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The Production and Determination of Physico–Chemical Properties of Biodiesel Derived from Beech wood (*Gmelina Arborea Roxb*) Seed

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Abstract: Gmelina arborea Roxb seed oil were extracted and transesterified using methanol as the solvent in presence of a catalyst to produce biodiesel. The yield of the oil and the biodiesel produced was determined and found to be 40.650% and 57.143% respectively. ASTM-D1959 (ISO3961) standard procedure was used to determine the physico–chemical properties of the biodiesel, which include the kinematic viscosity, specific gravity and density, pour point, cloud point, flash point, and refractive index. Predictions of four important chemical properties of biodiesel viz acid value, iodine value, saponification number and cetane index were performed based upon fatty acid profiles of *Gmelina arborea* biodiesel. Acid value obtained was found to be 0.329 mg KOH/g which is within the acceptable limit of equal or less than 0.50 mg KOH/g in both EN14214 and ASTM D6751 standard fuels. Iodine value of biodiesel was found to be 40.326 g I_2/100 g oil which is far below the maximum limit of 120 prescribed in EN14214, and saponification number of the biodiesel derived from *Gmelina* was determined to be 92.5 $mgKOH/Kg$. The cetane index of *Gmelina arborea* biodiesel obtained is 50.5, which is higher than the minimum required value specified in ASTM-D6751, but slightly below the minimum value specified in EN14214.

Keywords: Beechwood, Biodiesel, Gmelina Arborea Roxb, Physico – Chemical, Transesterification, Triglycerides.

1.0 Introduction

Gmelina arborea Roxb is a big forest tree popular for its wood used for making furniture and as building materials. It is a fast growing tree, which grows on different localities and prefers moist fertile valleys with 750-5000 mm rain fall. The tree attains moderate to large height up to 40 m and 140 cm in diameter. This tree is commonly planted as a garden and an avenue tree; growing in villages along agricultural land and on village community lands and wastelands. Flowering takes place during February to April whereas fruiting starts from May onwards to June. The fruit is up to 2.5 cm long, smooth, dark green, turning yellow when ripe and has a fruity smell. Fruit contains very little kernel but the kernel is quite rich in oil (53 wt. %) [1].

Current trends focus on the search for alternate fuel (biodiesel) for replacing fossil fuels due to the increase in the price and environmental concerns about air pollution [2]. Biodiesel is defined as the fatty acid methyl ester formed by the transesterification of vegetable oil (edible, non-edible), used cooking oil and animal fats with methanol, either pure or blended with fossil fuel [3]. The advantages of utilizing biodiesel replacing conventional fuel are that biodiesel is non-toxic, biodegradable, renewable and less pollutant in emissions. Engine life can be prolonged by reducing the frequency of engine part replacement and increasing the lubricity [4].

Biodiesel fuels derived from agricultural materials have the potential to provide a clean-burning alternative to dwindling sources of petroleum. Rudolph Diesel's first engine was designed to run on peanut oil, and Henry Ford envisioned plant-based fuel as the primary fuel for transportation and partnered with Standard Oil to develop biofuel production and distribution. However, currently the only type of biodiesel fuel that can be used in vehicles in the United States and Canada without violating manufacturer's warranties is B5, a blend of 5 percent biodiesel and 95 percent regular diesel [5]. Most diesel engines run just fine on blends of up to 30 percent biodiesel.

Biodiesel refers to 100% pure fuel (B100) and specific standards given by the American Society of Testing and Materials (ASTM) International (D 6751). However, it is often used to describe blends of biodiesel with petroleum diesel. Such blends are generally referred to as "B10," "B20," "B50," etc., where the number indicates the percent of biodiesel used.

Conventional manufacturing of biodiesel is by means of the transesterification of oils with methanol in the presence of catalyst, such as alkali (KOH, NaOH) [6, 7]. The basic transesterification reactions are as follows:

Oils (triglycerides) + Methanol → Biodiesel + Glycerol

Different processes have been found to be applicable in the synthesis of biodiesel, they include micro emulsion process, thermal cracking process and the most conventional way is transesterification process as mentioned earlier. This is because of the fact that this method is relatively easy, can be carried out at normal conditions, and gives the best conversion efficiency and quality of the converted fuel [8].

The process of transesterification can be represented by the following chemical equation.

