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Biodiesel Potentials and Lubricating Properties of *Citrus sinensis* Seed Oil

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Abstract: Potentials of *Citrus sinensis* seed oil were evaluated for its biodiesel and lubricating properties. The oil of *C. sinensis* seed was extracted using n-hexane and then transesterified using various methanol: oil ratios. The physicochemical properties of the oil and the resultant biodiesel, such as viscosity, acid value, iodine value, free fatty acid value, pour point, cloud point, smoke point, specific gravity and surface tension, were determined. The raw oil exhibited a low oxidative stability, while the biodiesel ratio with the highest methanol content had a biodiesel potential that could compete favourably with that of fossil diesel. The test for the burning efficiency of the respective biodiesel ratios indicated that the ratio with the lowest alcohol content had the best burning efficiency. This was evident from its relatively low flash point. The study concluded that the non-edible oil obtained from the seeds of *C. sinensis* could serve as a highly reliable substitute for the production of very good quality biodiesel fuels.

Keywords: Biodiesel, Lubricating Properties, Seed Oil, Citrus Sinensis, Physicochemical Properties

1. Introduction

Over the ages, generation and utilization of heat by man progressed from solar radiation by the sun, geothermal source, the use of biomass, and discovery and use of coal to replace biomass. Later, discovery of petroleum products which are being used in various ways by humans for generating heat in cooking gadgets, powering internal combustion engines and reducing frictions in parts of engines also followed. For several decades since the discovery of fossil fuel, humans have depended on it as a source of energy and the industrial revolution of the earlier decades was catalyzed by availability of gaseous, liquid and solid fossil fuels.

There are three major concerns with respect to the use of petroleum-based fuels. One, fossil fuel as a petrochemical energy stock is non-renewable and can be exhausted with time as a result of continuous and various utilizations [1-3]. This, in part, explains the rising cost of conventional petroleum products as a result of their global depletion. Besides, of grave concern is the fact that exploration and exploitation of fossil fuel could lead to serious environmental degradation. Also associated with combustion of petroleum products is the problem of emission of higher levels of noxious pollutants into the environment than vegetable derived biofuels [2]. To forestall the impending energy shortage and associated challenges, it becomes imperative for scientists to be proactive and rise up to the exigencies of sourcing and developing alternative fuels that could solve some of the highlighted environmental and economic problems [4-6].

Environmental legislation by occupational safety and health administration (OSHA) and other international regulation authorities discourage the use of mineral oil-based lubricants and environmentally harmful additives and have actually recommended vegetable oils as alternatives from which biofuels and lubricants can be developed. This is because biofuels from vegetable oils are more environmentally friendly, non-toxic, renewable, widely available and readily biodegradable in nature [5, 6]. According to Rudnick [7], vegetable oils possess excellent potentials as lubricants and functional fluids as a result of their triacylglycerol structure, long fatty acid chains, presence of polar groups and closed packed monomolecular or multimolecular layer resulting in a surface film that provides desirable qualities as a lubricant. Other advantages include very low volatility due to the high molecular weight of the triglyceride molecule and excellent viscosity properties.

Biofuel, such as biodiesel, is a fuel derived from biomass containing carbon fixed through a natural process known as photosynthesis. Currently, biodiesel is fast gaining wide acceptance in several countries of the world to the extent that respective governments are giving out incentives to encourage rapid growth of the biodiesel industry [8]. For instance, Brazil has promulgated a law that makes it compulsory for every diesel sold in the country to contain at least 10% biodiesel [9]. Biodiesel is an alkyl ester derived from the reaction between oil from an oil-bearing biomass (such as Soybean, peanut, Jatropha, *Hura crepitans*, Mustard seed, *Citrus sinensis*, palm fruit, sunflower, hemp, vegetable oil, animal fat and algae oil and animal fat) and a monohydric alcohol in the presence of a catalyst, releasing glycerol as a byproduct [10-13]. The monohydric alcohols mostly used for the production of biodiesel are low molecular weight alcohol, such as methanol, ethanol, propanol and isopropanol. Methanol is mostly used because it has the least molecular weight among the monohydric alcohols [6, 12, 14], thereby giving the resultant biodiesel the name Fatty Acid Methyl Esters (FAMEs) [15].

Biodiesel can be used alone or be blended with petroleum based diesel due to the fact that they both have similar characteristics. Generally, advantages of biodiesel over the conventional diesel oil include the fact that biodiesels combine more favourable combustion output due to higher cetane number with viscosity that is related to that of conventional biodiesel, better lubricating power and the absence or very limited amount of sulphur. These characteristics bring about lower emission of sulphur oxides and carbon (IV) oxide and higher ignition property.

