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Application and analysis of biodiesel produced from refined rubber seed oil as an alternative fuel

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Abstract The production of carbon dioxide from the conventional fuel is eliminated in biodiesel because all of the carbon dioxide that would have been released during combustion is sequestrated out of the atmosphere during crop growth, thereby making the biodiesel more environmentally friendly. This study was on the production and analysis of biodiesel from refined rubber seeds obtained from the rubber research institute in Benin, Edo State Nigeria. The rubber seeds collected were cleaned and air-dried to constant weight. The rubber seed oil (RSO) was extracted using n-hexane solvent with soxhlet apparatus. From the analysis of the extracted refined RSO which was transesterified with ethanol using Potassium Hydroxide, the following physicochemical properties were obtained: the acid value, the saponification value, the Iodine value, the specific gravity, the free fatty acid value, the pH value, the peroxide value and the refractive index. These values were compared to the values of the corresponding physicochemical properties of crude RSO, and it was confirmed that the both sets of values were similar. The refined RSO was characterized according to ASTM standard based on the following properties: Flash point, water and sediment value, kinematic viscosity, sulphated ash value and the acid number value, it was confirmed that these values were in line with the ASTM standard values except for the flash point value that fell below the ASTM standard. This study confirmed that RSO from Nigeria is a viable feedstock for biodiesel production and the shortfall in the flash point value can be corrected by proper ethanol-oil blend and improved refining.

Keywords Biodesiel, Rubber seed oil, refined, fossil fuel.

Introduction and Background

The large increase in industrialization and motorization in recent years has resulted in a great demand for petroleum products and petroleum based fuels are obtained from limited reserves. Conventional fossil fuel is very expensive and this has added burden on the economy of the importing nations. With crude oil reserves estimated to last only for a few decades, there has been an active search for alternate fuels. The combustion of fossil fuels increases as energy demands increase although fossil fuels are limited just as research directed towards alternative fossil fuels are limited [1]. The depletion in crude oil reserves arising from the extensive consumption of fossil fuel has caused an increased awareness of environmental issues resulting from such depletion, hence the craving for an alternative renewable and eco-friendly source of energy arises. One of such energy source is the biodiesel. Biodiesel is a form of diesel fuel manufactured from vegetable oils, animal fats, or recycled restaurant greases. It is safe, biodegradable, and produces less air pollutants than petroleum-based diesel. It can be used in its pure form (B100) or blended with petroleum diesel, some of its advantages over petroleum diesel is that the production of carbon dioxide from the conventional fuel is eliminated in biodiesel because all of the carbon dioxide that would have been released during combustion is sequestered out of the atmosphere during crop growth. The biodiesel molecules are simple hydrocarbon chains containing no sulphur or aromatic substances associated with fossil fuels. They contain higher amount of oxygen (up to 10%) that ensures more complete combustion of hydrocarbons [2]. They are domestically produced from non-petroleum, renewable resources and can be used in most diesel engines, especially newer ones. It produces less air pollutants (other than nitrogen oxides) and less greenhouse gas emissions (e.g., B20 reduces CO_2 by 15%) and it's biodegradable, non-toxic and safer to handle [3].

The objective of this research is to produce biodiesel from a non-edible raw material, hence the rubber seed oil, to obtain the RSO (Rubber Seed Oil) by Solvent extraction using n-hexane for maximum yield and to refine the crude RSO before biodiesel production to meet ASTM standard.

As a result of the birth of industrial revolution in the late 18th and early 19th Century, energy has become a crucial reason for humans to protect economic growth and maintain standard of living. The extension of industrial revolution in Europe had been largely contributed by the abundant availability and accessibility of coal as the primary source of energy. On the other hand, the arrival of automobiles, airplanes and electricity had been made possible by the energy use of petroleum in the 20th century. Marked to this date, energy has been continuously obtained from conventional sources (fossil fuels). Currently, we are facing problems like depletion of fossil fuel, increasing demand for diesel and uncertainty in the availability of fossil fuel [4]. There is excess use of fossil fuel and it is predicted that in another 80 years, mankind will face huge problems.

