



Research Article

**EFFECTS OF PROCESS VARIABLES ON THE YIELD AND VISCOSITY OF METHYL ESTERS DERIVED FROM *PRUNUS AMYGDALUS*, *DYACRODES EDULIS* AND *CHRYSOPHYLLUM ALBIDIUM***

**Chizoo ESONYE\*<sup>1</sup>, Okechukwu Dominic ONUKWULI<sup>2</sup>,  
Akuzuo Uwaoma OFOEFULE<sup>3</sup>**

<sup>1</sup>Department of Chemical/Petroleum Engineering, Federal University, Ndufu Alike Ikwo, Abakaliki-NIGERIA; ORCID: 0000-0001-7902-3149

<sup>2</sup>Dept. of Chemical Engineering, Nnamdi Azikiwe University, Awka-NIGERIA

<sup>3</sup>Dept. of Pure and Industrial Chemistry, University of Nigeria, Nsukka-NIGERIA; ORCID: 0000-0001-7546-8335

**Received: 09.04.2018 Revised: 14.08.2018 Accepted: 17.08.2018**

**ABSTRACT**

This paper investigates the significance of the operating conditions on the production of methyl esters from seed oils of sweet almond (*Prunus amygdalus*), African star apple (*Chrysophyllum albidium*) and African pear (*Dyacrodes edulis*). The effects of various process conditions such as catalyst amount, reaction temperature, methanol/oil molar ratio and reaction time on biodiesel yield and its viscosity were studied. The result shows that African pear seed oil methyl ester (APSOME), sweet almond seed oil methyl ester (SASOME) and African star apple seed oil methyl ester (ASASOME) production is optimized at a mixing rate of 140rpm, atmospheric pressure, temperature of 65°C, reaction time of 65 minutes, methanol to oil molar ratio of 8:1 and catalyst concentration of 1.5wt%, 2.0wt% and 2.0wt% respectively. The alkaline methylic transesterification gave 94.50%, 95.50% and 85.70% yields of esters with viscosity of 2.60mm<sup>2</sup>/s, 2.45mm<sup>2</sup>/s and 2.40mm<sup>2</sup>/s respectively. The physico-chemical properties of the seed oils showed improved fuel qualities upon transesterification compared well with ASTM and EN standards. The GC-MS result showed mainly unsaturation characteristics. A total of 37.74% saturated fatty acid (SFA), 41.42% monounsaturated fatty acid (MUSFA) and 13.90% polyunsaturated fatty acids (PUSF) were found to be contained in SASOME. ASASOME contains 27.71% SFA, 53.30% MUSFA and 18.99% PUSFA while APSOME contains 14.78% SFA, 75.50% MUSFA and 6.41% PUSFA. These results attest the viability of the selected tropical seed oils in biodiesel production.

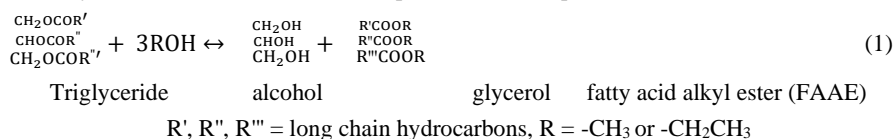
**Keywords:** Transesterification variables, biodiesel yield, viscosity, sweet almond, african star apple, African pear.

**1. INTRODUCTION**

Biodiesel production from a variety of vegetable oils and its merits as an alternative renewable energy source to mineral diesel has been well reported in the literature [1-3]. Interest in biodiesel production has mainly based on how to optimize the yield and improve its quality like

\* Corresponding Author: e-mail: esonye.chizoo@funai.edu.ng, tel: +234(0)803 872 5463

viscosity to make it possess close specifications with mineral diesel. Atabani *et al* [4] has reported that kinematic viscosity is the most important property of any fuel as it indicates the ability of a material to flow. It therefore affects the operation of the fuel injection equipment and spray atomization particularly at low temperature when the increase in viscosity affects the fluidity of the fuel. The large molecular mass and chemical structure of biodiesel makes it to have about 10-15 times greater viscosity than diesel fossil fuels. Some literatures thought that higher viscosity of biodiesel can affect the volume flow and injection spray characteristics in the engine and at low temperature. It may even compromise the mechanical integrity of the injection pump drive system. It is therefore very imperative to consider studies in the areas of optimizing transesterification variables as they affect not only the yield but also the viscosity of the biodiesel as a mark of its quality. There is no specification for the biodiesel yield but the higher the yield the more viable the feedstocks while the maximum allowable limit for viscosity according to ASTM and EN standards is 1.9-6.0mm<sup>2</sup>/s and 3.5-5.0mm<sup>2</sup>/s respectively. At present the homogeneous base-catalyzed transesterification with methanol (methanolysis) of vegetable oils resulting in the corresponding fatty acid methyl ester (FAMES) is the predominant techniques used for the industrial production of biodiesel [5]. The process of transesterification brings about drastic change in viscosity of the vegetable oil as the high viscosity component glycerol is removed and hence the product has low viscosity close to the liquid fossil fuels. The biodiesel production is totally miscible with mineral diesel in any proportion. The flash point of the seed oil is lowered after transesterification and the cetane number is improved. The general reaction of the base catalyzed transesterification can be represented as in equation 1.



Reaction temperature is an important factor that affects the yield of biodiesel. Higher temperature increases the reaction rate and shortens the reaction time due to reduction in viscosity of oils. However, the increase in reaction temperature beyond the optimal level leads to decrease of biodiesel yield, because higher reaction temperature accelerates the saponification of triglycerides [6] and affects the yield [7].

Again, one of the most important parameters affecting the yield of biodiesel is the molar ratio of alcohol to triglycerides. Stoichiometrically, 3 moles of alcohol and 1 mole of triglycerides are required for transesterification to yield 3 moles of fatty acid methyl/ethyl esters and 1 mole of glycerol. In order to shift the reaction to the right it is necessary to either use excess alcohol or remove one of the products from the reaction mixture, the second option is usually preferred for the reaction to proceed to completion. The reaction rate is found to be highest when 100% excess methanol is used [7]. Methanol, ethanol, propanol, butanol and amyl alcohol can be used in the transesterification reaction but amongst these alcohols methanol is applied more frequently as its costs is low and it is physically and chemically advantageous (polar and shortest chain alcohol) over the other alcohols. Many investigations have reported that the molar ratio depends on the type of catalyst and percentage of free fatty acid (FFA) of the seed oil (an acid catalyst reaction requires higher molar ratio than alkali-catalyzed reaction to achieve the same ester and the higher the free fatty acid the higher the molar ratio) [8].

