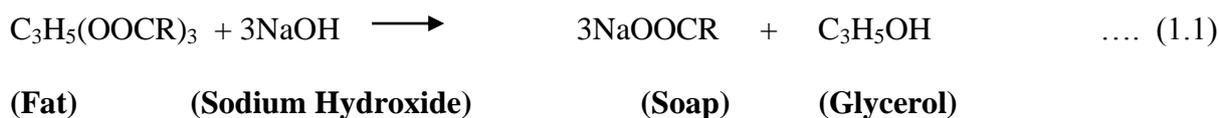


CHAPTER ONE

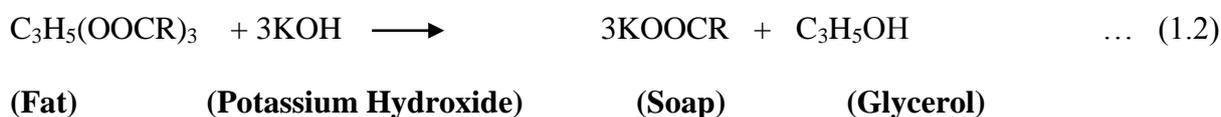
1 INTRODUCTION

1.1 Background of the Study

Lubricating grease is produced by dispersing thickening agents in mineral or synthetic oil. Several thickening agents exist but soap-base is the most popular. Several soap bases like sodium, lithium, calcium, aluminum etc. are used in lubricating grease production. Soap comprises of the metallic salts of long chain monocarboxylic acids. Generally, soap making is based on alkaline hydrolysis of fat and oil in a reaction known as saponification, according to the equations (1.1) and (1.2).



OR



These soaps give different properties to the grease and they have different formulations, structure, and characteristics. Other thickening agents include Organoclay, Polymer, Silica etc. All these soaps are formulated from manufactured alkalis. However, there is a prospect of formulating lubricating grease from alkalis derived from the ashes of agricultural waste such as plantain peel, since local soap production has been achieved using these alkalis as reported by Nwoko, (1980) and Onyegbado et. al (2002). According to Adewuji, et al (2008), several agricultural wastes of vegetable origin yield high potash when combusted. These materials include plantain peels, cassava peels, palm bunch, wood, cocoa pod, banana leaves, maize cob, 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 (equations 1.3 and 1.4). These agricultural wastes are readily and locally available in abundance.



As at present, these local alkalis are not used in grease production since no stoichiometry has been developed for them. The local production of potash from these agricultural wastes has been observed to be a cheaper alternative source of this much needed chemical used in the production of soap and other alkalis based products (Adewuji et al, 2008). 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 (Umeh-Idika and Maduakor; 2013) However Onyeagbado (2004) has produced solid odourless soap using alkali extracted from plantain peel ash. The ash derived alkali contains varying concentrations of different metals. Since emulsion of Ca, Li and many other metal soaps and their mixtures are used in most lubricating greases and are often called thickener (Thorsten et al., 2002), the soap made from alkali derived from plantain peel ash could be useful as a thickener in lubricating greases and will be more economical than those from inorganic sources. The presence of other metals besides K and Na at higher concentrations limits the foamability of the soaps and Olabanji, et al (2012) suggested that this could be an advantage to use them as grease thickeners since foamability is not a desirable quality in lubricating greases.

Although at present, palm oil and palm kernel oil for local soap production (as source of fat and oil) in Nigeria are readily available, nearly all the alkali for soap making is imported

(Onyegbado et al 2002). Edewor (1984) estimated an annual availability of over 30,000 tonnes of KOH derivable from cocoa-pod waste alone, in the country, which more than meet the importation requirements of KOH and NaOH of 26,000 tonnes in 1985 but the knowledge gap in developing the formulation for using this type of alkali has hampered the technical, economic and social benefits derivable from their use. Onifade (1994) asserted that the dumping of cocoa-pod wastes in concentrated heaps on the farms (the usual practice in Nigeria) was adverse to soil fertility and that hogs and other livestock could not completely remove the total wastes available, as fodder. According to (Umeh-Idika and Maduakor, 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, even their proper disposal is a waste of resources which are potential source of raw materials needed in soap making. Therefore, such agricultural wastes could be converted to potash and used for soap making and consequently, lubricating grease production.

1.2 Objective

The objective of the study is:

To produce lubricant grease using alkali derived from plantain peel ash and determine the combination of reactants that give the best grease consistency.

1.3 Justification of the study

Studies have been conducted on production of soap using alkalis from ashes of agricultural wastes (Onyeagbado et al, 2004, Onifade, 1994, Olabanji et al, 2012) but there are little or no information on production of lubricant grease from any of these alkalis. It is therefore pertinent to conduct studies on the production of lubricant grease using plantain peel ash as the source of alkali. This will provide the information on the consistency of the grease it can

produce and know whether this consistency falls within the acceptable standards. Plantain peel ash was chosen as the source of the bio-alkali because there is sufficient scientific information available from the analysis of its alkali from various sources (Nwoko, 1982, Onyegbado et. al. 2002, and Oluremi et al, 2012). This will enhance straightforward research on its suitability as a good grease thickener, without recourse to auxiliary analysis of the bio-alkali extract.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Lubrication and Lubricants.

Lubrication is the branch of science that deals with the application of lubricants to moving machine parts. The functions of lubricants are as follows;

- i. To reduce friction between moving parts, and so minimize the frictional effect of metal-to-metal contact.
- ii. To act as a cooling medium by absorbing and dissipating excessive heat generation. For example, it has been estimated that the big-end bearing of an internal combustion engine requires approximately 90 times as much lubricant to keep it cool as it requires for the actual reduction of friction (Culpin, 1981).
- iii. To act as a seal for pistons in internal combustion engines, so as to make the combustion chamber gas tight.
- iv. To remove dirt from engine parts, thus keeping them clean and efficient.

These elements move in relation to each other, either by sliding, rolling, approaching, receding, reciprocating, and angular or by combination of these motions. Improper, inadequate or excessive, lubrication results in premature failure of machine elements and consequent high maintenance costs and lower profitability in industries. In fluid dynamics, lubrication theory describes the flow of fluids (liquids or gases) in a geometry in which one dimension is significantly smaller than the others. Interior flows are the elements of machines that require lubrication are those in relative motion namely: gears, bearings, slides, guides-ways, pistons/cylinders, cam/cam-followers, flexible couplings, pulley/wire ropes etc. those where the boundaries of the fluid volume are known, and include those inside bearings. Here

a key goal of lubrication theory is to determine the pressure distribution in the fluid volume, and hence the forces on the bearing components. The working fluid in this case is often termed a lubricant.

Free film lubrication theory is concerned with the case in which one of the surfaces containing the fluid is a free surface. In that case the position of the free surface is itself unknown, and one goal of lubrication theory is then to determine this. Surface tension may then be significant, or even dominant. Issues of wetting and dewetting then arise. For very thin films (thickness less than one micrometre), additional intermolecular forces, such as disjoining forces, may become significant. Mathematically, lubrication theory can be seen as exploiting the disparity between two length scales. The first is the characteristic film thickness, H , and the second is a characteristic substrate length scale L . The key requirement for lubrication theory is that the ratio $\epsilon = H/L$ is small, that is, $\epsilon \ll 1$. The Navier-Stokes equations (or Stokes equations, when fluid inertia may be neglected) are expanded in this small parameter, and the leading-order equations are then (equations 1.2 and 2.2)

$$\frac{\partial p}{\partial z} = 0 \quad \dots (2.1)$$

$$\frac{\partial p}{\partial x} = \mu \frac{\partial^2 u}{\partial z^2} \quad \dots (2.2)$$

Where x and z are coordinates in the direction of the substrate and perpendicular to it respectively. Here P is the fluid pressure, and u is the fluid velocity component parallel to the substrate; μ is the fluid viscosity.

Lubricants are introduced to reduce friction between moving surfaces and may also have the function of transporting foreign particles. The property of reducing friction is known as lubricity.

A good lubricant possesses the following characteristics:

1. High boiling point.

2. Low freezing point.
3. High viscosity index.
4. Thermal stability.
5. Corrosion prevention.
6. High resistance to oxidation.

There are four main types of lubricants. These are solids (e.g. graphite), liquids (e.g. oils), plastics (e.g. grease) and gases (e.g. air).

