



Transesterified *Citrullus lanatus* (watermelon) Seeds oil as Biodiesel: Preparation and Characterization

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Abstract

This work studied the two-step method for the production, characterization and determination of alkyl ester composition of Citrullus lanatus seed oil. The seed contained 44.5–46% crude lipid. The oil contained high amount of free fatty (FFA's) acids (9.14%) with (18.28 mgKOHg⁻¹) acid number. The high FFA's content of the oil necessitates pretreatment (esterification, using H₂SO₄ catalyst) before alkali catalyzed transesterification using sodium hydroxide. The methyl esters produced were analyzed for physicochemical and fuel property tests. Fatty acid methyl ester composition were determined using GC—MS. Some important fuel parameters which include; viscosity, cloud point, flash point, diesel index, acid number and glycerol level determined; fall within the acceptable limits of ASTM standard specifications. The most abundant fatty acid in watermelon seed oil is linoleic (46.32%), then oleic (16.58%), palmitic (10.75%) and stearic (7.95%) acids. The results indicates that, citrullus lanatus seed oil possess qualities that qualifies it for use as biodiesel feedstock.

Keywords: *Two-step method; Citrullus lanatus oi; saturation/unsaturation levels; esterification; acid number.*

1.0 INTRODUCTION

Energy is an essential driving force towards socio-economic development of a society. Its impact touches every aspect of human endeavors such as health, transportation, agriculture and many more. Fossil fuels are the major source of energy today in most parts of the world. Its combustion generates emissions which are hazardous to the environment and adversely affect human health as reported elsewhere (Sokoto *et al.*, 2013). Due to gradual depletion of world petroleum reserves and its negative impact on the environment, there is a need for suitable alternative fuels for use in diesel engines

(Nag and Bhattacharyya, 1995). In view of the foregoing problems, vegetable oil becomes a promising alternative to petroleum-derived fuels because it is renewable, biodegradable, environment friendly and can be produced easily in rural areas where modern forms of energy are required (Padhi & Singh 2007, Farag *et al.*, 2013). In recent years, researchers have made effort to use vegetable oils directly as fuel in engines; but it turned out that, various problems were associated with the use of straight vegetable oils as fuel. These problems ranged from injector coking, ring sticking, high viscosity and thickening of the engine lubricant

(Sinha and Misra 1997, Masjuki, 1993). The aforementioned experiences led to the use of modified vegetable oil as an engine fuel. Vegetable oil can be converted into a diesel-like fuel in various ways which include; oil blends, pyrolysis, micro-emulsification etc. However, transesterification process was found to be the most viable oil modification process (Altin *et al.*, 2001). Transesterification (alcoholises) is the reaction of a fat or oil with an alcohol to form esters and glycerol. A catalyst is usually used to improve the reaction rate and yield. Excess alcohol is used to shift the equilibrium to the products side. Alcohols used in the transesterification process, are methanol, ethanol, propanol, butanol and amyl alcohol. Methanol and ethanol are mostly used. Methanol appears to be a good candidate due to its low cost, physical and chemical properties such as polarity, and shortest chain (Gerpen *et al.*, 2005). Biodiesel, is defined as monoalkyl esters of fatty acids derived from vegetable oil or animal fat via transesterification process. It exhibits a number of

promising qualities which includes, reduction of exhaust emissions. This transesterified and renewable fuel (Biodiesel) have proven to be a viable alternative to diesel fuel (Sharma & Singh, 2008). Watermelon species are wild weeds in some areas and domesticated in other places. The plant species contained seeds embedded within their fruits that have no established application within the locals but dumped as refuse. The seeds are thrown or dumped as garbage to decay. Decomposition of the seeds produced gases that are unpleasant to the immediate environment. Consequently, *Citrullus* seeds are assessed for use as bio-fuel source so as to convert waste to use and generate alternative route to energy supply.

