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Characterization of Watermelon (*Citrullus Vulgaris*) and Calabash (*Lagenaria Vulgaris*) Seeds Oil as Potential Feedstock for Biodiesel Production

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ABSTRACT

Potential of oilseeds for liquid transport fuel (biodiesel) is based on the knowledge of their oil characterization. In this paper, the proximate composition and oil characteristics of Watermelon (*Citrullus vulgaris*) and Calabash (*Lagenaria vulgaris*) seeds were studied using standard methods and considered alongside their yields to assess their suitability as feedstock for large-scale biodiesel production. The whole seeds were sorted, de-shelled, dried, milled, sieved and oil was extracted from the seeds using Soxhlet extractor with n-hexane. Results show the watermelon and calabash seeds contains total ash 6.70±0.10% and 6.0±1.02%; moisture, 4.00±2.16% and 2.39±0.14%; crude lipid, 41.05±1.30% and 58.0±3.57%; crude protein, 30.63±0.40% and 21.28±2.2%, respectively. The percentage extracted oil yield was found to be 48% and 40.5% for watermelon and calabash seeds respectively. These show that both watermelon and calabash seed have good oil yields and may have potentials for biodiesel production.

Keywords: Watermelon (*Citrullus vulgaris*); Calabash (*Lagenaria vulgaris*); proximate analysis; physicochemical analysis; crude lipid; and biodiesel.

1.0 INTRODUCTION

The window for limiting climate change to 1.5 °C is rapidly closing at the same time global average temperatures and fossil fuel emissions continue to rise and there are predictions that anthropogenic carbon dioxide (CO_2) emissions from global natural gas and oil use are likely to hit an all-time high in 2020 (IPCC, 2018; GCP, 2019). Even stable emissions at today's rates, let alone rising ones, make temperature targets of 1.5° and 2.0 °C less likely to obtain and more challenging and expensive to reach (Peters, *et. al*., 2017). Global fossil CO_2 emissions have grown three years consecutively: +1.5% in 2017, +2.1% in 2018, and +1.5% in 2019 (Jackson *et. al*., 2019). It is estimated that by the end of the year, emissions from industrial activities and the burning of fossil fuels will pump an estimated 36.8 billion metric tons of CO_2 into the atmosphere and total carbon emissions from all human activities, including agriculture and land use, will likely cap off at about 43.1 billion tons (Peters *et. al*., 2019). Since pre-industrial times, the earth has already warmed 1.1 °C and 2014–2019 is the hottest five-year period on record for average global surface temperatures (WMO, 2019).

Oils derived from plant seed sources remain important for their nutritional, industrial and pharmaceutical applications (Chouhan, 2011) and can extensively be used for biodiesel production (Aremu *et. al*., 2015). Biodiesel, fatty acid methyl esters of seed oils and fats, has been found suitable for use as fuel in diesel engine (Atabani, *et. al*., 2012). It is renewable and produces much fewer harmful emissions than conventional fossil based diesel (Dwivedi *et. al*., 2011). Thus, its significant utilization instead of fossil based diesel would lead to a decrease of the carbon dioxide (CO_2), sulphur dioxide (SO_2), and particulate matter emissions (Galadima and Muraza, 2014).

Currently, inedible oils are now being sought, from algae (Galadima and Muraza, 2014) as well as other crops and sources (Ashraful *et. al*., 2014), to help reduce the cost of biodiesel in order to make it competitive to conventional fossil based diesel (Haas, 2005). Watermelon (*C. vulgaris*) and Calabash (*L. vulgaris*) contains large quantities of seeds and the seeds oil is receiving growing interest due to their high concentration of bioactive lipid components, which have shown various industrial benefits.

2.0 METHODOLOGY

2.1 Sample Collection and Preparation

Calabash (*Lagenaria vulgaris*) and Watermelon (*Citrullus vulgaris*) seeds were collected from Gayari, Gummi Local Government area and Talata Mafara, Talata Mafara Local Government area of Zamfara State, Nigeria, respectively. The seeds were identified at the Botany Unit, Department of Biological Sciences, Usmanu Danfodiyo University, Sokoto. The seeds were dried and grounded into powder using mortar and pestle for oil extraction.

