www.rericjournal.ait.ac.th

Characterization and Flow Behaviour of Sandbox (*Hura crepitans Linn*) Seed Oil and its Methyl Esters

Solomon O. Giwa*[1], Kayode O. Adama*, Collins N. Nwaokocha*, and Olorunfunmi I. Solana[+]

Abstract – In this study, sandbox seed (*Hura crepitans Linn*) oil methyl ester (SSOME) was synthesized from Sandbox seed oil (SSO) using the classical reaction parameters (reaction time of 1 h, reaction temperature of 60°C, oil/methanol ratio of 1:6) with a yield of 82.73 ± 0.53%. The fuel properties of SSOME were determined based on standards. In addition, the flow behavior of SSO and SSOME was studied using a rheometer with shear rate range of 0-250 s^{-1} at 25, 40 and 55°C. The result showed that the fuel properties were found to satisfy recommended EN 14214 and ASTM D6751 specifications, expect for the oxidation stability. It was also observed that both SSO and SSOME exhibited pseudo plastic flow behavior at low shear rate (0-140s^{-1}) and they also displayed Newtonian flow behavior at shear rate range of 140-250 s^{-1}, all at 25, 40 and 55°C. This study reveals that the flow behaviors of SSO remains unchanged by transesterification process and those of SSO and SSOME are also not altered by increasing shear stress. With similar fatty acid profile and fuel properties to those of soybean and sunflower oils, SSO appears a potential feedstock for biodiesel production.

Keywords – Flow behaviour, fuel properties, methyl esters, oil, sandbox.

1. INTRODUCTION

The main sources of energy throughout the world are petrochemical, coal, hydroelectricity, and nuclear energy [1]. The fossil-derived fuel is wanting as a natural resource in many countries of the world with most of them in serious search of an alternative fuel for energy security. Over the years, petroleum-based fuel consumption has led to the emission of greenhouse gases into the environment and this has resulted in global warming of the earth surface. Diesel fuel is important in the industrial, transportation, and power generating sector of any economy which makes it to be in high demand worldwide. To reduce the problems associated with petroleum-based fuel, biodiesel has been considered as one of the alternative fuels to be used as a good replacement for diesel fuel [2]. Biodiesel is a liquid fuel obtained from oil-based biological material. Edible oils from soybean, rapeseed, palm and sunflower often used for food purposes have been predominantly used as biodiesel due to the increasing need for an alternative fuel to substitute diesel [3]-[4]. This scenario has affected the uses, price, production and availability of these oils for human consumption [5], which has spurred studies into the use of waste cooking oils and inedible oils in the production of biodiesel [3]-[6]. The raw materials used for biodiesel production are dependent on their availability in a particular geographical region [7]. Consequently, soybean, palm oil, rapeseed, coconut are used in United States, Thailand and Malaysia, Europe and Philippines, respectively. Less expensive oil (inedible oils and waste cooking oils) seems a good alternative since the use of edible oils for biodiesel production account for over 70% of the cost of production.

Rheology has to do with how materials act in response to applied forces and deformations. Materials (fluids, liquids and gases) present a certain resistance to deformation which results in the material viscosity [8]. Rheological behaviour of products or materials involves elasticity, viscosity, plasticity and the flow of matter. Predictive and behavioural information for different materials can be determined by measuring rheological properties, in addition to the knowledge of formulation changes and the effect of processing [9]. The rheological property of oil depends on factors which include time, temperature, pressure, shear rate, concentration, molecular weight, chemical properties, additive and catalyst [9].

Studies on the rheological behaviour of vegetable oils [9]-[10], vegetable oils (VOs) blended with other VOs [11], VOs blended with diesel oil [12]-[13], methyl esters of VOs [14]-[15] and, methyl and ethyl esters of VOs blended with diesel fuel [16]-[18] have been conducted. These studies have measured rheological properties such as cloud point, density, enthalpy, kinematic viscosity, lubricity, dynamic viscosity, surface tension, and pour point of VOs, methyl and ethyl esters with or without blending with diesel oil.

Viscosity as an important property of any fuel is an indication of its ability to flow. It is of significant influence in the mechanism of atomization of fuel spray in the operation of an injection system. In addition, viscosity increases as the temperature decreases, and biodiesel and its blends demonstrate a temperature-dependent behavior similar to diesel, in spite of the higher viscosity [19]. The effect of temperature is usually obvious on viscosity and it is even more significant than shear rate. It was found that the

*Department of Agricultural and Mechanical Engineering, College of Engineering and Environmental Studies, Olabisi Onabanjo University, Ibogun Campus, P.M.B. 5026, Ifo, Ogun State, Nigeria.

+Department of Food Science and Technology, Obafemi Awolowo University, P.M.B. 13, Ile-Ife, Osun State, Nigeria.

