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Effect of Cocoa Shell Ash as an Alkalizing Agent on Cocoa Products

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Abstract: Alkalized cocoa nibs were produced using cocoa shell ash as an alkalizing agent. Conventionally, imported alkalizing agents are used to produce alkalized/dutched nibs in cocoa processing industries. Cocoa powder and cocoa butter were produced from nibs treated with cocoa shell's ash as an alkalizing agent and compared with products from two industries which used imported alkali as the dutching agent. Cocoa products made from cocoa nibs alkalized with ash for the shell were evaluated for physicochemical properties in comparison with product from Oluji and Stanmark Industries located in Southwestern Nigeria. Flame photometry method was used to determine components of the ash. The pH value of cocoa powder were 6.72 and 6.56 for Oluji and Stanmark samples respectively while 6.59 was reported for the Experimental cocoa powder sample. Percent fat content was 11.56 for Stanmark, 12.20 for Oluji and 10.56 for the Experimental sample. Colour reflectance was highest in Stanmark sample with 8.69 while the least was recorded for Experimental sample (7.18). Percent ash was 6.58, 8.16 and 7.13 for Stanmark, Oluji and Experimental samples respectively. Fat parameters for cocoa butter from the three samples were found to be within International standard for cocoa butter. Percent fatty acid ranged from 1.46 to 1.59. Saponification value was 193 mg KOH g^{-1} sample for Experimental sample, while Stanmark and Oluji cocoa butter had 196 and 198 mg KOH g^{-1}, respectively. Percent unsaponifiable matter content was 0.30 each for Stanmark and Oluji with 0.39 for Experimental sample. Iodine value was between 35.11 and 38.07 Wij's. Peroxide value ranged from 26-29 ME kg^{-1}. Major components of cocoa shell ash were found to be potassium, 3.1 g/100 g and sodium, 7.2 g/100 g while sodium carbonate was 33.1 g/100 g. The pH of the ash was 10.8. There were no significant differences ($p<0.05$) in all the sensory parameter for cocoa powder. Although, chocolate aroma was found to be less pronounced in the Experimental sample when assessed by sensory panelists, it did not significantly affect the overall acceptability.

Key words: Cocoa shell ash, alkalising agent, cocoa product

INTRODUCTION

Cocoa is grown in Nigeria by small holders particularly in Ondo state where over 60% of national total output is produced (Akinwale, 2003). It provides an essential source of earning for the people and also enhances the growth of the country's economy as a whole through the provision of job opportunities for large number of Nigerians, together with the activities of foreign investors either in the manufacturing or exporting of cocoa (Akinwale, 2003).

The neglect suffered by non-oil sector of the Nigerian economy with the advent of oil boom in the 60s adversely affected the activities of the stakeholders in the cocoa trade. Cocoa, which prior to the oil boom in Nigeria used to be one of the most important economic crop suffered neglect (Arueya, 1991). Other factors like low yield, ageing tree, climatic and biological factors including soil degradation and problem of international cocoa price fluctuations aggregately resulted in loss of interest in the industry by the cocoa growers and manufacturers alike. However, due to the importance of this crop, successive governments have tried one system or the other in an attempt to evolve a permanent solution (Unten and Ushijima, 1991). The present government has shown tremendous determination in reviving cocoa production as a way of diversifying the economy which prompted the Cocoa Re-birth programme of the Federal Government that was launched some months ago in Nigeria.

In addition, a strategy to increase income for those involved in the cocoa trade is to identify and commercialise new product(s) or application that will not interfere with the main seed crop. Some of the products identified include: seed pulp and products from pod husk (Samsiah *et al*., 1991). As part of the effort to identify other applications of cocoa and its products, this research work focused on the utilization of cocoa shell-ash (known to be rich in potash) as a substitute for potassium carbonate commonly used in the industry during the Dutching process. Cocoa shell is a waste product from the manufacture of cocoa powder and cocoa butter (Adomako, 1995). There is dearth of information on its

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application and most cocoa processors pay huge amount to effectively dispose of or incinerate cocoa shell. However, it was interesting to know from our preliminary work that after incineration, ash obtained from the cocoa shell has useful application in dutching process due to its alkalizing power. The objectives of this research therefore were to assess application of shell-ash as an alkalizing agent in the processing of raw cocoa to cocoa powder and butter, also to compare the effect of the alkalization on the physicochemical properties of cocoa products.

