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EXTRACTION AND ASSESSMENT OF PHYSICOCHEMICAL PROPERTIES OF ROSIGOLD MANGO (*MANGIFERA INDICA*) SEED KERNEL OIL FOR BIORESIN PRODUCTION

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Abstract

This paper presents research report on extraction and assessment of physicochemical properties of Rosigold mango kernel oil. This is with a view to using the oil for bioresin production so as to mitigate some of the problems associated with petrochemical resins currently used for bulk of composite production activities. The seeds of the mango were identified and collected from the wastes discarded by marketers and consumers in Bauchi town. The Oil was obtained using soxhlet extraction with n-Hexane as solvent. The oil was characterized for yield, relative density, free fatty acid value, acid value, iodine value, and saponification value. Mean values of the characteristic parameters were: oil yield 19.6%, relative density 0.874 g/cm^3, free fatty acid value 3.09 mg NaOH/g oil, acid value 6.18 mg KOH/g oil, iodine value 60.7 mg iodine/100 g oil and saponification value 143.6 mg KOH/ g oil. Analysis and comparison of these results with the physicochemical properties of palm oil, Soya bean oil and Hemp seed oil respectively, revealed that the iodine value of Rosigold mango seed kernel oil is higher than palm oil, but lower than Soya bean and Hemp seed oils respectively. Bioresin production is heavily dependent on the degree of unsaturation of the oil which is reflected by the iodine value. However, the overall results suggested that Rosigold mango seed kernel oil is suitable for bioresin production since the minimum iodine bench mark for renewable oil suitable for bioresin production is 50 mg iodine/100 g oil. The extracted oil has an added advantage in that the source (mango seed) is a waste material that is readily available, affordable and sustainable in Nigeria and many other countries.

Keywords: Composite material; Petrochemical resin; Rosigold mango seed kernel oil; physicochemical properties; Bioresin.

1. Introduction

Mango (*Mangifera Indica*) fruit is one of the agricultural produce obtained in commercial quantity in Nigeria and many other countries. It is the commonest fruit found in all nooks and crannies in Nigeria especially during the peak of the harvesting season (March - July) every year. According to Food & Agricultural Organization (FOA), (2008), majority of mango fruits produced in Nigeria and many other countries are for consumption and only few are used for industrial purposes for making juices, concentrates, jams and fruit bars. The seeds of the fruits are discarded by the consumers and users as wastes.

Kittiphoom and Sutasinee (2013) reported that mango consumption and processing yield over 150,000 to 400,000 tons of the wastes worldwide. Fahimdanesh and Bahrami (2013) also reported that mango processing yields about 40-50% of by-products. One of the by-products is the seed which houses the oil-containing kernel. The constituent fatty acids found in mango seed kernel oil molecule are Stearic acid (40-45%), oleic acid (40-46%), Palmitic acid (4-5%) and arachidic acid (1-2%). The other important features of the oil are: Melting point (30 - 42°C), unsaturated fatty acids (42–44 %) and saturated fatty acids (52–56 %). Information from Kittiphoom and Sutasinee

(2013) and Fahimdanesh and Bahrami (2013) gives an insight into the quantity of mango seeds wastes across the globe and the possible use of the oil for industrial purposes including bioresin production.

Kichen Butterfly (2014) reported that there are eight varieties of mango fruits in Nigeria and over one hundred and fifty across the globe. Among these eight varieties, the five common ones are Alphonso, Rosigold, Heidi, Springfels and Keitt mangoes respectively. The report also has it that ripe mango is popular edible fruit all over the world. The fruit consists of a thick exocarp (peel), a resinous edible mesocarp (flesh) and a woody endocarp (pit). The skin and pulp constitute about 85% while the remaining 15% is of stone (seed) which houses the kernel that contains oil.