[1]Corresponding author; Tel: +2348091757240.
E-mail: sologiwa2002@yahoo.com;
solomon.giwa@oouagoiwoye.edu.ng.

viscosity of bio-edible oils converges and approaches low viscosity oil as the temperature increases [9]. For peanut oil-diesel fuel blends and biodiesel blends with diesel oil, a similar behavior was also reported [9]. The increase in temperature has a propensity to increase molecular interchange (motion) and reduce attractive forces between molecules. Oil viscosity has a direct relationship with some chemical characteristics of the oil, such as the degree of unsaturation and the chain length of the fatty acids that make up the triglycerides [10]. Viscosity slightly decreases with increased degree of unsaturation and this is the primary reason why oils are used as biodiesel [11].

Hura crepitans Linn (sandbox) is a tropical plant belonging to the family Euphorbiaceous. In Nigeria, this plant is known as "odan Mecca" by the Kabba people of Kogi State and "aroyin'' by the Ijesha people of Osun State. Hura crepitans is a widely occurring self-regenerating ornamental plant in the tropics and frequently planted in towns and villages as cover tree. It has a short, densely crowned spines on the trunk and branches, and the long-stalked leaves with notably closely parallel pinnate nerves. This tree flowers usually at the beginning and at the end of rainy season. Hura crepitans can be used as purgative. Its oil-bearing seed is under-utilized, marginalized or neglected despite its high oil content (over 50%). It is non edible, available at little or no cost of purchase and can be planted on marginal lands.

Consequently, this study focused on the use of sandbox seeds (*Hura crepitan L.*) as a raw material for biodiesel production. The oil and corresponding methyl ester from it was characterized. In addition, the flow behaviours of its oil and methyl esters were studied to have a proper understanding of their (oil and methyl esters from sandbox seeds) application in energy systems.

2. MATERIAL AND METHODS

2.1 Materials

Dry unshelled pods of sandbox were collected from the Campus of Covenant University, Ota, Ogun State, Nigeria. The seeds were carefully removed from the pods and deshelled. The creamy white cotyledons of the sandbox seeds were sun-dried to remove moisture and pulverized in monilex blender into a fine powder. The size reduction (milling) was carried out in order to provide a good surface for easy extraction of the oil from the powderized sandbox seeds. Reagents used for the transesterification process include methanol (99.5% purity), sodium hydroxide (85% purity), anhydrous sodium sulphate (98% purity) and n-hexane (99% purity), which were purchased from Belward Scientific (Nig.) Ltd., Ikeja, Lagos, Nigeria. Pure fatty acid methyl esters were purchased from Sigma Chemical Co. (USA). The chemicals were of analytical grades.

2.2 Extraction of Sandbox Seed Oil

About 1000 g of the grounded sandbox seeds was weighed using weighing balance and charged into the soxhlet apparatus in 40 g batches. The extraction was carried out using 400 ml of n-hexane in the soxhlet extraction apparatus for 8 h. The solvent was removed via a rotary vacuum evaporator at 40 - 50°C. The residue was weighed and stored at 20°C until it was analyzed. The weight of the sandbox seed oil (SSO) extracted from 40g of the sandbox seed was determined to calculate the lipid content according to AOAC official method 963.15 (AOAC, 1998). After the completion of the extraction process, the oil was stored in a cool, dry and safe place wrapped with aluminum foil in a conical flask until usage.

2.3 Pre-treatment of Sandbox Seed Oil

The SSO had a slightly high FFA of 7.29% (corresponding to an acid value of 3.65 mg KOH/g) which can cause soap formation when the oil is transesterified using alkaline catalyst. Moreover, alkaline catalyzed transesterification requires that the FFA be <2%. This necessitated the pre-treatment of the oil using previously reported procedure [18] to reduce the FFA to 1.16% (acid value of 0.58 mg KOH/g) prior to the commencement of the base catalyzed transesterification process.

2.4 Physicochemical Properties of Sandbox Seed Oil

The physical and chemical properties were conducted in accordance with standard test methods described in the AOAC [20]. The properties are; density, kinematic viscosity, iodine value, and acid value. These were conducted in triplicate and the average values reported.

2.5 Transesterification Reaction

A weighed amount (150 g) of SSO poured into a reactor was heated to a temperature of 60°C with the aid of a heater and a thermometer. An appropriate amount of methanol (44.05 g; 1:6 oil/methanol molar ratio) was measured and poured in a beaker with the required quantity of NaOH (1.5 g; 1%wt. oil) pellet added to it. The content of the beaker was manually stirred (vigorously) until the NaOH is completely dissolved in the methanol which would give a sodium methoxide mixture. The sodium methoxide was poured into the reactor containing the heated oil and the entire content in the reactor stirred at the rate of 360 revolution per minute (using magnetic stirrer) and temperature maintained at 60^{o}C. The heating and stirring was stopped after one hour and the resulting product poured into a separating funnel and allowed to settle down overnight. It was observed that the resulting mixture from the reaction had settled into two distinct layers of glycerol (bottom layer) and pale yellow crude sandbox seed oil methyl esters (SSOME) (upper layer). The separating funnel was opened to collect the glycerol into a container while the crude SSOME was collected in a separate container. The crude SSOME was heated on a rotary vacuum evaporator (at 80^{o}C for 1 h) to remove the excess methanol after which it was gently washed with warm distilled water (three times with two drops of diluted hydrochloric acid at the first wash) to remove residual catalyst or soaps. It was then dried with anhydrous sodium sulphate and filtered, and the resulting product (purified SSOME) stored in cool, dry place. The procedure was repeated three times and the average yield reported.