MATERIALS AND METHODS

Materials: Dried fermented cocoa beans were purchased from Igba Village near Ondo town, Southwestern Nigeria. Muslin cloth was obtained from a market. Cocoa shell ash was obtained from the incineration site of Stanmark Cocoa Processing Company at Ondo. Chemicals used were of Analytical grade.

Methods

Sample preparation and analysis: The dried fermented cocoa beans were cleaned and extraneous matters were picked out. The flowchart of cocoa processing is as shown in Fig. 1. The percent moisture content was measure with moisture meter. The ash was dissolved in distilled water at 70°C to make 25% solution (w/v). The ash solution was filtered using Whatman 150 mm filter paper. The pH of the solution was measured with Metrohm pH meter after standardization with buffers at pH 4 and 7. Colour reflectance of cocoa powder was determined by Chromameter. The alkali solution was mixed with cleaned cocoa nibs and nibs were autoclaved at 121°C for 10 min. The alkalized cocoa nibs were pasteurized in a hot air oven (Memmert) at 140°C for 130 min. Percent moisture content was monitored as drying progressed using Halogen moisture analyzer (MB 35) until moisture content was 2%. The nibs were later cooled to 40°C. The nibs were milled with Corona attrition mill, finess was determined on 75 micron sieve (200 mesh size). The cocoa liquor obtained was homogenized with Laboratory stomacher blender.

Fat extraction: The cocoa liquor was mixed with petroleum ether (Boiling point, 40-60°C range) for a contact period in a stainless steel container. The mixture was filtered and cocoa residue obtained was dried at 65°C. The residue was milled with attrition mill on 45 micron sieve. Cocoa butter was recovered from the filtrate by distillation method and trace of petroleum ether was eliminated by drying.

Moisture content: The percent moisture was determined on OHAUS MB35 Halogen moisture analyzer (Tanita-Mitsubishi). Three grams of sample were weighed in the dish and enclosed in the equipment. The percentage moisture was read as displayed after drying.

Fat content: The fat content was determined by the standard method described by Pearson (1981). Weighed sample was tied and dropped in cellulose thimble attached to Soxtec ™2045 and extracted with petroleum ether. The solvent recovered was used to rinse the sample over time. The sample was later dried to remove traces of solvent and extracted fat calculated.

Ash content: Percent ash was determined using the procedure of AOAC (1990). Samples were weighed into previously dried and weighed crucibles. The ashing was done in a muffle furnace preset to 550°C.

Free fatty acid determination: The method of AOAC (1990) was used with 95% ethanol and one drop of 0.1 N NaOH using phenolphthalein as indicator. After boiling the solution with sample material, it was titrated against 0.1 N NaOH with two drops of phenolphthalein.

Saponification value: The saponification values of cocoa butter samples were determined using AOAC (1990) procedure. Ethanolic potassium hydroxide was introduced into the sample with some quantity of anti-bumping granules and the flask was connected to a reflux condenser. The solution was titrated against 0.5 M HCl using phenolphthalein as indicator. Calculation was based on blank titration.

Unsaponifiable matter: The unsaponifiable matter content was determined using AOAC (1990) procedure. The sample was prepared and connected to a reflux condenser on heater and saponified for one hour. The resulting soap solution after cooling was extracted with petroleum ether and 50% ethanol. The last washing was confirmed alkali-free with phenolphthalein indicator. The unsaponifiable solution was then dried in hot air oven at 105°C for 15 min. Acetone was later introduced and further dried in the oven.

