CHARACTERIZATION OF SOAP PRODUCED FROM SHEA BUTTER AND PALMKERNEL OIL MIXTURE WITH SEED HUSK ASH DERIVED ALKALI

BY

MATTHEW, Ejiatta Patience
NSU/MSC/ICH/0012/16/17

M.Sc INDUSTRIAL CHEMISTRY

JUNE, 2021

CHARACTERIZATION OF SOAP PRODUCED FROM SHEA BUTTER AND PALMKERNEL OIL MIXTURE WITH SEED HUSK ASH DERIVED ALKALI

BY

MATTHEW, Ejiatta Patience

NSU/MSC/ICH/0012/16/17

A DISSERTATION SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES NASARAWA STATE UNIVERSITY, KEFFIIN PARTIAL FULFILMENT FOR THE REQUIREMENT FOR THE AWARD OF DEGREE OF MASTER OF SCIENCE DEGREE (M.Sc) IN INDUSTRIAL CHEMISTRY

DEPARTMENT OF CHEMISTRY

FACULTY OF NATURAL AND APPLIED SCIENCES, NASARAWA STATE UNIVERSITY, KEFFI

NIGERIA

DECLARATION

I hereby declare that this dissertation has been written by me and it is a report of my research work. It has not been presented in any previous application for the award of Master of Science in Industrial Chemistry. All quotation are indicated and sources of information specifically acknowledged by means of reference

PFE . 19/07/2021

.....

MATHEW, Ejiatta Patience

NSU/MSC/1CH/0012/16/17

CERTIFICATION

This dissertation title "Characterization of soaps produced from shea butter and palmkanel oil mixture with melon seed husk ash derived alkali" meet the regulation governing the award of Master Degree in Industrial Chemistry, of the school of postgraduate studies, Faculty of Natural and Applied Sciences, Nasarawa State University, Keffi, and is approved for its contribution to knowledge.

.....	20/07/2021
Prof. P. C. Madu	Date
(Chairman, Supervisory committee)	
.....	02/08/2021.
Dr. S. I. Audu	Date
(Member, Supervisory committee)	
.....	2/8/2021
Prof. B. W. Tukura	Date
(Head of Department)	
.....	02/08/2021
Dr. O. D. Opaluwa	Date:
(Intenal Examiner)	
.....	02/08/2021
Prof. U. M. Gurku	Date:
(Dean, of faculty)	
.....	6/7/2021
Prof. S. J. Salami	Date:
(External Examiner)	
.....	02/08/21
Prof. J. A. Ayuba	Date:
(Dean, School of Post Graduate studies)	

DEDICATION

The research work is dedicated to almighty God my creator, my strong piller, my source of inspiration, wisdom, knowledge and understanding. He has been the souce of my strength through this program and on his wings only have I soared. I also dedicate this work to my parents, Mr and Mrs Emanuel Ejiatta who has encouraged me all the way and whose encouragement has made sure that I give it all it takes to finish that which I have started. To my late sponsor AVM Muktar Mohammed and also Dr Gwumi Sebastian who supported me in this quest, thank you. My love for you all is beyond measure. I love you all.

ACKNOWLEGEMENTS

I remain most grateful to express my immeasurable gratitude to God Almighty, the author and finisher of our faith, the great provider, who made it a reality

I also express my deepest appreciation to my supervisor Prof. P. C. Madu and my co-supervisor Dr. S. I. Audu, for their encouragement, dynamic supervision which made the completion of this research work a reality.

I also want to appreciate Prof . B. O. Atolaiye, who had been of advice from the beginning to the end of this program.

My gratitude also goes to my entire family, who stood by me in love and difficult moment of life during the program.

May the Almighty God bless u all in several folds.

TABLE OF CONTENTS

Cover Page.....i

Title Page.....ii

Declaration.....iii

Certification.....iv

Dedication.....v

Acknowledgements.....vi

Table of Contents.....vii

List of Tables.....xii

Abstract.....xvii

CHAPTER ONE
INTRODUCTION

1.1 Background of the Study.....1

1.2 Statement of the Problem.....3

1.3 Aim of the Study.....3

1.4 Objective of the Study.....3

1.5 Scope and Limitation of the Study.....4

1.6 Significant of the Study.....4

CHAPTER TWO
LITERATURE REVIEW

2.1 Soap.....5

2.2 Types of Soap Based on Process, Properties and Compositions.....9

2.2.1 Glycerin Soaps.....10

2.2.2 Transparent Soap.....10

2.2.3 Liquid Soaps.....10

2.2.4 Tablet or Bar Soaps.....10

2.3 Types of Soap Based on Usage.....10

2.3.1 Antiseptic Soaps and Bathing Soaps.....10

2.4 Raw Materials for Soap making 11

2.4.1 Fats and Oils.....11

2.4.2 Olive Oil.....12

2.4.3 Palm Oil.....12

2.4.4 Coconut oil.....12

2.4.5 Jojoba 12

2.4.6 Shea butter.....13

2.4.7 Mango butter.....13

2.4.8 Aloe Vera butter 14

2.4.9 Cocoa butter.....14

2.4.10 Calendula flower.....15

2.4.11 Castor oil.....15

2.4.12 Sweet almond Oil.....15

2.4.13 Sunflower Oil.....15

2.4.14 Alkali.....15

2.4.15 Other Soap Ingredients.....16

2.5 Types Soap Making Process 16

2.5.1 Hot process.....17

2.5.2 Cold process.....17

2.6 The Soap-Making Process 18

2.6.1 Saponification.....19

2.6.1.1 Continuous Saponification Process 19

2.6.1.2 Glycerin Removal.....20

2.6.1.3 Soap Purification 20

2.6.1.4 Finishing 21

2.6.1.5 Soap Removal 21

2.6.1.6 Salt Removal.....22

2.7 Related Literature 22

CHAPTER THREE
MATERIALS AND METHODS

3.1 Materials.....27

3.2 Method 27

3.2.1 Sample Collection and Preparation.....27

3.2.2 Extracting Alkali from Melon Seed Husk 28

3.2.3 Determination of Potash Concentration of the melon seed husk Extract 28

3.2.4 Determination of Relative Density.....29

3.2.5 Determination of Saponification Value.....29

3.2.6 Determination of Iodine Value.....30

3.2.7 Determination of Free Fatty Acids (FFA) and Acid value 31

3.2.8 Determination of Acid Value.....31

3.3 Production of Soap Using Produced Alkali.....32

3.4 Characterization of Produced Soap and Commercial Soap.....32

3.4.1Determination of Moisture Content.....32

3.4.2 Determination of Ash Content.....33

3.4.3 Determination of pH 33

3.4.4 Emulsification Test.....33

3.4.5 Foam Test 34

3.4.6 Foam Stability / Foam Height 34

3.4.7 Hardness of Soap.....34

3.4.8 Test of Acceptability of the Soaps.....34

CHAPTER FOUR
DATA PRESENTATION AND ANALYSIS

4.1 Data Presentation.....35

4.2 Data Analysis.....40

4.2.1 Concentration of Melon Seed Husk Ash.....40

4.2.2 Physicochemical Properties of Shea Butter Oil (SBO) and Palm- kernel Oil (PKO)...40

4.2.3 Physicochemical Properties of Produced Soap 42

4.3 General Acceptability of prepared Soap and Commercial Soap.....44

CHAPTER FIVE
SUMMARY, CONCLUSION AND RECOMMENDATIONS

5.1Summary.....46

5.2 Conclusion.....46

5.3 Recommendations.....47

REFERENCES.....48

LIST OF TABLES

Table **Page**

4.1 Concentration of KOH and pH Value of Melon seed husk extract.....35

4.2 Physicochemical Properties of Shea Butter Oil (SBO), Palm-Kernel Oil (PKO) compared with FAO standard value and other reference findings.....36

4.3 Physicochemical Properties of Prepared and commercial soap 37

4.4 The General Acceptability of the prepared Soaps and commercial soap by the Panelist....38

ABSTRACT

The research involved the production of soap from melon seed husk ash using shear butter oil (SBO) and palm kernel oil (PKO). Alkali was extracted from the melon seed husk and used for the purpose of soap production. The physicochemical parameters of the oils, the produced and commercial soap were analyzed for ash content, pH, foam stability, texture, moisture content, foam height, foam test, emulsification test and colour using standard methods prescribed by AOAC. The relative density values where 0.89g/ml (SBO) and 0.90g/ml (PKO), sponification value of the oils where;175.30 mgKOH/g (SBO) and189.08 mgKOH/g (PKO) while iodine values were 54.0 I_2/100g (SBO) and 50.72 I_2/100g(PKO), The Free fatty acid (FFA) content were 5.39mgKOH/g (SBO) and 1.62 mgKOH/g (PKO), Acid value;11.70 mgKOH/g (SBO) and 3.50 mgKOH/g (PKO). The result obtained compared well with standard value recommended by FAO. The relative density within the range of 0.89 – 0.91 g/ml , sponification value 189 – 199 mgKOH/g and iodine value 50 – 55 I_2/100g while the free fatty acid $\leq$ 20 mgKOH/g and acid value $\leq$ 30 mgKOHH/g and other reference finding meant for soap production . The soap produced by using the oils at a ratio of 50:50 (SBO: PKO) had very good properties and compared favourably with that of commercial soap. The soap was evaluated using 15 student respondents; the data where analysed using frequency distribution and percentage, the quality of the soap was also evaluated based on colour, odour, lathering ability and texture, it was found that the soap produced is good compared to commercial soap. The result obtained from the physicochemical analysis of the produced soap using shear butter and palm kernel oil ratio (50:50) with purified alkali made from melon seed husk ash was successfully achieved. The study showed significant acceptability of the locally made soap by respondent individuals and for these reason the use of raw materials from vegetable matter should be encouraged for soap production to save the country's foreign exchange and it possibility of large scale production of this alkali should be evaluated over the high cost of imported alkali.

CHAPTER ONE

INTRODUCTION

1.1 Background to the Study

Soap is a common cleansing agent well known to everyone. Many authors defined soap in different ways, as any cleaning agent, manufactured in granules, bars, flakes, or liquid form obtained by reacting salt of sodium or potassium of various fatty acids that are of natural origin (salt of non-volatile fatty acids) (Warra, *et al.,* 2013). Soap can also be said to be any water-soluble salt of fatty acids containing eight or more carbon atoms. Soaps are produced for various purposes including washing, bathing, medication etc. The cleansing action of the soap is due to the negative ions on the hydrocarbon chain attached to the carboxylic group of the fatty acids (Okeke *et al.*, 2009). The affinity of the hydrocarbon chain to oil and grease, while carboxylic group to water is the main reason, soap is being used mostly with water for cleaning purposes (Adaku *et al.*, 2013). In addition to the basic raw materials, other substances are added to the soap in order to improve its application. For example, soap made for medicinal purposes, medicinal importance medicinal ingredients are added to it to produce medicated soaps (Antezana *et al.,* 2015).

