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Synthesis and Physico-chemical Studies of Base Catalyzed Methanolysis of Some Virgin Tropical Seed Oils

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ABSTRACT

The physico-chemical characterization of *Prunus amygdalus, Dacryodes edulis* and *Chrysophillum albidium* seed oils were investigated, together with their methyl esters. The vegetable oils were extracted by applying the solvent extraction method, using n-hexane. *Prunus amygdalus* had the highest oil yield (60.1%), followed by *Dyacrodes edulis* (55.76 %) and least from *Chrysophillum albidium* (13.67%). The oils and their biodiesel were then analyzed for acid value, free fatty acid, specific gravity, ash content, iodine value, peroxide value, saponification value, kinematic viscosity, flash point, smoke point, titre value, cloud point, moisture content and refractive index. Accordingly, *Dyacrodes edulis* seed oil had the highest acid value of 6.57 and required two-step transesterifictaion. The produced biodiesels were discussed in the light of ASTM D 9751, ASTMD 6751 and DIN 14214. These showed yields of 94.36%, 93.03% and 86.49%, cetane numbers of 70.40, 55.20 and 64.57 and calorific values of 31,178.39 KJ/kg, 34,421.50 KJ/kg and 32,838.38 KJ/kg for *Prunus amygdalus, Dacryodes edulis* and *Chrysophyllum albidium,* respectively. Other fuel-related properties showed highly improved qualities upon transesterification and compared well with ASTM and EU standards. The overall results showed that the seed oils are viable for biodiesel production.

***Keywords*:** Vegetable oils, Physico-chemical Parameters, Transesterification; Biodiesel, Extraction

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1. INTRODUCTION

Direct use of vegetable oil as fuel for diesel engine has been observed to cause particle agglomeration and injector fouling due to its high viscosity and low volatility that is about 10 to 20 times greater than the values obtained from petroleum diesel. There are four techniques applied to reduce the high viscosity of vegetable oils and they are: dilution with pure ethanol or diesel fuel, micro emulsion with immiscible liquids, pyrolysis or thermal degradation of vegetable oils and transesterification. Among all these methods, transesterification seems to be the best option since the process can significantly reduce the high viscosity of vegetable oils (Fan, 2008). Furthermore, the physical properties of biodiesel produced by this simple process are very close to the petroleum diesel fuel. Transesterification is the displacement of alcohol from ester by another alcohol in process similar to hydrolysis except that alcohol is employed instead of water (Srivatava and Prasad 2000). The transesterification process consists of a sequence of three consecutive reversible reactions which include conversion of triglycerides to monoglycerides. The glycerides are converted to glycerol and yield one ester molecule in each step. Since this reaction is reversible, excess amount of alcohol is often used to help drive the equilibrium towards the right. In the presence of excess alcohol, the forward reaction is pseudo-first order reaction and the reverse reaction is a second order reaction. Equation 1-3 consists of the sequential process while Equation 4 is the summary of the processes.

$$\text{Triglyceride (TG)} + \text{R'OH} \underset{K_2}{\overset{K_1}{\leftrightarrow}} \text{Diglyceroide (DG)} + \text{R'COOR}_1 \tag{1}$$

$$\text{Diglyceride (DG)} + \text{R'OH} \underset{K_4}{\overset{K_3}{\leftrightarrow}} \text{Monoglyceride (MG)} + \text{R''COOR}_2 \tag{2}$$

$$\text{Monoglyceride (MG)} + \text{R'OH} \underset{K_6}{\overset{K_5}{\leftrightarrow}} \text{Glycerol (GL)} + \text{R'''COOR}_3 \tag{3}$$

$$\begin{array}{lcccccl} CH_2OCOR & & & & CH_2OH & & R'COOR \\ | & & & & | & & \\ CHOCOR & + & 3ROH & \leftrightarrow & CHOH & + & R''COOR \\ | & & & & | & & \\ CH_2OCOR & & & & CH_2OH & & R'''COOR \end{array} \tag{4}$$

Triglycerides ester in oil **Alcohol** **Glycerol** **Fatty acid alkyl ester (FAAE)**

The choice of the catalyst and the nature of alcohol determine the type of initial species and the nature of Fatty Acid Alkyl Ester (FAAE) to be formed. Equation 5-9 shows the conventional mechanism of transesterification reaction process.

