# PHYSIOCHEMICAL PROPERTIES OF BLACK SOAP FROM OIL PALM EMPTY FRUIT BUNCHES

Comment [PSO1]: See my suggested title in the Reviewer's Comments


## Abstract

Comment [PSO2]: Suggest to make all single line spacing.

The use of oil palm biomass in black soap production was carried out. The soap was prepared using different oils (Palm kernel oil (PKO), Tallow oil (TO), Palm oil (PO), Palm fatty acid distillate (PFAD) and their blends. The physiochemical properties of the different oils and their blends were studied. The moisture content, bulk density, foaming stability, pH, solubility of metallic salts and surface tension of the different black soaps produced were analyzed. The results of the oils and their blends had free fatty acid values between 2.56-49.48%, saponification values of 231.4-450.20(KOH/g) and relative densities of (0.97-1.008g/ml. The results indicated that the moisture content ranged from 6.0-7.4% for all soaps, with the lowest (6.0%) observed in PKO, the highest (7.4%) observed in soap made with PO and PKO:PFAD:TO:PO blend. The bulk density of the soaps ranged from 0.55-0.94g/cm$^3$. The PKO: PFAD soap had the highest foam stability of 7.4cm and PKO soap (2.08cm) the lowest. The soap produced with various oils and their blends showed a neutral pH range of 7.25 -7.38. The metallic salts NaCl, KCl and $HgCl_2$ were soluble in the soap solution with no precipitate formed while $Mncl_2$, $PbCl_3$, and $CuCl_2$ salts precipitated out of the soap solution. The surface tension of water was lowered at different rates by the soaps. The black soap produced with the different oils met the standard quality specification for commercial soaps.



**Keywords:** *Palm kernel oil, Tallow oil, Palm oil, Palm fatty acid distillate, Empty fruit bunches.*




## 1.0 INTRODUCTION:

Comment [PSO3]: The word "African" should be in the paper title.

African black soap is a native organic soap formed by saponification of natural oils and fats with alkaline solution obtain from wood ash, which is known for its disinfectant and detergency action. It is generally used by various tribes in Nigeria and West African countries and are called different names, such as OseDudu in Yourba, Sabulunsalo in Hausa, Nchamkuta in Igbo, Anago soap in Ghana (Getradeghana, 2000). The production of soap from ash derived alkali has been an age-old gift in Nigeria and West African countries (Bella, 2008). Alkali derived from wood ash offer cheap alternatives to the synthetic ones (Ogunsuyi and Akinayo, 2012). Agricultural wastes such as empty palm bunch, cocoa pod, plantain peels, banana leaves, maize cob, wood, sugar beet wastes and many others has been reported to contain a reasonable quantity of alkali ash (Ogunsuyi and Akinayo, 2012). The source of ash and oils greatly determines the properties of the black soap produced (Ikotun, *et al.*, 2017). The common oils used for the production of soaps through saponification reactions are animal tallow, palm fatty acid distillate, coconut oil, palm oil, palm kernel oil and linseed oil. The physicochemical properties of soaps depend on

several factors such as the concentration and type of alkali, the type of oil used and the extent of saponification reaction. Empty fruit bunches (EFB) are wastes generated during processing of palm oil, they are mainly used as source of energy in the mill. The burning of empty fruit bunches in open air results ashes which contain oxides of potassium and sodium which give their corresponding hydroxides upon dissolution in water, which is a major component in black soap production (Ogunsuyi and Akinayo, 2012; Zauro*et al*., 2016).

The African oil palm (*Elaesisguineesis Jaca*) is one of the main sources of vegetable oil. Two distinct oil types; the palm oil (mesocarp oil) and the kernel oil the (seed oil) are obtainable from the oil palm tree (Atiku, *et al*., 2014). This research is focused on the utilization of EFB ash alkali, its effectiveness in generating soaps with different oils and their blends and the physiochemical analysis of the soaps produced.

## 2.0 MATERIALS AND METHODS

**Materials:** The materials/reagents used in this work were: Tallow oil (TO), palm kernel oil (PKO) sourced randomly from Benin City, Edo state, Nigeria, palm fatty acid distillate (PFAD), palm oil (PO) and empty fruit bunches (EFB) obtained from Nigerian institute for oil palm research (NIFOR), Benin city, Edo state Nigeria. All reagents used were of analytical grade.