In this study, *Citrullus lanatus* (watermelon) is a member of *cucurbitacea* family whose seed oil and alkyl esters have been investigated for use as biodiesel. Additionally, the qualities of oil and methyl esters prepared from *Citrullus lanatus* were examined.

2.0 MATERIALS AND METHODS

The seeds of *Citrullus lanatus* (watermelon) were purchased from custom market in Maiduguri town of Borno State, Nigeria. They were identified at the Herbarium of the Department of Botany, Usmanu Danfodiyo University; Sokoto. The sample seeds were dried and crushed to powder using pre-washed and dried metallic mortar and pestle. Oil was extracted from the powdered sample seeds using Soxhlet extractor with n-Hexane as solvent. The oil extracted was conserved in a dry glass bottle and kept for analysis.

2.1 Analysis of *Citrullus Lanatus* Oil (CLO)

The extracted crude seed oil was analyzed for the following properties: percentage yield, acid number, viscosity @40°C, ash content, saponification and Iodine values in accordance with the AOCS (1997) methods.

2.2 Chemicals and Reagents

Chemicals and reagents of analytical grade used in this analysis were obtained from Sokoto Energy Research Centre Laboratory, Usmanu Danfodiyo University Sokoto; (Nigeria). These chemicals include, Sodium hydroxide (NaOH) pellets,

methanol (CH₃OH), Sodium Sulphate (Na₂SO₄) crystals, Silica gel and Sulfuric acid (H₂SO₄). Other materials used included, Seed oil, filter paper and aluminum foil.

2.3 Biodiesel Preparation

Two-step method was employed for synthesis of biodiesel from *Citrullus lanatus* oil (CLO). The optimal conversion of CLO with high free fatty acid content needs pretreatment reaction (esterification) which was performed using H₂SO₄ as catalyst (2%) with methanol (methanol:oil 6.5:1) for 60minutes at 50°C. Then sodium hydroxide catalyst was employed for the transesterification process. Methanol to CLO molar ratio of 4:1 methylation process was carried out by dissolving 1.74g of NaOH (to neutralize the H₂SO₄) in 60cm³ of methanol. This was mixed with the esterified CLO in a 500cm³ round bottom flask stoppered with a cork. The mixture was stirred for 5 minutes, then heated on a water bath at 55°C for 45minutes and transferred into a separating funnel, then allowed to separate under gravity overnight. Two distinct layers were observed, with the lower layer decanted; the upper layer was further heated to remove residual methanol and then neutralized with dilute sulfuric acid. The biodiesel obtained was washed several

times using hot distilled water to remove all the acid used. The resultant alkyl esters were dried using heated silica gel and anhydrous sodium sulphate. The percentage yield of methyl esters were estimated using equation 1 below:

$$\text{Yield of alkyl esters(\%)} = \frac{\text{grams of the alkyl esters}}{\text{grams of the oil used in reaction}} \times 100 \dots\dots\dots 1$$

2.4 Determination of Fuel Properties of CLO

Alkyl esters: The fuel properties of biodiesels produced were determined according to ASTM (1985 and 1999) and European Organization (EN14214) Standard methods. The fuel properties determined include kinematic viscosity, cloud point, flash point, sulphur content, acid value, aniline point, diesel index and free glycerin level which were determined in accordance with ASTM D 445, ASTM D 2500, ASTM D 93, ASTM D 2622, ASTM D 664, ASTM D 97, and ASTM D 6584 respectively.

2.5 Analysis of produced methyl esters using GC-MS

MS: Analysis of alkyl esters composition of *Citrullus lanatus* were accomplished using 6890N series model, AGILENT GC-MS machine. One microliter of alkyl ester sample was introduced into the gas chromatograph using a micro syringe at injector

temperature of 250 °C. The column temperature was programmed from 120 °C to 250 °C at a linear flow rate of 5 °C/min, hold 5 min at 260 °C. The chromatographs obtained were scanned and the biodiesels components were identified based on software matching with mass spectra.

