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Prospect of African Bush Mango, kapok, Sesame, and Avocado Seeds Oils as a Feedstock for Biodiesel Production over $CaSO_4/Al_2O_3$ Catalyst

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***Abstract**: Oils extracted from the seeds of African bush mango (Irvingiag abononsis), Sesame (Sesamum indicum), Avocado (Persea americana) and Kapok (Ceiba pentandra) were transesterified with $CaSO_4/Al_2O_3$ catalyst to biodiesel. High biodiesel yield was obtained from African Bush Mango Oil (90.54±2.01%) with the lowest yield from the Sesame (85.90±3.14%). The fatty acid methyl esters profile indicates methyl-9,12-octadecadienoate and methyl-11-octadecenoate as the major compounds in the produced biodiesels. The physico-chemical properties of the produced biodiesels (kinematic viscosity, flash point, cloud point, acid value etc) conform to the ASTM standard specification, except cetane value which is below the standard specification. The oil content of the seeds, Avocado (18.56 %), Kapok (32.90%), Sesame (56.77 %), and African Bush Mango (54.00%) was appreciable, indicating the viability of the seeds as source of oil for biodiesel production. The result obtained shows the efficacy of $CaSO_4/Al_2O_3$ as a catalyst for biodiesel production.*

***Keywords:**Biodiesel; African Bush Mango, Avocado, Transesterification, Calcium Sulphate*

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I. Introduction

It is evident that petroleum is the major source of energy that anchor industries, transportation, agriculture as well as other domestic activities such as cooking, heating etc. However, the depletion of petroleum reserves and the negative impact of fossil fuels to environmental have led to the search for renewable and alternative sources of fuel. Nowadays, biomass has been focused as an alternative energy source as it maintains the level of carbon dioxide in the atmosphere constant through the process of photosynthesis. The carbon dioxide emitted during the combustion of biomass would be absorbed during the process of photosynthesis [1]. Bio-fuels are considered as an alternative fuels that could minimize greenhouse gas emission as well as complimenting the fossil fuels [2]. The presence of oxygen molecules within the biofuel molecules makes them to have better oxidation and combustion characteristics than the fossil fuels [3]. It is evident, that there are numerous forms of renewable energy sources, but biodiesel remain most promising fuel that could be used in the existing vehicular combustion engines. Biodiesel is a liquid form of bio-fuel mostly produced from animal fat or plant-based oil via transesterification reaction with aliphatic alcohols [4]. The transesterification process is most often catalyzed with either alkaline, acidic, enzymatic or heterogeneous catalysts [5] Hydroxides and alkoxides of group IA and IIA metals (NaOH, KOH, $Ca(OH)_2$, $Mg(OH)_2$, $NaOCH_2CH_3$, $KOCH_2CH_3$ etc.) are also extensively used as catalysts for transesterification process [6]. Although efficient conversion of oil to biodiesel can be attained within a moderate reaction time with the homogeneous alkali catalysts, the recovery of the catalyst is difficult and also their activity is generally affected by free fatty acid concentration in the feedstock even in trace quantities [7]. The homogeneous acid catalysts such as sulphuric acid (H_2SO_4), hydrochloric acid (HCl), phosphoric acid (H_3PO_4) and some organic acids have also been classified as unreliable due to the problems of slower reaction rate, high reactant ratios (oil to alcohol), separation and corrosion [6]. The numerous problems associated with homogeneous catalysts stimulated researchers to explore other options with a great emphasis on conversion efficiency and greener catalyst system. Silitonga et al., [5] reported that heterogeneous catalysts have many advantages over homogeneous catalysts. It eliminates the problems of separation, corrosion, toxicity and catalyst regeneration.

Therefore, the objective of the present study is to exploit the potential of calcium sulphate ($CaSO_4$) loaded over alumina (Al_2O_3) support for the transesterification of Avocado, Kapok, Sesame and African Bush Mango seed oils.

II. Materials And Methods

The seeds of African Bush Mango and Avocado were collected from Taraba and Benue states Nigeria, while that of Kapok and Sesame were collected in Sokoto and Zamfara states, respectively. The seed kernels were sun-dried, and then ground to a powder using mortar and pestle. The oils were extracted from the powdered samples using soxhlet extractor with n-hexane as a solvent. Equation (1) was used to calculate the percentage oil yields $\text{Oil Yield}(\%) = \frac{\text{Weight of the Oil (g)}}{\text{Weight of the Sample (g)}} \text{X} 100 \ldots\ldots\ldots\ldots\ldots 1$

2.2 Catalyst Preparation:

Twenty grams (20.00g) of calcium sulphate was weighed, and then transferred into a 250 cm^3 beaker containing 50 cm^3 of distilled water. The mixture was stirred for 30min on magnetic hot plate stirrer at 300rpm, and then 80.00g of Alumina added. The mixture was stirred thoroughly while heated on a hot plate until a homogeneous mixture was obtained. The resulted mixture was dried in an oven at 105°C for 5hrs and calcined at 200°C for 2hrs in a furnace [8].