Going by the report obtained from Wikipedia the free Encyclopedia, (2015), Rosigold mango originates in Southeast Asia. The fruit ripen early, from middle to late March. The fruit are cylindrical in shape, weighs about 11 oz (slightly bigger than Alphonso mango).

It has less fibre when compared with Alphonso, but costlier (2 pieces for ₦50 in Bauchi town) and less sweet. It is the second commonest mango in Nigeria after Alphonso mango. The seeds are proportional to the size of the mangoes. The seed kernels are relatively big but not directly proportional to the size of the seeds in some cases.

Mango seed kernel oil, like other renewable oils has numerous physical and chemical (physico-chemical) properties inherent in them. *Information on relevant physico-chemical properties of oil* determines to a large extent the suitability of the oil for any application (Sadiq *et al.*, 2016*)*. Th*e* few studies conducted by some researchers on physicochemical properties of mango seed kernel oil were centered on the possible use of the oil either for biodiesel production, eatable oil or for other industrial uses rather than bioresin production.

Resin is a viscous and transparent liquid either from organic or inorganic source that will transform (cured and hardened) into solid when treated with suitable catalyst, accelerator with or without heat. Those from inorganic sources (crude oil or chemicals) are commonly called synthetic resins while those from organic sources (plant or animal) as bioresin or renewable resins.

Composite material is a tailor-made material consisting of two or more distinct material phases combined into one engineering material. The purpose of the combination is to optimize the materials properties while at the same time mitigating the effects of some of the less desirable characteristics (Astron, 1997). One of the two major constituents of composite material is polymer matrix commonly called resin. Traditional Fiber Reinforced Polymer (FRP) composites manufacturers use thermosetting resins as the polymer matrix (binder) to holds the structural fiber firmly in place. The most common thermosetting resins widely used today for wide range of engineering activities are the polyester, vinyl ester and epoxy resins respectively (Stong, 1999).

Despite the numerous engineering applications of composite materials in the fields of air, land and sea transportation among others, petrochemical resins (synthetic resins) have serious drawbacks in terms of sustainability, renewability, biodegradability, initial processing cost, energy consumption and health hazards among others (Sadiq et al., 2016). The British Plastic Federation (2011) reported that the bulk of the resins and many other polymers matrices used for composite activities are produced from non renewable petrochemicals substances like xylene, ethylene, propylene; styrene, benzene and vinyl chloride by polymerization processes. Similarly, the Organisation for Economic Co-operation and Development (OECD) (2004) reported that the global productions of petrochemical resins have been declining not only because of the depletion in fossil fuels and uncertainty in its prices but also due to environmental and health concerns especially during the production processes.

The bulk of the resins used in Nigeria are imported materials. Despite the adverse effects of importation on our economy, the resins are still costly (₦1, 200 per litre) and not readily available for use, (Sadiq, 2008)

Increasing global use of composite materials for wide range of engineering applications and the adverse effects associated with petrochemical resins call for concerted efforts by researchers across the globe to source for alternative materials that are renewable and sustainable for composite resins.

The aim of this work is to extract and asses the physico chemical properties of Rosigold mango seed kernel oil for resin production. The bioresin is to serve as alternative resin to the petrochemical resins (synthetic resins) currently used for fibre reinforced composite material manufacturing activities. This will help to mitigate some of the problems (renewability, sustainability and health issues) associated with petrochemical resins. In addition to contribution to knowledge in that direction, the work will also help to minimize our dependence on the petroleum base resins and consequently cushion the adverse effects of synthetic resins on health, environment and economy.

2. Materials and Methods

2.1 Extraction of Oil.

Having identified Rosigold mango seeds (by size and shape), they were collected from the wastes discarded by marketers and consumers in Bauchi town. The seeds were sun-dried for one week for easy cracking and removal of the kernel from each seed by hammering lightly. The kernels were ground (using melon manual grinding machine) and sieved to particle size of about 2-5mm suitable for soxhlet oil extraction. The oil was extracted using Soxhlet oil extraction apparatus with n-Hexane as solvent as described in Kyari (2008).The Rosigold mango fruit, seeds and kernels are shown in plates 1 to 3 while plates 4 to 6 show the ground kernels ready for oil extraction, Soxhlet apparatus set up for oil extraction and a sample of the extracted oil.