Biodiesel formation is also affected by the amount and type of catalyst. Most commonly used catalyst for biodiesel production is sodium hydroxide (NaOH) or potassium hydroxide (KOH) [6]. The type and amount of catalyst required in the transesterification process usually depend on the quality of the feedstock and method applied for the transesterification process. For a purified feedstock, any type of catalyst could be used for the transesterification process. However, for feedstock with high moisture and free fatty acids contents, homogenous transesterification process is suitable due to high possibility of saponification process instead of transesterification

process to occur. The yield of fatty acid alkyl esters generally increase with increasing amount of catalyst. This is due to availability of more active sites by additions of larger amount of catalyst into the transesterification process. However on economic perspective, larger amount of catalyst may not be profitable due to cost of the catalyst itself. Therefore, similar to the ratio of oil to alcohol, optimization process is necessary to determine the optimum amount of catalyst required in the transesterification process [9, 10]. Many research works have been carried out on the effect of these parameters on the yield of esters from various vegetable oil sources [2]. However, some feedstocks are yet to be investigated. It is therefore necessary to understand the optimum conditions for respective feedstocks conversion since the standard conditions of processing them into biodiesel is highly depended on their physico-chemical compositions which differs from feedstock to feedstock and when the same feedstock is globally considered, geographical and climatic conditions where the feedstocks are obtained makes them differ in quality characteristics. African star apple is one of the indigenous wild fruit trees with enormous potentials for establishment [11]. It belongs to the family of *sapotacea* and naturally occurs in Nigeria, Uganda, Niger Republic, Cameroon and Cote d'ivoire [12]. It grows as a wild plant which has up to 800 species and make up almost half of the order Ebernales [13] and has become a crop of commercial value in recent times. 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 [14]. It is found mainly in the rural and urban centers in the month of December to April [15]. African Star apple is among the under-utilized fruits in Nigeria and seed of this plant have been rarely exploited for production of oil for commercial purposes despite the fact the seed has been reported to contain up to 25% oil [16]. The seeds are thrown away after the consumption of its juicy pulp [15]. Only few attempts on the extraction of oil from *Chrysophyllum albidum* in Africa are documented. The effect of solvent blending on the characteristics of oil extracted has been studied, the extraction and classification of lipid through phytochemical screening has been reported, and the extraction and characterization of the oil at 65°C for 3-4 hours has equally been investigated [17-19].

Sweet almond seed is another important feedstock with potential viability. Almond plants are included in the family *Rosaceae* in addition to *prunoideae* (apples, pears), *prunoideae* (apricot, cherry, peach and plum) and *rosoideae* (blackberry, strawberry) fruits [20]. The almond is native to the Mediterranean climate region of the Middle East. It was spread by humans in ancient times along the shores of Mediterranean into northern Africa and southern Europe and recently transported to other parts of the world notably California, United States [21]. World production of almond was 2.9 million tonnes in 2013 with United States as the largest producer of 1.8 million tonnes [22]. The two major varieties of almonds are the bitter almond (*Prunus amygdalus "amara"*) and the sweet almond (*Prunus amygdalus "dulcis"*) which found useful application in culinary purposes and making of oils and flavourings respectively [23]. Almond fruit consists of four portions: comprising the kernel or meat, middle shell, outer green shell cover or almond hull with a thin leathery layer referred as brown meat or seed coat [24]. Sweet almond tree is found in the south eastern and south southern part of Nigeria. They provide shades to homes, offices and the environment. Their fruits litter the environment and are picked either by children or disposed off as wastes and as such their use as feedstock for biodiesel production would also serve as a waste disposal option. The extraction and characterization of the seed oil biodiesel from sweet almond obtained from Nigeria has been investigated [20]. The study revealed that the seed oil has an oil yield of 51.45%, acid value of 1.07mg KOH/g and fatty acid composition of oleic acid (69.7%), linoleic acid (18.2%) and palmitic acid (9.3%). The result equally showed that the cold flow properties were -3 and -9 for the cloud point and pour point respectively with the specific fuel properties found to satisfy both EN 14214 and ASTM D6751 biodiesel standards.

African pear otherwise called African plum or Safou, locally called ube among the Igbos in southern eastern part of Nigeria belongs to the family of *Burseraceae* and botanically known as *Dyacrodes edulis*. It is indigenous fruit tree grown in humid low lands and plateau regions of West central African and Gulf of Guinea country [25, 26]. 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 3cm in diameter and contains a leathery shelled stone surrounded by a pulpy pericarp of about 5mm thick. It is this portion that is eaten either raw or cooked and the seeds discarded [27, 25]. Besides the pulp contains 48% oil and a plantation can produce 7-8 tonnes of oil per hectare [28]. However, no much work has been done in the use of African pear seed oil as a feedstock for biodiesel production and other commercial purposes.

The purpose of this study is therefore to produce methylic biodiesel from the seed oils of Sweet Almond, African Star Apple and African Pear and investigate the effect of oil/methanol molar ratio, temperature of reaction, reaction time and catalyst concentration on the biodiesel viscosity and yield and equally ascertain the physico-chemical parameters as well as the fatty acid distribution of the biodiesel produced at the optimum conditions.

## 2. MATERIALS AND METHODS

### 2.1. Materials

Sodium hydroxide (99% Sigma-aldrich), potassium hydroxide (lobachemie, gmbH 85%), methanol (Merck, Germany 99.5 % purity), carbon tetrachloride (chloroform), Wij's solution (iodine monochloride), potassium iodide solution and phenolphthalein (Merck Germany) were all of analytical grade. The fresh fruits were sourced from Onitsha city in Anambra State of Nigeria.

### 2.2. Experimental Procedure

The fruits were washed properly and separated manually into seeds and pulp. The seeds were sun-dried in the open for 7 days before being ground into meal using electric grinder. A known weight (3.5kg) 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 24h. 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 dry up the remaining solvent completely. The oils were degummed to remove phosphophides and lysophasidic acids. 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 before using it for biodiesel production.

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

The APSO acid transesterification (esterification) was necessary because of its high FFA. This was carried out using 50ml of methanol and 0.2ml of concentrated H<sub>2</sub>SO<sub>4</sub> 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 200ml warmed (preheated) APSO inside a 500ml conical flask and placed on magnetic stirrer with heater, continuously stirred for 1 hour 30 minutes for the acid transesterification to take place. The seed oils was subjected to base transesterification. The calculated amount of NaOH (Catalyst) and methanol was added for each reaction for the temperature and reaction time specified. The Base transesterification was carried out in a Soxhlet extractor fitted with thermo-regulator heater and stirrer. The calculated amount 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. After the base transesterification process the biodiesel was allowed to settle for at least 24h 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. 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. Anhydrous CaCl<sub>2</sub> was added to the biodiesel and heated gently at 50°C. The anhydrous CaCl<sub>2</sub> 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.

