Journal of Environment and Earth Science ISSN 2224-3216 (Paper) ISSN 2225-0948 (Online) Vol.5, No.12, 2015



A Study Of Distinctive Characteristics Of Soaps Made Of Saw Dust Ash (Lye) With Palm And Olive Oils And Their Oil Blends In Benue State Nigeria.

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ABSTRACT

In Benue State Nigeria saw dust is dumped in large quantities as waste while in other parts of the country it is used in producing ceiling boards and plywood. In order to further explore its use, palm oil and olive oil with saw dust ash as the source of alkali (lye) were used in the production of soap and the choice of traditional and modern laboratory methods was adapted. The characteristics of the soap products were determined and the average results compared. Blending of these oils with other oils to further study improvements or order wise in the quality of the soaps was also done . Parameters assessed were Moisture Content, Hardness of Soap , Total Fatty Matter, Total Free Alkali, Lathering Power, Free Caustic Alkali, Carbonate Alkali, pH and Cleansing Power. Comparative results show that Total Fatty Matter was 69 and 82% for palm oil and olive oil respectively while the Total Free Alkali %, Free Caustic Alkali % and Free Carbonate Alkali % were 7.8 and 6.9, 3.71 and 2.6 ,4.09 and 4.3% respectively. The Lather Volume (ml) was 460 and 630 respectively while the Lathering Power of palm and olive oils was 8 % and 10% respectively, Cleansing Power of palm and olive oils was 42.66% and 55.7 % respectively, pH of olive oil was 8.5 while that of palm oil was 9.1. Moisture and Hardness of soap samples from olive and palm oils showed Moisture Content 3.5 % for palm and 4.3% for olive and the Hardness showed palm olive soap soft while that from palm oil was hard. Blends of oils were also used, between olive oil and castor oil in a ratio 3:1 gave a Lathering Power of 9.7 while the Clean sing Power was 90.3% . coconut oil and olive oil blend of ratio 2:1 gave the Lathering Power of 10.5 % and its Cleansing Power 88.1%. The production of soap with olive oils and its blends stood out better than palm oil which in itself has become a matter of international interest. Palm tree exploitation began to raise serious environmental issues on land deforestation for palm tree cultivation and an international organization known as Roundtable on Sustainable Palm Oil (RSPO) was created in 2004 following concerns raised by non-governmental organizations about environmental impact issues related to palm tree cultivation for oil production P. Gunasegaran, (2011). This has further de emphasized palm oil use in soap production and increased efforts in research in other oils while the saw dust potentials remain untapped in Benue State Nigeria.

KEY WORDS Lye, Roundtable, molecular, Lathering and deforestation.

INTRODUCTION.

Saw dust is useful in the production of barroom floors, commercial charcoal briquettes and wood-fired systems which also accounts for a reasonable percentage of power production, R. Overend, (2010) (NREL data). Some power companies co-fire biomass with coal to save fuel costs and earn emissions credits. Felman and David (2005) and also using wood waste or other biomass in the fuel mix, enhancing their competitiveness in the marketplace. Dan Burden, (2012), it is also a filler in some low calorie foods. Green, Harvey (2006). Recent studies also indicate that quantities of available (presently unused) mill and urban wood residues exceed 39 million dry tons per year in the United States. This is enough material to supply more than 7,500 MW, doubling the existing bio-power capacity in the United States. Dan Burden, (2012). . To illustrate this point, this amount of power could supply the yearly electricity demand of the residential customers in all six New England states . Sawdust and shavings bonded with new and improved resins are molded into chair backs, toilet seats, furniture parts, croquet balls, pool balls, shuffleboard discs and more recently a nucleonic barrier-type of sawdust plastic has been developed. K W Brockschmint (1960). One of the key ingredients needed to make soap is fat. Until the early 1900s, most soap was made at home from leftover animal fats, until a shortage of fats occurred during World War I. In the new millennium, chemistry is much better understood and a wide variety of ingredients are available to create better soap with less difficulty than ever before. Vegetable oils produce soaps that are considered higher quality than animal fats. Palm oil is used for cooking, making cosmetics and as a biofuel, making it a highly sought-after resource. Unfortunately, the results of using so much palm oil for so many things is deforestation of the rain forests of Borneo and Sumatra, the only



