



Research Article

## Production of Biodiesel from Yellow Oleander (*Thevetia peruviana* (Pers. K Schum) Seed Oil

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### ABSTRACT

The production of biodiesel from *Thevetia peruviana* seed oil using two different catalysts (NaOH and KOH) was evaluated. The Physical and chemical properties after extracting the seed oil were determined and the following results were obtained (density; 0.896g/cm<sup>3</sup>, pH; 5.6, oil content; 32.5%, moisture content; 1.5%, specific gravity; 1.33, viscosity; 20mm<sup>2</sup>/s, and refractive index; 1.48) and (Acid value; 0.3 mg of KOH/g, free fatty acid; 0.45%, iodine value; 38.5gI/100g, saponification value; was 75mg/KOH) respectively. Different catalysts were prepared by dissolving separately (0.18g, 0.20g and 0.21g) w% of NaOH and another 0.18g, 0.20, 0.21g w% of KOH pellets each in 10ml of methanol to produce concentrations of sodium and potassium methoxide respectively. Furthermore, Yellow Oleander Oil (YOO) was divided into 6 portions (25ml each) and poured into 6 different beakers (100ml) and separately placed on a magnetic stirrer. The amount of biodiesel produced at different concentrations of NaOH catalyst was 20.3ml, 20.1ml, and 22.3ml and the amount of biodiesel produced at different concentration of KOH were 24.2ml, 22.1ml, and 21.0ml. The conversion yield of the biodiesel catalysts was 81.2%, 80.4% and 89% for the NaOH catalyst and 96.8%, 88.4% and 84.0 for the KOH catalyst. The properties of the biodiesel such as flash point were 68°C, pour point was 3°C, cloud point was 7°C, cetane number was 98, the acid value was 0.5mg of KOH/g, density was g/cm<sup>3</sup>, Iodine value was 3gI/100g, saponification value was 104, viscosity was 1.5mm<sup>2</sup>s, the refractive index was 1.49. The results obtained from the study indicate that the physicochemical properties of the synthesized biodiesel are in agreement with the ASTM standard specifications. Both catalysts gave a considerable yield with KOH having a higher yield than NaOH in almost all the concentrations used. *Thevetia peruviana* can be considered a highly promising feedstock for biodiesel production.

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## INTRODUCTION

Currently, most of the world's energy needs are supplied through petroleum, coal and natural gas sources. These sources are finite and non-renewable, and the current usage rates are fast depleting them. In addition, these non-renewable energy sources have several drawbacks such as; increased greenhouse gas emissions, high cost of processing, non-renewability and their production is hugely energy intensive. Consequently, there is a growing demand for alternative sources to petroleum-based fuels (Highina *et al.*, 2011). Alamu *et al.* (2007) have reported that Nigeria currently imports about 80% of its petroleum requirements. Unfortunately, in the Niger Delta region; the centre of oil production in Nigeria, severe environmental impacts has been ignored in the country's haste to develop the oil industry. This has generated hostilities from the local population, making successful oil prospecting very difficult for oil-producing companies in Nigeria. In addition, it has led to an increase in the cost of production of the oil reserves in the region. Biodiesel can facilitate clean air, which is readily usable in existing engines with no or very minor modifications. Biodiesel production is capable of generating employment and income for citizens and the country at large (Patrick *et al.*, 2013). Biodiesel is a diesel fuel derived from plants or animal oils, usually composed of methyl esters of long-chain fatty acids (the detailed chemical composition and the length of the chain of fatty acids in particular depend on the source of the oil). Biofuel is a type of fuel whose energy is derived from biological carbon fixation. Biofuels include fuels derived from biomass conversion, as well as solid biomass, liquid fuels and various biogases (Demirbas, 2009).

The fuel is biodegradable, non-toxic and has low emission profiles as compared to petroleum-based diesel. The use of biodiesel will allow the balance to be sought between agriculture,

economic development, and the environment (Meher *et al.*, 2004). This buttresses the need to exploit alternative renewable forms of energy to increase energy security. An alternative fuel must be technically feasible, economically competitive, environmentally acceptable and readily available. One possible alternative to fossil fuels is the use of oils of plant origin such as vegetable oils and tree-borne oil seeds to synthesize biofuels. Both edible and non-edible vegetable oils such as rice bran oil, coconut oil, *Jatropha curcus* oil, castor oil, cottonseed oil, Mahua, Karanjas well as oils like groundnut oil, palm oil can be used for the preparation of biodiesel (Highina *et al.*, 2011).