Soap making involves the use of sodium salts (Isaac, 2005). In addition to potassium and sodium salt, other metals such as calcium, magnesium and chromium are also used to produce metallic insoluble soap that are not used as cleaning agents, but are used for other purposes (Antezana *et al.*, 2015). The hardness of soap is a function of the metallic element present in the salt. For example soap made up of Sodium salts shows little hardness compare to potassium salts soaps, provided the same fat or oil is used in both cases (Phanseil *et al.*, 1998). These are

characteristically different from soaps made from divalent metals such as magnesium, calcium, aluminum or iron which are not water soluble (Kutom *et al.*, 1994). It is generally known that soap is produced by the saponification of a triglyceride (fat or oil). In this process the triglyceride is reacted with a strong alkali such as; potassium or sodium hydroxide to produce glycerol and fatty acid salts. The salt of the fatty acid is called soap. A typical saponification reaction process is represented in equation1.1 and 1.2

$C_3H_5(OOCR)_3 + 3KOH \longrightarrow 3KOOCR + C_3H_5(OH)_3$

Fat Potassiumhydroxid Soap Glycerol .....(1.1)

OR

$C_3H_5(OOCR)_3 + 3NaOH \longrightarrow NaOOCR + C_3H_5(OH)_3$

Fat Sodium hydroxide Soap Glycerol .....(1.2)

where: R represents the hydrocarbon chain or alkyl group.

Fatty Acids are straight-chain monocarboxylic acids. The commonest fatty acid used in soap making contains a range of C_{10}-C_{20} and most often have an even number of carbon atoms including the carboxyl group carbon. Examples of such saturated fatty acid is palmitic acid (CH_3-$(CH_2)_{14}$ -CO_2H) and an unsaturated fatty acid is oleic acid, $C_{17}H_{33}COOH$. The constituent component of fatty acids, are chiefly oleic ($C_{17}H_{33}COOH$), stearic ($C_{17}H_{35}COOH$), palmitic ($C_{15}H_{31}COOH$), lauric ($C_{11}H_{23}COOH$) and myristic ($C_{13}H_{27}COOH$) acids; Hydrocarbon oils or paraffin are not suitable for soap-making, as far as chemical combination with the caustic alkalis is concerned. The oils and fats which form soap are those which are a combination of fatty acids

and alkali. While glycerin is obtain as a by-product to the soap making industry (Warra *et al.*, 2013).

Several agricultural wastes are littered all over the environment and accumulation of these wastes poses a serious health hazard apart from being an eyesore. Throwing away some of these agricultural wastes as a form of disposal is a waste of resources. For these may be a source of raw materials in soap making.

1.2 Statement of the Problem

Several agricultural wastes are littered all over the environment and accumulation of these poses a serious health hazard apart from causing an imbalance in the ecosystem. Melon seed husk is said to be in abundance, and its presence in the environment poses an environmental problem. Most of the soap used in Nigeria today such as toilet soaps are produce using imported sodium hydroxide alkali. There is the need to source for an alternative to imported alkali. This can be sourced using an alternative alkali derived from melon seed husk for soap making which would be a way of reducing the high cost of imported alkali. The implication of this research work is that it will solve the problem of indiscriminate dumping of melon seed husk as an environmental pollutant and lower the cost of production of soap.

1.3 Aim of the Study

The aim of this research work is to produce soap using alternative alkali derived from melon seed husk ash.

1.4 The Objectives of the study

This includes to:

I. Extract and determine the potash content of the melon seed husk ash extract

II. Produce soap from extracted alkali using shea butter oil (SBO) and Palm kernel Oil (PKO) at the ratio of 50:50 (1:1)

III. Determine the physicochemical properties of oil, produced soap and commercial soap

IV. Determine the general acceptability of soap produced compared with commercial soap

1.5 Scope and limitation of the Study

The scope of this study is limited to the extraction of alkali from melon seed husk ash, determination of the potash content of the melon seed husk ash extract, production of soap from extracted alkali using shea butter oil (SBO) and palm kernel oil (PKO) at the ratio of 50:50 (1:1), physicochemical properties of shea butter oil, palm kernel oil, produced soap and commercial soap and the general acceptability of soap produced with commercial soap.

This study was limited to the use of melon seed husk ash from agricultural waste to produce alkali. Shea butter and palm kernel oil only was used in the production.

1.6 Significance of the study

The study sought to tackle the problem of solid agricultural waste management in the environment by utilizing the melon seed husk normally disposed as wastes in the production of alkali rather than the indiscriminate dumping. This was made to solve the environmental problem associated with melon seed husk. This study was also made to create value to melon seed husk through the conversion to alkali. The findings of this study will help to solve the problem of high cost of imported alkali, as alkali produced was derived from cheap available and abundant agricultural waste in the environment

CHAPTER TWO

LITERATURE REVIEW

2.1 Soap

Soap is one of the oldest chemical substance produced over two thousand years ago by saponification, animal fats with the ashes from plants. Although soap is mainly used as surfactant for washing, bathing, cleaning, they can also be used in textile spinning and as important constituent of lubricating grease. Now soap and detergent have become an integral part of our society. There has been continuous development in soap making technology starting with batch kettle making process in cottage industry and to present continuous modern soap making process using either fat saponification or by fatty acid neutralization utilizing a wide variety of natural and synthetic feed stock (Zhu *et al.*, 2004). Soaps are also key components of most lubricating grease which are usually emulsion of, calcium, sodium, lithium soaps and mineral oil. Soap is the alkali salt of fatty acid. Some of the important fatty acids used in soap manufacture are lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, linoleic acid, linolenic acid, reicinolenic acid.

Fatty acids have varying chain length and may be saturated or unsaturated. Fatty acid content of the oils vary. Unsaturated fatty acids give softer soap with lower melting point and are less stable while soap from saturated fatty acids are firm, slowly soluble, milder and have good detergency (Dixit, 2011). Total fatty acid is considered beneficial ingredient of toilet soap. The property of soap depends on the chain length of fatty acids in blend, amount of saturation and unsaturation, formulation and soap structure. A judicious blend of oils and fats are necessary to obtain soaps of ideal properties. Soaps are graded in terms of total fatty matter. Soap may be categorized as

bathing soaps or specialty soaps like baby soaps which are comparatively of high purity. Other categorization of soaps includes transparent soap which have high glycerin content, herbal and antibacterial soap. The Bureau of Indian standards (BIS , 2006), categorized soap on the basis of total fatty matter (TFM). In this case Grade I (Minimum 76%), Grade II (minimum 70%), Grade III (minimum 60%), bathing bar (minimum TFM 40%). Soft soaps are made by using potassium hydroxide instead of sodium hydroxide. Bathing bars may be made from partial soap and partial detergent or wholly synthetic detergent. Soaps are commonly made from fats and oil and sodium hydroxide. Oils and fats can be classified either lauric or nonlauric oils /fats. In soap making palm oil, coconut oil, caster oil, neem oil, kernel oil, ground nut oil, ricebran oil and animal fat especially tallow are used. Fatty acid present in tallow are mysteric acid, palmitic acid, stearic acid, oleic acid, linoleic acid whereas the coconut oil contains lauric acid, mysteric acid, palmitic acid, stearic acid. Different oils produce soaps of varying hardness, odour and lathering properties. Normally 75-85% tallow and 15-25 % coconut oil is used in soap making. C_{12} and C_{14} soaps lather quickly but they produce unstable, coarse bubble foam while C_{16} and C_{18} lather slowly but lead to stable, fine bubble foamed. For saponification , caustic soda is used. Some of the other ingredients in soap are talc as filler which also act as carrier for perfume, fragrance. Sodium silicate is used to give firmness to the soap, sodium carbonate, dyes to impart color (Dixit, 2011).

Home made soap using local raw materials is an ancient and amazing method that is used in producing soaps for the family use in the olden days. It is one of the soaps used in the family cleaning chores. But recently this skill of soap making is gradually fading away that the younger generation may not be able to enumerate the ingredients in soap making not to mention making the soap itself. The making of soap using vegetable matter has been an age old craft,

unfortunately the soaps that were made then, were soft, black, smelly and corrosive to the hands. So there is need for improvement. Soap is one of the cleaning materials needed by every family (Amyakoha, 2011). Soap is so important that there is hardly any family that does not use it in their daily activities either in the solid bars, liquid and detergent forms. Soaps are salts of fatty acids and it may be hard or soft soap depending on the type of ingredients used (Okeke, 2009). Soaps are made by the hydrolysis of fats with caustic soda (Sodium hydroxide), thus converting the glycosides of stearic, oleic and palmitic acids into sodium salts and glycerol. Soaps have a cleansing action because they contain negative ions composed of a long hydrocarbon chains attached to a carboxyl group (Okeke, 2009).

The hydrocarbon chain has an affinity for grease and oil and the carboxyl group has an affinity for water. That is why soaps are mostly used with water for bathing, washing and cleaning. They are also used in textile industries for textile spinning. The making of soaps from ash-derived alkalis has been an age-old craft in Nigeria and many West African countries (Nwoko, 1982). Ash - derived alkalis offer cheap alternatives to imported ones. According to Adewuji, *et al.* (2008), agricultural waste materials contain a good percentage of potash. Agricultural waste materials generated in homes and are found littering all over the environment constituting environmental nuisance to man ,are potential viable source which needs to be harnessed for other uses and to save the environment. These materials include melon seed husk, palm bunch waste, coco-pod, plantain peels, banana peels, maize cobs, cassava peels,wood,sugar beet waste and many others. When these materials are burnt in air, the resulting ashes contain oxides of potassium and sodium which when dissolved in water yield the corresponding hydroxides according to the equations:

$Na_2O + H_2O \longrightarrow NaOH$ 2.1

OR

$K_2O + H_2O \longrightarrow KOH$ 2.2

The local production of potash from these agricultural wastes has been observed to be a cheaper alternative source used in the production of soap and other alkalis based products (Adewuji *et al,* 2008). While Onyegbado, *et al.*, (2004) has observed that alkali obtained from plants origin were high in potash content and also good for soap production. Presently, the art of homemade soap using caustic soda is gaining acceptance because of emphasizes on entrepreneurship education in our educational system. Production of soap using agricultural wastes as becomes veritable source of gainful employment for individuals.

Soap is one of the most essential needs of man used for several purposes. Solid agricultural wastes for soap production have not been fully exploited. The production of home made soap is a very viable business opportunity for self employment, which home economics graduates can exploit. The recent emphasis on entrepreneurship in our educational institutions makes it imperative that opportunities that can be exploited for self-employment should never be neglected.

Melon (Citrullus colocynthis L.) is an important oil seed and perennial cash crop widely cultivated in many parts of Africa. The vegetable oil extracted from melon seed is primarily used for domestic consumption although medicinal uses and industrial applications for biodiesel, soap, detergents and margarine production, have been reported (Oluba, 2011). In addition, the seed cake is a rich source of protein and minerals for livestock feeds and nutritional supplements (Basu, 2010). Conversely, the extraction of vegetable oil from melon seeds produces enormous

$Na_2O + H_2O \longrightarrow NaOH$ 2.1

OR

$K_2O + H_2O \longrightarrow KOH$ 2.2

The local production of potash from these agricultural wastes has been observed to be a cheaper alternative source used in the production of soap and other alkalis based products (Adewuji *et al,* 2008). While Onyegbado, *et al.*, (2004) has observed that alkali obtained from plants origin were high in potash content and also good for soap production. Presently, the art of homemade soap using caustic soda is gaining acceptance because of emphasizes on entrepreneurship education in our educational system. Production of soap using agricultural wastes as becomes veritable source of gainful employment for individuals.