Plate 1: Rosigold mango fruit

Plate 2: Rosigold mango seeds

Plate 3: Rosigold mango seed kernels

Plate 4: Ground kernels ready for oil extraction

Plate 5: Rosigold mango kernel oil extraction with Soxhlet apparatus.

Plate 6: Sample of Rosigold Mango kernel oil extracted.

2.2 Determination of Percentage Yields of Oil Extracted

The percentage oil yield (Yp) was determined using International Standard Organization (ISO - 3657) method described in Kyari (2008) report. The oil extracted was weighed and the percentage yield was calculated on dry matter bases using percentage oil yield formula (Eqn 1). This procedure was repeated twice to obtain average result.

$$Y_p = \frac{Wo}{WS} \text{ x } 100 \qquad (1)$$

Where:

Y_p is Percentage oil yield, Wo is weight of oil and W_S is weight of sample on dry matter basis

2.3 Determination of Relative Densities of Extracted Oil

The relative density of the oil was determined in line with ISO method that uses distilled water and relative density bottle described in Ejilah (2010). The relative density bottle provided was washed, rinsed with acetone and dried at 45°C in oven. After the bottle was cooled to room temperature in desiccators, it was weighed empty using electronic weighing balance. The bottle was filled to a mark with distilled water and weighed again on the same electronic weighing balance. The water was poured out, bottle rinsed with acetone and dried in oven and then filled to the same mark with the pure mango seed kernel oil extracted. The specific gravity of the oil was calculated using relative density formula (Eqn. 2). The procedure was repeated twice to obtain average result.

$$\rho = \frac{w_3 - w_2}{w_1} \qquad (2)$$

Where:

ρ = Relative density of oil, W3 = weight of bottle and pure oil sample, W_2 = weight of empty bottle, W_1 = weight of equal volume of water = weight of bottle and distilled water - weight of empty bottle.

2.4 Determination of Free Fatty Acid Values of Oil

The free fatty acid value of the oil was determined using the Association of Official Analytical Chemists (AOAC, 1998)'s method described by Kyari (2008). About 1g of the oil was placed in 250ml conical flask and warmed. 25ml of methanol was added with thorough stirring and 2 drops of Phenolphthalein indicator and a drop of 0.14M NaOH solution were added. The contents were titrated with 0.14M NaOH solution until a light pink colour which persisted for one minute appeared. The volume of the end point was recorded. At the end of the titrations, the free fatty acid (FFA) was calculated from FFA formula (Eqn. 3). The procedure was repeated twice.

$$\text{FFA} = \frac{Tv \, xM \, x \, 28.2}{Wo} \qquad (3)$$

Where, Tv = Titre volume, $\text{Wo} = \text{Weight of oil}$ and M (0.14) is the morality of the base (NaOH) used.

2.5 Determination of Acid Values of Oil

The acid value of the oil was determined in line with Association of Official Analytical Chemists (AOAC, 1998) method described in Kyari (2008)'s report. In this method, the free fatty acid value of the oil was multiplied by a constant (1.99) to determine the acid value of the oil.

$$\text{AV} = \%\ \text{FFA x } 1.99 \qquad (4)$$

Where, AV = Acid value and FFA = free fatty acid of the oil.