2.2 Lubricating Grease

Lubricating grease is generally defined as “a solid to semi-fluid product or dispersion of a thickening agent in a liquid lubricant. Other ingredients imparting special properties may also be included” (NLGI, 1987). Grease from the early Egyptian or Roman eras is thought to have been prepared by combining lime with olive oil ([http://en.wikipedia.org/wiki/Grease_\(lubricant\)](http://en.wikipedia.org/wiki/Grease_(lubricant))). The lime saponifies some of the triglyceride that comprises oil to give calcium grease. In the middle of the 19th century, soaps were intentionally added as thickeners to oils (Thorsten et al, 2005). Over the centuries, all manner of materials have been employed as greases. Black slugs *Arion ater* were used as axle-grease to lubricate wooden axle-trees or carts in Sweden (Svanberg, 2006)

2.2.1 Fundamentals of Grease Formulation

Lubricating grease is a complex mixture of alkali, fatty acid (fats and oil), and lubricating oil. First the alkali reacts with the organic acid to form soap as shown in equations (1.1) and (1.2). The soap is heated to dehydrate and melt so as to have an intimate mixing with the lubricating oil to form grease. Soap production started around 2500 BC with boiling of fats

with ashes. The formula for soap consisting of water, alkali and cassia oil was written on a Babylonian clay tablet around 2200 BC (Willcox, 2000). 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. In other words, Soap has two dissimilar ends: a hydrocarbon chain, that is non-polar, and a carboxylate salt end, which is polar as shown in equation (2.3)



Sodium stearate, soap

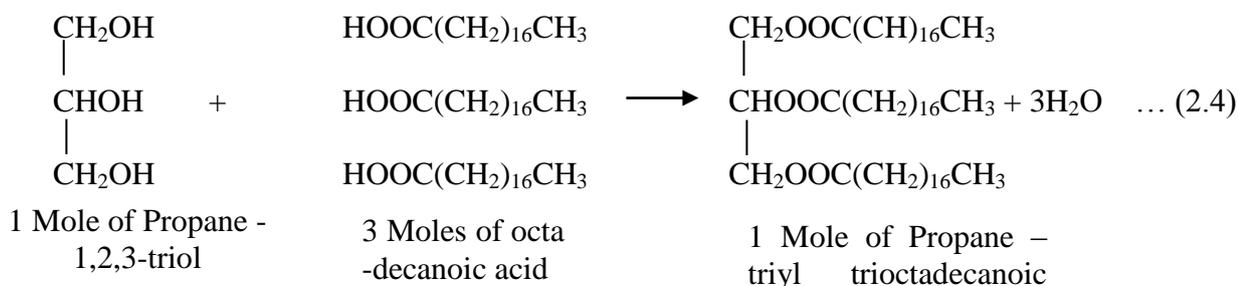
The non-polar hydrocarbon chain is soluble in fats and oil while the polar end is soluble in water (hydrophilic). So in grease formation, the non-polar hydrocarbon chain causes the soap to dissolve in the lubricating oil, thereby thickening it. Although the gelling action of all thickening agent is not fully understood (Nwagbara, 2005), most of the soap types are fibrous crystallites. Oil is believed to be held in the fibrous structure by capillary forces adsorption on the gel-formation molecules and physical entrapment within the interlacing fiber structure. Awoyale et al (2011) also asserted that base oil is trapped in the fibre network of the soap. The relative importance of each of these mechanisms depends on the type and degree of

dispersion of the thickener, the type and solvency of action of the oil, and the influence of any stabilizing agents and additives. Unfortunately, neither the chemical formula for grease nor the chemical equation that leads to its formation has been developed yet. Chemical formula and equation that leads to soap formation has earlier been given in this work.

2.2.2 Fat and Oil

Fats and oils are naturally occurring esters used as energy-storing compounds by plants and animals. They are derived from propane 1,2,3-triol, $\text{CH}_2\text{OH}-\text{CHOH}-\text{CH}_2\text{OH}$ (commonly known as glycerol or glycerine). This molecule has the capacity to combine with one, two or three molecules of carboxylic acid. In practice, most fats are triesters derived from propane 1,2,3,-triol and a variety of long-chain carboxylic acids, sometimes called fatty acids.

For example, a simple fat molecule is that derived from a mole of propane – 1,2,3-triol and three molecules of octadecanoic acid according to the equation (2.4)



In naturally occurring fats each molecule is derived from two or three different fatty acids. Table 2.1 gives some common fatty acids: fifty or so are found in nature, the vast majority having an even number of carbon atoms in their molecule (Hill and Holman, 1979).

Table 2.1: Some common fatty acids

Structure	Systematic name	Common name	Occurrence
$\text{CH}_2(\text{CH}_2)_{16}\text{COOH}$	Octadecanoic acid	Stearic acid	Mainly in animal fats
$\text{CH}_2(\text{CH}_2)_{10}\text{COOH}$	Dodecanoic acid	Lauric acid	Coconut oil, palm-kernoloic
$\text{CH}_2(\text{CH}_2)_{14}\text{COOH}$	Hexadecanoic acid	Palmitic acid	Most fats especially palm oil
$\text{CH}_2(\text{CH}_2)_7\text{CH}=\text{CH}(\text{CH}_2)_7\text{COOH}$	Octadec-9-enoic acid	Oleic acid	Most fats especially olive ore

Source: (Hill, and Holman 1979)

Fats containing large proportion of unsaturated acids tend to have low melting points: many are liquid at room temperature and these are called oils. They can be converted to solid fats by hydrogenation.

2.2.3 Liquid Lubricant

Lubricants commonly used in grease production are either derived from mineral oils or are classified as synthetic. The synthetic oils available are based on esters derived from animal or vegetable oils and other groups are derived from hydrocarbons (Liyedahl et al 1979).

However, lubricants that are derived from mineral oils predominate.

Mineral lubricants are obtained from crude petroleum and change very little on exposure to the air. A great variety of lubricants are produced, ranging from light to heavy oils. Crude oil is a complex mixture of hydrocarbons, mainly alkanes, cycloalkanes and aromatic. The residual oil from the primary distillation boils above 350°C and is a highly complex mixture

of involatile hydrocarbons. Most of it is used as fuel oil in large furnaces such as those in power station or big ships. A proportion of it, however, is used to make lubricating oil and waxes. Both these materials contain $C_{26} - C_{28}$ hydrocarbons; when pure these hydrocarbon are solid, but lubricating oil contains a complex mixture, each member of which depresses the melting point of the others so that the mixture is a liquid.

2.2.4 Types of Grease

There are seven types of grease available, each manufactured for special purposes. These include wheel bearing grease, universal joint grease, chassis grease, extended lubrication interval (ELI), multipurpose grease, extreme pressure grease (EP), and spindle grease. Generally speaking, greases are those lubricants, which at ordinary temperatures are in a solid, plastic state. Greases that are in a more fluid state are sometimes called semi fluid oils.

2.2.5 Classification

Greases may be classified according to their method and mode of manufacture; those obtained by saponification with a metallic base like sodium hydroxide and then mixed with mineral oil, those prepared by a cold process with calcium hydroxide and resin, and those obtained from residues composed of mixtures of fatty or mineral oils and the residual of petroleum distillation. In the chemical sense, the last mentioned is a solid mixture of oils and should not be considered grease because they are not formulated as grease (Billet, 1979). The use of only the first category of grease is recommended. Unlike petroleum jelly or any other type of grease, their soap content provided them with special qualities, namely, long persistence upon a surface and reduced viscosity during use. Their viscosity depends upon the viscosity of the dispersion medium, that is, the oil used in the manufacture of the grease. The base used for saponification has an important effect upon the lubricant's properties, and

accordingly, may constitute another criterion of classification. For example, grease with bases of calcium, sodium, aluminum, or lithium have different qualities as explained below.

1. Aluminum Soap Grease

Aluminum base greases are resistant at high temperatures and possess particularly adhesive properties, which minimize leakage. It is smooth, transparent grease with poor shear stability but excellent oxidation and water resistance, but tends to have poor mechanical stability and so is not suitable for rolling bearings (Mohammed, M.A.R 2013)

2. Calcium Soap Grease

It is one of the earliest known greases and is water resistant and mechanically stable. Calcium soap grease usually has a low dropping point; typically 95 °C. High temperatures cause a loss of water and a consequent weakening of soap structure, and therefore the use of this grease is limited to a maximum temperature of about 60 °C

3. Sodium Soap Grease

It is fibrous in structure and is resistant to moderately high temperature but not to water. Sodium soap grease has a high dropping point (175 °C) than calcium grease. In applications where high temperatures, dynamic stress, or centrifugal effects are significant, sodium-base greases are more efficient than calcium-base greases. However, they are emulsified by water.

