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Biochemical Characterization of Seed Oil in Sesame and Watermelon for Production of Biodiesel

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ABSTRACT

Biochemical characters of seed oil from sesame (*Sesanum indicum*) and watermelon (*Citrullus lanatus*) seed was carried out using standard physicochemical procedures. Ripe seeds of the two species were dehulled mechanically before extraction. Oil was extracted from the two seeds using n-hexane in a soxhlet extractor, then trans-esterified to biodiesel using single step alkali hydrolysis. The biodiesel so produced was analysed for physicochemical and fuel properties using ASTM (American Society for Testing and Materials) procedures. The oil extraction was carried out using solvent extraction method. The basic test for suitability of the oil obtained was carried out using transesterification processes. Sesame and watermelon seeds oil was heated to 60^0C, solution of methoxide ($NaOCH_3$) were also added and stirred continuously for an hour. It was left to settle for 24 hours. The biodiesel was obtained using the separating funnel, separating biodiesel from glycerine. The washed biodiesel was collected into a beaker and gently heated in an oven at 105^0C to evaporate the excess water and methanol in the diesel. The result of the test classified the biodiesel within the limits set for biodiesel properties by ISO14214 specification on biodiesel.

Keywords: sesame, watermelon, biodiesel, transesterification, ISO, ASTM

1.0 INTRODUCTION

About 36% of the world's energy comes from petroleum oil and 22% from gas (Rodriguez-Acosta *et al*., 2010). This growing consumption of energy throughout the world has also resulted in the dependent on fossil fuels such as coal, oil and gas. The use of fossil fuels also causes increasing pollution that leads to global warming and yet it is non-renewable. It is a common knowledge that the world's energy depleted in future several decades (Meres *et al.*, 2004). Consumer nations of fossil fuel have become dependent on foreign suppliers and their economies have become hostage to international events. The desire to be exonerated from dependency on fossil fuels created an interest in alternatives (Kalam and Masjuki, 2002) as reliance on imported petroleum and fluctuating prices is creating apprehension among users. Biodiesel is a promising alternative which is already in use in some countries (Singh and Singh, 2010). Due to the need to achieve sustainable biodiesel production, crops or other similar agricultural sources would have to be considered as potential source of biodiesel (Lea, 2003; Kheang and May, 2006). Consequently, there is an increasing need to search for oils from vegetative sources to augment the available ones and also to meet specific applications (Kyari, 2008). Hence, neglected and underutilized plant species readily comes to mind, as exploitation of this will greatly reduce poverty in developing countries. In Nigeria, there are some native oil seed plants which grow well in fallow lands and could be used as source of alternative to fossil fuel (Afolabi, 2008).

Biodiesel fuel (BDF) is defined as the mono-alkyl esters of long-chain fatty acids synthesized by transesterification of triglyceride in vegetable oils or animal fats with alcohol, and is therefore a renewable energy resource (Willson, 2001). BDF biodiesel (mixture of mono-alkyl ester of

saturated and unsaturated long chain fatty acids) is superior to conventional diesel (mixture of paraffinic, naphthenic and aromatic hydrocarbons) in terms of its sulphur content, aromatic content and flash point which is evident in their basic properties, affecting engine performance and pollutant emissions.. It is essentially sulphur free and non-aromatic while conventional diesel can contain up to 500 ppm SO_2 and 20–40 wt% aromatic compounds. These advantages could be a key solution to reduce the problem of urban pollution since transport sector is an important contributor of the total gas emissions.

2.0 MATERIALS AND METHODS

2.1 The study area

The study was conducted at Sokoto Energy Research laboratory, Usmanu Danfodiyo University, Sokoto. The University is located in Dundaye district of Wamakko Local Government Area of Sokoto State. The State lies within the Sudan savannah belt and is located in the North West geographical zone of Nigeria within longitude $11^0$3-$13^0$50E and latitude 4^0-6^0 40^1N. It covers a land area of 2,648.48 square kilometres. There are two distinct seasons in the State; the rainy season which starts usually around May and last till around September and the dry season from October to April. The annual rainfall is frequently erratic, poorly distributed and varies from 500 mm to 1300 mm per annum (SMANR, 1998).