### 2.3. Analytical Methods

The properties of the seed oils were determined in accordance with Association of Official Analytical Chemists [29] 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 the Rotary Evaporator Oven (BTOV 1423), the ash content by heating to dryness in Veisfar Muffle furnace and the refractive index by using Abbe refractometer (Model: WAY-25, Search tech. Instruments). All the analyses carried out on the physico-chemical parameters of the seed oils were done in triplicates and the mean values and standard deviations were calculated and provided. The fuel properties of the synthesized biodiesel at optimum conditions were determined by ASTM standards: the kinematic viscosity was determined by ASTM D-445 method, the density was determined by ASTM D-1298 method, and the pour point determination was made using ASTM D-97 methods. The flash point of the fuel was determined as ASTM D-93, the value of cloud point was estimated according to ASTM D-2500, and Acid value was measured following the ASTM D-664 method. Cetane number (CN) was calculated by the equations developed by Patel [30] (Equation 2-3), while the higher heating values were determined by using correlation applied by Sivaramakrishnan and Ravikumar [31] (Equations 4 to 7). The copper corrosion test was carried using copper strip test according to ASTM D130 method.

$$CI = 46.3 + \left(\frac{5458}{SV}\right) - 0.25(IV) \quad (2)$$

$$CN = CI - 2.6 \quad (3)$$

$$HHV = 0.0317\mu + 38.053 \quad (4)$$

$$= 0.4625\rho + 39.450 \quad (5)$$

$$= -0.025\rho + 63.776 \quad (6)$$

$$= 0.021FP + 32.12 \quad (7)$$

Where HHV- higher heating value,  $\mu$ -viscosity,  $\rho$ -density and FP-flash point, SV – saponification value, IV-iodine value and CI – cetane index and CN – cetane number. Equations 4, 5, 6, and 7 are for vegetable oil, biodiesel based on viscosity, biodiesel based on density and biodiesel based on flash point.

The fatty acid composition of the biodiesel samples was analyzed by gas-chromatography coupled with mass spectrometer. The gas Chromatographic analysis was made using GCMS-QP2010 plus, Shimadzu, Japan instrument. The GC column used was calibrated by injecting methyl ester standards, good separations were achieved by diluting the sample in a small amount of ethyl acetate. The carrier gas used was hydrogen and its flow rate was regulated at 41.27ml/min while the column flows at 1.82ml/min. The oven temperature was set at 80°C before ramping up at 6°C/min until 340°C. The identification of peaks was done by comparison of their retention time and mass spectra with mass Spectra Library (NIST05s LIB.).

A 6<sup>4</sup> factorial experimental design was used to ascertain the optimum conditions for reaction time (45, 50, 55, 60, 65, 70 minutes), catalyst concentration (0.5, 1.0, 1.5, 2.0, 2.5, 3.0 wt%), methanol/oil molar ratio (3:1, 4:1, 5:1, 6:1, 7:1, 8:1) and reaction temperature (45, 50, 55, 60, 65, 70°C). The choice of values were based on some preliminary investigations while optimization of the transesterification variables were done by considering each of them at a time while keeping others constant (catalyst concentration of 1.5wt%, methanol/oil molar ratio of 5:1, reaction time of 60minutes and reaction temperature of 60°C). The mixing rate and pressure were kept constant at 140rpm using magnetic stirrer (Moddel-124, Hp-1/8, max. speed - 4000rpm, India) and atmospheric pressure respectively.

### 3. RESULTS AND DISCUSSION

The properties of the seed oils and the biodiesel at optimum conditions as obtained from this work are shown in Table 1 and 2. The results of the biodiesel compared with ASTM D6751, EN14214 and ASTM D975 recommended standards. The density flash point, iodine number, cetane number, pour point, moisture content and the calorific value conform to the approved international standards and showed improved fuel qualities upon transesterification when compared with the parent seed oils.

Figure 1 contains the fatty acid compositions chromatogram of the methyl esters of sweet almond, African star apple and African pear seed oils obtained using GC-MS techniques at optimum conditions. The major fatty acids were oleic, palmitic, Stearic, linolenic and  $\alpha$ - linoleic for APSOME, oleic, palmitic, linolenic and eicosenic for ASASOME and oleic,  $\alpha$ - linoleic, palmitic, eicosenic, lignoceric, arachnidic, behenic, myristic, and  $\gamma$  – linoleic for SASOME. It shows that all the seed oils belong to oleic family. Other organic compounds found in the seed oils' methyl ester were less than 2.0% in composition.

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

S/n	Parameters	Results		
		Sweet almond seed oil	African pear seed oil	African star apple seed oil
1.	Oil yield (%)	60.10±2.41	56.40±2.24	13.43±2.60
2.	Colour	Golden	Pale yellow	Dark red
	Red units	4.0±0.25	2.10±0.13	5.4±0.56
	Yellow units	40.00±6.65	31.0±5.10	55±8.55
3.	Specific gravity	0.8552±0.008	0.8885±0.007	0.8346±0.005
4.	Moisture content (%)	0.58±0.05	0.54±0.045	0.77±0.058
5.	Refractive index	1.4472±0.008	1.4269±0.009	1.4515±0.009
6.	Saponification value (mg KOH/g)	1665.31±3.49	249.82±3.70	202.66±3.39
7.	Iodine value (g/100g)	36.27±0.66	51.06±0.58	38.17±0.58
8.	Peroxide value (milli eq. oxy/kg)	1.48±0.02	1.88±0.03	1.60±0.02
9.	Acid value (mgKOH/g)	2.805±0.35	6.57±0.25	2.88±0.30
10.	Free fatty acid as oleic (%)	1.397±0.27	3.36±0.30	1.43±0.29
11.	Ash content (%)	1.01±0.02	1.47±0.02	1.23±0.02
12.	Dynamic viscosity (cp)	7.80±0.34	8.30±0.29	8.90±0.25
13.	Smoke point (°C)	40(2.3)	30±1.7	35±1.5
14.	Titre point (°C)	52±1.79	36±1.72	45±1.76
15.	Flash point (°C)	156±2.24	148±1.22	136±1.79
16.	Cloud point (°C)	-2±0.12	10±0.23	-3±0.16

**Table 2.** Physico-chemical analysis of SASOME, APSOME and ASASOME at optimum conditions.

S/n	Parameter	Results			Standards		
		SASO FAME	APSO FAME	ASASO FAME	ASTM D 9751	ASTMD 6751	DIN 14214
1.	Biodiesel yield (%)	95.50	94.50	85.70	-	-	-
2.	Specific gravity	0.8491	0.8517	0.8195	850	880	860-900
3.	Moisture content (%)	0.02	0.031	0.026	-	-	-
4.	Refractive index	1.4402	1.4269	1.4438	-	-	-
5.	Acid value (mgKOH/g)	0.46	0.92	0.32	0.062	0.50	0.50
6.	Free fatty acid (%)	0.23	0.46	0.16	0.31	0.25	0.25
7.	Iodine value (mgKOH/g)	28.02	45.06	32.86	42-46	-	120max
8.	Saponification value (mgKOH/g)	161.05	242.51	189.03	-	-	-
9.	Ash content (%)	0.10	0.10	0.10	0.01	0.02	0.02
10.	Kinematic viscosity(mm <sup>2</sup> /s))	2.80	2.91	2.88	2.6	1.9-6.0	3.5-5.0
11.	Smoke point	34	24	25	-	-	-
12.	Fire point	40	27	36	-	-	-
13.	Flash point	136	125	126	60-80	100-170	120
14.	Cloud point	-2	10	-3	-20	-3 to 12	-
15.	Pour point	-6	4	-8	-35	-15 to -16	-
16.	Calorific value (KJ/Kg)	31.17	34.42	32.83	42-46	-	35
17.	Conductivity (Us/CM)	0.40	0.86	0.52	-	-	-
18.	Cetane index	73.0	57.80	67.16	-	-	-
19.	Cetane number	70.40	55.20	64.57	40-55	47min	51min
20.	Higher heating value(HHV) <sup>a</sup> (MJ/kg)	34.72	34.50	34.52	-	-	-
21.	Higher heating value(HHV) <sup>b</sup> (MJ/kg)	40.76	40.52	40.46	-	-	-
22.	Higher heating value(HHV) <sup>c</sup> (MJ/kg)	63.75	63.75	63.75	-	-	-
23.	Copper corrosion @ 3h/50 °C	Class 1	Class1	Class 1	-	-	-
23.	Copper corrosion @ 3h/50 °C	0.0028	0.0028	0.0028	0.05	0.05	-
24.	Sulphur content (%)						

