Characterisation And Transesterification Of *Allanblackia Floribunda* Seed Oil For Production Of Biodiesel

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Abstract- Oil was extracted from the seed of *Allanblackia floribunda* using hot water floatation method. The oil was characterized and used for production of biodiesel through transesterification process. Evaluation of the properties of the biodiesel obtained was done. Physicochemical properties of the oil were measured and the results obtained show that the oil is edible and can also be used for industrial purposes. The viscosity of oil was 30 Cm^2S^{-1}, density 914 kg/m^3, smoke point 210 ˚C, flash point 270 ˚C, cloud point 25 ˚C and refractive index of 1.464 nD_{40}. Transesterification was carried out at a temperature of 60 °C for 60 minutes with 6:1 mole ratio of the methanol to oil and 1 gram of KOH as catalyst. Results obtained from the evaluation of the biodiesel were compared with ASTM and EN standards and the values compared well. The fuel properties of the produced biodiesel met the specification given by standards. The yield of fatty acid methyl ester (FAME) obtained was 91.62% in GC-MS analysis. The study supports the production of biodiesel from *Allanblackia floribunda* seed oil as a viable alternative to the diesel fuel.

Index Terms- Transesterification, Biodiesel, Allanblankia floribunda, Seed Oil, Methyl ester

I. Introduction

The rise in energy demand and carbon dioxide emissions associated with the use of fossil fuels has driven the search for alternative energy sources which are renewable and have a lower environmental impact (Atabani *et al.,* 2013 and Ho *et al.,* 2014). Therefore, it is very clear that biodiesel will contribute immensely to the energy demands of the populace in the near future. Biodiesel has advantage of fossil fuel because of its non emission of carbon dioxide in the air so there will be complete elimination of carbon dioxide emissions lifecycle with the use of Biodiesel. When compared with petro-diesel, it reduces about half of the emission of particulate matter, unburned hydrocarbons, carbon monoxide, most part of the polycyclic aromatic hydrocarbons and entire sulphates on an average (Du *et al*., 2004). The biodiesel molecules are simple hydrocarbon chains, containing no sulfur, or aromatic substances associated with fossil fuels. They contain higher amount of oxygen (up to 10%) that ensures more complete combustion of hydrocarbons (Global Farmer, 2009).

Transesterification is the most common methods used in production of mono alkyl esters of vegetable oils and fats, which is now known as biodiesel when used for fuel purposes. (Bull and George, 2015). The methyl ester produced by transesterification of vegetable oil has a high octane number, low viscosity and improved heating value compared to those of pure vegetable oil which results in shorter ignition delay and longer combustion duration and hence low particulate emissions. The use of biodiesel will help the environment by reducing greenhouse gas emissions. Some of the well-known non-edible oil seed producing plants are Jatropha (*jatrophacurcas*), Karanj (*pongamiapinnata*), Castor (*ricinuscommunis),* Rubber (*heveabarasiliensis*) seeds. India, Indonesia, Malaysia and China are already producing biodiesel successfully from Jatrophacurcus and oil palm (Haque *et al.*, 2009).

Allanblackia floribunda seed also known as tallow tree seed belongs to the family *Guttiferae* and genus *Allanblackia*. It grows in parts of Central, East and West African countries including Nigeria, Ghana, Democratic Republic of Congo, Uganda and Tanzania in moist lowland and upland rainforest. It is an evergreen medium-sized tree, up to 30m tall with a cylindrical or slightly fluted trunk and a narrow crown supporting horizontal branches. It has a fairly smooth bark and simple opposite leathery leaves evenly distributed along the branches of the tree. A matured tree produces about 100-150 egg-shaped brown fruits of weight between 1.2 and 4.0 kg. The fruits contain 25-40 oil-rich brown seeds, with a seed containing 68-72% oil (Dike and Asuquo, 2012).

II. MATERIALS AND METHODS

Materials

The fruits of were obtained from Okehi in Etche local government area of Rivers state, Nigeria. The methanol and anhydrous potassium hydroxide (KOH) (Analytical grade) were obtained from the department of Chemistry, Rivers State University, Port Harcourt.

Extraction of oil from *Allanblackia floribunda Seeds*

Hot water flotation method described by Rosenthal *et al*., (1996) was used. It was followed with some modification made by Alenyorege *et al.,* (2015).