two islands where wild orangutans live and are now considered critically endangered. Elephants, tigers and rhinos may also be at risk. Organizations concerned for global conservation and wildlife preservation, such as the Cheyenne Mountain Zoo and the World Wildlife Federation, urge consumers to limit palm oil use . Allison Stevens (2014)

1. SAWDUST

Sawdust is a by-product of cutting, grinding, drilling, sanding, or otherwise pulverizing <u>wood</u> with a <u>saw</u> or other tool; it is composed of fine particles of wood and can present a hazard in manufacturing industries, especially in terms of its flammability. Added to decreased production and less supply to meet what had been the demand, there has been increasing demand for sawdust from the bio-energy sector as more consumers are incorporating pellet stoves and pellet-fueled hot-water boilers into their homes. This has led to increasing numbers of wood-pellet producers, especially in the the northern and northeastern states. The increased demand for sawdust and increased price for the commodity has primarily impacted livestock producers, particularly dairy farmers and hog producers who use sawdust as part of a composting system for decomposing quarantined carcasses. Ralph Overend (2010).



Figure 1 Pictue of saw dust

The burning of saw dust (dry basis) results into ash which contains calcium carbonate 45 percent as its major component, 10 percent potash, and 1 percent phosphate M.A. Awodun , (2007); there are also trace elements of iron, manganese, zinc, copper and some heavy metals. It is an effective liming material and source of soil organic matter, N, P, K, Ca and Mg . Some metallic oxides (e.g. mercuric oxide) even dissociate to elemental state and vaporize completely at wood fire temperatures . Potassium hydroxide can be indirectly made from saw dust ash , this form is known as caustic potash or lye. Because of this property, saw dust ash has also traditionally been used to make saw dust-ash soap , it also acts as a flux, reducing the melting point of the glaze and an effective as an odor control agent, especially in composting operations. Hume E (2006)

2. PALM OIL

Palm oil consists of the following acids , stearic 4-5% , myristic 1% , palmitic 43-45% , oleic 38-40% , linoleic 9-11% , contributes to: soap hardness, stable lather, conditioning, silky feel and quicker trace H . McGee. (2004. It makes a hard bar that cleans well and is also mild. It is a good substitute for animal tallow in all-vegetable soaps and processed from the flesh of the fruit of tropical oil palm plants. This oil is solid at cool temperatures, becomes slushy at warm temperatures and a golden, clear liquid at higher temperatures .





Figure 2 Palm kernel

Figure 3 Palm oil

Several studies have linked palm oil and cardiovascular disease including a 2005 study conducted in Costa Rica which indicated that replacing palm oil in cooking with polyunsaturated non-hydrogenated oils could reduce the risk of heart attacks, and a 2011 analysis of 23 countries which showed that for each kilogram of palm oil added to the diet annually there was an increase in ischemic heart disease deaths (68 deaths per 100,000 increase) though the increase was much smaller in high-income countries. However, further results from several studies indicate that palm oil provides health benefits, and its consumption does not increase the risk of cardiovascular disease

3.OLIVE OIL.

Commercial olive production generally occurs in two belts around the world, between 30° and 45° N latitude and between 30° and 45° S, where the climatic requirements for growth and fruitfulness can be found. Olive oil is classified into virgin, from first pressings that meet defined standards and pure, or edible, a mixture of refined and virgin. Olive Leaf Extract is one of greatest natural antibiotics on earth. Thomssen E. G. (2010) In addition to its potent antibiotic power, olive leaf extract provides the extra benefit of no side effects. It is effective against Shingles, Eczema, Acne, Rashes, Poison Ivy and other skin conditions . Fresh, unprocessed olives are inedible because of their extreme bitterness resulting from a glucoside that can be neutralized by treatments with a dilute alkali such as lye. Salt applications also dispel some of the bitterness. The processed fruit may be eaten either ripe or green. The olive fruit and its oil are key elements in the cuisine of the Mediterranean and popular outside the region.



