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Potentials of *Afzelia africana* Vegetable Oil in Biodiesel Production

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ABSTRACT

Vegetable oils are combustible materials of organic origin and have potentials for use as biodiesel. The potential of extractable vegetable oil from *Afzelia africana* in the production of biodiesel was investigated and its fuel properties were evaluated by the assessment of the physicochemical properties. Standard official methods were employed in extraction and characterization of oil from *Afzelia africana* (African oak) seed and it was found that it contained 18.50% crude lipid content on dry weight basis with a very high percentage of total fatty matter and a refractive index of 1.47 at 40°C. The acid value 4.49% was low in the oil sample while the peroxide value 6.40 meq g^{-1} was indicative of very low level of hydroperoxides which could initiate or propagate further oxidation of the oil, thereby improving the stability (oxidative stability) of the oil. The saponification value was 229.12 mg KOH g^{-1} while the iodine value indicates that the oil was non-drying and non volatile at room temperature. The value of the Cetane index was 55 and the estimated value of the heat of combustion revealed that burning the vegetable oil in a diesel engine will yield about 9209.45 cal g^{-1}. The fatty acid distribution in the seeds of *Afzelia africana* expressed as the percentage area of fatty acid methyl esters composition revealed lauric acid 0.69%, myristic acid 1.54, palmitic acid 33.45%, stearic acid 6.97%, oleic acid 12.25% and linoleic acid 41.25%, showing that the seed oil was predominantly composed of palmitic acid and oleic acid families. This result showed that the oil would be stable on exposure to atmospheric oxygen during storage and use. This stability is further confirmed by the low level of free fatty acids.

Key words: *Afzelia africana*, biodiesel, methyl esters, vegetable oil, physicochemical properties

INTRODUCTION

Vegetable oils come mainly from seeds. Within the seeds, oil is stored in the endosperm (castor oil, coconut oil), the cotyledons of the embryo (peanuts, soya beans, cotton) or in the scutellum (corn) (Simpson and Conner-Orgazally, 1986). Some vegetable oil seeds include groundnut, cotton seed, sunflower, palm, corn, castor linseed and rubber seed etcetera (Ikwuagwu *et al*., 2000).

Afzelia africana plant is called “akparata” in the Igbo speaking south-eastern part of Nigeria. The genus was named in honour of Dam Afzelius of Uppsala, who lived in Somalia. *Afzelia africana* is a very attractive medium sized tree, with bright green leaves that turn to attractive yellowish colour during harmattan seasons in Nigeria. It has upright crown and the dropping branches resemble an eucalyptus from a distance. *Afzelia africana* is a deciduous plant that bears 6-10 hard, shiny, oblong black bean-shaped seeds with red orange aril with extractable oil (Palgrave and Palgrave, 2002). The seeds are used as soup thickeners (Igwenyi and Akubugwo, 2010).

Vegetable oils are now processed into other industrial products for the benefit of mankind. These other applications of this nutrient in non-food or industrial sectors have mounted pressure on the food use of certain food materials. For example, carbohydrates are converted into biofuels and used as alternative biodegradable and environmentally friendly fuels. They are converted into ethanol used as fuel/blends for combustion engines and also as a raw material for the production of strong drinks and other industrial products. Vegetable oils are used as biodiesel, vanishes, raw material for paints, ink oil and so on (Igwenyi *et al*., 2008). Thus, the food use and industrial applications of plants and their products have increased over the years and this is associated with increase in world population. This has mounted pressure on their food uses and created a big problem in feeding the ever increasing world population (Wilcox and Leffel, 1987).

Vegetable oils and their methyl esters have long been considered as potential alternative fuels for diesel engines. In addition to ignition quality, the gross heat of combustion of oil is one of more important properties in determining its suitability for use in diesel engines (Krisnangkura, 1991). The use of renewable fuels also leads to a reduction of carbon dioxide (CO_2) in the atmosphere that contributes to the greenhouse effect (Arapatsakos *et al*., 2008).