Relying on conventional edible seed oils for biofuel production could lead to scarcity and price uptrend of edible oils [16]. To avoid this and for the fact that the tropical countries including Nigeria are endowed with non-conventional oil-rich seed-bearing plants among other natural resources [17], it is imperative to focus on readily available non-conventional seed oils that have, hitherto, been considered as waste but could offer both low production cost and large production scale [12, 18] for the development of lubricants and biofuels.

Juice from the ripe fruit of *Citrus sinensis* is popularly consumed either as an appetizer or as a blood purifier or because of its high content of Vitamin C. However, its seeds generated in large quantities throughout the year, which serve as the basis of this study, are often discarded as a waste. In the past, the oil from the seed has been used for soap making [19-20], but there is paucity of data on the lubricating properties of the extracted seed oil and biofuels developed from the oil. This fact necessitated the study of the lubricating properties of the oil and its biodiesel potential through transesterification.

2. Method

2.1. Collection and Preparation of Sample

Citrus Sinensis seeds were collected from the campus of the Obafemi Awolowo University, Ile-Ife and Odo-Ogbe market also in Ile-Ife, Osun State, Nigeria. The seeds were air dried to constant weight and manually decorticated. The decorticated seeds were further air dried to ascertain proper drying. The properly dried seeds were ground into fine particles with the aid of an electrically operated laboratory blender (Nakai Japan, model N9991). Lubricating oil (SAE 40) and diesel oil were purchased from Total filling station, Ile-Ife for lubrication properties and biodiesel potential comparisons, respectively.

2.2. Extraction of Oil

Extraction of oil from the dried and pulverized seeds was carried out using Soxhlet extractor according to the Association of Official Analytical Chemists' (AOAC) method (AOAC, 2004) [21] in which case 20 g of the milled sample was weighed at a time and packed into a cellulose thimble prewashed with acetone / n-hexane (1:1) mixture and allowed to dry in an oven at a temperature of 70°C for 2 h before used. Each extraction batch of the oil with n-hexane lasted 7 h on the average. After extraction, the content in the flask was concentrated by distilling off the n-hexane content using rotary evaporator to obtain a solvent-free crude oil.

2.3. Conversion of Oil to Biodiesel

About 20 g of oil was measured into a flat bottomed flask and placed on a magnetic stirrer. This was followed by the addition of a mixture of pure methanol and concentrated sulphuric acid for pre-treatment. With the aid of a bar magnet, the mixture was agitated at 500 rpm for about 1 hour. The mixture was transferred into a separating funnel in order to separate the oil from the upper methanol-water mixture. The pre-treated oil was replaced on the magnetic stirrer at a temperature of about 60°C and transesterification of all the vegetable oils was carried out with 5 mL of methanol in the presence of KOH as a catalyst to obtain a biodiesel sample tagged B4:1. The process was repeated with 25 g and 30 g of the oil to obtain B5:1 and B5:2 biodiesel samples. The method recommended by Van Gerpen et al. [22] was employed.

2.4. Percentage Yield of the Biodiesel

The percentage biodiesel yield was calculated using the relationship:

$$\% \text{ conversion} = \frac{\text{massof biodiesel produced}}{\text{mass of oil used}} \times 100$$

The physico-chemical properties of oil, biodiesel produced for both the raw and the degummed oils were carried out according to the AOAC and American Society for Test and Material (ASTM) methods outlined by Leevijit *et al*. [23].

2.5. Parameters Determined

With respect to the raw oil and biodiesel developed from the oil, the parameters determined were specific gravity, dynamic viscosity, cloud point, pour point, smoke point, flash point, surface tension, acid value, percentage free fatty acid value, iodine value and heating efficiency according to ASTM and AOAC methods as outlined by Leevijit *et al*. [23].