2.2 Extraction of Oils

Oil from the powered seeds (50g) was extracted using Soxhlet extraction methods (60°C, 8 h) with n-hexane (150 ml) as a solvent. The solvent was then removed using a rotary evaporator (35°C, 30 mmHg). The percentage crude oil (lipid) yield was calculated from Equation 1. The oil was stored at 20°C until required for experiments.

$$\%OY = \frac{W2}{W1} x100 \tag{1}$$

where,
%OY, is the percentage oil yield
W1, is the initial weight of the sample
W2, is the weight of the oil

2.3 Proximate Analysis

2.3.1 Determination of Ash Content

The ash content of the seeds was determined based on method described by (Daud *et. al*., 2015). The percentage ash content was calculated from Equation 2.

$$Ash\% = \frac{WAsh}{Wsample} \times 100 \tag{2}$$

Where,
WAsh, is the weight of ash; and
Wsample is the weight of the sample

2.3.2 Determination of Moisture Content

The percentage moisture content was determined based on the method described by (Daud *et. al*., 2015) and was also calculated from Equation 3.

$$Moisture\% = \frac{Wfs - Wds}{Wfs} \times 100 \tag{3}$$

Where, *Wfs* is the weight of the fresh sample and *Wds* is the weight of the dry sample

2.3.3 Determination of Crude Protein

Total nitrogen was determined by the Kjeldahl method and the result multiplied by 6.25 to give crude protein.

$$Nitrogen\% = \frac{mlacid \times Nacid}{Ws} \times 0.014 \times 100 \tag{4}$$

where, *mlacid* is the volume of the acid;
Nacid is the Normality of the standard acid

Crude protein content (%) = nitrogen content × 6.25

2.3.4 Determination of Crude Fibre

Thorough washing with boiling water and finally drying off followed the sequential hot digestion with acid and alkaline solution of defatted sample. This ensures the removal of all other material. The crude fibre was calculated from the equation below (Equation 5).

$$Crudefibre\% = \frac{WDresidue - WAresidue}{Ws} \times 100 \tag{5}$$

where, *WDresidue* is the weight of the crucible plus dried residue;
WAresidue is the weight of crucible plus ashed residue; and
Ws is the weight of the sample.

2.3.5 Determination of Crude Lipid

The crude lipid in the samples was determined by the Soxhlet extraction method using petroleum ether based on the standard method of (Daud *et. al*., 2015).

$$Crudelipid\% = \frac{Wlipid}{Wsample} \times 100 \tag{6}$$

where, *Wlipid* is the weight of the lipid and *Wsample* is the weight of the sample.

2.3.6 Determination of Carbohydrate Composition

The carbohydrate content was obtained by subtracting the sum of ash, moisture, crude fiber, crude protein, and crude fat from 100 as shown in Equation 7 (Efavi *et al*., 2018).

$$Carbohydrate\% = (Ash + Moisture + Fibre + Protein + Lipid) - 100 \quad (7)$$

2.4 Physicochemical Analysis

Physicochemical properties were determined as follows in order to know the characteristics of the oil.

2.4.1 Specific Gravity and Density

Procedure: 25 ml of pyrometer bottle was washed, dried and weighed. The bottle was filled with water and weighed. The bottle was emptied, dried and filled with the extracted seeds oil and weighed. The specific gravity (SG) and density (D) of the oil were calculated by the Equations as shown below.

$$SG = \frac{W25mlOil}{W25mlWater} \quad (8)$$

$$Density = \frac{W25mlOil}{VolumeWater} \quad (9)$$

2.4.2. Determination of Viscosity

This is the opposite of flow of liquid. It is expressed in mm^2/sec or Pa/s or kg/ms. Viscosity of the oil was determined using rotational viscometer. 100 ml beaker was filled to three-quarter of its capacity with calabash seed oil sample, heated to 40 ^oC and immediately placed on viscometer and a spindle of a viscometer was adjusted until it submerged into the sample. The viscometer was switched on after spinning; reading was taken from the scale.