*Thevetia peruviana* also known as Be-still Tree, Lucky nut tree, and yellow oleander, is a shrub or small tree which grows to about 1.5 - 2.3 m high. The leaves are spirally arranged, linear and about 13-15 cm in length (Ibiyemi *et al.*, 2002). The flowers are bright yellow and funnel-shaped with 5 spirally twisted petals. The fruits are somewhat globular, slightly fleshy and have a diameter of 4-5 cm. The fruits, which are green in colour, become black on ripening and contain one to four seeds in their kernel. Each fruit contains a nut that is divided longitudinally and transversely. Mature fruits contain about 22-23% kernel and the seeds have 60-65% oil content (Deka and Basumatary, 2011). This plant reproduces by seed. Locally, it is also propagated by cuttings, especially for use as a live hedge. This project seeks to study the production of biodiesel from the transesterification of Yellow Oleander Oil (YOO) using NaOH and KOH as the catalysts. Methanol was used as the solvent in the oil extraction process. The use of edible oil to produce Biodiesel is not feasible in view of a huge gap between demand and supply of such oil and due to the fact that it competes with human for food sources. Therefore, there is a need to explore alternative non-edible food sources for use in the production of biodiesel.

Thus, the objectives of this study were to produce biodiesel from *Thevetia peruviana* seed oil, to determine the physicochemical properties of the seed oil extracted and biodiesel produced, to determine the effect of catalyst (NaOH and KOH) on yield of the biodiesel.

## MATERIALS AND METHODS

### Seeds Collection

*Thevetia peruviana* fruits were collected from mature trees from the University of Maiduguri campus. The seeds were removed from the fruits, sun-dried for 3 weeks, and ground into powder using mortar and pestle. The dried powder was stored prior to analysis. All the laboratory activities were conducted in the Department of Chemical Engineering, University of Maiduguri, Nigeria.

### Extraction of oil

Soxhlet apparatus was used to extract oil, 1000g of the powdered seed sample using n-hexane as solvent at 60°C as described by Akbar *et al.* (2009). After the extraction, the solvent and oil mixture were separated by distillation. The solvent was recovered using a rotary evaporator, leaving the oil behind and the quantity of oil was measured using a measuring cylinder.

### Chemical and Physical Properties of the Oil and the Biodiesel Produced

Standard laboratory tests were carried out to determine the physical properties of the oil and the biodiesel produced from *Thevetia peruviana* seed oil. The percentage of the oil content was calculated using the equation of Linder *et al.* (2009). Moisture content as described by Ranganna (1986). Viscosity (Sanford *et al.*, 2009), density and refractive index using Abbe refractometer (Pomeranze and Meloan, 1987) were also determined.

Chemical properties such as acid value (AV) were determined using (Indian Standard Methods of Sampling and Test Butterfat's, 1995)., free fatty acid (FFA), and Iodine Value (IV) was determined using (Chindo *et al.*, 2010). For the determination of the Saponification

Value (SV), 2g of oil was placed in 250 ml of a round bottom flask and 25 ml of 0.5M ethanolic potassium hydroxide solution was added. A reflux condenser was attached and the flask content was refluxed for 30 minutes in a water bath with continuous swirling until it simmered. The mixture was titrated with 0.5 M hydrochloric acid using the phenolphthalein indicator while still hot. A blank determination was carried out under the same conditions. The saponification value was calculated using this equation.

(Equation 1): Saponification value (S.V.) =  $(B - T) \times 28.05/W$

B = blank titra

T= titra value

W = weight of the oil

### Biodiesel Production by Transesterification

This process involves the preparation of sodium and potassium methoxide using sodium hydroxide (NaOH) and potassium hydroxide (KOH) catalysts for various catalyst concentrations. Different concentrations of sodium and potassium methoxide catalyst were prepared by separately dissolving 1.8 g, 2.0 g, and 2.1 g of NaOH and KOH pellets each in 10 ml of methanol to produce (0.18ml, 0.20 ml and 0.21ml) concentrations of sodium and potassium methoxide, respectively.