The heat of combustion of a fuel is the quantity of energy released by burning a unit amount of the fuel and it is important with regards to fuel consumption. The heat of combustion of oils increases with the molecular weight and varies from about 5,900 cal g^{-1} for butyric acid to about 9,600 cal g^{-1} for stearic acid (Hall *et al*., 1978).

Another, measure of quality of oil used in combustion engines is the Cetane index or number. This is a measure of a fuel's ignition delay and can be defined as the time between the start of an injection engine and the first identifiable pressure increase during combustion of the fuel. Generally diesel engines run well with a cetane number from 40-55 (Owen *et al*., 1995). The Cetane number, therefore measures the ease with which a diesel fuel ignites under compression and diesel engine conditions (Heywood, 1988).

Some physicochemical parameters were considered which affect the oxidative stability of the oil under storage and usage as well as overall quality of the oil. Some of these parameters include oil content to check the presence of extractable oil and the quantity that can encourage industrial attention. Others include the acid value which varies with the source of the oil and the level of refining (Hammond, 1993) as well as the peroxide value which gives the amount of active oxygen (mg) present in 1 kg fat (Ikwuagwu *et al*., 2000). The iodine value is important as a measure of the degree of unsaturation and a determinant in the drying and non-drying property of the oil while the saponification value determines the amount of fatty acids that can be liberated on complete hydrolysis of the oil etcetera.

This study was therefore aimed at the investigation of fuel properties of the vegetable oil from *Afzelia africana* with a view to providing baseline data for further systematic scientific research.

MATERIALS AND METHODS

Test samples: All the samples used were fresh seeds purchased from foodstuff dealers in EKE ABA market, Abakaliki, Ebonyi State, Nigeria. They were processed traditionally (dried and roasted) and the shells of the seeds were removed manually and further dried in an oven at 60°C for 48 h. The study was carried out during the dry season period of 2010 in the Department of Biochemistry, Faculty of Biological Sciences, Ebonyi State University, Nigeria.

Oil extraction and characterization: Oil was extracted using petroleum ether (40-60°C) in a soxhlet apparatus and the solvent was later distilled off in a rotary evaporator. The acid value was determined as the number of milligrams of potassium hydroxide required to neutralize 1 g of the oil (AOAC, 1990). The peroxide value was determined following procedures described by Hamilton *et al.* (1992) as the amount of substance in a sample expressed in terms of mill-equivalents of “active or peroxide oxygen” per kilogram of fat or oil which oxidizes potassium iodide while the iodine value was determined according to Wij’s method as described by Ikwuagwu *et al.* (2000) as a measure of unsaturation in fats and is the number of grams of halogen added to the double bonds of 100 g fat and expressed as equivalent number of grams of iodine. The saponification value was determined by refluxing the oil with alcoholic potassium hydroxide (Hamilton *et al.*, 1992) while the amount of unsaponifiable matter was determined as the total quantity of matter present in the oil which after saponification by potassium hydroxide and extraction using diethyl ether, are not soluble in aqueous alkali and non-volatile at 103°C (Hoffman, 1986).

Determination of fatty acid profile: The fatty acid methyl esters of lipids were prepared according to the AOAC method 991.39 (AOAC, 1990). The analysis of fatty acid methyl esters were carried out with a Hewlett Packard Gas Chromatograph equipped with a hydrogen flame ionization detector and a capillary column; CP-Sil-88 Wcott fused silica 50 mx 0.25 mM id. (of 0.20 mM film thickness). The temperatures of injector and detector were 270°C. The initial column temperature was 170°C and then raised to 205°C at a rate of 1°C min^{-1}. Split ratio was 1/50. The carrier gas was hydrogen at a flow rate of 1 mL min^{-1}. The identification and quantification of fatty acid methyl esters was accomplished by comparing retention times of the peaks with those of standards.

Cetane number: Cetane number was estimated using the Klopfenstein simultaneous equation for esters of fatty acids (Klopfenstein, 1982).

Heat of combustion: Heat of combustion was estimated using the methods and equation that expressed the value in terms of constant volume at 15°C according to Hall *et al.* (1978).