Biodiesel is an initiative alternative source of energy that is being produced to overcome fossil fuel depletion, this can be seen from the effort that had been started over a century ago. Alternative fuel has been accepted as early as 1982 by holding the first international conference on plant and vegetable oils as fuels [5]. Even in Kyoto Protocol, the use of biodiesel throughout the world has been advised. The European Community in 1991 has proposed a tax reduction of 90% for the use of biofuels including biodiesel [6]. Biodiesel is beneficial as it is renewable, biodegradable, non-toxic and aromatic. It is also sulphur free and has potential in reducing levels of pollutants and probable carcinogens [7]. Due to having better properties than petroleum diesel itself, it can be concluded that the search for biodiesel is indeed beneficial to mankind as it has many advantages as a substitute.

Biodiesel can be used in heating applications such as home heating or industrial applications, it can also be used in transport applications if the vehicle has a diesel engine and on the farm in machines like tractors [8]. Biodiesel has become a valued commodity in powering auto vehicles; there are various economic and environmental advantages to utilizing this unique fuel in transportation [9]. Consumers today, more than other times have greater opportunity to purchase biodiesel, it is now possible to purchase biodiesel for use as transportation fuel or heating fuel. Prices for biodiesel vary by both location and manufacturer, in some countries biodiesel is now cheaper than regular diesel while in some areas it is more expensive than regular diesel [9]. The search for alternatives of fossil fuels is a major environmental and political challenge. A promising alternative source of fuel, namely biodiesel, has already been developed and is being used in some countries. Biodiesel is a chemical compound of methyl ester derived from raw or used vegetable oils and animal fats. It is considered "carbon dioxide neutral" because all of the carbon dioxide that would have been released during combustion is sequestered out of the atmosphere during crop growth. Recent environmental and economic concerns (Kyoto Protocol) have prompted resurgence in the use of biodiesel throughout the world. The superior lubricating properties of biodiesel increases functional engine efficiency. Their higher flash point makes it safer to store. When compared with petro-diesel it reduces about half of the emission of particulate matter, unburned hydrocarbons, carbon monoxide, most part of the polycyclic aromatic hydrocarbons and entire sulphates on an average [10]. Lower emission of sulphur dioxide, soot, carbon monoxide, hydrocarbons, polyaromatic hydrocarbons and aromatics are noted. NOx emissions from biodiesel are reported to range between plus or minus 10% as compared with petro-diesel depending on engine combustion characteristics. Biodiesel can be mixed with petroleum-based diesel in any proportion [11]. Biodiesel blends can be used in most compression-ignition (diesel) engines with little or no modifications.

Biodiesel is a fatty acid alkyl ester, normally produced by a process called transesterification. Transesterification is the replacement of an alcohol from an ester by another alcohol usually of low molecular weight [12]. It is a reversible reaction and the rate of conversion to the fatty acid alkyl ester is greatly affected by several factors such as type of catalyst, molar ratio of alcohol to oil, stirring, etc. Catalysts used in transesterification include alkalis, acids, enzymes and also heterogeneous catalysts. However, alkali catalysts (sodium hydroxide, sodium methoxide, potassium hydroxide, potassium methoxide) are more effective [13]. For oils with high free fatty acid content and moisture, acid catalyzed transesterification is more suitable. Therefore, the choice of catalyst for transesterification reaction is largely dependent on the nature of oil, such as level of purity, level of percent free fatty acid, etc. Transesterification reaction involving alkaline catalyst is known to give higher yield especially for pure oil (with low %free fatty acid) where low yield is likely to be the result with impure oils (with high % free fatty acid) [14]. Also, the difficulties observed in separation, both in refining and transesterification, of the oil and methyl ester, in the respective processes warrant the need for a more convenient and less laborious method of biodiesel production, while considering the yield of the product. Vegetable oils for biodiesel production vary considerably with location according to climate and feedstock availability. Generally the most abundant vegetable oil in a particular region is the most common feedstock. Biodiesel can be produced from food grade vegetable oils or edible oils, non-food grade vegetable oils or non-edible oil, animal fats and waste or used vegetable oils. Most times, biodiesel is prepared from edible oil like soybean, rapeseed, sunflower, safflower, canola, palmand fish oil [15].