Mechanisms of the Transesterifiction Reaction

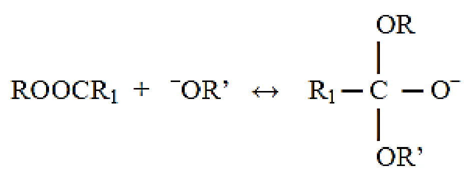
Mechanism of the transesterifiction reaction with an alkaline catalyst

Pre-Step $^{-}OH + R'OH \leftrightarrow R'O^{-} + H_2O$ (5)

or

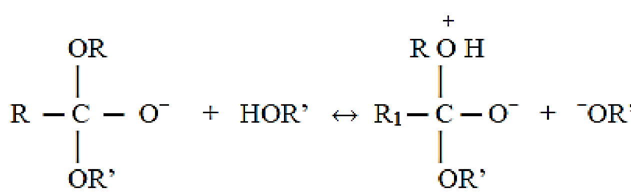
$NaOR' \leftrightarrow R'O^{-} + Na^{+}$ (6)

Step 1



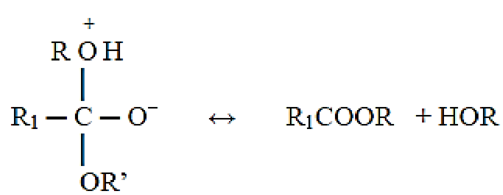
(7)

Step 2



(8)

Step 3



(9)

where: R-OH – triglycerides, R_1 – long alkyl group and R' – short alkyl group.

The transesterification process involves the use of vegetable oil; hence, efforts are geared towards harnessing vegetable oil sources from several tropical plants to promote the application of renewable energy policies in the world oils but oils that are not staple foods are preferable to prevent food-fuel crises.

Almond plants are included in the family *Rosaceae* in addition to *promoideae* (apples, pears), *prunoideae* (apricot, cherry, peach and plum) and *rosoideae* (blackberry, strawberry) fruits (Giwa and Ogunbona, 2014). There are two major varieties of almonds, the bitter almond (*Prunus amygdalus* "amara") and the sweet almond (*Prunus amygdalus* "dulcis") used mainly for culinary purposes and making of oils and flavourings respectively (Agunbiade and Olanlolukun, 2006). Sweet Almond (SA) fruit consists of three or correctly four portions of kernel or meat, middle shell, outer green shell cover or almond hull and a thin leathery layer known as brown meat or seed coat (Ali *et al.*, 2010).

Giwa and Ogunbona, 2014, has reported that *Prunus amygdalus dulcis* seed contains 51.45% oil, and yielded 85.90% biodiesel with oleic acid of 69.7%, linoleic acid of 18.2% and palmitic acid of 9.3% as predominant fatty acids. They reported that the fuel characteristics (cloud point; -3 °C and pour point; 9 °C) were within the limit of EN14214 and ASTMD6751 biodiesel standards. Sweet almond tree is predominant in the south eastern and south southern parts of Nigeria where they are basically grown for ornamental purposes. In these areas, the fruits litter the environment and are either picked up by children or disposed of as wastes and as such their use as feedstock for biodiesel production would also serve as a waste disposal option in these areas.

African Star Apple (ASA) is one of the indigenous wild fruit trees with enormous potentials for establishment (Ureigho and Ekeke, 2010). It belongs to the family of sapotaccea and naturally occurs in Nigeria, Uganda, Niger Republic, Cameroon and Cote d'ivore (Adewusi and Bada, 1997). In Nigeria it is referred to as *Udara in Igbo and Agbalumo* in Yoruba. It grows as a wild plant which has up to 800 species and make up almost half of the order Ebernales and has become a crop of commercial value in recent times (Oboh *et al.*, 2009; Ehiagbonare *et al.*, 2008). It is an evergreen tree that grows up to 40m high and about 2m in girth with a straight-long fluted bole with small buttress of the base (Jayeoba *et al.*, 2007). It is found mainly in the rural and urban centres in the month of December to April (Audu *et al.*, 2013).

The fruit when ripe is ovoid to sub-globose, pointed at the apex up to 6cm long and 5cm in diameter with an orange to golden yellow skin or peel. Within the pulp are three to five seeds which are not usually eaten. The seeds are dark brown shiny, obliquely ollipsoid to ovoid up to 2.8cm long and 1.2cm wide; its coat is hard, bony-shiny and dark brown when broken reveals white colored cotyledons. Its leaves are elliptic to oblong (Emmanuel and Francis, 2010). The seed oil of ASA has rarely been reported for industrial purposes though it has been reported that its seed has an oil content between 7 – 25%. It is among the underutilized fruits in Nigeria.

The African Pear (AP) otherwise called African plum or Safou, locally called *ube* among the Igbo's in southern Eastern part of Nigeria belongs to the family of Burseraceae and botanically known as ***Dacyrodes eludis***. It is indigenous fruit tree grown in humid low lands and plateau regions of West central African and Gulf of Guinea country (Ogunsuyi 2015; Isaac, 2014). In south eastern Nigeria, the trees are grown around homesteads and flowering takes place from January to April with the major fruiting season between may and October. It is an annual fruit of about 3 cm in diameter and contains a leathery shelled stone surrounded by a pulpy pericarp of about 5 mm thick. It is this portion that is eaten either raw or cooked and the seeds discarded (Bull and George, 2015; Ogunsuyi, 2015).