Statistical analysis: The results were presented as mean±standard deviation (x±SD).

RESULTS AND DISCUSSION

The mean value of the percentage composition of vegetable oil in *Afzelia africana* was 18.50% crude lipid content on dry weight basis as shown in Table 1. The comparative analysis

Table 1: Extraction and physicochemical characterization of oil from *Afzelia africana* seeds

Parameters	*Afzelia africana* (African oak tree)
Oil content	18.50±2.02
Moisture content	2.80±0.01
Total fatty matter	98.47±0.04
Refractive index at 40°C	1.47±0.01
Acid value (mg KOH g^{-1})	4.49±0.02
Free fatty acid (%)	3.47±0.05
Peroxide value (meq g^{-1})	6.40±0.02
Sap. value (mg KOH g^{-1})	229.12±2.20
Iodine value (Wij’s)	74.10±0.02
Cetane index	53.54
Heat of combustion (cal g^{-1})	9209.45

with oil seeds showed that the seeds can be classified as oil seeds or oil crop since it can serve as commercial source of vegetable oils. Vegetable oils come mainly from seeds. This value for the oil content of the seed (18.50%) was higher compared with results of oil contents of *Brachystegia eurycoma* (5.87%), *Tamarindus indica* (7.20%) and *Mucuna flagellipes* (3.77%) by Ibironke *et al.* (2005) but comparable to results of nutritive properties of dehulled and undehulled samples of *Brachystegia eurycoma* and *Detarium microcarpum* which ranged from 14.00 to 18.5% by Uhegbu *et al.* (2009). The values were also comparable to 15% reported in *Detarium microcarpum* by Akpata and Miachi (2001) and 8.30% in *Mangifera indica* (Eddy and Udoh, 2005), 2.80 and 3.1% fat content of *Canavalia gladiata* seeds (whole and cotyledon, respectively) (Sagarika *et al.*, 1999). The oil composition was however lower than 54.26% reported for Turkish sesame seeds (Unal and Yalcin, 2008) and 48.00-50% reported for *Sesame indicum* L. (Mohammed and Hamza, 2008), which are oil seeds that can provide a commercial quantity of oil for the industries. The oil content was also found to be lower than castor seed 50%, cotton seed 30%, linseed 40% and palm kernel 50% (Carr, 1989).

The very high percentage (98.47%) of total fatty matter in the oil in Table 1 indicates that the oil was rich and predominantly fatty materials. The seeds of *Afzelia africana* had refractive index of 1.47 at 40°C. Refractive index of a fat is the ratio of speed of light at a defined wavelength to its speed in the fat itself. This value varies with wavelength and temperature and also varies with the degree and type of unsaturation as well as the type of substitutions of component fatty acids and with accompanying substances. Refractive index is widely used in quality control to check for the purity and adulteration of fatty materials and to follow hydrogenation and isomerization (Hoffman, 1986).

The acid value 4.49% was low in the oil sample. This value was comparable to the values of 3.0, 12.2, 0.8, 2.1 and 2.5 reported for sunflower, cotton seed, groundnut, olive oil and coconut oils respectively used as edible and industrial oils (Engler *et al.*, 1983). It was also observed that there were no significant differences with the values reported by Anhwange *et al.* (2004) for *Detarium microcarpum* and *Moringa oleifera* (Lam). The value was comparable to 1.68-5.05 reported by Igwenyi *et al.* (2008) for *Raphia vinifera* seed pulp oil and 9.0-21.6 reported by Ikwuagwu *et al.*, (2000) for rubber seed oil used in the preparation of biodiesel. This result showed a potential for the industrial application of the oil in biodiesel production. The values however accounted for the low level/presence of free fatty acids in the oil as an indicator of the little presence and low extent of hydrolysis by lipolytic enzymes and oxidation (Ranken and Kill, 1993). The value is comparable to the free fatty acid value of <10 reported in the survey of plant oil engines and fuel specifications for running on rapeseed oil (Krause, 1998). The low value showed that the oil if exposed without addition or treatment with antioxidants will be stable over a long period of time and protected against rancidity and peroxidation. This low level of the free fatty acids is an indication that the components were predominantly composed of triacylglycerols and presence of natural antioxidants (Ikwuagwu *et al.*, 2000; Igwenyi *et al.*, 2008).

