

Production and Characterisation of Biodiesel from *Vitellaria Paradoxa* Seed Oil Using CuO/Kaolin as Catalyst

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ABSTRACT

Biodiesel, a form of diesel fuel is an alternative fuel similar to the conventional diesel (fossil) fuel; it can be produced from vegetable oils, animal fats and oils, tallow and waste cooking oils. In this research work, *Vitellaria paradoxa* seed oil was obtained, and used for the production and partial characterization of biodiesel. The results for the biodiesel produced showed that the biodiesel has a pale yellow colour, percentage yield of 84.37 %, iodine value of 46.95 I₂/100g, peroxide value of 700 meq kg⁻¹, acid value of 13.46 mgKOH/g, FFA value of 15.43 w/w, saponification value of 141.65 mgKOH/g, calcium of 5.5 mg/kg, magnesium of 3 mg/kg, specific gravity of 0.89, sodium of 2.3 mg/kg, potassium of 2.4 mg/kg, and the kinematic viscosity of 4.2 mm²/s respectively. The results for AAS analysis showed that, the concentration of Al, Pb, Cu, Zn, Cr, Mn, Fe, Co, Ni and V are 1.55 ± 0.01 nm, 1.76 ± 0.03 nm, 0.69 ± 0.02 nm, 0.17 ± 0.01 nm, 0.06 ± 0.02 nm, 0.18 ± 0.01 nm, 2.75 ± 0.03 nm, 0.01 ± 0.01 nm, 0.02 ± 0.01 nm and 0.77 ± 0.03 nm respectively. Also, the GCMS and FT-IR results revealed that the major composition of the biodiesel produced are methyl esters, however, these results obtained were consistent with EN and ASTM standards as well as other literatures as compared.

Keywords: Biodiesel, production, characterization, seed oil, GCMS, FT-IR

Introduction

Global energy crisis, constant increase in the prices of petroleum products and its non-renewability, environmental issues arising from oil spillage and noxious gases been emitted into the atmosphere are some of the problems of conventional fossil energy sources (Amish *et al.*, 2009). Hence, the search for alternative sources of new, sustainable and renewable energy such as biomass, solar, hydro, biofuel, hydrogen as in the case of fuel cell powered vehicle, wind and electrical energy has become necessary. Upon all the above mentioned sources, biofuel have shown more prospects, this is

because it is biodegradable, renewable and its sources are infinite and abundant (Demirbas, 2003).

The demand for petroleum products and its derivatives on daily basis is highly on the increase, which is highly related to the increasing human population and the quest for better standard of living. The rise in prices of petroleum fuel and increasing threat to the environment, have stimulated global interest in developing alternative, non-petroleum; renewable fuels that have the potential to solve many of the current social problems and concerns (Demirbas, 2005).

It is of no doubt that most of the activities we do and the needed services that enhance our standard of living are energy dependent, thus their optimal delivery can be achieved through stable and sufficient energy. Acknowledging this fact has made many countries and nations around the globe to start investigating possibilities of using alternative fuels as a replacement or substitute to petroleum and its derivatives (Carrareto *et al.*, 2004). The essential minimum requirement for biofuels to be more sustainable alternative for fossil fuels is that they should be produced from renewable raw materials and that their use has lower negative environmental impact (Carrareto *et al.*, 2004).

Vegetable oil is one of the renewable fuels which have become more attractive recently because of its environmental benefits; vegetable oils are renewable and potentially inexhaustible source of energy with an energetic content close to diesel fuel (Demirbas, 2003). With recent uncertainties concerning petroleum availability and increase in its price, there is renewed interest in vegetable oil fuels for diesel engines (Demirbas, 2003).