Soap is one of the most essential needs of man used for several purposes. Solid agricultural wastes for soap production have not been fully exploited. The production of home made soap is a very viable business opportunity for self employment, which home economics graduates can exploit. The recent emphasis on entrepreneurship in our educational institutions makes it imperative that opportunities that can be exploited for self-employment should never be neglected.

Melon (Citrullus colocynthis L.) is an important oil seed and perennial cash crop widely cultivated in many parts of Africa. The vegetable oil extracted from melon seed is primarily used for domestic consumption although medicinal uses and industrial applications for biodiesel, soap, detergents and margarine production, have been reported (Oluba, 2011). In addition, the seed cake is a rich source of protein and minerals for livestock feeds and nutritional supplements (Basu, 2010). Conversely, the extraction of vegetable oil from melon seeds produces enormous

quantities of lignocellulosic waste commonly called melon seed husk (MSH). Currently, MSH is combusted in open air or dumped in refuse dumps and landfill sites thereby exacerbating the prevalence of greenhouse gases (GHG) and environmental burden of pollutant emissions on the environment (Ogbe, 2012).

The utilization of MSH for water treatment, compost material, soil remediation, and weed suppressants is widely reported in literature (Achigan-Dako *et al.,* 2008). Palm kernel oil is mainly lauric acid containing saturated fatty acids of C_6-C_{18} chain. It has a sharp melting point when heated. Higher quality soap is produced using 10-15% lauric acid (Berger *et al.*, 1986). Alkalis are water soluble base, usually hydroxide or oxide of potassium or sodium. Alkali can be produced locally from ashes as "potash" by extraction with water. It is generally believed that the highest soluble metal is potassium A, though this depends on the species of the plant material and the type of soil where the plant grows (Onyegbado, *et al.*, 2002). Several studies have been carried out on the potash content of some plant materials such as: cocoa husks (Afrane, *et al.*, 1992), fresh plantain trunk (Ankrah *et al.*, 1974), unripe plantain peel (Onyegbado *et al.*, 2002), ripe plantain peel, groundnut shell and sorghum chaff (Taiwo *et al.*, 2001). The used of ashes obtained from agricultural materials as source of industrial alkali have reported (Olabanji *et al.*, 2012).

2.2 Types of Soap Based on Process, Properties and Compositions

Hard and soft soaps undergo some processes, hardness is achieved through the addition of hardening agents, and so many natural soaps tend to be softer. Hard soap can be produced by repeat regrinding and re-forming, known as triple milling. Keeping the moisture content low helps the hardness of the soap, but this is often achieved by accelerated curing in very low humidity condition.

2.2.1 Glycerin soaps

Glycerin is normally produced during the soap making process. It is humectants, which means it attracts water. Therefore soaps with glycerin in them tend to make the skin feel moister. At the same time glycerin soaps tend to have more water in them and attract water from the atmosphere, therefore 'sweating' in humid conditions. Most commercial soaps have glycerin component removed during manufacture, as it can be sold separately.

2.2.2 Transparent soap

This soap uses slightly different components and usually some form of alcohol in the process. The process is conducted at higher temperatures, facts change the process and hence, the resulting product. Not all transparent soaps are glycerin soaps.

2.2.3 Liquid soaps

These are actually quite difficult to make and many of the commercial liquid soaps are just in fact detergents. They are in liquid state.

2.2.4 Tablet or bar soaps

These are generally solid soaps.

2.3 Types of Soap Based on Usage

Either based on the ingredients used by the manufacturer or producer soap can be used for different purposes, which cover cleaning, washing to bathing. The types of soap based on usage are:

2.3.1 Antiseptic soaps and bathing soaps

Antiseptic soap, sometimes called antibacterial soap or anti-fungal soap, is regular soap in liquid or solid form that contains some kind of ingredients that reduce the chance of infection when applied to the skin. These products also have antimicrobial properties, meaning they kill or

inhibit the growth of microbes like bacteria, virus, or fungi. Alcohol, triclosan, and tetrasodium EDTA are three antiseptics commonly used in soap, and they are all examples of antibacterial antiseptics, meaning they have been effective against bacteria. Other antiseptics have anti-viral properties, and some are anti-fungal and can be used to treat or prevent fungal infections like athlete's foot, ringworm, or vaginal yeast infections. Many antiseptics have a combination of these various properties. Some essential oils, such as tea tree oil, contain naturally occurring antiseptics called terpenes that have antibacterial, anti-fungal, and antiviral properties. These various kinds of antiseptic ingredients are also used in soap (Wisegeek, 2013).

Some scientists and medical professionals are critical of the increasing use of antiseptic soap and the addition of antibacterial ingredients to so many cleaning products. They believe that this practice might lead to more strains of bacteria becoming resistant to antibacterial agents, eventually causing antibiotic medications to become less effective. This could make it more difficult to treat serious medical conditions caused by bacteria, like staph infections and pneumonia. For example, many microorganisms are already resistant to triclosan, meaning that even though it is a proven antibacterial agent, it may not be as effective as stated by some soap manufacturers because many strains of bacteria are immuned to it (Wisegeek, 2013).

2.4 Raw Materials for Soap making

2.4.1 Fats and oils

All animal fats and vegetable oils are used for soap making. They should be as free as possible from unsaponifiable matter be of a good colour and appearance, and in a sweet, fresh condition (Simmon and Appleton, 2007). Oil derived from another sources such as mineral oil, cannot be used. Soap can be made by using only one kind of fat or oil, by blending animal and vegetable oil or blending more than one vegetable oil. Animal fats are hard fats. Soap that uses only animal

2.4.4 Coconut oil

Coconut Oil is considered a gift. Its discovery has contributed to higher grade soaps in addition to its rich, moisturizing lather. If used in too high portions it can be drying. Many of these natural oils have replaced lard in high quality soaps.

2.4.5 Jojoba

Jojoba is a perennial woody shrub grown primarily in the desert regions of the southwestern United States and north-western Mexico. Native Americans have long used jojoba to help heal sores and wounds. Today, jojoba oil is still most commonly used for cosmetic purposes, particularly for the maintenance of healthy skin. Jojoba oil helps promote healing of the skin in many ways. It has antimicrobial properties, which means it actually discourages the growth of some bacterial and fungal microbes that attack the skin. In addition, the chemical composition of jojoba closely resembles that of the skin's natural sebum, so it is easily absorbed and rarely causes allergic reactions, even in the most sensitive individuals.

2.4.6 Shea butter

Shea Butter is from the nut of the Shea tree, also known as "The Tree of Life". The Shea tree (locally known as ori) only grows in the savannah region of Africa. It grows up to 60 feet and can live up to 200 years. The Shea Tree produces its fruits once a year. The nut in the centre of the fruit when crushed and traditionally processed by boiling and extracting the oil, is what yields the vegetable fat known as Shea Butter. She butter contains vitamins A, E, and F, and fatty acids, which provide healing abilities superior to cocoa butter. This natural butter has proven cell regenerative, moisturizing, and anti-aging properties, which restore shine and beauty to skin and hair. Effective in preventing stretch marks, wrinkles, inflammation, eczema, and dryness from razor irritation. Easily absorbs into the skin without clogging pores.

Shea butter has been used for centuries in Africa for cooking, and also as skin treatment for its amazing ability to renew, repair, and protect the skin against harsh climates. African healers and beauties like Cleopatra have known about Shea butter for thousands of years. Shea butter is also called "Women's Gold," because extracting the butter from the nuts gives income to hundreds of thousands of rural African women.

2.4.7 Mango butter

Mango butter is extracted from the shelled fruit kernel of the mango, which is a tropical evergreen. This butter is highly emollient, softening and soothing to the skin. Mango butter has protective effects against UV radiation and also helps treat skin rash, eczema, insect bites, and poison ivy. Mango butter can help protect and heal skin from the damage caused by sunburn and frostbite. While mango butter is excellent for skin, it is often mixed with other ingredients because it is much harder than Shea butter

2.4.8 Aloe Vera butter

Aloe Vera Butter is a combination of coconut oil and aloe Vera. It is a soft, white butter with a low melting point. Aloe Vera Butter has similar qualities to Aloe Vera Gel in that it soothes and helps heal dehydrated skin conditions such as eczema, psoriasis, sunburn and windburn. It can be added to moisturizing soaps, creams, lotions, lip balms and body butters, and can be used on its own as a body balm or after-sun treatment.

2.4.9 Cocoa butter

Cocoa butter is obtained from the same bean as chocolate and cocoa. Cocoa butter lays down protective layer that holds moisture to the skin, making it a good skin softener.

2.4.10 Calendula flower

Calendula flower creams and washes are used to disinfect minor wounds and to treat infections of the skin. The antibacterial and immune stimulant properties of the plant make it extremely useful in treating slow-healing cuts and cuts in people who have compromised immune systems. The herb stimulates the production of collagen at wound sites and minimizes scarring. Gargling calendula water may ease sore throat. The Calendula infused oils are made to add to natural creams/lotions.

2.4.11 Castor oil

Castor oil is derived from the bean produced from the castor plant. Like olive and jojoba oils, castor oil acts as humectants by attracting and retaining moisture to the skin.

2.4.12 Sweet almond oil

Sweet Almond Oil is known for its many skin benefits. While it is used for all skin types, sweet almond oil is particularly effective for dry skin that is prone to itching and irritation. The oil is a nice choice for the natural oil cleansing method because it is light, moisturizing and doesn't leave a greasy residue on the skin once it absorbs.

2.4.13 Sunflower oil

Sunflower oil is very high in essential fatty acids. It helps to moisturize, regenerate and condition the skin. It is good oil for mature, sensitive, dry or damaged skin. Non oily feel in lotions, saves, and lip balms as well as an excellent moisturizer and massage/baby oil. (DMBB, 2013)

2.4.14 Alkali

Alkalis are basic substances that cause the desired chemical reaction. Common alkalis used are caustic soda (sodium hydroxide) and potash (potassium hydroxide). The alkalis used in soap making can be from two sources:

i. Lye, caustic soda, or potash, purchased at the market: or

ii. Lye, obtained by leaching or passing water through the ashes of plants.

2.4.15 Other soap ingredients

Borax, soda, ammonia, kerosene, naptha, and rosin are sometimes added to increase the quantity of suds and improve the appearance of the soap. They are not necessary. Perfumes are added to make soap smell more pleasant. Either essential oils or artificial perfumes can be used. Some essential oils commonly used are lavender, geranium, winter green, citronella, clover lemon, rose, almond, caraway, and banana. The oil or perfume is stirred into the soap just before the Soap is poured into molds. The quantity of perfume used depends on the size of the batch of soap being produced, the intensity of the perfuming agent, and the strength of the desired final Scent. The amount used can vary from a few drops to 15 grams or more.