Besides the pulp contains 48% oil and a plantation can produce 7-8 tonnes of oil per hectare (Awuno *et al.,* 2002; Shikha and Rita, 2012). The pericarp has the characteristics of butter and contains 48% oil in the pulp. Ogunsiyi *et al*., 2015, obtained 59% oil from its seed which had an optimum biodiesel yield of 64% with the following amount of fatty acids (monounsaturated fatty acid – 76%, saturated fatty acid – 24%). Bull and George, 2015 in their study, obtained 80% biodiesel yield though the oil yield was not reported. However, no much work has been done in the use of African pear seed oil as a feedstock for biodiesel production.

Therefore, this study is undertaken to assess the viability of the seed oils from Sweet Almond, African Pear and African Star Apple in biodiesel production since their seeds are treated as wastes to enhance their economic potentials.

2. MATERIALS AND METHODS

2. 1. Materials

2. 1. 1. Reagents and Chemicals

Sodium hydroxide (99%, Sigma-Aldrich), potassium hydroxide (loba chemie, GmbH) 85%), methanol ((Merck, Germany 99.5 % purity)**,** carbon tetrachloride (chloroform), Wij's solution (iodine monochloride), potassium iodide solution, phenolphthalein (Merck Germany), powdered iodide (Fishon, England), hexane (99% purity, Merck Germany), sulphuric acid (98% min., Sg: 18300 BDH), hydrochloric acid, iodine**,** glacial acetic acid**,** iodine tetrachloride**,** starch indicator**,** potassium chloride**,** ethanol.

2. 1. 2. Apparatus and Analytical Equipment

Petri dishes, thermo regulator heater with Stirrer (Heizung chauffage, MGW-LAUDA, D6970, Lauda Konigshoffen, Germany). electric digital precision weighing balance (Ohaus, Adventurer, model – AR 3130), pH meter (Hanna pH meter, model: 02895, India), rotary evaporator oven (model BTOV 1423), veisfar muffle furnance (PEW, Path Electrical Mumbai, India), fenantic portable viscometer (model VL Brookfield Eng. Labline, USA), abbe refractometer (model: WAY-25, Search tech. Instruments), semi-automatic cleveland flash point tester, oxygen bomb calorimeter (model XRY-1A), top load balance (Binatone; model KS-7020), water still (2Lit/hr,model No: 7652, Medica Inst. Mgt Coy, India), concentric rings, thermostatic water bath (model no; 6801TI, 6 holes, medica Inst. Mgt Coy, India), pH meter, digital (Exstick, India), heating mantle (0-100 °C, Labline sunbine, India) and sohxlet extractor (BEHR, Labor- Technik Ez100).

2. 2. Test Materials/Sample Collection

2. 2. 1. Source of Seeds

The Fresh fruits were sourced from Onitsha City in Anambra State of Nigeria. Anambra State is located in the South Eastern part of Nigeria, linked with Delta State by the popular River Niger Bridge and shares boundaries with Enugu, Imo and Delta States. Geographically, Anambra State is located between latitude 5°37' 60N and longitude 7°10' 0E with equatorial type of climate.

2. 2. 2. Sample Preparation

The Fruits were washed properly and separated into seeds and pulp. The Clean seeds were sun-dried in the open for 7 days (for African Pear) while for Sweet Almond and African Star apple, the hulls containing the seeds were sun dried for 5 days to ensure free movement of the seed and indication for readiness for smooth seed separation. The seed were manually separated from hulls by cracking and the seeds collected were sun-dried in the open for 7 days.

Automatic Milling Machine was used to crush the seeds to obtain a size of 1.18 mm sieve size in order to weaken or rupture the cell walls to release the fat for extraction. The ground meal was further placed on solar dryer for a period of 3 days to remove residual moisture.

2. 3. Oil Extraction

2. 3. 1. Solvent Extraction

A known weight of the dried meal of seed was packed in a big fractionating column up to three quarter level and n-hexane was poured well above the level of the meal in the column. It was closed with aluminum Foil and sealed with masking tape and then left for a period of 24 hrs. The mixture of oil and solvent was collected and filtered into a beaker. This was repeated to extract more oil from the meal. After which the oil was recovered using rotary evaporator to distill off the solvent. After distillation, the oil was left in the open to totally dry up the remaining solvent. The same process was applied for the other two fruit seed meals.

2. 3. 2. Oil Degumming

The oils were degummed to remove phosphosphide, lysophasidid acids which are strong emulsifiers which lower the yields of neutral oil. This was done by mixing the crude oil with about 3% of warm water and the mixture was agitated mechanically for 30 minutes at 70 °C. This hydrates the phospholipids and gums thus making them insoluble in the oil. They were thereafter separated by settling.

2. 3. 3. Physico-Chemical Characterization of the Oil

The physic-chemical properties of the seed oils were determined in accordance with Association of Official Analytical Chemist (AOAC, 1990) method (the acid value by AOAC Ca5a-40, saponification value by AOAC 920:160; iodine value by AOAC 920:158 and peroxide value by AOAC 965.33) while the viscosity was determined by using Oswald viscometer apparatus, the density by using density bottle, moisture content by oven method, the ash content by heating to dryness in Veisfar Muffle furnance and the refractive index by using abbe refractometer (Model: WAY-25, Search tech. Instruments).