Biodiesel, biogas and bioethanol are examples of biofuels (Alenezi *et al.*, 2010). One important feature is that they can be blended at any proportion with any fuel obtained from petroleum whose properties conform to the end use. For example, biodiesel with diesel fuel, bioethanol with gasoline can all be blended (Anandan *et al.*, 2005). Biodiesel is a methyl ester which can be produced from vegetable oil, animal fats etc (Berchmans and Hirata, 2008). Vegetable oil, been one of the sources of biodiesel is abundant in Nigeria this is because most seeds contain vegetable oil which can be used to make biodiesel (Henning, 1996). Worldwide concern and effort have begun in the development of renewable and economically viable alternative fuel sources in order to cut down dependence on fossil fuels as primary source of energy for both domestic and industrial uses, some of these alternative and renewable sources of energy include solar energy, hydroelectric power, fuel cells, wind power and bio-fuels (Bouaide, *et al.*, 2007).

Bio-ethanol and biodiesel are the two well known biofuels derived from agricultural crops and products (Ma, 1999). Although bio-ethanol is made by fermentation, mostly from carbohydrates, biodiesel are fuels that are made of mono-alkyl ester of long chain fatty acids derived from vegetable oils or animal fats (Vincent *et al.*, 2007). Biodiesel is nontoxic, biodegradable, produced from renewable sources and contributes minimal amount of net green house gases, such as CO₂ and NO₂ (Bouaida *et al.*, 2007). Thus biodiesel may be considered as a very good and promising alternative source of energy (Demirbas, 2007).

The current feedstock of biodiesel production is vegetable oil, animal fat and micro algal oil. Vegetable oils currently being used as a sustainable commercial feedstock oils for the production of biodiesel includes sunflower oil (De los Rios, 2011) soya bean oil (Watanabe, 2002, and Du, 2004) cottonseed oil, (Wu, 2007 and Liang *et al.* 2010) rapeseed oil (Kusdiana, 2001) peanut oils, coconut oil, palm-kernel oil (Crabbe, 2001) and fried oil (Demirbas and Kara, 2006). Most of these oils used so far for the production of biodiesel are edible oils, expensive and may thus be counterproductive if used in large scale for the production of biodiesel (Niotou *et al.*, 2008; Yusuf, 2011).

Thus, a dependence on the production of biodiesel from edible oils will result into scarcity of food for man and livestock. Putting this fact into consideration has necessitated the use of non-edible oils from cheap sources such as waste cooking oils. For example, Rhadha and Manikandan (2011) in their research on the production of biofuel from neem oil discovered that the optimum condition to achieve maximum yield of biodiesel was at a temperature of 55°C and a molar ratio of 1:12 of oil to methanol after conducting their experiment at different temperatures and with different molar ratio of oil and methanol. They determined the kinematic viscosity and acid value of the biodiesel and demonstrated that the biodiesel produced reduced smoke and carbon monoxide emissions.

Materials and Methods**Materials****Table 1: List of apparatus used**

S/No	Apparatus	Model	Manufacturer
1	Beakers	Glass	Pyrex glass England
2	Separating funnel	Glass	Pyrex glass England
3	Measuring cylinder	Glass	Pyrex glass England
4	Stirring rod	Glass	Pyrex glass England
5	Retort stand	Metal	Gallanvan company
6	Filter paper	Paper	Whattman, China
7	Conical flask	Glass	Pyrex glass England
8	Weighing balance	PE-200	Ohaus, China
9	Heating mantle	K-300	United Kingdom
10	Water bath	HH-S	China
11	Centrifuge machine	K-3000	China
12	Flame photometer	M-410	Sherwood
13	Viscometer	2020	Cannon Company

Reagents

The reagents that were used for this research were analytically graded and are given in the table 2.

Methods

The processes for biodiesel production are as follows:

Percentage biodiesel yield

Two grams of the catalyst (CuO/Kaolin) was weighed using an electric weighing balance and transferred into a beaker containing 20cm³ of

The apparatus/equipments that were used in this research are listed in table 1.