2.6 Fatty Acid Composition of Sandbox Seed Oil

The fatty acid profile of SSO and, the free and total glycerol contents of SSOME were determined using gas chromatography based on procedure reported in previous literature [21].

2.7 Fuel Properties of Sandbox Seed Oil Methyl esters

Biodiesel fuel properties of SSOME were determined using standard test methods according to ASTM D6751 and EN 14214 standards. The following fuel properties were measured; acid value (ASTM D664), iodine value (EN 14111), kinematic viscosity (ASTM D445), density (ASTM D5002), flash point (ASTM D93), cloud point (ASTM D2500), oxidation stability (EN 14112), pour point (ASTM D97) while the cetane number was empirically determined. These were carried out in triplicates (except cetane number) and the average reported herein.

2.8 Rheological Equipment Calibration and Measurement

The dynamic viscosity of SSO and SSOME was used to study their rheological behavior using Haake rheometer RS689 model. Measurements of shear rates (0 - 250 s^{-1}) and temperatures (30, 45 and 60°C) were taken using a PPTi 60 spindle and the temperature was controlled within ±1.0°C. The flatness of the sample plate was calibrated using water level before operating the rheometer. After automatically initializing the zero point of measurement and giving a gap of 0.5 mm, samples were smeared on the sample plate for testing and thereafter measurements were taken.

3. RESULTS AND DISCUSSION

3.1 Properties of Sandbox Seed Oil

The oil content of the sandbox seed was found to be 56.13%. This value is slightly less than that of American hazelnut (C. americana) (62.2%) and slightly less than those of Siberian almond (51%), egusi melon (50%), palm kernel (50%), sweet almond (51%) [18], [22], [23]. The quality of the SSO expressed in terms of the physicochemical properties is provided in Table 1. The oil properties measured are; acid value (3.65 mg/KOH, before pre-treatment; 0.58 mg/KOH), iodine value (74.82 g I_2/100g), FFA (7.29%, before pre-treatment; 1.16%, after pre-treatment), density (902 kg/m^3), and kinematic viscosity (22.05 mm^2/s). The values obtained for kinematic viscosity and density were compared with conventional oils and found to be in good agreement with those values [24].

3.2 Fatty Acid Profile and Yield of Sandbox Seed Oil

Figure 1 shows the FA composition of SSO determined using gas chromatography. The predominant FA was found to be linoleic acid (C18:1; 59.6%) while other FA components were oleic (C18:2; 22.1%), palmitic (C16:0; 11.7%), stearic (C18:0; 3.5%) and linolenic (C18:3; 3.1%). The oil of sandbox seeds contains the same FAs as those of soybean oil, sunflower oil and egusi melon seed oil with linolenic acid as the dominant FA [25]. The saturated (palmitic and stearic acids) and unsaturated (oleic, linoleic, linolenic acids) FA contents of the oil were 15.2% and 84.8%, respectively. This indicates that this oil is highly unsaturated. In this study, an average yield of 82.73 ± 0.53% was achieved. Previous studies on the transesterification of crude oils of karanja [26], acorn kernel oil [27], rice bran [28], egusi melon seed [25] and sweet almond [21] gave 84, 90, 83.31, 82.5 and 85.9% ester yield, respectively. Considering the above, the yield obtained in this present study is within range of previous studies and can be said to be in agreement with them.

Table 1. Sandbox seed oil quality.

Property	Sandbox seed oil
Density (at 15°C; kg/m^3)	902 ± 3.14
Kinematic viscosity (at 40°C; mm^2/s)	22.05± 1.29
Acid value (mg KOH/g)	3.65± 0.32[a]; 0.58± 0.051[b]
Free fatty acid (%)	7.29± 0.56[a]; 1.16± 0.22[b]
Iodine value (g I_2/100g)	74.82± 2.39

[a]Before oil treatment; [b]After oil treatment

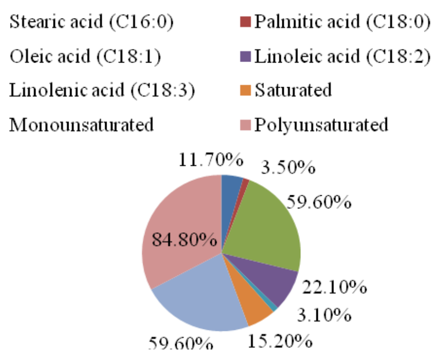

Fig. 1. Fatty acid profile of sandbox seed oil.