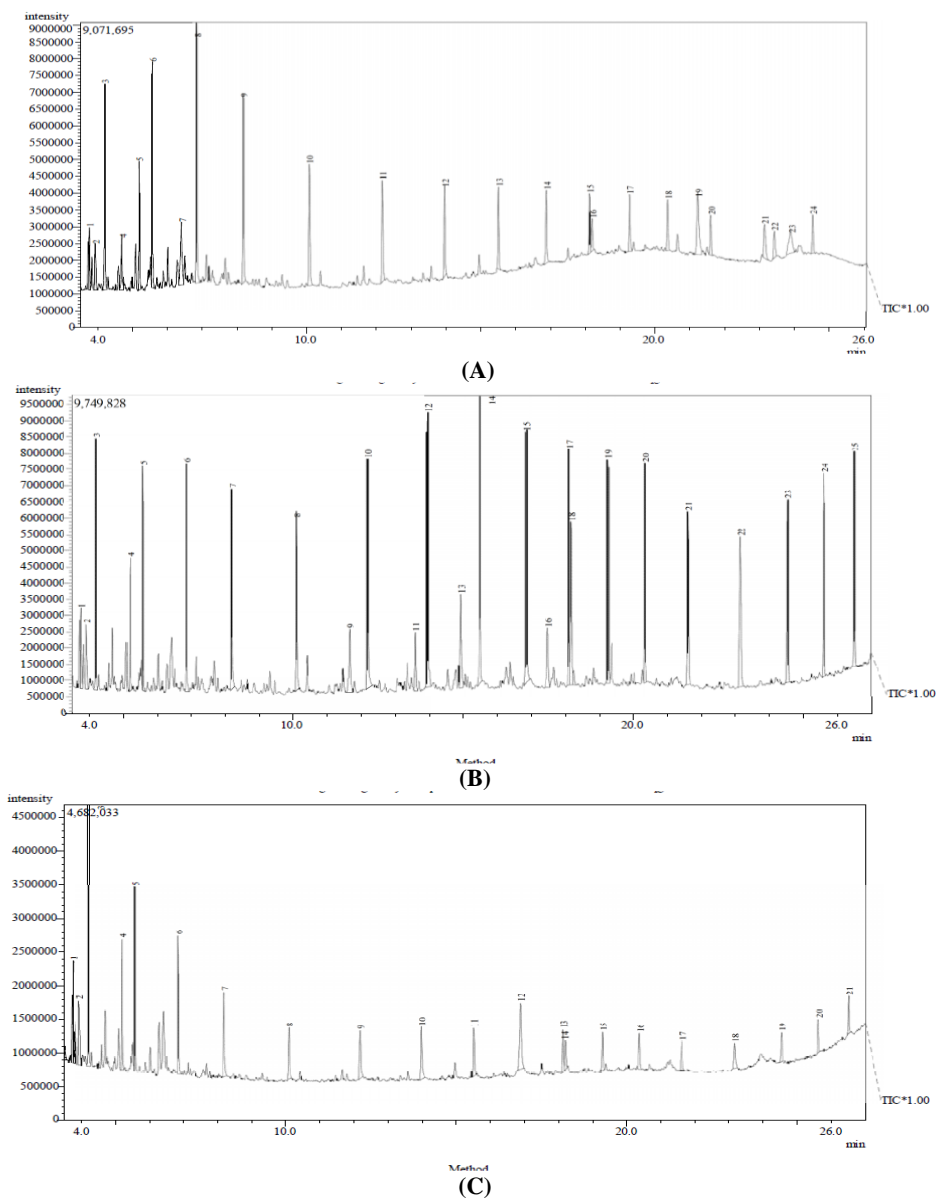


Figure 1. GC-MS chromatogram of SASOME (A), APSOME (B) and ASASOME(C)



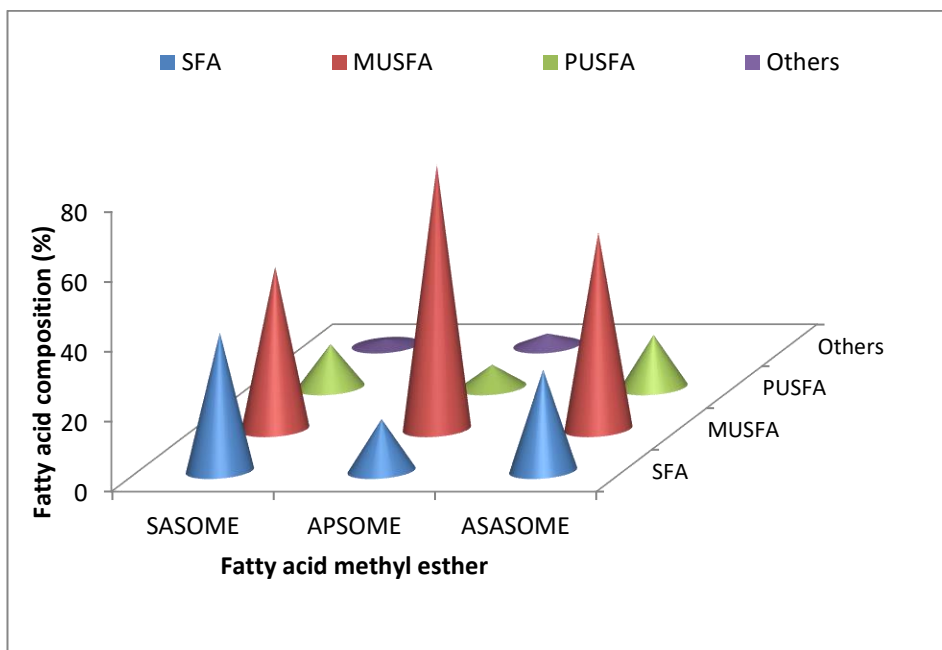


Figure 2. Fatty acid composition of the seed oil methyl esters.

Figure 2 contains the distribution of the fatty acid compositions of the methyl esters. A total of 37.74% saturated fatty acid (SFA), 41.42% monounsaturated fatty acid (MUSFA) and 13.90% polyunsaturated fatty acids (PUSF) were found to be contained in SASOME. ASASOME contains 27.71% saturated fatty acids, 53.30% monounsaturated fatty, acids and 18.99% polyunsaturated fatty acids while APSOME contains 14.78% saturated fatty 75.50% monounsaturated fatty acids and 6.41% polyunsaturated fatty acids. It implies that APSOME and ASASOME would have less density, less viscosity, lower cetane number and heating number as well as lower thermal efficiency and would emit lower HC and CO and smoke compared to SASOME that is more saturated.

