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Biodiesel Production from Ground Nut Oil

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Abstract
Ground nut oil is widely grown in northern Nigeria and is a potential source of feed stock for biodiesel production. However, not much work has been done on the conversion to biodiesel and its characterization. The purpose of this study is to cover the gap in knowledge by extracting the oil, transesterifying it to biodiesel and characterizing it. To achieve this, the ground nut oil which contains high amount of free fatty acid was pretreated with hydrochloric acid as catalyst and anhydrous methanol at a molar ratio of 9:1 to reduce its free fatty acid to 1.5% before tranesterification with sodium hydroxide as catalyst at a molar ratio 6:1. The oil and biodiesel were characterized and it gave for example, a kinematic velocity 6.6 mm2/s, flash point of 182oC and cetane number 51 which are close to the properties of diesel fuel thus making it an alternate fuel for diesel engines. Gas chromatography analysis shows that it is 68.7% unsaturated and contains mainly the oleics.

Keywords: biodiesel, ground nut oil, oleics, pretreatment, transesterification.

INTRODUCTION

Global warming and the consequential changes in weather pattern manifested in the form of wide spread flooding, gully erosion, massive mudslide, environmental degradation and increasing cost of fossil fuel have given the necessary impetus to switch to vegetable oils as alternative fuels for diesel engines. Vegetable oils however, are not suitable for direct use in diesel engines because of high viscosity, poor cold flow properties and low cetane number (Ma and Hanna, 1999; Ramadhas, 2009). It can however, be made useable by either blending with diesel fuel or transesterifying with alcohol to methyl ester called biodiesel (Bello, 1999; Bello, 2003; Erantan and Canakci, 2009). Biodiesel has been defined as the mono alkyl esters of vegetable oils and animal fats (NBB, 1997; Knothe, 2005). It has properties that are close to those of diesel fuel and in addition, has agricultural origin, highly biodegradable, environmental friendly and emits lower harmful exhaust emissions (Canakci and Van Gerpen, 1999). One of the vegetable oils suitable for biodiesel production is ground nut (*A. hypogaea*) oil that is widely cultivated in northern Nigeria. It is a leguminous crop that is cultivated mostly in the sub tropic and tropic regions of the world. The pods are attached to the roots and are very rich in oil, which is extracted by roasting, grinding and pressing. The oil is commonly used as cooking oil because of its high protein content.

MATERIALS AND METHODS

Oil extraction

Ground nut oil was extracted in a soxhlet extractor with n-hexane as the solvent. The ground nuts were procured from a local dealer and dried in the sun for five days at 35^{o}C to reduce moisture content to about 7% (Ebewere et al., 2011). There after the nuts were milled to reduce diameter and expose more area for higher oil extraction (Goodrum and Kiloha, 1986; Sayyar et al., 2008). The oil was leached for 8 hours at 60^{o}C and the hexane in the oil was removed using a vacuum rotary extractor operated at 75^{o}C. The oil obtained was weighed and the percentage oil yield was calculated by equation 1.

$$Oil\ yield\ \% = \frac{Weight\ of\ oil\ extracted}{weight\ of\ seed\ kernels\ used} x100 \quad 1$$

Characterization of the Oil

The properties of the oil were first measured to determine if pretreatment was necessary or not before alkaline transesterification. It was found that the free fatty acid value (FFA) of the oil was 23.68 mg KOH/gm (oleics) which is too high for alkaline transesterification as it can react with the catalyst to form soap which can inhibit methyl ester yield (Ramadhas, 2009).