3.3 Fuel Properties of Sandbox Seed Oil Methyl Esters

3.3.1 Kinematic viscosity

Viscosity is the most important property of biodiesel since it affects the operation of fuel injection equipment, especially at low temperatures when an increase in viscosity affects the fluidity of the fuel. Biodiesel has a viscosity close to that of diesel fuel. The KV of biodiesel is significantly influenced by the feedstock used. For SSOME, the KV was determined to be 4.03 mm^2/s. The higher viscosity of biodiesel may cause operational problems (such as engine deposits) which led to the transesterification of VOs to reduce their viscosities. From Table 2, it could be seen that this value fits well into the ASTM D6751 and EN 141214 standards. The KV of soybean and sunflower were 4.12 mm^2/s and 4.16 mm^2/s [25], respectively. As seen in Table 2, the KV of SSOME was 4.03 mm^2/s while the KV of its oil was 22.05 mm^2/s. This implies 81.72% reduction of the parent oil (SSO).

3.3.2 Density

Density is another important property of biodiesel. It is the weight of a unit volume of fluid. Fuel injection equipment operates on a volume metering system, hence a higher density for biodiesel results in the delivery of a slightly greater mass of fuel. The density of biodiesel produced from sandbox seed oil was 891 kg/m^3. This value is within the range of 860-900 kg/m^3 specified by EN 14214 standards, but no specification is stipulated for density by ASTM D6751. Also, the density of SSOME is slightly above that of soybean and sunflower (Table 2).

3.3.3 Flash point

Flash point (FA) of a fuel is the temperature at which it will ignite when exposed to a flame or spark. Biodiesel offers safety benefits over petroleum diesel because it is much less combustible, with a greater FP, compared to petroleum diesel (77°C). Biodiesel has lower volumetric heating values (about 12%) than diesel fuels but has a high FP [29]. The biodiesel produced from SSO had a FP (175°C) greater than conventional diesel (77°C) by 98°C. The value of the FP obtained for this work conformed to both biodiesel standards as shown in Table 2. The FP of SSOME is higher than those of sunflower and soybean oil (Table 2).

3.3.4 Cetane number

The cetane number measures the tendency of the fuel to self-ignite at the temperature and pressure in the cylinder when the fuel is injected. A high CN implies short ignition delay. The CN number of biodiesel is generally higher than conventional diesel. Biodiesel CN depends on the feedstock used for its production. The longer the FA carbon chains and the more saturated the molecules, the higher the CN [1]. A higher CN indicates that the fuel is more ignitable. The CN of SSOME was empirically determined [1] its value is 51.4 which slightly exceeds the minimum cetane number prescribed in ASTM D6751 and EN 14214 (Table 2). The CN of biodiesel produced from oils with analogous FA profile such as soybean and sunflower were 54 and 51 respectively which are also in good agreement.

3.3.5 Acid value

Acid value is a measure of the FFA content in the biodiesel and is expressed as the milligram of KOH required to neutralize the FFAs in 1 gram of the sample. The AV of the SSOME produced in the present work was 0.29 mg KOH/g (Table 2). AV of SSOME satisfied this specifications (0.5 mg KOH/g) and hence an indication of good biodiesel quality in this regard. As seen in Table 2, the AV of SSOME (0.29 mg KOH/g) is slightly higher than those of soybean oil biodiesel (0.12 mg KOH/g) and sunflower biodiesel (0.15 mg KOH/g), and the values conforms to ASTM D6751 and EN 14214 standards.

3.3.6 Iodine value

The iodine value is an index of the number of double bonds within a mixture of FA contained in biodiesel. Therefore, it is a measure of the total unsaturation of a fatty material measured in grams of iodine per 100 g of sample when iodine is formally added to the double bonds. The IV of SSOME was 76.2 g I_2/100g. The result satisfied the specification of 130 g I_2/100g (maximum) recommended by EN 14214 standards, as shown in Table 2. The IV of SSOME as seen in Table 2 is low compared to sunflower and soybean oil biodiesels.

3.3.7 Cloud and pour points

The cold flow properties of SSOME were obtained by measuring CP and PP. No specification was recommended for CP and PP in the biodiesel standards, although ASTM D6751 requires that CP be reported. A major disadvantage of biodiesel compared to diesel fuel is its inferior cold flow properties, which is aggravated by the presence of higher-melting saturated FAs in biodiesel [30]. In addition, the amount of the saturated FAs contained in biodiesel has been reported to have proportionate effect on its low temperature properties [25]. SSOME, with low saturated FA content of 15.2%, exhibited relatively low CP (-1.0°C) and PP (-6.0°C) values (Table 2). These properties of SSOME are comparable to those previously reported for methyl esters of almond oil, canola oil and soybean oil, which are known to exhibit relatively low temperature properties due to the low content of SFA inherent in them [21], [31].

3.3.8 Oxidation stability

The oxidation stability (OS) of biodiesel is a measure of its shelf life. A minimum Rancimat induction period (110°C) of 3 h is recommended for ASTM D6751 while a limit of 6 h or greater is specified in EN 14214. An OS of 2.47 h was obtained for SSOME, which was lower than that recommended by ASTM D6751 and EN 14214 (Table 2). This value of OS is attributable to the higher content of polyunsaturated FAs (C18:2, 22.1%; C18:3, 3.1%) which oxidize at significantly faster rates than monounsaturated FAs (C18:1, 59.6%) [25]. OS of SSOME can be improved by the addition of antioxidants or the blending of the biodiesel with diesel fuel.