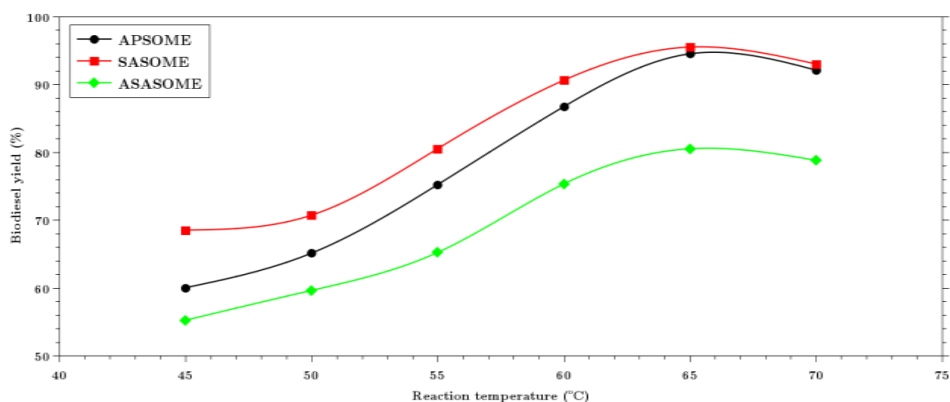


Figure 3. The effect of reaction temperature on biodiesel yield.

Figure 3 shows the effect of temperature on the biodiesel yield of the feedstocks. The reaction rate and yield were observed to follow an increase trend until 65°C because increase in temperature increases the energy of the reacting molecules and also improves the miscibility of the alcoholic polar media into a non-polar oily phase which could result in much favoured reaction. After the maximum yields obtained at 65°C as the optimum temperature the yield decreased. These results agree with the fact that transesterification should be processed between 60 – 70°C [32]. Also at elevated temperatures, saponification reaction is favoured over transesterification [33] because methanol vapourizes when heated beyond its boiling point of 68°C. These could equally be the reason for the decrease in yield with increase in temperature beyond 65°C as obtained in this study. Therefore transesterification being a reversible reaction follows Le-Chateliers principles and favours backward reaction at higher temperatures.

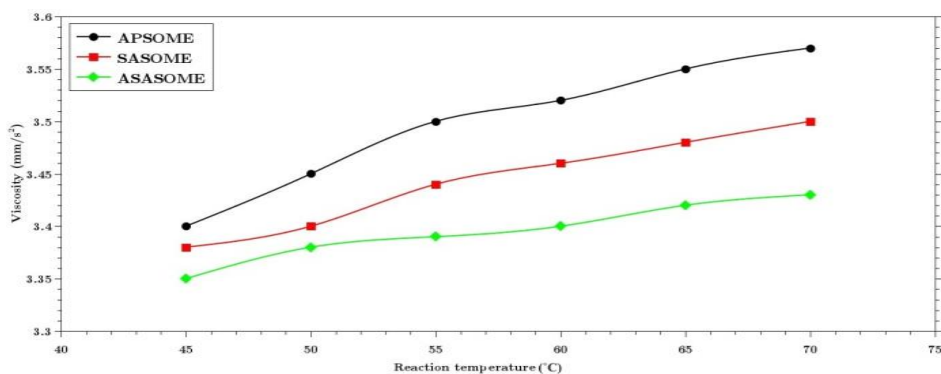


Figure 4. The effect of reaction temperature on viscosity.

The viscosity of the biodiesel samples increased slightly with increase in reaction temperature (Figure 4). Since the saponification reaction is more favoured at elevated temperature, more soap which is more viscous would be formed as the temperature increases and this could explain why the viscosity kept on increasing with increase in temperature. However, at 65°C where there is highest yields of 80.50%, 95.50% and 94.50% for ASAOME, SASOME and APSOME, their viscosity of 3.42mm<sup>2</sup>/s, 3.48mm<sup>2</sup>/s and 3.55mm<sup>2</sup>/s still compares with ASTM and EN standards

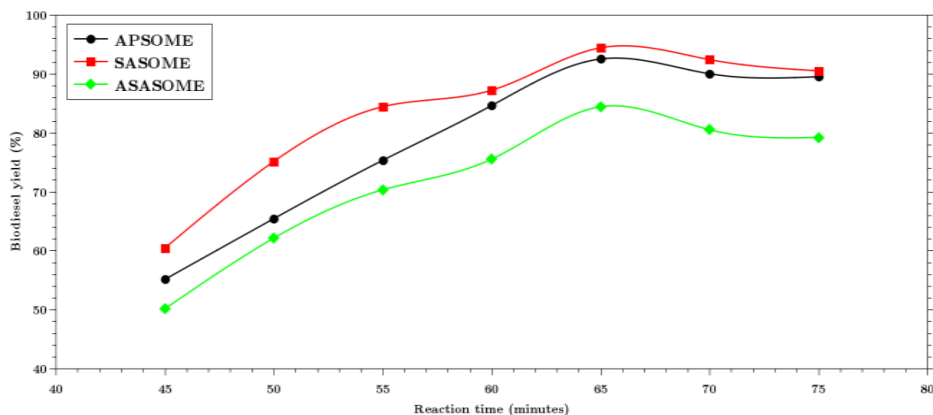


Figure 5. Effect of Reaction time on Biodiesel yield.

The effects of reaction time on biodiesel yield showed maximum yield of 84.50%, 94.40% and 92.50% for ASASOME, SASOME and APSOME respectively at 65 minutes but with additional five minutes reaction time, 4.60%, 2.10% and 2.70% decrease in yield respectively were observed. It was observed that the yield continued to increase with increase in reaction time but as the product concentration increases, the equilibrium shifts backwards to nullify the effect of this constraint because longer reaction time leads to the reduction of the end product because the reversible reaction resulted in loss of ester as well as soap formation. This observation is supported by previous reports in the literature [6, 9] and the trend of the result is shown in Figure 5.

The viscosity is observed to decrease with increase in reaction time but had a slight increase from 65 minutes to 70 minutes reaction time in the case of ASASOME before it became steady (Figure 6). Lowering the viscosity of triglycerides is one the key essence of transesterification process. The lowest achievable kinematic viscosity were 2.0mm<sup>2</sup>/s, 2.88mm<sup>2</sup>/s and 2.91mm<sup>2</sup>/s for ASASOME, SASOME and APSOME respectively which gave 65.30, 64.18 and 67.30 percentage decrease in the kinematic viscosities of the respective parent seed oils. Hence, it could be asserted that as the reaction proceeds, the viscosities decrease while FAME yield increases till 65 minutes, after which the reverse becomes the trend.

