, 2019; Kumar et al., 2019; Ni et al., 2020; Yusuff and Owolabi, 2019). Transesterification is the most popular reaction used for the conversion of oil into biodiesel. It involves the reaction of an alcohol in most cases butanol with the triglycerides present in oils, fats or recycled grease forming biodiesel and glycerol (Hideki et al., 2001; Fernando et al., 2018).

Currently, world is facing with problems of energy sustainability, environmental challenges, rising fuel prices and so on (Okedu et al., 2005; Black, 2010; McKenzie et al., 2012). Fuels are known for polluting air by emission of SO_2, CO_2, particulate matters and other gases (Alvarez et al., 2012). However, biodiesel is proved to be the best replacement for diesel because of its unique properties like significant reduction in greenhouse gas emission, non sulphur emission, non-particulate matter pollutants, low toxicity and biodegradability. This is a major challenge and the use of biodiesel as an alternative source of fuel would be able to overcome this problems and their effect (Ahmad et al., 2019; Chebbi et al., 2019; Chen et al., 2019; Kumar et al., 2019; Sánchez-Arreola et al., 2019).

Clay is an earth material that is plastic when moist but hard when fired, and composed mainly of fine particles of hydrous aluminum silicates and other minerals (Rao, 2013). Based on composition, it is crystallized aluminum silicate which contains other impurities. Secondary components of clay can be quartz, zircon, apatite, granite, etc. Clays often contain mixtures such as iron hydroxides and organic substances. Swelling is a very important feature of clay minerals that enables their wide application in various industries in the field of geotechnical engineering, environmental engineering and other industrial applications. High degree of efficiency for M^+ cation exchange is the result of charge imbalances in clay structure caused by exchange of Al^{3+} for Si^{4+} in the tetrahedral sheets, and of Mg^{2+} for Al^{3+} cations in the octahedral sheets. In addition, study of clay chemistry is also of great relevance to the chemical industry, as many clay minerals are used as catalysts, catalyst precursor or catalyst substrates in a number of chemical processes, like automotive catalysts and oil cracking catalysts (Francisco et al., 2018; David et al., 2019).

In a bid to explore on some of the seed oils that could give better biodiesel quality, we decided to extract oil from *Cola lepidota* seeds which have experienced a post-harvest loss of over 40%. Therefore, this study is aimed at producing biodiesel from *Cola lepidota* seed oil and characterizing the biodiesel produced as alternative to petroleum diesel through tests for fuel quality parameters. The results obtained from this study will encourage the cultivators to expand on their scale of production and ultimately create opening for empowerment.

MATERIAL AND METHODS

Sample collection and preparation

The *Cola lepidota* seeds were bought from Rumuokoro Daily Market in Obio/Akpor local Government area of Rivers State, Nigeria. The fruit pulps were separated from the seeds, washed with distilled water and the seeds obtained were oven-dried at 105°C until constant weight. The seeds were milled with manual grinder and stored for extraction. The clay sample used in this study was collected from Ugwuta (Isi Ogo) cave of Unwana new site in Afikpo North local Government area of Ebonyi State, Nigeria. The physicochemical properties of the clay have been characterized by Obi and Agha, (2016) and presented in Tables 1 and 2.