2.4.3 Determination of Color

The color of the oil samples was determined by observation using several independent competent individuals and the color was correlated using color charts.

2.4.4 Determination of Acid Value

Acid value is the amount of potassium hydroxide in mg that would neutralize the free acid in gram of the sample. It is expressed in (mg KOH/g). This was determined by mixing 25ml of petroleum ether with 25ml of ethanol and 4 drops of phenolphthalein indicator into a conical flask containing 5g of the oil sample and was titrated with aqueous 0.1M KOH and was shaken properly until a pink colour, which persist for 15 seconds was obtained. Equation 10 calculated this.

$$AcidValue = \frac{Titre(ml) \times 0.1 \times 56.10}{Wsample(g)} \quad (10)$$

2.4.5 Determination of Free Fatty Acids (FFA)

Free Fatty Acid: It is a number that is usually calculated as oleic acid, also expressed in (mg KOH/g). This was calculated from Equation 11.

$$FFA = \frac{AcidValue}{2} \quad (11)$$

2.4.6 Determination of Saponification Value

This is the number of milligrams of potassium hydroxide (KOH) required to neutralize the free fatty acids resulting from the complete hydrolysis of 1g of the sample. It is measured in (mg/g).
Exactly 1g of the oil sample were added into a conical flask containing 25 ml of 0.1M alcoholic KOH solution. The flask was sealed and heated in the oven for 5 minutes at 105^{o}C. 1ml of phenolphthalein solution was added and then titrated with 0.5M HCl until the solution becomes colorless. Blank titration (without oil) was also carried out and the saponification value calculated thus (Equation 12).

$$SaponificationValue = \frac{(B - S) \times 0.5 \times 56.10}{Wsample} \quad (12)$$

where: B = blank titre value,
S = sample titre value.

2.4.7 Determination of Iodine Value

This is a measure of the degree of unsaturation in any vegetable oil or animal fat. It is the weight of iodine absorbed by 100 parts by weight of the sample. It is expressed in (mg/g). The oil sample was poured into a dry glass- stoppered bottle of about 250 ml capacity and a small rod was added. The weight (g) of the oil was calculated by dividing the highest expected iodine value by 20.10 ml of carbon tetrachloride and 20ml of wiji's solution was added into the bottle and dissolved. The stopper (moistened with potassium iodine solution) was inserted and kept in the dark for 30 minutes. 15 ml of potassium iodide solution and 100 ml of water was mixed and titrated with 0.1M of thiosulphate solution using starch as indicator just before the end point. A blank was carried out at the same time commencing with 10 ml of carbon tetrachloride.

$$IodineValue = \frac{(B - S) \times 1.269}{Wsample} \quad (13)$$

where, B = blank titre value,
S = sample titre value

2.4.8 Determination of Peroxide Value

This is the measure of its content of oxygen. It is expressed in Mol/kg. This was determined by adding 1g of oil sample and 1g of powdered potassium iodide into 2 test tubes containing 20ml of solvent mixture each (2 vol. glacial acetic acid + 1 vol. of chloroform) i.e. (60:30). Step 1 was carried out in a blank tube (without sample). The tubes were placed in a water bath and allowed to boil vigorously for 30 seconds. The contents were poured quickly into a conical flask containing 10 ml of 5% potassium iodide solution. The tubes were washed with 5ml of water each and poured into each conical flask with contents, and 4 drops of phenolphthalein was then added into each conical flask and was titrated with 0.002M thiosulphate until a colour change was obtained. It was calculated from the Equation below (Equation 14).

$$PeroxideValue = \frac{(B - S) \times 0.02 \times 1000}{Wsample} \quad (14)$$

where: B = blank titre value,
S = sample titre value

3.0 RESULTS AND DISCUSSIONS

3.1 Proximate Analysis

The result of the proximate composition of watermelon and calabash seeds is presented in Table 1.