3.3.9 Other properties

Linolenic acid content of SSOME was determined to be 3.1%. This value is well within the EN 14214 specification since it is considerably lower than the 12% (maximum) it recommended. Furthermore, the SSOME synthesized from SSO satisfied the free (0.011%) and total (0.192%) glycerol specifications prescribed in both EN 14214 and ASTM D6751 biodiesel standards (Table 2).

3.4 Flow Behaviour of Sandbox Oil and its Methyl Esters

Viscosity is a vital fuel property which depends on the make-up of the parent oil in terms of FA profile and thus, the fatty ester composition of equivalent alkyl ester. A Newtonian fluid is one in which the viscosity is constant and does not dependent on the shear rate at a specified temperature. On the contrary, a fluid is non-Newtonian when its viscosity is not constant. In addition, fluids are said to be thixotropic or rheopectic when their viscosities depend on time. Nevertheless, when viscosity is independent of time the fluids are called pseudoplastic, dilatant, plastic and Bingham plastic. For this study, the viscosity of SSO and SSOME is used to investigate their behaviours under increasing shear rate between 0 and 250 s^{-1}.

Table 2. Fuel properties of sandbox seed oil methyl esters.

Property	Unit	Limits		SSOME
		ASTM D6751	EN 14214	
Density; 15°C	kg/m^3	-*	860-900	891± 3.29
Kinematic viscosity; 40°C	mm^2/s	1.9-6.0	3.5-5.0	4.03± 0.31
Flash point	°C	130 min	120 min	175± 2.42
Cloud point	°C	Report	-*	-1± 0.076
Acid value	mg KOH/g	0.5 max	0.50 max	0.29± 0.032
Linolenic acid content	% (mol/mol)	-*	12.0 max	0.31± 0.029
Iodine value	g I_2/100g	-*	120 max	76.2± 1.36
Oxidative stability	h	3 min	6 min	2.47± 0.34
Pour point	°C	-*	-*	-6± 1.02
Cetane number		47 min	51 min	51.4
Free glycerol	mass %	0.02 max	0.02 max	0.011± 0.0018
Total glycerol	mass %	0.24 max	0.25 max	0.192± 0.017

*Not specified

3.4.1 Flow behaviour of SSO

Viscosity is known to be strongly correlated with the structural variables of the fluid particles [10]. The viscosity of oil has a linear relationship with some physicochemical properties of the oil, which include the degree of unsaturation and the chain length of the fatty acids that make-up the oil. Figure 2 provides the changes in shear stress against shear rate at 25°C. It can be seen that as the shear stress increases with shear rate, the viscosity of SSO increases. The flow index (n) of 1(unity) is estimated for Figure 2 and this indicates that viscosity of SSO is constant under varying shear rate. As can be observed in Figure 2, a linear relationship exists between shear stress and shear rate which implies that SSO exhibits a Newtonian flow behavior. In addition, Figure 3 gives a clearer view of the nature of flow exhibited by SSO. As the shear stress increases with a corresponding increase in shear rate, a rapid decrease in viscosity is observed from shear rate of 0 to 140 s^{-1} (Figure 3). This flow behavior is known as pseudoplastic and it is noticed at low shear rate of below 140 s^{-1}. Also from Figure 3, a Newtonian flow behavior is exhibited above shear rate of 140 s^{-1} with the display of constant viscosity of the oil. This part of Figure 3 just discussed witnesses high shear rate from increasing shear stress. The flow index reported in this study is estimated using the Equation 1.

$$\tau = \vartheta \gamma^n \quad ` \qquad (1)$$

For rheological study of the viscosity of SSO at temperatures of 40 and 55°C, similar flow behaviors (pseudoplastic from 0-140 $s^{-1}$and Newtonian from 140-250 s^{-1}) are observed when shear stress is increased with increase in shear rate. It is also noticed that the increase in temperature of SSO resulted in viscosity reduction and this is in agreement with what has been reported in literature [9], [19]. Several studies have reported Newtonian flow behaviors for a good number of vegetable oils investigated for their rheological properties, which is subject to the stress rate used in the study [9], [10], [32].This indicates that the present study is in agreement with previous studies. Conversely, at low shear rate, Bingham flow behavior was reported [11] against the pseudoplastic flow behavior obtained at low shear rate in this study and other previous studies [9], [10], [32].

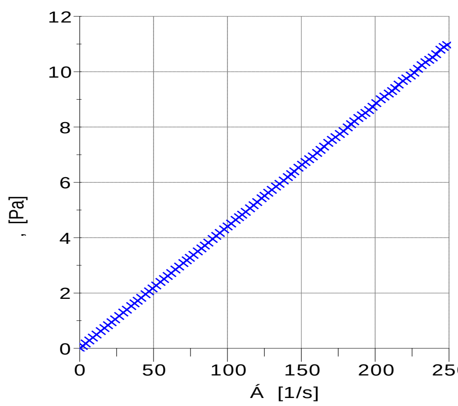

Fig. 2. Rheogram of shear stress versus shear rate of sandbox seed oil at 25°C.