2.5.1. Specific Gravity

The specific gravity was carried out through the aid of a 25 mL density bottle. The bottle was thoroughly washed, dried, stoppered and weighed empty. The bottle was then filled to the brim with distilled water and stoppered. The water oozing out of the bottle was wiped dry with tissue paper and the bottle was weighed again. The weight of the water was recorded as the value at room temperature. The same step was followed at 30, 40, 50, 60, 70, 80, 90 and 100°C by placing the density bottle in a water bath for about ten minutes and cooled before weighing. In each case, duplicate measurements were obtained. The procedure above was repeated using oil at the same temperature range. The specific gravity was then calculated using this equation:

$$Specific\ gravity = \frac{Weight\ of\ the\ Oil}{Weight\ of\ equal\ volume\ of\ water}$$

2.5.2. Dynamic Viscosity

The determination of the dynamic viscosity of the oil sample, biodiesels and distilled water were carried out within a temperature range of 28°C to 100°C using an Oswald Kinematic viscometer immersed in a water bath. The readings were taken in triplicates at each temperature and the average value was taken. The viscosity of the samples was calculated from the expression:

$$\eta o = \frac{\eta\text{w}.\rho\text{oto}}{\rho_w t_w}$$

where η_o = coefficient of viscosity of oil; η_w = coefficient of viscosity of water; ρ_o and ρ_w = density of oil and water respectively; and t_o and t_w = times of flow of oil and water respectively.

2.5.3. Cloud Point and Pour Point

In order to determine the cloud and pour points of the biodiesel, a test tube filled with oil was put in a beaker filled with ice-chips and then clamped to a retort stand. A thermometer was inserted and used to stir the biodiesel sample in the test tube. The stirring was allowed to persist and the temperature increase every 20 seconds was closely observed until the biodiesel becomes cloudy. The temperature at which the biodiesel sample becomes cloudy was taken as the cloud point. The pour point was obtained as the temperature at which the oil begins to pour from the test tube when the test tube is slightly bent.

2.5.4. Surface Tension Determination

The surface tension was determined using the drop number method. This was done at room temperature with the aid of a 10 mL pipette. The number of drops of distilled water and oil from the pipette was counted. Average of the triplicate measurements in each case was taken. The surface tension of the oil was determined using the expression below:

$$\frac{\gamma\text{o}}{\gamma\text{w}} = \frac{\eta\text{w}\ \rho\text{o}}{\eta\text{o}\ \rho\text{w}}$$

$$\text{or}\ \gamma\text{o} = \gamma\text{w}.\frac{\eta\text{w}\ \rho\text{o}}{\eta\text{o}\ \rho\text{w}}$$

where γ_o and γ_w = surface tensions of oil and water respectively; η_o and η_w = number of drops of oil and water respectively; and ρ_o and ρ_w = densities of oil and water respectively.

2.5.5. Flash Point and Smoke Point

The flash and smoke points were determined using 5 mL of the biodiesel sample in a crucible placed on a hot plate. A thermometer clamped to a retort stand was inserted into the crucible in such a way that the mercury bulb was slightly immersed in the sample. The temperature at which the first smoke came out from the crucible was noted and recorded as the smoke point while the lowest temperature at which the sample caught fire from a lighted match was recorded as the flash point. The procedure was carried out in triplicate.

2.5.6. Acid Value and Free-fatty Acid Value

Few drops of phenolphthalein were transferred into a beaker containing ethanol before subsequent dropwise addition of 0.1 M KOH until a pale pink colouration was obtained. About 1.5 g of the oil sample was weighed into a conical flask followed by the addition of 12.5 mL of the neutralized ethanol solution before the resultant mixture was boiled on a water bath. Afterwards, this was titrated (while hot) with 0.1 M KOH solution until the solution turns almost colourless. The titre value was accurately recorded. The titration was done in triplicate. The acid value (A. V.) and percentage free fatty acid (% FFA) value were obtained from the expressions:

$$\text{A.V} = \frac{\text{Titre value (mL) x N x 56.1}}{\text{Weight of oil}}$$

$$\%\ \text{FFA (as oleic acid)} = \frac{\text{Titre value (dm}^3\text{) x N x 282 x 100}}{\text{Weight of oil}}$$

where N = normality of KOH.

2.5.7. Iodine Value Determination

A 0.25 g oil sample was weighed into a conical flask. Accurately measured 10 mL of chloroform and 25 mL of Hanus reagent were added. The resultant mixture was placed in the dark for about 30 mins with occasional shaking. This was followed by the addition of 10mL of 15% KI before subsequent dilution with 100 mL of distilled water to wash down any free iodine on the side of the flask. Thereafter, a 25 mL portion of the solution was titrated against 0.1 N sodium thiosulphate ($Na_2S_2O_3$) solution until the yellow solution turned colourless. Two drops of freshly prepared 1% starch solution was added as indicator and the titration continues until the blue colour observed after the addition of the starch solution disappears. The titration and blank were done in triplicates and the iodine value was obtained using the expression:

$$\text{Iodine value (I.V)} = \frac{(B - S) \times N \times 126.9}{W}$$

Where B = blank titre value
S = sample titre value
N = normality of $Na_2S_2O_3$
W = weight of oil in grams