Colouring matter can also be added. For example, vegetable or aniline dyes can be used to make soap. They are stirred evenly into the soap mixture before pouring it into molds. The colour obtained from aniline dyes has a tendency to fade slightly when soap is exposed to bright light (Francioni *et al.*, 2002)

2.5 Types of Soap making processes

There are two known soap making processes. These are the hot and cold method.. Both the hot and cold soap making processes involve mixing fats with a strong alkali. Both processes include the use of the same ingredients, such as liquid fat; which are oil from the plant (such as olive and palm), Solid fat; which are animal fat or shear butter, Lye; which are alkali consisting of sodium hydroxide or potassium hydroxide, goat milk, fragrance and colorants; which are used for aesthetic purpose.

2.5.1 Hot process

Solid and liquid fats are combined in a stainless-steel pot and heated until the solid fats melt, around 43 °C. A lye solution is created by dissolving lye (Sodium Hydroxide) into goat's milk in a stainless steel or glass bowl. The combination of the lye and the milk creates an exothermic reaction that heats the mixture to roughly 93 °C. The mixture is then cooled to 43 °C. The lye and fat mixtures are combined at a high temperature and mixed vigorously. The mixing is complete when trace is reached. Trace occurs when the mixture is thick enough to maintain slight shape. The mixture is immediately heated to 68 °C for approximately two hours until the gel phase is reached. The gel phase is marked by a dramatic change in opaqueness of the mixture. This is where saponification occurs. Essential oils (fragrance) are added to the mixture. The hot mixture is poured into molds where it sits until it is cooled. Once the soap is cooled, it is removed and cut into the desired shape. This soap is ready for use (Avon *et al.*, 2013)

2.5.2 Cold process:

Solid and liquid fats are combined in a stainless-steel pot and heated until the solid fats melt, around 43 °C. A lye solution is created by dissolving lye (Sodium Hydroxide) into goat's milk in a stainless steel or glass bowl. The combination of the lye and the milk creates an exothermic chemical reaction that heats the mixture to roughly 93 °C. The mixture is then cooled to 43 °C. The lye and fat mixtures are combined at a high temperature and mixed vigorously. The mixing is complete when trace is reached. Trace occurs when the mixture is thick enough to maintain slight shape. Essential oils (fragrance) are added to the mixture. The mixture is poured into molds and insulated. Insulation can be as simple as wrapping the molds in a thick towel. When the soap is cooled and hardened (about 24 hours after mixing), it is removed from the molds and

cut into its final shape. The pieces are placed on a curing rack in a well ventilated area where the saponification process will occur. The soap is cured for an additional 6-8 weeks. The common test for saponification completion is touching the soap to the tongue, if the soap irritates the tongue upon contact, the curing is not yet complete. (This is not to standard and not recommended due to toxicity.); (warra *et al.,* 2013)

2.6 The soap-making process

A chemical reaction between the goat's milk and lye allows saponification to occur, resulting in soap. In the hot process, saponification occurs while the mixture is held at 68 °C until the gel phase occurs. The gel phase is visually indicated by a dramatic change in opaqueness of the mixture, taking roughly two hours. If the soap mixture does not reach or maintain this temperature, saponification will not occur and the soap will not be safe due to the presence of remaining lye. If the temperature is increased over 68 °C, the mixture will burn, resulting in unusable soap. On the contrary, saponification during the cold process occurs after the soap mixing process, during an extended curing period which can last up to two months (Avon *et al.*, 2013). Due to the availability of appropriate resources and low start-up capital, soap-making can be a lucrative and successful venture in sub-Saharan Africa (Warra *et al.*, 2013). The cold process is recommended by small-scale enterprise soap makers in low-resource contexts, particularly in tropical regions due to quick solidification of local oils (Pleasant *et al.*, 2012). Engineers without Borders-UK published a soap making manual and recommended the cold process for their chapters participating in projects in Tanzania, South Africa, and Nigeria. Specifically, in Uganda, small soap and detergent businesses have been successful (All African *et al.*, 2007). Also, the soap making process consists of reaction of animal fats along with several, oil with sodium or potassium hydroxide, the traditional soap making process consists of

direct saponification of oil and fats in batch process. The commercial process consist saponification in a kettle pan boiling batch process or a continuous process The production of soap comprises saponification (soap making), removal of glycerol, soap purification, finishing which consist of mixing and homogenisation of the soap base with additive such as perfumes, coloring matter, skin grooming substances and final extrusion, cutting shaping and packaging. The basic steps in soap manufacture are saponification, glycerine removal, soap purification and finishing (Dixit, 2011).

2.6.1 Saponification

The word "Saponification" is derived from the Latin word "saponins", meaning' soap' though the word has a wide application. For example, in papermaking, many components of wood pitch may become saponified under alkaline papermaking conditions (Dixit, 2011). A mixture of tallow (animal fat), coconut oil, sodium hydroxide and salt are mixed in fixed proportion and fed to a reactor (Kettle or pan) with and heated with steam. Effective mixing and proper blending of raw material is very important to ensure a consistent reaction. The soap batch is boiled using steam sparging. The soap produced is the salt of a long chain carboxylic acid (Dixit, 2011).

2.6.1.1 Continuous saponification process

Continuous saponification process has now replaced old batch process for making soap. Although there are varieties of commercial systems available, however all the processes rely on high speed saponification using intense mixing and continuous separation of soap, lye and glycerol, drying and finishing of the soap. In the continuous process the blended oils and fats along with appropriate amount of caustic lye and salt is continuously fed to the pressurized, heated autoclave (temperature 120 °C and pressure 200 kpa). The saponification process is very

fast and proceeds very quickly requiring about 30 minutes or less (Dixit, 2011). After saponification in autoclave with short residence time the reaction product are fed to cooling mixer where further saponification is completed. The soap stream from the cooling mixer is sent to the static separator where lye phase containing, glycerol, caustic soda and salt are separated from the soap layer. The soap layer still contains glycerine which is washed in a washing column with lye and salt solution to remove impurities and allow further separation of glycerol. The soap solution is added at the bottom column while the fresh caustic lye is added at the top for washing (Dixit, 2011).The final separation of lye with soap is achieved in centrifuge. The soap from the crutcher is fed to feed tank where it is preheated in heat exchanger and then sprayed into the spray dryer for drying. Removal of excess moisture from vapor and entrained soap is achieved. Soap is separated by passing the vapor in a cyclone. The dry soap is fed to noodles which is screw extrodudes. The extruded soap is cut into small noodles. The measured base soap for through the vortary air value blower is fed to noodles. The soap from nodule silo is fed to noddles through sigma mixer and roll mill. After milling it goes to pre plodder, vacuum chamber and final plodder, bar cutter and packing, wrapping and storage (Dixit, 2011).

2.6.1.2 Glycerin removal

Upon completion of saponification , additional salt to the wet soap causing it to separate out into soap and glycerin in salt water as soap is not very soluble in salt water. Glycerin is very valuable in soap production, so effective removal is a very important process. Upon addition of salt the single phase soap is converted to two layers. The bottom layer is high level of salt, glycerol and only small amount of soap while the top layer is soap which is allowed to settle for several hours. Aqueous solution called lye is drawn from the bottom which consists of most of the glycerin

which is sent to the glycerin recovery plant where glycerol is recovered and purified (Dixit, 2011).

2.6.1.3 Soap purification

The soap remaining in the kettle still contains some glycerin which is removed by adding small amount of caustic soda in the wash column. The soap and lye are separated. The lye removed is reused in the process. The top neat soap layer still contains some caustic soda which is neutralized with a weak acid such as citric acid. The separated soap containing water is further dried by heating under vacuum (Dixit, 2011).

2.6.4 Finishing

Finally; additives such as preservatives, color and perfume are added and mixed in with the soap and it is shaped into bars for sale (Dixit, 2011).

2.6.7 Soap removal

The spent lye contains a small quantity of dissolved soap which must be removed before the evaporation process. This is done by treating the spent lye with ferrous chloride. However, if any hydroxide ions remain the ferrous ions react with them instead, so these are first removed with hydrochloric acid:

$$HCl + NaOH \rightarrow NaCl + H_2O \quad \text{.....2.3}$$

The ferrous chloride is then added. This reacts with the soap to form an insoluble ferrous soap:

$$FeCl_2 + 2RCOONa \rightarrow 2NaCl + (RCOO)_2Fe \quad \text{.....2.4}$$

This precipitate is filtered out and then any excess ferrous chloride removed with caustic:

$2NaOH + FeCl_2 \rightarrow Fe(OH)_2(s) + 2NaCl$ 2.5

This is filtered out, leaving a soap-free lye solution (Dixit, 2011).

2.6.8 Salt removal

Water is removed from the lye in a vacuum evaporator, causing the salt to crystallize out as the solution becomes supersaturated. This is removed in a centrifuge, dissolved in hot water and stored for use as fresh lye. When the glycerine content of the solution reaches 80 – 85percent, it is pumped to the crude settling tank where more salt separates out (Dixit, 2011).

2.7 Related Literature

In view of the high cost of imported alkali and also the high cost of commercial soaps, several studies have been carried out on the potash content of some plant materials such as: cocoa husks (Afrane *et al.*, 1920), fresh plantain trunk (Ankrah *et al.*, 1974), unripe plantain peel (Onyegbado *et al.*, 2002), ripe plantain peel, groundnut shell and sorghum chaff (Taiwo *et al.*, 2001).The use of ashes obtained from these agricultural materials as source of industrial alkali have been reported (Olabanji *et al.*, 2012). Research has shown that plantain peel ash has been used to produce soap of good quality.

Experiment have also been out using locally available raw materials in soap production. The soap was prepared using sheabutter oil (SBO), palm kernel oil (PKO) and plantain peels. The physicochemical parameters of the oils were analysed. The saponification values of the oils 176.30 mgKOH/g (SBO) and 198.10 mgKOH/g(PKO), and the iodine values 55.4 I_2 /100g (SBO) and 50.58 I_2 /100g (PKO) agreed with those found in literature. The free fatty acid (FFA), acid value and Relative density were found to be 1.71mgKOH/g, 3.60

mgKOH/g and 0.90 mgKOH/g for PKO and for SBO the corresponding values were 5.49 mgKOH/g,11.78 mgKOH/g and 0.91 mgKOH/g respectively. The alkali was extracted from the plantain peels ash and used to saponify the oils for the production of soap. The soap produced was analysed by testing its hardness, moisture and foaming stability. The results indicated that the soap produced by the oil showed very good properties, hence regarded better compared to the soap produced by SBO and PKO separately (Zauro *at al.*, 2016).

Also in a related experiment carried out using millet stalks for extracting 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 (41.2 g/100g), acid value (1.46 mg/KOH), ash content (9.2%), colour (white), texture (hard and rough), emulsification test (observed), foam test (form lightly with moderate persistence), foam height (1.8cm). These properties tested showed that the soap prepared using traditional method gave a better quality soap which could be compared with any other soap (Atiku *et al.*, 2014).