3.4.2 Flow behaviour of SSOME

Figures 4 and 5 shows the shear stress against the shear rate and viscosity of SSOME versus the shear rate all at temperature 25°C, respectively. In Figure 4, an increase in shear stress with a corresponding increase in shear rate is observed. This depictsa straight line between the two variables (shear stress and shear rate), which is an indication that the viscosity of SSOME at 25°C does not depend on the shear rate and thus, a Newtonian flow behavior is obtained. With flow index of unity (1) estimated for SSOME at 25°C, this corroborates the fact that SSOME demonstrates a Newtonian flow behavior. For this study, the estimated flow indices of SSOME at various points (20, 50, 60 and 90) in the plots of shear stress against shear rate at 25, 40 and 55°C is presented in Table 3.

From Figure 5, two distinct regions are observed. The first region is from shear rate of 0 s^{-1} to 140 s^{-1}(low shear rate) while the second is from 140 s^{-1} to 250 s^{-1} (high shear rate). For the first region, a remarkable reduction in SSOME viscosity as the shear rate increases is noticed from 0 s^{-1} to 140 s^{-1} and this is indicative of the pseudo plastic flow behaviour of SSOME. The second region observed from shear rate of 140 s^{-1} displays constant viscosity with increase in shear rate. This implies that SSOME exhibits Newtonian flow behaviour and it is therefore evident that both pseudoplastic and Newtonian flow behaviours are exhibited by SSOME with increasing shear rate from 0 and 250 s^{-1} (Figure 5).

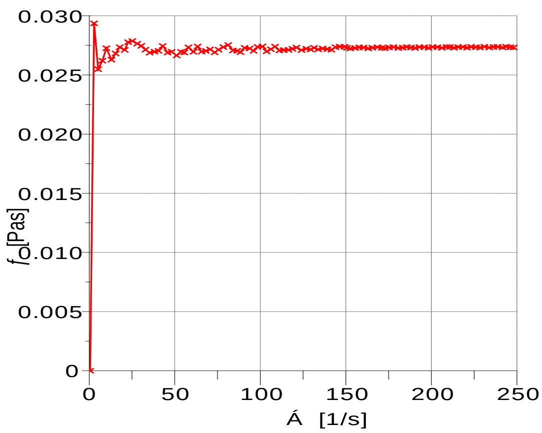

Fig. 3. Rheogram of viscosity versus shear rate of sandbox seed oil at 25°C.

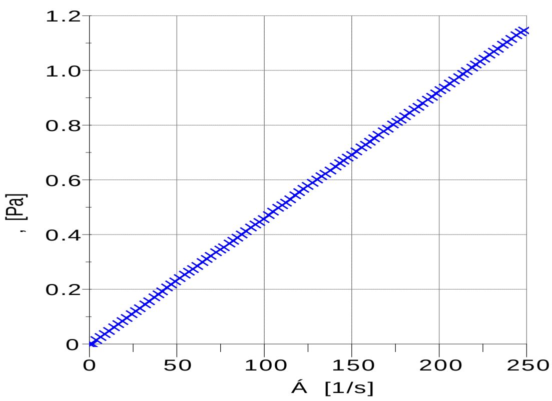

Fig. 4. Rheogram of shear stress versus shear rate of sandbox seed oil methyl esters at 25 °C.

For rheological property of SSOME in terms of viscosity investigated at 40 and 55°C, similar trend of results is obtained regarding the viscosity and shear stress against shear rate at 25°C as earlier discussed. Obviously, pseudoplastic flow behaviour followed by Newtonian flow behaviourat 0-140 s^{-1} and 140-250 s^{-1}, respectively, is characterized by this study. It is clearly noticed with the increase in temperature from 25 to 55°C that the viscosity of SSOME decreases as the temperature increases. This observation is in consonance with and earlier studies that viscosity of biodiesel decreases with increase in temperature [16], [17], [19].

Furthermore, it is noticed that the flow behaviours (pseudoplastic and Newtonian) of SSOME in this study agrees with that of castor oil biodiesel [8], [21]. However, for the castor oil biodiesel, the pseudo plastic and Newtonian behaviours observed were at low shear rate (0 and 80 s^{-1}) [8]. The pseudo plastic and Newtonian flow behaviours were at0 - 20 s^{-1} and 20 - 80 s^{-1}, respectively.

It is worth noting in this present study that similar flow behaviours (pseudoplastic and Newtonian) are observed at 25, 40 and 55°C for both SSO and SSOME. These results depict that transesterification reaction which does not alter fatty acid profile of oil that goes into methyl esters production, does not change flow behaviours of oil (SSO) and methyl esters (SSOME). Thus, this supports the fact that the main purpose of transesterification process is to reduce the viscosity of oil for its suitability as fuel [25]. It can be deduced also that the application of equal shear stress on oil (SSO) and methyl esters (SSOME) at the same temperature does not affect their flow behaviours.