Materials and Methods

In this research, various processes were carried out for biodiesel production from refined rubber seed oil. The equipment used in this experiment are Soxhlet apparatus, Bunsen burner, Refractometer, Blender, Beaker, Test tubes, Separating Funnel, Laboratory dry oven, Volumetric flask, Measuring cylinder, Pipette, Conical flask, Wash bottle, Stand clamp, Evaporating dish, Density bottle, Mechanical stirrer, Weighing balance while the reagents used are n-hexane, Distilled water, Ethanol, Potassium iodide, Sodium thiosulphate, Potassium hydroxide, Glacial acetic acid, and Sulphuric acid. The rubber seeds were collected from Rubber Research Institute in Benin, Edo State, Nigeria. The rubber seeds collected were cleaned and air-dried to constant weight for 24 h to ensure moisture was removed. Then the seeds were deshelled and blended into a paste using a blender.

The rubber seed oil was extracted from the paste using n-hexane solvent for 6 h with soxhlet apparatus. In the degumming process, 100 ml of acetic acid was poured into 40 g of rubber seed oil and shaken thoroughly to mix. The mixture was allowed to settle for 24 h in a separating funnel. The two immiscible liquids were observed in the separating funnel and separated.

Biodiesel Production

0.25 g of potassium hydroxide KOH (catalyst) was dissolved in 60 ml ethanol and the degummed rubber seed oil. 100 g of the RSO was transferred to 250 ml conical flask, in water bath shaker with temperature control, and heated at 50 °C. The reaction component was allowed to stay for 24 h. After settling, the reaction mixture was transferred to a separating funnel to separate glycerol. The ethanol was removed from both methyl ester (biodiesel) and glycerol layer by heating at 90 °C for 30 min. Washing was done by adding 30 % (v/v) of warm water to the crude biodiesel and stirred for 5 min. The mixture was allowed to settle for another 24 h to separate the soap layer from the biodiesel phase. This process was repeated for three times to properly remove all trace of soap present in the biodiesel. The washed biodiesel was placed in an oven at 70 °C for 6 h to remove all traces of water. The flash point, acid value and kinematic viscosity were determined using standard methods (ASTM).

Analysis of Biodiesel

A sample of biodiesel was placed on clever land open cup tester and Bunsen burner is used to supply heat to the apparatus at the temperature of 50 °C. With thermometer inserted, the temperature at which the test flame caused the vapour above the sample to ignite was then recorded. The analysis of kinematic viscosity was carried out by introducing 50 ml of biodiesel into a clean dried viscosity tube. This was done by inverting the tube thinner arm into the oil sample and then using suction force to draw up the oil to the upper timing mark of the viscometer. For water and sediment determination, 100 ml sample of undiluted biodiesel was centrifuged at a relative centrifugal force of 800 N for 10 min at 21 °C to 32 °C (70 ° to 90 °F). After centrifugation, the volume of the centrifugation, the volume of water and sediment which has settled into the tip of the centrifugal tube is read to the nearest 0.005 ml and reported as the volumetric percent of water and sediment.

Sulphated Ash was determined by placing 1ml of sulphuric acid on a platinum crucible of known weight. 10 ml of RSO based biodiesel was also placed on the crucible. The crucible and its contents were weighed accurately and recorded. Then they were transferred to a furnace and the temperature was raised to 800 ^{o}C for about 10 min. Afterwards, the crucible with the charred remains was taken out and cooled in a desiccator before weighing. Sulphated ash is determined from the difference between the weight of the crucible before being put in the furnace and the weight after cooling.