The peroxide value in meq g^{-1} for *Afzelia africana* was 6.40. There was no significant difference when compared to the value of 7.45-8 meq KOH g^{-1} in *Sesame indicum* L. reported by Mohammed and Hamza (2008). The value was indicative of very low level of hydroperoxides which could initiate or propagate further oxidation of the oil thereby improving the stability (oxidative stability) of the oil and corroborates the result of the free fatty acid values. The value was comparable to the peroxide value of less than 3 meq g^{-1} reported in the survey of plant oil engines and fuel specifications for running on rapeseed oil (Krause, 1998). The peroxide value is also comparable to 2.00-6.00 reported by Igwenyi *et al.* (2008) for *Raphia vinifera* seed pulp (mesocarp) oil and the reports of Ikwuagwu *et al.* (2000) for rubber seed oil and Engler *et al.* (1983) for sunflower oil. This showed that the oil would be stable and this stability is further confirmed by the low level of free fatty acids. This is attributable to the presence of natural antioxidants in the oil which are effective in slowing down the rate of oxygen absorption by reacting with the fatty acid peroxy free radicals (Hoffman, 1986). This property of the oils which are comparable with those of rapeseed, sesame, sunflower and groundnut seeds suggests their suitability and use as edible oils (Ibironke *et al.*, 2005).

The saponification value in mg KOH g^{-1} was 229.12. The saponification value was comparable to 189-191 mg KOH g^{-1} reported by Mohammed and Hamza (2008) for *Sesame indicum* L. seeds grown in Jigawa State of Nigeria and 179-220 mg KOH g^{-1} reported by Anhwange *et al.* (2004) for *Detarium microcarpum* and *Moringa oleifera*. An increase in saponification value in oil increases the volatility of the oil. It enhances the quality of the oil because it shows the presence of lower molecular weight components in 1 g of the oil. The saponification value is the number of milligrams of potassium hydroxide required to neutralize the fatty acids liberated on complete hydrolysis or saponification of 1 g of the oil. It is inversely proportional to the molecular weight of the oil since 1 g of oil or fat containing low molecular weight fatty acids will have more molecules than oil or fat containing higher molecular weight fatty acids. The principle in the methods of Jacobs (1958) revealed that the number of milligrams of KOH required to saponify the oil will be greater in the former than in the latter case. Therefore, the higher the saponification value, the more the lower molecular weight fatty acids and the better the quality of the oil.

Iodine number of oil is a measure of its degree of unsaturation and is a useful criterion for purity and identification. The iodine value indicates that the oil was non-drying with iodine number lower than 100 (Kochhar, 1986). Non-drying oils are not volatile at room temperature and does not pose any danger of inflammability. It showed that the oils were not made up of very low molecular weight fatty acids as non-drying oils are predominantly composed of oleic and palmitic acids. This result further confirms the result of the fatty acid profile of the oil. It is also in line with the results of Adeyeye and Ajewole (1992) for cereals which indicated the predominance of stearic, oleic and linoleic acids in sorghum, millet, maize and rice.

The value 74.10 Wij's (Giod/100 g) for the iodine value was lower than the maximum value of 115 Giod/100 g reported in the recommendation of quality standards for rapeseed oil to be used as fuel in internal combustion engines (Krause, 1998). However, the values were comparable to the values for edible vegetable oils (Simpson and Conner-Orgazally, 1986) but was lower than 155.00-205.00 for linseed, 135.00-150.00 for safflower, 120.00-143.00 for soya bean and 110.00-143.00 for sunflower (Ranken and Kill, 1993; Hoffman, 1986) and 69.40-76.50 reported by Igwenyi *et al.* (2008) for *Raphia vinifera* seed pulp oil which were utilized in the production of biodiesel.

