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Production of Biodiesel from Fluted Pumpkin (Telfairia Occidentalis Hook F.) seeds Oil.

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Abstract. In this study, the work done on the extraction of oil from fluted pumpkin (*Telfairia Occidentalis Hook F.*) seeds, its transesterification methyl ester (biodiesel) and characterization is reported. The oil was extracted in a soxhlet extractor using normal hexane as solvent. The oil properties were measured and the free fatty acid was 3.59 mg KOH/g which is high for alkaline transesterification hence the oil was neutralized with hydrochloric acid before transesterification using with 3 g of sodium hydroxide per litre of methanol as catalyst and methoxide/oil in the volume ratio of 6:1. Gas chromatography analysis shows that the oil and its methyl ester contains primarily the short chain fatty acids oleic (C18:1), linoleic (C18:2). The fuel properties were evaluated following the American Society for Testing and Materials (ASTM) methods for biodiesel. The fuel properties are very close to those of diesel fuel hence can be used as alternative fuel for diesel engines. Of particular importance is the high flash point which makes it a safe fuel and the low pour point will allows it to be used in cold climate.

Keywords: Fluted pumpkin seed oil; free fatty acids; transesterification; biodiesel; characterization.

1.0 Introduction

There is serious concern worldwide on the level of pollution caused by internal combustion engines exhaust emissions and high price of crude oil. This has led to search for alternate fuel for diesel engines. The search has been focused on vegetable oil because of its renewable source from agriculture and the fact that it is abundantly available and evenly distributed all over the world. Attempts to used vegetable oils to fuel diesel engines gave rise to problems mainly due to high viscosities, different chemistry of combustion, and lubrication oil contamination due to incomplete combustion. The differences in chemistry of combustion is manifested in the form of poor cold flow properties, poor atomization, coking tendencies, carbon deposits, cold starting problems, and wear in direct injection engines [1], [2], [3] and [4]. Thus giving rise to the need for a method of converting vegetable oil to esters which is generally called biodiesel [5] and [6]. The most viable method for overcoming the disadvantages of vegetable oil is to convert to esters. The transesterification process uses alcohol in the presence of a catalyst to chemically break down the molecules of the vegetable oil. The glycerol from the triglycerides are removed and replaced with radicals from the alcohol, which transforms the branched molecular structure of vegetable oil into smaller straight chain molecular structure, identical to but much longer than that of diesel fuel. The transesterification results into the formation of mono-alkyl esters called biodiesel with glycerol as by-products [7] and [8]. Transesterification reduces the molecular weight and the viscosity while also increasing the volatility but maintains the cetane number and heating value [9] and [10]. Additional advantages include reduction in most harmful exhaust emissions, improved biodegradability, inherent lubricity, higher flash point and domestic source [11].
One of such vegetable oil sources is Fluted Pumpkin shrub plant (*Telfairia Occidentalis Hook F.*) which belongs to the cucurbitacase family and is characterized by its thick and fleshy fruits. It is a creeping vegetative shrub plant that spreads low across the ground and has large lobed leaves and long twisted

tendrils [12]. Sometimes the shoots are made to climb and spread on beds made with wooden stalk at a height of 1.5 to 2 m. The leaves are rich in vitamins and essential minerals and highly nutritious, hence used for the preparation of vegetable soups and salad [13], [14], [15], 16]. A stem can support two to five fruits and the fruits are very large, measuring about 100 - 200 cm in length and 10 - 20 cm in diameter and are characteristically shaped by 10 longitudinal ridges on the surface. The fruits can have up to 196 seeds enclosed in the mesocarp and measures about 3 cm in length. It is widely grown in southern Nigeria mainly because of the leaves and some of the varieties flourish in the wild. If all the sources are harnessed, it would provide a major source of oil that can be converted to biodiesel within a farm.

2.0 Materials and Method.

2.1 Materials and oil extraction

The seeds purchased from the market were planted in the backyard garden in July 2010 and a fruit, shown in Fig.1 was harvested in January 2011. The 190 seeds removed from the fruit were dried in the sun to reduce the moisture content. An anhydrous methanol (of purity 99.95%, density 0.7850 g/mL and water content 0.04%) and sodium hydroxide of analytical grade were purchased from Finlab laboratory in Akure, Nigeria. The oil was extracted in a soxhlet extractor using normal hexane as solvent at a temperature of 60 ^{o}C and the leaching process lasted 8 hours. The oil was separated from the hexane using a rotary vacuum evaporator, dried and weighed for the determination of the oil yield.