The acid number was determined by weighing accurately 10 ml of RSO based biodiesel into a 250 ml flask and 50 ml of a mixture of equal volume of ethanol and ether which had been neutralized with potassium hydroxide (0.l mol/L) was added. After the addition of phenolphthalein/ ethanol was heated until there was dissolution, it was titrated with (0.l mol/L) potassium hydroxide while constantly shaking the contents of the flask until a pink colour which persisted for 15 sec was obtained.

Physicochemical Analysis of the Rubber Seed Oil

The physicochemical analysis of the rubber seed oil was carried out the following parameters were checked and determined; Refractive Index, odour, colour, pH, and clarity. The odour, colour and clarity was done by physical identification while for the refractive index, 4 drops of Rubber Seed Oil was taken and placed on a refractometer and the reading taken. The pH was determined by the use a pH meter dipped into the rubber seed oil and the reading was recorded.

Determination of Relative Density at 30 °C

A 50 ml capacity density bottle of known weight was washed, cleaned and dried. Then the bottle was filled with water, weighed and the weight recorded. The density bottle was dried again and now filled with the rubber seed oil sample, weighed and the weight recorded. This was used to calculate the relative density of the oil.

Determination of Acid Value

2 g of the RSO sample was dissolved in 50 ml of neutralized solvent of equal volume of diethyl ether and absolute ethanol. The resultant solution was titrated with 0.1 ml KOH solution using phenolphthalein as indicator.

The acid value was calculated using the expression;

$$\text{Acid Value (AV)} = \frac{(V \; x \; M \; x \; 5.61 \; x \; 0.14)}{2} \qquad (1)$$

Where

V = Volume of titrant (KOH) in ml

M = Molarity of standard KOH

W = Weight of samples in grams

Determination of Iodine Value

The sample under determination was weighed and dissolved in 15 ml of carbon tetrachloride, agitated thoroughly and then allowed to stand for about 30 min in the dark. 100 ml of distilled water and 20 ml of potassium iodide was added to the mixture and filtered with 0.1 M standard sodium thiosulphate using 0.5 % (W/V) starch solution as indicator. Blank solution was also carried out in similar manner. The iodine value (IV) was calculated as follows;

$$IV = \frac{(b-a) x \; M \; 12.69}{W} \qquad (2)$$

Where

M = Molarity of standard sodium thiosulphate

W = Weight of sample in grams used

b = Volume in ml of sodium thiosulphate titrated in blank

a = Volume in ml of sodium thiosulphate titrated in test.

Determination of Free Fatty Acid

4 g of sample was dissolved with 50 ml neutral solvent of equal volume of ethanol and diethyl ether in a 250 ml conical flask. This solution was titrated with 0.2 M KOH using phenolphthalein as indicator. The Free Fatty Acid (FFA) was expressed in terms of oleic acid and was expressed by the formula;

$$FFA = \frac{V \; x \; M \; x \; Ma}{10W} \qquad (3)$$

Where

M = Molarity of KOH

Ma = Molecular weight of oleic acid (282)

W = Weight of sample in grams

V = Volume of KOH in ml

Determination of Saponification Value

2 g of the sample under determination was dissolved into a l5 ml, 0.5 M ethanolic potassium hydroxide solution in 250 ml round bottom flask with a reflux condenser. The flask was heated in a steam bath and occasionally swirled to effect saponification as the solution starts to boil; the heating was done for 30mins. After heating, the hot soap solution formed was titrated with standard 0.5 M hydrochloric acid using phenolphthalein as indicator. A blank titration was also done in the same manner. The saponification value (S.V) was expressed as;

$$S.V = \frac{28 \; x \; M \; x \; (b-a)}{W} \qquad (4)$$

Where

M = Molarity of hydrochloric acid

W = Weight of sample in grams

b = Volume in ml of hydrochloric acid titrate blank

a = Volume in ml of hydrochloric acid titrate test.