2.5.8. Heating Efficiency

An improvised wick lamp was used to determine the heating efficiency of the oil, biodiesel and conventional diesel. Under a fume cupboard, some quantity of fossil diesel was transferred into the fuel chamber of the lamp and the wick was lighted and placed under a tripod stand fitted with wire gauze. A beaker containing 100 mL of distilled water was placed on the tripod stand and the initial temperature, θ_1, of the water was noted. The temperature of the water was monitored for five minutes with constant stirring. The temperature of the water, θ_2, at the expiration of five minutes was recorded. Triplicate determination of such temperature change was determined. The procedure was repeated using raw oil and various biodiesel ratios as the fuel. The quantity of heat, Q, was calculated using the formula:

$$Q = mC\theta$$

Where m = mass of the fuel
C = Specific heat capacity of water
θ = temperature difference = $\theta_2 - \theta_1$

Heating efficiency was determined by comparing the Q value of the oil and the biodiesel with that of the fossil diesel.

3. Results and Discussion

3.1. Percentage Yield, Appearance and Taste of Citrus Sinensis Oil

The oil of *Citrus sinensis* seed has a faint yellow appearance with a characteristic bitter taste. The bitter taste could be attributed to the presence of alkaloids and resins. The percentage yield of the oil is 61.42%, a value well above the one reported earlier [17].

3.2. Percentage Yield of Biodiesel by Various Oil: Methanol Ratios

The percentage yield of biodiesel increases with increase in alcohol (methanol) content because the increase in alcohol content reduces the content of soap generated during the transesterification. In other words, increasing the methanol content favours transesterification and reduces the possibility of saponification. The methanol: oil ratio of 6:1 gave the highest biodiesel yield of (72.17%), followed by that of 5:1 (65.10%), while that of 4:1 (63.19%) was the lowest (Figure 1).