2.2 Sample collection and preparation

Ripe fruits of watermelon were purchased from Kasuwar-daji in Sokoto north local government area, Sokoto. Fresh seeds of sesame were purchased from Sokoto central market. The two were taken to departmental herbarium for authentication by a taxonomist where voucher specimen was deposited at the herbarium. Similarly, a sterile sharp knife was used to cut the ripe watermelon fruit and the seed were removed carefully and the pulp of the fruit was discarded. The spoilt/bad seeds were also removed from the fresh sesame seed. Both water melon and sesame seeds were air dried for two weeks, and later carefully blended using an electric blender to remove unwanted particulate substances and the final product was an averagely coarse aggregate.

2.3 Biodiesel Production from Two Step Acid-Base Trans-esterification

Pre-treatment of Seed Oil

This was 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 glycerine 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 other to enhance optimum separation of the vegetable oil into its corresponding esters (Christ, 2007).

2.3.1 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°C to remove the excess methanol.

2.3.1.1 Trans-esterification process

1.0 Mixing of alcohol and catalyst

Procedure:

0.5 g 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 (Christ, 2007).

2.0 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 shacked vigorously for 1 hour in order to obtain a homogeneous mixture.

2.4 Separation of the Biodiesel and Glycerine:

2.4.1 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 product exist which are glycerine and biodiesel, in which the biodiesel was formed at the top and the glycerine at the bottom. To achieve full separation of the mixture, the quantity of the glycerine produced varies according to the oil used, the process involved and the amount of excess alcohol used. Both the glycerine 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 glycerine 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 (Christ *et al.,* 2007).

2.5 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). Percentage of biodiesel yield, colour, Acid value, iodine value, saponification value, percentage free fatty acid, ash content, moisture content and cetane number of the biodiesel were determined.

2.5.1 Percentage yield determination of biodiesel

The quantity of biodiesel yield was determined using the formula $\%\ Biodisel\ produced = \frac{weight\ of\ biodiesel}{weight\ of\ seed\ used} x\ 100$

Colour

The colour was determined by Oganonetip method, where ten people were called up to visualize the physical appearance of the biodiesel (AOAC, 1975).

2.6 Determination of acid value of the oil

Acid value of the oil was determined using the method of AOAC (1975). Alcoholic KOH (0.5 M) was standardized using 1 M H_2SO_4. An aliquot (2 g) of the n-hexane oil extract was weighed into a conical flask. This was followed by the addition of 20 ml of hot neutralized ethanol and the mixture boiled on a water bath. On addition of the hot neutralized ethanol to the oil, the pink solution became colourless due to the acid content of the oil. The solution was then titrated while hot to neutrality with 0.5 M alcoholic KOH using phenolphthalein as indicator. The titre values were taken after triplicate run and the mean value recorded. The acid value was then calculated using a conventional formula below:

Acid value = $\frac{VXNX56.1}{M}$

where;

V = volume of ethanolic KOH used

N = molarity of ethanolic KOH used

M = weight of oil.

2.7 Determination of ash content of the biodiesel

Ash content of the biodiesel was determined using the method of AOAC (1984). 1g of the sample was weighed into porcelain crucibles which have been washed, dried in an oven at

100°C, cooled in a desiccator and weighed. They were then placed inside a muffle furnace and heated at 600°C for 4 hours. After this, they were removed and cooled in a desiccator and then weighed.

% Ash = $\frac{A-B}{C}$x$\frac{100}{1}$ = weight of crucible + ash

where;
A= weight of crucible
B= weight of original sample

2.8 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).

Procedure: The oil sample was poured into a dry glass- stopper 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. 10 ml of carbon tetrachloride and 20 ml 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. 15 ml of potassium iodide solution and 100 ml of water was mixed and titrated with 0.1 M 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.