A similar experiment was also carried out using four agricultural by-products namely Cocoa pod husk (CPH), Kola pod husk (KPH), Plantain peel (PP), and Orange peel (OP) were examined for their potential as alternative source of potash for soap production. These materials were ashed and the samples were subjected to hot aqueous extraction.Extracts from the ashed samples were characterized of their inorganic elements viz calcium, sodium, potassium and magnesium. Results indicated that these samples contains appreciable amount of potassium, a precursor material for soap production with CPH giving the highest value (41%).The percentage amount of the potash is of the order CPH > KPH > PPA > OPA.Liquid soaps were thus prepared from the

extracts of CPA, KPH, PPA and OPA. Physical and chemical characteristics of the resulting soap products were carried out. The overall quality of the products compared well with that of the standard with exception of OP which showed little variations.Indications therefore abounds that these agricultural residues are suitable material or alternatives for convectional alkalis for soap production(Yahaya *et al.*, 2012)

In addition, an experiment was carried out the making of soap using vegetable matter (palm bunch waste). The dried palm bunch matters were subject to total combustion, soaking, filtering and recrystallizing the ash-residue to obtain a colourless filtrate and pure extract of the alkali. Coconut oil was extracted from coconut seeds using hot –water extraction process. Soaps were produced using both the conventional and modified methods. Conventional saponification process was modified to improve on the quality of the soap produced with the extracted alkali hence, generating a neater soap which was milky in appearance. The following parameters were determined: free alkali content, total fatty matter, moisture content, lathering ability, cleansing power, matter insoluble in water, matter insoluble in ethanol. The free caustic alkali content of the black soap produced through the conventional method was found to be 0.09%, while 0.26% and 0.98% were recorded respectively for the improved and synthetic-alkali soaps. The total fatty matter content of the black soap was 55.45%, which was over two folds of 23.00% and 21.69% observed in the improved and synthetic –alkali soaps. Moisture content of modified soap was 29.05%, which was remarkably higher than 9.53% recorded for black soap and 6.65 for the synthetic-alkali soap. The lathering ability was found to be 5.00ml for black soap and 15.00ml and 10.00mL for the other soaps. The improved soap produced with purified palm bunch ash-derived alkali was comparatively of a better quality than its conventional black soap counterpart considering some physico-chemical properties such as matter insoluble in water, matter insoluble

in ethanol, unsaponified neutral fat and lathering characteristics of the soaps (Ogunsuyi *et al.*, 2012)

Similarly an experiment was carried out to investigated, the potential of Jatropha curcas L. seed oil and lye its ash for soap making. Oil was extracted from the seeds using Soxhlet extractor and n-hexane. Lye solution was obtained by boiling ash of Jatropha with distilled water. The physicochemical properties (saponification value, Iodine value, acid value and peroxide value) of the oil (and its blend with palm oil) were found to be consistent with reported values in literature. The oil content and its relative density were also found to be 31.17% and 0.88g/cm^3 , respectively. Soap samples were prepared by treating the oil and the prepared lye solution. Their physicochemical properties (moisture content, total alkali content, total fatty matter, pH, foam ability and cleansing ability) were found to be comparable with reported properties for laundry soaps. The findings indicated that the lye solution from ash of Jatropha and its seed oil result in soap materials that have acceptable qualities (Legesse *et al.*, 2015)

Finally, a research work was carried out aimed at producing soap using agricultural raw materials (Rubber seed oil, Kolanut pods and Almond leaves). The kolanut pods and almond leaves were air-dried, burnt to ashes and alkali was extracted from them by dissolving the ashes in water and later filtered. The kernels from the rubber seed were pounded with mortar and pestle to form a paste. Oil was extracted from the rubber seed paste using n-hexane. The alkali from the kolanut pods and almond leave ashes were made to react with the prepared RSO to form the soaps. The soap samples so produced were analyzed to determine their chemical composition and efficacy. The values obtained from the analysis of the soap samples has revealed that soap produced from locally source agro based waste has a quality very similar to any standard soap. The deviation in the values of the prepared soaps from the standard soap (Joy soap) may be due

CHAPTER THREE

MATERIALS AND METHODS

3.1 Materials

The materials and reagents that were used in the research work includes: Melon seed husk ,sheabutter (SBO) / palm kernel oil (PKO)(50:50), Ethanol, diethyl ether, KOH, l methyl orange, Na_2CO_3, anhydrous Na_2SO_4, iodine monochloride, glacial acetic acid, CCl_4, HCl, KI, Sodium thiosulphate, phenolphthalene , others include: weighing balance, set of sieve, oven and furnance.

3.2 Methods

3.2.1 Sample collection and preparation

The Melon seed husk, 1000g quantity used in this research was collected from melon seed deshelling center in Keffi central market, Nassarawa State, Nigeria. The sample was washed severally with water to get rid of dirt from the peels. The cleaned melon husk was dried in the sun for two weeks and then oven dried using a DHG-9101-15A, laboratory dry oven, Changzhou, china at 40 ^{0}C to a constant weight after which it was burned into ashes using muffle furnace at 550^{o}C for 5hours. This was done using the method of AOAC (2005).

1.0 kg of shea butter oil and 1.0 kg of palm kernel oil were purchased from keffi central market, Nigeria and mixed in ratio 50:50 by weight.

3.2.2 Extraction of alkali from Melon Seed Husk

Melon seed husk ash (200g) was taken using calabash sieve of particle size of 1.06×10^{-4} m that was placed on a clean receiving bucket, 2.5 dm^3 of distilled water was then added and the set up was allowed to stand for 48 hours at 60 °C until the filtrates drain out to get the extracted alkali. The slurry prepared under above condition was kept for 48hours in further attempt to ensure maximum extraction of the alkali. Subsequently the slurry was filtered to obtain the extract. Addition of water continues until the volume of filtrate was up to 4.0 dm^3 (Onyegbado, *et al.*, 2002).

3.2.3 Determination of potash concentration of the melon seed husk

Distilled water (100 cm^3) was measured into a beaker, 5.0 g of the ash was added into the beaker and stirred properly for 30 seconds after which it was boiled and allowed to cool. The solution was then filtered using whatman No 44 filter paper, 25 cm^3 of 0.1M hydrochloric acid (HCl) was measured using the burette and 2 cm^3 of the solution was measured into a clean conical flask, a drop of methyl orange indicator was added. The molarity of the extracted alkali was determined by titration using 25 cm^3 of 0.1M HCl in the burette, until the colour changes to pink. The molarity of the extracted alkali was determined using the method (Umeh ,*et al.*, 2013). The amount of KOH in the extract was calculated from the equation 3.1

$$V_{KOH} = \frac{FW_{KOH}N_{KOH} - V_{ex}}{100cm^3} \qquad 3.1$$

where,

V_{KOH} = Amount of KOH in a given volume of extract

FW_{KOH} = Formula weight of KOH

N_{KOH} = molarity of KOH

Vex = volume of extract

3.2.4 Determination of relative density of shea butter and palm kernel oil

Shea butter oil (20 cm^3) sample was measured and transferred into a cylinder of known weight. The weight of the cylinder and its contents was measured and the density of the oil was calculated using the method (Aiwizea, *et al.*, 2012). The same experimental procedure was repeated using palm kernel oil. The relative density was calculated using equation 3.2

Relative Density = Weight of the sample (g) / Volume of the sample (cm^3) 3.2

3.2.5 Determination of Saponification Value of shea butter and palm kernel oil

Shea butter oil sample (2.0g) was added to 250cm^3 flask with 30cm^3 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, 1cm^3 of phenopthalein was added and titrated with 0.5M HCl untill a pink end point has reached (Gunston *et al.*, 1986 and Atiku *et al.*,2014). The same experimental procedure was repeated using palm kernel oil. Saponifiication value was calculated from the equation 3.3

$$S.V = \frac{28\ 0.5\ (V_2 - V_1)\ M}{W} \qquad 3.3$$

where:

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 blank

3.2.6 Determination of iodine value of the oil samples

Shea butter oil and palm kernel oil (0.4g) respectively was weighed seperately into a conical flask and 20cm^3 of carbon tetrachloride was added to dissolve the oil. Then 25cm^3 of dam's reagents (distilled water with 6 month shelf life) 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, 20cm^3 of 10% aqueous potassium iodide and 125cm^3 of distilled 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 (Gunstone, 1986 and AOQAC, 2000). The iodine value (I.V) is given by the expression in equation 3.4

$$I.V = \frac{12.69\,(V_2 - V_1)}{W} \qquad 3.4$$

where;

N = Normality of sodium thiosulpahte

V_1 = volume of sodium thiosulpahte use for blank titration

V_2 = volume of sodium thiosulpahte used for sample titration

W = mass of the sample used (g)

3.2.7 Determination of free fatty acids (FFA) and acid value of the oil samples

Shea butter oil and palm kernel oil (1.0g) respectively at separate run was boiled with 50cm^3 of ethanol and allowed to cool, 2 drops of phenolphthalein indicator were added and then titrated against 0.1M NaOH until pink colour was obtained (William, 2012). The free fatty acid was calculated using equation 3.5.

$$\% \text{ FFA} = \frac{T \times 2.82}{W} \qquad 3.5$$

where;

W = weight of sample

T = Average titre value

3.2.8 Determination of Acid Value of the oil samples

Shea butter oil and palm kernel oil (10.0g) respectively at separate run was weighed into conical flask and 50cm^3 of denatured alcohol (ethanol and diethyl ether in ration 1:1) was added and shaken, 2 drops of phenolphthalein indicator were added and then titrated against 0.1N sodium hydroxide (AOQAC, 1990 and 2000). The acid value can be calculated using the equation 3.6

$$A.V = \frac{100 \times 2.82 \times V}{W \times 1000 \times 1} \qquad 3.6$$

where;

V= Volume of NaOH used in sample titration

W = weight of sample

OR

Acid value = % FFA X 1.99 3.7

3.3 Production of soap using produced alkali

Extracted alkali (2.0 dm^3) was put in a cleaned cooking pot, 50cm^3 of equal mixture of shea butter and palm kernel oil at a ratio of 50:50 was added a little at a time, at an interval of 10cm^3 for five times, this was boiled at 60°C, the resulting mixture was stirred continuously with a wooden stirrer until all the surface of the mixture was covered with foam, the lather volume was kept increasing until it reached its peak and essential fragrant were added to the mixture. Heating process was stopped and the soap was allowed to cool into a solid mass designed to give the shape of a required mould (Sani and Hassan, 2007)

3.4 Characterization of Produced Soap and Commercial Soap

3.4.1 Determination of moisture content

The produced soap (5.0g) was collected and dried in an oven for four hours at 150 °C, until the weight of the sample became constant (Ademiluyi *et al.*, 2008). The moisture content was calculated using equation 3.8

$$Xo = \frac{W_1}{W_2} \times \frac{100}{1} \quad 3.8$$

where, X_0 = Moisture constant

W_1 = weight of soap after drying

W_2 = weight of soap before drying

3.4.2 Determination of ash content

The ash content of the produced soap was determined by weighing 5.0 g of the soap into a crucible and heated in a muffle furnace at 60^0C for 6 hours. The ash in the crucible was cooled and weighed (William *et al.*, 2012).Ash content was calculated using equation 3.9

$$\% \text{ ash} = \frac{W_C+(W_a - W_e)}{W_s} \times 100 \qquad 3.9$$

where;

W_e = Weight of empty crucible

W_a = Weight of ash

W_s = Weight of the soap

W_c = Weight of crucible

3.4.3 Determination of pH

The pH of produced soap was determined using a pH meter (827 pH lab model). 10 g out of the produced soap shavings was weighed and dissolved in distilled water in a 100cm^3 volumetric flask and made up to mark to produce the soap solution. The electrode of the pH meter was inserted into the soap solution and the pH was recorded as described by Umar *et al.*, (2002).

