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Production of Soap Using Locally Available Alkaline Extract from Millet Stalk: A Study on Physical and Chemical Properties of Soap

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Abstract: *Millet stalks where used to extract alkaline using traditional method. The alkaline extract was used in the preparation of soap using traditional method. The resulting soap was subjected to physicochemical test. Saponification value (171 mg/KOH/g), iodine value (41.2g/100g), acid value (1.46mg/KOH), ash content (9.2%), colour (white), texture (hard and rough). This implies that the white colour of soap is as a result of bleaching of the oil sample and also the soap is hard due to the presence of high concentration of k^+ ions in the prepared soap, emulsification test (observed), foam test (form lightly with moderate persistence), foam height (1.8cm). Reactions with metals NaCl, KCl and NH_4Cl (form white ppt) but soluble in water, Ca^{2+}, fe^{2+}, mg^{2+} form (white gelatineous ppt) and form insoluble complex with water. Reaction of soap with 1 drop of phenolphtalein gave (pink colour) and the reaction of the soap with 3M HCl gave (colourless solution) to ascertain the quality of soap produced. These properties tested showed that the soap prepared using traditional method gave a better quality soap which could be compared with any other soap.*

Keywords: *Alkaline extract, Millet stalk, Soap, Saponification, Traditional method.*

1. INTRODUCTION

The African oil palm *Elaesis guineesis* (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. The oil palm belongs to the family *palmae*. The family consists of about 225 general with over 2600 species. The palm belongs to subfamily *Cocoideace* of which it is the important member [1]. The uses of palm oil are for edible purposes, large proportion of oil palm is also consumed in the manufacturing of soaps, candles, lubricants and in planting industry, sometime it is used as fuel for internal combustion engines [1]. The aim of this study was to

determined physicochemical properties of palm oil, such as Saponification value, iodine value, acid value, ash content and to prepare soap that is of high quality with minimal damage to human skin.

2. METHODS

2.1. Sample Collection and Treatment

The millet stalk was collected from a farm in Mungadi village, Kebbi State of Nigeria. The sample was then oven dried (DHG-9101-15A, laboratory dry oven, Changzhou, China) at 40 ^{0}C to a constants weight after which they were burned into ashes using muffle furnace at 550^{o}C for 5 h by official method [2].

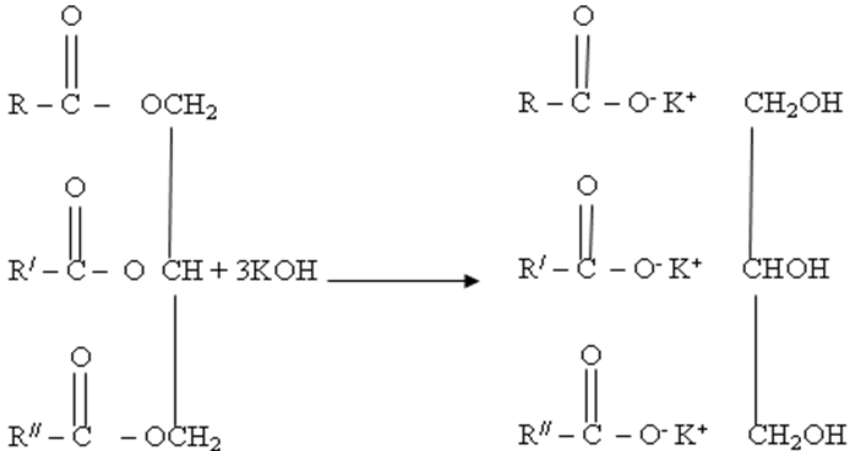
2.2. Traditional Method of Extracting Alkaline from Millet Stalk Ash

200g of millet stalk ash were taken using calabash siever that was place on cleaned receiving bucket. Water was then added, and the set up was allowed to stand until the filtrates dried out. Addition of water continues until the volume of filtrate was up to 4 liters. The filtrate was then concentrated on a cleaned cooking pot, to about one – quarter of its original volume. 50ml of the oil was added slowly into the concentrated solution and resulting mixture was stirred vigorously to avoid sedimentation process. 10ml of the oil was added after each interval of 10 mins for four times. The stirring continued until all the surface of the mixture was covered with foam and the lather volume kept increasing until it reached its peak. Heating process was stopped and the soap was allowed to cool into a solid mass [3].