**Preparation of oil samples and their blends:** The oils samples (PKO. PO, PFAD and TO) were dried at 40°C for 2h and blended in a ratio of 1:1 as follows; PKO:PO, PKO:TO, PKO:PFAD, PKO:PO:TO:PFAD.

**Extraction of Alkali from Empty Fruit Bunches (EFB):** Empty fruit bunches were sun dried for 7 days to ensure the reduction of moisture from the sample. The EFB were burnt at a temperature of 450-550°C for a period of 6h for proper ashing. The ash was loaded in an empty rice bag and was washed with water till the pH of the filtrate was 7.0. The filtrate obtained was allowed to stand for 24 hours thereafter decanted. The filtrate was poured into a soap pan and heated with firewood to evaporate the excess water leaving behind a residue.

**Physiochemical analysis on the oil samples**

**Determination of Saponification Value:** The number of mg of potassium hydroxide needed to saponify 1 gram of oil/fat is term as saponification value. The saponification value was carried out according to the AOCS method 2000. 5g of the oil was weighed and placed into a 250ml conical flask, 50ml of alcoholic-KOH was added and connected to an air condenser. This was allowed to boil gently until the sample was completely saponified for 1h. The flask was allowed to cool, phenolphthalein indicator was added. The KOH solution was titrated with 0.5N hydrochloric acid (HCl) until the pink colour disappears and the final volume recorded. Saponification value (SV) was determined according to AOCS method 2000.

**Determination of Iodine Value:** 0.2g of the oil sample was placed in a flask that contained 20 ml of carbon tetrachloride, 25ml of Wiji's iodine solution was further added. The flask was covered, shaken and kept in the dark for 1hr at room temperature. Then 20 ml of potassium

**Comment [PSO4]:** Reframe the yellow highlighted portion to read: "The burning of …results in ashes containing oxides of …which upon dissolution in water give their corresponding hydroxides which is a major component in African black soap production".

**Comment [PSO5]:** Is it "heated with firewood" or rather "heated with wood fire"?

**Comment [PSO6]:** The equation used for the calculation of SV should be stated at the end

**Comment [PSO7]:** The equation used for the calculation of IV should be stated at the end

iodide solution and 100 ml of distilled water were added. 'The liberated iodine was slowly titrated against 0.IN sodium thiosulphate solution until the yellow colour disappeared. At this point, about 1-2 ml of starch solution was slowly added and titration continued until the blue-black colour was discharged. This process was repeated without oil (blank titration). Iodine value was calculated according to AOCS method 2000.

**Determination of Free Fatty Acid (FFA):** 0.5g of oil was boiled with 50ml of ethanol and allow to cool, 1-2 drops of phenolphthalein indicator were added which was titrated against 0.1N NaOH to obtain a pink colour. The free fatty acid was calculated according to AOCS method 2000.

**Determination of Relative Density:** The relative density was calculated according to the method of Aiwizea and Achebob, (2012). The oil samples were transferred into a 50 ml density bottle of known weight. The density of the oil was calculated as follows:
Relative density = weight of sample (g) / weight of sample (ml).

**Saponification Reaction**

The saponification process involves the esterification of the concentrated alkali solution with the different oils and blends separately at a ratio of 1:1.5. The oil was added to the alkali solution at 300°C with continuous stirring until the entire soap mass is black. The soap was poured into molds and allowed to solidify (Atiku*et al.*, 2014).

**Comment [PSO8]:** Not scientific. There should have been a test to determine complete saponification by measurement of unsaponified oil. Also, reaction equation should be presented.

**Analysis of soap**

**Determination of Foamability Test:** 2.0g of each soap shavings was added to a 500ml measuring cylinder containing 100ml of distilled water. The mixture was shaken vigorously so as to generate foams. After shaking for about 2 minutes, the cylinder was allowed to stand for about 10 minutes. The height of the foam in the solution was measured and recorded (Isah, 2006).

**Comment [PSO9]:** The shaking should have been automated to have same frequency and time because the extent and time of shaking determine the foamability

**Determination of Moisture Content**

Moisture content was determined by drying 10g of the soap sample to a constant weight at 105 ºC according to AOAC (2000). It was allowed to cool and then reweighed until constant weight is obtained.

**Determination of pH:** pH of the soap prepared was determined using a pH meter (PHS-3C). Ten percent of the soap solution was prepared using the soap shavings. The electrode of the pH meter was inserted into the solution. The pH was recorded as described by Umar (2002).

