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ORIGINAL RESEARCH ARTICLE

PHYSICO-CHEMICAL PROPERTIES OF YELLOW OLEANDER *(THEVETIA PERUVIANA)* AND THEIR EFFECTS ON THE QUALITIES OF BIODIESEL

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ABSTRACT

This study investigated the effects of physico-chemical properties of Yellow oleander (Thevetia peruviana) on quality of biodiesel. The seeds were processed and extraction of oil was carried out using solvent extraction method. Biodiesel was produced from the extracted oil using trans esterification process. Physical and chemical properties of Thevetia peruviana biodiesel were determined using the ASTM standard test procedures. Results showed that the biodiesel contained little sulphur (3.0 mg/kg) and exhibited a high cetane number of 55 that exceeded the standard limit of 47 and 51 prescribed for EN 14214 and EN 590 respectively, which is a good indication of fuel's ignition and combustion quality. Kinematic viscosity of the biodiesel at 40°C was 4.81 mm^2/s, which was within the range specified by EN 14214. The density at 15°C was found to be 0.89g/cm^3 which was well within the range specified by EN 14214. 0.16 mg/g of acid level was obtained for the bio-diesel, which conformed to the standard set by Calorific value of the biodiesel produced from Yellow oleander seed oil was obtained as 40.42 kJ/g which indicated good fuel properties such as density, ignition quality, viscosity, cetane number, heating value and flash point. Carbon residue of the biodiesel was 0.14 mass %. Quality of the biodiesel produced conform to biodiesel and petroleum diesel standards of EN14214 and EN590 respectively.

1.0 Introduction

Due to rapid population growth and economic development, the worldwide energy demand is constantly increasing. The energy demand is fulfilled mainly from the conventional energy resources like coal, petroleum and natural gas. But, the petroleum reserves concentrated in certain regions of the world are fast depleting day by day and at the current usage rate, these sources will soon be exhausted (Barua et al., 2014; Basumatary, 2013; Khan et al., 2009; Vyas et al., 2010).The search for alternative sources of fuel to supplement or replace fossil fuels so as to cater for their increasing demands, uncertain availability and to reduce the related pollution problems of their combustion, has drawn our attention towards fuels of biological origin (Encinar et al., 1999), which provide regenerable feedstocks. The most common fuel being

developed and used at present is the biodiesel, which is fatty acid methyl esters (FAMEs) of seed oils and fats.

Biodiesel has been chosen as one of the interesting alternative fuels and has been receiving a lot of attention throughout the world as it is a renewable, biodegradable, non-toxic and environment-friendly fuel (Basumatary and Deka, 2012; Basumatary, 2013; Basumatary et al., 2013). Biodiesel, an alternative and renewable fuel for diesel engines, consists of mono-alkyl esters of long chain fatty acids, more commonly methyl esters and is typically made from nontoxic, biological resources such as edible and non-edible vegetable oils, animal fats, waste cooking oils and oil from algae by transesterification with methanol (Basumatary and Deka, 2012; Basumatary, 2013; Basumatary et al., 2013; Takase et al., 2014). Biodiesel produces lower emissions, possesses high flash point, better lubrication and high cetane number and has very close physical and chemical characteristics to those of conventional diesel fuel allowing its use either on its own (pure biodiesel, B100) or mixed with petroleum based diesel fuel (preferred ratio 5– 20%, B5–B20) with very few technical adjustments or no modification (Basumatary, 2013; Basumatary et al., 2014; Biswas et al., 2010; Fazal et al., 2011). A myriad of edible and non-edible oils could be used as bio-diesel feed stocks, but traditionally, biodiesel has been produced from edible oils due to their low free fatty acids. However, their use has elevated some issues such as food versus fuel and many other problems that have negatively affected their economic viability. Therefore, exploration of non-edible oils may significantly reduce the cost of biodiesel especially in poor countries which can barely afford the high cost of edible oils. One of these non-edible feed stocks is Theveta peruviana (yellow oleander) oil (Basumatary, 2013).

