

Production of biodiesel from watermelon (*Citrullus lanatus*) seed oil

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Abstract

This work is about the production of biodiesel from watermelon (*Citrullus lanatus*) seed oil. The oil extraction was done using solvent extraction method. The basic test for suitability of the obtained watermelon oil was carried out. Using trans-esterification process, watermelon oil was heated to 60°C, solutions of methoxide (NaOCH₃) were also added and stirred continuously for an hour. It was left to settle for 24 hours. After shaking, the mixture was poured into a separating funnel and was allowed to stand for 24 hours. The biodiesel was obtained using the separating funnel, separating biodiesel and glycerine. The washed biodiesel was collected into a beaker and gently heated in an oven at 105°C to evaporate the excess water and methanol in the biodiesel. The results of the test classified the watermelon biodiesel within limits set for biodiesel's properties by ISO 14214 specifications on Biodiesel.

Keywords

Biodiesel, Watermelon seed oil; Methoxide; Glycerine; Trans-esterification; Solvent extraction; Methanol; Evaporate

Introduction

In simple words, biodiesel can be defined as a natural and renewable domestic fuel made from vegetable oil. Biodiesel can also be defined technically, as a fuel comprised of

mono-alkyl esters of long chain fatty acids derived from vegetable oil or animal fats, and is typically made by reacting lipids with an alcohol. The “mono-alkyl ester” in the biodiesel is the product of the reaction of a straight chain alcohol, such as methanol or ethanol, with fat or oil (triglyceride) to form glycerol (glycerine) and the esters of long chain fatty acids. The world’s major sources of energy today are petroleum, coal and natural gas which are fossil-derived and non-renewable which have been and is the major source of development in some countries. The world at large also depends on petroleum products as the main energy source. The way countries are over-dependence on petroleum products has caused increase in emission of combustion which generates pollution into the environment and the use of the energy sources over many years have also resulted in the rise of global temperature levels also known as global warming which is due to high levels of carbon that are released as by-products and exhaust gases. There are also serious cases of oil spillage which tends to destroy the immediate or remote marine life and environment where petroleum resources are found. Most of the political and socio-economic problems facing countries today are because of the instability of petroleum product [1]. Due to these problems it has become necessary to diversify and find alternative sources for fuel. Rudolph Diesel was the first to test peanut oil in his combustible ignition engine in the 1800’s, during this period various oils were extracted from different plants used to run the engines such as melon seed oil, jatropha seed oil, soya bean, palm oil, sunflower, peanut oil, corn oil, sugar cane and olive oil which are produced in large quantities for use as fuel substitutes. The advantage of biodiesel fuel is that it is a renewable energy source unlike petroleum-based diesel. Another main biodiesel fuel advantage is that it is less polluting than petroleum diesel and the lack of sulphur in 100% biodiesel extends the life of catalytic converters. Its primary advantage is that it is one of the most renewable fuels currently available and it is also non-toxic and biodegradable. It can also be used directly in most diesel engines without requiring extensive engine modifications. Biodiesel fuel can also be used in existing oil heating systems and diesel engines without making any alterations. The lubricating property of the biodiesel may lengthen the lifetime of engines.

Several methods of biodiesel production process includes ultra and high shear in-line or batch reactors, ultrasonic reactor, microwave process, lipase catalyzed process, and super critical process and the methods of oil extraction from the seed can be by mechanical screw press, solvent extraction and intermittent extraction technique such as the soxhlet extraction.

