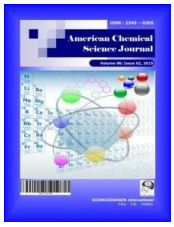

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Production of Biodiesel from Calabash Seed Oil

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Authors' contributions

This work was carried in collaboration among the authors. Authors HI and YT interpreted results, compiled the write up and supervised the work. Authors UAA and KON extracted and refined the oil. Authors JNA, DCN and OBA did the esterification and transesterification. Authors ASZ and SA wrote the script. All authors read and approved the final manuscript.

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ABSTRACT

Biodiesel has gained support and recognition as a fuel to replace and blending agent with fossil diesel. In search of non-edible seed oil feedstock that can be used for biodiesel production, an investigation was carried out with calabash seed oil. This is the type of calabash used by Arugungun fishers and Fulani women fresh cow milk hawkers. The seed yielded 39.3% oil by mechanical press. The oil was transesterified with methanol using heterogeneous catalyst (magnesium oxide supported by alumina) with catalyst loading of 0.6, 0.8, 1.0, 1.2 and 1.4% (w/w of oil) at 60ºC for 60 minutes. The products had esters content of 90.43, 77.92, 93.64, 96.00 and 83.48% respectively. The viscosity falls between 5.0 and 5.7 mm^2/s which is within ASTM and EN standards. The biodiesel yield of 61.8, 62.3, 69.7, 69.5 and 78.1% were also recorded. This oil can be a potential for biodiesel production.

Keywords: Biodiesel; calabash oil; potential; production.

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1. INTRODUCTION

Biodiesel is a bio-based diesel fuel that has received worldwide acceptance as a substitute and also a blending agent to fossil diesel. It is a mono-alkyl ester which is produced mainly by transesterification of vegetable oils or animal fats. This reaction is carried out by heating feedstock (oil or fat) and alcohol with suitable catalyst. Over time, edible oils were used but this has resulted to food crisis causing the research on biodiesel production to shift to non-edible seed oils and even the waste oils [1]. The used oils are cheap but require a lot of effort and cost to refine them for good biodiesel production as they contain high free fatty acid value. The fatty acids cause the formation of soap which affects the progress of the reaction and also the separation of the products [2]. Used or waste oils have to be filtered and refined before it can be transesterified. The raw vegetable oils or fats are too thick or rather have high viscosities. Transesterification therefore, thins the oils and fats or lower the viscosities.

The calabash, bottle gourd, or white-flowered gourd, *Lagenaria siceraria* (synonym *Lagenaria vulgaris* Ser.), also known as opo squash or long melon, is a vine grown for its fruit, which can either be harvested young and used as a vegetable, or harvested mature, dried, and used as a bottle, utensil, or pipe. The fresh fruit has a light-green smooth skin and a white flesh. Rounder varieties are called calabash gourds. They grow in a variety of shapes: they can be huge and rounded, small and bottle shaped, or slim and serpentine, more than a metre long. There are also the hard, hollow fruits of the calabash tree, *Crescentia cujete*, whose fruits are also used to make utensils, containers, and musical instruments [3]. In some countries, the dried shell of the fruit is used to make bowls and fruit containers, decorated with paintings or carvings. Bushel gourd is a large round gourd; 12 to 16 inches high with 20-inch diameter, when dried have approximately ½-inch thickness [4].

Already, the common edible vegetable oils are expensive; their use for biodiesel production would further increase their prices [5] and also cause food crises. Calabash also known as Lagenaria siceraria is a creeping plant found growing in Northern Nigeria [6]. This type of calabash produces large spherical fruits commonly found in Gombe, Jigawa, kebbi, Sokoto and Zamfara States in Northern Nigeria used by Arugungun fishers and Fulani women fresh cow milk hawkers is as shown Fig. 1. It is used as containers and storage vessels by some rural settlers in Northern Nigeria [6]. The center is filled with seeds that contain oil with exciting properties for cosmetic use [7]. The fruit is wild harvested, cold-pressed and filtered to obtain clear oil. Table 1 presents some of the physicochemical properties of calabash oil.

