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Full Length Research Article

Assessment of Physicochemical Properties of Biodiesel from African Grapes (*Lannea microcarpa* Engl.& K.Krause)

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ABSTRACT: The African Grape (*Lannea microcarpa*) seed oil was extracted and subjected to fuel properties tests according to standard method for oil and fuel analysis to evaluate its suitability as oil crop for biodiesel production in Nigeria. The oil was transesterified using alkali hydrolysis to biodiesel. The yields of the oil and its methyl ester were 41.20 ±1.32% and 85 ± 1.30% respectively. The biodiesel produced was analysed for its physicochemical properties and yielded the following properties; kinematic viscosity at 40°C (5.80 cSt), acid value (1.66 $mgKOHg^{-1}$), flash point (96 °C), cloud point (+9°C), sulphur content (0.03 wt %), and free glycerol (0.54%). The results obtained showed that most of the important properties were within the recommended standards for a biofuel grade biodiesel and suggest the potential of *L. microcarpa* seeds as a source of biodiesel.
Keywords: African Grape, *Lannea microcarpa,* Seeds, Oil, Biodiesel

INTRODUCTION

Global energy crisis, unstable prices of petroleum products, environmental concerns arising from oil spillage and noxious gaseous emissions into the atmosphere are the major problem of conventional fossil energy source (Barnwal and Sharma, 2005; Amish *et al*., 2009). Therefore, the search for alternative sources of new, sustainable and renewable energy such as biomass, solar, hydro, wind has become necessary. The demand for petroleum is on the increase daily, possibly due to increasing world population and the quest for better living standard. The rise in prices of petroleum fuel and increasing threat to the environment, have generated an international interest in developing alternative, non-petroleum; renewable fuels that have the potential to solve many of the current social problems and concerns (Demirbas, 2005). On the other hand, most of the needed services that enhance our standard of living are energy dependent, thus their optimal delivery can be achieved through sufficient energy. This realization made many countries to investigate possibilities of using alternative fuels to petroleum and its derivatives (Carrareto *et al.,* 2004). The essential minimum requirement for biofuels to be more sustainable alternative for fossil fuels is that they should be produced from renewable raw materials and that their use has a lower negative environmental impact (Janulis, 2008).

Vegetable oil is one of the renewable fuels which have become more attractive recently because of its environmental benefits. Vegetable oils are renewable and potentially inexhaustible source of energy with an energetic content close to diesel fuel(Demirbas, 2003). With recent uncertainties concerning petroleum availability and increases in its price, there is renewed interest in vegetable oil fuels for diesel engines (Demirbas, 2003).

Lannea microcarpa commoly known as African grape, Wild Grape or "*Faaru*" in Hausa belongs to the family Anacardiacea. It is found in the savanna and the drier forest re-growth zone of West Africa. The unripe fruits are green in color while ripe ones are purplish black. The seed has 22-28% moisture content and oil yield of 38-41% (Ellis *et al*., 1990; Bugaje and Idris, 2010). The fruits are edible and traded commercially and wine can be produced from fermented pulp while pigment from the leaves provide a source for natural dyes (Bein, 1996). The seeds are not economically useful and are often discarded as a waste into the environment. Information on oil yield and biodisel potential of this plant has not been documented in the literature. There is the need for the exploration of its potential in bio-diesel production. The objective of the study was to determine the physico-chemical properties of both oil and biodiesel of *L. microcarpa* and assess its potential in the replacement of fossil diesel.

MATERIALS AND METHODS

Sample Collection and Preparation

Ripe fruits of wild grape were obtained from Dabai in Zuru Local Government Area of Kebbi State, Nigeria. The fleshy mesocarp and the outer cover of the fruits were removed and the hard nutshell was separated. Large amounts of water were mixed for several hours with the fruits, the mesocarp and exocarp washed off, and the clean nuts separated. The seeds were sundried for seven days and then dried nuts were ground followed by sieving to get fine kernel-rich powder and were stored in polyethene bags and used for oil extraction. The oil content of ground seed powder was extracted with n-hexane using soxhlet apparatus.