4. Lithium Soap Grease

It is normally smooth in appearance but may exhibit a grain structure. Lithium soap grease offers both the water resistance of calcium soap grease and high-temperature properties of

sodium soap grease. They are water resistant and can be used at temperatures up to approximately 120°C this makes them useful in a wide range of applications and for this reason they are called multi-purpose greases. The vast majority of bearing used in industries have running temperatures well within the capability of the lithium soap thickened greases.

5. Mixed Soap Grease

It is generally manufactured by saponifying the fatty material with mixed alkalis derived from metals. One of the soaps usually predominates and determines the general character of the greases while the other modifies the structure in some way. This results, for example, in changes in texture and improved mechanical stability.

6. Complex Soap Grease

It is formed when two dissimilar acids are attached to the same metal molecules, thus restricting complexes to only polyvalent metals. There are several types of complex grease, such as, calcium complex grease, aluminum complex grease, and lithium complex grease. Calcium-complex greases commonly include a minor proportion of calcium acetate with fatty acid soap thereby forming multipurpose greases with dropping points above 260 °C.

7. Non Soap Grease

Many non-soap greases are present.

A. Polyurea

It is the most important organic non soap thickener. It is a low-molecular weight organic polymer produced by reacting amines with isocyanates, which results in an oil soluble chemical thickener. The polymer-thickened greases are used when semi-fluid type grease is

required, for example in certain gearbox applications where leakage is a problem (Billet, 1979).

B. Organo–Clay

It is the most commonly used inorganic thickener. Its thickener is modified clay, insoluble in oil in its normal form, but through complex chemical processes, converts to platelets that attract and hold oil. Organo–Clay thickener structures are amorphous and gel-like rather than the fibrous, crystalline structures of soap thickeners. This grease has excellent heat resistance since clay does not melt. The clay-thickened greases are very useful in special high temperature, low speed applications, such as the lubrication of oven chain and kiln car wheel bearings. However, the presence of the mineral oil limits their upper temperature use to approximately 200°C.

Others

Sometimes, for special applications, fluids other than mineral oils are used. The silicone greases lubricate bearings that have to operate under extremes of heat and cold. Carbon black is used as a thickener in some high temperature petroleum and synthetic greases. Organic powders and pigments, which are stable at elevated temperatures, are being used increasingly (Billet, 1979). Tables 2.2 and 2.3 show the properties and compatibilities of different grease soaps respectively

Table 2.2 Properties of different Greases

	Lithium	Calcium conv.	Calcium anhyd.	Al	Lithium complex	Calcium complex	Aluminum complex	Polyurea	Organo Clay
Dropping point	177- 204	96-104	135- 143	110	260	260	260	243	260
Max. Temp.	135	93	110	79	177	177	177	177	177
Water resistance	o/++	+ /++	++	++	+ /++	o/++	+ /++	+ /++	o/++
Oxidation stability	o/++	- /++	o/++	++	o/++	- /+	o/++	+ /++	+
Rust protection	- /++	- /++	- /++	+ /++	o/++	o/++	+ /++	o/++	- /++
Pump ability	o/++	+ /++	o/++	-	+ /++	o/+	- /o	+ /++	+
EP properties	v	v	v	-	v	v	v	v	-

Source: www.tribology-abc.com/abc/grease.htm

0 means no effect, - means negative effect, + positive effect, ++ highly effective, v means very good.

Hence 0/++ means from no effect to highly effective depending on the type of additive.

+ /++ means effective to highly effective, - /++ means from negative effect to highly effective

Table 2.3 Grease compatibility chart

	Lithium complex	Lithium	Al. Complex	Calcium complex	Barium	Sodium	Bentone	Silica gel	Polyurea
Lithium complex	-	V	X	V	X	X	x	v	V
Lithium	V	-	X	V	X	X	x	v	V
Al.complex	X	X	-	X	X	X	x	v	X
Calcium complex	V	V	X	-	V	X	x	x	X
Barium	X	X	X	V	-	X	x	v	X
Sodium	X	X	X	X	X	-	x	x	X
Bentone	X	X	X	X	X	X	-	v	X
Silica gel	V	V	V	X	V	X	v	-	X
Polyurea	V	X	X	X	X	X	x	x	-

Source: www.tribology-abc.com/abc/grease.htm

v is for compatibility, x is for non-compatibility

2.2.6 Consistency.

Consistency in greases is analogous to viscosity in oils, the corresponding coefficient being defined in the same way as that of viscosity. Sometimes the reciprocal relation between the velocity gradient normal to the direction of motion and the tangential force on the unit of surface is used. This reciprocal relation is called mobility. The term consistency is also used to define the properties of greases: structure (smooth, fibrous, spongy), elasticity (rigid, elastic), and ductility (fibrous, soft). Consistency depends on different factors such as the nature and quality of the metallic soap content, percentage of free fatty acids, percentage of alkaline substances used in the saponification process, speed of cooling, temperature of

dispersion, method of manufacture, temperature during storage, action to which it has been subjected during use, and water content. In general, soap content is the most important factor. Grease with a high percentage of soap has a high consistency. The consistency of greases during operation is modified by time of use and by the degree of mixing and stirring. Any grease or plastic materials having consistency that depends on the shearing actions to which they have been previously subjected are customarily referred to as thixotropic (Nolan, 2004).

The friction developed in bearings, the operating temperature of the bearings, the flow of grease, and the carrying capacity, all depend on consistency, which should be considered the fundamental property of these lubricants. In contrast to oils, the consistencies of greases exhibit large variations, depending on the parameters just mentioned. Additives, the most important of them being graphite and mica, are used to enhance the lubricating qualities of greases. Chalk, talcum, and gypsum are used to enhance their dynamic operating characteristics (Nicolae, 1962). Consistency is determined by measuring the flow of grease through a capillary tube at various pressures. Its value varies because the relation between pressure and flow is nonlinear, as in the case of viscous fluids, but in general, consistency depends on pressures. Consequently, determinations must be carried out at various pressures. Another laboratory method of determining consistency is by measurement of the depth to which a standard body subjected to a given force penetrates into a mass of grease.

Establishment of the melting point and the leaking point of grease are of practical importance because the maintenance of grease films within bearings depends on these points. The melting and leaking points also depend on the soap content, for they increase with the quantity of soap in the grease and on the mineral oil and water content of the greases. The

flash point of grease is defined in the same way as for oils. A large proportion of fats, or of free fatty acids, facilitates oxidation and alteration of the lubricants. Grease used in ball bearings should be sufficiently stable to resist centrifugal forces, which tend to separate the component substances. It is also important to determine the corrosive action of greases in establishing their possibilities for utilization. This is done by spreading the lubricant on a copper plate and noting the colour modification of either the metal or the grease (Nicolae, 1962).

2.2.7 Consistency Number (Grades)

Greases are neither Hookean solids, nor Newtonian fluids, but are “in-between” viscoelastic (semi-fluid) materials that display differing physical properties depending on the applied conditions (Nolan, 2004). In selecting engine oil, the first concern is the appropriate viscosity. A grease, is however, graded by its hardness, and not by its viscosity. It is expressed in terms of American Society for Testing of Material (ASTM) penetration or National Lubricating Grease Institute (NLGI) consistency number. ASTM penetration is a numerical representation of an actual test of an object as it sinks into grease under a specific test condition. NLGI's classification defines nine grades, each associated to a range of ASTM worked penetration values, and measured using the test defined by standard ASTM D217 “cone penetration of lubricating grease”. This involves two test apparatus. The first apparatus consists of a closed container and a piston-like plunger. The face of the plunger is perforated to allow grease to flow from one side of the plunger to another as the plunger is worked up and down. The test grease is inserted into the container and the plunger is stroked 60 times while the test apparatus and grease are maintained at a temperature of 25 °C. Once worked, the grease is placed in a penetration test apparatus. This apparatus consists of a container, a specially-configured cone and a dial indicator. The container is filled with the grease and the

top surface of the grease is smoothed over. The cone is placed so that its tip just touches the grease surface and the dial indicator is set to zero at this position. When the test starts, the weight of the cone will cause it to penetrate into the grease. After a specific time interval the depth of penetration is measured. It is measured in tenths of a millimeter.

