Evaluation of Momordica Balsamina Seed Oil for its Potential as Feedstock for Biodiesel

Production

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Abstract

This paper sought to evaluate the potential of oil obtained from balsam apple (Momordica *balsamina*) for biodiesel production. Oil was extracted from the seed using n-hexane in a soxhlet extractor, then transesterified to biodiesel using single step alkali hydrolysis. The biodiesel so produced was analyzed for their physicochemical and fuel properties using American Standards for Testing and Materials procedures. GC-MS was used to quantify the Fatty acid methyl esters yield. Percentage oil yield was 33.21 ± 0.18 %. The physicochemical properties of the oil showed high acid values (M. balsamina $9.958 \pm 0.5 \text{ mg/KOH/g}$). The percentage oil degumming was 10.12 ± 0.6 %. Some critical fuel parameters for the biodiesel produced from the oil showed compliance with American Standards for Testing and Materials and European standard specifications. The result of biodiesel produced showed; Colour 2.9 \pm 0.0, cetane number 57.699 \pm 0.23, flash point 137 \pm 0.00 °C, cloud point 1.0 \pm 0.00 °C, pour point -0.4 \pm 0.0 °C, sulphur content 0.021 ± 0.01 ppm, kinematic viscosity 3.82 $\pm 0.0 \text{ mm}^2/\text{s}$ and specific gravity $0.8615 \pm 0.0 \text{ g/cm}^3$. The percentage yield of biodiesel was 89.12 ± 0.04 %. Stearic acid methyl ester, a saturated ester, was dominant with percentage of 14.03 % in the biodiesel produced. The yield of the oil is high enough and comparable with other oils that have been used for biodiesel production. It can be inferred that oil from Momordica balsamina is suitable for biodiesel production.

Keywords: *Momordica balsamina*, transesterification, biodiesel, cetane number.

1.0 Introduction

There is a need for alternative energy sources to petroleum based fuels due to the depletion of the world's petroleum reserves, global warming and environmental concern which makes it necessary to develop renewable energy sources of limitless duration and smaller environmental impact than the traditional one. One possible alternative to fossil fuel is the use of fuels or diesel produced from oils of plant origin like vegetable oils and tree - borne seed oils. These have been found suitable for utilization in diesel engines. [1].

Recently, environmentalists have started to debate on the negative impact of biodiesel production from edible oil due to large-scale production of biodiesel from edible oils which may bring global in balance to the food supply and market demand [2]. Non-edible plant oils have been found to be promising crude oils for the production of biodiesel since world annual vegetable oil production is about 0.107 billion tons [3]. Among non-edible oils already used for biodiesel production, castor and pea nut oils is drawing more attention globally. The oils are not fit for nutritional purposes due to its relative effect in humans (Roth and Kormann, 2000). This property is ascribed to the fact that castor oil contains up to 90 % of linoleic acid. Lower-cost feedstock is needed since biodiesel from food-grade oils is not economically competitive with petroleum-based diesel fuel. Hence, in this paper non edible vegetable oil from Momordica balsamina seed oil was assessed as potential alternative fuel for economic development and to solve environment issues. The plant balsam apple Momordica balsamina is a member of Cucurbitaceae family generally grown in the tropical regions of Africa and it is an annual to perennial in nature. It is locally known as balsam apple (English), Garahuni (Hausa), Akbon-ndewe (Igbo) and Ejirin (Yoruba) [4]. When ripe, the fruits (25-60 mm) burst apart automatically into three valves that curl back (also opens when the tip is touched), revealing numerous seeds covered with a brilliant scarlet, extremely

sticky coating. The seeds are embedded into a sweet edible red fleshy pulp test like watermelon [5].

2.0 Materials and Methods

2.1 Sample collection and preparation

Sample (1800g) was collected from the seeds of balsam apple; *M. balsamina* in Kawo Area within Kaduna metropolis Nigeria. The leaves and seeds were identified in the Herbarium section of Biological Science Department, Ahmadu Bello University Zaria with a Voucher numbers 1139 and was kept for future reference. The seeds were peeled to obtain the kernels, which was air dried at room temperature (25 °C) and pulverized using locally constructed pulverizer to a fine powdered form and stored in an air tight plastic containers under room temperature (25 °C).