2.6 Determination of Iodine Values of Oil

The Iodine value (mg/100g oil) was determined by titration using ISO method as reported in Kyari (2008). 21 g of the oil and 30ml Hanus solution were placed in a 250ml conical flask and stoppered. The contents were thoroughly mixed by shaking and later placed in a drawer for thirty minutes (for complete reaction) after which was titrated with 0.1N Sodium triosulphate ($Na_2S_2O_3$) until the solution became light yellow. 2ml of 1% starch indicator was added and the titration continued until the yellow colour almost disappeared. The iodine value was calculated from Eqn. 5. The procedure was repeated twice.

$$IV = \frac{(B-S) \text{x N x } 12.69}{W} \quad (5)$$

Where: IV = Iodine value of oil, B = bank titre (without oil) = volume (ml) of $Na_2S_2O_3$ used

S = sample titre (with oil) = volume of $Na_2S_2O_3$ used

N= normality of Sodium triosulphate = 0.1

W= weight of oil = 1g.

2.7 Determination of Saponification Value of Oils

The Saponification value (mg KOH/g oil) was determined by titration using ISO 3657 method described in Kyari (2003)'s report. 2g of the oil was placed in a 250ml conical flask and 25ml of 0.5M ethanol potassium hydroxide solution was added. A reflux condenser was attached and the flask contents were refluxed for 30 minutes on a water bath while swirling until it started to boil gently. The warm contents in the flask were titrated with 0.5M hydrochloric acid while phenolphthalein served as the indicator. The saponification value of the oil was calculated using Eqn. 6. The procedure was repeated twice to obtain average value.

$$SV = \frac{(B-S) \text{x } 28.05}{W} \quad (6)$$

Where: SV = Saponification value of oil, B = titre volume (ml) of blank sample (without oil), S = titre volume (ml) of sample (with oil) and W = weight of oil = 2g

3. Results and Discussion

The average results of the physicochemical properties of Rosigold mango kernel oil are presented in Table 1.

Table 1: Physico-chemical properties of Rosigold mango kernel oil

S/No.	PARAMETERS	AVERAGE VALUES
1	Percentage yield of Oil (g oil/100 g dry matter)	19.6
2	Relative density of oil (g/cm^3)	0.874
3	Acid value (mg NaOH/g oil)	6.18
4	Iodine value (mg iodine/100 g oil)	60.7
5	Saponification value (mg KOH/g oil)	143.6
6	Free fatty acid (mg NaOH/g oil)	3.09

Figures 1 to 6 show the histograms comparing the variations of the physicochemical properties of the extracted mango kernel oil (MKO) and some similar oils (palm oil, soya bean oil and hemp seed oil) reported by other researchers for bioresin production

Mango kernel oil (MKO) like other renewable oils has numerous physical and chemical properties inherent in it. However, the physicochemical properties that will give an insight into the suitability of the oil for bioresin production are found in Table 1.

The oil yield in this work is 19.6%.This implies that the Rosigold mango kernel contains only 19.6% oil while the others substances in it summed up to 80.4%. The 19.6% figure is low when compared with those reported on palm oil (30.2%), Hemp seed oil (32.4%) and soya bean oil (21.4%) by Nursyazana (2014), Nathan (2013) and Encyclopedia (2014) respectively. Figure 1 shows the histogram illustrating the variations of the yields of the oil extracted and those three that have been reported for bioresin production. However, the value of oil yield extraction helps to sharpen decision on whether to proceed with more extraction or change to other fruits or seeds with possible better yields. Considering the fact that the source of the oil is a waste material discarded by consumers and users, the low yield value may be tolerated since the seeds are abundantly available for use with virtually no cost.

The relative density of Rosigold mango seed kernel oil (MKO) in this work is 0.874 g/cm^3. Although the figure is slightly low, it compared favourably with the relative densities of palm oil (0.931g/m^3), Hemp seed oil (0.893g/m^3) and soya bean oil (0.908g/m^3) reported by Nursyazana (2014), Nathan (2013) and Encyclopedia (2014) on oils that have been used for bioresin production. The mango kernel oil figure (0.874 g/cm^3) implies that the oil is less dense than water due to absent of heavy element or hydroxyl groups in it. Figure 2 shows the histogram illustrating the variations of the relative densities of the oil extracted and those three that have been reported for bioresin production. According to Kakani and Amit (2004), value of relative density of any oil gives an idea about it heaviness (dense nature) when compared with that of distilled water. As expected, resins generally should be light in weights so as to contribute to the overall light weight of the composite product and this has to start from the raw material (oil) itself.