NLGI uses a consistency number 000 to 6 to classify the grease, with use of ASTM penetration test results. For example, a grease having the consistency number 000 is soft, like ice cream at a room temperature of 25⁰C, whereas, grease having consistency number 6 is hard-like butter just removed from a refrigerator. NLGI #2 grease is suitable for most ambient temperature for either light or heavy applications. However, for extremely low ambient temperature, NLGI 0 or 1 is recommended. The National Lubricating Grease Institute (NLGI) of America and the American Society for Testing of Materials (ASTM) provide the standards and equivalent measurement to assist in the use of lubricating greases for automotive, industrial plant, machinery and equipment selection in general. The corporate and equivalent values as provided by the two bodies are shown in Table 2.4 The consistency of industrial greases are classified by the distance in tenths of a millimeter, that a standard cone penetrates a sample of the grease under standard conditions at 25°C

Table 2.4 NLGI consistency number and equivalent ASTM penetration value.

NLGI Consistency (Grade no.)	ASTM Worked Penetration at 25°C (Penetration in 0.1 mm)	Appearance	Consistency food analog
000	445 – 475	Fluid	cooking oil
00	400 – 430	semi-fluid	Applesauce
0	355 – 385	very soft	Mustard
1	310 – 340	Soft	tomato paste
2	265 – 295	“normal” grease*	peanut butter
3	220 – 250	Firm	vegetable shortening
4	175 – 205	very firm	frozen yogurt
5	130 – 160	Hard	smooth pate
6	85 – 115	very hard	cheddar cheese

Source: www.tribology-abc.com

“Normal” grease* means the most common grease.

NLGI grades 0, 1 and 2 are applied in highly loaded gear transmissions; grades 1 through 4 are often applied in rolling bearings where grade 2 is the most common (www.tribology-abc.com). The quality of the grease is governed by the fluid used, the ratio between the fluid and thickener, the chemical structure of the thickener and its additives. Non-soap grease can be made but are not significant in general lubrication.

2.2.8 Dropping point.

The dropping point of soap-thickened lubricating grease is the temperature at which it passes from a semi-solid to a liquid state under specific test conditions. It is an indication of the type of thickener used, and a measure of the cohesiveness of the oil and thickener of grease. (Totten, G.E., 2006). Dropping point is used in combination with other testable properties to

determine the suitability of greases for specific applications. It is applicable only to greases that contain soap thickeners. Greases with other thickeners, such as many synthetic greases, do not change state. Instead, they separate oil, and the dropping point as a phase transition does not apply. It is useful to assist in identifying the grease as to type and for establishing and maintaining bench marks for quality control. The results are to be considered to have only limited significance with respect to service performance because dropping point is a static test. Cooperative testing indicates that, in general, dropping points by Test Method D2265 and Test Method D566 are in agreement up to 260°C. In cases where results differ, there is no known significance. However, agreement between the manufacturer and purchaser as to test method used is advisable. (<http://www.astm.org/Standards/D2265.htm>)

The dropping point test procedures are given in ASTM standards D-566 and D-2265. The test apparatus consists of a grease cup with a small hole in the bottom, test tube, two thermometers, a container, stirring device if required and an electric heater. The inside surfaces of the grease cup are coated with the grease to be tested. A thermometer is inserted into the cup and held in place so that the thermometer does not touch the grease. This assembly is placed inside a test tube. The test tube is lowered into the container which is filled with oil in D-566 and has an aluminum block in D-2265. Another thermometer is inserted into the oil/block. To execute a test, the oil/block is heated, while being stirred, at a rate 4.4 °C to 6.7 °C per minute until the temperature is approximately 16.7 °C below the expected dropping point. The heat is reduced until the test tube temperature is 2.2 °C or less than the oil/block temperature. Once the temperature has stabilized the sample is inserted. The dropping point is the temperature recorded on the test tube thermometer, plus a correction factor for the oil/block temperature, when a drop of grease falls through the hole in the grease cup. If the drop trails a thread, the dropping temperature is the temperature at which the thread breaks.

2.2.9 Additives

Chemical additives similar to those used in lubricating oils also are added to grease to improve their performances such as oxidation resistance, rust protection, extreme pressure properties etc. In a study by Mohammed, (2013) he concluded that the best weight percentages to all types of grease which give good properties are 1.5% extreme pressure additive, 3% graphite, 1% molybdenum disulfide, 2.5% carbon black. On the other hand, he noted that the best weight percentage for corrosion inhibitor is 1% to lithium-calcium grease, 2% to lithium grease, and 3% to sodium grease. He also concluded that there is no need to add corrosion inhibitor to calcium grease.

Although 1-naphthyl (phenyl) amine is the common choice as an oxidation inhibitor at about 0.1-0.5% concentrations, other amines; phenolic, phosphate, sulfur and selenium inhibitors are also used. A common procedure involves trying a number of commercial additives in varying concentrations to determine the least expensive means of obtaining satisfactory oxidation inhibition. In many greases 0.2-0.3% of an amine metal deactivator is also added to avoid staining of copper and to minimize any catalytic effect of copper on oxidation of the grease (Nicolae, 1962). Although, most greases offer some inherent protection against rusting of coated surface, additives e.g., amine salt, metal sulfonate and cycloparafin salts (naphthenate), esters, and nonionic surfactants, are used to provide added resistance against water and salt-spray corrosion. A dispersion of sodium nitrite has been especially effective in some multipurpose grease (Nicolae, 1962). Extreme Pressure (EP) additives are not required in greases for most ball and roller-bearing applications nor for general purpose industrial use, but they are necessary to minimize wear of bearings under shock load conditions characteristics in steel rolling mills, for many gear applications, and for sliding conditions that involve boundary lubrication- Solid powders are added as fillers in greases for extreme

conditions of boundary lubrication. Among those employed are graphite, molybdenum disulfide, talc and zinc oxide (Nicolae, 1962). The lubricant industry has come a long way in relatively short period of time to limit the use of dangerous substances such as lead, asbestos and chlorinated solvent that were once common place (Kieke and Klein, 2004). Glycerol also is present in many lubricating greases. Frequently, the glycerol remains after the formation of the metallic soap thickener when natural fats are employed as raw materials. Even with some soap that are produced from fatty acids, glycerol may be added for its stabilizing effect on the soap structure when used in combination with a small amount of water (Billet, 1979).

2.2.10 Choice of grease as Lubricant

In lubricating any given mechanism, a fundamental choice must be made. Will the lubricant be a liquid, a solid or an intermediate product, grease, which may range from semi-fluid to semi-solid? The choice is made, in fact, by the machine designer, who looks at expected operating conditions and the properties of available lubricants and decides on the lubrication system to be used. The designer finds several advantages in using greases. One is cost. Greases assist seals. Oils require more effective, more expensive seals. If vertical shafts are involved, effective sealing of oil is quite difficult and costly. Sealing greases is less complex and more economical. Another significant cost saving is due to the decreased complexity and space required when grease is used. To lubricate a bearing with oil, we frequently find an oil-filled sump below the bearing and a pumping device, which lifts the oil from the sump to the bearing. The oil then drains back to the sump. Compare this with the corresponding grease lubricated bearing. Neither pump nor sump is required. Housing around the bearing holds a small supply of grease, which does not drain away. Such a device, which is less complex and more compact, would be less expensive than oil lubricated bearing.

Many other characteristics of grease are helpful to both designer and user of the equipment. Some of the advantages in using grease are highlighted as follows:

1. Low Speed Combined with High Pressure

Grease is usually the preferred lubricant when bearings are operating at speeds below 100 rpm at high load. If very high-viscosity oil is used, an adequate lubricating film would be formed. However, such oil has very poor pumpability and often cannot be employed. Lower viscosity oil would not form an adequate lubricant film under these conditions. Because of their high apparent viscosity at low speeds, grease would form a lubricant film of adequate thickness. Such a film, despite the high load would lubricate successfully under these adverse circumstances.

2. When Machine Parts Are Badly Worn

A mechanism designed for oil probably will be lubricated with oil for the life of the machine. However, as equipment grows older, wear causes machine clearances to increase until adequate oil films can no longer be maintained in service. At this juncture, a change to grease is helpful since with increased clearance, shear rate of the moving mechanism - bearing, gear or whatever - decreases. At low shear rate, grease films are much thicker than oil films, providing adequate lubrication. A change to lubricating grease permits the machine to continue in service at least until a maintenance shutdown can be scheduled. Some gear cases designed for use with gear oil have operated for years with greases ranging from NLGI #000 to #2 in consistency

3. When Noise Reduction Is Important - As machines become worn, gears, bearings and shafts develop looseness. Loose, sloppy fits lead to noisy operation. Under such

circumstances, the thick films provided by grease cushion the excessive movement and significantly reduce the noise level. Though most lubrication is carried out with oils under many situations encountered in service, the properties of grease are superior, making them the lubricants of choice.