3.0 RESULTS AND DISCUSSION

The crude CLO contained 9.14% free fatty acid (FFA) which is higher than limit suitable for alkali-catalyzed transesterification (Freedman *et al.*, 1986). Hence, two-step method was employed for biodiesel production. Table 1, shows how acid value of CLO varies with time. The amount depicts values before addition of H₂SO₄ (catalyst) for esterification and after esterification.

Oil content of a particular seed is an important qualifying factor for its use as feedstock for biodiesel production especially for the plant seeds under investigation. The results presented in Table 2 showed *Citrullus lanatus* seeds to have oil content of 44.50 ± 0.25%. The oil yield is higher than 36.7± 0.15% for *Lagenaria vulgaris* seeds as reported (Sokoto *et al.*, 2013) and 39.22% reported for bottle gourd seeds (Hassan and San, 2010). However, oil yield of 48.0% was recently reported for *Citrullus l.* seeds elsewhere (Ogunwole, 2015).

Table 1: Acid number change of CLO during Esterification Reaction.

Reaction time (mins)	Acid number (mgKOHg ⁻¹)
0	9.14
5	23.6
30	19.4
60	15.6
120	13.8
240	13.8
300	13.8

The oil content of this plant seed is appreciably high compared to other seeds in use for biodiesel production. Therefore, *Citrullus lanatus* seeds could find application if adapted as source of oil for alkyl

ester production. The oil produced was analyzed for various quality parameters before conducting the transesterification reaction. The quality parameters tested are shown in Table 2.

Table 2: Analysis of quality of extracted *Citrullus lanatus* oil

Parameter	Yield
Crude lipid (%)	44.50±0.25
Viscosity@40 °C (cSt)	26.41±1.15
FFA (%)	9.14±0.00
Ash content (%)	0.48±0.05
SV(mgKOHg ⁻¹)	201.61±1.81
Iodine value (gI ₂ /100g)	98.52±6.86

Values are mean ± SD triplicate analysis of samples, SV=Saponification value, Free Fatty Acid Content.

Free fatty acid level of vegetable oils is a guiding factor that affects the optimum conversion of the oil to its alkyl esters and dictates the choice of catalyst for transesterification reaction (Sokoto *et al.*, 2013 and Deshmukh and Bhuyar, 2009). Table 2 showed FFA value of 9.0 ± 0.14 (%) for *Citrullus l.* oil. This value is high and far above the $>3\%$ regarded as minimum for clean raw oil. As reported elsewhere (Deshmukh and Bhuyar, 2009), the oil could not be transesterified via alkali single step transesterification as the acid present would render the alkali-catalysts to catalyze saponification reaction. Thus, two-step method of transesterification was employed in this study. Iodine value of oil is indicative of its chemical stability. The result in Table 2 shows the Iodine value of CLO. It suggests that, alkyl esters derived from the oil would be moderately stable going by

the iodine value recorded. However, its methyl esters may likely undergo oxidation on exposure to excess air or long storage time. The value obtained in this study is below what was reported for melon seed oil ($121.65 \text{ gI}_2/100\text{g}$) by Ogunwa *et al.*, 2015.

One of the purposes of transesterification reaction on oils was to reduce viscosity in order to achieve a property that makes the oil more suitable for use as fuel. The standard value of viscosity for biodiesel as specified by ASTM D6751 is $1.9\text{--}6.0 \text{ cSt @ } 40^\circ\text{C}$. The viscosity of transesterified *Citrullus l.* oil (biodiesel) in this study is lower than that of the parent oil (Table 2). In the present study (Table 3) *Citrullus l.* methyl esters had viscosity value (5.1 ± 0.35) that fall within the recommended standards limit of ASTM biodiesel specification.