The acid value is a measure of total acidity of the lipid, involving contributions from all the constituent fatty acids that make up the glyceride molecule. The lower the acid value of oil, the fewer the free fatty acids it contains which makes it less exposed to the phenomenon of rancidification (Ekpa and Ekpe, 1995). Acid value of oil gives idea about the oil tendency to spoilage and shelf life and thus its quality, (Ejilah, 2010). The acid value of MKO in this work is 6.18 mg KOH/g oil. This value is higher than the palm oil (2.86 mg KOH/g oil), hemp oil (2.15 mg KOH/g oil) and soya bean oil (1.05 mg KOH/g oil) reported by Nursyazana (2014), Nathan (2013) and Encyclopedia (2014) respectively. Figure 3 shows the histogram illustrating the variations of the acid values of the oil extracted and those three that have been reported for bioresin production. The high acid value of MKO indicates that it has high free fatty acids and carboxylic acid group in it. This implies that oil is more saturated when compared with those above. This high acid value of the oil limits its usefulness for bioresin production. According Asuquo et at. (2012), acid value measures the degree of saturation of oil and high acid value indicates high saturation level of free fatty acid and carboxylic acid group present in the oil.

The iodine value of MKO in this work is 60.7 mg iodine/100g oil. The figure is slightly higher than palm oil (53.8 mg iodine/100g oil) and much lower than hemp seed oil (163.5 mg iodine/100g oil) and soya bean oil (135.7 mg iodine/100g oil) reported by Nursyazana (2014), Nathan (2013) and Encyclopedia (2014).Figure 4 shows the histogram illustrating the variations of the iodine values of the oil extracted and those three that have been reported for bioresin production. Going by the report of (Wool, 2005), high iodine value of oil simply implies high degree of unsaturation and thus more the double (C=C) bond. According to Nathan (2013), the double bonds in the oil are used as reactive sites in the epoxidation reaction (leads to bioresin production) and other functionalized processes. A successful epoxidation reaction will see a high proportion of the C=C converted into epoxide oil which serves as raw material for bioresin production. Going by this it implies that the MKO is better than palm oil for bioresin production than the other two oils (hemp seed oil and soya bean oil). However, considering the abundant availability of the mango fruit seeds waists and comparatively low cost in obtaining them for oil extraction, the low iodine level of the oil may be tolerated since the minimum bench mark of iodine value of oil for bioresin production is 50mg iodine/100g oil.

In this work the saponification value of the oil is 143.6 mg KOH/g oil. This value is lower than the values reported by Nursyazana (2014), Nathan (2013) and Encyclopedia (2014) on palm oil (203.9 mg KOH/g oil), Hemp seed oil (190.2 mg KOH/g oil),) and soya bean oil (185.4 mg KOH/g oil) respectively. Figure 5 shows the histogram illustrating the variations of the saponification values of the oil extracted and those three that have been reported for bioresin production. According to Ejilah (2010), saponification value of oil helps to determine the magnitude of potassium hydroxide (in mg) needed to neutralize the acids and saponify the esters contained in 1 g of the lipid. High saponification value of oil indicates high Lauric acid content of that oil which determines its suitability for making soap, Alkyl resin, wetting agents, Detergents etc. According to (Kittiphoom and Sutasinee, 2013), saponification value of oil is a useful tool for the evaluation of the chain length (molecular weight) of fatty acids occurring in the triacylglycerols in oil. Low saponification value of oil indicates a very high content of low molecular weight triacylglycerols. However, oil with high saponification value is better for bioresin production than the one with low value.