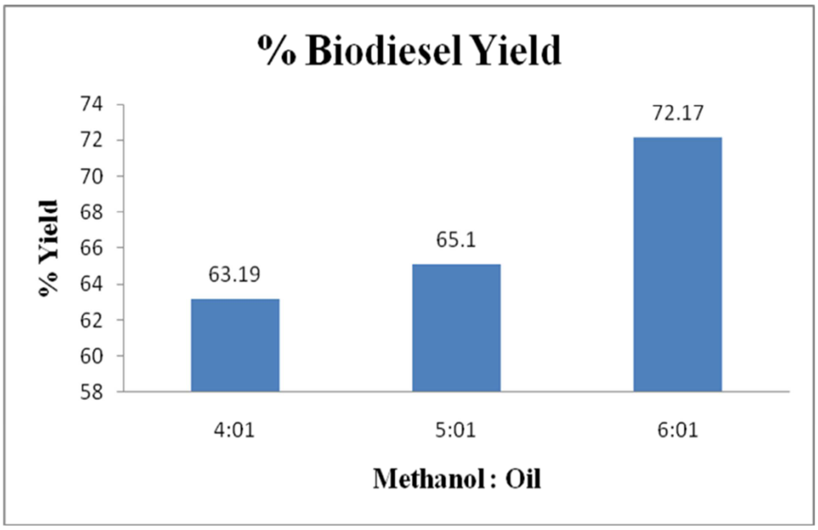

Figure 1. *Effect of methanol: oil on biodiesel yield.*

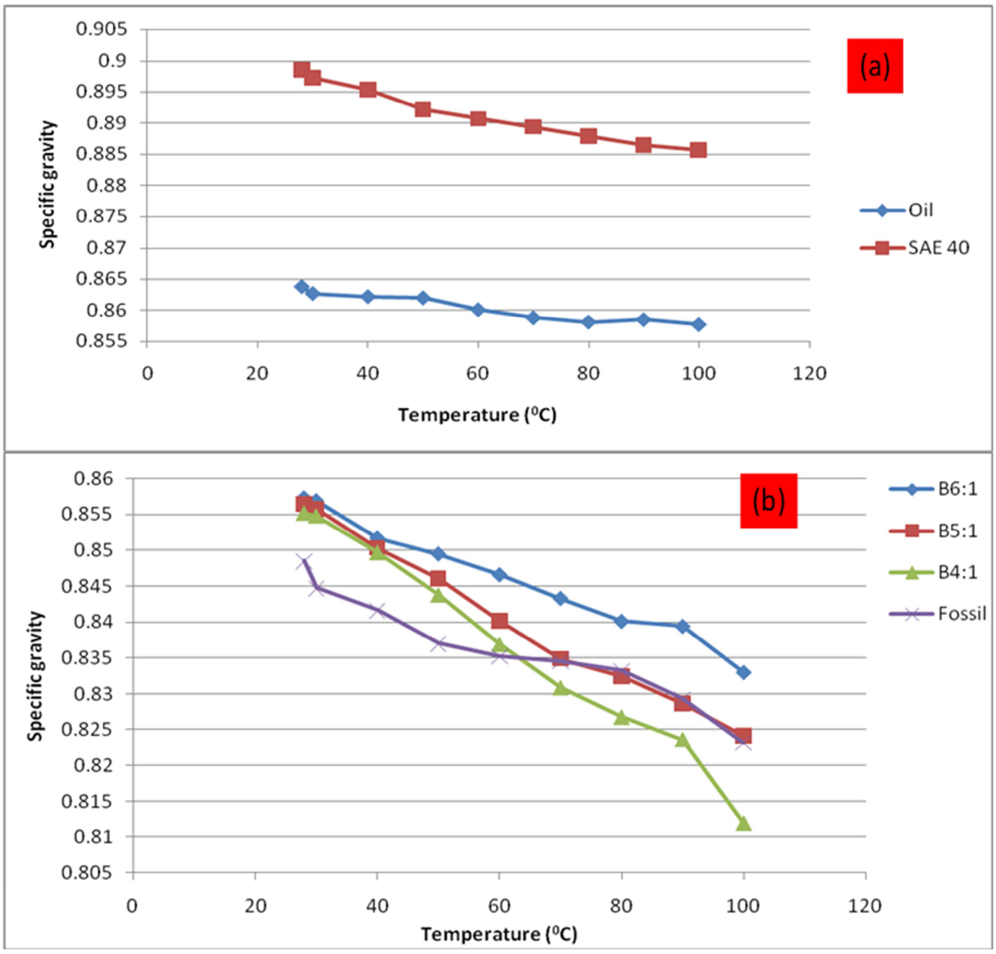

Figure 2. *Plots of specific gravity of (a) Citrus sinensis oil and (b) biodiesel ratios with temperature.*

3.3. Specific Gravity/Relative Density

Specific gravity, a temperature dependent parameter, is simply the ratio of the weight of a substance to that of an equal volume of water at a specific temperature. From this study, the specific gravity value of both oil and biodiesels decreased with increase in temperature. The specific gravity of oil (0.8638) was lower than that of the SAE 40 lubricating oil (0.8985) (Figure 2a), implying that the oil might find application as a lubricant in light machineries. Also, it was observed that the specific gravity of biodiesel increased with increase in methanol: oil ratio, and the biodiesel produced showed higher sensitivity to temperature changes compared to fossil diesel. At temperatures between 70 and 100°C, biodiesel ration of B5:1 had its specific gravity closer to fossil diesel (Figure 2b), an indication that the biodiesel might have related efficiencies in internal combustion engines.

3.4. Viscosity (Centipoise)

Viscosity is a physical property of a fluid which reflects its tendency to flow at specified temperatures [24]. It is an important property of a motor oil because changes in viscosity affect the ability of the oil to lubricate and protect the moving parts of an internal combustion engine. It was observed from this study that the viscosity values of *Citrus sinensis* oil (22.4717 at room temperature and 4.5861 at 100°C) were much lower than that of SAE 40 lubricating oil (42.3241 at room temperature and 13.4509 at 100°C) (Figure 3a). According to SAE viscosity chart at 100°C, the values of viscosity obtained for the extracted oil pointed to the fact that it could be suitable as SAE 10W and not as SAE 40. The viscosity of biodiesel ratios decreased with increase in methanol fraction (Figure 3b). The reason for this might be due to increase in solubility of oil as methanol content increases. The viscosity of biodiesels fell within the range set by ASTM (1.6 – 6.0) [25] at 40°C (Table 1). Viscosity of $B_{6:1}$ biodiesel (2.6981) was closer to the viscosity of fossil diesel (2.3621) at 40°C implying that the biodiesel can be a potential alternative fuel to the conventional biodiesel. The relationship between viscosity and temperature can further be explained using the Gourd *et al*. [26] expression:

$$H = A + SQ$$

where H = dynamic viscosity; A = constant; S = slope; Q = Log (1 + t/135); and t = temperature in °C.