Table 1. Properties of calabash oil

Fatty acd (%)	Calabash seed	Bottle gourd seed	Lump-in-neck bottle gourd	Citrullus linatus	Citrullus colocynthis
Lauric	9.12	0.11	0.5100	0.0350	-
Capric	-	-	0.0013	-	-
Myristic	5.36	0.16	0.1640	0.0045	-
Palmitic	2.12	0.02	-	12.9000	10.10
Palmitoleic	0.01	-	0.0240	-	-
Stearic	2.54	0.10	-	7.7800	9.58
Oleic	20.20	25.90	29.5000	16.6000	18.40
Linoleic	58.20	65.80	62.2000	61.6200	60.90
Linolenic	1.70	1.08	0.0110	0.6100	0.61
Arachidic	-	0.005	-	-	-
Mono unsaturated	58.20	26.13	29.5560	16.6000	18.40
Oleic/linoleic (O/L)	0.35	0.39	0.47	0.27	0.30

Source [8]

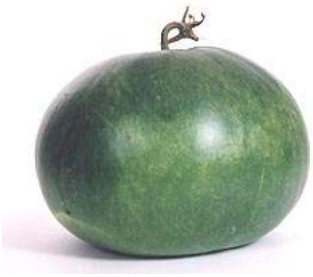

Plate 1. The most popular calabash (bushel gourd) in Northern Nigeria

The most useful part of this big spherical calabash is the shell fruit. After opening the shell, only few quantities of the seeds is reserved for planting while the remaining larger quantity is thrown away. In this investigation, the calabash seed oil was transesterified with methanol using bulk calcium oxide catalyst. The transesterifications were carried at 60ºC for 60 minutes, 13.5% methanol with 0.6, 0.8, 1.0, 1.2 and 1.4% (w/w of oil) catalyst loading. The biodiesel properties of the products were analyzed to determine its suitability for biodiesel production. The analyses of the biodiesel products carried out include; esters content, specific gravity (density), biodiesel yield and viscosity. The fatty acids content of the oil was also estimated.

2. MATERIALS AND METHODS

The materials used for this study include; conical flask, burette, magnetic stirrer, separating funnel, viscometer, density bottle, GC-MS machine and the host of others. The reagents used were analytical grade methanol, potassium hydroxide, propan-2-ol, sulphuric acid and calcium oxide catalyst.

2.1 Refining of the Feedstock

1.0 g of the calabash oil was dissolved in 25 ml propan-2-ol. After stirring, two drops of phenolphthalein were added. The solution was titrated against 0.1 M potassium hydroxide to pink colour. The acid value (free fatty acid) was calculated from the titre value. The oil was esterified with a mixture of sulphuric acid and methanol. The mass of methanol used was calculated as 2.25 x %FFA x mass of oil and that of sulphuric acid as 0.05 x %FFA x mass of oil. These were mixed and added to the oil at 60ºC [9]. The temperature was maintained at 60ºC for 60 minutes. The product was transferred into separating funnel and left to settle. The organic layer was collected at the bottom and tested for acid value again. The process was repeated washed and dried until the acid value reduced to 0.58.

2.2 Transesterification

100 ml of the refined oil was heated to 60^{o}C, a mixture of 13.5 g methanol and 0.6 g calcium oxide catalyst were added and the temperature was maintained at 60ºC for 60 minutes. The procedure was repeated with 0.8, 1.0, 1.2 and 1.4 g of the catalyst keeping other parameters constant. The products were filtered poured into separating funnel to settle. The Biodiesel was dried on hot plate to remove residual methanol.

2.3 Ester Content Test

2 ml of each sample was diluted with n-hexane. The resulting mixture was filled into a sample bottle and inserted into the GC-MS machine. The machine was run and the chemical components of the sample were analyzed. The methyl esters content was calculated from area% of the GC-MS analysis [10]. This analysis was performed on GCMS-QP2010 PLUS SHIMADZU/JAPAN in the Quality Control Unit of NARICT, Zaria.

2.4 Viscosity

100 ml beaker was filled to three-quarter of its capacity with biodiesel sample, heated to 40^{o}C 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. This analysis was carried out with Brookfield SYNCHRO LECTRIC VISCOMETER in the Department of Chemical Engineering, Ahmadu Bello University, Zaria.