Tranesterification Procedure

Transesterification was carried out using a laboratory scale biodiesel processor in internal combustion engine laboratory of the Federal University of Technology, Akure, Nigeria. The Methanol and sodium hydroxide used were procured from Finlab laboratory in Akure, Nigeria. Methanol was used as the reagent because it is a low cost and short-chain alcohol that reacts fast. The pretreatment was done using hydrochloric acid 1%(w/w) as catalyst and anhydrous methanol at a molar ratio of 9:1, stirred at 400 rpm and at 60^{o}C for 1 h. The product of reaction was pour into a decanter to settle for 3 h after which

the content separated into two layers with the top mainly water and methanol and the bottom transesterified oil. The oil had a free fatty acid value to 1.5%. Alkaline transesterification was next done using anhydrous methanol at a molar ratio of 6:1 and 3g/liter of sodium hydroxide as catalyst. The processor was stirred at 600 rpm and at a temperature of 60 ^{o}C for 2 hours, after which the mixture was poured into a decanter and allowed to settle for 3 hours so that the reaction can be driven to completion and for the mixture to separate into methyl ester and for the glycerol at the bottom to be drained off by gravity. The excess methanol in the ester was removed in a flash evaporator. To remove any impurity, the methyl ester was washed in distilled water of volume ratio 3 to 1 three times. Finally, the washed methyl ester was dried by passing it through anhydrous sodium sulphate (Na_2SO_4)(Shinas et al.,2009).

Fatty Acid Profile

The fatty acid composition of the ground nut oil biodiesel was investigated using gas chromatography analyzer, GC-17A model by Shimadzu inc., Japan, with HP 5/Bp. 5-capillary column 30 m long and 0.25 mm in diameter. The injector was maintained at 230 °C and the detector temperature at 240 °C. Nitrogen was the carrier gas at a flow rate of 45.0 ml/min and pressure of 2.0 psi. The oven temperature was set at 40°C, held for 1 minute, programmed to 120°C at 20°C/min for 25 minutes and then to 230 °C at 35°C/ min for 35 minutes. The total run time was 68.14 minutes. The proportion of the various fatty acids is shown in Table 1.

Determination of Fuel and Physiochemical Properties

The oil yield was 35% and biodiesel yield was 96%. The fuel and physiochemical properties of the ground nut oil and its fatty acid methyl ester (FAME) were determined following American Society for Test and Materials (ASTM) and American oil Chemist Society (AOCS) methods and undertaken in Multi-environmental management laboratory, Ikorodu, Lagos, Nigeria and Chemistry laboratory of the Federal University of Technology, Akure, Nigeria.

Density and relative density: The density and relative density were measured using hydrometer to IP-160/ASTM D-1298. The measurements were made three times and then averaged.

Cold Flow properties: In measuring the Pour point, a 45 ml sample initially at 45^{o}C was cooled in Herzog HCP852 at specified rate and examined at interval of 3^{o}C to check if the sample is still flowing. The cloud point was determined by a cloud point meter which comprises of a waveguide sensor of a total-reflection type, the wave guide sensor including a wave guide having an incidence channel, an emergency channel and a detection surface all formed on a substrate, the incidence and emergency channels intersecting along the detection surface, an incidence optical fiber connected to the entrance of the incidence channel, and an emergency optical fiber connected to the exit of the emergence channel; and a cooling/heating means in contact with the waveguide sensor for cooling/heating the waveguide sensor within a desired temperature range.

Kinematic viscosities: The kinematic viscosity was determined with a Herzog GmbH MP-480 that involves measuring the time for a fixed volume of the fuel to flow under gravity through a capillary at a known and closed temperature.

Kinematic viscosity = Calibration constant (mm^2/s^2) x mean time of flow (s).

Flash Point: Flash point measurements were done according to method ASTM D6751 using Kehler Model K-16270 (Pensky-Martens Closed Flash Tester).

Heating Value: The lower heating value was obtained using the oxygen bomb calorimeter (Parr Instrument Company, US.) following the ASTM D240 method.

Cetane Number: The cetane number of the biodiesel was calculated using equation 2 (Willard, 1976).

$$CI = -420.34 + 0.016G^2 + 0.192G(\log T_{50}) + 65.01(\log T_{50})^2 - 0.0001809T_{50}^2, \quad 2$$

where G is the API (American Petroleum Institute) specific gravity and T50 is the distillation temperature as 50 vol.% fuel sample distilled and condensed in a unit of °F.