3.4.4 Emulsification test

Gas oil (4 drops) was taken into a test tube and 5cm^3 of the produced soap solution was added and mixture in the test tube was shaken briefly to observe emulsification (Umar *et al.*, 2002).

3.4.5 Foam test

Produced soap solution (5 cm^3) was placed in a test tube and corked followed by shaking vigorously after which the relative amount of lather observed was recorded (Mabrouk, 2005).

3.4.6 Foam stability / foam height

Produced soap (2.0g) was shaved and put into 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 with the time in which the form collapsed (Mabrouk, 2005).

3.4.7 Hardness of soap

The hardness was determined locally by physical appearance and texture of the soaps, using hand to feel the hardness or the texture of the soap.

3.4.8 Test of acceptability of the soaps

Fifteen students from Nasarawa State University Keffi were randomly selected. The two soaps were separately placed on the palm of their hands. They were asked to rub the soaps between their hands and say whether they liked the soap extremely, very much, moderately, slightly, neither liked nor disliked the soaps, disliked moderately, very much or extremely, all their feeling were recorded (Akpan, *et al.*, 2006).

CHAPTER FOUR

DATA PRESENTATION AND ANALYSIS

4.1 Data Presentation

The result of the concentration of potash and pH value of the melon seed husk extract is presented in Table 4.1, while the physicochemical properties of shea butter oil (SBO), palm-kernel oil (PKO) compared with FAO standard references and other research work is represented in Table 4.2. The physicochemical properties of the prepared soap are presented in Table 4.3, while that of the commercial soap is presented in Table 4.4. The general acceptability test of the produced soap and commercial soap by the panelist is presented in Table 4.5.

Table 4.1: Concentration of KOH and pH Value of Melon seed husk extract

Sample	Concentration of KOH	pH Value
Melon Seed Husk extract	$63.57g/dm^3$	10.31

Table 4.2: Physicochemical Properties of Shea Butter Oil (SBO), Palm-Kernel Oil (PKO) compared with FAO standard value and other reference findings

Parameter	SBO	PKO	Reference Research finding
Relative Density (g/ml)	0.89	0.90	0.89 – 0.91(FAO, 2015, Amaoo *et al.*, 2004)
Saponification Value (mgKOH/g)	175.30	189.08	189 – 199 (Kyari *et al.*, 2008; Aremu *et al.*, 2010; Atiku *et al.*, 2014; FAO, 2015; Zauro *et al.*, 2016)
Iodine Value (I_2 /100g)	54.00	50.72	50 – 55(FAO, 2015 ;(Kyari *et al.*, 2008)
Free Fatty Acid (mgKOH/g)	5.39	1.62	≤20 (FAO, 2015, Zauro *et al.*, 2016
Acid Value (mgKOH/g)	11.70	3.50	≤30) (FAO, 2015)

SBO: Shea Butter Oil

PKO: Palm Kernel Oil

Table 4.3 Physicochemical Properties of Produced Soap and Commercial Soap

Parameter	Produced Soap	Commercial soap
Ash Content (%)	9.20	9.00
pH	10.17	9.21
Foam Stability (min^{-1})	4.15	4.40
Moisture Content (%)	4.70	4.50
Form Height (cm)	3.35	3.35
Texture	Hard	Hard
Foam Test	Foam sticky with longer persistence	Foam sticky with longer persistence
Emulsification test	Emulsification was observed	Emulsification was observed

Table 4.4 The General Acceptability of the Soaps by the Panelist

Soap Rating	Commercial Soap	%	Melon Seed Husk Ash Soap (Produced Soap)	%
Likes extremely	7	46.6	4	26.6
Like very much	5	33.3	5	33.3
Like moderately	1	6.7	4	26.7
Like slightly	-	-	1	6.7
Neither like nor dislike	1	6.7	1	6.7
Dislike slightly	1	6.7	-	-
Dislike moderately	-	-	-	-
Dislike very much	-	-	-	-
Dislike extremely	-	-	-	-
Total	15	100	15	100

4.2 Data Analysis

4.2.1 Concentration of melon seed husk ash potash

Several waste materials such as plantain peel, melon seed husk, cassava peel, coco pods etc have been shown to yield high percentage of potash which is suitable for soap making. It was also discovered that the process of combustion contributes to the quality of the potash. When the peel or seed husk are slowly combusted they will not burn completely and this affects the concentration of the potash (Kirt *et al.,* 1994). The concentration of potassium concentration in melon seed husk ash was found to be 63.57g/dm^3 while the pH is 10.31as in Table 4.1 and these compare favorably with other research work of Umeh *et al.*, (2013).The finding of the study revealed that melon seed husk ash has higher concentration of potassium hydroxide (KOH) . This result of the analysis of melon seed husk ash produced an alternative source of caustic soda for soap making as it was in line with the work of Kirth and Othemer (1994).

4.2.2 Physicochemical properties of shea butter oil (SBO) and palm- kernel oil (PKO)

The physicochemical properties of both SBO and PKO show that they had acceptable properties and values which compared favorably with FAO standard values and other research finding as represented in Table 4.2.

The Relative densities of these oils are almost the same, the value for SBO and PKO was found to be 0.89g/ml and 0.90g/ml respectively. The values obtained agree with FAO standard value range of 0.89 – 0.91 g/ml as shown in Table 4.2 and also the value obtained by other research work (Amaoo *et al.*, 2004). The saponification value for SBO is 175.30mgKOH/g which was observed to be within reported value of other research finding (Amaoo *et al.*, 2004) and also within the range of FAO standard value as shown in Table 4.2 while that of PKO is 189.08mg/KOH/g which also agree with FAO standard value range of 189 – 199mg/KOH/g and

other reference research work (Kyari *et al.*, 2008; Aremu *et al.*, 2010 and Zauro *et al.*, 2016), as shown in Table 4.2. The value obtained for the oils are useful in making soap and will produce soap which is relatively hard and soluble in water. This is also in line with the research work of Atiku *et al.*, (2014).

The Iodine value for both SBO and PKO are found to be 54.0 I_2 /100g and 50.72 I_2 /100g respectively as shown in Table 4.2. The values obtained was found to be within the FAO standard values and other research findings (Kyari, 2008 & FAO, 2015). It is observed from the above saponification and iodine value obtained, that results are complementary. The oil with high saponification value has low iodine value and vice versa. Therefore, we expect this blend to produce good quality soap with the combined properties of the two oil particularly for blend ratio of 50:50 . Usually oil with low iodine value produce hard soap for example, coconut oil and PKO give hard soap with large bubbles which is short lived oil with medium iodine value e.g palm oil (PO) and Beef tallow oil (BTO) give short live bubbles (Olabanji *et al.*, 2012).

Acid value (AV) measured the quality of fatty acid in oil. Low acid value in oil indicates that the oil will be stable over a long period of time and protected against rancidity and its suitability in soap making (Aremu *et al.*, 2015). The acid value obtained in this work for both SBO and PKO was found to be 11.70mgKOH/g and 3.50mgKOH/g respectively as shown in Table 4.2. The values obtained are observed to be within the standard set by FAO (FAO, 2015) which is ≤ 20mgKOH/g. There for, 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 (Atiku *et al.*, 2014)

For free fatty acid, 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 (Umar *et al.*, 2002).

The value obtained by both oil (SBO and PKO) was found to be 5.39 mgKOH/g and1.62 mgKOH/g respectively as shown in Table 4.2; and this is observed to be within other research finding (FAO, 2015 and Zauro *et al.*, 2016). All these values indicate that the two oils are good for soap production.

4.2.3 Physicochemical properties of produced soap

The ash content of the prepared soap (9.20%) and that of the commercial soap found (9.0%) compared reasonably well with the result for the commercial soap and both values obtained falls within the range of other research study of Atiku *et al.*, (2014) and FAO (2015) standard value of 9.10%.

The pH of the produced soap (8.71) and that of commercial soap (9.21) indicate that the soap samples are strongly basic in nature, even though the pH is not skin friendly because skin friendly pH soap supposed to have pH 7-8 , but NAFDAC recommended a pH of 8 (Umar *et al.*, 2002). The pH values of both soap are found to be within the range of other research study (Atiku *et al.*, 2014).

The produced soap has a foam stability value of 4.15min as shown in Table 4.3, while the foam stability of the commercial soap was found to be 4.40min as shown in Table 4.3. These values compare favorably with order research finding of (Zauro *et al.*, 2016). 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 (Phansteil *et al.*, 1998).

Locally processed soap known is soft was due to the presence of high concentration of K^+ ions in the soap; due to these the result was found to be relatively hard. The hardness and rough texture of the soap could be due glycerol removal through the process of salting out, both the prepared and commercial soap are hard based on their texture as shown in Table 4.3, as a result of these, both soap are found to have similar properties of hardness and for these reason compared favorably with each other properties. It is also noted that the length of hydrocarbon chain , number of double bonds and the nature of the fatty acid composition determine the hardness or softness of the soap (Umar, M. A.,2002).

The moisture content of the prepared soap was found to be 4.70% as presented in Table 4.3 while the moisture content of the commercial soap was found to have value of 4.50% as shown in Table 4.4 and compared favorably with other research finding of Zauro *et al.*, (2016) and FAO,(2015) standard value of 4.60%.

The foam height of the prepared soap was 3.10 cm while that of the commercial soap was 3.35 cm as shown in Table 4.3. Based on the above, the foam height value was observed to be within the same range of other research work of Zauro *et al.*, (2016) which gives a good similarity to both result values.

The foam test of the prepared soap and commercial soap, as shown in Table 4.3 Compare favorably finding other research work (Atiku *et al.*, 2014) .

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

both the prepared soap and that of the commercial soap as shown in Table 4.3.The colour of both soaps was also observed to be white as shown in Table 4.3; these could be due to salting out process.