2.2 Extraction procedure

Two hundred gram (200 g) of air dried and pulverized plant seeds of *M. balsamina* was weighed out and packed into a thimble, which was in turn placed into soxhlet extractor. Extracting solvent n-hexane (500 cm³) and anti - bumping chips were put into a 1000 cm³ round bottomed flask and heated on heating mantle at 60 $^{\circ}$ C. The extraction was allowed to continue for one hour (1hr). The solvent in the round bottomed flask were collected and concentrated in vacuo using a rotatory evaporator at 40 $^{\circ}$ C. The process was repeated to obtain the mean of the percentage extraction and enough oil for further analysis.

% Extraction = <u>Weight of oil extracted</u> $\times 100$

Weight of sample

2.3 **Pre-treatment of the Oil (Acid Degumming)**

Two hundred (200 gram) of *Cucurbita maxima* oil was weighed and heated to 70 $^{\circ}$ C on a heating mantle. 25 % citric acid was prepared by dissolving 250 g citric acid in 1000 cm³ of distil water and was added in the ratio of 3:1 citric acid to oil then mixed for 5 min. This was centrifuge for 30 min for separation of gums and other impurities which settled at the bottom. Oil at the top of the centrifuge test tubes, was decanted and reheated [6]

2.4 Physicochemical Properties of the Seed Oil

2.4.1 Determination of the saponification value

The American Standard for Testing and Material (ASTM) method- (D 5558-95) was used for the determination of the saponification values of the vegetable oil. The oil (5 g) was weighed into Erlenmeyer flask and 0.5 M ethanolic KOH was prepared by dissolving 7 g of KOH in 250 cm³ ethanol and 25 cm³ of the prepared 0.5M ethanolic KOH was added and the resulting mixture was refluxed for 60 minutes. The resulting solution was subsequently titrated against 0.5 M HCl prepared by diluting 10.7 cm³ HCl in 250 cm³ of distil water using phenolphthalein as indicator. The resulting end point was obtained when the pink colour changed into colourless. The same procedure was used for the blank. The Saponification value (SV) was then calculated using the expression;

Saponification value (S.V.) = $\frac{5.61 \text{ (B-S) x M of HCl}}{\text{Weight of sample}}$

(Source: ASTM-D 5558 (95))

Where;

B – Vol. of HCl required by blank
S – Vol. of HCl required by sample
M – Molarity of HCl
5.61– Molar mass of KOH

2.4.2 Determination of acid value

Acid value of the oil was determined by ASTM method (ASTM – D 974(00). The oil (0.5 g) of the oil was weighed into 250 cm³ conical flask and 50ml of neutralized ethyl alcohol was added, prepared by neutralizing a solvent mixture of 25 cm³ ethanol and 25 cm³ diethyl ether with 0.1M ethanolic KOH prepared by dissolving 1.4 g KOH in 250 cm³ of ethanol using phenolphthalein as indicator. The mixture was added to the oil and heated on a water bath to dissolve the oil. The solution was then titrated against 0.1 M KOH prepared by dissolving 1.4 g of KOH in 250 cm³ of the free fatty acid was calculated respectively as follows;

Acid Value = $\underline{A \times M \times 56.10}$ W (Source: ASTM-D 974 (00)) Where, A = ml of 0.1M KOH consumed by sample M = Molarity of KOH W = weight in grams of the sampleThen, Free fatty acid = <u>Acid Value</u>

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2.4.3 Determination of iodine value

The oil (0.5 g) was weighed into conical flask and 20 cm³ of carbon tetrachloride was added to dissolve the oil. 25 cm³ of Wijs reagent was added into the flask using a measuring cylinder in a fume chamber and a stopper was inserted, the content of the flask was vigorously swirled and kept in the dark for 35 minutes. 20 cm³ of 10 % aqueous potassium iodide prepared by diluting 10 cm³ of potassium iodide in 90 cm³ of distill water was added into the content of the flask using a measuring cylinder. The content was titrated with 0.1M sodium thiosulphate solution prepared by dissolving 3.95 g of anhydrous Na₂S₂O₃ in 250 cm³ of distill water. Few drops of 1 % starch indicator were added and the titration continued by adding the sodium thiosulphate drop wise until coloration disappeared after vigorously shaking. The same procedure was used for the blank test. The Iodine Value (I.V) is given by the expression;

Iddine Value (I.V) = $126.9C (V_1 - V_2)$

Where,

C = concentration of sodium thiosulphate V_1 = volume of sodium thiosulphate used for blank V_2 = volume of sodium thiosulphate used M = mass of sample 12.69= Constant.