The production of biodiesel is basically a trans-esterification reaction [2]. According to [3], microwave ovens for the microwave method of production of biodiesel can be used to provide the heat needed for trans-esterification process. This process was used in the production of biodiesel from jatropha oil (curcas oil). The jatropha seeds' oil was heated to 60°C, a solution of potassium methoxide also at 60°C was added and stirred continuously for one hour. It was left to settle for 24 hours. Thereafter, the upper layer which is the biodiesel was decanted into a separate beaker while the lower layer which comprised glycerol and soap was collected from the bottom of the separating funnel. [4]. The solvent extraction method was also used in extraction of watermelon seed (*Citrullus lanatus*) oil in order to determine its physic and chemical properties for relevant uses. The seeds were extracted from the fruits, washed and dried in an oven at 70°C for 48 hours for easy removal of the husk. Moisture content per 100gm sample was determined directly on the seeds by oven drying at 55°C for 12 hours until constant weight was achieved. The cleaned de-husked melon seed were dry-milled and kept in a desiccators till when needed. A 100gm of pulverized sample was extracted in a thimble of the soxhlet apparatus. The samples were extracted with hexane in a ratio of 1: 6 w/v at 60-65°C. The resulting oil mixtures were subjected to distillation and desolventised using a rotary evaporator at 35°C. The extracted oil was further air-dried to remove residual solvent vapour and measured. Proximate analysis of refractive index, iodine value, saponification value, free fatty acid, peroxide and acid values were determined for each sample in triplicate in accordance with the association of official analytical chemist procedures.

The aim of this research work was to produce biodiesel and to characterize the produced biodiesel from water melon seed.

Material and method

Procedure for watermelon oil extraction

The watermelon seeds were removed manually and carefully blended using an electric blender. The blended samples were sieved to remove unwanted particulate substances and the final product was an averagely coarse aggregate. The initial moisture content was calculated at first using the formula:

$$mc = \frac{w_1 - w_2}{w_1} \times 100 \quad (1)$$

where mc is moisture content, $w1$ is the weight of the sample before extraction and $w2$ is the weight of the sample after extraction.

1. 10g of the milled samples were taken in pairs and wrapped in a filter paper and inserted into the soxhlet chamber.
2. 250ml of N-hexane was poured into the round bottom flask and heated for about 4 - 6 hours at 60°C (boiling point 40 - 60°C).
3. As heating continues, the solvent evaporates into the extraction chamber and goes up into the condenser and falls back as liquid there by washing/dissolving the fat/oil in the sample back to the round bottom flask. This continues to reflux until 6 hours is reached.
4. The watermelon seed oil was gotten by evaporating the solvent from the round bottom flask into the extraction chamber after the wrapped samples were carefully removed.
5. The wrapped samples were oven dried at 105°C for 30 minutes and allowed to cool, and then it was weighed.
6. The solvent was drained into its container for re-use.

Calculation:

$$\%oy = \frac{m_1}{m_2} \times 100 \quad (2)$$

where oy is oil yield.

Characterization procedure for the extracted watermelon seed oil

Physic-chemical properties are determined as follow in other to know the characteristics of the oil.

Specific gravity and density

Procedure: 25ml 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 watermelon seed oil and weighed.

Calculation:

$$SG = \frac{\text{weight of 25ml of oil}}{\text{weight of 25ml of water}} \quad (3)$$

$$\text{Density} = \frac{\text{weight of 25ml of oil}}{\text{volume of water}} \quad (4)$$

Acid value or Free Fatty Acid (FFA)

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 (mgKOH/g).

Procedure: 25ml of petroleum ether was mixed with 25ml of ethanol and 4 drops of phenolphthalein indicator into a conical flask containing 2g 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.

Free Fatty Acid: It is a number that is usually calculated as oleic acid, also expressed in (mgKOH/g).

Calculation:

$$\text{Acidvalue} = \frac{\text{Titre (ml)} \times 0.1 \times 56.10}{\text{Weight of sample used (g)}} \quad (5)$$

$$\text{FFA} = \frac{\text{Acid value}}{2} \quad (6)$$

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).

Procedure: 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 gotten by dividing the highest expected iodine value by 20. 10ml of carbon tetrachloride and 20ml of wiji's solution was added into the bottle and dissolved. The stopper which was moistened with potassium iodine solution was inserted and kept in the dark for 30 minutes. 15ml of potassium iodide solution and 100ml 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 10ml of carbon tetrachloride.