Table 2: List of Reagents

S/N o	REAGENTS	% PURITY	MANUFACTURER
1	Methanol	99.5	BDH
2	Nitric acid	68.0	BDH
3	Perchlorate acid	72.0	AR
4	Chlorofoam	99.0	BDH
5	Iodine solution	99.5	BDH
6	Potassium iodide	99.5	BDH
7	Starch solution	-	AR
8	Sodium thiosulphate	99.0	BDH
9	Acetic acid	98.0	BDH
10	Sodium hydroxide	99.0	BDH
11	Murexide indicator	-	AR
12	Murexide indicator	99.0	AR
13	Ammonium buffer solution	-	AR
14	Erichrome black T	-	AR
15	Ethanol	99.0	BDH
16	Phenolphthalin	-	AR
17	Potassium hydroxide	85.0	BDH
18	Hydrochloric acid	37.5	BDH

KEY: BDH = British Drug House

AR = Analytical Reagents

methanol. The mixture was stirred in the methanol; it was then poured into 200cm³ preheated shea butter seed oil in a 250cm³ beaker. The mixture was then placed on a digital thermostatic water bath and heated for three hours at 65⁰C with continuous stirring, the mixture was then removed from the digital thermostatic water bath and poured into a separating funnel attached to a retort stand and it was allowed to stand for 24 hours. After 24 hours

the mixture was observed to separate into three layers with the biodiesel at the top, glycerol at the middle and the catalyst at the bottom. The biodiesel was then separated and it was further centrifuged to recover more of the product. The percentage biodiesel yield was calculated using equation (7)

$$\% \text{ Yield} = \frac{\text{Mass of biodiesel}}{\text{Mass of oil}} \times 100 \dots \dots \dots 7$$

Determination of iodine value (IV)

Two grams of the oil was weighed in a conical flask and to it 10cm³ of chloroform and 25cm³ of iodine solution was added and then shaken. Also, blank solution was prepared alongside the sample solution and both solutions were kept in a dark locker for an hour. The solutions were brought out and to the sample solution 10cm³ of 10% KI, 100cm³ of distilled water and starch solution (indicator) were all added and shaken. Finally, both the sample solution and the blank solution were titrated against 0.1M sodium thiosulphate. The iodine value was calculated using equation (8)

$$IV = \frac{126.9 \times M \times (V_2 - V_1)}{\text{Weight of oil}} \dots \dots \dots 8$$

Where: V₂ = Titre value for blank solution

V₁ = Titre value for sample solution

M = Concentration of sodium thiosulphate

Determination of peroxide value (PV)

Two grams of the oil was weighed into a conical flask and to it, 15cm³ of chloroform and acetic acid each were added. This was followed by the addition of 10cm³ of KI, 30cm³ of distilled water and starch indicator were added and shaken. The blank solution was also prepared alongside the sample solution and both were titrated against 0.1M sodium thiosulphate solution. The peroxide value was calculated by equation (9)

$$PV = \frac{(V_2 - V_1)}{\text{Weight of oil}} \dots \dots \dots 9$$

Where: V₂ = Titre value for blank solution

V₁ = Titre value for sample solution

Determination of acid value (AV)

Two grams of the oil was weighed into a conical flask and 50cm³ of ethanol was added, the mixture was heated to homogenize the mixture and then 3 drops of phenolphthalein indicator was added and titrated against 0.1M of KOH, the acid value was calculated by equation (10)

$$AC = \frac{56.1 \times M \times \text{titre value}}{\text{Weight of oil}} \dots \dots \dots 10$$

Where: M = Concentration of KOH used.

Determination of Free Fatty Acid Value (FFAV)

Two grams of the oil was weighed into a conical flask and 50cm³ of ethanol was added, the mixture was heated to homogenize the mixture of the oil and the ethanol. Then, 3 drops of phenolphthalein indicator was added, shaken and titrated against 0.1M of NaOH solution, the free fatty acid value was calculated by equation (11)

$$FFAV = \frac{56.1 \times M \times \text{titre value}}{\text{Weight of oil}} \dots \dots \dots 11$$

Where: M = Concentration of NaOH used.