2.4.4 Determination of refractive index

Abbey refractometer was used in this determination. A drop of the sample was transferred into a glass slide of the refractometer. Water at 30 °C was circulated round the glass slide to keep its temperature uniform. Through the eye piece of the refractometer, the dark portion viewed was adjusted to be in line with the intersection of the cross. At no parallax error, the pointer on the scale pointed to the refractive index. This was repeated and the mean value noted and recorded as the refractive index.

2.5 Transesterification

A modified method of biodiesel reaction was employed in terms of timing, catalyst, temperature, methanol to oil ratio and a biodiesel reactor, which differs from the convectional biodiesel method by [24]. 100 g of the pretreated oil was heated to 60 0C and transferred into the jurk of a master chep blender. 20 g methanol containing potassium hydroxide 1 % w/w (1g) of oil to form potassium methoxide was added. The stirring speed was kept constant at 10000 rpm using a time interval of 2, 4 and 6 mins to avoid over heating the blender. 16 g potassium methoxide solution was initially added representing 80 % and stirred for 4 min and the remaining 4 g was added at the 4 th min representing 20 % to complete the 6 th min, because the reaction was very slow at the beginning due to mixing and dispersion of alcohol into the feedstock.

2.6.0 Determination of Fuel Properties of Biodiesel

2.6.1 Determination of pour point

The pour point was determined by ASTM method (ASTM D - 97). The oil sample was poured into the test jar to the level mark. The test jar was closed with the cork carrying the high – pour thermometer. The position of the cork and the thermometer were adjusted for the cork to fit tightly, the thermometer and the jar were coaxial and the thermometer bulb was immersed 3mm

below the surface of the sample. After this, the test jar was placed into the cooling medium. The sample was cooled at a specified rate and examined at interval of 3 °C for flow characteristics until a point was reached at which the sample showed no movement when the test jar was held in a horizontal position for 5 seconds. The observed reading of the thermometer was recorded. 3 °C was added to the recorded temperature and the result was recorded as the pour point

2.6.2 Determination of kinematic viscosity

The temperature of the viscometer bath was adjusted to 38.9 °C. A calibrated thermometer was held in upright position and inserted into the bath by a holder. A clean dry calibrated viscometer was selected and carefully flushed with a dry nitrogen gas to remove the moist room air. A sample of the biodiesel was drawn up into the working capillary of the viscometer and the timing bulb was then allowed to drain back as an additional safeguard against moisture condensing or freezing on the walls. The charged viscometer was inserted into the bath at a depth such that at no time during the measurement of the flow time was any portion of the sample in the viscometer less than 20 mm below the surface of the bath. The viscometer together with its content was allowed to remain in the bath for 30minutes to reach the test temperature (38.9 °C). A suction bulb was used to adjust the head level of the biodiesel to a position in the capillary arm of the viscometer about 7 mm above the first timing mark. The biodiesel was then allowed to freely flow and the time required for the meniscus to pass from the first to the second timing marks was noted with a stop watch. The procedure was repeated to make a second measurement of flow time and the average of these determinations was used to calculate the kinematic viscosity. The viscometer was thoroughly cleaned with sample solvent

and dried by vacuum. The procedure was repeated for the other samples of the biodiesel (ASTM D 445-97)

Calculation:

v = C x t
Where,
v = kinematic viscosity, mm²/s
C = calibration constant of the viscosity, (mm²/s)/s
t = mean flow time

2.6.3 Determination of Cloud point

The cloud point was determined using ASTM D2500. A cylindrical test tube was filled with the biodiesel to a specific level (5 cm³) and clamped with a wooden clamp bearing thermometer. The test tube was placed on the ice/salt bathe and the set up inspected at intervals for cloud formation. The temperature at which a distinct cloudiness appeared at the bottom of the test tube was observed and recorded as the cloud point of the biodiesel.