Extraction of oil

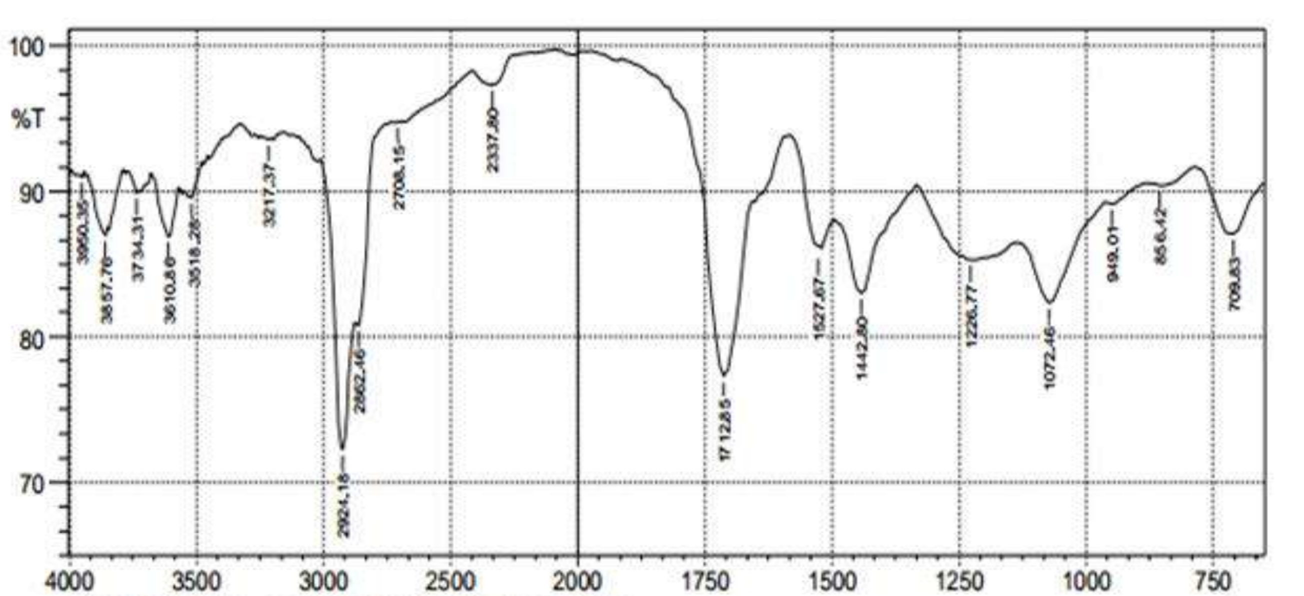

Fig. 2: Fourier Transform Infra-Red of the extracted *cola lepidota* seed oil [X-axis = Transmittance (%) and Y-axis = Wavenumber (cm^{-1})]

The oil was extracted from *Cola lepidota* seed using petroleum ether by soxhlet extractor. The percentage yield of the oil obtained was calculated using relation shown in Eq. 1.

$$\text{Yield (\%)} = \frac{\text{weight of oil obtained}}{\text{weight of sample}} \times 100 \qquad (1)$$

The oil obtained was used to produce biodiesel and was further characterized using the Fourier Transform Infrared Spectroscopy (FTIR) and scanning electron microscopy (SEM).

Biodiesel synthesis

The clay catalyst (0.4 g) was added to 5 ml of butanol. The mixer was agitated for 1h and then filtered. The butoxide was poured into a 150 mL conical flask and tightly corked throughout the process to prevent evaporation of butanol and absorption of moisture by the mixture. The extracted oil was heated in a round bottom flask at a temperature of 60˚C. The transesterification reaction was carried out by pouring the butoxide into the heated oil which was agitated then transferred into a separating funnel and was allowed to stand for 24 h. At the end of 24 h the biodiesel was separated from glycerol using a separating funnel. The glycerol which was the heavier liquid was collected at the bottom, while the lighter liquid (biodiesel) was further washed with warm water thrice. The biodiesel obtained was further characterized for specific gravity, cloud point, flash point, pour point, kinematic viscosity, API (American petroleum index) gravity and diesel index.

RESULTS AND DISCUSSION

The FTIR results of the characterization of the extracted oil are presented in Figure 2. C-N stretching aliphatic amine at 1072.46 cm^{-1}, CH_2X alkyl halides at 1226.77 cm^{-1}, C-C stretching (in ring) aromatics at 1442.80 cm^{-1}, N-O asymmetric stretching nitro compounds at 1527.67 cm^{-1}, C=C stretching α, β unsaturated esters at 1712.85cm^{-1}, C-C stretching aromatics at 2924.18 cm^{-1}, O-H stretch or free hydroxyl alcohols or phenols at 3610.86 cm^{-1}. The result from the SEM presented in Figures 3, indicate that the morphological form of the biodiesel was amorphous which means that the biodiesel can freely flow like corresponding petrol diesel.

Biodiesel characterization

The specific gravity value obtained was 0.862 g/cm^3 (Table 4). This value lies within the American Standard for Testing Materials**.** The result from this work showed a kinematic viscosity of 4.8 mm^2/s which was quite in agreement with the ASTM standard. Viscosity of a fuel is related to the fuel lubricity. Low viscosity fuels are unlikely to provide satisfactory lubrication in fuel injection pumps; these often lead to seepage and increase in wear (Raja et al., 2011). High viscosity in fuel are responsible for atomization of fuel, incomplete combustion and increased exhaust emissions, choking of the injections thereby forming larger droplets on injector, ring carbonization and accumulation of the fuel in the engine (Wang et al., 2006).