In this work the free fatty acid value of the oil is 3.09 mg NaOH/g oil. This value is high when compared with those reported on palm oil (1.06), Hemp seed oil (1.79) and soya bean oil (2.08) by Nursyazana (2014), Nathan (2013) and Encyclopedia (2014) respectively. Figure 6 shows the histogram illustrating the variations of the free fatty acid of the oil extracted and those three that have been reported for bioresin production. According to Amos-Tautua and Onigbinde (2013), free fatty acid content of oil is responsible for formation of soap and high water content in oil leads to increase in free fatty acids level because water in oil will oxidize in the present of air and water and many of the alkyl groups of the triacyl glyceride oxidize to fatty acid. Free fatty acid like the acid value of oil limits the degree of unsaturation of oil and thus undesirable elements in bioresins production.

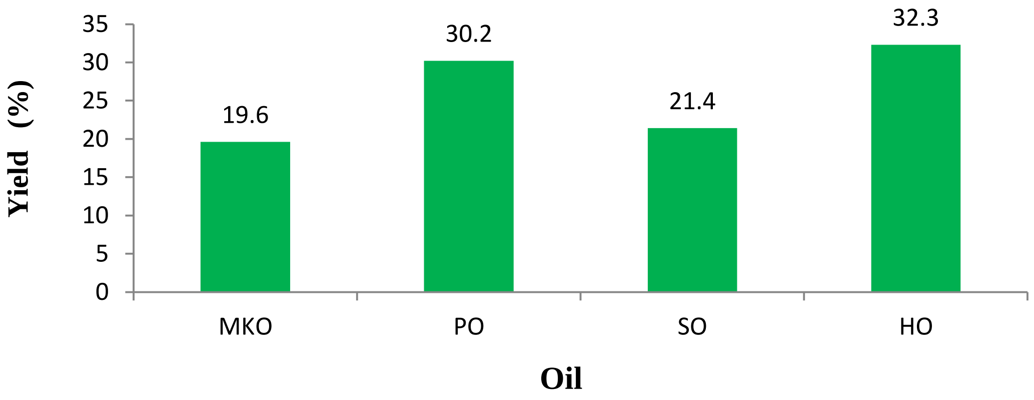

Figure 1: Variations of the percentage yields of the extracted oil and some reported ones

KEYS: MKO: Rosigold mango seed kernel oil, PO: Palm oil, SO: Soya bean oil, HO: Hemp seed oil

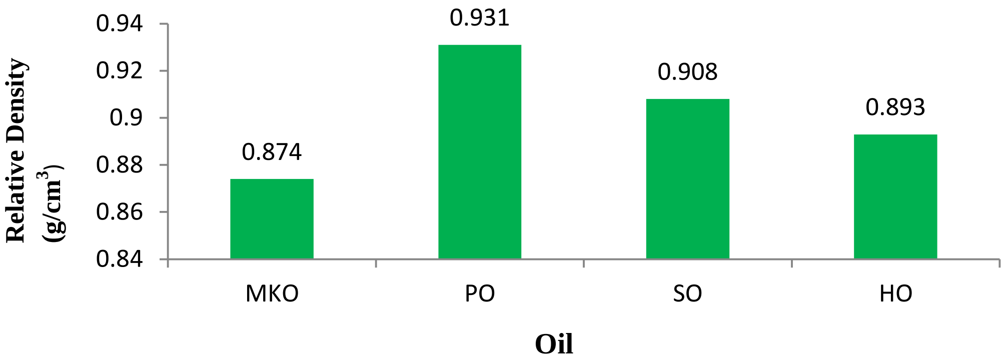

Figure 2: Variations of relative densities of extracted oil and some reported ones