**Reaction of Soap with Metals:** To 5ml of the soap solution in test tubes, 2ml of 4% NaCl, KCl, $PbCl_3$, $CuCl_2$, $MnCl_2$ and $HgCl_2$ were added separately, each of the test tube was shaken, the precipitate formed was observed (Mabrouk, 2005).

**Bulk Density**: Approximate method of Aiwizea and Achebob (2012) was used to determine the bulk density of the soaps. The soap samples were packed into a cylinder of known weight and volume. The weight of the cylinder including its contents were measured and the bulk density calculated.

**SURFACE TENSION OF THE SOAPS:** The surface tension of the soap solution was determined according to the method of Ruff (2015) by measuring the capillary action and density of each of the soap solutions. After which the surface tension of the soap solutions were calculated using the formula;$S = \frac{phga}{2}$ Where; s = surface tension, $ph$ = density of soap solution, $g$ = acceleration due to gravity and a = capillary rise.

**Capillary action of soap solution**

In measuring the capillary action of the soap, ten percent of the soap solution was prepared and poured into clean petri-dish. A capillary tube was gently placed to stand in the solution on the petri dish. A rule was used to measure the liquid rise in the capillary tube. The procedure was repeated for each of the soap solutions and measurements were recorded.

**Density**

The density of each of the soap solution was determined using a density bottle. The density bottle was filled up with the soap solution. The weight and volume of each of the soap solutions were measured and used to estimate the density.

**3.0 Results and Discussion**

**Table 1: Result of some physiochemical properties of the oil samples**

| PARAMETERS | PO | PFAD | PKO | TO | PKO: PO | PKO:PFAD | PKO: TO | PKO:PO:PFAD:TO |
|---|---|---|---|---|---|---|---|---|
| **FFA (%)** | 2.56±0.1 | 8.45±0.15 | 11.00±0 | 8.74±0.05 | 8.45±0.5 | **49.48±0.15** | 7.47±0.35 | 31.81±0.6 |
| **RELATIVE DENSITY(g/ml)** | 0.97 | 1.012 | 0.978 | 0.988 | 1.002 | 0.982 | 1.004 | 1.008 |
| **SAPONIFICATION VALUE (KOH)/g** | 231.41 | 441.79 | 416.54 | 450.20 | 437.58 | 458.62 | 409.53 | 370.26 |
| **IODINE VALUE (g/100g)** | 53.4 | 43.7 | 18.97 | 46.2 | 36.25 | 31.5 | 45.67 | 40.54 |

The pH of the alkali extract is 8.15 with a concentration of $6.75x10^{-3}$M.

Table 1 above shows the physiochemical properties of the oils and their blends. The free fatty acid (FFA) value of the oils ranges from 2.5-11% with palm oil being the lowest and Palm kernel oil the highest. The FFA of the oil blends revealed PKO: PFAD to be the highest (49.48%) followed by PKO: PO: PFAD: TO (31.81%) and PKO: TO (7.47%) as the lowest.

Relative densities of the oils and their blends (Table 1 above) ranged from 0.97-1.01g/ml which agrees with FAO standard and values obtained by other researchers (0.860-0.73 g/ml) (Zauro*et al.*, 2016; Amoo*et al.*, 2004). The saponification values of the oils and their blends ranged from 231.41 to 437.58 (KO H)/g as seen in table 1. Although, this value is extremely high for oil consumption, however, for soap production purposes it is acceptable. This is an indication that the oils and blends could be used in soap making as the values falls within accepted range as reported by Natural soap directory (2009). Iodine value is one of the parameters used in accessing the quality of oils for soap making. Oils with very low iodine number yields soap that are hard and insoluble in water (Pavila, *et al*., 1982). Table 1 shows the iodine value of all the oil samples and their blends. This result indicates that the oils can be used in the production of hard and soluble soaps.

**Comment [PSO10]:** This is not the correct concept of Iodine value. It is a measure of degree of unsaturation. Go back to literature.