Yellow Oleander Oil (YOO) was charged in the reactor pre-heated to a temperature of 130°C, 75ml of the preheated oil was divided into three (3) portions (25ml each) and poured into three 100ml beakers and separately placed on a magnetic stirrer. Prepared potassium methoxide at different concentrations (0.18ml, 0.20ml and 0.21ml) was added to each portion of the oil. The beakers were tightly secured using aluminum foil paper and the magnetic stirrer was switched on, with moderate agitation for 60 minutes. The mixtures were poured from the

beakers into separating funnels separately. The reaction mixture was allowed to stand overnight while phase separation occurred by gravity settling into golden/pale liquid methyl ester, unreacted methanol and the catalysts were at the top, the lower layer comprising of glycerol and other impurities (at the bottom).

The biodiesel was carefully separated by opening the tap of the funnels. Glycerol having a higher density and viscosity drops down and leaves the biodiesel inside the funnel which later was collected by using the tap of the funnel. The same procedure was repeated with sodium methoxide. The biodiesel was washed separately with water, as detailed in Alamu (2007). The conversion of triglycerides to methyl esters was determined through the material balance of the reaction and the percentage yield conversion of the biodiesel was calculated using the following equation:

(Equation 2): % Conversion = actual yield/theoretical yield

### Properties of biodiesel produced from *Thevetia peruviana* seed oil

The properties of biodiesel, such as flash point, cloud point, pour point, and cetane number, were determined using the following methods. Flash point; the oil sample was filled into the test cup and the lid was placed on the cup and set on the stove, making sure it is properly secured. The thermometer was inserted and the heat was applied to the oil sample at the rate of 5-6 °C/min. The light of the flame tester was on and was applied by operating a mechanism in the cover which controls the shutter and the test flame burner so the flame is lowered into the vapour space of the cup and was left for one second. The application of the flame started when the temperature was 28°C until the expected flash point was reached. The same procedure was done for *Thevetia peruviana* seed oil. The pour point of Biodiesel was determined by replacing the fuel sample with the equipment until the whole fuel sample showed no movement (i.e., freeze). The capped test tube was observed in a horizontal position for five seconds. The possible point was determined by (D-2500).

**Table 1:** Physical and chemical properties of *Thevetia peruviana* oil

Properties		Values
Physical	Oil content (%)	32.5
	Moisture content (%)	1.5
	Physical state	Liquid (at 25°C)
	Colour (visual inspection)	Pale yellow
	Refractive index	1.48
	Specific gravity	1.33
	Density (g/cm <sup>3</sup> )	0.896
	Viscosity (mm <sup>2</sup> /s)	20
	pH	5.6
Chemical	FFA (%)	0.45
	Iodine value (gI <sub>2</sub> /100g)	38.5
	Acid Value (mg of KOH/g)	0.3
	Saponification value (mg/KOH)	75

**Table 2:** Amount of Biodiesel Produced using NaOH and KOH Catalysts

Catalyst (%)	Biodiesel (ml)		Yield (%)	
	NaOH	KOH	NaOH	KOH
0.18	20.3	24.2	81.2	96.8
0.2	20.1	22.1	80.4	88.4
0.21	22.3	21.0	89.0	84.0

**Table 3:** Properties of *Thevetia peruviana* oil and its Biodiesel Compared with ASTM Standards for Biodiesel and Diesel fuel limit

Test property	<i>Thevetia peruviana</i>		ASTMD6751	ASTM D975
	oil	Methyl ester	limit Biodiesel	limit Diesel fuel
Flashpoint (°C)	130	68	130	60-80
Pourpoint (°C)	-	3	-15 -10	-35-15
Cloudpoint (°C)	7.5	7	-	9
Cetane number	110	98	48-65.	40-55
Acid value mg of KOH/g	0.3	0.5	0.8 max	-
Density (g/cm <sup>3</sup> )	0.896	0.906	0.860-0.900	-
Iodine value (g I <sub>2</sub> / 100g)	38.5	3	-	-
Saponification	75	104	-	-
Viscosity (mm <sup>2</sup> s)	20	1.5	1.9-6.0	1.9-4.0
Refractive index	1.48	1.49	-	-