Yellow oleander commonly known as milk bush, shown in Figure 1, is an evergreen, dicotyledonous shrub which is believed to have originated from the forest of tropical America, precisely from Central America, but has naturalized in the tropical and subtropical regions of the world ((Olaoye, 2000).)It is abundantly available in Nigeria, where it is mainly grown as an ornamental plant. The seed of the plant contains about 60% oil and the defatted seed cake is about 37% protein (Olaoye, 2000).

Figure 1: Thevetia peruviana fruit

The importance of Thevetia peruviana has revolved around the clinical, toxicological and pharmacological aspects. Probably this is the reason for limited research on oil and protein of Thevetia that would have promoted its industrial and domestic potentials. Though literature is available on Thevetia plant and its soil characteristics (Ibiyemi et al., 2002), a few studies are

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available on its physicochemical properties. Therefore, this study aims at investigating the effect of physical and chemical properties of Thevetia peruviana on quality of biodiesel produced from its oil.

2. Materials and Methods

2.1 Collection and Preparation of Thevetia peruviana Seeds

The ripe and matured Thevetia peruviana was harvested and collected from Thevetia peruviana plants in Iseyin metropolis, Iseyin Local Government Area of Oyo State, Nigeria. The succulent green outermost layer of the fresh fruits was removed manually using a knife to peel off the outer layer from the seed and the seeds separated from the peels manually. The peeled seeds were then decorticated manually using a stone to impact force on the seed in order to open the seed shell and free the seed kernels from its compartments. The mixture of the contents was winnowed to separate the seed kernels from the empty shells. The cleaned seed kernels collected were then sun dried for about 7 days in order to reduce its moisture content to about 10-11% wet basis required for oil bearing seed processing. The dried seed kernels were pound in a mortar and pestle into paste (cake) in order to weaken or rupture the kernel walls to facilitate oil extraction using solvent extraction method. The grind seed kernel paste was then packed in a plastic container for further processing.

For oil extraction, 250 g of Thevetia peruviana paste was placed on the cotton wool inside the thimble and 300 ml of n-Hexane was poured into the round bottom flask and processed. The heating chamber was switched on and set to the predetermined heating temperature and the heating process allowed for the required predetermine heating time. The vapour condensed and accumulated in the thimble and gets siphoned into the distillation flask. After the heating process, the thimble was carefully removed to collect the mixture of both n-Hexane and oil extracted. The mixture collected was then separated using rotary evaporating device. The procedure was repeated up to 14 more times with the same quantities of Thevetia peruviana paste and n-Hexane to obtain enough oil quantity for the biodiesel production. The n-Hexane removed was stored and reused for subsequent extraction operation, while the oil collected was stored for biodiesel production. Oil yield was determined using Equation (1).

$$\%\ \text{Oil yield} = \frac{\text{Weight of oil obtained (g)}}{\text{Weight of sample (g)}} \times 100 \qquad (1)$$

2.2 Conversion of Extracted oil to Biodiesel

Free fatty acid of the oil was firstly determined in order to use the value in biodiesel production using trans-esterification method. Methanol and sodium hydroxide were mixed inside the conical flask at a ratio of 1:10, that is 1% of methoxide to 10% of oil and the sodium hydroxide was allowed to completely dissolve in the methanol and heated to 40oC on the hot plate. One litre of the oil extracted was taken into flat bottom flask and heated to the 50oC temperature on the hot plate. The warmed methoxide was poured into the oil slowly, heated and stirred vigorously using magnetic stirrer for the required time and temperature. The mixture was poured into the container and allowed to cool to 40°C temperature (Canakci and Gerpen, 2001).

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2.3 Biodiesel separation, washing and drying processes

The mixture obtained after the transesterification process was transferred into a separating funnel which was mounted on a retort stand to separate biodiesel from glycerol. The lower layer (glycerol and soap) was collected from the bottom of the separating funnel. After the separation, the mono methyl ester (Biodiesels) separated still contain traces of sodium hydroxide, methanol, and glycerol. This was established by seeing traces of foams and other particles in the biodiesel indicating that it was not 100 % pure. Warm water was then used to wash the biodiesel to remove any excess glycerol and soap that remain in the funnel. This was done by mixing the hot water with the biodiesel several times and then separating the water from the biodiesel until the clear water was seen below the biodiesel in the separating funnel. Then, the biodiesel was dried by placing it on a hot plate where excess water was removed at 110oC. The quantity of biodiesel collected was measured and recorded. The procedures were repeated by varying the required molar ratio of Thevetia peruviana oil to methanol (12:1, 10:1 and 8:1); heating time (55, 60 and 65 minutes) and heating temperatures (55, 60 and 65 °C) (Canakci and Gerpen, 2001).