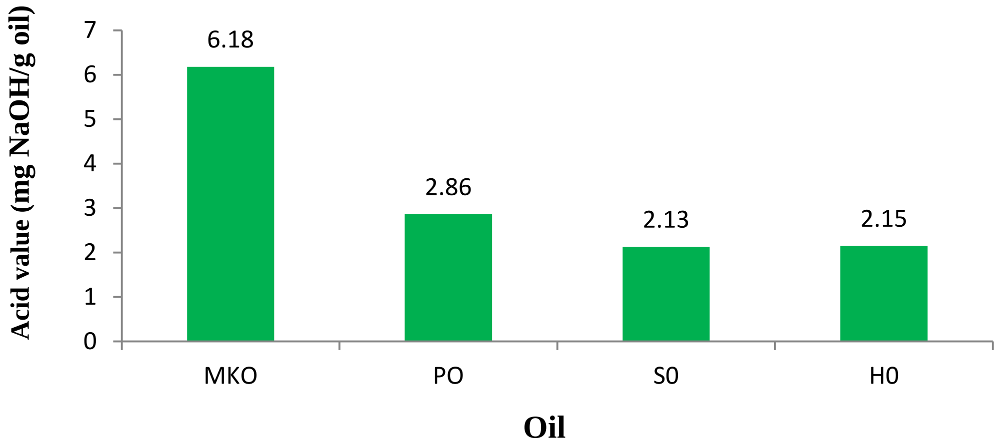

Figure 3: Variations of the Acid values of the extracted oil and some reported ones

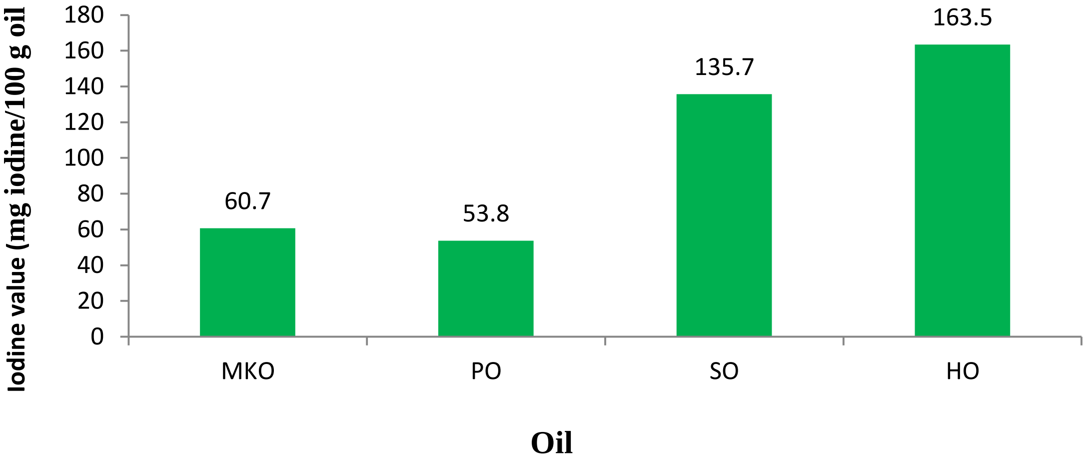

Figure 4: Variations of the Iodine values of the extracted oil and some reported ones