Table 3: Analysis of fuel properties of the methyl esters produced from *Citrullus lanatus* Oil

Parameters	Yield	ASTM Limits *	Petrodiesel
Viscosity@40°C (cSt)	5.1 ± 0.35	1.9—6.0	1.3—3.1
API gravity	28.29	-	
Cloud point (°C)	5.24 ± 0.74	NS	NS
Flash point (°C)	128 ± 0.88	>130	65.0
Sulfur content (wt%)	0.03 ± 0.00	0.050	0.05
Aniline point (°C)	28.2 ± 2.44	45--65	----
Diesel index	37.60 ± 0.00	45—55	47
Free glycerol (%)	0.22 ± 0.03	0.03	--

Source: *(Rashid *et al.*, 2010; Sokoto *et al.*, 2013), NS = Not specified.

Cloud point is an indication of first wax appearance in biodiesel. The cloud point observed for *Citrullus l.* methyl ester is $5.24 \pm 0.74^\circ\text{C}$ (Table 3). Biodiesel is less convenient to use at low temperature than petro-diesel. The result shows that, the value obtained is less than methyl tallowate (CP 16°C) (Foglia *et al.*, 1997) but close to rapeseed methyl esters (CP 3°C) which exhibit better cold flow properties (Rashid and Anwar, 2008). CP result recorded is higher than what was reported elsewhere (CP -3°C) for watermelon seeds (Ogunwole, 2015).

Flash point is an important factor to consider during handling and storage of fuels. It is indicative of flammability level of fuels. In this study, *Citrullus l.* biodiesel had a value of $128 \pm 0.88^\circ\text{C}$ (Table 3).

This value is slightly less than that of melon seed oil methyl ester (Egusi), 132.0°C as reported by Ogunwa *et al.*, 2015. Yet, the result falls within the prescribed limits of the ASTM standard. Seed oils contain different kinds of saturated and unsaturated fatty acids. Fatty acid composition of *Citrullus l.* oil as compared to *Jatropha*, soybean and rape seed oils are shown in Table 4.

Sulfur content of *Citrullus* oil methyl ester was determined using Energy-Dispersive X-ray fluorescence spectrometry method (ASTM D 2622). Sulfur level was arrived at $0.03 \pm 0.00 \text{ wt\%}$, as shown in Table 3.

Table 4: Composition of fatty acid methyl esters (approximate wt %) derived from *Citrullus* oil when compared to reported literature

Fatty acid methyl esters	Reported from literature				This work
	M/Formula	Jatropha ^b	Rape ^a	Soybean ^a	<i>Citrullus l.</i>
Hexadecanoic acid methyl ester	C ₁₇ H ₃₄ O ₂	18.22	2.70	10.30	10.75
Octadecanoic acid methyl ester	C ₁₉ H ₃₈ O ₂	5.14	2.80	4.70	7.95
9-Octadecenoic acid methyl ester	C ₁₉ H ₃₆ O ₂	28.46	21.90	22.5	16.58
9,12-Octadecadienoic acid methyl ester	C ₁₉ H ₃₄ O ₂	48.18	13.10	54.10	46.32
13-Docosenoic acid methyl ester	C ₂₂ H ₄₂ O ₂	0.00	50.90	0.00	0.00
Non-methyl esters	C _x H _y O _z				18.28
Total saturated.		23.36	5.50	15.10	18.70
Total unsaturated.		76.64	94.50	84.90	63.00

^a:[Solomon *et al.*, 2010], ^b:[El-Diwani *et al.*, 2009].

Balanites oil biodiesel was reported (Deshmukh and Bhuyar, 2009) to have 0.03%, while *Jatropha* oil methyl ester showed 0.036 wt% (Achten *et al.*, 2009) and sunflower oil methyl ester 0.012 wt% (Rashid *et al.*, 2008) sulfur level. This suggests biodiesels from every source are not sulfur free. Presence of sulfur in biodiesels could have originated from feedstock oils whose level varies from oil to oil. The sulfur may be from the phospholipids present in vegetable oils and glucosinolates present in *Jatropha* based biodiesels (Knothe, 2006). The level of sulfur here is within the ASTM standard acceptable limits.