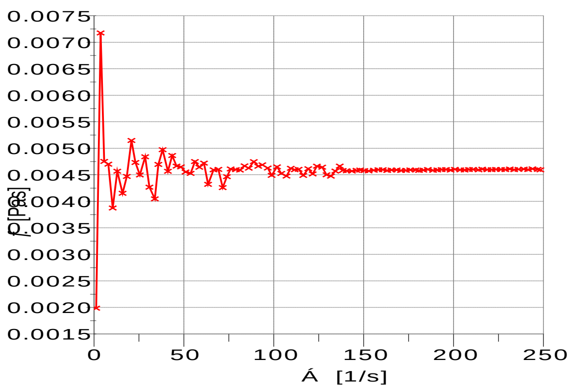

Fig. 5. Rheogram of viscosity versus shear rate of sandbox seed oil methyl esters at 25°C.

Table 3. Indices of sandbox seed oil methyl esters.

Temp. (°C)	Point	τ (Pa)	γ (s^{-1})	υ (mPas)	n
25	20	0.225	48.34	4.649	1.0003
	50	0.578	124.00	4.662	0.9999
	60	0.679	148.00	4.589	0.9999
	90	1.029	223.60	4.601	1.0000
40	20	0.171	48.51	3.533	0.9994
	50	0.446	124.40	3.584	1.0001
	60	0.520	147.90	3.519	0.9998
	90	0.782	223.80	3.493	1.0000
55	20	0.096	48.77	2.412	0.9954
	50	0.248	124.70	2.574	0.9978
	60	0.298	147.60	2.626	0.9997
	90	0.450	224.10	2.630	1.0005

4. CONCLUSIONS

SSOME was synthesized from SSO using the classical reaction parameters (reaction time of 1 h, reaction temperature of 60°C, oil/methanol ratio of 1:6) with a yield of 82.73 ± 0.53%. The quality and fuel properties of SSOME determined were found to satisfy stipulated EN 14214 and ASTM D6751 specifications, expect for the oxidation stability. For this study, pseudo plastic flow behaviours were exhibited at low shear rate of 0 - 140 s^{-1} while Newtonian flow behaviours were displayed at shear rate of 140 - 250 $s^{-1}$for both SSO and SSOME at temperatures of 25, 40 and 55^{o}C. This result is in agreement with previous studies on rheological behaviours of oils and methyl esters. SSO is non-edible with similar FA profile and close biodiesel fuel properties to those of soybean oil, sunflower oil and cotton seed oil, and thus presents itself as an alternative to these oils for biodiesel production. This oil appears a potential feedstock for biodiesel production since it has no demand for food use and can be cultivated on marginal lands.

ACKNOWLEDGEMENTS

The contribution of Olushola Fagbohun of the Department of Agricultural and Mechanical Engineering of Olabisi Onabanjo University during the course of the research is hereby acknowledged.

NOMENCLATURE

τ =shear stress
ϑ = dynamic viscosity
γ = shear rate
n = flow index

REFERENCES

[1] Ramos M.J., Fernandez C.M., Casas A., Rodriguez, L. and Perez, A., 2009. Influence of fatty acid composition of raw materials on biodiesel properties. *Bioresource Technology* 100: 261-268.

[2] El-Diwani G., Attia N.K. and Hawash S.I., 2009. Development and evaluation of biodiesel fuel and by-products from jatropha oil. *International Journal on Environmental Science and Technology* 6: 219-224.

[3] Balat M. and H. Balat. 2008. A critical review of biodiesel as vehicular fuel. *Energy Conversion Management* 49: 2727-2741.

[4] Demirbas A., 2007. Importance of biodiesel as transportation fuel. *Energy Policy* 35: 4661-4670.

[5] Rashid U., Anwar F., Moser B.R. and Ashraf S., 2008. Production of sunflower oil methyl esters by optimized alkali-catalyzed methanolysis. *Biomass Bioenergy* 32: 1202-1205.

[6] Mariod A., Klupsch S., Hussein I.H., and Ondruschka B., 2006.Synthesis of alkyl esters from three unconventional Sudanese oils for their use as biodiesel. *Energy Fuels* 20: 2249-52.

[7] Pinto A.C., Guarieiro L.L.N., Rezende M.J.C., Ribeiro N.M., Torres E.A., and Lopes W.A., 2005. Biodiesel: an overview. *Journal of Brazil Chemical Society* 16: 1313-30.

[8] Conceicao M.M., Candeia R.A., Dantas H.J., Soledade L.E.B., Jr., V.J.F. and Souza A.G., 2005. Rheological behavior of castor oil biodiesel. *Energy and Fuels* 19: 2185-88.

[9] Nik W.B.W., Ani F.N., Masjuki H.H., and Giap S.G.E., 2005. Rheology of bio-edible oils according to several rheological models and its potential as hydraulic fluid. *Industrial Crops Production* 22: 249-255.

[10] Rubalya V.S. and P. Neelameagam. 2008. A Study of rheological behavior and oxidative stability of rice bran and corn oil using FTIR spectra. *International Journal of Pure Applied Physics* 4: 77-86.