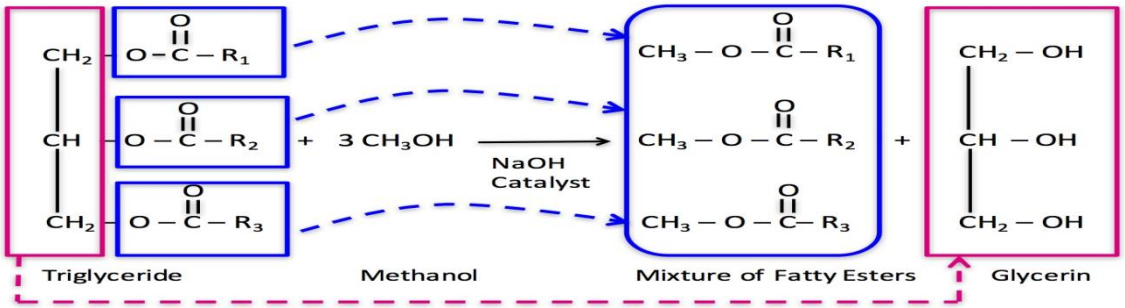

Figure 1; Transesterification chemical equation [9]

Alcohol combines with the triglycerides to form glycerol esters. A catalyst is usually used to improve the reaction rate and yield. Since the reaction is reversible, excess alcohol is required to shift the equilibrium to the product side. Among the alcohols that can be used in the transesterification process are methanol, ethanol, propanol, butanol etc.

[10] conducted the experimental analysis of the engine with various types of biodiesel and their blends and concluded that blending require much effort and time. It has been found that biodiesel can be use in blend with fossil diesel and used inside compression ignition engine without modification. The blend can be in any ratio ranging from 0 – 99, where the number signifies the volume of the biodiesel in percentage.

Fatty acid profile of biodiesel from Gmelina arborea seed oil was determined and reported by [1]. The biodiesel consists of 15.09 wt.% of methyl palmitate (C16:0), 44.88 wt.% of methyl oleate (C18:1), 11.16 wt.% of methyl stearate (18:0), 15.95 wt.% of methyl gondoate (C20:1), 4.21 wt.% of methyl arachidate (C20:0) and 8.67 wt.% of methyl behenate (C22:0).

The physico-chemical properties of fuel are the fuel specifications that define and set the quality standards. The physico-chemical properties that were studied include: cloud point, pour point, flash point, density, viscosity cetane number, iodine value, free fatty acid value and saponification value.

2.0 MATERIAL AND METHODS

2.1 Materials and Equipment

Gmelina Arborea Roxb (Verbenaceae) seeds, methanol, n–hexane, Soxhlet extractor and accessories. All other solvents and chemicals used were of analytical grade, and they were procured from commercial sources and used as such without further treatment.

2.2 Methods

Seed selection, Collection and Preparation of seeds, Oil Extraction, Biodiesel Production and Biodiesel Characterization.

2.2.1 Gmelina seed selection, collection and processing

The *Gmelina* samples (both green and yellow) were collected locally from Owukpa in Ogbadibo local government area in Benue State, Nigeria and brought to Abubakar Tafawa Balewa University, Bauchi - Nigeria to separate the nut from its pulp and shell (de–pulping). The seeds were sun-dried for one week. After drying, the samples were grinded using corona blender to break the cell wall for easy oil extraction. The samples were then dried using the Mermmet oven, stored in air tight containers and were labelled adequately.

Methanol, sodium hydroxide, potassium hydroxide and hydrochloric acid were obtained from the chemistry Department of Abubakar Tafawa Balewa University, Bauchi - Nigeria.

Petroleum ether, diethyl ether, phenolphthalein indicator, glacial acetic acid, chloroform, distilled water, carbon tetrachloride, iodide solution were purchased from a reputable chemical shop in Wunti market, Bauchi, Bauchi

State. Potassium iodide (KI) and sodium thiosulphate were obtained from the same place. The organic solvent used for the oil extraction was n-hexane. All the reagents were commercial grade and were used without further purification.

2.2.2 Extraction of oil from gmelina arborea roxb seeds

The processing of vegetable oil is commonly done by chemical extraction, using solvent extracts, which produces higher yields and is quicker and less expensive. The most common solvent is petroleum – derived hexane. Hence, solvent extraction method was adapted for this research using a soxhlet extractor as shown in figure 2.