Iodine and peroxide Values: The iodine and peroxide values were analyzed, based on the methods of the American Oil Chemists' Society (AOCS cd8, 1980) by titration with 0.01 N sodium thiosulfate for the mixture of tested fuel and chemical reagents until they were light blue and light yellow, respectively.

The iodine value and peroxide value were then calculated by equations (2) and (3).

$$Iodine\ value = \frac{(B-T)xCx0.001269}{Y} \quad 3$$

$$Peroxide\ value = \frac{(T-B)xCx1000}{Y} \quad 4$$

where B and T are denoted as the amounts (in mL) of sodium thiosulfate titrated for the blank sample and tested sample, respectively; C is the molar concentration (in mol/L) of sodium thiosulfate; and Y is the weight (in g) of the tested sample.

Acidic number: The acid number, which is the amount of KOH required to neutralize 1 g of fat and expressed as mg KOH/g, was determined by titrating with 0.01 N potassium hydroxide for the mixture of tested fuel and chemical reagents until the appearance of the color pink.

RESULTS AND DISCUSSION

Fatty acid profile of the oil consists of 77.7% oleic series and is 79.7% unsaturated, which reduces to 68.7% after transesterification. The results are shown in Table 1. The properties of the oil and its biodiesel were characterized following the American Society for Test and Materials protocols and the results are shown in Table 2.

Density: The densities of biodiesels are generally higher than those of fossil diesel fuel and the values depend on their fatty acid composition as well as on their purity. Density increases with decreasing chain length and increasing number of double bonds. Knowledge of density is important as it gives an indication of fuel type and mass of a given volume. It also affects the performance of pumps and atomizers (Goodger, 1975). GNO density of 956 kg/m3 reduced to 922 for the B100.

Cloud Point and Pour Point: Cold temperature behavior of biodiesel is an important quality criterion, as frozen fuel may cause blockage of the fuel lines and filters and starve the engine of fuel. The two most important criteria are the cloud and pour points. Cloud point is the temperature at which wax first becomes visible when the fuel is cooled while Pour Point is the temperature at which the amount of wax out of solution is sufficient to gel the fuel, thus it is the lowest temperature at which the fuel can flow. The cold point characteristics of biodiesel products depend on chain length and degrees of unsaturation, with long chain saturated fatty acid esters displaying particularly unfavorable cold temperature behavior Ramadhas et al.,2005). The cloud, pour and cold filter plugging points are above zero which limits their application in cold regions.

Flash point: This is the lowest temperature to a barometric pressure of 101.3 kPa at which a liquid sample produces sufficient vapour for the air-vapour mixture above the surface to flash momentarily on exposure to a standard source of ignition. It is a measure of flammability of fuels and thus an important safety criterion in transport and storage. The flash point of pure biodiesels is usually higher than the ASTM limits, but fall rapidly with increasing amount of methanol. Ground nut oil has a flash point of 165^{o}C and the value for FAME is 141^{o}C which although are below the minimum for biodiesel, are higher than that for diesel fuel.

Viscosity: Kinematic velocity is the dynamic viscosity/relative density. The kinematic viscosites of the GNO and FAME are 244.52 and 6.6 mm^2/s respectively. Viscosity is an important property of biodiesel since it affects the operation of fuel injection equipment, particularly at low temperatures when the increase in viscosity affects the fluidity of the fuel or leakage at high temperature when too thin.

Heating value: The lower heating values for GNO and FAME are 39.30 MJ/kg and 39.6 MJ/kg respectively and are slightly less than that of diesel fuel which is consistent with the trend for biodiesel. The lower heating value of vegetable oils depends on the composition of the fatty acids, where grown and its vintage among other factors. It increases if the length of the fatty acids increases, and does so to an even greater extent if the content of oxygen in the oil decreases (Laza and Bereczky, 2010). However, Knothe (2005) reported that it decreases as the volume of double bond increases.