## RESULTS AND DISCUSSION

The result of the physicochemical properties of *Thevetia peruviana* seed oil was determined (Table 1). The physical and chemical properties determined include oil moisture content, oil content, refractive index, viscosity, iodine value, saponification value and acid value. The physicochemical characterization of *Thevetia peruviana* oil shows that the oil content of *Thevetia peruviana* seeds is 32.5%, which is lower than that reported by Deka *et al.* (2011) and Yarkasuwa *et al.* (2013) with an oil content of 63% and 67% of *Thevetia peruviana* seed using soxhlet extraction, respectively. The variation in oil content may be due to differences in the variety of plants, collection, ripening stage, and harvesting time of the seed. The oil moisture content was 1.5%, higher than that of Oseni *et al.*, (2012) as 0.09 %, but lower than the value obtained by Yarkasuwa *et al.*

(2013) as 2.2%, a lower moisture content indicates that the seed will have a long shelf life and may reduce the amount of free fatty acid in the biodiesel (Gerpen *et al.*, 2004). The specific gravity of the oil is 1.33, indicating that it is denser than water. It could also be an indication of the purity of the oil and is important in detecting adulterated oil. Viscosity is defined as the resistance of a liquid to flow. High viscosity means high resistance to flow, while low viscosity means low resistance to flow. The viscosity value of *Thevetia peruviana* oil at 40°C was 20mm<sup>2</sup>/s as shown in Table 1. The viscosity of oil plays a vital role in the determination of oil properties especially for an engine to work properly a lower value of viscosity is required since the viscosity of biodiesel must be lower than that of vegetable oil, Yarkasuwa *et al.* (2013) reported a drastic reduction in viscosity (at 40°C) from the crude seed oil of *Thevetia*

*peruviana* (47 mm<sup>2</sup>/s) to the FAEE (5.10 mm<sup>2</sup>/s) and FAME (5.21 mm<sup>2</sup>/s) was observed. Emily (2009) reported that viscosity increased with molecular weight but decreased with increasing unsaturated levels and temperature.

Table 2 shows the effect of catalysts on transesterification of *Thevetia peruviana* seed oil at various concentrations and the percentage yield of the biodiesel. Potassium hydroxide (KOH) produces a better yield of biodiesel than NaOH at a concentration of 0.18 and 0.2. in which KOH yielded 96.8% and 88.4% while NaOH yielded 81.2% and 80.4%, but at a concentration of 0.21 NaOH produces a higher yield of biodiesel (89.2%) compared to biodiesel produced using KOH catalyst (84.0%), Silitonga *et al.* (2014) reported the highest biodiesel yield produced by *Calophyllum inophyllum* 98.53% by using 1 wt% KOH as the catalyst. The results also show that, the amount of biodiesel produced by both catalysts decreases as their concentration increases except for KOH at a concentration of 0.23, the biodiesel yield increases. From the results above, both catalysts gave a considerable yield with KOH having a higher yield than NaOH in almost all the concentrations used, this results deviate from the work of (Boateng *et al.*,2012), who work on biodiesel produced from soya bean oil using NaOH as the catalyst. The higher yield produced by KOH catalyst may be due to the fact that KOH dissolves faster and completely in methanol than NaOH. This result shows that *Thevetia peruviana* seed oil can be harnessed for the commercial production of biodiesel.

Table 3 shows the properties of oil and its biodiesel produced compared with ASTM standard for biodiesel and diesel fuel limit. The physical and chemical properties of the biodiesel determined include kinematic viscosity, flash point, cloud point, pour point, iodine value, cetane value, saponification value and acid value as presented in Table 3, The ignition and combustion quality of biodiesel can be attributed