2.3 Physicochemical Properties of the Oils:

Physicochemical properties of the extracted oils (Acid value, saponification value, iodine value, FFA, and molecular weight were determined according to the method reported by Sokoto et al. [9]. The ester value was calculated using equation (2) as reported in literature [10].

$$\text{Ester Value}(\%) = \text{Saponification Value} - \text{Acid Value} \ldots\ldots\ldots\ldots\ldots 2$$

2.5 Transesterification Process:

Prepared solution of methanol (50 cm^3) and $CaSO_4/Al_2O_3$ (1g) was added into 250 cm^3 of the warmed oil in a 500 cm^3 round bottom flask. The flask was placed into a thermo-set water bath at 60°C for resident period of 6hrs; the flask was shaken intermittently to ensure homogeneity of the reacting mixture [11]. At the end of the experimental time, the content in the flask was transferred into a separating funnel and allowed to settle for 24hrs. The glycerol was separated from the biodiesel using separating funnel while the catalyst was separated using a centrifuge. The produced biodiesel was washed four times with warm distilled water (50^0C) for removal of any residual glycerol, methanol, catalyst, and soap; then dried over anhydrous sodium sulphate. The percentage biodiesel yield was calculated using equation (3) as reported in literature [12].

$$\text{Biodiesel Yield}(\%) = \frac{\text{Weight of the Biodiesel (g)}}{\text{Weight of the Oil (g)}} \text{X} 100 \ldots\ldots\ldots\ldots\ldots 3$$

2.6 Fuel Properties of the Produced Biodiesel:

Specific gravity of the produced biodiesels was determined according to the method reported Ved and Padam [13] API gravity was calculated from specific gravity reported by Gerpen *et al.*, [14]. Equation (4) was used to calculate the cetane number of the samples from saponification and iodine values [15].

$$\text{Cetane Nunber} = 46.3 + \frac{5458}{SV} - 0.225(\text{IV}) \ldots\ldots 4$$

The kinematic viscosity was determined according to ASTM D445 method. The viscometer was inserted into a thermo-set water bath (40 ^oC) and was allowed to stand for 30mins. The sample was pumped into the capillarity tube of the viscometer and allowed to remain in the bath until it reached the test temperature (40^0C). The free follow of the sample from meniscus to knob through the viscometer was measured with respect to time. The procedure was repeated three times and average value was taken. Equation (5) was used to calculate the kinematic viscosities of the samples [11].Kinematic Viscosity (mm^2/sec)=C×t…….5

Flash point, cloud point, water and sediments, sulphur content was determined according to ASTM methods as cited in Indhumathi *et al.,* [11]

2.7 Fatty Acid Methyl Ester Analysis:

The Fatty Acid Methyl Ester analysis was performed by using GC-MS-Q2010 PLUS. 2μL of biodiesel sample was injected into the Elite column-5MS. The injection was performed in split mode (10:1). The oven temperature was initially held at 140ºC for 5min, later increased to 240ºC at 4ºC/min, and then held for 5min. The injector, transfer, and source temperature were set at 250ºC, 200ºC and 150ºC, respectively. The carrier gas was helium and the total scan time was 35min [16].

III. Results And Discussions

The percentage oil yield obtained showed that the seeds of sesame (56.77±2.66) and African bush mango (54.05±3.35) have the highest oil yield compared to the seeds of the Kapok (18.56±1.54) and Avocado (18.56±1.54). The percentage oil yield of the seeds is appreciable which indicate that the seeds could be good sources of oil which could be used for biodiesel production. Avocado seeds have the least oil content which implies that its oil content is not appreciable in comparison with kapok, sesame, and African bush mango. High oil yield is one of the factors that determine the viability of feedstock as potential raw material for biodiesel. The high the oil content of the seeds the most likely it is profitable for biodiesel production.

3.1 Physicochemical Properties of the Oils:

Physicochemical properties determine the oil quality as well as its possible applications. These properties include acid value, saponification value (SV), iodine value, free fatty acid, ester value and molecular weight (MW). The results of physicochemical properties are presented in Table 1.