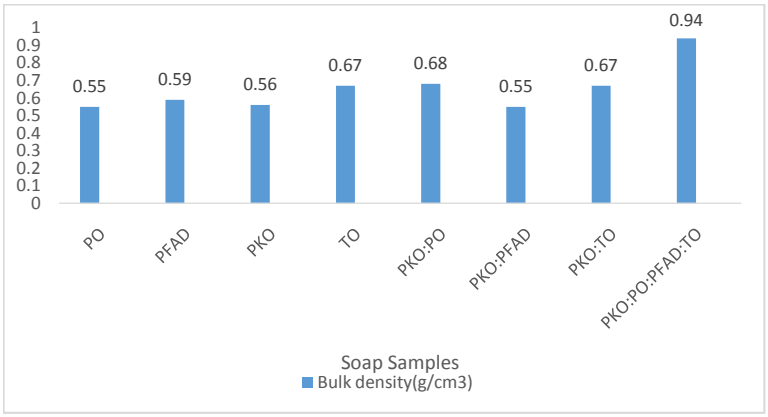


**Figure 1: Bulk density of the different soap samples.**

In figure 1, PKO:PO:PFAD:TO soap had the highest density value of 0.94 g/cm$^3$ while other soaps fall within the range of 0.55 g/cm$^3$ to 0.68 g/cm$^3$. The bulk density of soaps indicates whether a particular soap will float or sink when placed in water. From the results obtained, the bulk density of the PKO:PO:PFAD:TO soap is in agreement with the report of Allard (2005) were the Dawn soap density was 0.932g/cm$^3$.

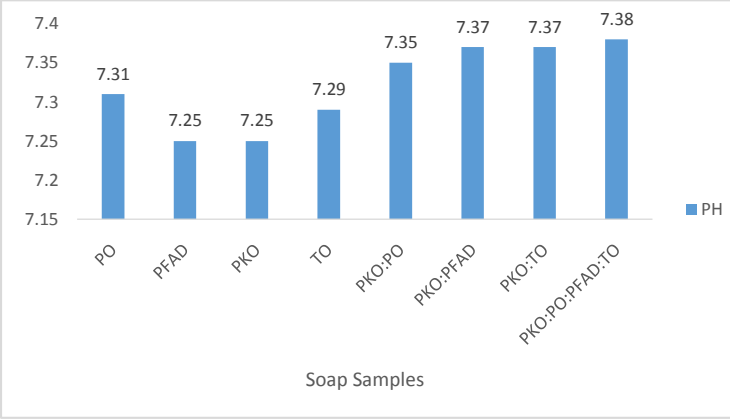


**Figure 2a: pH of soap samples.**

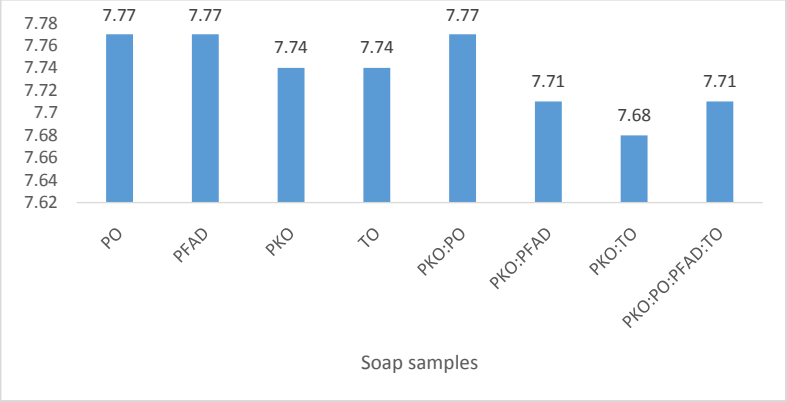


**Figure. 2b: pH of the soap at seven (7) weeks of storage**

The pH of the different soaps ranged from 7.25-7.38 as shown in Figure 2a. There is a slight increase of the pH values (7.68- 7.77) of all soap samples at seven (7) weeks of storage as seen in Figure 2b. The results obtained at production and at seven weeks of storage falls within the accepted and recommended pH values of a neutral and skin friendly soap. According to Umar (2002), NAFDAC recommends soaps with pH values of 7-8.