The iodine value confirmed the stability of the oil and points to a low degree of unsaturation and a further confirmation of its low peroxide value and fatty acid profile since non-drying oils do not undergo oxidation. Iodine values increase with the degree of unsaturation as the number of grams of halogen added to the double bonds of 100 g fat and expressed as equivalent number of grams of iodine. It is applied in monitoring progress of hydrogenation, degree of fractionation and for identity characterization of fats (Hoffman, 1986).

The Cetane index value was estimated and found to be within the maximum range for diesel engines as diesel engines run well with cetane number between 40 to 55 (Owen *et al.*, 1995). This

Table 2: Percentage (% area) fatty acid composition of processed seed of *Afzelia africana* samples

Parameters	*Afzelia africana* (African oak)
C12 (Lauric acid)	0.6867
C14-0 (Myristic acid)	1.5398
C16:0 (Palmitic acid)	33.6470
C18:0 (Stearic acid)	6.9692
C18:1 (Oleic acid)	12.6458
C18:2 (Linoleic acid)	41.2511

is advantageous as a future diesel fuel since it has a high cetane rating (55) and can be produced as a biofuel. Cetane index is a measure of injection delay, a time between the start of injection and the start of combustion (ignition). It follows then that the vegetable oil from *Afzelia africana* therefore can ignite easily and quickly which gives it a positive attribute and a potential diesel fuel for combustion engines (Heywood, 1988).

The estimated value of the heat of combustion of the oil according to the method of Hall *et al.* (1978) was about 9209.45 cal g^{-1}. This showed that combustion of a little volume of the methyl ester of the oil will yield a tremendous amount of energy to drive the pistons of diesel engines, there by providing enough power to propel the engine. This is comparable to the recommendations for oil standards for use in a heavy duty combustible diesel engine (Krause, 1998; Klopfenstein and Walker, 1983).

The fatty acid distribution (Table 2) in the seeds of *Afzelia africana* expressed as the percentage area of fatty acid methyl esters composition yielded 41.25% linoleic acid, 12.65% oleic acid, 6.97% stearic acid, 33.65% palmitic acid, 1.54% myristic acid and 0.69% lauric acid, indicating the predominance of linoleic, palmitic and oleic acids. These values were however comparable to 26.50 oleic acid and 45.10 g/ 100 g (41.10%) linoleic acid reported for *Xylopia aethiopica* by Barminas *et al.* (1999). The results were also comparable to 15.10-24.80% palmitic acid, 29.90-41.80% oleic acid and 35.90-51.30% linoleic acid reported by Maestri *et al.* (1996) for sorghum cultivars from Argentina.

It was observed that the seed oil was predominantly composed of palmitic acid and oleic acid families. This result showed that the oil would be stable and this stability is further confirmed by the low level of free fatty acids. This is attributable to the presence of natural antioxidants in the oil which are effective in slowing down the rate of oxygen absorption by reacting with the fatty acid peroxy free radicals. The high saponification value in oil indicates that an increase in the volatility of the oil. It enhances the quality of the oil because it shows the presence of lower molecular weight components in 1 g of the oil which can give high amount of energy on combustion. However, there was a nutritional advantage of the seeds because they contained good level of the essential fatty acid linoleic acid. The body requires essential fatty acids for the synthesis of useful substances. The body can however synthesize linolenic acid and arachidonic acid if provided with linoleic acid (Voet and Voet, 2004). Essential fatty acids are very important in maintaining cell membrane structure and in capillary wall integrity and form starting materials for the synthesis of other unsaturated fatty acid derivatives such as prostaglandins (Igwenyi, 2008).

CONCLUSION

Afzelia africana contains extractable oil and the physicochemical and fuel properties of the methyl esters showed potentials in biodiesel production. The oil can release high amount of heat on combustion and the cetane index shows that the oil can ignite easily in a combustion engine.

The iodine and peroxide values showed increased stability of the oil during storage and transportation. Biodiesel is a safe biodegradable and renewable fuel from biomass, which reduces the emissions of most air pollutants. It is much less polluting than petroleum diesel. They can replace conventional fuels, completely or partially, in the internal combustion engines.

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