Table 1: Physicochemical Properties of the Oils

Properties	Avocado Oil	Kapok Oil	Sesame Oil	Bush Mango Oil
Acid Value (mgKOH/g)	7.56±0.60	18.70±0.85	5.30±0.24	7.40±0.76
SV (mgKOH/g)	186.6±7.19	193.8±10.60	187.5±8.23	195.1±8.85
Iodine Value (gI_2/100g)	82.00±2.23	79.77±4.51	75.20±3.14	61.90±2.61
Free Fatty Acid (%)	3.78±0.05	9.35±0.36	2.65±0.11	3.70±0.58
Ester Value	178.99±12.68	175.10±10.15	182.20±16.70	187.73±13.48
M W (g/mol)	940.26±23.32	906.51±28.13	935.69±25.65	900.59±26.77

The values are expressed as mean ± standard deviation of the replicate measurements.

3.3 Percentage Biodiesel Yield:

Transesterification African bush mango oil with $CaSO_4/Al_2O_3$ resulted to higher percentage biodiesel yield (90.54±2.01%) in comparison to Avocado, kapok and sesame oils with biodiesel yield of 88.73±0.98%, 87.05±0.70%, and 85.90±3.14% respectively. The biodiesel yield obtained is comparable to the maximum biodiesel yield (81%) reported from milk bush transesterification using calcined snail shell as catalyst [17]. Similarly, Birla et al. [18] reported biodiesel yield of 87.28% from the transesterification of waste frying oil using calcined snail shell as a catalyst Hence $CaSO_4/Al_2O_3$ could also be a good catalyst for transesterification reaction. Its catalytic activity could be due to its high ability to withstand catalyst poison [6].

3.4Fuel Parameters of the Produced Biodiesels:

The biodiesel fuel properties describe the quality of biodiesel fuel. The results of fuel properties of the produced biodiesel (Table 2) indicates that the specific gravity of the produced biodiesels were within the range of 0.863 to 0.980 which correspond to the specific gravity of a biodiesel fuel range (0.86 to 0.90) [19]. Viscosity measures the internal friction or resistance to flow of a liquid fuel. The viscosities of the produced biodiesels were significantly different with African Bush mango (5.70^a ±0.40) having significantly higher kinematic viscosity than the other biodiesels Avocados (2.42^c ±0.03), Kapok (4.32^b ±0.02), sesame (3.35^b ±0.03; though all the viscosities fell within the ASTM range (1.9 - 6.0 mm^2/sec @ 40ºC). The conformity of the viscosities values obtained from the present study with standard specification for biodiesel infers that the oil from feedstock could be suitable for biodiesel production, likewise the used catalyst. The flash points of the produced biodiesel are below the maximum limit (Table 2) prescribed by ASTM. Thus it can be safely handled and stored. The cetene values of the produced biodiesel (Table 2) are lower than the minimum cetane number prescribed in ASTM D6751 (47) indicating that they will have shorter ignition delay. The pour point of the produced biodiesel conforms to ASTM D6751 (-15ºC to 16ºC) specification. This indicates that the fuel can flow freely through pipes even at very low temperatures. According to United States biodiesel standard (ASTM D6751), the content of water and sediment in biodiesel must be less than 0.05% volume by volume. From the result obtained, it is clear that the content of water and sediment in accordance with American standard.

Table 2: Fuel Parameters of the Produced Biodiesels

Parameter	ASTM Standard	Avocado	Kapok	Sesame	Bush Mango
S.G	0.86 - 0.90	$0.887^{b} \pm 0.009$	$0.868^{b} \pm 0.001$	$0.980^{a} \pm 0.05$	$0.883^{b} \pm 0.003$
API Gravity	-	$28.03^{c} \pm 0.94$	$31.52^{b} \pm 0.12$	$23.14^{b} \pm 0.59$	$28.75^{d} \pm 0.11$
Diesel Index	-	$30.27^{c} \pm 1.21$	$34.04^{b} \pm 0.04$	$24.99^{b} \pm 0.29$	$31.05^{c} \pm 0.96$
Cetane Number	47 min	$31.79^{c} \pm 0.56$	$34.51^{b} \pm 0.19$	$27.99^{b} \pm 0.67$	$32.36^{c} \pm 0.16$
K V(mm^2/sec)	1.9- 6.0	$2.42^{c} \pm 0.03$	$4.32^{b} \pm 0.02$	$3.35^{b} \pm 0.03$	$5.70^{a} \pm 0.40$
Flash Point^{0}C	93 **m**in	$150^{c} \pm 2.00$	$140^{c} \pm 3.00$	$137^{b} \pm 2.00$	$133^{b} \pm 1.00$
Cloud Point^{0}C	-3 - 12	$6.30^{c} \pm 0.10$	$3.50^{a} \pm 0.10$	$6.70^{a} \pm 0.30$	$2.50^{a} \pm 0.10$
Pour Point^{0}C	-15 - 16	$-5.40^{c} \pm 0.30$	$-5.00^{c} \pm 0.2$	$-2.70^{b} \pm 0.10$	$-5.30^{b} \pm 0.20$
A V(mgKOH/g)	0.05 max	$0.36^{a} \pm 0.01$	$0.97^{a} \pm 0.05$	$0.07^{b} \pm 0.02$	$0.23^{b} \pm 0.015$
W S (%)	0.05 max	0.02^{b}	0.02^{b}	0.05^{a}	0.02^{a}
Sulphur (%)	0.05 max	$0.03^{a} \pm 0.002$	$0.03^{a} \pm 0.01$	$0.04^{a} \pm 0$	$0.04^{a} \pm 0.01$
I V(gI_2/100g)	-	$62.20^{a} \pm 0.60$	$73.10^{a} \pm 1.20$	$53.50^{a} \pm 0.50$	$58.30^{a} \pm 0.80$