Results and Discussion

The results of the analysis carried out on the refined rubber seed oil for the production of biodesiel are explained in the following tables and graphs shown. From the table 1 obtained, comparisons were made for the acid value, saponification, iodine value, specific gravity, viscosity, free fatty acid, pH value, peroxide value, refractive index of the crude RSO and the refined RSO. According to figure 4 in the appendix, degumming increased the iodine value of the rubber seed oil (RSO) while it reduced the saponification value.

Table 1: Physicochemical Properties of the Rubber Seed Oil (RSO)

Parameters	Crude	Refined
Acid value	24.40	23.60 (mg KOH/g)
Saponification	210.75	210.36 (mg KOH/g)
Iodine Value	109.40	110.30 (1g/100g)
Specific Gravity	0.889	0.899
Viscosity	28.24	26.75 (Mm^2/s)
Free Fatty Acid	12.80	12.20 (mgKOH/g)
pH Value	9.5	8.4
Peroxide Value	15.1	15.3 (meq/g)
Refractive Index	1.456	1.459

Table 2: Physical Properties of the Rubber Seed Oil (RSO)

Parameters	Refined RSO
Odour	Unpleasant
Clarity	Cloudy
Colour	Golden yellow

Table 3: Analysis Result of the Rubber Seed Oil Based Biodiesel

Property	Test method (ASTM)	ASTM Specified value	Experimental Value for Biodiesel	Unit
Flash Point (coc)	D93	130 minimum	128.0	^0C
Water and Sediment	D2709	0.050	0.06	% Volume
Kinematic Viscosity @40°C	D445	1.9-4.1	3.90	mm^2/s
Sulphated ash	D874	0.020	0.010	% Mass
Acid number	D664	0.50	0.48	Mg KOH/g

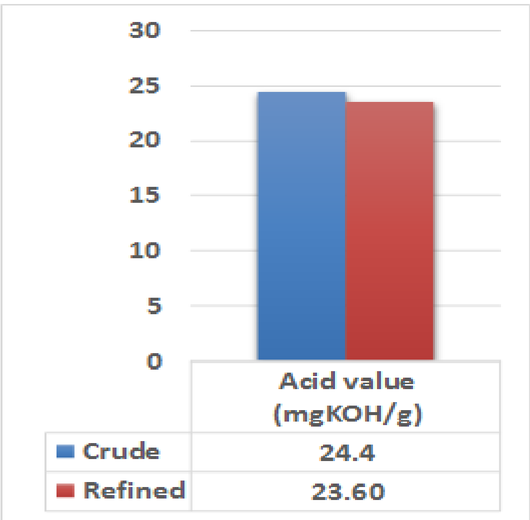

Figure 1a: Acid value of crude and refined RSO

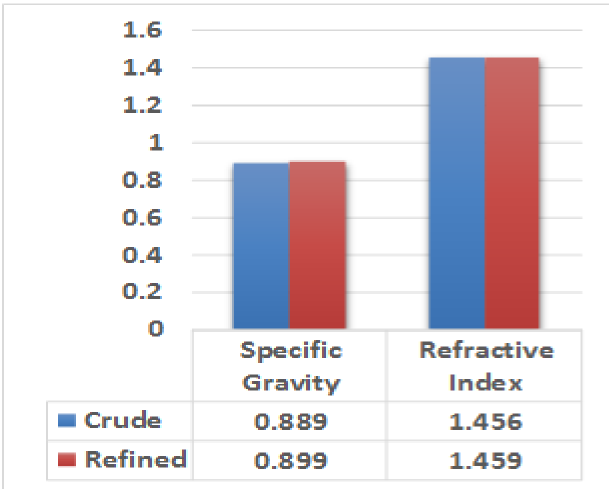

Figure 1b: Specific gravity and refractive index of crude and refined RSO

The bar graph figure 1a shows the acid value of the Crude Rubber Seed Oil (RSO), 24.40 mgKOH/g, is higher than the acid value of the degummed RSO 23.60 mgKOH/g. This change in value may be due to the fact that the gum from the rubber seed oil is also acidic.