Cetane Number: Cetane Number (CN) is a measure of the ignition quality of diesel fuels and one of the prime indicators of the quality of diesel fuel. It relates to the ignition delay time of a fuel upon injection into the combustion chamber, it influences ease of starting, duration of white smoke after start up, drivability before warm up and intensity of diesel knock at idle. Biodiesel has a higher cetane number than diesel fuel because of its oxygen content (Ladammatos and Goacher, 1995) and also because the fatty acids present in the fuel have very high octane number. Cetane number increases with increasing length of both fatty acid chain and ester groups, while it is inversely related to the number of double bonds. It has been shown (Van Gerpen, 2005) that the cetane number of biodiesel depends essentially on the distribution of fatty acids in the feedstock. The longer the fatty acid carbon chains and the more saturated the molecules, the higher the cetane number. The calculated cetane number of the GNO of 26 increased to 51 for the FAME. That of FAME is above the minimum limit for biodiesel.

Peroxide value: This is an indication of oil auto ignition and high value is means high degree of rancidity. The peroxide value is 18 for the oil and 6.4 for the biodiesel.

Acid number and Free Fatty Acid value: This is the quantity of base required to titrate a sample to a specified end point. It is a measure of free fatty acid in biodiesel. Excessive free fatty acid in the fuel can be corrosive and may be a symptom of water in the fuel or poor production or subjected to oxidative degradation. Excessive free fatty acid in the fuel can inhibit the transesterification process and lead to soap formation. The acid values of the oil and FAME are 15.37 mg KOH/gm and 3.37 mg KOH/gm respectively.

Refractive index: The refractive index was 1.468 and reduced to 1.366 after transesterification. Refractive index is a measure of purity of the fuel.

Sulfated Ash: This is the alkaline catalyst residue remaining after a fuel sample has been carbonized, and the residue subsequently treated with sulfuric acid and heated to a constant weight. It is a measure of the mineral ash residue when a fuel is burned. It is an important test for biodiesel because it is an indicator of the quantity of residue metals in the fuel that came from the catalyst used in the transesterification process. Especially for base catalyzed transesterification in which the sodium hydroxide and potassium hydroxide commonly used have low melting points and may cause engine damage in combustion chamber, injector deposits or fuel system fouling. The sulfated ash for FAME is 0.010 %(mol/mol) and lower than the 0.05 ASTM maximum limit.

Phosphorus content: Phosphorus in biodiesel originates from phospholipids (animal and vegetable material) and inorganic salts contained in the feedstock. Phosphorus has adverse effect on long term activity of exhaust emission catalytic systems and therefore limited by specification. The value for the oil is less than the maximum of 10 mg/kg specified by EN standard

Table 1. Fatty acid profile of ground nut oil and its methyl ester

Acid	Form	Oil	B100
Palmitic	C16:0	8.0	12.4
Stearic	C18.0	2.9	5.8
Oleic	C18:1	44.9	42.9
Linoleic	C18:2	32.8	23.7
Arachidic	C20:0	5.6	4.0
Behenic	C22:0	3.8	5.0
Erucic	C22:1	1.0	2.0
Lignoceric	C24:0	1.0	2.0
Total Saturation		20.3	29.2
Total unsaturation		79.7	68.7

Table 2. Properties of ground nut oil and its methyl ester

Property	Ground nut oil	Ground nut oil Biodiesel
Density (Kg/m^2)	956	922
Specific gravity	1.10	0.96
Cloud Point(^oC)	8	10
Pour point(^oC)	-3	-6
Flash point(^oC)	458	182
Heating Value(MJ/kg)	39.30	39.6
Cetane number	26	51
Sulphated Ash (%)	0.05	0.010
Phosphorus (mg/kg)	2.13	4.17
Kinematic viscosity(mm^2/s)	244.52	6.6
Refractive index	1.468	1.366
Acid Value	15.37	3.366
Peroxide Value	18.0	8.4

CONCLUSIONS

Ground nut oil can be converted to methyl esters and the properties are within the limits for biodiesel. The pour point is -6^{o}C which means it cannot be used when temperature can fall below this value. The cetane number is just above the maximum for biodiesel. In view of the similarity of the properties to those of diesel fuel, it can hence be used as alternative fuel for diesel engines.

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