Values on the same column with the same superscript are not significantly different while those with different superscript show a significant difference at 95% confidence intervalIV = iodine value; KV= Kinematic viscosity; AV= Acid value; WS= water and sediment

3.5 Fatty Acid Methyl Ester of the Produced Biodiesels

The profile of fatty acid methyl ester (Figure 1) showed that the relative percentage area covered by ester compounds are 61.66%, 58.88%, 81.42% and 64.92% for Avocado, Kapok, Sesame and African Bush Mango, respectively. The profile revealed that all the four samples can be used as raw materials for biodiesel production since the percentage of the ester compounds (biodiesel) are dominant over the non-ester compounds. The methyl-11-octadecenoate is the most abundant fatty acid methyl ester in Avocado, Kapok and Sesame oils biodiesel with relative percentage area of 11.58%, 15.75%, and 16.12% respectively, while methyl hexadecanoate is the most abundant fatty acid methyl ester in African bush mango oil biodiesel with relative percentage area of 10.13%. The relative percentage area covered by saturated compounds are 39.93%, 35.55%, 42.45% and 37.37% for avocado, kapok, sesame and African bush mango, respectively. This shows that the dominant and majority of ester compounds in all four samples are not unsaturated as they contain Carbon-carbon single bond in their structures. It has been suggested by many researchers that saturated short chain esters are most suitable for biodiesel. Polyunsaturated esters are not required in biodiesel used as fuel due to their high tendency to polymerize and causes blockage in engine injection system [20].

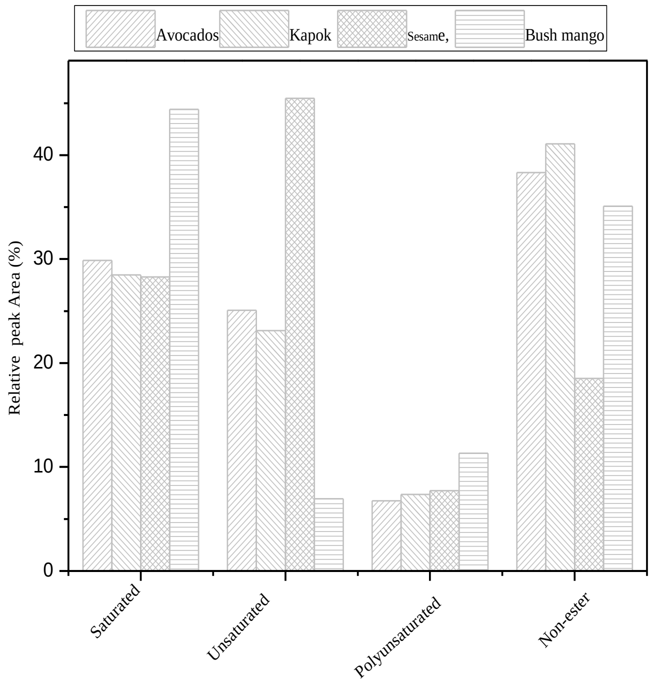

Figure 1: Class of Fatty Acid Methyl Esters Profile of the Biodiesels Produced

IV. Conclusions

The results obtained in this study have shown that heterogeneous catalyst calcium sulphate over alumina ($CaSO_4/Al_2O_3$ can be used for transesterification reaction of seeds oil of African bush mango, Sesame, Avocado, and Kapok. The study also revealed that the quality of the produced biodiesel conform to the ASTM limits, indicating that all the four samples are a good substrate for biodiesel production.

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