Calculation:

$$\text{Iodinevalue} = \frac{(B - S) \times 1.269}{\text{Weight of sample (g)}} \quad (7)$$

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

Peroxide value

This is the measure of its content of oxygen. It is expressed in Mol/Kg.

Procedure: 1g of oil sample and 1g of powdered potassium iodide was added 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 10ml 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.

Calculation:

$$\text{Peroxide value} = \frac{(B - S) \times 0.02 \times 1000}{\text{Weight of the sample (g)}} \quad (8)$$

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

Saponification value

This is the number of milligrams of potassium hydroxide required to neutralize the free fatty acids resulting from the complete hydrolysis of 1g of the sample. It is measured in (Mg/g).

Procedure: 1g of the oil sample was added into a conical flask containing 25ml of alcoholic potassium hydroxide solution. The flask was sealed and heated in the oven for 5 minutes at 105°C. 1ml of phenolphthalein solution was added, the excess alkali was then titrated with 0.5M HCl when hot. A blank was carried out at the same time (without oil).

Calculation:

$$\text{Saponification value} = \frac{(B - S) \times 0.5 \times 56.10}{\text{Weight of the sample}} \quad (9)$$

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

Viscosity

This is the opposite of flow of liquid. It is expressed in mm²/sec or Pa/s or kg/ms. The viscosity of the oil was determined using rotational viscometer.

Biodiesel production

Pre-treatment of watermelon seed oil

This is done so as to achieve the highest glycerine quality through reduction of the

impurities, improving the availability of the apparatus through reduction of the gums and the resulting caking in the thermal glycerin process. For higher economy of the apparatus through discharging less phosphate into the waste water, higher glycerine yield due to a lower material organic non-glycerol (MONG) content through lowest free fatty acid content and to obtain an optimum cold stability of the biodiesel through reduction of the wax content in the extracted oil, pre-treatment is carried out on oils that have high free fatty acid content in order to enhance optimum separation of the vegetable oil into its corresponding esters.

Procedure: 1% of H_2SO_4 (sulphuric acid) was added with 30 ml of methanol into a conical flask containing 100ml of the oil sample.

The mixture was stirred vigorously for 30 minutes using a magnetic stirrer. Then poured into a separating funnel and allowed to separate for about 10 hours.

The impurities formed a top layer while the treated oil formed a layer below and was collected in a beaker and oven dried for 2 hours at $105^\circ C$ to remove the excess methanol.

Trans-esterification process

1. Mixing of Alcohol and catalyst

Procedure: 0.5g of sodium hydroxide pellet was mixed with 30 ml of methanol inside a strong heat resistance glass beaker. The mixture was heated gently at a temperature lower than the boiling point of the methanol this was done to assist in dissolving the pellet in the methanol thereby obtaining a chemical solution known as methoxide ($NaOCH_3$). Excess alcohol is normally used to ensure total conversion of the fat or oil to its esters.

2. The methyl ester mixture:

Procedure: The methoxide solution was mixed in a beaker containing 100 ml of the treated cotton seed oil and poured into a rubber container and was shaken vigorously for 1 hour in order to obtain a homogeneous mixture.

3. Separation of the Biodiesel and Glycerin:

Procedure: After shaking, the mixture was poured into a separating funnel and was allowed to stand for 24 hours. Once the separation is complete two major products exist which are glycerin and biodiesel, in which the biodiesel was formed at the top and the glycerin at the bottom. To achieve full separation of the mixture, the quantity of the glycerin produced varies according to the oil used, the process involved and the amount of excess alcohol used. Both the glycerin and biodiesel products have a substantial amount of excess alcohol that was used

in the reaction. The raw biodiesel was washed with water to remove some traces of soap and other contaminants and the water was allowed to settle down before removing it by draining. The washed biodiesel was collected into a beaker and gently heated in an oven at 105°C to evaporate the excess water and methanol in the biodiesel. The biodiesel yield was 70 ml at the end of the purification process while the jelly- like residue known as glycerin was the bi-product and which is useful in organic and chemical industries for the production of soap, cosmetics and cleansers. The Biodiesel was obtained using the separating funnel.