Determination of Saponification Value (SV)

Two grams of the oil was weighed into a conical flask and 50cm³ of ethanolic potassium hydroxide was added and the mixture was warmed to homogenize the mixture. 3 Drops of phenolphthalein was added and the blank solution was also prepared alongside, both the blank and sample solutions were titrated against 0.5M of HCl, the saponification value was calculated by equation (12)

$$SP = \frac{56.1 \times M \times (V_2 - V_1)}{\text{Weight of oil}} \dots \dots \dots 12$$

Determination of Specific Gravity (SG)

An empty beaker (250cm³) was washed, dried, weighed and tagged (W₀). The biodiesel sample (30cm³) was transferred into the beaker and weighed (W₁). The weight of the oil was determined by subtracting the weight of the initial empty beaker from the weight of the final beaker with oil. The biodiesel was substituted with water after washing and drying the beaker and weighed (W₂). The specific gravity was calculated by the equation (13)

$$SG = \frac{W_1 - W_0}{W_2 - W_0} \dots \dots \dots 13$$

Determination of Calcium (Ca) by EDTA titration

One centimeter cube of the sample was taken into a conical flask and 19cm³ of distilled water was added and shaken, then 1cm³ of 10% NaOH and a tip of murexide indicator was added shaken very well and titrated against 0.01M of EDTA, the value of Ca was calculated by equation (14)

$$Ca (mg/kg) = \frac{\text{titre value} \times M}{\text{Volume of sample}} \dots \dots \dots 14$$

Where: M = Concentration of EDTA used.

Determination of Magnesium (Mg) by EDTA titration.

One centimeter cube of the sample was taken into a conical flask and 19cm³ of distilled water was added and shaken, then 5cm³ of ammonium buffer solution was added and followed by drops of Eriochrome black T solution as an indicator, the whole mixture was shaken very well and titrated against 0.01M of EDTA solution, the value of Mg was calculated by equation (15)

$$Mg \left(\frac{mg}{kg} \right) = \frac{\text{titre value} \times M}{\text{Volume of sample}} \times 100 \dots \dots \dots 15$$

Where: M = Concentration of EDTA used.

Determination of Sodium (Na) and Potassium (K) by flame photometry.

Two gram of the oil was weighed into a crucible and heated on a hot plate until it turned completely into ash, It was then brought down from the hot plate and was allowed to cool to room temperature. Then, 5cm³ of 20% HCl was added to dissolve the ash residue and was made up to 50cm³ with distilled water into a sample bottle. On the other hand serial dilution solutions of both Na and K of different concentrations were also made. These serial dilution solutions and the sample solution were taken to the flame photometer which was first calibrated with distilled water, these solutions were run in the machine and their transmittances were recorded. A graph of concentration against transmittance was plotted, and the transmittance of both Na and K were extrapolated from the graph to find their concentrations. The concentrations of Na and K were calculated from the equation (16)

$$Conc. = X_{ppm} \times D.F \dots \dots \dots 16$$

Where: Xppm = the extrapolated value

$$D.F = \text{dilution factor} = \frac{\text{volume of sample}}{\text{weight of sample}}$$

Determination of Kinematic Viscosity

Fifty centimeter cube of the biodiesel produced was charged into the viscometer via a suction valve in a viscometer bench apparatus, the viscometer was set at a temperature of 35⁰C and the sample was allowed to come through the bath after 15 minutes. Suction force was then applied to the viscometers thinner arm to draw the sample slightly above the upper timing mark. Afflux time of the sample as it flows freely from the upper timing mark to the lower timing mark was recorded, the viscosity of

the biodiesel was then determined via the equation (17) (Benedict *et al.*, 2018).

$$\text{Kinematic viscosity} = \frac{\text{Time of fall} \times \text{Stoke constant} \dots \dots \dots 17}{\dots \dots \dots}$$

Atomic Absorption Spectroscopy Analysis (AAS).

Two gram of the oil was weighed in a crucible and 10cm³ of concentrated nitric acid was added. 2cm³ of concentrated perchlorate acid was also added to the mixture and it was then heated on a hot plate to digest the sample. The mixture was removed from the hot plate after complete digestion and it was allowed to cool to room temperature. The resulting mixture was filtered into a sample bottle using a filter paper and the sample was taken to the Central Advance Laboratory of Usmanu Danfodiyo University, Sokoto for the determination of Al, Pb, Cu, Zn, Cr, Mn, Fe, Co, V and Ni at a wave length of 396.152nm, 405.781nm, 324.754nm, 213.857nm, 425.433nm, 403.076nm, 371.993nm, 340.512nm, 309.311nm and 352.454nm respectively.