4. To Decrease Dripping and Spattering of Lubricant

Greases assist seals. Thus, grease tends to stay in its housing and not leak or drip out. This is particularly true as seals become worn. The effect on house-keeping is obvious. In processing foods, pharmaceuticals or other products for which contamination must be avoided, grease minimizes problems.

5. To Decrease Frequency of Lubrication

Machine design frequently requires the placement of bearings where they cannot be easily serviced without shutting down production. In these applications, grease can provide lubrication for long periods of time with only infrequent lubrication. Electric motors in plants are often lubricated annually or even less often. Some electric motors and gears are lubricated for life at the factory. Obviously, infrequent lubrication requires high quality greases.

6. To Seal out Contaminants

Since greases make seals more effective, they assist in keeping out contaminants. In mining operations and steel mills, dust, dirt and water must be excluded. In paper mills, corrosive water and pulp are potential contaminants. In chemical plants and many other environments, corrosive gases and liquids must be kept out. If corrosive contaminants do enter the bearing cavity, grease is more protective of the metal surface than oil would be. When a machine is

stopped, oil drains away from bearing surfaces, leaving them essentially unprotected. Grease does not drain away from those surfaces. Thus a protective grease film remains on the bearing surfaces to protect against corrosion.

7. For Intermittent Operation - The fact that oil drains away when a machine is stopped, but grease does not, is significant also whenever equipment operates intermittently, changes speed, or reverses direction. On start-up, bearings are dry until oil has been drawn in between surfaces, forming a lubricating film. Grease does not drain away when the device is stationary; on start-up, a lubricating film forms immediately. Thus, for intermittent operation, grease protects against wear that would be found with oil as the lubricant.

8. To Suspend Solid Additives - Some solids have lubricating properties in varying degrees when mixed with oils or greases, the mixture often performs better than the oil or grease alone does. Typical solids are graphite, molybdenum disulfide and zinc oxide. When mixed with oil, the solid tends to settle out leaving little, if any, in suspension. The solids can be ground very fine at considerable cost; yet the amount remaining in suspension is small. When mixed with grease, even coarse solids remain in suspension indefinitely at any proportion desired.

9. High Temperature

Many industrial operations subject equipment and lubricants to very high operating temperatures. Kiln car, Ladle car and Furnace door bearings are examples. Oil lubrication tends to develop too thin a film and poses a significant fire hazards. High temperature greases sometimes, containing solids give quite satisfactory lubrication.

10. Shock Loading

Shock loading is an instantaneous and severe increase in stress. Such loading tends to rupture a thin lubricant film, leading to rapid wear. Grease appears to cushion against such sharp rupturing of the film. Shock loading occurs, for example, in rolling mills when a thick slab hits rollers, which have been preset to a lesser thickness (Sote 1997).

2.3 Grease Manufacturing Methods.

For over 4,000 years, man has made use of solid or semi-solid materials for lubrication. During this time, many methods, ranging from a simple hand-stirred pot over an open fire to a continuous manufacturing process, have been used for their manufacture. This work concentrated on three methods of manufacturing lithium hydroxystearate grease. These methods are the **Stratco** Contactor process, the **Texaco** Continuous Process and the **Atmospheric Kettle** process.

2.3.1 Stratco Contactor Process

The STRATCO Contactor consists of a pressure vessel; a circulation tube and a hydraulic head assembly with the mixing impeller and driver. The outstanding feature of the Contactor is its highly turbulent circulation in a closed cycle path. All energy input through the mixing impeller is expended within the materials being mixed and there is virtually no pressure differential between the Contactor's inlet and outlet. The high dispersion mixing in the Contactor is achieved by the hydraulic head assembly. Frequent and forced changes in the velocity and direction of flow occur around the impeller area. The material feed flows directly to the impeller from where it emerges uniformly mixed and dispersed. Turbulence is established between the stationary shear vanes and the blades of the impeller, resulting in a zone of high shear and intense mixing.

As the material passes through the impeller, its velocity is greatly increased. At the discharge side of the impeller, the slightly swirling stream is violently impinged against the diffuser vanes. The vanes then straighten the stream into axial turbulent flow and the direction of flow is reversed at the bottom of the hydraulic head. A double walled circulation tube is installed inside the Contactor to create a continuous flow path for the soap concentrate. Material is pulled down through the center of the circulation tube by the impeller and then forced through the annular space formed by the circulation tube and Contactor wall. The outside of the Contactor is jacketed. Heat transfer oil is circulated in both the jacket and inside the circulation tube to provide heating or cooling. An alternate design can use high-pressure steam. The impeller is connected to a two-speed motor normally turning at 1200 rpm. A mechanical seal seals the shaft from the process materials. This seal can be replaced from outside the Contactor without removing the head or the motor.

The STRATCO Contactor process is similar to the atmospheric kettle process but is slightly more sophisticated. Dry materials are charged through the top manway of the Contactor, while base oils are normally pumped in through meters or added through weigh tanks. The dry materials added to the Contactor may consist of acids and glycerides, such as hydrogenated castor oil, beef tallow or other combinations, along with the lithium hydroxide and some water. The Contactor is then sealed and heating commenced. This startup operation requires about 20 minutes. Normally, the amount of raw materials initially charged to the Contactor results in producing a soap concentrate in the Contactor containing approximately 30-weight percent soap. However, for some conventional lithium soap greases, a soap concentrate containing up to 40-weight percent soap can be produced.

The water added, as well as the water of reaction, increases in the Contactor's operating pressure. Pressures in the range of 4.8 to 6.9 bars are typical of those used for efficient and

essentially complete saponification. This pressure prevents foaming of the soap concentrate as well as accelerating the saponification reaction. The Contactor pressure is maintained by manually venting or by automatic controls as the temperature rises. Very rapid heating occurs during saponification when the ingredients are circulated between the circulation tube and the shell. The temperature in the Contactor rises to 204.4oC in approximately 30 minutes. Upon reaching the desired maximum temperature, the pressure is vented to atmospheric conditions. Cooling or quench oils are then added to reduce the temperature below the soap crystallization temperature. At this point, the Contactor's contents are transferred to an atmospheric kettle and the grease is finished with additional oils and additives. As outlined above, the complete process of charging the raw materials, cooking, quenching, transferring the soap concentrate and rinsing requires less than two hours. This procedure results in maximizing the volume of soap concentrate produced in a single Contactor over a given period of time. An alternate procedure is to partially or completely finish the grease in the Contactor. This option takes advantage of the high shear milling action of the Contactor's impeller. Many times such further processing in the Contactor will eliminate the need to mill NLGI #1 grade greases. The Contactor can be utilized to prepare almost every metallic soap based grease. Other than adjusting operating conditions as appropriate, the only additional step required to take advantage of this flexibility is more complete rinsing between the different soap batches.

In summary, the Contactor permits the grease manufacturer to use an unlimited variety of raw materials. The ability to perform these operations under pressure accelerates saponification while allowing complete control of all the manufacturing variables. This includes minimizing the amount of excess water required to accomplish complete and efficient saponification. The STRATCO Contactor is supplied in many sizes 617 to 8,113 litres

operating volumes. Various small pilot units are also supplied with the most popular size being a 55.1litres unit.

2.3.2 Texaco Continuous Grease Process

The Texaco Continuous Grease Process (TCG) is well documented in the literature. It is basically composed of three major sections: the reactor, the dehydration and the finishing sections. All raw materials for the TCG must be in liquid form. The process described for manufacturing lithium grease uses a hot, stirred, 15,285 litres solution of 14% hydroxystearic acid in oil maintained at about 99.5°C. The lithium hydroxide is dissolved in water in 1,762 litres stirred tank containing about 9.3% lithium hydroxide monohydrate. A third feed tank holds oil at about 173°C. The liquid raw materials from the feed tanks are metered to the reactor where they are heated to 350°C. High recirculation rates and residence times are maintained in the reactor to ensure complete reaction. The recirculation system is adjusted to maintain a high pressure of up to 6.9 bars by passing through partially closed valves. The stream is then directed to the dehydration section where additional heat and often times additional hot oil from a storage tank are added. This section removes the water or other volatiles under reduced pressure at a temperature of 185°C. The stream is then cooled by the addition of cold oil followed by coolers in the finishing section. Additives are also metered in at this point. The TCG includes a consistometer, which senses the amount of finishing oil needed to produce a particular grade of grease. The finished grease is then milled and sent to bulk storage tanks. TCG plants are built in several sizes for processing 1,360 to 2,268 Kg of grease per hour. The raw material feed tanks are sized from 1,762 to 5,285 litres each. The unit can be used to manufacture several types of grease.