Production of Biodiesel

Oil sample extracted was used for biodiesel production using a base-catalyzed transesterification reaction. Oils containing low free fatty acids level, therefore would require 0.30-1.5% of the oil weight as base catalyst. It would require one-fifth of its weight or volume of alcohol for treating triglycerides to produce (biodiesel) fatty acid methyl esters (Gerpen *et al*., 2005**).** Anhydrous NaOH was added to methanol, stirred continuously till it dissolved. Previously extracted wild grapes oil (triglyceride) was placed in a flask and warmed. The methanolic NaOH solution was added to the oil. The mixture was agitated at 55^{o}C, and then transferred to a separating funnel. This stood for 1 hour to allow for separation of glycerol (a dark brown colored liquid) and biodiesel (a light yellowish less dense liquid). Excess methanolic NaOH solution was added to the fatty acid methyl ester and stirred again, the mixture was allowed to stand overnight for gradual separation. After the removal of glycerol, the (biodiesel) methyl ester was washed with warm slightly acidic water to remove alcohol, catalyst, as well as neutralizes the biodiesel to level the pH (Gerpen *et al.,* 2005**)**. The methyl ester was treated with silica gel and filtered. It was further subjected through a vacuum filtration funnel loaded with sodium sulphate crystals to obtain dry biodiesel for characterization (Dalai, 2004). The oil was transesterified into biodiesel using methanol catalyzed by sodium hydroxide. The volume of biodiesel recovered from the oil was measured. The properties of biodiesel produced were determined using AOCS (1997) official methods of analysis. Properties determined included yield, density, kinematic viscosity, acid value, sulphur content, cloud point, pour point and flash point. The percentage biodiesel yield was determined using the equation:

$$\text{Biodiesel yield } (\%) = \frac{\text{mass}(g) \text{ of biodiesel recovered}}{\text{Mass } (g) \text{ of Oil}} \times 100$$

RESULTS AND DISCUSSION

The colour of oil changed from dark brown to reddish brown after transesterification,. The important properties of wild grapes oil, Jatropha oil, methyl ester, petro-diesel and methods used to determine them are presented in Tables 1 & 2. The percentage yield of biodiesel produced from wild grape seed oil is presented in Table 2. The yield of methyl ester (85.30 ±1.30) is relatively good compared to reported data from literature using NaOH and methanol.

The high yield of biodiesel obtained indicates the potential as a feedstock for biodiesel industry. However, percentage yields of biodiesel can be affected by different reaction conditions and subject to modification. The density of petroleum products is usually expressed as specific gravity. Density measurement at 20^{o}C for biodiesel of wild grape oil is 0.88 g/cm^{3}. The value is slightly higher than that of diesel fuel (0.82—0.85), but is within the ranges (0.86—0.90) recommended for fatty acid methyl esters (FAME) EN: 14214, 2008. Knowledge of density gives a broad indication of the fuel type and for a known fuel type; this property may serve as a general inspection check for the presence of contaminants **(**Hassan *et al.,* 2006).

Table 1: Physicochemical properties of African grape Oil as compared to Jatropha Oil.

Property	African grape Oil
Oil yield (%)	41.20±1.32
Moisture content (%)	0.82 ± 0.15
Kinematic viscosity @ 40^{o}C (cSt)	33.10 ± 0.41
Pour point (^{o}F)	35.60 ± 2 .45
Ash content (%)	0.64 ± 0.01
Density (g/cm^{3})	0.9069 ± 0.00
Saponification value (mgKOHg^{-1})	153.40 ± 2.45
FFAs (as oleic) (%)	4.20 ± 0.25

Table 2: Physicochemical properties of African grape methyl ester

Property	Methyl Ester
Methyl ester yield (%)	85.30±1.30
Density (gcm^{-3})	0.88
Kinematic viscosity @ 40^{o}C (cSt)	5.8
Cloud point (^{o}C)	+9
Sulphur content (wt%)	0.03
Flash point Penski-Martins (^{o}C)	96
Acid value (mgKOHg^{-1})	1.66