Results

The results of some parameters of biodiesel are as follows

Table 3: Some biodiesel parameters as compared to EN and ASTM standards.

S/No	Parameters	Biodiesel	EN	ASTM
1	% Yield	89.4		
2	Iodine value (I ₂ /100g)	46.95	Max. 120	
3	Peroxide value (meq kg ⁻¹)	700		
4	Acid value (mg/KOH/g)	13.46	Max. 050	Max. 050
5	Free fatty acid value	15.43	800	860-900
6	Saponification value (mgKOH/g)	141.65		
7	Calcium (mg/kg)	5.5	5	5

8	Magnesium (mg/kg)	3	5	5
9	Specific gravity	0.89		0.85-0.91
10	Sodium (mg/kg)	2.3	5	5
11	Potassium (mg/kg)	2.4	5	5
12	Kinematic viscosity (mm ² /s)	4.2	3.5-5.0	1.9-6.0
13	Colour	Pale yellow		

Table 4: Concentration of some heavy metals in the biodiesel produced

S/No	Metals	Concentrations (mg/kg)
1	Al	1.55 ± 0.01
2	Pb	1.76 ± 0.03
3	Cu	0.69 ± 0.02
4	Zn	0.17 ± 0.01
5	Cr	0.06 ± 0.02
6	Mn	0.18 ± 0.01
7	Fe	2.75 ± 0.03
8	Co	0.01 ± 0.01
9	Ni	0.02 ± 0.01
10	V	0.77 ± 0.03

Table 5: GCMS Percentage fatty acid methyl esters present in the biodiesel produced.

S/No	Methyl esters	%
1	Hexadecanoic acid methyl ester	1
2	n-Hexadecanoic acid	2.65
3	9, 5-Octadecanoic acid methyl ester	1.34
4	9-Octadecanoic acid methyl ester	10.22
5	Methyl state	12.11
6	Oleic acid	37.23
7	Octadecanoic acid	27.61
8	Olean-12-en-3-ol acetate	2.31
9	13-Hexyloxacyclotridecan-2-one	0.77

10	12-Oleane-3-yl acetate	3.55
11	Lup-20(29)-en-3-ol acetate	0.86
12	Stigmast-7-en-3-ol	0.80

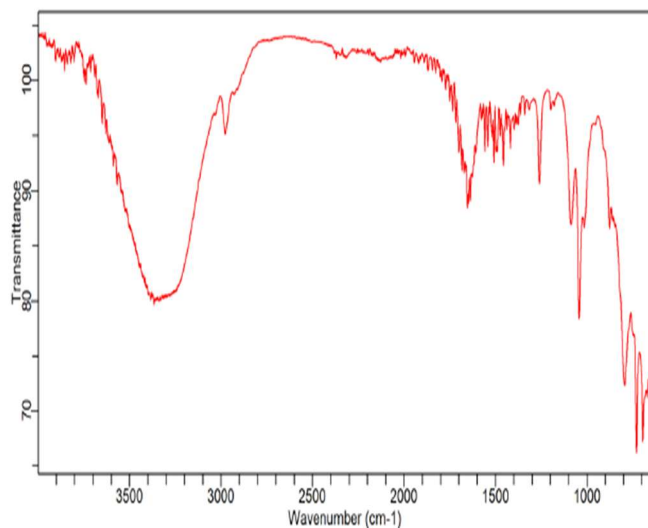


Figure 1: The FT-IR spectrum for the biodiesel produced.

Discussion

The biodiesel (methyl ester) produced was pale yellow in colour and much less viscous than the *Vitellaria paradoxa* seed oil that was used to produce it with a percentage yield of 89.4% which is moderately higher than that of Yelwa *et al.* (2018) 73.5%. This value is considered as reasonable recovery yield, the iodine and peroxide values of the biodiesel produced were found to be 46.95gI₂/100g and 700 meq kg⁻¹ which are lower than 56.49gI₂/100g and 800 as reported by Nurhayati *et al.* (2017).