2.6.4 Determination of Flash point

The flash point was determined using ASTM D93. Seta MultiflashPensky-Martens Flash Point Module Part Number 34100-2 was used to determine the flash point. The automatic PMCC module conforms precisely to national and international Pensky-Martens Closed Cup flash point test methods. It comprises a heated cup and lid, and a DIPS pod containing the dipping mechanism, gas and electric ignitors, fire detection system and a stirrer. The Pensky- Martens module was used with the Multiflash Universal Base unit (p/n 34000-0). The base unit recognises the Pensky-Martens module is connected and instantaneously sets up standard test parameters and calibration data

2.6.5 Determination of Cetane number

The cetane number was determined based on the formula proposed by Demirbas 2009 as there was no enough biodiesel to carry out the test. The formula is given below.

$$CN = \frac{46.3 + 5458}{S.V - 0.225 \times I.V}$$

Where,

S.V = Saponification of the biodiesel

I.V = Iodine Value of biodiesel

2.6.6 Determination of Specific gravity

Specific gravity bottle was washed, rinsed with acetone and dried at room temperature in a dessicator and the weight of the empty bottle determined using an electronic weighing balance. The weight of the bottle filled with water was recorded. The same procedure was repeated with the oil and the specific gravity computed as follows;

Specific gravity = W2 - W1

$$W3 - W1$$

Where,

W1 = weight of empty bottle

W2 = eight of bottle + oil

W3 = weight of bottle + water

2.7.0 GC- MS Analysis of the Biodiesel Produced

GC-MS analyses were carried out at the National Institute of Chemical Technology (NARICT) in Basawa Zaria Kaduna state Nigeria. The Biodiesel was analyzed using GCMs model QP2010 plus Shimadzu equipped with detector and slit injection system the initial temperature was maintained at 60°C for 3 minutes and was gradually increased to 250oC. 1.6ul of solution was injected for analysis and the sample injection temperature was maintained at 250°C throughout the experimental period the carrier gas Helium flow, was 2ml per minute.

3.0 RESULTS

Table 1: Physicochemical properties of the seed oils

Oil property	Unit	M. balsamina	
		(Balsam Apple)	
010 + +	0/	22.21 + 0.190/	
Oil Content	%	$33.21 \pm 0.18\%$	

Saponification Value	mgKOH/g	207.57 ± 0.02
Iodine Value	$gI_2/100g$	171.31 ± 059
Peroxide value	Meq/kg	1 ± 0.2
Acid value	mgKOH/g	9.958 ± 0.5
Relative density	Dimensionless	0.874 ± 0.0
Refractive index	Dimensionless	1.481 ± 0.0
Free fatty acid	Percentage	4.979 ± 0.6
Unsaponifiable value	mgKOH/g	2.98 ± 0.0
Gums	%	$10.12 \pm 0.6\%$

Table 2: Result of GC-MS for Biodiesel Produced from Balsam Apple (BOME)

Fatty Acid	<mark>Carbon Number</mark>	<mark>Molecular</mark> Formular	% Composition
Azelaic Acid	C10:2	$C_{11}H_{20}O_2$	0.72

Linoleic Acid	C18:2	$C_{19}H_{34}O_2$	11.48
Palmitic Acid	C16:0	$C_{17}H_{34}O_2$	7.94
Stearic Acid	C18:0	$C_{19}H_{38}O_2$	14.03
Alaidic Acid	C18:1	$C_{19}H_{36}O_2$	8.43
Cerotic Acid	C26:1	$C_{27}H_{54}O_2$	10.18
Behenic Acid	C22:0	$C_{23}H_{46}O_2$	10.18
Eicosanoic Acid	C20:1	$C_{21}H_{42}O_2$	4.68
Eicosatrienoic Acid	C20:2	$C_{21}H_{54}O_2$	8.09
Linolenic Acid	C18:2	$C_{19}H_{32}O_2$	9.67
Non-methyl esters			14.6
Total			