Figure 4 Olive plant

New research has shown that olive leaf helps protect the skin for aging. Olive leaves and olive oil have several different antioxidant, antifungal and antibacterial properties all of which help free the skin from the damage of free radicals that can lead to skin aging, skin cancer, skin rashes and skin diseases

4. LYE

Lye is a liquid obtained by leaching ashes (containing largely potassium carbonate or "potash"), or a strong alkali which is highly soluble in water producing caustic basic solutions. Wilson and Joseph (2014.) . It is commonly the alternative name of sodium hydroxide (NaOH) or historically potassium hydroxide (KOH). Lyes



are used to cure many types of food, including olives , oranges, eggs and cakes and are also valued for their cleaning effects. Sodium hydroxide is commonly its major constituent and it is used as commercial and industrial cleaners and clogged drain openers, due to its grease-dissolving abilities by decomposing greases via alkaline ester hydrolysis, yielding water soluble residues that are easily removed by rinsing. It can also be used to digest tissues of animal carcasses . In the event that lye solution touches the skin use of vinegar on the affected skin is also a first aid remedy .



Figure 5 Pellets of sodium hydroxide.

The reaction between sodium hydroxide and a few metals is also hazardous. Aluminum reacts with lyes to produce hydrogen gases. Since hydrogen is flammable, mixing a large quantity of a lye such as sodium hydroxide with aluminum in a closed container is dangerous—especially when the system is at a high temperature, which speeds up the reaction. In addition to aluminum, lyes may also react with magnesium, galvanized zinc, tin, chromium, brass or bronze—producing hydrogen gas.

5 SOAP

A soap is a salt of a fatty acid. The molecule has a long hydrocarbon chain with a carboxylic acid group on one end, and the other which has an ionic bond with metal ion, usually sodium or potassium. The hydrocarbon end is non polar which is highly soluble in non polar substances and the ionic end is soluble in water. A. K, Hamirin and K, Peang-Kean, (1996). The structure of the soap molecule is represented below:

Fatty acids are straight-chain monocarboxylic acids, and the most common range in size from 10-20 carbon atoms and most often have an even number of carbon atoms including the carboxyl group carbon. The carbon-carbon bonds in saturated fatty acids are all single bonds, while unsaturated fatty acids have one or more carbon-carbon double bonds in their chains. One example of a saturated fatty acid is palmitic acid, CH_3 - $(CH_2)_{14}$ - CO_2H . Fatty acids are also seldom found as free molecules in nature but are most often a part of a larger molecule called a triglyceride which consist of a three-membered carbon chain (glycerol backbone) with a fatty acid bonded to each of the three carbon atoms in the glycerol backbone. The bond between the fatty acid and the glycerol backbone is referred to as an ester linkage.



Figure 6 Natural soap Photo Credit Hemera Technologies/AbleStock.com/Getty Images (2014)



The cleaning action of soaps is their ability to emulsify or disperse water-insoluble materials and hold them in the suspension of water. This ability is seen from the molecular structure of soaps E. G. Thomssen (2010. When soap is added to water that contains oil or other water-insoluble materials, the soap molecules surround the oil droplets which get dissolved in the alkyl groups of the soap molecules while the ionic end allows it to be dissolved in water. As a result, the oil droplets are to be dispersed throughout the water and can be washed away. There are various fatty acid varieties, each differing in molecular composition. When used in soap making, each fatty acid variety will make a soap that has its own unique characteristics. Pure Soap opens pores, unclogs and cleans the pores. Many skin irritations like dryness, flaking, redness, itching and rash are more often caused by the chemicals used in commercial soaps, some of the chemicals used include petroleum products and chemical fragrances. Pure soap has healing properties and helps to fade scars, stretch marks and age-lines over time.