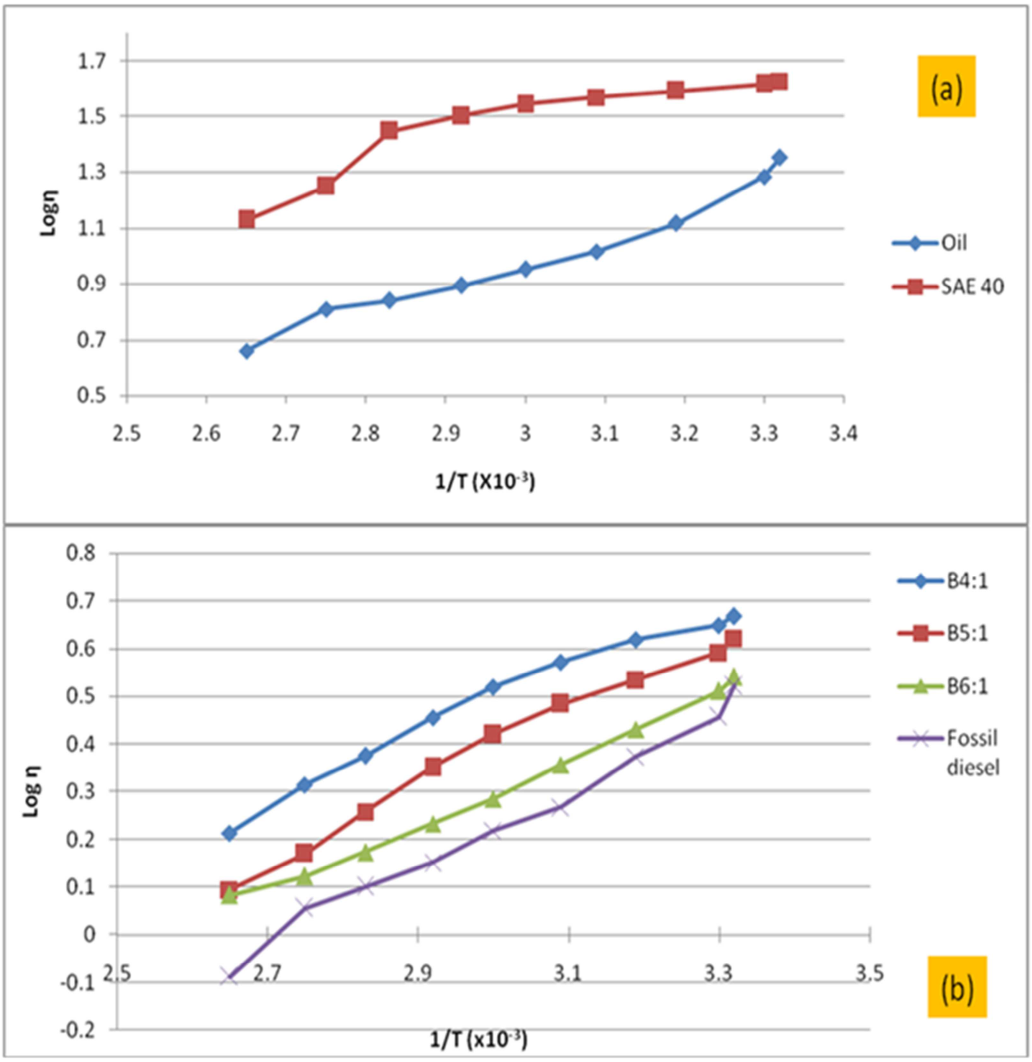

Figure 3. *Graph of H against Q of (a) Citrus sinensis oil and (b) biodiesel ratio.*

Table 1. *Dynamic viscosity (x 10^{-2}) of Citrus sinensis oil and its biodiesel ratios.*

Sample		**Temperature (°C)**			
		28	**30**	**40**	**50**
Oil		2247.17±0.74	1924.43±0.00	1310.02±1.29	1036.99±0.74
$B_{4:1}$		465.46±1.30	444.90±1.98	416.38±1.50	373.10±1.29
$B_{5:1}$	Viscosity values	417.93±1.48	391.04±0.00	342.42±1.94	305.11±1.91
$B_{6:1}$	(centipoise)	347.02±0.74	324.55±0.00	269.81±1.47	227.47±0.73
Fossil Diesel		332.50±0.49	286.43±0.00	236.21±0.53	185.25±0.09
SAE 40		4232.41±1.34	4123.52±4.32	3908.41±5.67	3707.54±0.54