4.3 General Acceptability of Soap made with Alkali Extract from Melon Seed Husk Ash

The result of the laboratory analysis of ash of melon seed husk to produce alternative source of caustic soda for soap making is in line with the work of Kirk and Othemer (1994). The Hedonic scale of rating was used to evaluate different qualities of melon seed ash soaps and commercial soap in terms of their texture, colour, odour lathering ability and general acceptability. The data collected during analysis showed that, the respondents liked the soap samples very much. This is as a result of improved colour, texture, odour and lathering quality. The soap made with well filtered ash solutions and palm kernel and Shea butter oil has improved colour and increased lathering ability as was observed from the sensory evaluation on colour , 26.6% of respondents extremely liked the colour of melon seed husk ash soap and 33.3% liked the colour of melon seed husk ash soap very much as shown in Table 4.4

The results obtained in the present study are in agreement with the findings of Onyeghado *et al* (2000),that clearer filtration in the extraction stage, virtually removed all black particles from the extract and also eliminates any metallic ions in the ash extract, which could colour the resulting soap. The findings of this study is of the view that the colour improvement observed by the panelists were as a result of filtering the alkaline solutions with cotton wool and also the use of shea butter oil (SBO) and palm kernel oil (PKO) at equal ratio. The findings also revealed that the lathering ability of the soaps were generally liked by the respondents, this is due to the fact that the ashes contain very high quantity of alkali which when completely saponified with shea

butter oil and palm kernel oil lathers very well. This is in line with the submission of Onyekwere (1996), who observed that soaps made with alkalis derived from vegetable matter ash when reacted with shea butter and palm kernel oil are found to be soft and hard , had good lathering abilities and cleaning properties. The odour of the soap was improved with the use of shea butter oil/palm kernel oil and perfume; this in agreement with Onyekwere (1996) who stated that bleaching the oil removes the characteristic odour of palm oil in the soap produced. The result obtained from the sensory evaluation on the general acceptability of the respondents showed that the soap were generally accepted by the panelist because of the improvement on the colour, odour, texture and lathering ability which was achieved with the use of shea butter oil/ palm kernel oil, clearer filtration of the solutions and the added perfume.

CHAPTER FIVE

SUMMARY, CONCLUSION AND RECOMMENDATION

5.1 Summary

Soap samples were produced using sheabutter (SBO), palm kernel oil (PKO) in a ratio of 50:50 with melon seed husk ash. The physicochemical properties of the oil and soap was analysed for, relative density, saponification value, iodine number, free fatty acid, acid value, ash content and pH. The physical properties of the soap were also analysed for foam stability, hardness, and foam height. The hedonic scale rating was used by giving out questioner to evaluate the quality of produced and commercial soap in terms of their texture, colour, odour, lathering ability and general acceptability. The data collected during analysis showed that, the respondents liked the soap sample very much.

5.2 Conclusion

The results obtained from the physicochemical analysis of the produced soap using shear butter and palm kernel oil ratio (50:50) with purified alkali made from melon seed husk ash was successfully achieved using an improved conventional method adopted for black soap production. The study showed significant acceptability of the locally made soap by respondent individuals. The qualities of soaps thus produced clearly indicated that exploitation of vegetable matter to generate alkali for soap production is worthwhile. Apart from the fact that our environment would be free of these agricultural wastes that often render them untidy, it will save the environment from the potential harmful effect of pollution that is commonly associated with these solid agricultural wastes. In addition, the heavy dependence on synthetic chemicals for soap production would drastically be reduced if concerted effort is made on improving this locally source of raw material for soap making.

5.3 Recommendations

Based on the findings, the study recommended that;-

The use of raw materials from vegetable matter should be encouraged for soap production to save the country's foreign exchange.

The possibility of large scale production of this alkali should be evaluated over the high cost of imported alkali.

Graduates of Industrial Chemistry should exploit the self-employment opportunity in the area of local production of soap for self-reliance

REFERENCES

Achigan-Dako, E.G., Fagbemissi, R., Avohou, H.T., Vodouhe, R.S., Coulibaly, O. & Ahanchede, A. (2008). Importance and Practices of Egusi Crops (Citrullus lanatus (Thunb.) Matsum. & Nakai, Cucumeropsis mannii Naudin and Lagenaria siceraria (Molina) Standl. cv.'Aklamkpa') in sociolinguistic areas in Benin. *Biotechnol Agron Soc. Environ.* 12(4):393 - 403.

Adewuji, G.O, Obi –Egbedo, N.O & Babayemi, J.O., (2008). Evaluation of ten different, African wood species for Potash Production. *International journal of physical sciences* .3 (2); 63 – 68.

Affrane ,Y.A (1982). Leaching of caustic potash from cocoa husk ash.*journal of environmental cience*. Vol 12. Pp56

Afrane, G. (1992) Leaching of caustic potash from cocoa husk ash. *Bioresour. Technol.*, 41: pp101-104.

Ankrah, E.K., (1974). Chemical studies of some plant wastes from Ghana, *Journal of Science, Food and Agricultural,* 25: pp1229-1232

African Development Bank Group (2012). Rural Enterprises Project II in Ghana – Transforming the Lives of the Rural Poor, *https://www.afdb.org/en/news-and-events/rural-enterprises-project-ii-in-ghana-transforming-thelives-of-the-rural-poor-9203/*

Akpan ,R.S & Joannis ,T.M (2006). Assesment of soap produced from agro waste. *journal of environmental cience*. Vol 42. Pp55

Akbar, E., Yaakob. Z & Kamarudin, S.K. (2009). Characteristic and Composition of Jatropha Curcas Oil Seed from Malaysia and its Potential as Biodiesel feedstock. *Eur J Sci Res.* 29: 396–403.

All Africa, Uganda(2007). Kyambogo Student Starts Small-Scale Soap Industry.

Amaoo , A.M & Joshua , F.M (2004). Physicochemical properties of oil. *Association of Official analytical chemist.*vol 3 .pp 71.

Aremu ,M.O & Hashim ,I (2015).Pysicochemical characteristic of oils extract from some Nigeria plant foods.A review.*Chemical and process Engineering Research.*vol 32. Pp 22

Amyakoha, E. U (2009). New Entreptreneurship education and wealth creation strategies 2nd Edition. *Practical tip for Economic Empowerment and survival Nsukka; Great AP Express Publishers Ltd, 12th edition.*Vol 3.pp34

Amyakoha, E. U (2011). Home Economics for Junior Secondary Schools Onisha. *African first Publishers Plc.* Vol 4.

Association of Official Agricultural Chemists (AOAC) (2000). Oils and Fats Preparation of test sample, *17th edition Official Method* 981.11. 12-15

Association of Official Agricultural Chemists (AOAC) (1990). Officer analytical method of analysis, 14th edition, *Association of Official analytical chemist, washinton* D.C.Vol 3.

Association of Official Agricultural Chemists (AOAC) (1984). *Officer analytical method of analysis, Association of Official analytical chemist, washinton* D.C.Vol 5

Association of Official Agricultural Chemists (AOAC) (2005). Official analytical method of analysis, 18th edition Maryland USA, *Association of Official Analytical chem. Int* .Vol 6

Atiku, F.A., Fakai, I.M., Wara, A.A., Birnin Yauri, A.U & Musa, M.A (2014). Production of Soap using Locally available Alkaline Extrcted fro Mjllet Stack. A study on physical and chemical properties of soap. *International Journal of Advance Research in Chemistry science (IJARCS)* .Vol 1ISSUES7, PP 1- 7.

Austin G.T. (1975). Soap and Detergent. Shreve's Chemical Process Industries, 5th Edition, *McGraw Hill Publication.* Pp 529

Avon, M.A., & Adams, M. (2013). A Grosso, The Everything Soap making Book: *Recipes and Techniques for Creating Colorful and Fragrant Soaps*, pp 69 – 132.

Basu, N.B., Georgia , D,Jame ,W.J,Sally, E. T,Ntalia, V.I.L,Stefono, Z, Mary ,Y,Murugesu, S, Andrea ,R & Suresh, P.R (2010).Nutrient Load exported from managed catchment reveal emergent biogeochemical stationarity.*Geophysical Research Letter.*vol37. pp23

Berger, M.D., Bhatt, B & Combes, R.W. (1986). Carbonterachloride-induced toxicity in isolated hepatocytes. Journal of chemical research.Vol 6, pp313- 323.

Benge, M. (2006). Assessment of the Potential of Jatropha Curcas, (biodiesel tree) for energy Production and other uses in Developing Countries. *USAID Report.* Pp 56-59.

Brittaine, R., & Lutaladio, N. (2010). Jatropha: A Small holder Bio energy Crop: The Potential for pro-Poor Development. Rome, Italy: *Food and Agriculture Organizational Journal.* Pp 14-18

Cavitch , T., & Miller, S. (1994). *The Natural Soap Book.* Storey Publishing, ISBN 0-88266-888-9.

Chalmers, L & Bathe, P. (1978). Chemical Specialties, *Domestic and Industrial.2nd edition.* PP.57

Dixit, S. (2011). Toilet Soaps and Bathing Bars. *Chemical Business.* PP 18

Desert Moon Bath & Body (DMBB) (2013). Beneficial Properties of Oils, Butters, EWB-UK, "Training Hand Over Pack: Cold Process Soap Making," *https://www.yumpu.com/en/document/view/36474897/cold-process-soap-making-ewb-uk-training-hand-overpack*

FAO, (2015). Joint FAO/WHO food standard programme codex Alimentarius commission thirty eight session CICG, *Report of the Twenty forth session of the codex committee on fats and oil melaysia* .vol 4 .pp56

Flynn, J.H & Wall, L.A. (1966). A Quick, Direct Method for the Determination of Activation Energy From Thermo gravimetric Data. *Journal of Polymer Science Part B: Polymer Letters. 4(5):PP 323. doi:10.1002/pol.1966.110040504.*

Foo, K., & Hameed, B. (2012). Preparation and Characterization of Activated Carbon From Melon (Citrullus vulgaris) seed hull by microwave-induced NaOH activation. Desalination and Water Treatment. 47(3):pp 130-133.

Francioni, J. B & Callings, M. L. (2002). Soap Making." Louisiana State Extension Circular. *Retrieved from www.http://ebook browse.com/gdoc.php?id=w ww.http://ebookbrowse. com/g doc.php?id=355456856&url=e36e883294bb5b9bcd6 11ff0a00130aa [Accessed 22nd January, 2018].*

George Godwin United, U.K. pg. 1-15.

Giwa, S., Abdullah, L.C. & Adam, N,M. (2010). Investigating "Egusi"(Citrullus colocynthis L.) seed oil as potential biodiesel feedstock. *Energies*. 3(4): pp 607-618.

Giwa, S.O., Chuah,. L.A, & Adam, N.M. (2014). Fuel Properties and Rheological Behavior Of Biodiesel From Egusi (Colocynthis citrullus L.) seed kernel oil. *Fuel Processing Technology*. 122(0): pp 42-8.

Gunstone , F.D., Harwood, J.L & Padley , F.B (1986). *The lipid hand book, champam and hall limited, London.Vol 1986, pp 236 – 261.*

Henning, R. (2000). The Jatropha Booklet. Choma: GTZ-ASSP Project Zambia. Pp 60-75

Isaac, A. (2005). The Macmillan Encyclopedia London: *published by Macmillan London Limited.11th edition. Vol 6.pp 45.*

Israel, A.U., Obot, I.B., & Asquo, J.E. (2008). Recovery of Glycerol from Spent Soap Lye. by-E *Journal of Chemistry. 5(4) : pp 940-945.*

James, A. K (1997). *Reigel's Handbook of Industrial Chemistry 9th Edition, CBS Publication. Pp 55-59*

Jarret, R.L. & Levy, I.J. (2012). Oil and Fatty Acid Contents in Seed of Citrullus lanatus Schrad; *Journal of Agricultural and Food Chemistry*.vol 60 (20): pp 5199-5204.

Kirt,E & Koppel, A (1994). Willow Vegetation filters for municipal wastewater experiment in Estonia.*Journal of environmental science*.pp 45.