6.1 MAKING OF LYE.

(traditional method)

A plastic bucket was used and elevated so that underneath a leaching hole was made small enough and lined by a thick layer of charcoal for the ashes not to fall in order to collect the lye water . Boiled water half of the capacity of the bucket was poured gently over the ashes. As soon as the water made contact with the ash it started hissing and bubbling. A chicken feather was placed in the lye in order to test its strength the feather did not dissolve, the lye was not strong enough and could not be used for soap. It had to be re-boiled until the chicken feather dissolved in it. Using a fresh, whole egg placed in the lye water when it was cold it sank meaning the lye was not strong enough. The lye water was heated in order to concentrate it and the process had to be repeated until it floated halfway . The lye water was placed in the sun until the water was evaporated to lye crystals for soap making recipes.

6.2 MATERIALS / REAGENTS

Olive oil , Groundnut oil, Palm oil, Caustic soda(sodium hydroxide), Sodium carbonate(soda ash) , Sodium sulfate, Ammonium sulfate, Colour to taste, Perfume, Methyl orange indicator, Phenolphthalein indicator, 0.1M sulphuric acid, 96% ethanol, Diethylether, Barium chloride, Distilled water, Sodium chloride , Potassium dichromate($K_2Cr_2O_7$) , Ferrous ammonium sulfate, Anhydrous sodium sulfate , 1,10-phenalphtralein and Wood ash.

6.3 SOAP PREPARATION

(Hot method)

Lye concentration was determined by titrating it with 0.1m Sulphuric Acid with the lye at pH 9 using Phenolphthalein indicator . Palm and olive oils were measured out 100ml each and heated to near boiling. A 250ml breaker containing 40g of thoroughly heated palm oil was mixed with hot lye water and heated with stirring into the hot soap solution. The mixture was allowed to cool into a solid mass and was collected. . The same process was repeated for olive oil.

6.4 SOAP ANALYSIS.

(ASTM D460-91(2014), Standard Test Methods for Sampling and Chemical Analysis of Soaps and Soap Products, 2014,) These included moisture content, Total fatty matter, Total free alkali ,Free caustic, carbonate alkali pH and lathering power.

6.41 MOISTURE CONTENT

Approximately 5 g of samples was accurately weighed using analytical balance (sensitivity 0.1 mg) into dried, moisture dish and dried in an oven for 2 hr at 101^{-0C} and repeated until a constant weight mg/g of sample was reached. The % moisture was calculated using the following formula weight of crucible + sample - weight of crucible = weight of sample after heating . % Moisture = weight of sample before heating – weight of sample after heating x 100



6.42 TOTAL FATTY MATTER (TFM)

Total Fatty Matter (TFM) is defined as the total amount of fatty matter, mostly <u>fatty acids</u>, that can be separated from a sample after splitting with <u>mineral acid</u>, usually <u>hydrochloric acid</u>. The fatty acids most commonly present in soap are <u>oleic</u>, <u>stearic</u> and <u>palmitic</u> acids and pure, dry, sodium oleate.

The total fatty matter was analysed according to Stilman (1973) by dissolving 50g of both soap samples in 50ml of hot distilled water and the volume adjusted to 100ml, the solutions were allowed to cool and then made acidic (methyl orange indicator) with 0.1m sulphuric acid. The solutions were extracted with another three 25ml of diethyl ether and then with another three 225ml portions of diethyl ether. The ether extract were combined with and dried with 1.0g of anhydrous sodium sulphate. The combined ether extract was filtered into a tarred 250ml flask and the ether was allowed to evaporate. The weight of the total fatty matter was obtained by subtracting the weight of the ether extract from initial weight of soap sample.