Characterization of the biodiesel

The characterization analysis and comparative test were carried out using a low sulphur content fossil (petroleum) diesel as the standard control according to the American Standard Test Method for Diesel (ASTM-D). Specific gravity, density, viscosity, acid, iodine and saponification values were determined using the same procedure as the characterization of the extracted watermelon seed oil.

Flash point and fire point

The flash point was determined using a small strong heat resistance glass cup and a heating mantle. The sample was poured into the cup and heated gradually while being stirred to distribute heat uniformly in the cup and the temperature was monitored using a thermometer. At regular interval temperatures, the cup was exposed to naked flame, the temperature at which the biodiesel increases the flame like a flash but does not supports combustion was recorded, which was the flash point of the sample. The temperature at which the biodiesel catches fire (supports combustion) was noted and recorded which gives the fire point of the sample.

Cloud point and pour point

The sample was poured in a test tube to a certain level and a thermometer was inserted and sealed alongside with the test tube. It was then placed in a freezer and monitored at intervals, the temperature at which some traces of cloudy suspension appear in the test tube was noted which is the cloud point of the sample and the temperature at which the biodiesel solidifies (freezes) was noted which is the pour point of the sample.

Refractive index

This was determined using a device called Refractometer

Cetane number

This is a measurement of the combustion quality of diesel fuel during compression ignition.

Calculation:

$$\text{Cetane Number} = 46.3 + (5458/S) - (0.225 \times I) \quad (10)$$

where S and I stands for saponification and iodine value respectively.

Colour

The colour was determined by oganonetip method, there where ten people called up to visualize the physical appearance of the biodiesel and took the average and was concluded to be golden yellow.

Results and discussion

The results of the physic-chemical properties of the oil and the biodiesel produced from watermelon seed oil is presented in Table 1 and 2 respectively. The physic-chemical analysis of the solvent extracted watermelon seed oil includes; Saponification value of 191.89 mgKOH/g, the value obtained was higher than that of *Dennettia tripatala* fruit oil (Pepper fruit) 159.33 which is suitable for soap making and also higher than that of beeswax 93 mgKOH/g. This indicates that the oil could be used in soap making.

Table 1. Physicochemical Properties of the Watermelon Seed Oil Produced

Properties	Watermelon Seed Oil	ASTMD Standard
Specific Gravity	0.944	0.916
Density (g/cm ³)	1.38	0.918 – 0.926
Kinematic Viscosity (mm ² /sec)	1	35
Free Fatty Acid (mg/g)	5.048	25max
Saponification value (mg/g)	191.89	189 - 198
Iodine Value (gI ₂ /100g)	157.15	123
Oil Yield (%)	48	<0.09
Moisture Content (%)	5.8	
Peroxide Value (mMol/Kg)	8	< 9
Acid Value (mgKOH/g)	10.096	10

Table 2. Fuel Properties of Biodiesel Produced From watermelon Seed Oil

Properties	Produced Biodiesel	ASTMD Standard (ASTMD975)	Conventional (ASTMD6751)
Specific Gravity	0.89	0.85	0.88
Density (g/cm ³)	0.8	0.82 - 0.845	0.86 - 0.90
Kinematic Viscosity (mm ² /sec)	1.05	2-3	1.9 - 6.0
Free Fatty Acid (mg/g)	1.683	0.27	0.50max
Acid Value (mgKOH/g)	3.66		
Saponification value (mg/g)	154		
Iodine Value (gI ₂ /100g)	0.867	128.5	130max
Moisture Content (%)	0.025	0.05 max	0.05max
Biodiesel Yield (%)	49.8	Reported value	Reported value
Flash Point (°C)	107	60-80	130-170
Fire point (°C)	123	68	100-170
Cloud Point (°C)	-1	-15 to -5	-3 to -12
Pour Point (°C)	-3	-35 to -15	-15 to 10
Refractive Index	1.46	1.664	1.245 - 1.675
Cetane Number	44.47	40 - 55	47 - 65