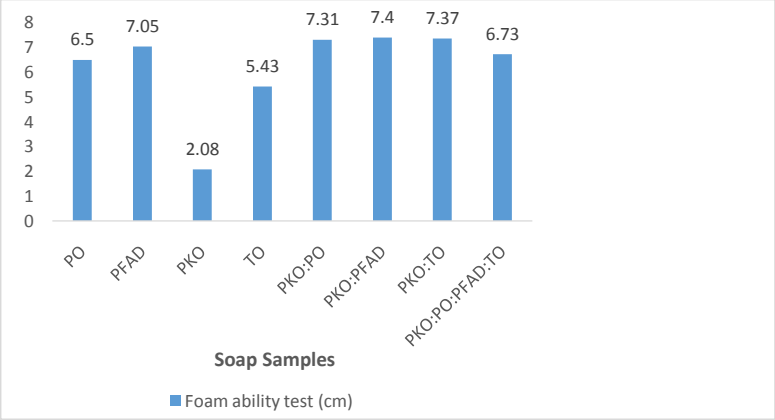


**Figure 3a: Foam ability test**

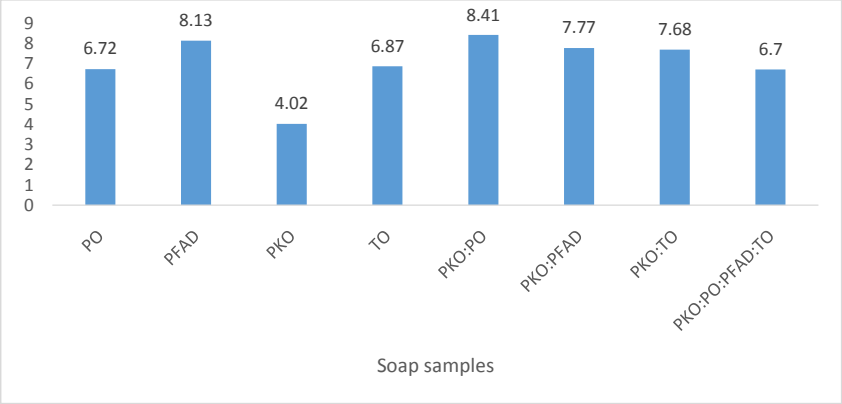


**Figure 3b: Foam ability of all soap samples after 7 weeks**

Figure 3a is the bar chart plots of the foam ability tests carried out on the soap samples. The bars represent the heights of the foams formed. The bars in the figure reveals that the foamability of the soap samples increases in the order of PKO:PFAD>PKO:TO>PKO:PO>PFAD> PKO:PO:PFAD:TO>PO>TO>PKO. The foamability of the PO soap is in agreement with the report of Mohammed and Usman (2018) which reported that increase in the foamability of soaps as it cures/ages while the value of the PKO soap (2.08cm) in this study is lower than the value reported by Mohammed and Usman (2018). Figure 3b reveals increase in the foam ability after seven weeks of curing (the process of allowing saponification to complete and for water to evaporate out). This suggests that curing is a major factor in improving the quality of soaps produced.

The moisture content of the samples is presented in the figure 4. The moisture content was determined after four (4) days. The chart shows PKO:PO:PFAD:TO and PO soaps having the highest moisture content of 7.4%. Followed by PKO:TO soap (6.8%), PFAD, TO, PKO:PO, PKO:PFAD soaps were in comparable range of (6.2-6.5%) PKO soap (6.0%) was the lowest.
Reports of Kuntom, (1996) and Ivy, (2013) reveal moisture content of 14% and 41% respectively in PKO soap produced. Also, Onyango (2014) reported moisture content values of 10.91-22.69% of certain commercial soaps. The disparity in moisture content values stated in numerous literatures could be allied with the differences in the production methods embraced by each scholar. In addition, it could also be credited to the time frame in which the test was carried out. Time frame plays an important role in the determination of moisture content of soaps. This is because as the soap undergoes curing process water in the soap is continuously being lost through evaporation (Kevin, 2008) but the reverse is the case with black soap because it is hydroscopic in nature.