2. 4. Biodiesel Production

2. 4. 1. Preheating the oil

The oil was heated fairly at 80 °C for 30 minutes using Gallenkamp Magnetic Stirrer thermostat hot plate (Weiss Technik England) to reduce the viscosity of the oil.

2. 4. 2. Preparation of Sodium Methoxide

This was prepared by adding 2% weight of oil of NaOH to 175 ml of methanol and stirred at 300 rpm until it dissolved completely for about two minutes in the reaction vessel.

2. 4. 3. Transesterification Reaction

The Sweet Almond seed oil and Star Apple Seed Oil were subjected to direct base transesterification reaction while African Pear Seed Oil was subjected to two-step transesterification because of its high FFA. The two-step transesterification involves Acid transesterification followed by base transesterification.

2. 4. 3. 1. Acid transesterification

The transesterification was carried out using 50 ml of methanol and 0.2 ml of concentrated H_2SO_4 mixed together inside a 250 ml conical Flask. The conical Flask was inserted into a water bath at 50 °C. The mixture was later added to 200 ml warmed (preheated) APSO inside a 500 ml conical flask and placed on magnetic stirrer with heater, continuously stirred for 1 hour 30 minutes for the acid transesterification to take place.

2. 4. 3. 2. Base Transesterification:

The SASO, ASASO and acid esterified APSO were subjected to base transesterifiction. The calculated amount of NaOH (Catalyst) and methanol was added for each reaction for the temperature and reaction time specified. The Base transesterifiction was carried out in a Sohxlet extractor fitted with thermo-regulator heater and stirrer. One hundred millilitre of oil was measured into the flask and was heated to the specified temperature. The Sodium methoxide was then poured into the flask containing oil and was immediately covered. The temperature was maintained for the specified time at constant agitation.

2. 4. 4. Separation of Biodiesel

After the base transesterifiction process the biodiesel was allowed to settle for 24hours inside a separating funnel to allow clear separation of biodiesel from glycerin by gravity. The layer on the top is the biodiesel while the bottom layer is the glycerol. The Biodiesel separation was carried out by decanting as the glycerol was drained off while the biodiesel remained.

2. 4. 5. Biodiesel washing

Warm distilled water at 50 °C was added to the separated biodiesel and the mixture was shaken vigorously. The water was allowed to drain through the bottom of the separating funnel. This was carried out five times until a clear biodiesel was obtained.

2. 4. 6. Biodiesel Drying

Anhydrous $CaCl_2$ was added to the biodiesel and heated gently at 50 °C the anhydrous $CaCl_2$ was later separated from the biodiesel to obtain a clean dry biodiesel. The volume of the biodiesel obtained from each sample was determined while the percentage yield of biodiesel was calculated.

2. 4. 7. Physico chemical Characterization of the Biodiesel

The physico-chemical analyses of the seeds oil biodiesel were carried out using the Association of official Analytical Chemists method (AOAC, 1990). The analysis carried out includes: Pour point, cloud point, cloud point, flash point, refractive index, specific gravity, moisture content, viscosity, iodine value. The Cetane Index (CI) was determined using correlation given by Krisnamgkura (1986) (Equation 10), Cetane Number (CN) was calculated by the equation developed by Patel (1999) (Equation 11), the FAME content in percentage was obtained by using correlation developed by Felizardo *et al.* (2006) (Equation 12), while the Higher Heating values were determined by using correlation applied by Sivaramakrishnan and Ravikumar, (2012) (Equations 13 to 16).

$$CI = 46.3 + (5458/SV) – 0.25IV \quad (10)$$

where: SV –Saponification Value, IV-Iodine Value

$$CN = CI-2.6 \quad (11)$$

where: CI – Cetane Index

$$FAME\ \% = -45.055 \ln\mu + 162.85 \quad (12)$$

where: μ – kinematic viscosity

$$HHV = 0.0317V + 38.053 \text{ for vegetable oil} \quad (13)$$
$$= 0.4625V + 39.450 \quad \text{for biodiesel based on Viscosity} \quad (14)$$
$$= - 0.0259\rho + 63.776 \quad \text{for biodiesel; based on density} \quad (15)$$
$$= 0.021FP + 32.12 \quad \text{for biodiesel based on flash point} \quad (16)$$

where: V-viscosity, ρ - density and FP – Flash point

3. RESULTS AND DISCUSSION

Table 1. Physico-chemical properties of SASO, APSO and ASASO

Sn	Parameters	Results		
		Sweet Almond	**African Pear**	**African Star Apple**
1.	Colour	Golden	Pale yellow	Dark red
2.	Specific gravity	0.8552	0.8885	0.8346
3.	Moisture content (%)	0.57	0.55	0.79
4.	Refractive Index	1.4472	1.4269	1.4515
5.	Saponification Value (mg KOH/g)	165.50	250.72	201.66
6.	Iodine Value (g/100g)	35.77	50.96	37.57
7.	Peroxide Value (milli eq. oxy/kg)	1.48	1.88	1.60