Table 1: Physical properties of the clay (Obi and Agha, 2016)

pH	Surface area (m^2/g)	Specific gravity (g/cm^3)	Pore volume (m^3/g)	CEC (meq/100g)
2.8	133.4	2.16	0.45	18.8

Table 2: Composition of the clay used as catalyst (Obi and Agha, 2016)

Element	Concentration (mg/L)	Oxide composition (%)
Al	159.593	32601
Si	232.143	47.380
Mg	14.320	2.919
Ca	5.902	1.203
Na	7.952	1.621
K	1.006	0.205
Fe	10.454	2.042
Ti	0.643	11.409
Loss on ignition	-	11.409

Table 3: Vibrational bands of the biodiesel produced using *C. lepidota* seed oil

S/N	Bands (cm^{-1})	Explanation
1	1072.46(m)	C-N stretching aliphatic amine
2	1226.77(b)	CH_2X alkyl halides
3	1442.80(m)	C-C stretching (in ring) Aromatics
4	1527.67(s)	N–O Asymetric stretching nitro compounds
5	1712.85(s)	C=C Stretching α, β unsaturated esters
6	2862.46(m)	C–C stretching alkane
7	2924.18(s)	C-C stretching aromatics
8	3610.86(s)	O–H stretch or free hydroxyl alcohols or phenols

Where, s = strong, m = medium, b = broad

Table 4: Comparison of fuel quality parameter of biodiesel obtained from *C. lepidota* seed oil with petroleum diesel and International Standards (ASTM)

Parameter	Values obtained	ASTM (D6751) limits	Diesel
Specific gravity (g/cm^3)	0.862	0.86-0.90	0.8503
Viscosity (mm^2/S)	4.8	1.9-6.0	3.2
API value (°C)	30.24	>10	
Flash point (°C)	80	100-170	37
Cloud point (°C)	-2	-	2
Aniline point (°C)	68	-	
Diesel index	1.424	-	

The API value is very important in determining the suitability of the biodiesel for both domestic and industrial applications. This is a measure of how heavy or light a diesel liquid is compared to water; if the biodiesel API is greater than 10, it is lighter and floats on water; if it is less than 10, it is heavier and sinks. The result from this work showed an API value of 30.24 °C. This value showed that the produced biodiesel was in conformity with the standard values. It also revealed the fluidity of the biodiesel produced.