Table 4: Analysis Result of the Rubber Seed Oil Based Biodiesel

Property	Test method (ASTM)	ASTM Specified value	Experimental Value for Biodiesel	Unit

Flash Point (coc)	D93	130 minimum	128.0	^{0}C
Water and Sediment	D2709	0.050	0.06	% Volume
Kinematic Viscosity @40°C	D445	1.9-4.1	3.90	mm^2/s
Sulphated ash	D874	0.020	0.010	% Mass
Acid number	D664	0.50	0.48	Mg KOH/g

The graphical representation figure 1b clearly shows a negligible increase in the specific gravity of the refined RSO. Also, the refractive index of the degummed oil, 1.459, is negligibly higher than that of the crude RSO 1.456. Therefore, refining has little or no effect on the specific gravity and refractive index of rubber seed oil.

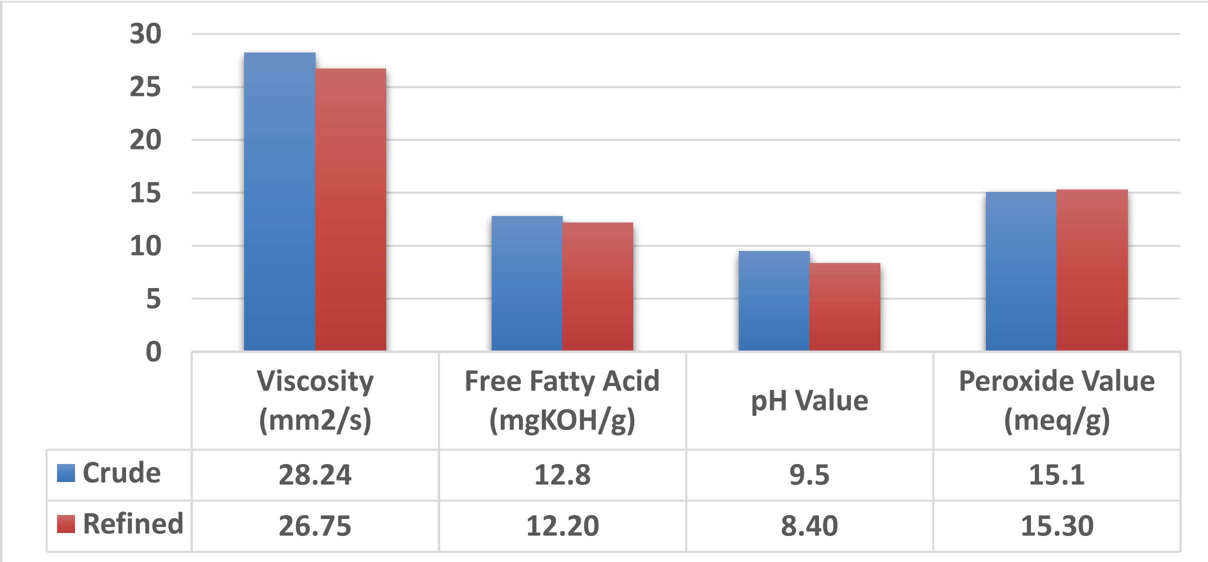

Figure 2: Viscosity, FFA, P^H value and Peroxide Value of crude and refined RSO

The figure above clearly indicates that refining reduced the viscosity of the RSO. The Free Fatty Acid (FFA) content and pH value of the RSO was also reduced while there was an increase in the peroxide value of the RSO.