6.43 TOTAL FREE ALKALI (TFA)

Alkalinity is the name given to the quantitative capacity of an $\underline{aqueous}$ solution to neutralize an \underline{acid} . The excess alkali used in making soap is termed as free alkali usually include NaOH, additional alkaline substances like sodium carbonate and silicates.

Total free alkali was determined using the method described by Stilman (1973). The soap sample (10g) was digested in freshly boiled ethanol (200ml) on steam and then filtrated with standard 0.1m sulphuric acid to phenolphthalein end point. The total free alkali was calculated as Na_2O x volume in lit

6.44 FREE CAUSTIC ALKALI (FCA)

Over steam bath a 100ml of barium chloride was added to the hot soap solution and was filtrated with 0.1m sulphuric acid to phenolphthalein end point. The amount of free caustic alkali in the soap sample was calculated as Na_2O using the relationship, weight (g) of caustic alkali= molarity of acid x formular weight of Na_2O x volume in liters used.

6.45 FREE CARBONATE ALKALI

Free carbonate alkali was determined by subtracting the free caustic alkali from total free alkali =TFA-FCA.

6.46 THE LATHERING POWER

Sample 1g was placed in 500ml measuring cylinder and distilled water added to 100ml mark, the soap was allowed to soften and shaken vigorously to foam. The volume of the lather was noted together with the time taken for the foam to subside completely Ekpa (1995),

6.47 Cleansing power-

The cleansing power of a soap solution is associated with the ability of a small amount of soap to lower the surface tension of water. The soap solution is able to wet an object more easily, emulsify the oil or grease and disperse the suspension in the aqueous medium.

A drop of oil was placed on four separate strips of filter paper. The filter papers with the oil spot were immersed in a separate test tubes containing soap solution (2g soap shavings/100ml distilled water) each was shaken vigorously for 1 minute The filter papers were removed and rinsed with distilled water and the degree of cleanliness in each filter paper was observed.



6.48 _PH

Soap sample 2g was dissolved in 50ml of distilled water. The electrode of the pH meter was rinsed thoroughly with distilled water. It was then immersed in soap solution, the pH of the solution was recorded as the pointer of the pH meter stabilized

7.0 RESULTS.

Parameters	Coconut oil + Olive oil 2:1	Palm oil	olive oil Olive +	· Castor oil 3:1
Total fatty matter%	89	69	82	91
Total free alkali%	6.1	7.8	6.9	5.8
Free caustic alkali%	2.1	3.71	2.6	1.9
Free carbonate alkali	4.0	4.09	4.3	3.9
Lather volume (ml)	620	460	630	650
The lathering power (hrs	10.5	8	10	9.7
Cleasing power %	88.1	42.66	55.7	90.3
Moisture content %	4.5	3.5	4.3	4.6
Hardness SOFT		HARD	SOFT	SOFT
PH 8.9		8.5	9.1	9.0

8.0 CONCLUSION

Sawdust has been a high-priced market with U.S. mills producing 135-million board-feet of material per day (2006 U.S. Forest Products Laboratory, Madison, WI) and in Nigeria it is yet to find its proper usage and therefore requires further research. While Palm oil, , olive oils and their blends used by soap makers are relatively expensive to obtain , the availability and quantity of saw dust as raw material in Benue State subsidizes their production cost . They gave good quality soap - hard bar with a rich creamy lather , characteristic odor and quality obtained comparable to those produced commercially. The use of palm oil in food and soap products has attracted the concern of environmental activist groups. Palm tree exploitation began to raise serious environmental issues on land deforestation for palm tree cultivation and an international organization known as Roundtable on Sustainable Palm Oil (RSPO) was created in 2004 following concerns raised by non-governmental organizations about environmental impact issues related to palm tree cultivation for oil production P. Gunasegaran, (2011) and work with the palm oil industry to address these concerns. The



Palm oil growers have however been critical of the organization because of the costs associated with certification while the market demand of certified palm oil remains low. These and other activities in the industry have caused the focus to shift away from palm oil to other less attractive oils.

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