2.3.3 Atmospheric Kettle Processing.

Nearly all grease plants utilize atmospheric or open kettles. Many kettles are fabricated with simple agitators, which come close but do not scrape the walls of the kettle. Later designs use a counter rotating blade system with hinged wall scrapers. Some are also constructed to operate under higher than atmospheric pressures but most are open to the atmosphere. Like the STRATCO Contactor Process, atmospheric kettle processing can utilize essentially all of the dry and/or liquid raw materials known for grease making. Processing becomes critical with respect to maintaining sufficient water and time to dissolve all of the lithium hydroxide and force complete saponification. This problem is particularly evident when saponifying glycerides such as beef tallow and hydrogenated castor oil. Incomplete saponification leaves fragments or partial esters, which affect certain grease properties. Incomplete solution of all the lithium hydroxide sometimes leaves small particles in the grease.

Approximately 10 to 12 times more water is required to saponify the glycerides in the open kettle process than with the STRATCO Contactor. Even with this amount of excess water, all of the available glycerides are not used to form the soap thickener. Finally, processing time in the open kettle is prolonged because of this large amount of water and poor heat transfer and slow agitation characteristics of kettles. Kettles are fabricated in various sizes.

2.4 Prospect of Using Plantain Peel Ash as the Source of Alkali.

It has been stated earlier that ashes of agricultural materials can be a source of industrial alkali. The present work is devoted to investigating the suitability of plantain peel ash as a source of alkali for lubricating grease production. Research has shown that plantain peel ash has been used to produce soap of good quality. Hence, it is believed that soap produced from the ash can equally be a good grease thickener.

2.5 The Plantain

The plantain, scientifically named *musa Paradisiaca* is a very starchy banana that is usually used in cooking (www.all-creatures.org/recipes/I-plantain.html). It is a fast - growing plant 3-5m high with herbaceous stem. The fruits grow in bunches of up to 200 fingers each (www.fao.org). Plantains are widely grown across the world's tropical regions. They are major food crops in developing countries, and are also an important export crop to industrial countries. They are easy to grow and production is relatively stable. In addition, the fruits are highly nutritious, containing large amounts of carbohydrates and minerals such as phosphorus, calcium, and potassium as well as vitamins A and C. They are also important sources of revenue for many small-scale farmers. About 90% of the world's plantains are grown on small farms and consumed locally. An estimated 20 million people eat plantain as their major source of dietary carbohydrate. They are particularly important in East Africa, where they constitute the main staple food for about 50% of the population. In that part of the world, the annual consumption reaches over 400 kg per person.). Almost 75% of the world's plantains were grown in Africa. Uganda is the largest producer of plantains and produces about 9 million tons per annum (www.fao.org). The fruits can be fried, baked, or roasted, and are also sold in pulp form, as chips, and in confectionery. In some countries, they are used to produce alcohol. The leaves and pseudo stem are also often used, for example, for wrapping food, for thatching, and in textile manufacture. The fruits can also be used as animal feed. The major pests are the banana weevil and parasitic nematodes. Studies have revealed that if plantains are infected with both weevils and nematodes, yield losses may reach 85%. Another major constraint of plantain is that the fruits are highly perishable. At ambient tropical temperatures, plantain has an average market life of 1 - 10 days, compared to several weeks for yam, for example. In Nigeria, plantains are grown at the following states of the federation; Rivers, Cross River, Imo, Anambra, Ondo, Lagos, Ogun, Oyo, kwara,

Benue, Plateau, Kogi, Abia, Enugu, Edo and Delta with annual production of 1,855,000 Metric tons

2.6 Potassium Hydroxide

The major constituent of plantain peel ash is potassium hydroxide (Onyeagbado et al 2002). Potassium hydroxide is a chemical compound with formula KOH. Pure potassium hydroxide forms white, deliquescent crystals. For commercial and laboratory use, it is usually in the form of white pellets. A strong base, it dissolves readily in water, giving off much heat and forming a strongly alkaline, caustic solution. It is commonly called caustic potash. It closely resembles sodium hydroxide in its chemical properties and has similar uses, for example, in making soap, in bleaching, and in manufacturing chemical, but is less widely used because of its higher cost. Potassium Hydroxide is prepared chiefly by electrolysis of potassium chloride; commercial grades of it sometimes contain the chloride as well as other impurities. It is a major industrial chemical used as a base in a wide variety of chemical processes. It is used as a catalyst in reactions like the production of biodiesel. The advantage of using potassium hydroxide (KOH) and not sodium hydroxide (NaOH) is that NaOH “clumps” and KOH does not. Some uses of KOH include acrylate ester copolymer coating, defoaming agents used in the manufacture of paper, formulation aid for food, PH control agent, polyethylene resins, and textile processing. Other uses include in veterinary medicine, in disbudding calves horns and to dissolve scales and hair; in human medicine, to diagnose fungal infections, and as a wart and cuticle solvent; in manufacture of cleansers. This chemical is also used in washing powders, some denture cleaners, non-phosphate detergents, and drain or pipe cleaners. A very significant use of KOH in terms of significance to the average home consumer is that alkaline batteries use an aqueous solution of KOH as an

electrolyte. Thus, potassium hydroxide helps to power flashlights, smoke detectors, and other battery powered household items.

2.7 Bio-Alkali

Bio-alkali is the alkali derived from the ashes of burnt biomaterials. Agricultural materials contain a good percentage of mineral salts. These include calcium, phosphorous, iron, sodium, potassium and so on, as shown in Table 2.3 When these materials are burnt in air, carbohydrates, fats, proteins and vitamins will all burn away. The resulting ashes contain oxides of these minerals. Some of these are basic oxides of potassium and sodium, which when dissolved in water yield their corresponding hydroxides (alkali) according to the equations (1.1) and (1.2)

Table 2.5 Mineral Salt composition of some raw foods mg/100g edible portion

Food Product	Calcium	P	Fe	Na	K
Plantain	7	30	0.7	5	385
Rice	32	221	1.6	9	214
Soya bean	226	4	8.4	0.5	1677
Wheat (whole grain)	1308	1016	0.6	532	1745
Yam tuber	20	69	0.6	-	600
Cowpea (mature dry)	74	426	5.8	35	1024
Groundnut (peanut)	59	409	2.0	5	674
Sorghum (whole grain)	23	263	3.6	-	-

Source: Enwere (1998)

Alkali is derived from the Arabic word “al-kali” which means the dust or ashes (Bajah and Godman 1976). This was based on its earlier mode of extraction. Soda (Sodium carbonate) was made by burning marine plants to ashes and extracting the soda from them, while potash (Potassium carbonate) was made by burning wood in iron pots and extracting the potash from the ashes. The name “Potash” actually came from the compound word “pot-ash” (Bajah and Godman 1976) The method of making these “mild” alkalis into “caustic” alkalis by treatment with lime was practiced in the time of Pliny (www.simplestarpages.com) in connection with the manufacture of soap, and it was known that the ashes of shore-plants yielded a hard soap and those of land plants a soft one. But the two substances were generally confounded as “fixed alkali” (carbonate of ammonia being “volatile alkali”), till Duhamel du Monceau in 1736 established the fact that common salt and the ashes of sea-plants contain the same base as is found in natural deposits of soda salts (“mineral alkali”), and that its body is different from the “vegetable alkali” obtained by incinerating land-plants or wood in iron pot and extracting the potash (hence the name, pot-ash, and hence a derivation of potassium).

Later, Martin Heinrich Klaproth (Bajah and Godman, 1976) finding vegetable alkali in certain minerals, such as Lucite, proposed to distinguish it as potash, and at the same time assigned to the mineral alkali the name natrium, which survives in the symbol, Na, now used for sodium. The word alkali supplied the symbol for potassium, K (kalium). Analysis of alkalis derived from vegetable matter ashes by Nwoko (1980) and others (Onyekwere, 1996, Kuye and Okolie, 1990), showed that the extract was chiefly potassium hydroxide with some quantities of sodium hydroxide. Other metallic ions present constituting as a whole about 2% of the metallic ions present, were Ca^{++} , Cr^{++} , B^{++} , Zn^{++} , Fe^{++} , Pb^{++} and Ni^{++} . Tests have shown that bio-alkali produces harder soap than those produced from pure potassium

hydroxide, and this is because of the presence of the above metallic ion and notably sodium (Onyeagbado et al 2002).