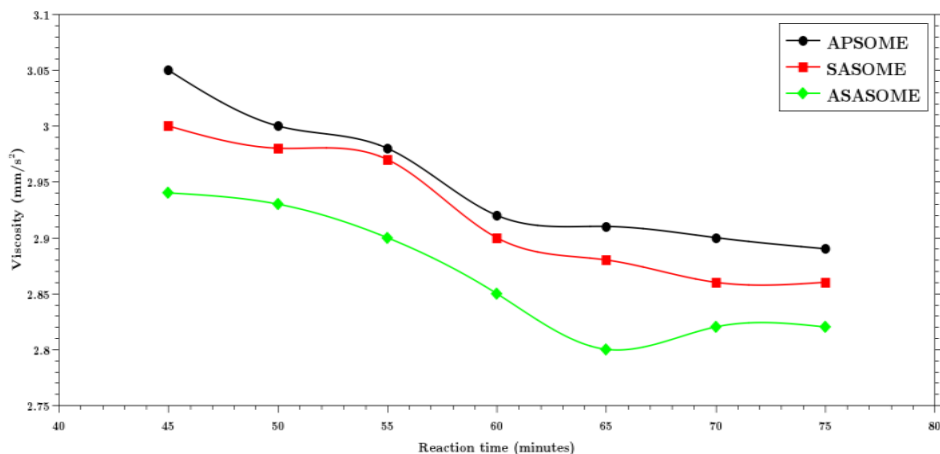
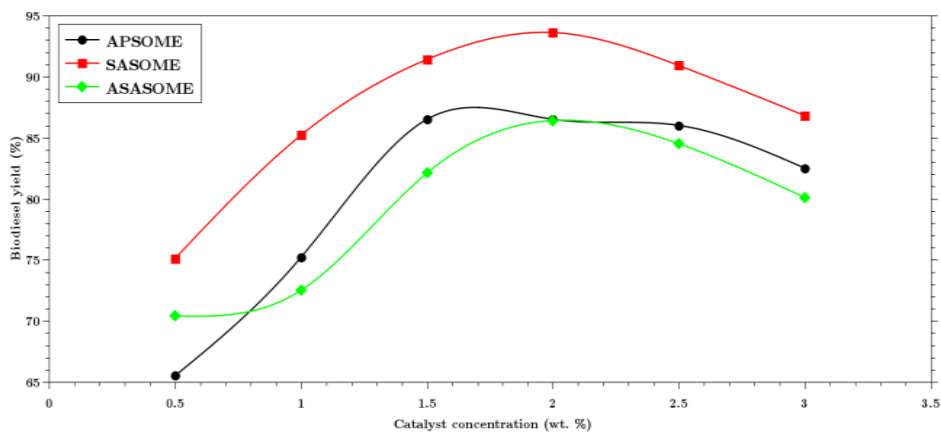
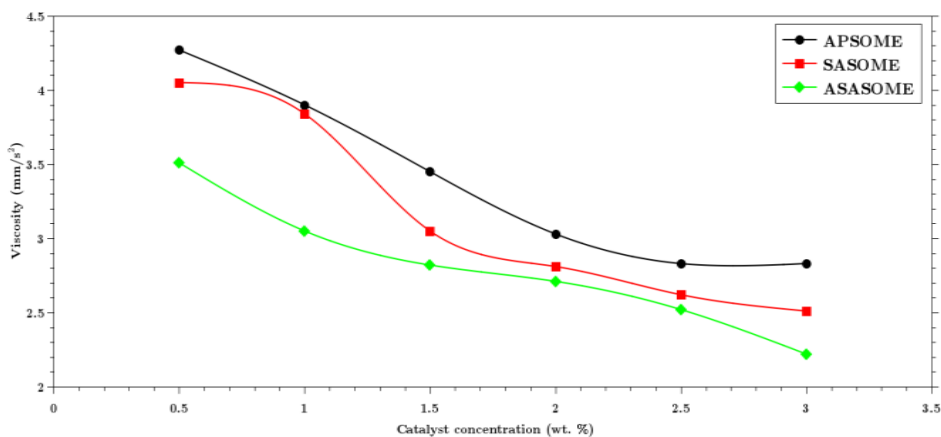


Figure 6. Effect of reaction time on viscosity.



**Figure 7.** Effect of catalyst concentration on biodiesel yield.

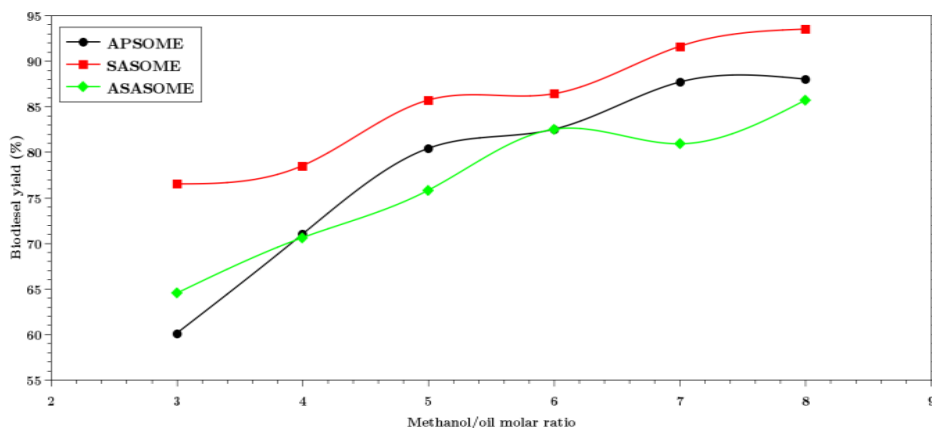
The optimum catalyst amount was found to be 1.5wt% for APSOME and 2.0wt% for both SASOME and ASASOME. Catalyst amount lower and higher than 1.5wt% proves to have no positive impact on the yield of APSOME. Also, catalyst concentration lower and higher than 2.0wt% shows no optimum methyl ester yield for SASOME and ASASOME. After 1.5wt% and 2.0 wt% catalyst amount, the yield starts to decrease fairly for APSOME and steeply for the other two respectively (Figure 7). This could be due to the fact that the higher concentration of NaOH leads to saponification of triglycerides. Also the formation of water when the catalyst is added inhibits transesterification and favours hydrolysis [6].



**Figure 8.** Effect of catalyst concentration on viscosity.

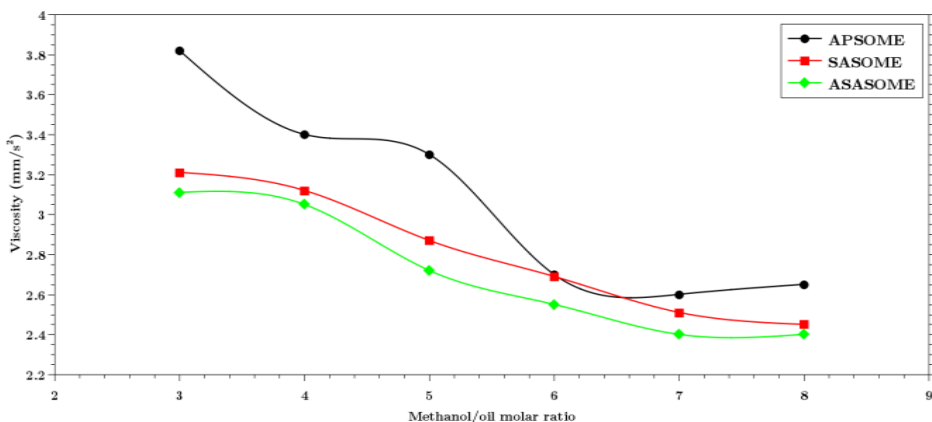
The viscosity of the produced FAME kept on decreasing until after 1.5wt% catalyst concentration when it became almost steady for APSOME and SASOME (Figure 8). However, for all the seed oils, the effect of catalyst concentration on viscosity became less noticeable after 1.5wt% catalyst concentration. Beyond 2.0wt% catalyst concentration, the yield decreased from maximum values of 86.40% and 93.60% for ASASOME and SASOME respectively but APSOME achieved its maximum yield of 86.50% with 1.5wt% catalyst concentration though at

higher viscosity of 3.45mm<sup>2</sup>/s against 2.71mm<sup>2</sup>/s and 2.81mm<sup>2</sup>/s obtained on the case of ASASOME and SASOME respectively.