to its cetane number, where a fuel with high cetane number is considered desirable and this can be attributed to the number of the carbon chain of the diesel. It would be observed from Table 3, that the biodiesel produced has a cetane number of 98 which is higher than the ASTM D6751 minimum limit of 48-65 min; as also observed by Deka and Basutumary (2011). The density of the biodiesel was 0.906g/cm<sup>3</sup>. The density obtained for biodiesel is slightly higher than the ASTM D6751 prescribed standard. These results deviate from the findings of (Deka and Basutumary, 2011; Yunusa *et al.*,2013). The acid value of *Thevetia peruviana* biodiesel was found to be 0.57 mg of KOH / g, which is correlated with the acid value reported by Dekar and Basutumary (2011) and below the ASTM D6751 set maximum limit. The 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. In table 3, *Thevetia peruviana* biodiesel had a cloud point value of +7°C. This amount is slightly higher than that of Neat Biodiesel (-15 to +5°C) as reported by Yunusa *et al.*( 2013). However, the value obtained in this study is within the range recommended for fatty acid methyl esters by the ASTM D6751 standard. The flash point is a measure of residual alcohol in B100 and is a determinant for the classification of flammability. In this study, the biodiesel sample of *Thevetia peruviana* shows a flash point value of 68<sup>0</sup>C, which is within the range of diesel fuel 60-80°C as reported by Gerpen *et al.* (2004), but less than that of biodiesel fuel 130°C as prescribed by the ASTM D6751 standard. The flash point for biodiesel has been set at 93°C (200 °C) minimum; this suggests that biodiesels are not highly flammable, but would require

safety precautions like any fuel during usage, storage, and transportation (Hassan and Sani, 2006).

In Table 3, the saponification value, which is an indication of the average properties of the presence of lower fatty acids (saturated acid), was 104. This value is lower than the value obtained by Yarkasuwa *et al.* (2013), who worked on biodiesel produced from *Thevetia peruviana* oil. However, a high saponification value indicates that oil has normal triglycerides and is a very useful parameter in production industries.

The refractive index of the oil is 1.48, slightly higher than the values obtained by Usman *et al.* (2009), Deka *et al.* (2011), and Ogunneye *et al.* (2014); as 1.44, 1.463 and 1.461 respectively. The refractive index is an indication of the purity level of the oil. Hence, comparing the observed index with that of the standards can be used as an indication of purity as well as identification. It also correlates with the degree of unsaturation and is also an indication of a lower degree of glycosides, which according to Mordechay *et al.* (2006) may be correlated with a higher amount of free sterols.

Density is one of the most important properties of fuels, because injection systems, pumps, and injectors must deliver the amount of fuel precisely adjusted to provide proper combustion; fuel injection pumps the fuel by volume, not by mass, and a denser fuel contains a greater mass in the same volume. Density is a key fuel property that directly affects fuel performance as well as some of the engine properties, such as cetane number, heating value and viscosity of biodiesel. The density of the fuel also affects the quality of atomization and combustion and is dependent on fatty acid composition and purity. The density of the seed oil was found to be  $0.896 \text{ g/cm}^3$ . A lower FFA value (0.45%) of yellow oleander seed oil was observed compared to those reported by Sahoo and Das (2009)

(1.35%) and Oseni *et al.* (2012) (1.96%), this may be due to the nature of the seed used.

The acid value of *Thevetia peruviana* oil was found to be 0.3, the acid value determines the level of free fatty acid, and the low acid value is due to the presence of saturated fatty acid (Manasa, 2005). The iodine value obtained from *Thevetia peruviana* seed oil falls within the range of 50-99 g/100 g for nondrying oil, as reported by Manasa (2005). Oils are classified into drying, semi-drying and non-drying according to their iodine values, since the iodine value of *Thevetia peruviana* seed oil is 38.5gI/100g which is lower than 100 g/ 100, it could only be classified as a non-drying oil. The lower iodine value indicates the presence of more monounsaturated fatty acids than polyunsaturated acids (Eqbal *et al.*, 2011). The iodine value affects the properties of biodiesel by having high oxidative stability, and a higher cetane number but poor low-temperature properties.

## CONCLUSION

This research work revealed the production of biodiesel from *Thevetia peruviana* seed oil by transesterification with methanol using NaOH and KOH as catalysts. The type of catalyst and concentrations used for transesterification of the oil played an important role in the production of biodiesel since biodiesel produced with KOH gives a higher yield (96.8%) at a lowest concentration (0.18) compared to that produced with NaOH (81.2%). Properties such as the kinematic viscosity at 40 °C, density at 25 °C, flash point, pour point, cloud point, acid value and cetane number were investigated and reported. The fuel properties of the biodiesel produced are found to be within the range of ASTM D6751 standards. Therefore, *Thevetia peruviana* seed oil can be a potential feedstock alternative to produce biodiesel.

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