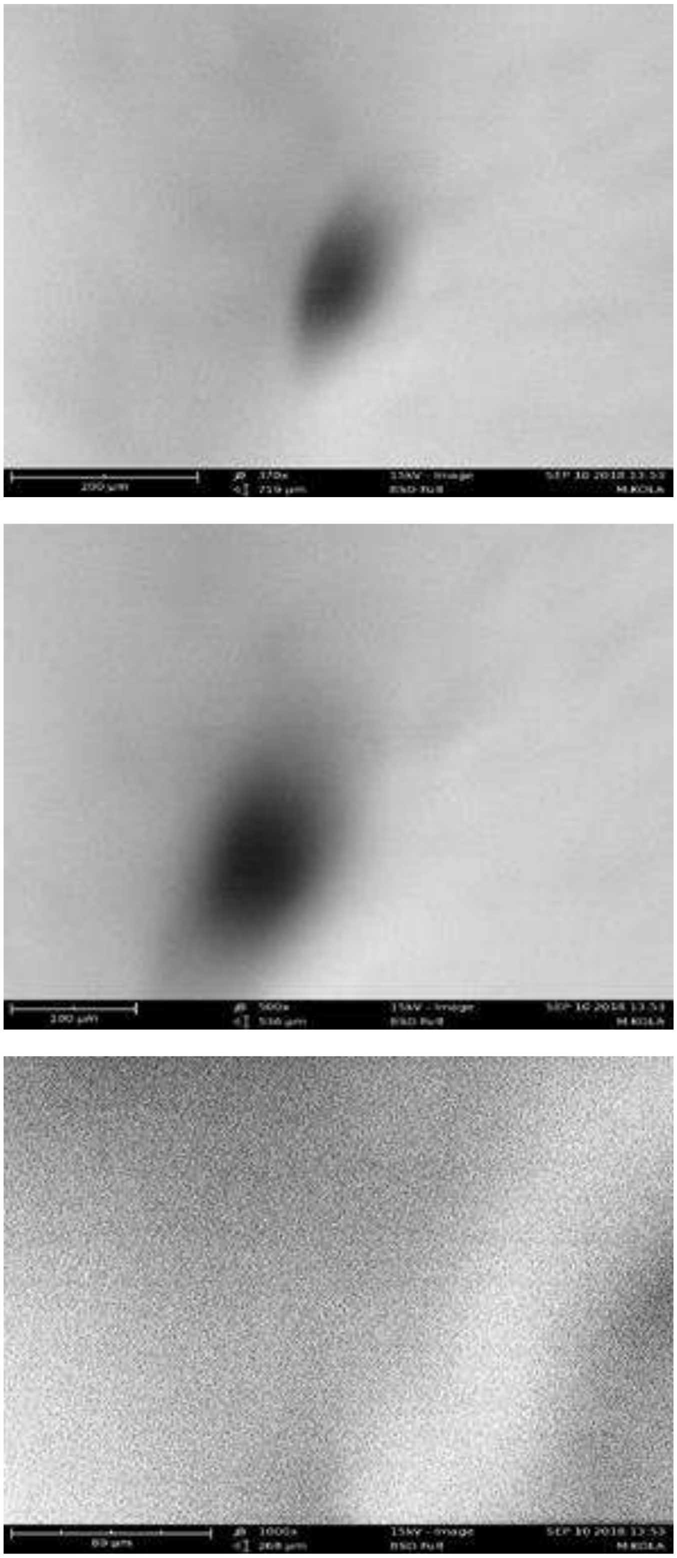

Fig. 3: SEM at magnification of 500x, 370x and 1000x

The flash point obtained from this work was 80˚C. Research work shows that high flash point ensure more safety in handling, transportation and storage (Candeia et al., 2009). Therefore the low value obtained from the biodiesel, showed that it was not highly flammable. The ASTM D6751 standard does not specify a cloud point for biodiesel. However, the cloud point must be tested and revealed to the buyer. The cloud point value for *Cola lepidota* oil over clay catalyst was -2°C as shown on Table 4. This value was lower compared to petroleum diesel which was 2°C. This implies that the biodiesel obtained from *Cola lepidota* oil will be suitable for temperate region that have extreme weather conditions.

The aniline point from this study was found to be 68˚C which showed that the biodiesel obtained was a high speed diesel and contained 40% of aromatic structures (Atzemi et al., 2019). The diesel index indicates the ignition quality of the fuel. It is found to correlate, approximately to the cetane number of commercial fuels. The value obtained from this study was lower than 50 and therefore will result to smoky exhaust (Atzemi et al., 2019), but with modifications and blending can be corrected. Finally, this study reveals that the presence of a heterogeneous catalyst (kaolinite clay) produced better biodiesel as the fuel quality parameters were comparable with the standard values, which could possibly be used for biodiesel production for practical application. Due to negative impact of fossil fuels, environmental is damaging and there is a need for alternatives to green fuels. Biodiesel production from renewable sources is considered a green and eco-benign for substitution of petro-diesel (Abukhadra et al., 2019a; Abukhadra et al., 2019b; Aghel et al., 2019; Allami et al., 2019; DeMarini et al., 2019; Dhanasekar et al., 2019; Du et al., 2019; Elkelawy et al., 2019; Hazrat et al., 2019; Silveira et al., 2019).

CONCLUSIONS

Biodiesel produced has similar properties to petroleum diesel. The flash point (80°C) was much higher than that of petroleum diesel which makes it safer to store and handle. The viscosity of 4.8 mm^2/s, cloud point of - 2°C and specific gravity of 0.862 g/cm^3 were comparable to the biodiesel standard (ASTM D6751) and therefore can be used as an alternative source of fuel with little modification or blending to correct the anomaly in the diesel index i.e. making the exhaust to be smooth. This study reveals that in the nearest future, the use of biodiesel produced from agro-materials for both domestic and industrial activities will overtake the fossil fuel. The large scale production of these agro-products will create employment opportunities for both skilled and unskilled workers.

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