8.	Acid value (mg KOH/g)	2.805	6.57	2.88
9.	Free Fatty Acid as oleic (%)	1.402	3.28	1.44
10.	Ash Content (%)	1.02	1.50	1.22
11.	Viscosity (cp)	6.05	5.82	5.55
12.	Smoke point (°C)	40	30	35
13.	Titre point (°C)	52	36	45
14.	Flash point (°C)	157	149	135
15.	Cloud point (°C)	-2	10	-3
16.	Yield (%)	60.15	55.70	13.36

Table 2. Result of the Seed Oil FAME Physico-chemical Characterization Compared with Standards

Parameter	Results			Standards		
	SASO FAME	APSO FAME	ASASO FAME	ASTM D 9751	ASTMD 6751	DIN 14214
Biodiesel Yield (%)	94.36	93.025	86.49	-	-	-
Specific gravity	0.8491	0.5517	8195	850	880	860-900
Moisture content (%)	0.02	0.031	0.026	-	-	-
Refractive Index	1.4402	1.4269	1.4438	-	-	-
Acid value (mgKOH/g)	0.46	0.92	0.32	0.062	0.50	0.50
Free fatty acid (%)	0.23	0.46	0.16	0.31	0.25	0.25
Iodine value (mgKOH/g)	28.02	45.06	32.86	42-46	-	120max.
Saponification value (mgKOH/g)	161.05	242.51	189.03	-	-	-
Ash Content (%)	0.10	0.10	0.10	0.01	0.02	0.02
Viscosity (cp)	2.84	2.31	2.19	2.6	1.9-6.0	3.5-5.0

Smoke point	34	24	25	-	-	-
Fire point	40	27	36	-	-	-
Flash point	136	125	126	60-80	100-170	120
Cloud point	-2	10	-3	-20	-3 to 12	-
Pour point	-6	4	-8	-35	-15 to -16	-
Calorific Value (KJ/Kg)	31,178.39	34,421.50	32,838.38	42-46	-	35
Conductivity (Us/CM)	0.40	0.86	0.52	-	-	-
Cetane Index	73.0	57.80	67.16	-	-	-
Cetane Number	70.40	55.20	64.57	40-55	47min	51min
Higher Heating Value (HHV)[a] (MJ/kg)	34.72	34.50	34.52	-	-	-
Higher Heating Value (HHV)[b] (MJ/kg)	40.76	40.52	40.46	-	-	-
Higher Heating Value (HHV)[c] (MJ/kg)	63.75	63.75	63.75	-	-	-

[a] - Based on Flash point, [b] - based on Viscosity, [c] - based on density, min-minimum, max- maximum

3. 1. Oil and Biodiesel Yield

The oil content is a key factor influencing the choice of plant seeds as potential feedstock for biodiesel and other industrial products. The percentage oil yield from SA and AP (60.15% and 55.70% respectively) appear more encouraging for biofuel purposes than ASA seed oil yield of 13.36% which is quite low when compared with most oil feedstocks (peanut – 50%, sesame seed – 5-% olive seed – 40%, castor seed - 50%, sunflower seed – 35%) as reported by Ofoefule *et al.*, (2013). This indicates that the ASA seed may not be a good seed of abundant oil for biodiesel production but genetically modified breeds may be developed which could produce seeds with higher oil yields.

3. 2. Oil Colour

The golden and pale yellow colours of SASO and APSO are of high aesthetic qualities while that of ASASO is dark red. The results are the same with the colours obtained by earlier researchers while ASASO compares well in colour with *Luffa Cylindrica* and *Cucumis melo* (Ibeto *et al.*, 2012).

3. 3. The moisture contents

The high moisture content of vegetable oil is an indication of poor processing practice; it promotes oil oxidation rancidity and equally affects the biodiesel yield negatively.

The results obtained for SASO – 0.59%, APSO – 0.55% and ASASO – 0.79%, are all quite low compared with 5.32% obtained by Ofoefule *et al.*, 2013 for tiger nut seed oil and 5.006% by Isreal, 2008 for Almond seed oil. Lotero *et al.*, 2005 has advised for moisture content of vegetable oils to be lower than 0.5% in order to obtain up to 90% yield of biodiesel. The values obtained in this study had no negative effect on the quality of methyl esters produced from any of the seed oils.