2.4 Physicochemical Properties of Thevetia peruviana Oil and Biodiesel

The physical and chemical properties of Thevetia peruviana oil and biodiesel were determined using the ASTM standard test procedures. The fuel properties of biodiesel such as Ignition quality, viscosity, Cetane number, heating value, flash point and carbon residue were compared with commercially available diesel. Moisture determination, FFA content, Density, Ignition quality, viscosity, Cetane number, heating value, flash point, carbon residue of biodiesel were determined in the laboratory and compared with both biodiesel and petroleum diesel standards.

2.4.1 Moisture determination of seed kernel

About 2 g of the Thevetia peruviana seed kernel was weighed into a previously weighed crucible. The crucible plus sample was then transferred into oven set at 100°C to dry to a constant weight for 24 hours, the crucible plus sample were removed from the oven and transferred into desiccators to cool for 10 minutes and weighed. The moisture content (d.b.) was evaluated from Equation (2).

$$\% \text{ moisture content (d.b.)} = \frac{W_2 - W_3}{W_3 - W_1} x\ 100 \qquad (2)$$

where:

W_1=Weight of empty crucible, (g)

W_2 =Weight of sample plus crucible before drying, (g)

W_3 =Weight of crucible plus oven dried sample, (g)

2.4.2 Flame test of oil

The nature of the flame of burning oil sample was determined by heating the oil in a stainless saucer, and placing a clean white ceramic plate above the oil sample and the ceramic plate was removed after a period of about 10mins and the presence of soothe was observed using ASTM Standard D93.

2.4.3 pH of the oil

pH of the Thevetia peruviana oil was determined using Soil and Water Analyzer using ASTM Standard D6751.

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2.4.4 Ash content of oil

About 2.0 g of the Thevetia peruviana oil was weighed into a porcelain crucible. It was then transferred into a muffle furnace set at 550ºC and was left 4 hours for it to turn to white ash. The crucible and content were then cooled in the air to about 100°C, then at room temperature in desiccators and was weighed using ASTM Standard D6751.

2.4.5 Density of biodiesel

Density of the biodiesel was determined using a density bottle at 25oC. This was determined by weighing the sample and comparing it with its volume. The ratio of the mass of the fuel to its volume was then determined by Equation (3) using ASTM standard D93.

$$\rho = \frac{M}{V} \quad (3)$$

where:

ρ= Density (kg/m^3)

M = Mass of the sample (kg)

V = Volume of the sample (m^3).

2.4.6 Ignition quality of biodiesel

The Cetane Number (CN) of the fuel is one such important parameter which is responsible for the delay period. Ignition quality tester was used to determine the cetane number using ASTM standard D445.

2.4.7 Viscosity of biodiesel

Sample dispersed with concentration ranging from 0.4 to 2.0% (w/v) are prepared with distilled water at room temperature. The dispersion was hydrated for 2 h at room temperature under continuous stirring (monostir magnetic stirrer). The viscosity of the hydrated dispersion was measured at 25°C using the NV sensor of the Haake – Rotovisco viscometer (Haake – Rotovisco GMBH Germany) using ASTM standard D445.

2.4.8 The congealing temperature of oil sample

The congealing temperature was determined by putting 10ml of the oil sample in a 100ml beaker and inserting a laboratory thermometer into the oil and putting it in a freezer. The oil was closely monitored as the oil sample starts getting jelly, and the temperature at which gelation took place within the oil was also noted.