Generally speaking, alkalis are soluble bases. A base is a metallic oxide, or hydroxide, which neutralizes an acid to form a salt and water only. In solution, the bases form hydroxides. Common alkalis and their formulae are Sodium hydroxide (Caustic soda) NaOH, Potassium hydroxide (Caustic potash) KOH, Ammonia solution NH_4OH and Calcium hydroxide (Lime water) $\text{Ca}(\text{OH})_2$. Alkalis have very low concentration of hydrogen ions when dissolved in water, and their pH values are above 7 (Sambal's Science Web 2006). Sodium carbonate (correctly speaking, is a salt) is included as an alkali in showing the uses of alkalis (Baja and Godman 1979). Ammonia solution also strictly speaking is not a hydroxide (Holderness and Lambert, 1976). A solution of sodium carbonate has an alkaline reaction, and it can be used in place of an alkali to neutralize an acid. The reaction is not neutralization by definition, as carbon dioxide is evolved. Both sodium and potassium carbonate have alkaline reactions with indicators, and they are called mild alkalis. The remaining alkalis are called caustic alkalis because they have a corrosive action when concentrated.

2.7.1 Properties and Uses of Alkalis

(a) Properties

The properties of alkalis are as follows;

- (i) They neutralize acids to form salt and water
- (ii) They change red litmus to blue, methyl orange to yellow and phenolphthalein to pink
- (iii) They give off ammonia gas (not ammonia solution) when they are warmed with an ammonium salt
- (iv) They have soapy feel
- (v) They have bitter taste

(b) Uses

Alkalis are used in large quantities in most chemical industries. Bases are less important commercially. Some of the more important uses of alkalis are as follows;

- (i) Caustic soda and potash are used in the production of soap, paper, artificial silk, mercerized cotton and lubricating grease.
- (ii) Sodium carbonate is used in water softening and also in the manufacture of glass and soap
- (iii) Lime is used in the manufacture of fertilizer
- (iv) Ammonia is used in making household cleaners

2.7.2 Extraction of Bio Alkali

Caustic solution is also known as “lye water”. There are various methods of extracting bio alkali. Two are described here.

Method 1

The method described here was originally prepared and printed as a booklet, at the request of Christians in Burma, to help in situations where normal supplies of soaps are not readily available; and where caustic soda is hard to come by. This information was needed because soap can be powerful in stopping the spread of certain diseases (Peter, 1986).

(a) Ashes

Dried palm bunches, dried out banana peels, cocoa pods, kapok tree wood, and oak wood, (or for really white soap, apple tree wood) make the best lye ashes. Ordinary wood used in cooking will do also. Whatever wood is used, it should be burnt in a very hot fire to make very white ashes. When cold, these are stored in a covered plastic bucket or wooden barrel, or stainless steel container. If these are not available, a clay pot-jar which has been fired in a pottery-making kiln (not just dried in the sun) will do.

(b) Soft Water

Water from a spring or from showers of rain is called “soft water”, because it does not have metallic or acidic chemicals in it. This makes it useful for soap making, as there are no other chemicals in it which would get in the way of making soap. Ordinary bore well or river water can be used for making soap, but this will sometimes need a washing soda or baking soda added to it. Otherwise, some of the chemicals in the water will get in the way of making the soap. If ordinary water is to be used, it will be necessary to test if soda needs to be added by simply trying to make soap bubble up (foam) in it. If the soap easily foams up, the water is probably ok as it is. Otherwise adding a little bit of soda at a time, stirring it to make it disappear, until the water will foam the soap up, will be necessary.

(c) Safe Containers

Any of the types of containers, buckets, barrels or jars described in the Ashes or Soft Water sections are called “Safe containers”

(d) Making Lye Water

A large barrel or drum to be used to make the lye water can have a tap or hole at a level a little above the bottom, and some kind of filter placed on the inside, around the opening. The barrel will be filled with white ashes to about 10cm or 0.1m below the top, and boiled soft water poured over the ashes. More cold (soft) water should be added slowly until liquid drips out of the barrel top. The tap should be closed or the hole blocked. More ashes could be added to top the barrel up again, and more soft water but so much water should not be added that the ashes swim. This should be left to stand for four or more hours (or even over night if there is time). Then the lye water should be allowed to drip into safe containers by opening the tap or unplugging the hole. When the brown lye water stops coming out of the barrel, or

ash container, then more soft water should be poured through the ashes, collecting the lye which comes out in a separate “safe” container (as this lye may be weaker than the first lot). This process is repeated until no more brown liquid comes out of the ashes. The lye is stored in a safe container and the ashes dug into the vegetable garden. It should never be stored in aluminum or tin container. They are badly corroded by the caustic solution.

(e) Lye Water Strength

If an egg or potato floats just below half way, or a chicken feather starts to dissolve in it, the lye water is at the right strength for local soap production. If the egg will not float, then the lye water could be boiled down to make it stronger. If the egg seems to pop up too far, the lye water is too strong, and a little bit of soft water (a cup at a time) would be added stirring the lye water, until the egg floats so that its head pops up.

Method 2

This method was reported by Onyegbado et al (2002) of the Department of Chemical Engineering, University of Port Harcourt, Nigeria, to improve the quality of ash-derived alkali soaps in order to make them amenable to all the uses previously listed for potassium based soaps. The lye water produced can also find other application where alkali uses are required. The apparatus and materials used included an oven, weighing balance, a large shallow tray called “combustion pan”, a sieve set, a spectrophotometer and laboratory glassware.

Unripe plantain peels were collected from Choba village, near Port Harcourt, Nigeria. They were dried in an oven at 100 °C for two days to constant weight. The peels were thus said to be “bone-dried”. The bone-dried peels were placed in an open “combustion pan” and heated till the peels ignited. The ignition temperature, which was presumably very high, could not

be measured with a mercury-in-glass thermometer. A metallic rod with a wooden handle was used to turn the burning peels, thus ensuring uniform combustion. The ashing lasted three hours. Another sample of the “bone-dried” peels was not ashed but ground into a fine powder. No alkali was detected when this sample was leached with distilled and deionized water. The ash sample was homogenized by crushing by hand and then sieved to remove large particles. Kuye and Okorie (1990) had shown that a particle size of 1.06×10^{-4} gave the highest concentration of potassium hydroxide when slurry of the ashed sample containing 0.15kg of the ashes in 2.5dm^3 of distilled and deionized water was kept for eight hours at 60°C . In their study, the slurry prepared under the above conditions was kept for forty-eight hours in a further attempt to ensure maximum extraction of the alkali. Subsequently, the slurry was filtered to obtain the extract. Spectrophotometric analysis of the extract for metallic ions was done using an atomic absorption spectrophotometer (AAS) available at NAFCON, Onne, Rivers State, Nigeria. The percentage compositions of the metal ions in the extract were approximately as follows;

Sodium ion = 15.86%, Potassium ion = 84.14%. Other ions were insignificant

2.7.3 Industrial Manufacture of Alkali

Sodium hydroxide and potassium hydroxide are obtained from electrolysis of sodium chloride and potassium chloride respectively. Since both alkalis are extracted the same way, this work will only discuss the standard electrolytic process for the manufacture of sodium hydroxide. This is described in several textbooks.

Sodium hydroxide is obtained when a solution of sodium chloride is electrolysed. In solution, sodium chloride ionizes thus;



The water molecules also ionize slightly



At the cathode, the hydrogen ions are discharged in preference to sodium, while at the anode; the chloride ions are discharged in preference to the hydroxyl ions.

Three types of cells have been devised for the production of sodium hydroxide electrolytically: These are the diaphragm cell, the mercury cathode cell, membrane Cell

(a) The Diaphragm Cell:

The cell consists essentially of a porous diaphragm, closely covered on the outside with steel gauze, which acts as the cathode shown in Fig.(2.1). The anode, which is made of graphite, dips into the concentrated solution of sodium chloride (brine) in the porous diaphragm. The brine gradually percolates through the diaphragm. During the electrolysis, chlorine is liberated at the anode and hydrogen at the cathode. Sodium ions collect at the cathode. The discharge of hydrogen ions (from water in the brine) leaves hydroxyl ions at the cathode; sodium and hydroxyl ions, together with water, form sodium hydroxide solution. Sodium hydroxide solution drips from the diaphragm and collects in the outer compartment of the diaphragm. On heating the concentrated solution in iron pans, fused sodium hydroxide is obtained, from which pellets or flakes are made.