3. 4. The Saponification Values

The saponification value serves as important parameters in determining the suitability of the oil for soap making and inversely proportional to the molecular weight of the oil (Audu *et al.,* 2012). Therefore it can be deduced that the value of 165.50 mg KOH/g, 250.72 mg KOH/g and 201.68 mg KOH/g for SASO, APSO and ASASO could indicate that SASO would be more useful in biodiesel production, followed by ASASO and APSO because APSO would have more tendency of soap formation than ASASO while ASASO would produce more soap during transesterification than SASO. The values obtained are in appreciable consistency with the literature values especially from ASASO: Audu *et al.,* 2013 obtained 193.7 mg KOH/g, Musal *et al.*, 2015 obtained 228 mg KOH/g though Agbede *et al.,* 2012 obtained 327 mg KOH/g while Ochigbo and Paiko 2011 got 246.84 mg KOH/g. The value 165.50 mg KOH/g obtained for SASO indicates that it is made up of low concentration of triglycerides (Adepoju and Olawale, 2014) or high proportion of fatty acids of low molecular weight (Musa *et al.,* 2015). The value is more than twice the value 65.92 mg KOH/g reported for *Luffa Cylindrica* by Ibeto *et al.,* 2012 and higher than 161.1 mg KOH/g reported by Ofoefule *et al.,* 2012 for tiger nut. The Saponification value of 250.72 mg KOH/g was obtained from APSO and it appeared highest among the three seed oil samples used. The high result is in agreement with the values of 250 mg KOH/g and 253 mg KOH/g reported for edible oil like palm kernel oil and coconut oil respectively as reported by Musa *et al.*, 2015 but far higher than the value of 171.10 mg KOH/g reported by Ogunsuyi, 2015 from African Pear. The saponification value of the methyl esters quite decreased when compared with the values obtained from the seed oils and follows the trends observed in tiger nut oil (Ofoefule *et al*., 2013) and corn oil (De lima *et al*., 2013). The value obtained from APSOME was the lowest (161.05 mg KOH/g).

3. 5. The iodine Values

The iodine values obtained are 50.96 mg KOH/g, 37.57 mg KOH/g and 35.77 mg KOH/g for APSO, ASASO and SASO respectively. Iodine value is the measure of degree of unsaturation of an oil (Nzikou *et al.*, 2009). Iodine value is classified thus, greater than 130 (drying) between 150 and 130 (semi-drying) and less than 115 non-drying. Therefore, all the three oil samples are all non-drying oil samples. The iodine value according to EN 14214 (European committee for standardization) should be less than 120 g I_2/100 g sample for the seed oil to be suitable as feedstock for biodiesel production while oils having high unsaturation of fatty acids, when heated are prone to polymerization of the glycerides, causing formation of deposits and thereby compromising oxidative stability, (Mittelbach, 1996). Therefore, the values obtained for the three seed oils, do not suggest high unsaturation. Also Giwa and Ogunbona, 2014 obtained 92.3 mg KOH/g for SASO, Audu *et al.,* 2013 obtained 33.18 mg KOH/g and 83.56 mg KOH/g for ASASO and *Luffa Cylindrica,* Musa *et al.,* 2015 obtained 30.0 mg KOH/g for ASASO. Literature value for APSO is rare. The iodine value is an index of the number of double bonds within a mixture of fatty acid contained in biodiesel. Therefore, it is a measure of the total unsaturation of a fatty material. The iodine value of SASOME, APSOME and ASASOME are 28.02 mg KOH/g, 45.06 mg KOH/g and 32.86 mg KOH/g respectively showing slight decrease in the values obtained from the parent seed oils. The above values satisfy the specification of 120 g I/100 g (maximum) recommended by EN14214 standards. Iodine value of APSOME is highest and this indicates that it may possess the highest fatty acid among the three methyl esters produced. The values are lower than 98.38 for tiger nut biodiesel (Ofoefule *et al.,* 2013) which indicates higher saturation in the results obtained in this research.

3. 6. Peroxide Values

Peroxide value is an index of rancidity and hence provides information on oil quality and stability. The values obtained were 1.48 meq oxy/g, 1.88meq oxy/g and 1.60meq oxy/g for SASO, APSO and ASASO respectively. These low values clearly suggest that the seed oils are stable and may not readily become rancid during storage (Audu *et al.,* 2013). High peroxide value in vegetable oil suggests absence of low levels of antioxidant. Also Codex Alimentarius Commission has recommended a maximum value of 10 meq oxy/kg for such edible oils such as groundnut seed oils. The values obtained here would therefore work within the limit stipulated for vegetable oils and biodiesel and are in consistence with the values obtained previously for ASASO by Audu *et al.,* 2013 (1.96 meq oxy/g), Akubugwo and Ugbogu, 2007 (1.80 meq oxy/g), Musa *et al.* 2015 (1.45 meq oxy/g), Adebayo *et al.,* 2012 (1.57 meq oxy/g) and 45.20 meq oxy/g obtained by Ogunsuyi, 2015 for APSO. The higher value obtained by Ogunsuyi, 2015 could be attributed to method of processing and handling of the raw seeds. However, Audu *et al.,* 2013 obtained 5.3 meq oxy/g for *Luffa Cylindrica.*