2.5 Density

The sample biodiesel was cooled to 15^{o}C using piece of ice blocks. An empty relative density bottle was first weighed, reweighed when filled with water and reweighed when filled with sample biodiesel. The relative density of the sample was calculated and converted to density.

3. RESULTS AND DISCUSSION

The products were separated into three layers and the upper most layers had the largest quantity of the product. The three layers were collected separately. All the three layers of 1.0% catalyst loading were analyzed with GC-MS. The bottom layer contained alkanes ranging from decane to tridecane, alcohol such as 6, 9-

pentadecadien-1-ol and 9, 12 octadecadien-1-ol, 7-tetradecenal, diglyceride; .beta.-Monolinolein and acyl chloride; Linoleic acid chloride as presented in Fig. 1. The upper layer had methyl ester. The middle layer had 66.07% methyl esters, 1.0% free fatty acid, 7.5% alkanals, 3.6% alcohols, 11.482% epoxides, and 6.03% diglycerides as shown in Fig. 2. There was no glycerol from any of the products as usual with solid base catalyzed biodiesel production [2]. The existence of these three layers was not ascertained probably due to the presence of wax or gum.

The biodiesel yield increased steadily with increase in catalyst loading as shown in Fig. 3. The coefficient of determination of was 89% indicating that the changes in the biodiesel yield were actually responsible by the changes in catalyst loading. The methyl ester content did not exhibit the dependency relationship on the catalyst loading. This was so because its coefficient of determination was 0.7% indicating that changes in esters yields was not responsible by the changes in catalyst loading. However, the highest methyl esters content of 96.0% was obtained with 1.2% catalyst loading and the lowest was 77.9% with 0.8% catalyst loading as shown in Fig. 3. The highest yield 96% was short of 0.5% lower than the minimum EN standard of 96.5% [2]. This calabash seed oil can be used for commercial biodiesel processing.