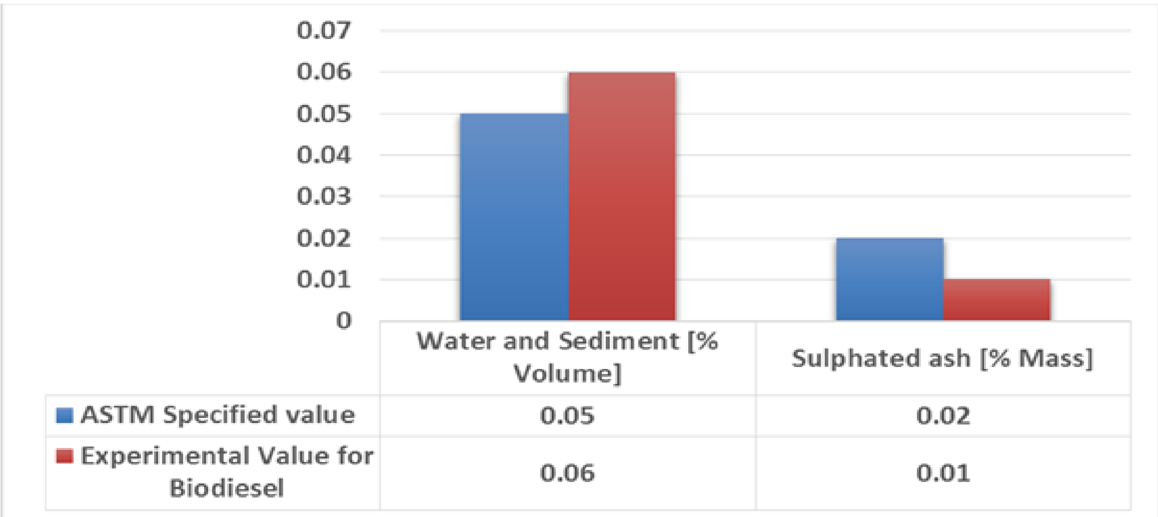

Figure 3: Water/sediment volume and sulphated ash of the produced biodiesel compared to ASTM specified

Figure 3 shows that The ASTM required value for water and sediment of a biodiesel is 0.050% volume and 0.06% volume was obtained. This value is slightly (by 0.01%) above the required standard. Also, the sulphated ash specified value is 0.020% mass and the RSO based biodiesel value is 0.010% mass which is a slight variation.