Table 3: Fuel Properties of Biodiesel Produced from Balsam Apple (Mean \pm SD)

Fuel parameter	BOMEs	ASTM Limits	European Standard
(%)Yield of Biodiesel	89.12 ± 0.06	-	-

Colour	2.9 ± 0.0	3.5	-
Specific gravity g/cm ³	0.8615 ± 0.0	-	-
Kinematic viscosity (mm ² /s)	3.82 ± 0.0	6.0 Max	3.5-5.0
Pour point (°C)	-0.4 ± 0.0	NS	NS
Cloud Point (°C)	1.0 ± 0.0	NS	NS
Flash point (°C)	137 ± 0.0	130 min	<120
Sulphur content (ppm)	0.021 ± 0.01	0.050	-
Cetane number	57.699 ± 0.23	Min47	-

NS = Not specified BOME = Balsam Oil Methyl Ester

4.0 Discussions

The results of the physical and chemical properties of *Momordica balsamina* oil seed studied is presented in Table 1. The percentage oil content of *Momordica balsamina* is 33.21 ± 0.18 %. According to Food and Agricultural Organization (FAO) as reported by

[7], any seed containing greater than 17 % of oil is considered to be an oil seed and can be utilsed as feedstock for biodiesel production, as such *M*omordica *balsamina* seeds are good feedstock for biodiesel.

The relative density of the *Momordica balsamina* oil was found to be 0.874 ± 0.0 , which is higher than the relative density of Africa star apple seed oil 0.711 [8] and Horse eye seed oil 0.847 [9]. The higher relative density observed in the *Momordica balsamina* seed oil when compared with other literatures is due to the fatty acid composition, minor components and temperature. Since the relative density of seed/vegetable oils are dependent on this factors as reported by [10]. This in turn will affect the viscosity of the *Momordica balsamina* seed oil resulting in poor atomization of the biodiesel produced from the seed oil in the engine performance.

The refractive index of the oil is 1.473 ± 0.0 . This value is lower than that of beniseed oil (1.474) [11]. The refractive index of an oil is the ratio of speed of light at a defined wavelength to its speed in the oil/fat itself [12]. The difference in the refractive index of the *M. balsamina* oil compared with similar seed oils reported in literature is due to the variation in wavelength and temperature, degree of unsaturation and substitutions of component fatty acids.

The acid value of *Momordica balsamina* was found to be 9.958 ± 0.5 mgKOH/g. The acid value of oil was higher in comparison to the acid value of Egusi seed oil (4.0 mgKOH/g) [13] and rubber seed oil (8.17 mgKOH/g) [14]. These indicate that the oil

will be unstable over a long period of time and will not be protected against rancidity and peroxidation. This could be attributed to lack of natural antioxidants in the seeds such as vitamins C and A as well as other possible phytochemicals like flavonoids [12]. The lower the acid value, the lower the free fatty acid, the more suitable, the oil for transesterification process.

The saponification value for was found to be 210.38 ± 0.02 mgKOH/g, which is lower when compared with *cocos nucifera* or coconut oil 246 mgKOH/g [14]. However biodiesel derived from oil with high saponification value causes exhaust emissions during burning in the engine [15].

The iodine value was found to be 182.74 ± 0.4 gI₂/100g, which is higher than the iodine value of refined 87.72 gI₂/100g and unrefined castor oil 84.8 gI₂/100g [11]. This indicates that the oil studied is suitable for biodiesel production since low iodine value of vegetable oil produces biodiesel with high cloud and pour points; higher cloud and pour points means poor engine performance in cold temperatures [13].

The viscosity for the oil was found to be $25.0 \pm 0.0 \text{ mm}^2$ /sec, which is lower compared to the viscosity of *Cucurbita pepo* oil 93.65 mm²/sec [16] and *black benised* seed oil 33.2 mm²/sec [17]. According to [18] viscosity increases with molecular weight, as such *Momordica balsamina* is having high molecular weight, which in turn will affect injection lubrication, increase engine deposits and fuel atomization [19]

The peroxide value of *Momordica balsamina* was 1 ± 0.2 Meq/kg and is considered lower compared with Melon seed oil 5.63 Meq/kg [20] but higher than groundnut seed oil 0.74 Meq/kg that have been used in biodiesel productions [21]. The peroxide value of *Momordica balsamina* indicates that *Momordica balsamina* will have less level of deterioration when attacked or exposed to oxygen, since peroxide value indicates the level at which deterioration will take place as a result of oxidation owing to the availability of oxygen during storage [22].