2.4.9 Flash-point of biodiesel

Flash point measures the lowest temperature at which application of the test flame causes the vapor above the sample to ignite. It is used to assess the overall flammability hazard of a material. Specifically, flash point is used in safety regulations to define "flammable" and "combustible" materials. It can be determined using Pensky-Martens Closed Cup Tester. Higher values indicate materials that are less likely to ignite accidentally. D 975 requires a minimum of 52°C. The biodiesels would be considered significantly safer with temperatures between 128°C and 167°C using ASTM Standard D93.

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2.4.10 Calorific value of biodiesel

The calorific value measures the available energy in a fuel and a critical property of fuel intended for use in weight-limited vehicles. This was determined using bomb calorimeter using ASTM standard D445.

3. Results and Discussion

3.1 Physicochemical Properties of Yellow Oleander Oil and Biodiesel

The analysis of the physicochemical properties of the yellow oleander oil extracted is as presented in Table 1. The table shows that the oil extracted from yellow oleander kernel was found to be suitable for biodiesel production as its free fatty acid value was found to be 1.21 mg KOH/g. Oil yield was found to be 62.44% which is within the range reported for the seed. Iodine value of Thevetia peruviana oil (68.2 g I2 /100 g) was also far below the maximum limit of 120 prescribed in EN 14214. The acid value of Thevetia peruviana was found to be 0.16 mg of KOH/g. pH value was found to be 6.8 neutral which means the oil is save for biodiesel production as stated by Adebayo et al. (2011). The oil was congealed at 4°C and was also frozen.

Table 1: Some physicochemical properties of yellow oleander oil

Properties	Unit	Yellow oleander oil
Free fatty acid	mg KOH/g	1.21
Iodine value	I_2/100g	68.2
Acid value	mg/g	0.16
Moisture content	wt %	1.86
Oil yield	wt %	62.44
Specific gravity		0-89
Congealing temperature	°C	4.0
Freezing temperature	°C	1.0
pH value		6.8

Table 2 shows the analysis of the physicochemical properties of the biodiesel produced from the Thevetia peruviana oil extracted.The biodiesel contain little sulphur and has exhibited a higher cetane number of 55 that exceeds the minimum limits of 47 and 51 prescribed in EN 14214 and EN 590 respectively, which is a good indication of fuel's ignition and combustion quality. The kinematic viscosity of the biodiesel at 40°C was 4.81mm^2/s. This is within the range specified by EN 14214. The density at 15°C was found to be 0.89g/cm^3 which is well within the range specified by EN 14214. It is prescribed in ASTM D6751 and EN 14214 that the maximum limit of acid value for biodiesel should not exceed 0.50 mg of KOH/g. The European standard EN 14213 for use of biodiesel as heating oil prescribes a minimum heat of combustion of 35.0 kJ/g. The calorific value of the biodiesel obtained was 40.42KJ/g.

Biodiesel with petroleum diesel standards from Yellow oleander seed oil was found to be 40.42 kJ/g indicating good fuel properties. The carbon residue of the biodiesel was 0.14 mass%. The results also conform to the one gotten by (Adebayo et al., 2011).

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Table 2: Comparison of Physicochemical Properties of Yellow Oleander

Properties	Unit	Biodiesel standard	Petroleum diesel	Yellow oleander biodiesel
Specification		EN 14214	EN 590	NS
Density 15	°C (g/cm^3)	0.86 - 0.90	0.82 - 0.845	0.89
Viscosity (@ 40°C)	mm^2/s	3.5 - 5.0	2.0 - 4.5	4.81
Flash point	°C	120 min	55 min	142
Sulphur	mg/kg	10 max	350 max	3.0
Carbon residue	% mass	0.3 max	0.3 max	0.14
Cetane number		51 min	51 min	55
Calorific value	kJ/g	35		40.42
Biodiesel yield				83.17

4. Conclusion

This study has shown that biodiesel produced from Thevetia peruviana oil is a potential replacement for fossil diesel while the production and effective usage of biodiesel will help to reduce the cost of protecting the atmosphere from the hazards in using fossil diesel and hence will boost the economy of the country. The quality of the biodiesel produced conformed to standards set for biodiesel standard EN14214 and petroleum diesel standard EN590.

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