Characterization of the *Allanblackia floribunda* seed oil

Moisture content, Density, cloud point, melting point, Smoke point, flash point, Viscosity, free fatty acid content, Acid value, Peroxide value, Saponification valueand Iodine value of the oil were determined using the methods described by the American oil chemist society official Method of analysis (AOCS, 2012) and Official analytical methods of analysis, 14th edition, Association of Official Analytical Chemists, Washington D.C. AOAC, (2012).

Transesterification Procedure of *Allanblackia floribunda* oil

The transesterification experiment was carried out in batch method at a reaction temperature of 45 using 0.5g Potassium hydroxide catalyst concentration of v/v to *Allanblackia floribunda* oil at 6:1 ratio methanol to *Allanblackia floribunda* oil and a reaction time of 60min. The experimental procedure was conducted according to methods explained by previous researchers (Aranisola *et al*., 2012 ; Deng *et al*., 2011 and Bull and George, 2015).

Biodiesel analysis

The physiochemical properties analyzed were: density, kinematic viscosity, flash point, cloud point, and Saponification value according the ASTM standard methods.

Biodiesel yield

The biodiesel yield was calculated from the Fatty Acid Methyl Ester (FAME) and oil weights

$$\text{Yield, \%} = \frac{\text{TotalweightofFAME}}{\text{Totalweightofoilsinthesample}} \times 100$$

(Kansedo *et al*., 2009)

III. RESULTS AND DISCUSSION

Physiochemical Properties of *Allanblackia floribunda* oil.

Physicochemical properties of *Allanblackia* oil are presented in the tables below.

Table 1: Physical properties of *Allanblackia* seed oil (ASO)

Parameter	ASO
Refractive index (nD_{40})	1.464
Slip melt point (°C)	42.5
Cloud point (˚C)	25
Density (kg/m3)	914
Moisture content (%)	0.16
Smoke point(°C)	210
Flash point(°C)	270
Viscosity (cm^2/s,), @40°C:	30

Table 2: Chemical properties of *Allanblackia* seeds oil

Saponification Value (mgKOH/g)	198
Iodine Value(wijs)	39
Free Fatty Acid (%)	1.15
Peroxide Value (mEq/kg).	0.86

Table 3: Physiochemical Properties of Biodiesel from *Allanblackia* Seed Oil

Parameter	**ASOB**	**ASTM D 6751**	**EN 14214**
Clarity	Clear liquid	Clear liquid	Clear liquid
P^H	8.3	8.0	7.8
Density, kg/m^3	880	870-900	860-900
Flash point°C	142	>130	>120
Kinematic Viscosity 40°C mm^2/sec^{-1}	5.1	1.9-6.0	3.5-5.0
Cloud point, °C	14		
Free Fatty Acid (FFA)%	0.05		
Saponification value (mgKOH/g)	192		

Key: ASTM D 6751 American standards and EN 14214 European Standards

ASOB: Allanblackia Seeds Oil Biodiesel.

Biochemical composition

Table 4: Fatty acid methyl ester profile of the produced biodiesel

Fatty acids	Structure (%)	Amount
	C6.0	11.18
Myristic (C14:0)	C14.0	10.69
Palmitoleic (C16:1)	C16.1	14.12
Stearic acid (C18:0)	C18.0	32.00
Oleic acid (18:1)	C18.1	11.18
Arachidic (C20:0)	C20.0	3.98
Eicosenoic (C20:1)	C20.1	8.47
Total		**91.62**

IV. DISCUSSION

Physical properties of *Allanblackia* seed oil

The results in table 1 show that the value of the refractive index of the oil was 1.464 (nD 40°C). The refractive index value obtained falls within the range reported for some fats in the nut family (1.45 -1.49) as reported earlier by Eckey, (1954). The melting point of *Allanblackia* oil was 42.5 °C and clouds at 25 °C. The melting point is relatively very high compared with cocoa butter, palm kernel oil and shear butter which have been reported to be between 32 - 36 and 25 - 30°C and 32 - 42°C respectively(Bockish, 1993). The relatively high melting point is an indication that the oil will be good for confectionary industry. The melting point of oil is related to their degree of unsaturation. The higher the degree of unsaturation, the lower the melting point. Density of the oil was 0.914 g/ml measured at 40 ℃. The density of vegetable oils is temperature dependent and decreases in value when temperature increases. The moisture content value was 0.16%. High moisture content is undesirable as it will lead to hydrolysis of the oil. Smoke point was 210℃. The flash point of the oil was 270 ℃. Flash point defines the temperature at which the decomposition products formed from frying oils can be ignited. Viscosity of *Allanblackia* oil measured at 40℃ was 30mm^2/s. Viscosity values estimate oil's relative thickness or resistance to flow. Viscosity is important to diesels and biodiesels because it has impacts on the operation of some engine components such as the fuel pump.