Diesel index (DI) is indicative of the ignition quality of a fuel. It is conceptually similar to the octane number used for gasoline. The DI of a fuel is related to the ignition delay time, i.e. time required for injection of fuel into the cylinder and onset of ignition. However, in this study the diesel index value for *Citrullus l.* methyl ester is 37.60 ± 0.00 (Table 3) is very close to what was reported by Achten *et al.*, (2008) for *Jatropha* oil methyl ester (38.0—51.0). Moreover, DI decreases with decreasing chain length and increasing branching (Knothe, 2006). The value obtained from this study agrees with what was reported by other authors.

The profile of fatty acids methyl ester composition of *Citrullus* oil as presented in Table 4, indicates methyl-9, 12-Octadecadienoate (Linoleic acid ester) as the dominant ester, followed by methyl-9-Octadecenoate (Oleic acid ester). Both esters are unsaturated and would exhibit some degree of instability with respect to peroxidation. The unsaturation level in the fatty acids (63.00 wt%) is close to that of *Jatropha curcas* (76.64 wt%) as reported elsewhere (El-Diwani *et al.*, 2009).

Biodiesel from this oil would be at operational advantage under cold weather conditions due to the presence of unsaturated fatty acids. The composition of the alkyl esters derived from *Citrullus* oil contain methyl hexadecanoate (Palmitic acid ester) and methyl octadecanoate (stearic acid ester) with lower percentages. The duo constitute 18.70 wt% of saturation level in the oil. Presence of unsaturation in the alkyl ester (*Citrullus* oil) makes it suitable for practical engine application particularly at moderate temperature operations (Canakci and Gerpen, 1999). However, high profile of unsaturated fatty acid methyl esters in oil would lead to easy oxidation of the fuel as well affect its fuel storage stability and thus may require anti-oxidant as additive. Tocopherol being a natural anti-oxidant found in all seed bearing plants helps in maintaining certain level of stability in biodiesel during storage; high level of unsaturated fatty acid methyl ester content makes it difficult to improve and maintain maximum oxidation stability during storage. Therefore, anti-oxidant can be added to improve the stability of the biodiesel produced from seed oil of *Citrullus lanatus*. The anti-oxidant is a chemical that delays the start or slows down the rate of oil oxidation by inhibiting the formation of free radical and hence contributes to the stabilization of the oil (Demirbas, 2008).

4.0 CONCLUSION

In this study, oils extracted from seeds of *Citrullus lanatus* were used as source of triglycerides to produce biodiesel by esterification and transesterification using methanol and sodium hydroxide. The results showed that; the seeds contained considerable amount of oil and the analysis of its methyl esters indicates that; biodiesel

derived possess parameters that are within the acceptable limits of ASTM standard specification