Figure 2; Soxhlet Extractor and Accesories

The soxhlet apparatus was assembled and refluxing was carried out for about 6 hours. The 10 g of grinded meal was extracted with n-hexane. The Extraction temperature was varied from 20^{o}C to boiling point of the solvent while the reaction time was varied between 5 and 60 min. The solvent to solid ratio was investigated from 2:1 to 5:1. At the end of the extraction, the micelle was filtered using a vacuum filtration (Millipore glass base and funnel) to remove suspended solids. Subsequently, the solvent was separated from the oil using rotary vacuum evaporator (Lab rota 4000) and was collected in the receiving flask. The oil that remained in the sample flask was weighed after the process was completed. The percentage of extracted oil was calculated using the expression below:

$$Y = \frac{W_0}{W_g}\, x\, 100 \qquad (1)$$

Where:

Y = oil yield (%)

W_0 = weight of pure oil extracted (g) and

W_g = weight of the sample of gmelina seeds.

This process was repeated 2-5 times with the seed meal (*Gmelina*) using fresh solvent each time in order to extract most of the oil. The oil was purified prior to transesterification.

2.2.3 Biodiesel production from the gmelina seed oil (GSO).

Biodiesel is produced through the chemical reactions of transesterification processes as reported in figure 1.

A measuring cylinder was used to measure 40 ml of methanol and transferred to a 250 ml beaker; an electric balanced was used to measure 1 g of potassium hydroxide. The potassium hydroxide was slowly added to the methanol. The mixture was gently stirred using a glass rod until the potassium hydroxide completely dissolved in the methanol. The residual was heated and mixed well using a stirrer. The mixture was then allowed to settle overnight. The next morning a lighter coloured layer of biodiesel was observed on the surface and a darker coloured layer of glycerol was observed at the bottom of the flask. The glycerol was then separated from the biodiesel. After the separation, the biodiesel undergo the following purification processes.

i. **Methanol Recovery:** The methanol used for the reaction was removed after the biodiesel and glycerine had been separated into two layers, preventing reaction reversal. The methanol is then cleaned and recycled back to the beginning of the process.

ii. **Removal of other by - products:** Products of the reaction include not only biodiesel, but also by – products such as soap, glycerol, excess alcohol, and trace amount of water. All of these by – products must

be removed to meet the standard. The density of glycerol is greater than that of biodiesel, and this property difference was exploited to separate the bulk of the glycerol co – product. Therefore once the biodiesel is separated from the glycerine, it goes through a purification process, removing all remaining alcohol and catalyst. To guarantee that the biodiesel is without colour, odour and sulphur, an additional **distillation** process may be implemented. The biodiesel washing sometimes leaves the biodiesel looking a bit cloudy. This means there's still a little water in it. It was heated slowly to 100^{o}C and held there until all moisture present was evaporated. This shown in figure 3.

Figure 3; the sample biodiesel produced

2.2.4 Biodiesel Characterization

Physical properties

The physical properties determined are;

The Kinematic Viscosity which was measured following the ASTM-D445 method using a calibrated Viscometer with a calibration constant of 0.1057.

The specific gravity and density following ASTM-D1298 by hydrometer method were both determined and estimated using the equations below.

$$SG = \frac{mass\ of\ oil}{mass\ of\ an\ equal\ volume\ of\ water} \quad (2)$$

$$Density = \frac{mass\ of\ oil}{Volume\ of\ biodiesel} \quad (3)$$

The flash point was determined by the method of ASTM-D93 using the Pensky-Martens closed cup tester. The sample of the biodiesel was heated in a close vessel and ignited. When the sample begins to burns, the temperature was recorded; cup tester measures the lowest temperature at which application of the test flame causes the vapour above the sample to ignite. The temperature at which the flash occurred was then recorded.

The pour point was determined following the procedure of ASTM-D97; a sample of the biodiesel was kept in the refrigerator for some time to freeze then placed in a heating mantle to melt. The temperature at the bottom of the test jar that is the temperature at which the biodiesel starts to pour is taken as the pour point.

The cloud point was determined using ASTM-D2500. The sample of the biodiesel was placed in a test jar to a mark and then placed inside a cooling bath. The temperature at the bottom of the test jar at which the biodiesel starts to form cloud was taken as the cloud point.

The refractive index was determined using Abbe's refractometer to determine moisture content of the oil sample. The refractometer was calibrated using distilled water then small sample of the oil was placed on it and the refractive index observed was taken and recorded.