2.1 Transesterification of the oil.

The fatty acid value of the oil was 3.5 gm KOH/g which was high and hence neutralized with HCL before transesterification. Methyl ester of the oil was produced by transesterifying the oil with methanol using sodium hydroxide as catalyst. 3.5 g/L of sodium hydroxide was added to methanol and mixed thoroughly to form sodium methoxide. The pumpkin seeds oil was heated to 110 ^{o}C to remove any water vapour present, cooled to 60 ^{o}C and mixed with the methoxide at a molar ratio of 6:1 in a 250 mL spherical flask equipped with reflux condenser, magnetic stirrer/heater. The mixture was stirred at 1100 rpm [17] for 2 hours and then allowed to settle for 8 hours after which the methyl ester and glycerol were separated using separating funnel. Excess methanol in the methyl ester was removed by flash evaporation at 90^{o}C for recycling.

2.2 Purification Process

After separation, the biodiesel was washed by adding 20 % volume of warm distilled water and agitated gently for 5 minutes. The mixture was allowed to settle and this gave a two-layer mixture from which the biodiesel was separated. The process was repeated two more times to give a clearer ester. The washing was done in other to remove impurities and any remaining residual methanol.

2.4 Condition for Optimal Biodiesel Yield

An iterative experimental design was used to determine the optimum amount of catalyst required and molar ratio of alcohol to oil in the transesterification of the oil for maximum biodiesel yield as follows;

- The mass of sodium hydroxide granulated was varied from 2.5 to 5 g in a step of 0.5 g
- Each mass was added to 1 litre of methanol and stir to form sodium methoxide.
- The methoxide was mixed with the oil in molar ratios 1:1, 2:1, 3:1, 4:1, 5:1 and 6:1 thus giving 36 samples which were all transesterified and the esters and glycerol separated and measured.

2.4 Fuel Characterization Tests.

The major fuel properties of the oil and its biodiesel were measured following the ASTM protocols for biodiesel [18].

2.5 Fatty Acid Analysis The relative weights of the composition of the methyl ester and the standard sample of free fatty acid were analyzed and compared by gas chromatography following the modified AOAC 965.49 and AOAC 996.06 official methods. 50 mg of the extracted fat content of the sample was esterified for 5 minutes at 95°C with 3.4 mL of 0.5M KOH in dry methanol. The mixture was neutralized by using 0.7M HCL and 3 mL of 14% boron triflouride in methanol was added. The mixture was heated for 5 minutes at a temperature of 90 °C to achieve complete methlation process. The fatty Acid Methyl Ester was thrice extracted from the mixture with redistilled n-hexane. The content was concentrated to 1 mL for gas chromatography analysis and 1 µL was injected into the injection port of the Gas Chromatography (GC). The fatty acid methyl esters were separated using HP 6890 Gas Chromatography analyzer powered by HP ChemStation Rev A 09.11 [1206] software and equipped with a flame Ionization Detector (FID) and HP INNOwax column (30 m x 0.25 cm x 0.20 µm film thickness) The carrier gas was nitrogen and the oven initial temperature was at 60 °C. The first ramping was at 10 °C/min for 20 min and maintained for 4 minutes. The second ramping was at 15 °C/min for 4 minutes and maintained for 10 minutes. The detector temperature was 320 °C while hydrogen and compressed air pressures were 22 and 35 psi respectively.

3.0 Results and Discussion

The oil content of pumpkin seed oil was 45% which is however lower than 55% for jatropha [19], 55% castor [20] and 60% for egunsi seeds oil [21]. The variation of catalyst weight and molar ratio is shown in Fig.2. It is clear that methyl ester yield increase with molar ratio and the maximum yield occurs at high molar ratio and catalyst weight. The biodiesel yield for a catalyst amount of 4.5 g/L and molar ratio of 6:1 from the transesterification process was 91%. Molar ratio tends to neutralize the effects of catalyst by reducing the tendency for soap formation. This result is close to the results obtained in [22-24]. However, excess molar ratio will slow the rate of separation of glycerin and the methyl ester because of increased in solubility. Any remaining glycerin in the ester will drive the equilibrium back to the reversed reaction [25]. Catalyst amount also affects the methyl ester yield. The best yield is at 4.5 g/L. However, at catalyst amount in excess of 6g/L the formation of gel will start to and yield will tends to zero. After transesterification, the measured properties of the resulting biodiesel were close to those of diesel fuel and within the limits for biodiesel of ASTM 06751-02. The relative density was determined following the D1298 procedure and is just higher than that of diesel fuel. The pour point which is the temperature at which the oil in the solid form starts to pour and cold point which is the temperature at which small solid crystals are first visually observed as the fuel cools are lower than for diesel fuel thus ensuring good cold flow performance even at very extremely cold temperature. Of particular importance is the flash point of 175 °C for the methyl ester compared to 55 °C for diesel fuel, which allows it to be classified as a non hazardous fuel.