Table 1. *Continued.*

Sample		**Temperature (°C)**				
		60	**70**	**80**	**90**	**100**
Oil		893.62±1.47	782.11±0.73	691.84±1.44	645.16±3.11	458.61±3.10
$B_{4:1}$	Viscosity	331.12±0.74	285.20±1.98	237.16±1.97	2.06.46±0.74	163.22±3.10
$B_{5:1}$	values	263.16±0.72	224.31±2.12	180.95±1.39	147.91±4.30	124.16±2.37
$B_{6:1}$	(centipoise)	192.73±0.72	170.86±0.00	148.78±0.71	132.51±6.87	121.11±2.49
Fossil Diesel		164.97±0.40	141.56±0.43	1.25.88±0.28	113.77±3.49	86.10±5.51
SAE 40		3489.01±1.24	3173.56±11.45	2798.76±17.56	1769.01±23.46	1345.09±0.67

3.5. Cloud Point, Pour Point, Smoke Point and Flash Point of Oil and Biodiesel

Cloud point and Pour point are the two properties used to measure the cold weather performance of a fluid. Cloud point is the temperature at which dissolved solids in a fluid precipitate, giving such fluid a cloudy appearance while the pour point is the lowest temperature at which the fluid tend to flow after solidification. A high cloud point means the oil or fuel would have the ability to turn cloudy at ambient temperature. From this study, it was observed that the cloud point of *Citrus sinensis* oil (4.8°C) and SAE 40 lubricating oil (4.3°C) were close which means both oil would behave similarly under cold conditions. The cloud and pour point of biodiesel were higher than that of fossil diesel (Table 2), but cloud point of biodiesel ratios increased with increase in methanol fraction with values falling within the ASTM (-3 to 12°C) [27] standard. Interestingly, all biodiesel ratios have lower cloud point and pour point than the one obtained from castor oil by Kumar et al. [28]. These facts suggests that these biodiesel ratios can be used at very low temperature.

It was observed that the flash point of *Citrus sinensis* oil (184.3°C) was higher than that of SAE 40 (172.0°C) (Table 2) which means the oil might not readily catch fire especially when used as a lubricant in engine parts. The flash point obtained for the oil met the set standard (>95) by ASTM (ASTM D1310) [27]. Smoke and flash points of biodiesel ratio increased with increase in methanol fractions and their values were higher than that of fossil diesel which means that they are safe for storage and to handle. The flash point of biodiesel ratios obtained in this study is higher than the European Union standard (120°C) and lower than the value reported by Hoseini et al. [12] and Kumar et al. [28].

Table 2. *Table showing the cloud, pour, smoke and flash points of oil and biodiesel.*

Sample	Cloud point (°C)	Pour point (°C)	Smoke point (°C)	Flash point (°C)
Oil	4.8±0.3	2.5±0.3	112.3±2.5	184.3±4.5
B4:1	2.7±0.2	-2.6±0.2	71.0±2.0	122.3±2.5
B5:1	3.2±0.2	-3.7±0.1	74.3±1.5	136.7±1.5
B6:1	3.7±0.3	-4.2±0.2	82.3±2.5	148.7±3.1
Fossil diesel	2.5±0.1	-14.7±1.2	65.3±2.5	75.3±3.1
SAE 40	4.3±0.2	-3.8±0.3	129.7±2.1	172.0±6.8

3.6. Surface Tension (N/m)

Surface tension is the force exerted along the plane of a surface per unit length [29]. It is a direct measure of surface interfacial energy [30]. The surface energy of a fluid relative to adjacent phases influences the transport and distribution of fluid, important parameter in the behavior of oil spreading rates [31]. New lubricating oil has relatively high surface tension, about 35dynes/cm (0.035 N/m) which is close to an average of 31.3 dynes/cm obtained for five notable vegetable oils [32]. The minimum standard value of surface tension for lubricant oil is 29.5 dynes/cm (0.0295 N/m) [33]. The surface tension for *Citrus sinensis* oil (0.028 N/m) is lower than the set standard for lubricating oil and that of SAE 40 oil. This might be as a result of the presence of high free fatty acid in the oil. It was also observed that the surface tensions of biodiesel ratios are lower than that of the fossil fuel. Biodiesel ration of $B_{6:1}$ has the surface tension that is closer to that of fossil fuel and it was also observed that surface tension increase with increase in methanol content.