After millet stalk were burned the ash contains potassium oxide K_2O. When this K_2O is mixed with water, the strong base potassium hydroxide (KOH) is formed.

$$K_2O + H_2O \longrightarrow 2KOH \quad (1)$$

Equation for the Reaction.



(2)

TRIGLYCERIDES (FAT OR OIL) A mixture of potassium carboxylates and glycerol (Soap)

Fig1. *Structure of potassium carboxylate and glycerol (soap)*

From the above equation, a triglyceride reacts with KOH to form a mixture of potassium carboxylates and glycerol. In the equation soap is a salt composed of mixture of carboxylate anions and univalent cation. A mixture of anions is formed because each triglyceride molecule contains a variety of fatty acid residue and because of particular fat or oil itself is a mixture of molecules. Potassium soaps are more soluble than sodium soaps and readily produce lather [4].

3. PHYSIOCHEMICAL AND CHEMICAL ANALYSIS OF PALM OIL AND SOAP

3.1. Determination of Saponification Value

2g of the oil sample was added to flask with 30ml of ethanol KOH and was then attached to a condenser for 30 minutes to ensure that the sample was fully dissolved.

After the sample had cooled, 1ml of phenopthalein was added and titrated with 0.5M HCl untill a pink end point has reached [5]. Saponifiication value can be calculated from the equation.

$$S.V = \frac{28\ 0.5 \times (v_2 - v_1)\ M}{W} \quad (3)$$

Were w = weight of the oil sample

M = molar mass of HCl

V_1 = volume of HCl used in real titration

V_2 = volume of HCl used in the blanck

56.1x0.5 = molecular weight of KOH

3.2. Determination of Iodine Value

0.4g of the sample was weighed into a conical flask and 20ml of carbon tetrachloride was added to dissolve the oil. Then 25ml of dam's reagents was added to the flask using a safety pipette in fume chamber, stopper was then inserted and the content of the solution was placed in dark for 2 hours 30 minutes. At the end of this period, 20ml of 10% aqueous potassium iodide and 125ml of water were added using a measuring cylinder. The content was titrated with 0.1m sodium thiosulphate solution on until the yellow colour almost disappeared.

Few drops of 1% starch indicator was added and the titration continued by adding thiosulphate drop wise until blue coloration disappeared after vigorous shaking. The same procedure was used for blank test [5]. The iodine value (I.V) is given by the expression.

$$I.V = \frac{12.69\ (v_1 - v_2)}{M} \quad (4)$$

Where C = contraction of sodium thiosulpahte

V_1 = volume of sodium thiosulpahte use for blank

V_2 = volume of sodium thiosulpahte used for determination

M = mass of the sample

3.3. Determination of Acid Value

10g of oil was weighed into conical flask and 50ml of denatured alcohol (ethanol and diethyl ether in ration 1:1) was added and shaken, 2 drops of phenolphthalein indicator was added, it was then titrated against 0.1N sodium hydroxide. The acid value can be calculated using the formula [6].

$$A.V = 100 \times 2.82 \times V/W \times 1000 \times 1 \quad (5)$$

V= Volume of NaOH used in sample titration

W = weight of sample

3.4. Determination of Free Fatty Acids

1g of oil was boiled with 50ml of ethanol and allows to cool, 2 drops of phenolphthalein indicator was added, it was then titrated against 0.1N NaOH until pink colour was obtained [7]. The free fatty acid was calculated formula.

$$\%\ FFA = \frac{T \times 2.82}{W} \quad (6)$$

Where w = weight of sample

2.82 = molecular mass of sodium hydroxide

T = Average titre value

3.5. Determination of Ash Content

5g of sample weighed into a pre – weighed crucible and placed in gallenkamp muffle furnace at 60^0C for 6 hours. The ash cooled and weighed in the crucible. The weight of the ash was obtained by difference between the ash content calculated as percentage of the initial dry weight of the sample [7]. Ash content can be calculated by using the formula

$$\% \text{ ash} = \frac{w_2 - w_1}{W_3} \times 100 \quad (7)$$

Where w_1 = weight of empty crucible

W_2 = weight of crucible +sample ash

3.6. PH Determination

The pH of soap prepared was determined using a pH meter (827 pH lab model). 10g of the soap shavings was weighed and dissolved in distilled water in a 100cm volumetric flask. This is made up to prepare 10% soap solution. The electrode of the pH meter was inserted into the solution. The pH was recorded as described by [8].