3. 7. Acid Value and Free Fatty Acid Values

Acid values provide an indication of age and quality of the oil or fat. The acid values were determined to be 2.80%, 6.57% and 2.88% for SASO, APSO and ASASO while the free fatty acid values were 1.405%, 3.28% and 1.44% for SASO, APSO and ASASO respectively. Many researchers have reported that free fatty acid (FFA) above 3% in oil require pretreatment for optimal conversion into biodiesel as high FFA results in losing the oil to soap rather than to biodiesel (Mushtaq *et al.,* 2014), hence, the AP seed oil requires two- step transesterification for optimal conversion to biodiesel this have to affect the biodiesel yield compared to the yields that would be obtained from SASO and ASASO. The FFA of APSO is lower than the value (12.33%) obtained by Ogunsuyi, 2015 for the same APSO and 4.49% obtained by Ofoefule *et al.,* 2013 for tiger nut. Okoye and Ibeto, 2010, obtained 47.12% and 51.4% from paw-paw and orange seed oils respectively. The difference observed in some cases here could be attributed to the age of the seed, geographical location where the seeds where obtained and storages conditions. However, considering FFA of the seed oils from this study, they can be used for industrial purposes such as the production of biodiesel and biolubricant. The following acid values were obtained after transesterification: 0.46 (SASOME), 0.92 (APSOME), and 0.32 (ASASOME). These values are within the limit of ASTMD 6751 and EN14214 as indication of good biodiesel quality. These values compare well with the results from other researchers though lower than 1.122 obtained from tiger nut biodiesel by Ofoefule *et al.*, 2013 and 2.81 on ASASOME by Audu *et al*., 2013. However, the high acid value recorded on the side of APSO (6.57) was reduced to 0.92 after the esterification process.

3. 8. Referactive index

When the biodiesel temperature is near to the cloud point, a cloudy state appears and refraction index changes showing that the refractive index is a significant parameter to evaluate the state of a biodiesel. The refractive index indicates the level of optimal clarity of crude oil sample relative to water. The values obtained were above 1.42 but below 1.46 and are within the values reported by some researchers (Audu *et al.*, 2013). This shows that the oil is not as thick as most drying oils whose refractive index fall between 1.425 and 1.485. However, the values obtained are higher than 6.91 for *Brachystegia eurycoma,* 0.73 for *Circubita Pepo,* 0.75 for *luffa Cyrindrica,* 0.71 for *Cucumis melo* but in the same range with 1.46 obtained for *Arachies hypogeal* (Ibeto *et al.*, 2012). Refractive index value obtained from the methyl esters were 1.4472 (SASOME), 1.4269 (APSOME) and 1.4575 (ASASOME) which are all above 0.77 obtained by Ofoefule *et al*., 2012 for tiger nut biodiesel, but compared well with 1.467 obtained for corn oil biodiesel by De lima *et al*., 2013.

3. 9. The specific gravity

The specific gravity values of all the oils were in the range of 0.83 to 0.88. These values are already close to the range of 0.87–0.90 for biodiesel (Ibeto *et al.*, 2012). The values of specific gravity of oil required for biofuel is very important for effective functioning of the injection engines through maintaining the optimal air to fuel ratio to promote efficient combustion and reduce particulate matter emissions (Ibeto et al 2012). Specific gravity values of the biodiesel produced were 0.8491, 0.8517 and 0.8195 for SASOME, APSOME and ASASOME respectively. Though the value of APSOME and ASASOME are slightly higher and lower than the results of Ogunsuyi, 2015 and Audu et *al.*, 2003 respectively, the values obtained are within the standard limit of ASTM6751 and DIN14214 (Table 2).

3. 10. The Viscosity

The viscosity of the seed oils were 6.05 cp, 5.82 cp and 5.55cp for APSO, SASO and ASASO respectively. The results are in consistent with 3.70 cp for APSO as reported by Ogunsuyi, 2015, and 4.23 cp for SASO as obtained by Giwa and Ogunbona, 2014. However, the high value obtained for APSO shows that it could be used as lubricants in engine parts in the tropics with little pretreatment. The viscosity of 2.84mm^2/s, 2.31 mm^2/s and 2.19 mm^2/s were obtained for SASOME, APSOME and ASASOME respectively. Viscosity is important in determining optimum handling, storage and operational conditions because biodiesel fuel need to have suitable flow characteristics to ensure that adequate supply reaches injectors at different operating temperatures. The values obtained are all comfortably within the 1.9 – 6.0 mm^2/s standards of ASTM. The values are slightly lower than 8.08 mm^2/s reported by Ofoefule *et al.*, 2013, on tiger nut, 4.23 mm^2/s reported by Giwa and Ogunbona, 2014 on SASOME and 5.6 mm^2/s reported by Bull and George on APSOME, but compared very well with 2.60 mm^2/s obtained by Ogunsuyi, 2015 on African pear. Moreover, the viscosities of the seed oils decreased considerably after transesterification which is very important for the efficiency of the engine. Many diesel engines use high technological injection pumps which do not tolerate very viscous fluids as these may clog fuel filters. Oil with high viscosity can form droplets on injection which causes poor atomization but oils with very low viscosity can produce biodiesel with low viscosity which may not provide sufficient lubrication for precision fill of the fuel injection pumps.