**Figure 9.** Effect of methanol/oil molar ratio in biodiesel yield

Stoichiometrically, three moles of alcohol are required for each mole of triglyceride in transesterification. However, in practice, this is not sufficient to complete the reaction. Higher molar ratio is needed to drive the reaction to completion at a faster rate. It was observed that ester yield increase with increase in molar ratio but among the molar ratio studied; molar ratio 8:1 gave the best result (Figure 9). At ratio higher than 8:1 methanol/oil molar ratio, the yield seemed to decrease slightly. This could be because of the diminution of the catalyst concentration by large excess of alcohol according to Liu *et al* [34].



**Figure 10.** Effect of methanol/oil molar on viscosity.

There was no notable difference in the viscosity of the biodiesel with increase in molar ratio (Figure 10). It is well known that the methanolysis of triglycerides is a heterogeneous biphasic reaction constituted by an emulsion of small drops of the alcoholic phase disperse in the continuous oily phase [35]. In the case of the methanolysis carried out here, as the volume of alcohol increases, the concentration of the catalyst in the alcoholic phase decreases for a given

mass of oil loaded into the reaction. It is generally accepted that the reaction starts at the liquid interphase so it is reasonable that as the catalyst concentration decreases the oil conversion decreases [5]. These results illustrate the importance of the excess of alcohol to preserve the catalytically active methoxide species during methanolysis reactions catalyzed by NaOH. This positive effect is mainly based on the shift of the hydroxide, methoxide equilibrium towards the formation of alkoxide [5]. Saponification could be the reason of conversion reduction in higher percentages due to presence of small amount of free fatty acids. Due to saponification in presence of alkaline catalyst, viscosity of mixture increases, this leads to effective catalyst concentration rate reduction in reaction and as a result conversion percentage reduced [36]. It is observed that if the molar ratio rises above a certain level, biodiesel production will reduce. The principal reason for this occurrence might be related to the amount of methanol increases in mixture which leads to more dissolution of glycerin and oil in the diesel and this will considerably influence its purity. Several studies have reported similar results about catalyst concentration increase and molar ratio [37].

**Table 3.** Optimum conditions for APSO, SASO and ASASO alkaline methanolysis.

Operating conditions	APSO	SASO	ASASO
Reaction time (mins.)	65.0	65.0	65.0
Reaction temperature (°C)	65.0	65.0	65.0
Catalyst concentrations (wt%)	1.50	2.0	2.0
Methanol : oil molar ratio	8:1	8:1	8:1
Mixing rate (rpm)	140	140	8:1
Methyl ester yield (%)	94.50	95.50	85.70
Kinematic viscosity(mm <sup>2</sup> /s)	2.60	2.45	2.40

The summary of the effects of the process variables gives an optimization criteria presented in Table 3. It shows that the methylic transesterification of the APSO, SASO and ASASO is optimized at a mixing rate of 140rpm and equal temperature, reaction time and methanol to oil molar ratio. The optimized catalyst concentration of APSO was 0.5wt% lower than that of the other two seed oils. At these conditions, the following methyl ester yields of ASASO had the lowest methyl yield which is above 85.00% while both APSO and SASO had methyl yields above 94.00%. The result of this study is in agreement with an optimized biodiesel yield of 94.36% obtained from sweet almond seed oil (SASO) using response surface methodology (RSM) on central composite design (CCD) approach at catalyst concentration of 1.5wt%, reaction time of 65 minutes, oil to methanol molar ratio of 1:5 and temperature of 50°C [38]. The viscosity of all the fatty acid methyl esters obtained were above 2.35 and below 2.65mm<sup>2</sup>/s.

#### 4. CONCLUSION

A comprehensive study on the process optimization of Sweet Almond, African Pear and African star apple seed oils alkali transesterification was performed. The GC-MS and physico-chemical parameters analysis of the optimum products showed that they are composed of mainly unsaturated methyl fatty esters and compared with the ASTM and EN norms. The influence of some major factors which are: reaction time, reaction temperature, methanol/oil molar ratio and catalyst concentration on the yield and viscosity of the methyl esters were observed. The African pear seed oil with high free fatty acid was subjected to two-step transesterification to reduce the FFA and increase its biodiesel yield. High biodiesel yields were obtained from the seed oils at low factor values. The viscosity of the methyl esters were all within the acceptable standards that promote fuel fluidity. This would promote low cost of production and good process control

conditions. All these show the viability of biodiesel production using the selected tropical feedstocks.