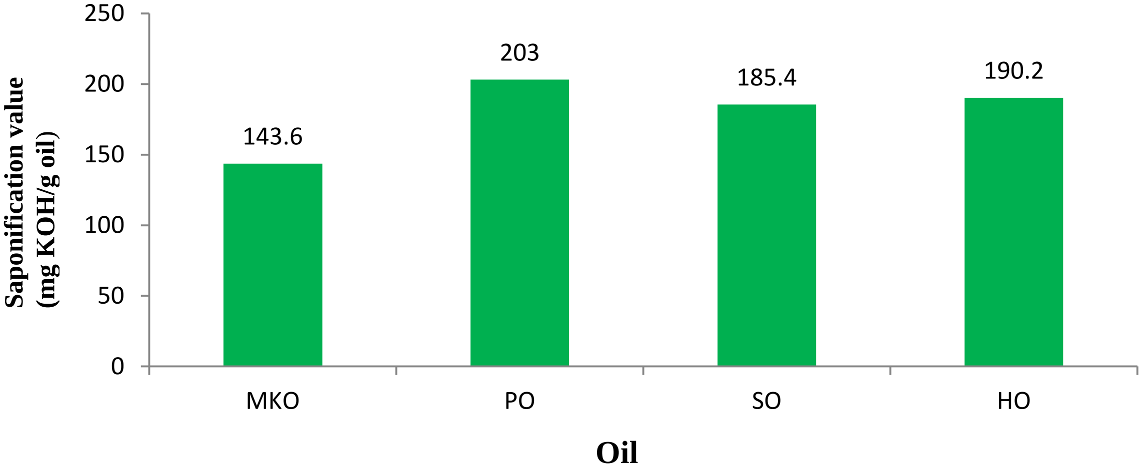

Figure 5: Variations of the saponification values of the extracted oil and some reported ones

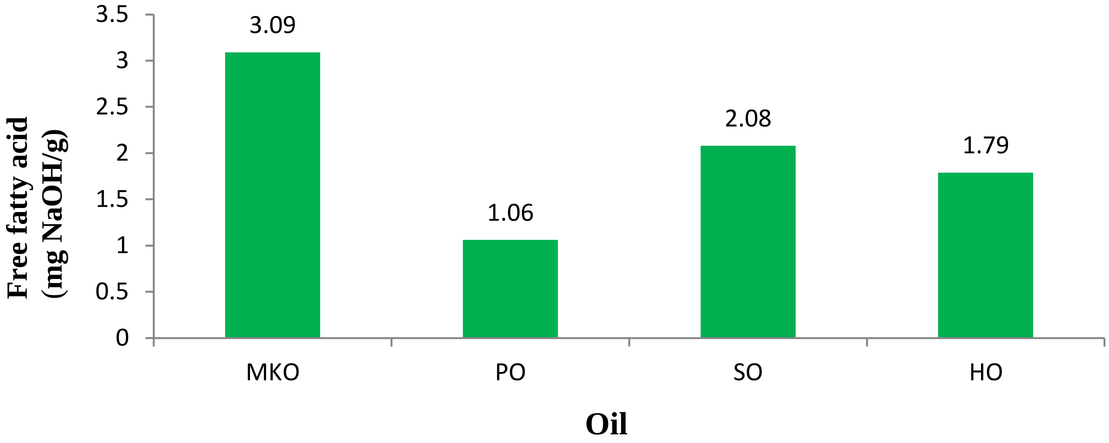

Figure 6: Variations of the free fatty acid (FFA) values of the extracted oil and some reported ones

4. Conclusion

The Rosigold mango kernel oil was extracted with average yield of 19.6%. Assessments and comparison of the characterized physicochemical properties results with those of three other oils (palm oil, Hemp seed oil and soya bean oil) that have been used for bioresin productions by some researchers, revealed that the oil yield and iodine values are low while the free fatty acid and acid values of the mango kernel oil are high. The other characterized parameters of the oil such as relative density and saponification values compete favourably with the above oils. However, considering the minimum iodine value bench mark of 50 mg iodine/100 g oil for oil suitable for bioresin production, Rosigold mango seed kernel oil is suggested to be suitable for bioresin production. Despite its low oil yield and iodine value, the oil has advantage over palm oil, Hemp seed oil and soya bean oil in that the source of it (mango seed kernel) is a waste material that is readily available, affordable and sustainable in Nigeria and beyond. Using the oil for bioresin production will not only give room for alternative resin that is renewable and sustainable, but will also help to ameliorates some of the challenges associated with total dependence on petrochemical resins thereby cushioning the adverse effects of synthetic resins on health, environment and economy.

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