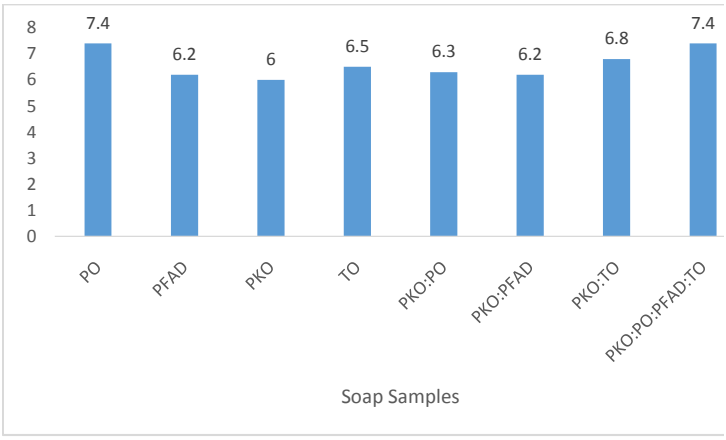


**Figure 4: Moisture content of soaps of different oils**

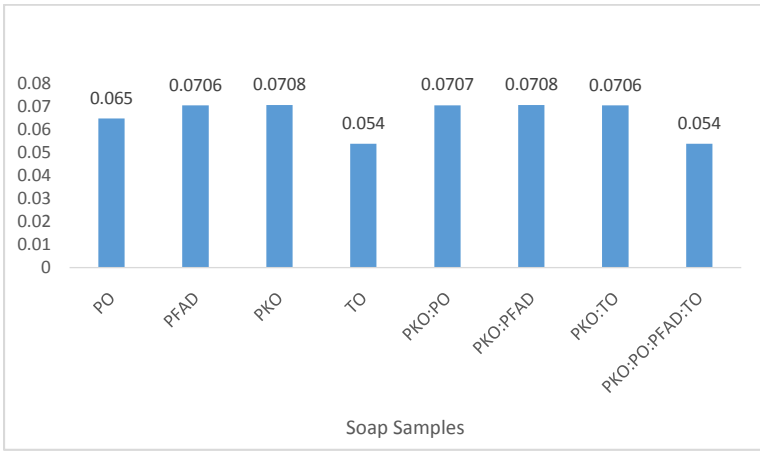


**Figure 5: Surface Tension of the different soaps.**

Surface tension is the ability of a liquid surface that allows resistance of an external force due to the cohesive nature of its molecules. Soap as a cleansing agent should be able to lower the surface tension of water so as to enable it wash off dirt. Figure 5 is the bar chart showing the surface tension of the soap samples. The result of the surface tension ranges from $5.4x10^{-2}$-$7.1x10^{-2}$N/m. This indicates that all the soap samples lower the surface tension of water thus are good cleansing agent. This result goes contrarily to the work of Roman *et al.* (2001) who

reported the surface tension of a liquid dish washer soap (A) and a liquid toilet soap (B) to be 0.0214N/m and 0.0245 N/m respectively.

**Table 2: Reaction of soap with metallic ions**

| SOAP/SALT | PO | PFAD | PKO | TO | PKO:PO | PKO: PFAD | PKO:TO | PKO:PO:TO: PFAD |
|---|---|---|---|---|---|---|---|---|
| $MnCl_2$ | White precipitate | White precipitate | White precipitate | White precipitate | White precipitate | White precipitate | White precipitate | White precipitate |
| $PbCl_3$ | White precipitate | White precipitate | White precipitate | White precipitate | White precipitate | White precipitate | White precipitate | White precipitate |
| KCl | No precipitate | No precipitate | No precipitate | No precipitate | No precipitate | No precipitate | No precipitate | No precipitate |
| NaCl | No precipitate | No precipitate | No precipitate | No precipitate | No precipitate | No precipitate | No precipitate | No precipitate |
| $CuCl_2$ | Blue precipitate | Blue precipitate | Blue precipitate | Blue precipitate | Blue precipitate | Blue precipitate | Blue precipitate | Blue precipitate |
| $HgCl_2$ | No precipitate | No precipitate | No precipitate | No precipitate | No precipitate | No precipitate | No precipitate | No precipitate |

Soap reaction with metallic ions is seen in table 2. A white precipitate was produced with $MnCl_2$ and $PbCl_3$ reaction with the soap. Manganese and lead chloride ions ($MnCl_2$ and $PbCl_3$) produced a white precipitate, copper ion ($CuCl_2$) gave a blue precipitate with all the soap solutions. No precipitate was seen when the soap reacted with NaCl, KCl and $HgCl_2$. This study is in contradiction with the work of Atiku*et al.* (2014) who reported that soap reactions with KCl and NaCl produced a white precipitate. This variation in this reaction maybe attributed to the different alkali source.

**Conclusion**

The results obtained from this study shows that the physiochemical properties of the oils and soaps tested are within the range of the standard values recommended by FAO. Also, the oils and blends used are good oils for traditional soap making. Although there were variations in the values of the parameters when compared to other similar investigations, however, these variations are not peculiar to results obtained in this study. Similar studies has shown the

variations are widespread among the results of investigations conducted previously. Conclusively, locally processed alkali from EFB used in this investigation can produce good and quality soaps that conform to any standard.



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