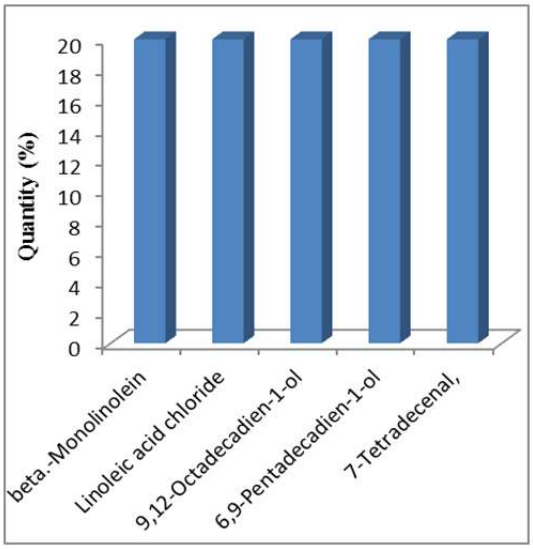

Fig. 1. Components of the bottom layer

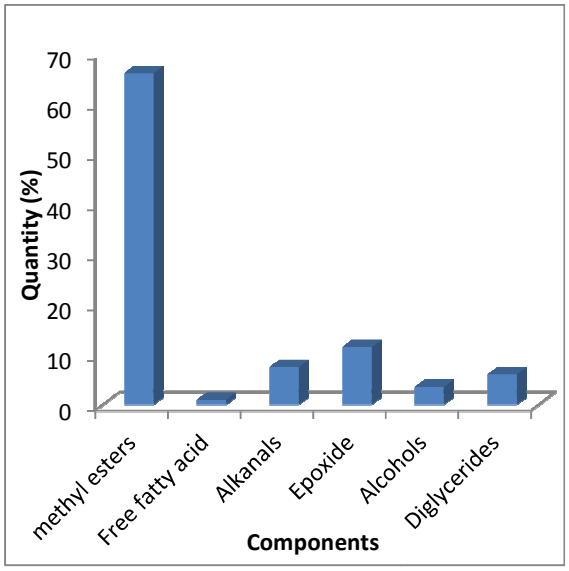

Fig. 2. Components of the middle layer

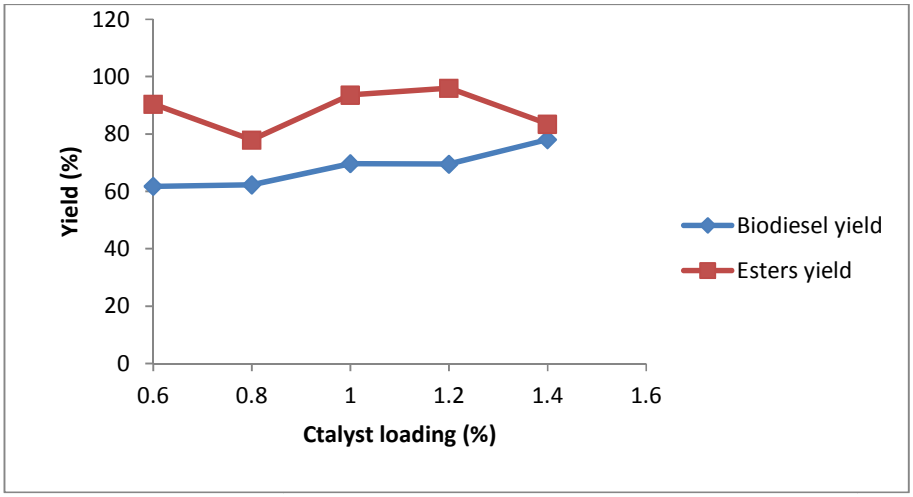

Fig. 3. Biodiesel yield with catalyst loading

The means value of the biodiesel yield and esters content (yield) were found to be 68.28% and 88.29% respectively. Also the standard deviations of the two were calculated to 5.96 and 4.20 as presented in Table 3.

The esters content of the biodiesel are tabulated in Table 3. From Table 3 the composition of saturated esters was found to be 59.98% while that of unsaturated was 40.02%. The ester with the highest composition was 18:1 (methyl oleate) composed of 36.23%. One can deduce that this calabash oil had glyceril tri-oleate or oleic acid as the highest component. From Table 3 we can draw out the possible fatty acids content of this calabash oil as presented in Table 4.

The relative oxidative rate can be estimated from Equation 1 [11]. Fig. 4 presents the comparative relative oxidative rate of the five products of bushel calabash seed oil biodiesel. The product from 0.8% catalyst loading was found to have weakest stability compared to others. The higher the oxidisability value, the less the stability of the sample. The product of 0.8% catalyst loading had highest quantity of 18:01 and 18:02 methyl esters, hence had higher tendency for oxidation.

$$OX = [0.02(\%O) + (\%L) + 2(\%Ln)]/100 \quad (1)$$

The biodiesel of this feedstock is most likely to be more stable as it contained less linolelaidate and no linoleate esters. According to Zuleta et al. [12] oxidative stability depends strongly on the concentration of linoleic and linolenic acid alkyl esters rather than on the concentration of saturated and monounsaturated alkyl esters. The oxidative rate of oleate:linolelaidate:linoleate according Christensen et al. [13] is 1:41:98. The product of 0.8% catalyst loading had the highest oxidisability and those from 1.2% and 1.4% had the least. The 0.8% catalyst loading had the highest oleate and linolelaidate (18:01 and 18:02), which accounted to its being the least stable product among others.

Table 2. Statistical analysis of biodiesel and esters yields

Catalyst loading	0.6	0.8	1	1.2	1.4	**μ**	**σ**
Biodiesel yield	61.8	62.3	69.7	69.5	78.1	68.28	
Esters yield	90.43	77.92	93.64	96	83.48	88.29	
Biodiesel yield variance σ^2	41.99	35.76	2.02	1.49	96.43		5.96
Esters yield variance σ^2	4.58	107.69	28.56	59.39	23.17		4.20