[11] Santos J.C.O., Santos I.M.G., and Souza A.G., 2005. Effect of heating and cooling on rheological parameters of edible vegetable oils. *Journal of Food Engineering* 67: 401-5.

[12] Goodrum J.W., Geller D.P. and Adams T.T., 2003. Rheological characterization of animal fats and their mixtures with #2 fuel oil. *Biomass Bioenergy* 24: 249-256.

[13] Tangsathitkulchai C., Sittichaitaweekul Y., and Tangsathitkulchai M., 2004. Temperature effect on the viscosities of palm oil and coconut oil blended with diesel oil. *Journal of American Oil Chemistry Society* 81: 401-5.

[14] Tate R.E., Watts K.C., Allen C.A.W. and Wilkie K.I., 2006. The densities of three biodiesel fuels at temperatures up to 300°C. *Fuel* 85: 1004-1009.

[15] Tate R.E., Watts K.C., Allen C.A.W., and Wilkie K.I., 2006. The viscosities of three biodiesel fuels at temperatures up to 300°C. *Fuel* 85: 1010-1015.

[16] Joshi R.M. and M.J. Pegg. 2007. Flow properties of biodiesel fuel blends at low temperatures. *Fuel* 86: 143-151.

[17] Candeia R.A., Freitas J.C.O., Souza M.A.F., Conceicao M.M., Santos I.M.G., Soledade L.E.B., and Souza AG., 2007. Thermal and rheological behaviour of diesel and methanol biodiesel blends. *Journal of Thermal Analysis Calorimetry* 87: 653-656.

[18] Giwa S.O., Luqman A.C., and Adam N.M., 2014. Fuel properties and rheological behavior of biodiesel from egusi (*Colocynthis citrullus* L.) seed kernel oil. *Fuel Process Technology* 122: 42-48.

[19] Candeia R.A., Silva M.C.D., Filho J.R.C., Brasilino M.G.A., Bicudo T.C., Santos I.M.G., and Souza A.G., 2009. Influence of soybean biodiesel content on basic properties of biodiesel–diesel blends. *Fuel* 88: 738-743.

[20] Firestone D., 1998. *Official methods and recommended practices of the American oil Chemists' Society*. London: Champaign.

[21] Giwa S. and C. Ogunbona. 2014. Sweet almond (Prunus amygdalus "dulcis") seeds as a potential feedstock for Nigerian Biodiesel Automotive Project. *Revista Ambiente and Água* 9: 37-45.

[22] Lane J.W., Hlina P., Hukriede K., Jersett A., Koirala D., Stewart A., and Waxman M.A., 2012. Probing Wisconsin highbush cranberry (*V. trilobum*), dotted horsemint (*M. punctata*), and American hazelnut (*C. americana*) as potential biodiesel feedstocks. *Industrial Crops Production* 36: 531-535.

[23] Wang L., 2013. Properties of Manchurian apricot

(Prunus mandshurica Skv.) and Siberian apricot (Prunus sibirica L.) seed kernel oils and evaluation as biodiesel feedstocks. *Industrial Crops Production* 50: 838-843.

[24] Demirbas A., 2009. Progress and recent trends in biodiesel fuels. *Energy Conversion Management* 50: 14-34.

[25] Giwa S.O., Chuah L.A., and Adam N.M., 2010. Investigating "Egusi" (*Citrullus Colocynthis* L.) seed oil as potential biodiesel feedstock. *Energies* 3: 607-18.

[26] Srivastava P.K. and M. Verma. 2008. Methyl ester of karanja oil as alternative renewable source energy. *Fuel* 87: 1673-1677.

[27] Karabas H., 2013. Biodiesel production from crude acorn (Quercus frainetto L.) kernel oil: An optimisation process using the Taguchi method. *Renewable Energy* 53: 384-388.

[28] Rashid U., Anwar F., Ansari T.M., Arif M., and Ahmad M., 2009. Optimization of alkaline transesterification of rice bran oil for biodiesel production using response surface methodology. *Journal of Chemical Technology and Biotechnology* 84: 1364-70.

[29] Srivastava A. and R. Prasad. 2000. Triglycerides-based diesel fuels. *Renewable and Sustain Energy Reviews* 4: 111-33.

[30] Moser B.R., 2012. Preparation of fatty acid methyl esters from hazelnut, high-oleic peanut and walnut oils and evaluation as biodiesel. *Fuel* 92: 231-38.

[31] Moser B.R. and S.F. Vaughn. 2010. Evaluation of alkyl esters from Camelina sativa oil as biodiesel and as blend components in ultra low-sulfur diesel fuel. *Bioresource Technology* 101: 646-53.

[32] Giap S.G.E., Nik W.M.N.W., Ahmad M.F., and Amran A., 2009. The assessment of rheological model reliability in lubricating behaviour of vegetable oils. *Engineering e-Transactions* 4: 81-89.

[33] Moser B.R., Knothe G., Vaughn S.F., and Isbell T.A., 2009. Production and evaluation of biodiesel from field pennycress (Thlaspi arvense L.) oil. *Energy Fuels* 23: 4149-55.