Kinematic viscosity is the resistance to flow of a fluid under gravity which is a basic specification for the fuel injectors used in diesel engines and when viscosity is high injectors do not perform properly (Gerpen *et al.,* 2005). The kinematic viscosity at 40°C for the biodiesel sample was 5.8 cSt. It is one of the most important property that qualifies a biofuel to serve as an alternative fuel. The recommended limits by ASTM D6751 ranges are 1.9—6.0 cSt for a fatty acid methyl ester. High viscosity in a fuel, leads to several problems such as incomplete combustion and formation of deposits at the tip of injection nozzles **(**Hassan *et al.,* 2006). An important reason for the transesterification of oils is to reduce their viscosity. The results obtained in this study suggest that, the biodiesel obtained from *L. macrocarpa* seeds was of good quality and within specification. Cloud point is important in that it defines the temperature at which a cloud or haze of crystals appears in the fuel under prescribed test conditions which generally relates to the temperature at which crystals begin to precipitate from the fuel in use. Biodiesel generally has a higher cloud point than petroleum based diesel fuel. From Table 2, biodiesel of wild grapes had a cloud point value of +9°C. This amount is slightly higher than that of Neat Biodiesel (-15 to +5 °C). However, the values obtained in this study are within the range recommended for fatty acid methyl esters. The impact of cloud point of biodiesel on the cold flow properties of the resulting blend should be monitored by users or producers alike to ensure trouble-free operation in cold climates. Cloud point can be modified by blending feedstock relatively high in saturated fatty acids with feedstock that has lower saturated fatty acid content resulting in a net lower cloud point for the mixture (National Renewable Energy Laboratory, 2004).

The sulphur content of biodiesel sample from wild grape seed oil was 0.03wt% (Table 2). This value is within the recommended maximum sulphur limits of 0.05wt % for Ultra Low Sulphur Diesel (ULSD) which was mandated for all on-highway diesel fuel in 2008 amongst EU member countries and the US. Biodiesel feedstock typically has very little sulphur. The effect of sulphur content on engine wear and deposits appears to vary considerably and depends largely on operating conditions. Sulphur is limited to reduce sulphate and sulphuric acid pollutant emissions for environmental reasons **(**Gerpen *et al.,* 2004). Although**,** flash point is not directly related to engine performance, it is of importance in connection with legal requirements and safety precautions involved in fuel handling and storage that is normally specified to meet fire regulations. It's an index of fire risk during storage under ambient conditions. Flash point is a measure of residual alcohol in B100 and is a determinant for flammability classification. In this study, the biodiesel sample of wild grape shows flash point value of 96, which is higher than Diesel fuel (60 to 80)°C, but less than that of biodiesel fuel (100 to 170)°C (Gerpen *et al*., 2004). The flash point for biodiesel has been set at 93°C (200°F) minimum. This suggests that, biodiesels are not highly flammable, but would require safety precautions like any fuel during usage, storage and transportation **(**Hassan *et al.,* 2006). Acid value is a direct measure of the level of free fatty acids that may be present in biodiesel. The biodiesel produced in the study had an acid value of 1.66 $mgKOHg^{-1}$ which is slightly above that of petro-diesel. Presence of high free fatty acids can lead to corrosion during storage or transportation and may be a symptom of water in the fuel. Acid value may increase as biodiesel fuel degrades due to contact with air or water (Gerpen *et al.,* 2005) which requires treatment that could lower acid content before use.

CONCLUSION

L. macrocarpa biodiesels are comparable to those of petro-diesel and the quality of biodiesel from this seed oil is comparable to that of ASTM standards for fuel grade biodiesel and Jatropha. The results suggest the potential of wild grapes seeds oil as a feedstock for biodiesel industry which could be exploited as an alternative source of fuel.

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