3.7. Emulsification Test

4 drops of mineral oil (gas oil) was taken into a test tube, 5ml of the soap solution was added to the oil in the test tube. The mixture in the test tube was shaken briefly and the extent of emulsification was noted [9].

3.8. Reaction of Soap with Metals

To 5ml of the soap in test tubes 2ml of 4% NaCl, KCl, NH_4Cl, $CaCl_2$, $MgCl_2$ and $FeCl_3$ were added, each of the test tube were shaken and precipitate formation were observed [9].

3.9. Test for Acidity / Alkalinity of Soap

To 5ml of soap in a test tube drop of phenolphthalein indicator was added and colour change was observed [9].

3.10. Reaction of Soap with Acid

To the solution in 2.3.9 above, 5ml of 3m dilute HCl was added to the test tube and colour change was observed [9].

3.11. Foam Test

To 5ml of the soap sample in a test tube, the sample was corked and shaken vigously, the relative amount of lather was observe and recorded [9].

3.12. Foam Ability Test

About 2.0g of the soap (shavings) was added to a 500cm^3 measuring cylinder containing 100cm^3 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 [10].

4. RESULTS AND DISCUSSION

4.1. Results

Table 1. *Result of physiochemical properties of palm oil and prepared soap*

S/N	Parameters	Palm oil	Prepared soap
1.	Saponification value (mg /KOH/g)	171.1	NA
2.	Iodine value (g/100g)	41.2	NA
3.	Acid value (mg/KOH)	1.46	NA
4.	Ash content (%)	NA	9.2%

5.	pH of prepared soap	NA	10.53
6.	Free fatty acids (%)	18.04	NA

NA: Not applicable

Physical Properties Test

From the product prepared (soap) it has been observed that it have the following physical properties as shown in the table below.

Table 2. *Result of physical properties test*

S/N	Parameters	Results
1	Texture	Hard and rough
2	Color	White
3	Foam test	Foam thickly with longer persistence
4	Emulsification test	Emulsification was observed
5	Foam height (cm)	1.8

Chemical Properties Test

From the reaction of soap with metals and acid the following information were obtained.

S/N	Parameters	Results
1	NaCl	White precipitate observed with foam
2	KCl	White precipitate observed with foam
3	Mg^{2+}	White precipitate that coat the surface of the solution was seen
4	NH_4Cl	White precipitate with foam
5	$CaCl_2$	White gelatinous precipitate observed
6	$FeCl_3$	Thick brown precipitate observed
7	Phenolphthalein	Deep pink colour observed
8	Reaction with HCl	Solution becomes colourless

4.2. Discussion

Saponification occurs when, first, three molecule of sodium hydroxide (NaOH) are dissolved in water (H_2O) and are splits apart, which results in three sodium ions (Na) and three hydroxyl groups (OH). Second, a triglyceride (fat) molecule ($C_3H_5(COOR)_3$) is split apart through hydrolysis, which results in free glycerol (C_3H_5) and three fatty acid tails (COOR). Third, the hydroxyl groups (OH) all bond to the free glycerol (C_3H_5) to form a molecule of glycerine ($C_3H_5OH_3$). Fourth, the three fatty acids (COOR) each bond with one of the three sodium ions (Na) to form three molecules of soap (3NaCOOR) [11]

Saponification value of palm oil in this experiment was determined to be 171.1 mg/KOH/g and it is an indication that the oil could be used in soap making because the value fall within the range as the literature reported [12].

The iodine value is one of the parameters used in accessing the quality of oil for soap making. Oils with very low iodine number yields soap that are hard and insoluble in water [13].

The pH of the prepared soap is 10.53 signifying that the soap is strongly basic in nature, even though the pH 10.53 is not skin friendly because skin friendly pH soap suppose to have pH 7-8, NAFDAC recommend pH of 8 [8].

Acid value in this work was observed to be 1.46 mg/KOH indicating that the palm oil used has strong acid content, the value is in line with the value obtained in soap making as reported [9].