Calculation:

Iodine value = $\frac{(B-S)\ (1.269XN)}{weight\ of\ sample\ (g)}$

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

2.9 Determination of saponification value

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

2.9.1 Procedure:

One (1) g of the oil sample was added into a conical flask containing 25 ml of alcoholic potassium hydroxide solution. The flask was sealed and heated in the oven for 5 minutes at 105^0C. 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). These were used to calculate the saponification value of the oil (Christ, 2007).

$Saponification\ value = \frac{(B-S)X0.5X56.10}{weight\ of\ sample}$

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

2.10 Determination of the cetane number of the biodiese

This is a measurement of the combustion quality of diesel fuel during compression ignition. The cetane number of the biodiesel was calculated via the use of empirical formula in the literature using the result of saponification number (SN) and the iodine value (IV) of biodiesel (AOCA, 2000)

Calculation:

Cetane Number (CN)=46.3+(5458/S)-(0.225x1)

where; S and I stand for saponification and iodine value respectively.

2.11 Determination of percentage free fatty acids (FFA) of the oil.

Ten (10) ml – 2 g of well-mixed sample was accurately weighed into conical flask after which 10 ml of neutralized 95%ethanol and phenolphthalein were added. This was then titrated with 0.1M NaOH, shaking constantly until a pink colour persisted for 30s. These were calculated using the formula below.

%FFA = $\frac{VXMx2.82}{w}$

where;
V = volume of NaOH,
M = Molarity of NaOH,
W = weight of oil, 2.82 = conversion factor for oleic acid.

3.0 Results

3.1 Physicochemical properties of sesame seeds biodiesel and watermelon seeds biodiesel

Result of the physicochemical characterization of the biodiesel has been presented in the Table 1 below:
Quantity of biodiesel produced;

Sesame seed biodiesel yield= $\frac{weight\ of\ biodiesel\ produced\ (\%)}{weight\ of\ sesame\ seed\ used} x \frac{100}{1}$

=58.6 g $\frac{58.6}{100\ g}$x$\frac{100}{1}$= 58.6 % of sesame seeds.

Watermelon seed biodiesel yield (%) =

$\frac{weight\ of\ biodiesel\ produced}{weight\ of\ watermelon\ seed\ used}x\frac{100}{1}$

=$\frac{48.4\ g}{100\ g}$ x$\frac{100}{1}$ = 48.6 % of watermelon seeds.

Table 1: Physicochemical properties of sesame biodiesel and watermelon seeds biodiesel with the ASTMD and EN standards

Parameters	Sesame Biodiesel	Watermelon Biodiesel	ASTMD 6751	EN
% of biodiesel yield	58.6	48.4		
Colour	Golden yellow	Light yellow		
Iodine value (gI_2/100 g)	60.1	51.6	_____	120 ma
Acid value	0.16	0.14		
mg/(KOH/g)	Trace	Trace		
Ash content				
Cetane number	69	68	47 min	51 min
Free fatty acid	0.20	0.20		
Saponification (mg/g)	151	163		

KEYS; ASTMD- American Standard Test method for diesel, EN- European Standard, Min- minimum, Max- maximum

4.0 DISCUSSION

The percentage biodiesel yield was 58.6% of sesame biodiesel and 48.4% of watermelon biodiesel while the colour of the biodiesel obtained was light yellow and golden yellow from sesame and watermelon seed respectively. The result of this study was not in agreement with reported 88.9 % on a study conducted with *Jatropha curcas* by Abdulmalik (2009), and this could be attributed to the species disparity.

Iodine value could be described as the measure of unsaturation of fats and oil. Thus, high iodine value of fats and oils indicates high degree of unsaturation and susceptibility to rancidity. In this study sesame seeds biodiesel has higher iodine value (60.1gI_2/100g) compared to those of watermelon (51.6 gI_2/100g) which all falls within the ASTM 067519 (130 max) and EN14214 (130 max). High iodine value is vital for biodiesel production due to the fact that heating highly saturated fatty acids results in poor polymerization of glyceride which could reduce the formation of deposits in engines, reduces the rancidity in the oil and makes it possible to preserve the oil and its biodiesel for long period of time.