Chemical Properties

Calculation of Acid value (ASTM-D664): The biodiesel sample was measured and poured in a beaker. A neutral solvent (a mixture of petroleum ether and ethanol) was prepared and 50 ml of it was taken and poured into the beaker containing the biodiesel. The mixture was stirred vigorously for about 20 minutes. 0.56 g of potassium hydroxide (KOH) pellet was measured and placed in a separate beaker and 0.1 M of KOH was prepared, 3 drops of phenolphthalein indicator is added to the sample and was titrated against 0.1 M of KOH till the colour change observed turned pink.

The acid value for the biodiesel was calculated using the formula given below;

$$AV = \frac{5.61 \times V \times N}{W_b}\left(mg\frac{KOH}{G}\right) \quad (4)$$

Where: V = volume of standard alkali used.

N = normality of standard alkali used.

W_b = weight of biodiesel used

Calculation of free Fatty Acid (FFA) value: The FFA was evaluated following the relationship below:

$$FFA = \frac{A.V}{2} \left(Mg\frac{KOG}{g}\right) \quad (5)$$

Calculation of Saponification value: The alcoholic KOH was freshly prepared by dissolving KOH pellet in methanol. 2 g of the biodiesel was measured and poured into a conical flask. 25 ml of the alcoholic KOH was added to it, a blank was used. The sample was well covered and placed in a steam water bath for 30 minutes, shaking it periodically, 1 ml of phenolphthalein was added to the mixture and titrated against 0.5 M of HCl to get the end point.

The saponification value of the biodiesel was determined using the following relation.

$$SV = \frac{(B-A)\times N}{W_g}\left(Mg\frac{KOH}{g}\right) \quad (6)$$

Where: B = volume of standard methanol potassium hydroxide used in blank titration;

A = volume of standard methanol potassium hydroxide used in titration with the oil

N = normality of standard acid;

W_b = weight of biodiesel used.

Calculation of iodine value: The iodine value is very important when biodiesel samples are analyzed as it is related to biofuel storage performance. The iodine value provides information about the unsaturation degree of the oil which directly affects its stability to oxidation. The main reason for auto-oxidation is the presence of double bonds in the chains of the fatty compounds. Higher unsaturated fatty acid on heating results in polymerization of glycerides. This can lead to the formation of deposits or deterioration of the lubricating property [5]. Hence, the limitation of unsaturated fatty acids in biodiesel is necessary. Iodine value of biodiesel obtained from *Gmelina arborea* seed oil was calculated theoretically (using equation 7) and found to be 40.326 g I_2/100 g oil which are far below the maximum limit of 120 prescribed in EN 14214.

$$\text{I.V} = \frac{0.1269(B-A)\ x\ N\ x\ 100}{W_b} \quad \left(\frac{gI_2}{100}\right) \quad (7)$$

Where: B = volume of sodium thiosulphate used in blank titration.

A = volume of sodium thiosulpate used in titration with oil.

W_b = weight of biodiesel used

N = normality of sodium thiosulphate.

Determination of peroxide value: 1 g of oil was weighed and pour into a clean drying boiling tube, 1 g of powdered potassium iodide and 20 ml of solvent mixture (2 volume of glacial acetic acid + 1 volume of chloroform) was added, the tube was placed in boiling water so that the liquid boils within 30 seconds and was also allowed to boil vigorously for not more than 30 seconds. The content was quickly poured into a flask containing 20 ml of potassium iodide solution; the tube was washed out with 25 ml of distilled water and was titrated with 0.002 M sodium thiosulphate solution using starch as indicator. A blank was also carried out at the same time.

Calculation of Cetane Number (ASTM-D613): Cetane Number is a measure of the fuel's ignition delay. Higher Cetane numbers indicate shorter times between the injection of the fuel and its ignition. Higher numbers have been associated with reduced engine roughness and with lower starting temperatures for engines. For calculating Cetane number of the biodiesel, this equation of Krisnangkura was used.

$$\text{C.N} = \frac{46.3 + 5458}{X - 0.225Y} \quad (8)$$

Where, X = S.N

Y = I.V

Determination of moisture content: In other to determine the moisture content in the biodiesel (%), 48.15 g of oil was weighed in a moisture pan, the weight of the pan and biodiesel was taken and was put inside an oven for 3 hours at a temperature of 45^0C. After every 1 hour, the sample was cooled and weighed until the weight before and after was approximately equal.