Table 3. Esters content of the biodiesel samples

MF	**Catalyst loading (%)**					**%**
	0.6	**0.8**	**1**	**1.2**	**1.4**	
5:00	0	0	0	0	9.00	1.80
8:00	0	0	0	0	0.28	0.06
10:00	5.94	4.33	6.88	5.73	6.84	5.94
13:00	6.17	5.69	6.88	5.73	6.84	6.26
14:00	0.42	0.29	0	0	0.72	0.29
15:00	6.37	4.33	6.88	5.73	6.12	5.88
16:00	17.82	17.52	12.01	16.17	18.06	16.32
16:01	0	1.26	0	0	0	0.25
18:00	5.57	5.68	3.47	13.78	10.81	7.86
18:01	28.48	49.01	48.02	37.38	18.27	36.23
18:02	1.758	3.38	1.08	1.04	1.44	1.74
20:00	1.50	3.79	0.61	5.01	0.71	2.32
20:02	0	0	1.08	0	0	0.22
21:00	4.69	0.32	0.31	0.29	0.44	1.21
22:00	16.60	4.41	12.49	4.73	5.35	8.72
22:01	0	0	0	0	9.00	1.80
24:00:00	0	0	0	0	0.28	0.06
26:00:00	4.69	0	0	4.44	5.36	2.90
27:00:00	0	0	0.31	0	0.44	0.15

Table 4. Estimated fatty acid composition of bushel gourd oil

IUPAC name	Common name	Formula	% composition
Pentanoic acid		C5:0	1.80
Octanoic acid		C8:0	0.06
Decanoic acid	Capric acid	C10:0	5.94
Tridecanoic acid		C13:0	6.26
Tetradecanoic acid	Myristic acid	C14:0	0.29
Pentadecanoic acid		C15:0	5.88
Hexadecanoi acid	Palmitic acid	C16:0	16.32
Hexadecenoic acid	Palmitoleic acid	C16:1	0.25
Octedecanoic acid	Stearic acid	C18:0	7.86
Octadecenoic acid	Oleic acid	C18:1	36.23
9,12-Octadecadienoic acid	Linoleic acid	C18:2	1.74
Eicosanoic acid	Arachidic acid	C20:0	2.32
Eicosadienoic acid		C20:2	0.22
Heinosanoic acid		C21:0	1.21
Docosanoic acid	Behenic acid	C22:0	8.72
Docosenoic acid	Brassidic acid	C22:1	1.80
Tetracosanoic acid		C24:0	0.06
Hexacosanoic acid	Cerotic acid	C26:0	2.90
Heptacosanoic acid		C27:0	0.15

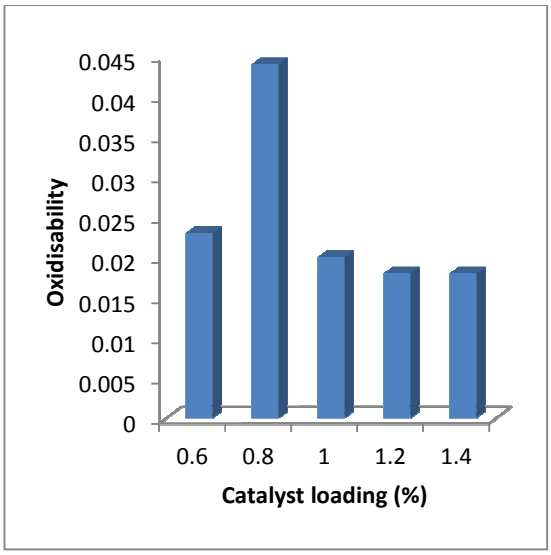

Fig. 4. Relative oxidative stability of the five products

The kinematic viscosity of all products fell within the ASTM standard as shown in Fig. 5. The ASTM standard lower and upper limit for viscosity is 1.9 and 6.0 mm^2/s respectively for biodiesel [14]. The presence of long esters of high molecular weights accounted for high viscosities of the samples [11]. Four of the products had viscosity of 5.0 mm^2/s and one had 5.7 mm^2/s; the product from 1.2% catalyst loading had viscosity slightly higher than EN standard by 0.7 mm^2/s. The EN standard upper limit for kinematic viscosity at 40ºC is 5.0 mm^2/s [14]. Viscosity of biodiesel is a very important parameter. It influences the ease of starting the engine, the spray quality, the size of the particles (drops), the penetration of the injected jet and the quality of the fuel-air mixture combustion [13]. This bushel calabash oil had good quality for biodiesel as it has high oil yield and high methyl esters content. It can surpass *Jatropha curcas* oil which has lower oil yield and very expensive.