The acid value of sesame seeds biodiesel was 0.20 mg/KOH/g and that of watermelon oil was 0.14 mg/KOH/g; each could be considered to be in accordance with the ASTMD6751 standard (0.5 max). Acid value measures the presence of corrosive free fatty acids and oxidation products. This is actually an important variable in considering the quality of biodiesel because the lower the free fatty acid, the better the quality of oil (Bailey, 1982).

Similarly saponification value of Sesame seed biodiesel was 151mg/g. The saponification value obtained from Sesame seed biodiesel is lower than that obtained from watermelon seed biodiesel 163mg/g and those of common seeds such as, *J. curcas* (202.40 mg/g), neem seed oil (195 mg/g) (Singh and Siroj, 2009), fluted pumpkin (151.48mg/g) and 257mg/g for coconut (Kyari, 2008), but higher than that of Pumpkin seed oil (44.88 mg/g), African bean oil (28.05 mg/g) (Eze, 2012).

The percentage free fatty acids of sesame and watermelon seeds biodiesel is 0.20 and 0.20 respectively. These lower percentage of free fatty of the biodiesel shows that the biodiesel is of great quality because the lower the free fatty acid, the better the quality of the biodiesel (Bailey, 1982). Vegetable oils containing high free fatty acids have significant effects on the trans esterification with methanol using alkaline catalyst. It interferes with the separation of fatty acid ester and glycerols (Ma and Marcus, 1999).

Biodiesel produced from *Sesame* seed oil and watermelon oil had cetane number of 69 and 68 respectively which is well above the minimum value of the ASTM D6751 (47 minimum) and EN 14214 (51 minimum) international biodiesel fuel standards. Cetane number (CN) is widely used as diesel fuel quality parameter related to the ignition delay time and combustion quality. High cetane numbers help to ensure good cold start properties and minimize the formation of white smoke. The CN of an individual compound depends upon the structure of the compound. The CN increases with an increasing chain length, for instance, methyl esters of lauric (CN 67), palmitic (CN 86) and stearic (CN 101) acids, and increasing saturation of fatty acid, for instance, methyl esters of stearic (101), oleic (59), linoleic (38) and linolenic (23) acids (Knothe *et al.*, 2006). The cetane number of *Sesame* seed oil biodiesel was found to be higher than some conventional biodiesels such as soybean oil biodiesel (Ramos *et al.,* 2009), sunflower oil biodiesel (Rashid *et al.*, 2008). This makes it a very good diesel for high speed diesel engine. Thus, the higher cetane number of *Sesame* seed oil biodiesel when compared to petro diesel (49) and other conventional biodiesel is due to long chain length of fatty acid alkyl ester of *Sesame* seed biodiesel (C_{16}), (C_{18}) ($C_{18:2}$), (C_{20}), (C_{30}) and higher saturated fatty acid alkyl ester (99.01%). Very small amount of ash was obtained from the sesame and watermelon biodiesel (trace) in which the ash content obtained could not be measured by weighing balance. In a similar research carried out on neem, the ash content was 11.10% (Zaku *et al.* 2012). These differences in results can be as a result of difference in grams of sample used or variety of seed.

5.0 CONCLUSION

Due to high availability of the seed, ability of the seed to grow easily, it can be considered a good resource for industrial process. The oil yield of the seed which is quite high when compared to other oil yielding seeds can be advantageous when used in the production of biodiesel. Some of the fuel properties investigated had shown, to a reasonable extent, that quality biodiesel can be produced from sesame and watermelon seeds. Hence improving sesame and watermelon cultivation more than its present state can be considered as to facilitate their incorporation as an additional feedstock for biodiesel.

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