Kissinger, H.E. (1956). Variation of Peak Temperature With Heating Rate in Differential Thermal Analysis. *Journal of Research of the National Bureau of Standards.* Vol 57(4): pp 217-221.

Kulyal, P., Tiwari, U.K & Shukla, A. (2011).Chemical Constituents Isolated from Seed Oil Of Jatropha Curcas. *Asian Journal Chem.* Vol 23: pp 2939

Kuntom, A., Siew, W. L., Tan, Y. A. (1994). Characterization of Palm Acid oil *J. Am. Oil ChemSoc, vol 71, pp 525-528.*

Kuntorn, A., Kifli, H. & Lim, P.K. (1996). Chemical and Physical Characteristics Of Soap Made From Distilled Fatty Acids Of Palm Oil And Palm-Kernel Oil. *J. Am. Oil Chern Soc. Vol* 73, pp 105-108.

Kyari ,M.Z & John , T.W(2008).Extraction and characterization of sees oils. . *J.Am. Oil Chern Soc.*Vol 5 .pp 9

Legesse , A , Habtamu, A & Tegene, T (2015). Use of Jatropha Seed Oil and Alkali Solution obtained from Its Ash for Soap Making. *J. Appl. Sci. Environ. Manage.* Vol. 24 (12). PP45

Ledakowicz, S & Stolarek, P. (2003). Kinetics of Biomass Thermal Decomposition. *Chemical Papers-Slovak Academy of Sciences. Vol 56(6): pp 378-381.*

Mak-Mensah, E. E.& Firempong, C. K., (2011). Chemical Characteristics of Toilet Soap Prepared from Neem (Azadirachta indica A. Juss), *Seed Oil.* pp3- 5.

Mabrouk,T.S (2005).Making usable ,quality opaque or transparent soap.*Journal of chemical education.* Vol 82(10).pp 1534.

Messemaker, L. (2008). Assessment of the Jatropha Value Chain and Its Potential for Pro Poor Biofuel Development in Northern Tanzania. M.Sc Thesis. *International development studies at the Faculty of Geosciences Utrecht University.*

Nwoko , S.G (1982). Quality Assessment of Soaps Produced from Palm Bunch Ash.*joournal chemical society of Nigeria.*vol 34. Pp32

Nyakuma, B.B. (2015). Solid Biofuel Potential of Acacia Mangium Leaves: Peer *J* 2167-9843.

Olabanji, O., Oluyemi, E. A & Ajayi, O.S. (2012) Metal analyses of ash derived alkalis from banana and plantain peels (Musa spp.) in soap making. *African Journal of Biotechnology,* 11(99): pp 16512-16518

Osagie,O.F and Enyi, C.C (2015). Utilization of agricultural waste (rubber seed oil, kolanut pods and almond leaves) for soap production. *International Journal of Geography and Environmental Management* Vol 1(8). PP 7

Ogbe, A. & George, G. (2012). Nutritional and Anti-nutrient Composition of Melon Husks: Potential as Feed Ingredient in Poultry Diet. *Research Journal of Chemical Sciences*. Vol 2231: pp 2606.

Ogunsuyi, H.O & Akinnawo, C.A (2012). Quality Assessment of Soaps Produced from Palm Bunch Ash-Derived Alkali and Coconut Oil. . *J. Appl. Sci. Environ. Manage*. Vol. 16 (4) 363-366

Okeke , S.U.N (2009). Home Economic for Schools and Collages, Onitsha: *Afriana first publishers Plc Nigeria.vol 8.*

Okieimen, F. & Onyenkpa, V.(2010). Removal of heavy metal ions from aqueous solutions with melon (Citrullus vulgaris) Seed Husks. Biological Wastes. Biomass gasification and Pyrolysis: *Practical Design and Theory. Academic Press. Vol 29(1):pp 11-16*

Oluba, O.M., Eidangbe, G.O., Ojieh, G.C., & Idonije, B.O (2011). Palm and Egusi Melon Oils Lower Serum and Liver Lipid Profile And Improve Antioxidant Activity In Rats Fed A High Fat Diet. *International Journal of Medicine and Medical Sciences.* Vol 3(2): pp 47-51. Olabanji, O., Oluyemi, E. A & Ajayi, O.S. (2012) Metal analyses of ash derived alkalis from banana and plantain peels (Musa spp.) in soap making. *African Journal of Biotechnology,* 11(99): pp 16512-16518

Onyegbado, C. O., Iyagba, E. T. & Offor, O. J. (2002) Solid soap production using plantain peels ash as source of alkali, *Journal of Applied Science and Environmental Management,* 6: 73-77

Onyegbado, C.O.,Iygba, E.T.& Offor, O.J (2004).Solid soap production using plantain peel ash as source of alkali. *Journal of applied science environmental management.*vol 6 pp 1

Ozawa, T. A. (1965). New Method of Analyzing Thermo gravimetric Data. *Bulletin of the Chemical Society of Japan.* Vol 38(11):pp 1881-1896.

Pallas Athene Soap. (2009*). High-Quality Sodium Hydroxide (NaOH) and Potassium Hydroxide (KOH) for Making Soap:* Organic, Vegan, Handmade Natural Soap. Available online at http://www.certified-lye.com/lye-soap.html [Accecced 20th January, 2019].

Pavila, L.D., Lapman, G.M & Krisz , G.S (1982). Introduction to Organic Laboratory Tecniques, 2nd Edition, *Sauders Publishser. Pp 113 – 114.*

Phansteil , O.N., Dueno , E & Xiaghong Wang, Q (1998). Synthesis of Exotic Soap in the Chemistry Laboratory. *Journal of Chemical Education. Vol (5): pp 612 – 614.*

Pratt, J., Henry, E., & Mbeza, H. (2002). Malawi Agro Forestry Extension Project Marketing & Enterprise Program, Main Report. *Malawi Agro Forestry.vol 47: pp 139.*

Sani ,N.A & Hassan, L.G (2007). Preparation an Analysis of the physical and chemical properties of from Lageneria (bottle groung) seed oli. *Nomada Tech. scope journal. Vol 7 (1):pp 23-32.*

Sharma, B. (2000). Industrial Chemistry (Including Chemical Engineering). *Meerut, India: GOEL Publishing House.*

Simmons, W. H. & Appleton, H. A. (2007). *The Handbook of Soap Manufacture. The Oil and Colour Trades Journal. London Scott, Greenwood & Son Offices 8 Broadway, Ludgate Hill, E.C.Also available online at http://www.gutenberg.org/files/21724/21724-h/21724-h.htm [Accessed on 2nd January, 2013].*

Slopiecka, K., Bartocci, P., & Fantozzi, F. (2012), Thermo Gravimetric Analysis and Kinetic Study of Poplar Wood Pyrolysis. *Applied Energy*. 97: pp 491-497.

Sun, W.G., Zhao, H., Yan, H.X., Sun, B.B., Dong, S.S, & Zhang, C.W. (2012).The Pyrolysis Characteristics and Kinetics of Jerusalem Artichoke Stalk Using Thermo gravimetric Analysis. Energy Sources, Part A: Recovery, Utilization, and Environmental Effects. Vol 34(7): pp 626-635.

Talabi. O. A., & Koleoso, O.A. (1984). Utilization of sheafat (A vegetable oil). *Federal Institute of Industrial research Manual, Oshodi, Lagos p. I-II.*

Taiwo, O. E. & Osinowo, F. A. O. (2001) Evaluation of various Agro-wastes for traditional Soap Production, *Bioresources Technology,* 79:pp 95-97

The Zimbabwean, Sweet Smell of Success,(2015). http://www.thezimbabwe an.co/2015/0 4/s weet-smell-ofsuccess-2/L Plesent, S Lincoln, Training Manual for a Village Soap-Making Operation by Vermont Soap (2012), *http://vermontsoap.com/training-manual-for-a-village-soap-making-operation/*

Umar , A,Berrevoets, C.A & Brinkmann, A.O (2002).physicochemical orange peels.*journal chemical society of Nigeria.*vol 9. Pp12

Umeh , G.N.,Nwibo, S.U., Nwofoke, C., Odoh, N.E., Eze, A.N., Egwu, P.N & Mbam, B.N (2019). Preference differentials for Agro - Entrepreneurship Among Youths in Eboyi State Nigeria. *Nigeria Agricultural Journals* .Vol 50 (2). Pp92-99.

Ugwumba, C. (2010). Allocative Efficiency of' Egusi'Melon (Colocynthis citrullus lanatus) Production Inputs in Owerri West Local Government Area of Imo State, *Nigeria Journal of Agricultural Science.1(1): pp 95-100.*

Warra, A. A (2013). Report on Soap Making in Nigeria Using Indigenous Technology and Raw Materials, *African Journal of Pure and Applied Chemistry* vol 7:4: pp 139-145.

Warra, A. A .Gunu, S.Y., Wawata, I.G., & Atiku, F.A (2011). Soap preparation from soxhlet Extrected Nigeria Cotton Seed Oil. *Journal of Advances in Applied Science Reasearch, 2(5): pp 617- 623.*

Warra, A. A .Gunu, S.Y., Wawata, I.G., & Hassan, L.G (2009). Physicochemical analysis and alkaline hydrolysis of some selected fat and Oil. *International Journal of physical Science. 4(1): pp 617- 623.*

Warra, A. A .Gunu, S.Y., Wawata, I.G., Hassan, L.G & Jega , S.A (2010).Cold process Synthesis and properties of soap preperd from diffent triacylglycerol sources *Nigeria Journal of Basic and Apply Science. 18(2): pp 315- 321.*

Wash basin Wonders. (2012). Saponification Table: *Handcraft Soap and Making Supplies.Avai lable at http:/ /webcache.googleusercontent.* zNIoQJ:www.washb asinwonders. com/saponificati on.htm l+& cd= 5&hl=e n&ct=clnk&gl=ngcom/search? q=cache:Cx8KVD [Accessed 1st January, 2018].

William, & Devine (1961). Oil Quality Characteristic of some Oil seeds, science Forum. *Journal of pure and Applied Science. 14, pp 17 – 23.*

William, A (2012). Comparison of the physicochemical properties of produced soap and commercial soap from agricultural waste. *Journal of chemical society of nigria.* Vol 3. Pp67.

Wisegeek. (2013). How to make Soap, Detergent Soap, Best Antibacterial Soap, Soap Making, Hand Made Soap. Available online at *http://www.wisegeek.org/what-is-antiseptic-soap.htm.[Accessed 1st January, 2018].*

Yahaya,L.E, Ajao,A.A, Jayeola,C.O, Igbinadolor, R.O & Mokwunye, F.C (2012).Soap Production from Agricultural Residues - a Comparative Study. *American Journal of Chemistry.* Vol 2(1):pp 7-10

Zauro, S.A & Philip ,K.P (2016).Production and analysis of soap using locally available raw materials.Int . *Jnr of App chm.*vol 96. Pp 41479- 41483

Zhu Y, H. & Zon, L.I.. (2004). A novel Gbeta-like protein, suppresses MAPK signaling pathway. *J Cell Biochem* 93(3): pp 579-87