## REFERENCES

- [1] Zanette, A. E., Barella, A. R., Pesgher, B.C.S., Treichel, H., Oliveira, D., Mazutti, A. M., Silva, A. E and Oliveira, J. V. (2011) Screening, Optimization and Kinetics of *Jatropha curcas* Oil Transesterification with Heterogeneous Catalysts, *Renewable Energy* 36,726-731.
- [2] Demirbas, A. (2009) Progress and Recent Trends in Biodiesel Fuels, *Energy Conversion and Management* 50, 14-34 .
- [3] Fukuda, H., Kondo, A. and Noda, H. J. (2001) Biodiesel Fuel Production by Transesterification of Oils *Bioscience Bioenergy* 91, 405-416.
- [4] Atabani, A. E., Silitonga, A. S., Bardruddin, I. A., Mahlia, I. M; Masjuki, H. H. and Mekhilef, S. (2012) A comprehensive review on biodiesel as alternative energy resource and its characteristics, *Renewable and Sustainable Energy Reviews* 16, 2070-2093.
- [5] Reyero, I., Arzamendi. G., Zabala S, and Gandia, M. L. (2015) Kinetics of the NaOH-catalyzed Transesterification of Sun Flower Oil with Ethanol to Produce Biodiesel, *Fuel Processing Technology* 129, 147-155.
- [6] Mathiayzhagan, M. and Ganapathi, A. (2011). Factors affecting biodiesel production, *Research in Plant Biology*, 1(2)1-5.
- [7] Anitha, A. and Dawn, S. S. (2010) Performance Characteristic of Biodiesel Produced from Waste Groundnut oil Using Supported Heteropolyacids, *International Journal of Chemical Engineering and Applications* 1(3), 261-265.
- [8] Ma, F. and Hanna, M. A. (1999) Biodiesel Production A review, *Bioresource Technology* 70, 1-15.
- [9] Jagadale, S. S. and Jugulkar, L. M. (2012) Review of Various Reactions Parameters and Other Factors on Production of Chicken Fat Based Biodiesel, *International journal of Modern Engineering Research* 2(2), 407-411.
- [10] Kansedo, J. B. (2009) Synthesis of Biodiesel From Palm Oil and Sea Mango Oil Using Sulfated Zirconia Catalysts, M.Sc Thesis, University of Sains, Malaysia.
- [11] Ureigho, U. N. and Ekeke, B. A., (2010) Nutrient Values of *Chrysophyllum albidium* Linn (African star apple) as a Domestic Income Plantation Species, *African Research Review* 4(2), 50-56.
- [12] Adewusi, H. G. and Bada, S. O. (1997) Preliminary information on the Ecology of *Chrysophyllum albidium* in West and Central Africa, In *Proceedings of a National Workshop on the Potentials of Star Apple in Nigeria* 16, 25.
- [13] Ehiagbonare, J. E., Onyibe, H. I. and Okoegwale, E. E. (2008) Studies on the Isolation of Normal and Abnormal Seedlings of *Chrysophyllum albidium*, a Step Toward Sustainable Management of the Taxon in the 21<sup>st</sup> century, *Sci. Res. Essay* 3(12), 567-570.
- [14] Jayeoba, O. J., Ige, M. M., Omolaiye, J. A., Gbadamosi S. O., Ogunbanjo, R. O. and Abiola, I. O. (2007) Chemical Composition and Physical Properties of African Star Apple (*Chrysophyllum albidium*), *ASSET* 7(1), 37-42.
- [15] Audu, T. O. K., Aluyor, E. O., Egualeoma, S. and Momoh, S. S. (2013) Extraction and Characterization of *Chrysophyllum albidium* and *Luffa cylindrical* Seed Oils, *Petroleum Technology Development Journal* 3(1), 1-7.
- [16] Musa, U., Isa, A. G., Mohammed, J. A., Mohammed, U. G., Usman, Z. and Alharsan, B. (2015) Extraction of *Chrysophyllum albidium* Seed Oil, Optimization and Characterization, *Chemical and Process Engineering Research* 30, 1-8.
- [17] Ochigbo, S. S. and Paiko, Y. B. (2011) Effects of Solvent Blending on the Characteristics of Oils Extracted from the Seeds of *Chrysophyllum albidium*, *I.J.S.N* 2(2), 352-358.

- [18] Sam, S. M., Akonye, L. A., Mensah, S. I., and Esenowo, G. J., (2008) Extraction and classification of lipids from seeds of *Persea Americana miller* and *Chrysophyllum albidum* G. Don, *Scientia Africana* 7 (2), 35-38.
- [19] Adebayo, S. E., Orheuba, B. A., Adeoye, P. A., Musa, J. J. and Fase, O. J. (2012) Solvent Extraction and Characterization of Oil From African Star Apple (*Chrysophyllum albidum*) seeds, *Academic Research International Nat. & Appl.*3(2),178-183.
- [20] Giwa, S and Ogunbona, C., (2014) Sweet Almond (*Prunus amygdalus dulcis*) Seeds as a Potential Feedstock for Nigerian Biodiesel Automotive Project, *Rev. Ambient Aqua* 9(1), 35-48.
- [21] Mark, R., (2006) Introduction to Fruit Crops, published online, retrieved from: <https://en.wikipedia.org/w/index.php>
- [22] FAOSTAT, (2014) Production/Crops for Almond with Shell Food and Agriculture Organization of United States, Statistical Division, 65-120.
- [23] Agunbiade, S. O. and Olanlokun, J. O. (2006) Evaluation of Some Nutritional Characteristics of Indian Almond (*Prunus amygdalus*) Nut". *Pakistan J. Nutr.* 5, 316-318.
- [24] Ali, J. E., Rashid, J. and Rana, J. E., (2010) The Importance of almond (*Prunus amygdalus L.*) and Its bye-products: Review, *Food Chemistry*, 120 (2), 349-360.
- [25] Ogunsuji, H. O. (2015) Production of Biodiesel Using African Pear (*Dacyodes edulis*) Seed Oil as a Feedstock, *Academia Journal of Biotechnology* 3(5), 085-092.
- [26] Isaac, I. O. (2014) Extraction, Characterization of African Pear (*Dyacrodes edulis*) Oil and Its Application in Synthesis and Evaluation of Surface Coating, *Driers* 1 (11), 14-22.
- [27] Bull, O. S. and George, D. Mc. (2015) Assessment of Fuel Properties of Biodiesel Obtained from African Pear (*Dyocrodes edulis*) Seed Oil, *Int. J. of Advanced research in Science, Engineering and Technology* 2(10), 894-898.
- [28] Shikla, K. and Rita, C. Y. (2012) "Biodiesel Production From Non-edible Oils: A Review, *J. Chem. Pharm. Res.* 4 (9), 4219-4230.
- [29] AOAC, (1990) Official Methods of Analysis, Association of Official Analytical Chemists, 13th edition, Washington D.C
- [30] Patel, V. (1999) Cetane Number of New Zealand diesel: Report, office of Chief Gas Engineer, Energy Inspection Group, Ministry of Commerce Press. Wellington, New Zealand.
- [31] Sivaramakrishnam, K. and Ravikumar, P., (2012) Determination of Cetane Number of Biodiesel and Its Influence on Physical Properties, *ARFN Journal of Engineering and Applied Sciences* 7(2), 205-211.
- [32] Moreira, A. I., Dias, J. M., Almeida, M. F. and Alvim -ferraz, C. M. (2010) Biodiesel Production Through Transesterification of Poultry Fat at 30°C, *Energy Fuels* 24(10), 5717-5721.
- [33] Varanda, M. G., Pinto, G. and Martins, F. (2011) Life Cycle Analysis of biodiesel production, *Fuel Processing Technology* 92 (5), 1087-1094.
- [34] Liu, Y., Lolero, E., Goodwin, J. G. and Mo, X. (2007) Transesterification of Poultry Fat With Methanol Using Mg-Al Hydrotalcite Derived Catalysts, *Applied Catalysis* 331, 138-148.
- [35] Jubiano, M., Rocha Jnr, J. G, and Bauerfelot, G. E. (2014) Biodiesel Synthesis With Alkaline Catalyst a New Refractometric Monitoring and Kinetic Study, *Fuel* 125,164-172.
- [36] Hingu, S., Golgate, P. R and Rathod, V. K. (2010) Synthesis of Biodiesel From Waste Cooking Oil Using Sonochemical-Reactors, *Ultrasonic sonochemistry* 17, 827-832.
- [37] Anwar, F. and Rashid, U., (2007) Production of Biodiesel Through Optimized Alkaline-catalyzed Transesterification of Rapeseed oil, *Fuel* 87, 267-273.
- [38] Esonye, C., Onukwuli, O. D. and Ofoefule, A. U. (2018) Optimization of Methyl Ester Production from *Prunus Amygdalus* Seed Oil Using Response Surface Methodology and Artificial Neural Networks, *Renewable Energy* 130, 62-71.