Ash content can be defined as a non-volatile inorganic matter; it is a substance which remains after subjected to high decomposition temperature. The 9.2% ash content obtained shows that the oils can be good sources of mineral Free fatty acid determines the suitability of the oil for edibility or industrial uses. In this study free fatty acid value was 18.04%. The value obtained for

palm oil is 171.1 which are used in making soap and produced soap which is relatively hard and soluble in water.

The determination of these parameters saponification value and acid value gave an insight about the amount of base consumed and also hardness or softness of the soap produced. The texture of soap depends on the nature of its fatty acids composition, length of hydrocarbon chain and number of double bound determines the hardness or softness of the soap. The most probable explanation to the variation in the texture of the soap could be due to the presence of glycerol and some impurities in sample of the soap [8].

Locally processed soap was known to be soft which could be due to the presence of K^+ ions in the soap. In this case, it was found to be relatively hard as a result of the high concentration of K^+ and presence of impurities derived from the millet ash Filtrates. The hardness and rough texture of the soap could be due glycerol removal through the process of salting out. The foam height was observed to be 1.8cm which is lower in comparism to shea butter seed oil (4.2) and higher than that of Castro seed oil which is 1.6 [14].

The colour of the soap could be due to salting out process that is why the soap maintained the white colour.

Fatty acids composition of oil used in soap formation can also determine the nature and stability of leather produced by different soaps, it was reported that, lauric acid, myrisic acid, which are all saturated fatty acids produce soap with flatty leather, higher cleansing power but of low stability, on the other hand linoleic acid produce fluty and stable leather soap with low cleansing power [15].

Sodium, and potassium salts of common soaps are soluble in water, the metal cations $mg^{2+,}$ ca^{2+} and $fe^{3+,}$ they are component of naturally hard water and form insoluble complex with (soap) which is one of the disadvantages of soaps over detergent. But NaCl, KCl and NH_4Cl do not form insoluble complexes with soap. The degree of precipitating agent used considering the precipitate formed, soap obtained through cold process is better recommend for use in hard water than other soap samples.

Pink colouration was observed on the addition of phenolphthalein to the soap sample, indicating that, they are all alkaline. The pink colour was as a result of the interaction between the OH^- ions form solution and H^+ ion forms the indicator. In the soap solution, the OH^- ion combines with H^+ ion form phenolphthelin to obtained unionized water molecule. This causes the equilibrium to shift to the right and the solution had pink colour. However, the intensity of pink colouration varied with the concentration on OH^- negative ions in the solution. Thus, a solution of high alkalinity shows dark pink colouration on addition 3M HCl, the sample solution turns colourless. This is because addition of the acid causes the increase in H^+ in the solution which in turn causes the equilibrium to shift in left direction more of H^+ is generated thus, the solution remains colourless.

Emulsification was observed, the emulsification of soap solution was as a result of hydrophobic interaction between the water in soap solution, oil droplets and long chain aliphatic hydrocarbon.

5. CONCLUSION

The result obtained from the physiochemical analysis of palm oil revealed that palm oil could be used as good oil for traditional soap making; palm oil is very popular for its ability to add hardness to soap and produce stable creamy leather. The low iodine value of the oil in the present study yield soap that is hard and insoluble in water. The acid value as well as the pH obtained is an indication that the soap is strongly acid in nature and can only be use for bathing purposes. The result obtained in relation to the alkaline produce shows that there is good probability to provide caustic potash from millet stalk, so there is the need to develop a suitable local technology which can be used to extract caustic potash from millet stalk. The ash content was observed to be 9.2% and the free fatty acid is 18.04. The texture of the soap was hard and rough as a result of removal of glycerol through the process of salting out, the colour of the soap is white and it foams thickly with moderate persistence emulsification was observed. Sodium chloride, potassium chloride, and ammonium chloride (NaCl, KCl, and NH_4Cl) are soluble in water and form white precipitate with the soap solution. The divalent and trivalent cations such as Mg^{+2} , Ca^{+2} and Fe^{3+} which are

component of hard water form insoluble complexes with soap and that is why soaps do not act well in hard water. The cations $Mg^{+2,}$ Ca^{+2} and Fe^{3+} will precipitate out the fatty acid salts as insoluble precipitates. That is why it takes more soap to clean in hard water than in "soft" water. The reaction of soap with 1 drop of phenolphthalein gave a deep pink colour and further reaction with 3M HCl, gives a clear colourless solution.

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