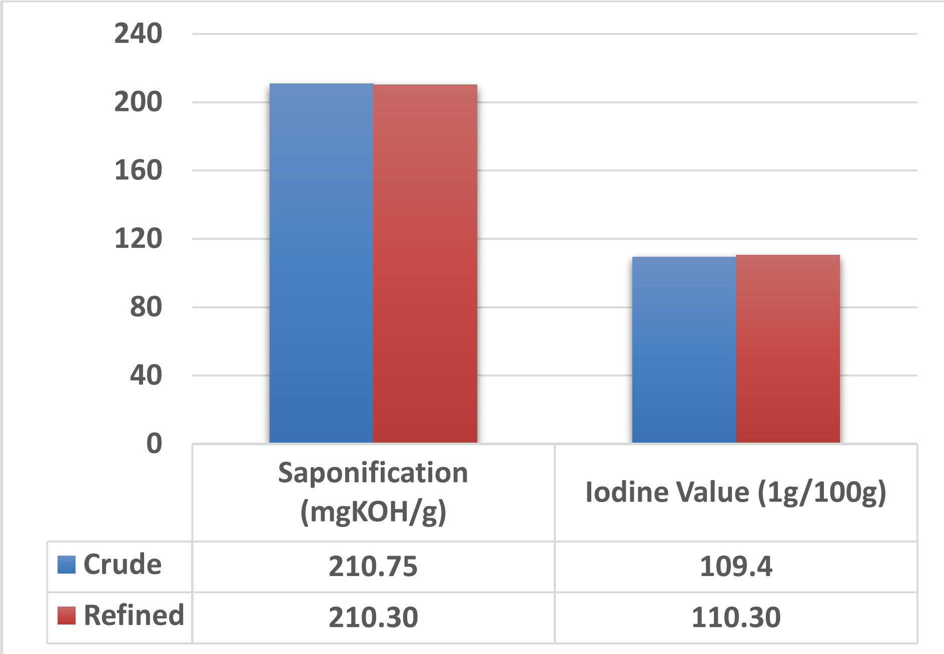

Figure 4: Saponification and Iodine value of crude and refined RSO

Conclusion

The characterization features of the rubber seed oil based biodiesel from this study show that our locally sourced rubber seed has the potential to be used as a viable feedstock for biodiesel production because the values obtained in the physicochemical analysis are similar to the standard ASTM values for biodiesel except for the flash point that fell a bit below the standard and this discrepancy can be corrected with proper ethanol-oil blend in the transesterification process and also with improved refining. Based on this research work, I recommend that rubber seed oil should be exploited for the production of biodiesel in Nigeria because it is environmentally friendly, renewable and can be a new source of income to Nigeria thereby boosting the economy.

References

[1]. Kumar, S. S., & Purushothaman, K. (2012). High FFA rubber seed oil as an alternative fuel for diesel engine, an overview. *International Journal of Engineering and Science*, *1*(10), 2278-4721.

[2]. Farmer, G. (2009). India Gives Biofuels a Chance to Grow. Available: http://globalfarmer.com.au

[3]. Zhang, Q., Feldman, M., Peterson, C.L. (1988). Durability of fuel with methyl ester of winter rapeseed oil. ASAE paper No. 88-1562.

[4]. Singh, B., & Sharma, Y.C. (2010). An ideal feedstock, kusum (Schleichera triguga) for preparation of biodiesel: optimization parameters. *Fuel, 89*, 1470-1474.

[5]. Singh, B., Sharma, Y.C., & Korstad, J. (2010). High yield conversion of biodiesel from a nonedible feedstock (*Pongamia pinnata*). *J. Agric. Food. Chem.*, *58*, 242-247.

[6]. Biodiesel the next generation sustainable fuel. Available: http://www.jatrophaworld.org/11.html

[7]. Akdemir, B. K. P. Ü. B., & Aytaç, S. (2006). A research on determining some performance values by using proportional mixture of vegetable oils and diesel fuel at a diesel engine. *JOTAF/Tekirdağ Ziraat Fakültesi Dergisi*, *3*(1), 16-24.

[8]. Schwab, A. W., Bagby, M. O., & Freedman, B. (1987). Preparation and properties of diesel fuels from vegetable oils. *Fuel*, *66*(10), 1372-1378.

[9]. Freedman, B. E. H. P., Pryde, E. H., & Mounts, T. L. (1984). Variables affecting the yields of fatty esters from transesterified vegetable oils. *Journal of the American Oil Chemists Society*, *61*(10), 1638-1643.

[10]. Du, W., Xu, Y., Liu, D., & Zeng, J. (2004). Comparative study on lipase-catalyzed transformation of soybean oil for biodiesel production with different acyl acceptors. *Journal of Molecular Catalysis B: Enzymatic*, *30*(3), 125-129.
[11]. Ikwuagwu, O. E., Ononogbu, I. C., & Njoku, O. U. (2000). Production of biodiesel using rubber [Hevea brasiliensis (Kunth. Muell.)] seed oil. *Industrial crops and products*, *12*(1), 57-62.
[12]. George, P. J., & Jacob, C. K. (2000). Natural rubber agromanagement and crop processing.
[13]. Ajibola, O. O., Eniyemo, S. E., Fasina, O. O., & Adeeko, K. A. (1990). Mechanical expression of oil from melon seeds. *Journal of Agricultural Engineering Research*, *45*, 45-53.
[14]. Gikuru, M., & Moriasi, L. (2007). A study of yield characteristics during mechanical oil extraction of preheated and ground soybeans.
[15]. Mathiyazhagan, M., Ganapathi, A., Jaganath, B., Renganayaki, N., & Sasireka, N. (2011). Production of biodiesel from non-edible plant oils having high FFA content. *International Journal of Chemical and Environmental Engineering*, *2*(2), 119-122.