3.7. Acid Value, Percentage Free Fatty Acid Value (% FFA) and Iodine Value of Oil and Biodiesel

Acid value gives information about enzymatic hydrolysis in oil. It measures the breakdown of triacylglycerols to free fatty acids, which has adverse effects on the quality of oil. In terms of fuel, acid value measures the amount of unreacted acids in the finished fuel and it's also an indicator of oxidized fuel [6, 34]. *Citrus sinensis* oil has high acid value (72.463 mg of KOH/g) and % FFA of 36%. The acid value of this oil is much higher than the maximum acceptable value of 4 mg of KOH/g set by Codex Alimentarius [35]. It is known that oils with FFA content higher than 5% decrease the transesterification yield, inhibiting the formation of methoxides by neutralization of part of the catalyst present and producing soaps within the reaction medium [22]. High free fatty acid of *Citrus sinensis* oil led to two step transesterification of the oil for production of biodiesel. The acid value of the *citrus sinensis* oil decreased after undergoing transesterification to form the biodiesel ratios but the acid value of these biodiesel ratios can still be considered higher than the set standard by European Union and American standard of 0.5 mg of KOH/g and 0.8 mg of KOH/g, respectively. This means there is still high hydrolytic cleavage of ester bonds occurring in the oil which can lead to early oil aging. It was observed that the acid value of biodiesel decrease with increase in methanol content (Table 3) which means that conversion of all the fatty acid to methyl ester in oil depends on the amount of methanol used during transesterification. Compared to the biodiesel acid value reported by Hoseini et al. [12], Kumar et al. [28] and Du et al. [36] using different feedstocks, the biodiesel ratios can be said to have very high acid value.

Iodine value is the measure or the degree of unsaturation in oil and could be used to quantify the amount of double bonds present in the oil which reflects the susceptibility of oil to oxidation [6, 37]. The higher the degree of unsaturation in oil, the easier it is for the oil to undergo oxidative deterioration since lipid oxidation occurs at the double bond site. High iodine value in fuel can lead to the formation of deposits or deterioration of lubricating property [38]. Iodine value of *Citrus sinensis* oil is high (277.488 I_2/100g) which means the oil will not be stable to oxidation and can deteriorate very fast. It was observed that the iodine value of biodiesel ratios decrease as the methanol content increases and biodiesel of $B_{6:1}$ has the lowest iodine value which falls below the limit set by European Union (120 I_2/100g) but much higher than the value reported by Banerjee et al. [6].

Table 3. *Acid value, % free fatty acid value and iodine value of oil and biodiesel.*

Samples	Acid value	% FFA value	Iodine value
Oil	72.463±0.809	36.650±0.4079	277.488±2.931
$B_{4:1}$	2.618±0.324	1.316±0.163	138.744±2.931
$B_{5:1}$	1.122±0.000	0.564±0.000	130.284±0.000
$B_{6:1}$	0.935±0.324	0.376±0.163	116.733±5.099
Fossil Diesel	0.158±0.015	0.079±0.007	74.569±0.839
SAE 40	1.589±0.162	0.799±0.081	82.908±2.931

3.8. Heating Efficiency

Heating efficiency was determined by measuring the amount of heat transferred to a specific volume of substance at a specific time. This parameter is important because it gives the knowledge of how efficient biodiesel will be for fuel substitution probably for domestic use in case of kerosene or petroleum diesel scarcity [39]. Heating efficiency of fuel was estimated in terms of the quantity of heat, Q, generated by the fuel within a specific length of time. The higher the value of Q generated ($Q = mC\theta$, where Q = quantity of heat, C = heat capacity of water, θ = temperature change), the higher the burning efficiency of the fuel.

It was observed that heating efficiency decreased with increase in methanol content which agrees to the flash point of biodiesel ratios (flash point increased with increase in methanol content) (Table 4). Therefore, the ratio with the lowest flash point ($B_{4:1}$) burned fastest. However, fossil diesel had a higher burning efficiency than all the biodiesel ratios.

Table 4. *Heating efficiency of oil and biodiesel.*

Samples	Q (kJ/mol)
Oil	0.5991±0.0429
$B_{4:1}$	1.1356±0.0493
$B_{5:1}$	0.9684±0.0521
$B_{6:1}$	0.8081±0.0429
Fossil Diesel	1.2261±0.0261

4. Conclusion

The oil derived from the seeds of *Citrus sinensis* had been demonstrated to possess a very high iodine value which is an indication that it would undergo oxidation readily. Among the biodiesels generated from various oil: methanol ratios, however, the biodiesel obtained from the oil: methanol ratio of 6:1 ($B_{6:1}$) demonstrated the highest resistance to oxidation and had the best biodiesel property. This study concluded that *C. sinensis* oil holds great potential for biodiesel production and there is the need to further explore the performances of degummed fraction of the oil in the production of biodiesel.

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