The Iodine value was 159.76g I₂/100g (greater than 100) which is within a range of semi-drying oils consisting predominately polyunsaturated fatty acids mainly oleic and lenoliec fatty acids. This class of oils whose iodine value is between 100-200 possesses the property of absorbing oxygen on exposure to the atmosphere; though they are not so sufficient to be qualified as drying oils. They thicken and remain sticky but do not form a hard dry film. They are used in the production of margarine and soap. An acid value of 10.096 mgKOH/g was obtained which is lower than that of olive oil 17 mgKOH/g and 10.3 mgKOH/g for shea nut butter. The Free Fatty Acid value is 5.048 mgKOH/g. It has a specific gravity of 0.944 which is less dense than water. This is slightly different with those obtained by [5] for jatropha (0.88), coconut oil (0.91) and mango oil (0.92). The extracted watermelon has a light yellow color because of the presence of pigments.

The viscosity of the produced watermelon seed biodiesel was 1.05mm²/s. High Speed Diesel (HSD) has viscosity of 1.3 - 4.1 at 40°C whereas the viscosities of Castor bean oil biodiesel and pongame oil biodiesel are 5.67 and 5.5 respectively, which is slightly higher than the viscosity of High Speed Diesel and watermelon seed biodiesel. It shows that the viscosity of watermelon seed biodiesel were comparable to HSD and other non-edible oils. Since viscosity is the rate of opposition of flow of a liquid, it makes it to be a very important property of biodiesel. Biodiesel have higher viscosity than conventional diesel, though higher viscosity leads to poorer atomization of fuel injectors but the obtained viscosity of the

biodiesel was found to be within the biodiesel standard of America.

The density of watermelon seed oil was 1.38g/cm³ which differ slightly from hemp, neem, 0.81 and 0.87 respectively, which are closer to the density of diesel (0.845). Watermelon biodiesel was found to be less dense than water and can be used as an alternative fuel as it tallies with the ASTM standard for Biodiesel (0.86 - 0.92).

Flash point is the temperature that indicates the overall flammability hazards in the presence of air; higher flash points make for safe handling and storage of biodiesel. The Flash Points of biodiesel of watermelon was 107°C, which is consistent with Palm oil Biodiesel but differ from Neem oil biodiesel (120°C) as reported by [6] which are higher than that of High Speed Diesel (60-80°C). For non-edible based seeds oils flash point are higher than fossil diesel [7].

Cloud point is the temperature at which a cloud of wax crystals first appear in the biodiesel when it is cooled. The pour point is the lowest temperature at which the biodiesel can still be moved. These properties are related to the use of biodiesel in colder region. The cloud point of the obtained biodiesel was -1°C as compared to -6°C for castor biodiesel and has a pour point of -4°C which differ from castor (-9°C) respectively. Pour point and cloud point of all biodiesel were almost within the specified range.

The percentage yield of biodiesel from the watermelon seed source is high, having 49% as compared to 75.3 for jatropha (curcas) oil [8]. This indicates that it is slightly lower than the biodiesel yield from jatropha oil.

Refractive index which is a dimensionless number that describes how light passes through the biodiesel was found to be 1.46 as it is consistent with biodiesel from soya bean oil [9].

The cetane number (44.47) was found to be lower compared with that of rape seed (49.21), jatropha (56.34). This shows that watermelon seed biodiesel has a higher combustion quality than rape seed biodiesel and jatropha biodiesel and was found within ASTM standards.

The colour of the obtained biodiesel was light yellow which is consistent with biodiesel from palm but differ from castor, as reported by [10].

Conclusively, the biodiesel was found to have higher cetane number and thermal stability, but low cold flow properties when compared to fossil diesel but was still within ASTM standard, thus biodiesel from watermelon seed oil proves to be one of the best

alternate fuel for diesel engine.

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