Chemical Properties

The results in table **2** show the summary of some chemical properties of *Allanblackia* oil. Saponification value was 198 mg KOH/g. Saponification values of oil is inversely related to the average molecular weight of the fatty acids in the oil. Generally, fats and oils with high proportion of shorter carbon chain lengths of the fatty acids have high saponification values (Kirk and Sawyer, 1991). Low molecular weight fatty acids have more glyceride molecules per gram of fat than high molecular weight acids and hence greater saponification value. Coconut oil contains appreciable quantities of low-molecular weight fatty acids and has high saponification value (251 - 264) (Aurand *et al.*, 1987). The saponification value obtained in this work was lower than that of coconut oil but close to that stated for palm oil (190 - 209) by (Bockish, 1993), indicating relatively higher molecular weight acids (Ellis *et al.*, 2007).The smaller the Saponification value the larger the average molecular weight of the triglyceride. The Iodine Value of fats and oils is an important characteristic which determines the degree of unsaturation. The iodine value of the*allanblackia* oil was 39wijs,is lower than the range of 50 - 55 specified by Codex Alimentarius (Codex Standard 2001, 2003) The values were relatively low indicating a low degree of unsaturation or high degree of saturation of the *Allanblackia* oil.
Peroxide value was 8.6 meq/kg. These values are within the acceptable limit of 10 mEq/kg for fat or oil stated by NIS, (1992), for edible oils.

Physiochemical properties of the Biodiesel

Table 3 shows the Physiochemical properties of biodiesel produced from *Allanblackia* oil compared with the biodiesel American standards ASTM D 6751 and European Standards EN 14214.The pH value was 8.3. This is a little bit higher than the set value by ASTM D 6751 and EN 14214. However, some countries accept pH range of 8-10.Monitoring pH provides a measure of the progress of the biodiesel reaction.

The Density of the biodiesel was 880 kg/m^3 which is within the standard range of standards given. Density and other gravities are important parameters for diesel fuel injection systems. The values must be maintained within tolerable limits to allow optimal air to fuel ratio for complete combustion. High-density biodiesel or its blend can lead to incomplete combustion and particulate matter as reported earlier by Galadima *et al.*, (2008).

The flash point for the biodiesel was well above the 130°C minimum ASTM recommended range and therefore no risk of fire outbreaks in case of accidents. Sulistyo *et al*., (2008) gave similar report. The kinematic viscosity of the biodiesel (5.1 mm^2 sec^{-1}) is within the recommended ASTM range of 1.9 to 6.0 mm^2 sec^{-1}. This means that the biodiesel can flow easily. This parameter is important to biodiesel because it has affects the operation of the fuel pump of engines. Cloud point was 14 ˚C. This is the temperature at which crystals first start to form in the fuel. At this point the engine cannot run and is a big problem in temperate region. It is therefore, important that cloud point of biodiesel be low. Free Fatty Acid content in the biodiesel was low 0.05%. High free fatty acid is undesirable as it an indication of deterioration. Saponification value is used in checking adulteration. Saponification value for the biodiesel was 192 mg KOH/g. High saponification value indicated that oils are normal triglycerides and very useful in production of liquid soap and shampoo. This may have contributed to the low yield of biodiesel produced due to separation challenges.

Fatty acid methyl ester profile of the produced biodiesel

Table 4 shows the values for the fatty acid methyl ester of the biodiesel produced.

V. CONCLUSION

The oil can be used in the confectionary industry. The low degree of unsaturation, acid and peroxide values indicates that the oil can be stored in plastic containers for a period of at least five months without deterioration. The cloud point of the oil suggests that it will not be good for paint production.. The physiochemical properties of biodiesel produced met the ASTM and EN standard specifications for biodiesel. The methyl ester of *Allanblackia floribunda* Seed oil can be successfully used for biodiesel production.

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