Kinematic Viscosity has strong influence on fuel flow and atomization characteristics. The kinematic viscosity of neat oil of 32.2 mm/s^2 reduced to 4.1 mm/s^2 for the methyl ester which although is slightly higher than that of diesel is still within the limits for biodiesel.

Heating value is the amount of heat released when a kg of the fuel is burnt at constant pressure or volume. In general, the heating value of biodiesel is 12.7 to 14.6 % of No.2 diesel [26]. The heating value of obtained is less than that for diesel and this is unexpected because like most biodiesel obtained from vegetable oils and animal fats the fuel contains the C18 carbon chains unlike the long chain C20 - C22 that usually have higher heating values[27]. Higher heating value would usually result in lower fuel consumption. The heating value is 9% less than that of diesel fuel and consistent with the trend for biodiesels.

The acid value of the raw oil of 3 mg KOH/g was high and was neutralized with HCL as high acid values above 1% tends to inhibit methyl ester yield. After transesterification, the value reduced to 0.5 mg KOH/g which is within the limits for biodiesel.

The carbon residue of a fuel is the tendency of carbon deposits to form under high temperature conditions in an inert atmosphere. The carbon residue when the methyl ester was burnt is 0.01% (mass) and is within the ASTM limits for biodiesel. Carbon residue is affected by impurities and additives present in the fuel. The methyl ester gave lower carbon residue than diesel and this has been attributed to the higher level of

oxygen content in the fuel which resulted into more complete combustion and hence reduced carbon residue [28]. The result of the properties measured and test methods are shown in Table 1.

3.1 Free Fatty acid profile

The chemical composition and properties of biodiesel depends on the length and degree of saturation or unsaturation of the fatty acid alkyl chains. The various structures of fatty acids impart different effects on physical properties on vegetable oils. For example, as the amount of unsaturation increases, the relative rate of oxidation will also increases [29]. Fatty acid composition and chain length affect properties such as Cloud and pour points, cetane number, Kinematic viscosity, oxidation, and $N0_x$ emissions. Thus the final properties of biodiesel will depend on the properties of the component free fatty acids present [30] Pumpkin oil biodiesel contains 45% Linoleic and 36% oleic acids which are unsaturated thus making the methyl ester unsaturated. The results obtained are close to those obtained by [31].

4.0 Cost Analysis

To determine the cost of producing pumpkin biodiesel, the computer model developed by [32], Hass which estimated the capital costs as well as operating costs for soya bean oil biodiesel plant of annual capacity of 34 000 m^3 was used. Table 3 shows the result obtained. The difference in costs is due to the higher cost of feedstock and lower labour costs in Nigeria.

5.0 Conclusion

Pumpkin seed oil can be transesterified to biodiesel with properties close to those of diesel fuel and within the ASTM limits for biodiesel. It can thus be used as alternative fuel for diesel engines. Of particular advantage is the high flash point which makes it a safe fuel. The low cloud and pour points makes it a suitable fuel for use in cold regions. However, because of the limited quantity that can be produced, is may for now serve as a source of blending fuel [33].

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Table 1. Relative properties of raw pumpkin oil, its methyl esters and diesel fuel.