Iodine value: The method of AOAC (1990) was used. Wij's iodine solution was added in a fume cupboard to cocoa butter sample (0.34 g) and carbon tetra chloride using mercuric chloride as a catalyst. After the reaction in the dark, potassium iodide and freshly distilled water were added and titrated against 0.1 N sodium thiosulphate. Two milliliter of 1% starch solution was introduced with

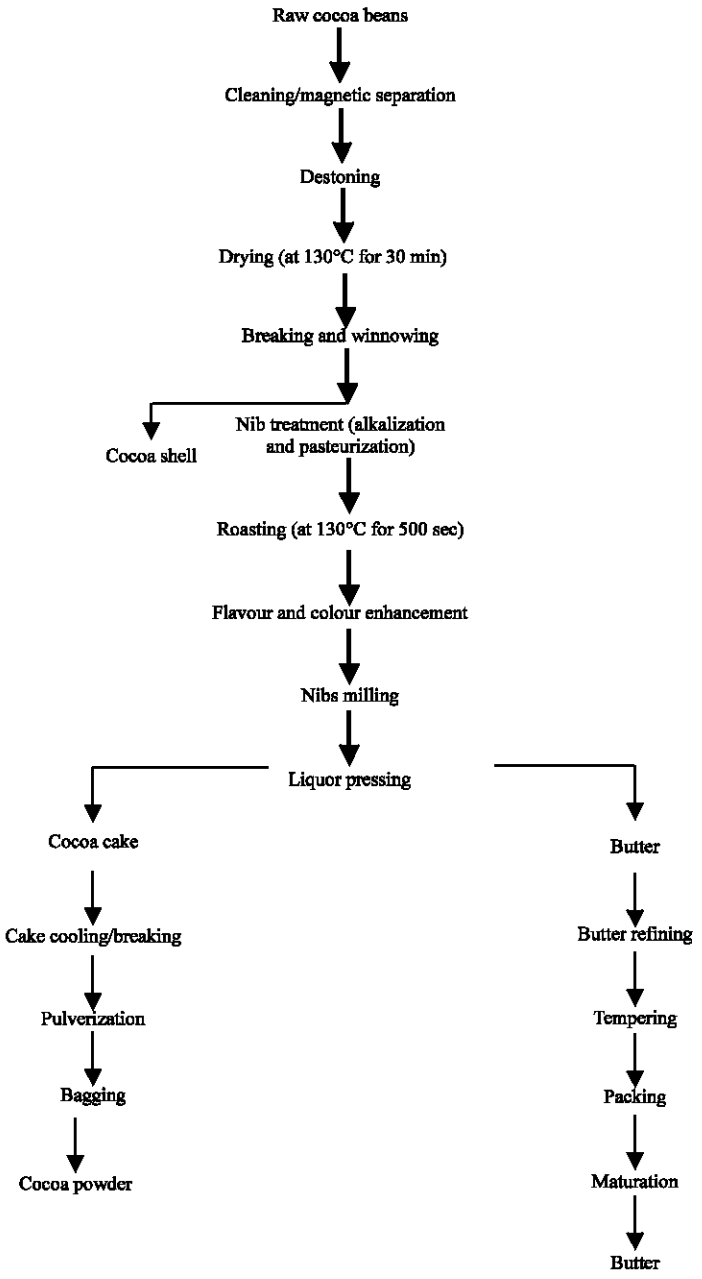

Fig. 1: Flow chart of cocoa processing

blue-black colour while the titration was continued until the blue colour was discharged. Calculation was based on blank titration.

Peroxide value: Peroxide value was determined using the procedure of the AOAC (1990). Weighed sample was placed in a flash with ground joint. Acetic acid/chloroform (ratio 3:2) was added and swirled to dissolve. Saturated potassium iodide solution was added and allowed to stand for 60 sec with occasional shaking. Thirty milliliter of double distilled water was added and the sample titrated against 0.1 N sodium thiosulphate and 1% starch with vigorous shaking until faint yellow colour was obtained.

Determinations on shell-ash: For ashing and mineral analysis, finely ground dried samples were ashed in a muffle furnace. Weighed sample for mineral analysis was

digested and made up to volume. From known volume of the digest solution sodium and potassium were determined using flame photometry method.

Sensory evaluation: Products (cocoa powder and cocoa butter) made from the three samples: Stanmark, Oluji and Experimental sample were evaluated for colour, flavour/aroma and overall acceptability. A hedonic rating scale of 1 to 9 where 1 = dislike extremely; 5 = neither like nor dislike; 9 = like extremely (Larmond, 1977).

The results for each attribute were averaged to give mean scores. Differences between the means obtained from ANOVA were ascertained using Duncan multiple range test. The computer programme used in the analysis was the statistical Analysis System (SAS, 1985). Significance was accepted at $p<0.05$.