Two products catalyzed with 0.6% and 1.4% catalyst loading had density of 0.906 g/ml while others had 0.922 g/ml as presented in Fig. 6. These values are slightly higher than upper limit of ASTM standard for biodiesel. The upper limit of density for biodiesel is 0.90 g/ml [14,15]. The presence of higher molecular weight esters could be responsible for high density. The density of the fuel is also important as it affects the quality of atomization and combustion [15]. The biodiesel density of this oil can be reduced by further work on the best method of transesterification of its oil. Degumming and dewaxing may improve its biodiesel product.

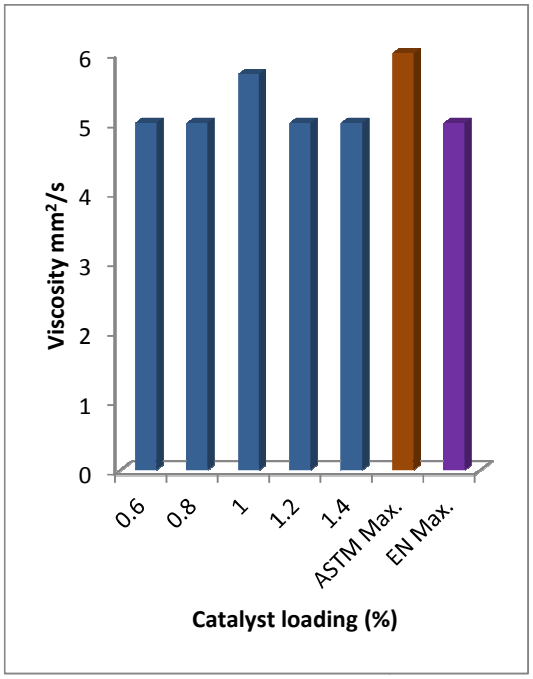

Fig. 5. Sample viscosities compared to standards

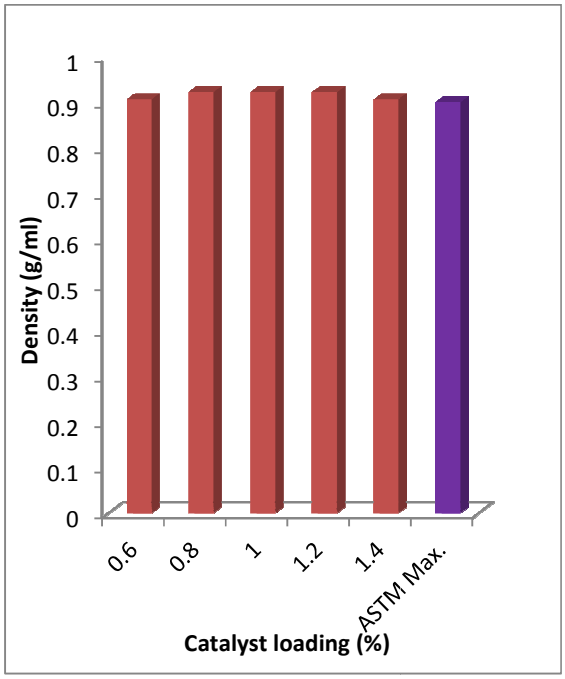

Fig. 6. Sample densities compared to ASTM standard

4. CONCLUSION

Biodiesel produced from bushel gourd calabash oil by heterogeneous catalytic transesterification had high methyl esters content of 96%, high yield of 78.1% and standard viscosity (ranging from 5.0-5.7 mm^2/s). The seed had high oil yield of 39.3%, hence it will be good for commercial biodiesel production. Its highest ester was methyl oleate with average of 36.23%. The biodiesel samples of this calabash oil had little quantity of linolelaide and no linoleate esters hence, could be more stable to oxidation. Its biodiesel product had three layers which may require degumming and dewaxing. It has the potential for commercial biodiesel processing.

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COMPETING INTERESTS

Authors have declared that no competing interests exist.

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