Property	**ASTM protocol**	**Pumpkin Oil**	**Pumpkin oil methyl ester**	**[31]**	**Diesel fuel**
Relative Density at 30 °C	D1298	0.921	0.877	0.8837 at 15°C	0.85
Pour Point (°C)	D2500	20	-32	_	-20
Cloud Point (°C)	D2500	12	-18	_	-12
Flash Point (°C)	D93	280	175	120	55
Acid Value (mg/KOH/g)	D664	3.56	0.48	0.48	-
Kinematic Viscosity (mm^2/s)	D445	32.22	4.13	4.41	3.5
Heating Value (MJ/Kg)	D240	38.32	40.21	38.08	45
Calculated Cetane number	-	30	51	-	-
Carbon residue (% mass)	D4530	0.15	0.03	0.175	0.01
Sulfated ash (%)	-	0.008	0.006	-	-
Acid value (mg KOH/gm)	-	16.56	0.48	0.48	-
Free fatty acid (%)	-	14.50	0.23	-	-
Water content (mg/kg)	-	584	495	490	-
Iodine value ($gI_2/100g$)	-	101	90	115	-
Peroxide value ($gI_2/100g$)	-	25	29	_	-
Oxidation stability (Hour at 110°C)	-	15	7.2	_	-
monoglycerine	-	0.003	0.015	_	-
Diglycerine	-	0.002	0.004	_	_
Triglycerine	-	98.75	0.006	_	_
Free glycerine	-	0.98	0.019	_	_
Total glycerine	-	9.740	0.231	_	_
Totalglycerine	-	98.76	0.0212	_	_
Methanol content (%)	-	0.001	0.128	_	_
Sodium (mg/kg)	-	8.90	1.80	1.50	-
Potassium (mg/kg)	-	4.2	1.00	0.5	-
Calcium (mg/kg)	-	4.70	0.35	-	-
Magnesium (mg/kg)	-	1.80	0.60	-	-
Phosphorous (mg/kg)	-	1.68	2.93	-	-
Sulphur (mg/kg)	-	-	2	-	-

Carbon (% kg/kg)	-	-	77.7	-	-
Hydrogen(% kg/kg)	-	-	11.7	-	-
Oxygen(% kg/kg)	-	-	11.7	-	-

Table 2. Fatty Acid Composition of Raw Pumpkin Oil and its Methyl Ester.

Free Fatty Acid	Form	Pumpkin Oil	Pumpkin Oil Biodiesel	[31]
Palmitic	C16:0	10.2	11	12.51
Stearic	C18:0	6.0	9.7	5.43
Oleic	C18:1	36.1	29.6	37.07
Linoleic	C18:2	45.2	45.3	43.72
Linolenic	C18:3	2.6	4.4	0.19
Total Saturated	-	-	20.7	-
Total Unsaturated	-	-	79.3	-

Table 3. Cost analysis of pumpkin oil biodiesel based on soya bean oil biodiesel

Cost component	**[a]Soya baen Oil biodiesel US$/litre**	**Pumpkin seed oil biodiesel US$/litre**
Total raw materials	0.5	1.0
Utilities	0.011	0.011
Labour	0.013	0.001
Supplies(operating and maintenance insurance)	0.004	0.004
General works(administration, taxes and insurance)	0.003	0.003
Depreciation	0.03	0.03
Total Costs	0.561	1.049
Glycerol credit	0.034	0.30
Gross operating cost	0.527	0.749

a Hass et al., 2006

Fig.1 Fluted Pumpkin Fruit

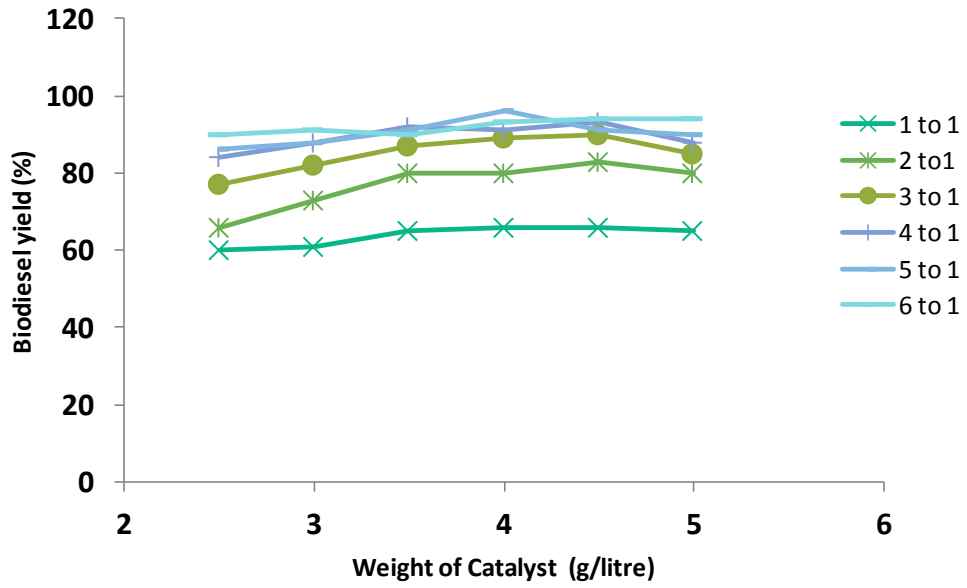

Fig. 2. Variation of pumpkin biodiesel yield with molar ratio and catalyst weight