RESULTS AND DISCUSSION

The data in Table 1 shows that percent moisture contents were 3.66% for Stanmark; 4.11% for Oluji and 1.56% for Experimental sample. The moisture content in the experimental sample was lower than value (3.0%) recommended by the International Cocoa Organization (2003). Stanmark and Oluji samples with higher moisture content may not have longer storage life. Although other factors together with moisture are responsible for wholesomeness of cocoa powder in storage. Abiola and Tewe (1991) reported that key factors for long shelf-life in cocoa powder are the control of the moisture content and the crystalline nature of the residual fat in cocoa powder. Cocoa powder is highly hydroscopic and both physical and chemical reaction may take place if high moisture level is allowed. The residual fat in the samples were 11.56, 12.20 and 10.56% for Stanmark, Oluji and Experimental samples respectively. The ICO specification for fat content is 11.00% Wood and Lass (1987) reported that high fat cocoa powder has 20-25% residual fat, while low fat cocoa powder has between 10-13%. High fat content has been implicated in reducing the shelf-life of cocoa powder which results in lump formation and discolouration during storage due to oxidative rancidity. The pH values for 10% slurry of powder samples were 6.56 for Stanmark, 6.72 for Oluji and 6.59 for the Experimental sample. These values were in agreement with value reported by Gerrard (1976) which ranged from 6.0-7.5. The values are higher than ICO (2003) specification of 5.7 in cocoa powder. Reports from these Cocoa Processing Industries revealed that cocoa powder of varying pH are produced according to the customer's requirement. Customers from Egypt require low pH powder (pH<6) while customers from Kenya prefer cocoa powder of pH from 6.8-7.5. Actually, the acidity of natural cocoa is neutralised during the dutching process and this also modifies the chocolate flavour. Colour reflectance ranged from 7.18 to 8.69. Findings at the cocoa industries revealed that the colour of cocoa powder to a large extent is dependent on the slaty level of the raw beans and alkalization of the nibs during processing. It has been reported earlier that Oluji company uses sodium carbonate and as revealed in elemental analysis of cocoa shell's ash used for experimental sample that sodium carbonate is the predominant alkali salt, the results from the two are similar. Stanmark company uses potassium carbonate. Ammonium carbonate is known to have darkening effect on the powder than potassium carbonate. Percent ash recorded was 6.58, 8.16 and 7.13 for Stanmark, Oluji and Experimental samples respectively. Ash content is an index of mineral content in a sample.

In Table 2, the free fatty acid of cocoa butter samples ranged from 1.44 to 1.59%. The values are within International standard. Wood and Lass (1987) opined that higher free fatty acid value is an indication that hydrolysis of triglycerides has occurred which usually result in softening of cocoa butter. Saponification value of 196, 198 and 193 mg KOH^{-1} was recorded for Stanmark, Oluji and Experimental samples respectively. The percent unsaponifiable matter was 0.30% for both Stanmark and Oluji while Experimental sample had 0.39%. Wood and Lass (1987) identified three principal methods of extraction of butter from cocoa mass as hydraulic pressing, expeller or extrusion press and solvent extraction. It was reported that best ability cocoa butter designated as prime press is made from hydraulic press of cocoa mass, expressed butter is next in grade while solvent extracted is invariably of lowest quality. The effect is due to the presence of high level of non-triglycerides since almost all lipid materials would have been extracted in solvent extraction. The iodine value for the samples ranged from 35.11 to 38.07 (Wij's). Iodine value is a measure of the degree of

Table 1: Physicochemical analysis on cocoa powder

Parameters	Stanmark	Oluji	Experimental sample
Moisture (%)	3.66±0.24	4.11±0.11	1.56±0.70
Fat (%)	11.56±0.13	12.20±0.10	10.56±0.22
pH (10% slurry)	6.56±0.17	6.72±0.13	6.59±0.14
Colour reflectance	8.69±0.04	7.80±0.07	7.18±0.05
Ash (%)	6.58±0.11	8.16±0.18	7.13±0.19