The acid value of the biodiesel produced was found to be 1.67mgKOHg⁻¹ which is slightly higher than 0.5 mgKOHg⁻¹ max of ASTM D6751 and EN 14214 standard limits respectively, acid value may increase as biodiesel fuel degrades due to contact with air or water which requires treatment that could lower acid content before use (Gerpen *et al.*, 2004). Also the free fatty acid which is influenced by the concentration of the acid value was also

found to be 15.43mgKOHg⁻¹ and the saponification value of the biodiesel was also found to be 141.65mgKOH/g which is consistent with the reports of Gerpen *et al.* (2004).

The sodium and potassium as well as calcium and magnesium concentrations were found to be 2.3mg/kg, 2.4mg/kg, 5.5mg/kg and 3mg/kg respectively. All these values were below the maximum limits (5mg/kg each) set by both ASTM D6751 and EN 14214. The value of the specific gravity of the biodiesel produced was found to be 0.89 which is within the range set by ASTM D6751 (0.85-0.91). The viscosity of the biodiesel produced which is a factor that influences the flow of the biodiesel due to internal friction of one part of the fluid over another as well as the atomization of the fuel upon the combustion chamber was found to be 4.2 mm²/s which is within the standard limits set by both EN 14214 and ASTM D6751 (3.5-5.0 mm²/s and 1.9-6.0 mm²/s) respectively.

The A.A.S. analysis that was carried out on the biodiesel produced to determine the concentrations of different heavy metals which include: Al, Pb, Cu, Zn, Cr, Mn, Fe, Co, Ni and V. It was found that Co has the least concentration (0.01mg/kg±0.01) and Fe has the highest concentration (2.75mg/kg±0.03) which may not be unconnected to the CuO/kaolin, heterogeneous catalyst that was used in the transesterification of the oil (*Vitellaria paradoxa* seed oil) Zuru *et al.* (2013).

Figure 1 is the FT-IR spectrum of the biodiesel produced from *Vitellaria paradoxa* seed oil, the peak at 3500 cm⁻¹ with stretching mode of vibration is ascribed to the presence of O-H groups, they are single bonded and at high energy region in the spectrum (Shiut *et al.* (2010). The peaks at 2850.41 cm⁻¹ and 2924.32 cm⁻¹ indicate symmetric and asymmetric stretching vibrations of C-H alkane groups respectively. They could be methyl (CH₃) or methylene groups in the esters chains of the biodiesel and they require high energy to cause stretching vibrations within their bond when compared to the ordinary C-H bending vibrations of alkene groups detected at low energy and frequency region (Shiut *et al.*, 2010). The characteristic peak

at wave number 1745.89 cm^{-1} which is strongest in the spectrum is attributed to C=O groups with the stretching mode of vibration. These groups indicate the presence of carbonyl functional groups in the biodiesel. The groups indicate the conversion of triglycerides in the oil to methyl esters (John, 2000). The band region of $1376.00 - 1459.40\text{ cm}^{-1}$ can be ascribed to the bending vibration of C-H methyl groups in the fuel, while the band at 1646.42 cm^{-1} is ascribed to C=C bending vibrations in the biodiesel (Shiut *et al.*, 2010). The characteristics peaks found in the region $1036.81 - 1248.60\text{ cm}^{-1}$ indicate stretching vibrations of C-O and C-O-C. They can also indicate the bending vibration of O-CH₃ in the spectrum (John, 2000).

The major composition of the biodiesel produced are esters which is a key factor that determine the suitability or otherwise the potential of a substance to be used as a feedstock for biodiesel production (Zuru *et al.*, 2013)

Conclusion

The biodiesel produced from *Vitellaria paradoxa* seed oil (shea butter) through transesterification reaction using methanol and CuO/kaolin as a heterogeneous catalyst was characterized and found to be within acceptable limits of EN 14214 and ASTM D6751 as well as some literatures, Thus, the percentage yield of the biodiesel was 89.4% which makes *Vitellaria paradoxa* seed oil (shea butter) a potential feedstock for commercial or industrial production of biodiesel.

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