3. 11. The Cloud point, Flash point and Smoke point

The seed oils have more favourable values for smoke point (SASO – 40 °C, APSO – 30 °C, ASASO – 35 °C), the titre point (SASO – 52 °C, APSO – 36 °C, ASASO – 45 °C), Flash point (SASO – 157 °C, APSO – 149 °C, SASO – 135 °C) and cloud point (SASO – (-2 °C), APSO – (10 °C), ASASO – (-3 °C)). These values are quite different from the values of 170 °C of smoke point and 182 °C of flash point obtained by Ogunsuyi, 2015 from APSO but in agreement with the result obtained by Bull and George, 2015 (144 °C of flash point and 2.7 °C of cloud point for APSO). The result obtained in this study implies that the seed oils would have high biofuel potential. The cold flow properties of the methyl Esters were measured by determination of cloud point (CP) and pour point (PP). These are important low temperature fuel parameters. Specifications for CP and PP are not in the biodiesel standards of DIN14214 though ASTMD6757 requires that CP be reported probably because each country has different climatic conditions. As reported here, SASOME and ASASOME have satisfactory CP and PP values of -2 °C, -6 °C and -3 °C, -8 °C, respectively, while APSOME has values of 10 °C, and 4 °C, which are quite within the -15 to +10 and -3 to +12 ASTM D6757 standards for CP and PP respectively. The different results could be as a result of the higher percentage of long-chain unsaturated fatty Acids in SASOME and ASASOME than APSOME (Giwa and Ogunbona, 2014). However, the values obtained from APSOME is in agreement with results of Bull and George, 2015 (CP – 2.7 °C, and PP 15.2 °C), Awolu and Layokun, 2013 (CP – 8 °C and PP – 4 °C). Moreover, since the pour point is the lowest temperature at which frozen oil can flow and is used to specify the cold temperature instability of fuel oil, this shows that the produced biodiesel from these seed oils would perform well in very cold and temperature regions.

3. 12. The Ash content

The Ash content of the biodiesel sample were the same and above the maximum limit of ASTMD and EN. This indicates that they may likely have very high mineral contents that would lead to presence of some air pollutants like SO_X and NO_X (Ofoefule et *al*., 2013). The values obtained as shown in Table 2 are far below the values obtained for tiger nut methyl esters and its blends by Ofoefule *et al*., 2013. The ash content of the methyl esters are lower than the values obtained from the corresponding vegetable seed oil samples showing improved fuel quality because of the transesterification process.

3.13 Calorific values

The Calorific values of 31,178.79, 34,421.50 and 32,838.36 KJ/Kg were obtained for the SASOME, APSOME and ASASOME respectively. These values are below diesel fuel ASTMD 975 standards but within the limit of EN DIN14213 standard of 35 MJ/kg minimum. These values supports the values obtained on higher heating values based on flash point (34. MJ/kg).

3. 14. Cetane number

Cetane number (CN) measures the tendency of the fuel to self-ignite at a particular temperature and pressure in the cylinder when the fuel is injected. The values obtained here are 70.40, 55.20 and 64.57 for SASOME, APSOME and ASASOME respectively. The values of the three seed oil biodiesel are within the minimum standard limits of ASTM and EN (47 and 57 respectively). It implies that SASOME would give lowest delay period and smoother engine operation followed by ASASOME and APSOME (Sivaramakrishnan and Ravikumar, 2012). The values obtained are equally above the standard set for petrol diesel (40 – 55) as indication of higher oxygen content which is typical of biodiesel fuel. Also Sivaramakrishnan and Ravikumar, 2012 obtained CN values of 63, 54, 45, 49, 54 and 62 for Babassu, Rapeseed, Soyabean, Sunflower, Peanut and Palm oil methyl esters respectively.

4. CONCLUSION

Prunus amygdalus and *Dyacrodes edulis* had good yields which show that they are very good and viable feedstock for biodiesel production. *Chrysophyllum albidium* though low in yield could be exploited for biodiesel production since they are derived from non-common food sources while the bye-products obtained from them could be useful for animal feed if properly processed. Also the biodiesel produced from *Chrysophyllum albidium* could be blended with petro-diesel to arrest the challenge of its low oil yield. *Dyacrodes edulis* had highest acid value among the three seed oils and would require two-step transesterification process for effective conversion of its oil to biodiesel. However, Transesterification process improved the fuel qualities of the vegetable oils and the physico-chemical quality parameters of the oil and the produced biodiesel showed excellent fuel properties and could be harnessed for biodiesel production.

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