5.0 REFERENCES

- Achten, W.M.J., Verchot, L., Franken, Y.J., Mathijs, E., Singh, V.P., Aerts, R. and Muys, B. (2009). *Jatropha* Biodiesel Production and Use (a Review). *Biomass & Bioenergy* (32):1063-84.
- Altin, R., Cetinkaya, S. and Yucsu, H.S., (2001). The potential of using vegetable oil fuels as fuel for diesel engines, *Energy Convers Manag*, 42: 529—538.
- AOCS, (1997). Official Methods and Recommended Practices of the American Oil Chemists' Society, 5th ed. AOCS: Champaign, Illinois.
- ASTM (1985). Standard Test Methods for Sulphur Contents: Book of ASTM Standard, Vol. 05
- ASTM (1999). ASTM Book of Standard Test Methods: American Society for Testing Materials. Philadelphia PA 268—271.
- Canakci, M. and Gerpen, V.J. (1999). Biodiesel Production via Acid Catalysis. *Trans ASE* 42: 1203—1210
- Demirbas, A. (2008). Comparison of transesterification methods for production of biodiesel from vegetable oils and fats. *Energy Converse. Manage*. 49: 125-30
- Deshmukh, S.J. and Bhuyar, L.B. (2009). Transesterified Hingan (Balanites) Oil as a Fuel for Compression Ignition Engines. *Biomass and Bio-energy*, 33: 108--12.
- El-Diwani, G., Attia, N. K. and Hawash, S.I. (2009). Development and Evaluation of Biodiesel Fuel and by-Products from *Jatropha* Oil. *International Journal of Environment, Science and Technology*, 6: 219--224.
- Farag, H.A., El-Maghraby, A. and Taha, N.A. (2013). Kinetic study of used vegetable oil for esterification and transesterification process of biodiesel production. *International Journal of Chemical and Biochemical Sciences* (3):1—8.
- Foglia, T.A., Nelson, I.A., Dunn, R.O. and Marmer, W.N. (1997). Low temperature properties of for alkyl esters. Thus, seeds of *Citrullus l.* are recommended as feedstock for biodiesel production. alkyl esters of tallow and grease. *J. Am.Oil.Chem. Soc.* 74: 951--955
- Freedman, B., Butterfield, R.O. and Pryde, E.H. (1986). Transesterification Kinetics of Soybean Oil. *JAOC* 63 (10): 1375--1380
- Gerpen, J.V. Shanks, B. and Pruszko, R. (2005). Biodiesel Production Technology. NRETL, 1617 Cole Boulevard; Colorado. USA.
- Hassan, L.G. and Sani, N.A. (2010). Preliminary studies on biofuel properties of bottle gourd (*Lagenaria siceraria*) seeds oil, *Nigerian Journal of Renewable Energy*, 11: 20--25
- Knothe, G. (2006). Analyzing Biodiesel: Standards and Other Methods, Review. *Journal of American Oil Chemist Society*. 83 (10): 823—825.
- Masjuki, H. (1993). Biofuel as diesel fuel alternative: An overview. *J Energy Heat Mass Transfer*: (15):293-304
- Nag, A. and Bhattacharyya, K.B. (1995). New utilizations of vegetable oils. *J Amer Oil Chem Soc.* 72 (12):1391—1398
- Ogunwa, K.I., Ofodile, S. and Achugasim, O. (2015). Feasibility Study of Melon Seed Oil as a Source of Biodiesel. *Journal of Power and Energy Engineering*, 3: 24—27.
- Ogunwole, A.O. (2015). Production of biodiesel from watermelon (*Citrullus lanatus*) seed oil. *Leonardo Journal of Sciences*, 27: 63—74.
- Padhi, S. K. and Singh, R. K. (2007). Characterization of mahua oil (*Madhuca indica*) for the preparation of biodiesel (mahua oil methyl ester), International Conference on Advances in Energy Research (ICAER), 12th to 14th December 2007, IIT Bombay.
- Rashid, U. and Anwar, F. (2008). Production of biodiesel through optimized alkaline catalyzed transesterification of rapeseed oil. *Fuel*; (87): 265—273.
- Rashid, U., Anwar, F., Jamil, A. and Bhatti, H. (2010). *Jatropha curcas* Seed Oil as a Viable Source for Biodiesel. *Pakistan Journal of Botany*, 42 (1): 575—582.
- Sharma, Y.C. and Singh, B. (2008). Development of biodiesel from *karanja*, a tree found in rural India, *Fuel*, 87: 1740—1742.

- Sinha, S. and Misra, N.C. (1997). Diesel fuel alternative from vegetable oils. *Chem Eng'g World*: 32 (10): 77-80
- Sokoto, M.A., Hassan, L.G., Salleh, M.A., Dangoggo, S.M. and Ahmad, H.G. (2013). Quality Assessment and Optimization of Biodiesel from *Lagenaria vulgaris* (Calabash) Seeds Oil. *International Journal of Pure and Applied Sciences and Technology*: 15 (1): 55-66.
- Solomon, G., Luqman, C.A. and Nor, M.A. (2010). Investigating “Egusi” (*Citrulluscolocynths l.*) seed oil as potential feedstock. *Energies*, (3): 607—618.