The unsaponifiable value for *Momordica balsamina* was found to be 3.20 ± 0.4 mgKOH/g, which is higher compared to African pear seed oil 2.62 mgKOH/g and Soy bean seed oil 0.837 mgKOH/g [23]. The high level of the unsaponifiable matter in the oils indicates the presence of good lubricating properties [24].

The percentage degumming after centrifugation of *Momordica balsamina* was 10.12 ± 0.6 %. This is above the percentage degumming of crude Canola oil 4.50 ± 0.0 % and crude Sunflower oil 3.20 ± 0.0 % [4]. The value indicates that there is high level removal of hydratable and non-hydratable phosphatides, and other impurities especially metals contamination (P and Ca specifically) and also improvement in the yield of biodiesel production [25].

4.3 Fatty acid methyl esters

The result of fatty acids methyl esters in Balsam Oil Methyl Esters (BOMEs) biodiesel shown in Table 2 indicate that stearic acid methyl esters been the dominant ester will help

in enhancing the stability of the biodiesel, it is a saturated compound and less susceptibility to peroxidation [26]. It is also observed that balsam oil methyl ester is having more long chain of acid methyl esters, as such the long chain of balsam oil methyl ester will have effect on the fuel properties of the biodiesel produced [27].

4.4 Fuel properties

The fuel properties of Balsam Oil Methyl Esters (BOMEs) produced is shown in Table 3. The percentage yield was recorded to be $89.12 \pm 0.06\%$, which is higher than the percentage yield of biodiesel produced from the oil seeds of *Gul Mohr* 87% [19]. The kinematic viscosity of the fatty acid methyl esters corresponded to biodiesel specification for both ASTM and European Standard limits, which indicate the presence of short chain unsaturated methyl fatty acid esters and is likely to produce less deposit when burnt in combustion engines [26].

The flash point of Balsam Oil Methyl Esters (BOMEs) conforms to the ASTM and (EN 2003) for biodiesel limit. This shows that the biodiesel produced has fewer tendencies to ignite accidentally, since flashpoint is the lowest fuel temperature at which application of ignition source causes the vapor of the fuel sample to ignite under the prescribed test conditions and also a parameter used to assess the overall flammability hazard of fuel [28].

The cetane number of the Balsam Oil Methyl Esters (BOMEs) was found to correspond to the biodiesel specification for ASTM Standard limits. The higher the cetane number the better it is in its ignition properties. Biodiesel has higher cetane number than conventional diesel fuel, which results in higher combustion efficiency [29].

The pour point of the Balsam Oil Methyl Esters (BOMEs) was found to be -0.3°C. There is no standard specification for pour point due to variation in atmospheric condition. The cloud point of Balsam Oil Methyl Esters (BOMEs) was found to be 1.1°C. Cloud point test characterizes the low temperature operability of diesel fuel. There is no standard specification for cloud point due to variation in atmospheric condition.

The specific gravity of Balsam Oil Methyl Esters (BOMEs) was found to be 0.8713 g/cm³ this is lower than the specific gravity of biodiesel produced from *Lagenaria Vulgaris* with specific gravity of 0.8879g/cm³ [26]. This indicates that the biodiesel produced can be handled and stored safely. It is an important physical property in handling and storing of fuels [22].

The sulphur content of Balsam Oil Methyl Esters (BOMEs) was 0.032ppm, and was found to correspond to the biodiesel specification for ASTM Standard limit of 0.050ppm.This indicates that the biodiesel produced could emit less SOx upon combustion [19].

5.0 Conclusion

The oil content of the plant seed shows economic viability of feedstock for biodiesel production and the physicochemical properties of the oil is promising with the exception

of saponification and free fatty acid values which were above their limits for biodiesel production. The percentage of biodiesel production from the oil was high with more long chain methyl esters.

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