3.0 Results and Discussion

The results of the test conducted for the determination of the Physico–chemical properties of the biodiesel are as shown below.

Table 1: Physico-chemical properties of Gmelina seeds oil

Physico-chemical parameters	Calculated values	Experimental Values
Density at 35^{o}C	-	0.7545 g/cm^{3}
Acid value	0.329 mg KOH/g	-
Free fatty acid	0.165 mg KOH/g	-
Peroxide value	-	9 mleq g-^{1}
Iodine value	40.326 g I_2 /100 g oil	-
Flash point	-	200.54^{o}C
Pour point	-	10^{o}C
cloud point	-	17^{o}C
Refractive index at 35^{o}C	-	1.441
Saponification value	92.5mg KOH/kg oil	-
Moisture content	-	8.7 %
Cetane number	50.532	-

Transesterification of seeds oil to biodiesel was carried out using methanol as the solvent in the presence of a catalyst (KOH), the oil yield obtained from the research was determined to be (40.650 wt.%) and that of biodiesel was determined to be 57.143% at a reaction temperature of 32°C.

The physico - chemical properties: The physico – chemical properties of the biodiesel were determined and presented in table 1.

Iodine value: The iodine value of biodiesel derived from *Gmelina* seeds oil was found to be 40.326 g I_2 /100 g oil, which is within the acceptable standard of (1 – 130 g I_2 /100 g oil).

Acid value: it is the degree of fuel compatibility with engine material component and was found to be (0.329 mg KOH/g) for *Gmelina* biodiesel which is within the acceptable limit. The acid value set by the relevant bodies for biodiesel is given to be equal or less than 0.50 mg KOH/g in both EN14214 and ASTM-D6751 standard fuels.

Saponification number: The biodiesel standards such as ASTM-D6751 and EN14214 have no specification regarding the saponification number. But from this research the saponification number of the biodiesel derived from *Gmelina* is 92.5 $mgKOH/Kg$. Comparing this result with the values gotten from other seeds like neem, moringa, jatropha it is within the same value.

Cetane index (CI): or number is an important parameter and a prime indicator of fuel ignition quality in diesel engines. The minimum requirement of cetane number prescribed in biodiesel standards ASTM-D6751 and EN14214 is 47 and 51 respectively. From this research, the experimental value calculated for the cetane index is (50.532). Biodiesel derived from *Gmelina* has fairly good cetane number and can be used with fossil fuel without causing any problem.

Flash point: The minimum temperature at which the biodiesel derive from *Gmelina arborea roxb* ignite was determined to be (200.54^{o}C). This temperature is considered high when compared to biodiesel from other sources. The reason for the high flash point is attributed to the high moisture content of the *Gmelina* biodiesel and also its viscosity.

Pour and cloud point: The pour and cloud point of biodiesel derived from *Gmelina* was determined to be equal to 10^{o}C and 17^{o}C respectively. This temperature is considered high but still good for tropical areas.

4.0 Conclusion

Biodiesels from *Gmelina arborea* seed oils were obtained by carrying out transesterification reaction using methanol in presence of a catalyst. Some properties of seed oil and biodiesel were determined. Calculations of four important chemical properties of biodiesel viz. acid value, iodine value, saponification number and cetane index were performed based upon fatty acid profiles of *Gmelina arborea* biodiesel. Acid value obtained from *Gmelina arborea* seed oil was found to be 0.329 mg KOH/g which is within the acceptable limit of equal or less than 0.50 mg KOH/g in both EN14214 and ASTM-D6751 standard fuels. Iodine value of biodiesel from *Gmelina arborea* seed oil was found to be 40.326 g I_2 /100 g oil which is far below the maximum limit of 120 prescribed in EN14214, and saponification number of the biodiesel derived from *Gmelina* was determined to be 92.5 $mgKOH/Kg$. The minimum requirement of cetane number prescribed in biodiesel standards ASTM-D6751 and EN 14214 is 47 and 51 respectively. The cetane index of *Gmelina arborea* biodiesel obtained is 50.5 which is higher than the minimum required value specified in ASTM-D6751, but slightly below the minimum value specified in EN14214. *Gmelina arborea* seed oil may be considered as potential non-edible feedstock for biodiesel production and further research needs to be done.

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