Table 2: Chemical composition of cocoa butter

Parameters	Stanmark	Oluji	Experimental sample
Free fatty acid (%)	1.46±0.12	1.44±0.11	1.59±0.10
Saponification value (mg KOH g^{-1} of fat)	196.33±0.32	198.06±0.27	193.36±0.21
Unsaponifiable matter (%)	0.30±0.29	0.30±0.28	0.39±0.18
Iodine value (Wij's)	35.11±0.24	37.31±0.14	38.07±0.20
Peroxide value (ME g^{-1})	26.00±0.21	26.89±0.22	29.00±0.37

Table 3: Selected physical and chemical composition of shell-ash used as alkalizing agent

Parameters	Shell-ash
Appearance	Brown
pH	10.8±0.60
Total ash (%)	90.5±1.01
Potassium (g/100 g)	3.1±0.10
Sodium (g/100 g)	7.2±0.15
Sodium carbonate (g/100 g)	33.1±0.13

Table 4: Sensory evaluation of cocoa powder from Stanmark, Oluji and Experimental samples

Products	Colour	Flavour/ aroma	Overall acceptability
Stanmark cocoa powder	6.8[a]	6.5[a]	7.8[a]
Oluji cocoa powder	6.8[a]	6.9[a]	7.9[a]
Experimental cocoa powder	6.8[a]	6.4[a]	7.5[a]

Mean for each attribute followed by the same superscript letter(s) are not significantly different higher values indicate greater preference

Table 5: Sensory evaluation of cocoa powder from Stanmark, Oluji and Experimental samples

Products	Colour	Flavour/ aroma	Overall acceptability
Stanmark cocoa butter	8.2[a]	6.8[a]	8.2[a]
Oluji cocoa powder	7.9[a]	5.0[a]	7.7[ab]
Experimental cocoa butter	8.0[a]	4.4[a]	7.8[ab]

Mean for each attribute followed by the same superscript letter(s) are not significantly different higher values indicate greater preference

unsaturation of the fatty acid components of the fat. The values were within acceptable minimum value of 34-38. Soybean oil in the category of semi-drying oil is within the range of 80-140 while drying oil like sunflower oil has a range within 125 and 200. The more unsaturated oils are, the more desirable in terms of nutritional quality although will usually be in liquid form but the greater the liability of the oil or fat to go rancid by oxidation. Cocoa butter as used in product like chocolate melts once in the month since the melting point (28°C) is lower than the body temperature (37°C). The peroxide value ranged between 26.0-29.0 ME g^{-1}. Although peroxide may not directly be responsible for off taste and odour, the peroxide concentration is useful for assessing the extent to which spoilage has advanced in foods.

The pH determined was 10.8 and observed to be brown in colour. Total ash was 90.5%, potassium and sodium were 3.1 and 7.2 g/100 g, respectively while sodium carbonate was estimated to be 33.1 g/100 g (Table 3).

The panelists did not have preference for a product over another (Table 4). The mean score for colour was 6.8 for each of the three products. Flavour/Aroma had 6.5, 6.9 and 6.4 for Stanmark, Oluji and Experimental samples respectively. The scores (7.8, 7.9 and 7.5) recorded for overall acceptability in Stanmark, Oluji and Experimental samples indicates that there was no preference. Tasters' scores for cocoa butter (Table 5) show that there was no significant difference ($p \leq 0.05$) in terms of colour. The scores were 8.2, 7.9 and 8.0 for Stanmark, Oluji and Experimental samples respectively. Flavour/Aroma had similar preference also. The scores were 6.8; Stanmark, 5.0; Oluji and 4.4; Experimental sample. The overall acceptability in cocoa butter shows that greater preference (8.2) was given to Stanmark product. Cocoa butter from Oluji and Experimental samples were comparable with 7.7 and 7.8 scores, respectively.

In conclusion, the results of analysis of the Experimental sample compared favourably with products from conventional cocoa press industries. The results showed that the use of the cocoa shell ash as an alkalizing agent may be adopted for dutching process. Application of the ash during processing of cocoa products does not have adverse effect on the physicochemical properties of the products. Although, chocolate aroma was found to be less pronounced (4.4) in the Experimental sample when assessed by sensory panelists (Table 5) it did not significantly affect the overall acceptability.

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