Table 1. Proximate Composition of the Watermelon and Calabash Seeds Oil

Properties	Watermelon Seed Oil	Calabash Seed Oil
Moisture	4.00 ±2.16	2.39±0.14
Crude Protein (%)	30.63±0.40	21.28±2.2
Crude Lipid (%)	41.05±1.30	58.0±3.57
Crude Fibre (%)	10.40±0.20	3.5±1.06
Ash Content (%)	6.70±0.10	6.0±1.02
Total Carbohydrates (%)	7.22±0.30	8.8±0.97

Values are mean +/- standard deviation of triplicate data.

3.3 Physicochemical Analysis

The results of the physicochemical properties of the oil from watermelon and calabash seeds are presented in Table 2. The oil yield estimation after extraction was found to be 45.0% and 40.5%, for watermelon and calabash seeds, respectively and the results are in the range of the standard oil yield 25 – 45% (Usman, *et. al*., 2013).

The physicochemical analysis of the solvent extracted watermelon and calabash seeds oil includes; iodine value, specific gravity, density, acid value, kinematic viscosity, free fatty acid, saponification value, and peroxide value.

The specific gravity of the oils was found to be 0.94 and 0.92 for watermelon seed oil and calabash seed oil, respectively. The value conforms to the standard value of less than 1.0 (Efavi *et al*., 2018).

Table 2. Physicochemical Properties of the Watermelon and Calabash Seeds Oil Produced

Parameters	Watermelon Seed Oil	Calabash Seed Oil
Colour	Golden yellow	Dark yellow
Specific Gravity (g/ml)	0.94	0.92
Density (g/cm^3)	1.38	0.90
Acid Value (mg KOH/g)	3.096	2.25
Kinematic Viscosity (mm^2/s)	20.47	21.65
Free Fatty Acid (mg/g)	6.34	5.15
Saponification value (mg/g)	191.89	207.57
Iodine Value (gI/100g)	120.15	145.8
Oil Yield (%)	45	40.50
Peroxide Value (meq/kg)	11.0	11.60
pH	5.73	5.51

The iodine value of the oils produced from the watermelon and calabash seeds shows that the oil may not be too susceptible to oxidation and quick rancidity. Given the threshold acid value of 1.0 mg KOH/g for fresh oils, it is obvious that watermelon seed oil (acid value 4.09) and calabash seeds oil (acid value 4.25) would have catalysis problem during transesterification (catalyst deactivation) and formation of soaps as side reaction (Pannerselvam, *et. al*., 2016). However, heterogeneous catalysts and addition of bases such as sodium could be used to solve these problems. The oils contain specific gravity of 0.94 (watermelon seeds) and 0.92 (calabash seeds). The high kinematic viscosity of the oils however, can be reduced during esterification. It has been shown that kinematic viscosity of watermelon oil could be reduced from 21.65 to about 5.8 mm^2/s in the produced biodiesel, a value that is comparable to that of the conventional fossil based diesel.

The iodine value, which indicates the degree of oil saturation shows that the oils are semi-drying and unsaturated and this makes it suitable for utilization in certain industrial applications (Usman, *et. al*., 2015). The low acid value and free fatty acids shows the ability of the oils to resist hydrolytic rancidity (Okonkwo and Okafor, 2016; Kennedy, *et. al*., 2015).

4.0 CONCLUSION

The high percentage oil yield of both watermelon and calabash seeds shows that the seeds are a viable oil source and suitable feedstock for biodiesel production. The oil quality parameters show that the oil from watermelon and calabash seed with a moderate degree of unsaturation is not susceptible to oxidative rancidity. The proximate and physicochemical parameters of the oil extracted from the watermelon and calabash seeds show that the oil conforms to standards for biodiesel production. Thus, both watermelon and calabash seeds oil can serve as a good and viable feedstock for biodiesel production.

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