(b) The Mercury Cathode Cell:

The cell consists essentially of graphite anodes dipping into a concentrated solution of brine in a container as shown in Fig.(2.2). A layer of mercury covers the floor of the cell and is kept flowing slowly through the cell. Chlorine is liberated at the anode, but sodium ions, being more easily discharged than hydrogen at the mercury electrode, form a solution of sodium in mercury (sodium amalgam). This amalgam flows to a trough in which it reacts with water to give sodium hydroxide solution and hydrogen. Mercury, which is also

regenerated in this reaction, is returned to the electrolytic cell to pass through the process again.



Solid sodium hydroxide is obtained as before. Sodium amalgam is represented by the symbol Na/Hg, as it is not a compound of definite atomic proportions.

(c) Membrane Cell

The Membrane Process

A membrane cell is a diaphragm cell with an improved diaphragm called a 'membrane'. This is made from polytetrafluoroethylene (PTFE), making it a plastic membrane, which has been modified to include anionic groups to act as an ion exchange membrane. The Membrane Cell is replacing the older techniques which used the Castner-Kellner Mercury cell (problems with mercury pollution) and the Gibbs Diaphragm cell (contamination of the NaOH produced with

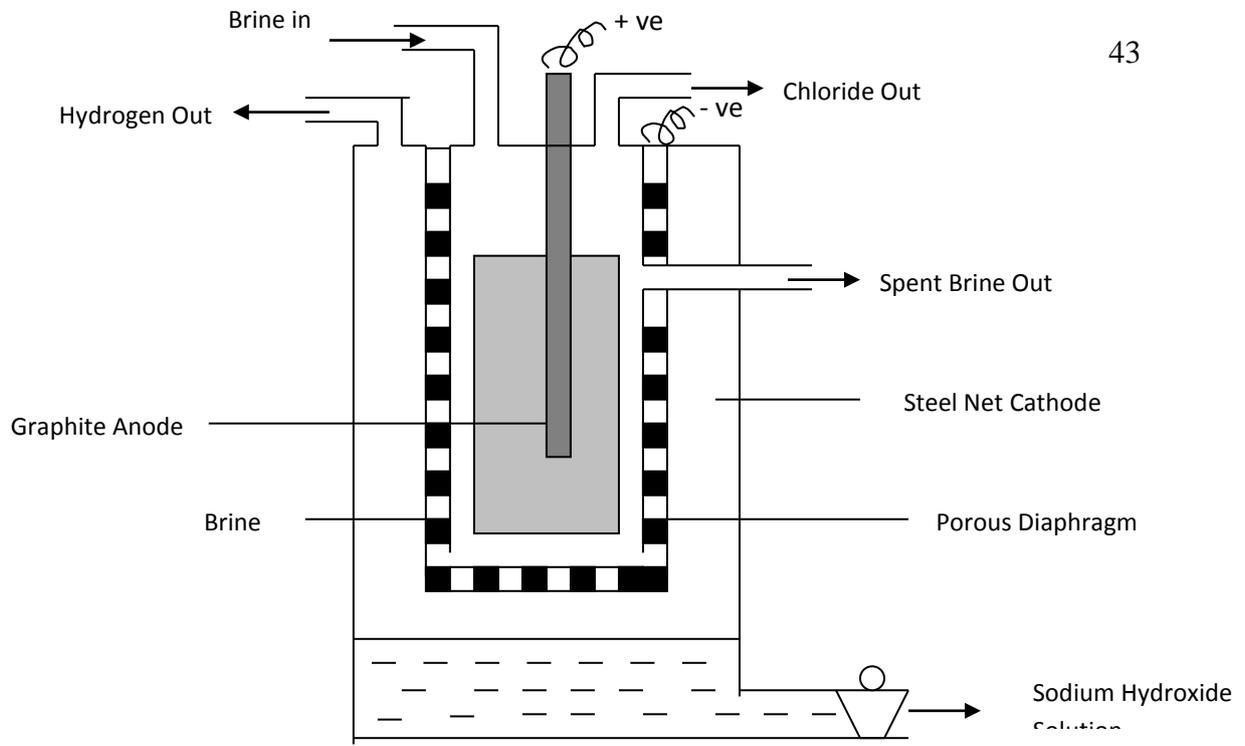


Fig 2.1: Diaphragm Cell (Source: Bajah and Godman, 1976)

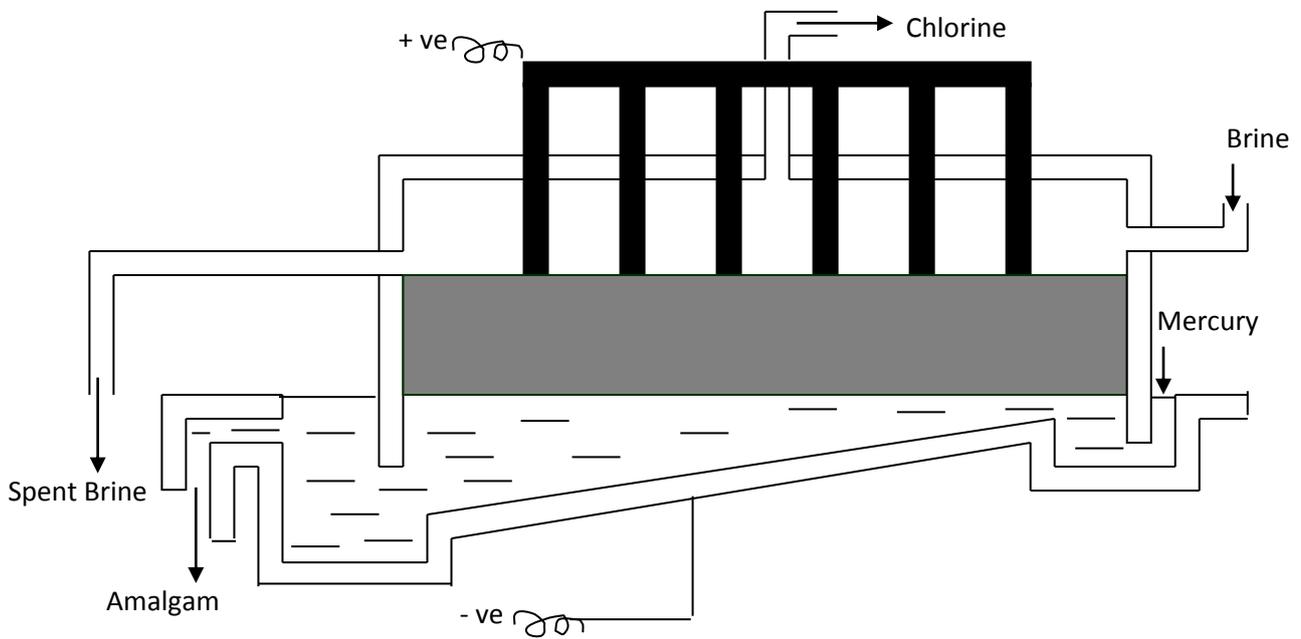


Fig 2.2: Mercury Cathode Cell (Source: Bajah and Godman, 1976)

the sodium ion migrates to the cathode compartment. Unlike in the diaphragm cells, only the sodium ions and some water migrate through the membrane. The unreacted sodium chloride and other inert ions remain in the anolyte. About 30-32% caustic soda is fed to the cathode compartment, where sodium ions react with hydroxyl ions produced during the course of the hydrogen gas evolution from the water molecules. This forms caustic, which increases the concentration of caustic solution to ~35%. The hydrogen gas, saturated with water, exits from the catholyte compartment. Only part of the caustic soda product is withdrawn from the cathode compartment. The remaining caustic is diluted to ~32% and returned to the cathode compartment.

The anode compartment therefore contains sodium hydroxide solution. In one type of cell (not the only one) 33% NaOH is taken out near the top of the anode compartment; some of this solution is taken for concentration and sale, and some are diluted with water to 30% concentration and returned to the bottom of the anode compartment. A diagram of this cell is given below in Fig.2.3.

The use of this process results in virtually pure sodium hydroxide (only contains about 0.02% of sodium chloride at most) being produced as there is no contamination by chloride, and there is virtually no oxidant in the spent brine. Furthermore, there is no working hazard of working with asbestos or mercury. This process of using electrolysis to develop sodium hydroxide, has been adapted in all chlor-alkali plants due to its very pure production of sodium hydroxide, similar costs to that of the diaphragm cell (reasonable) and it has negligible environmental impact. The process is much more preferable to that of the mercury and diaphragm processes and has proved to be the best technique for extracting sodium hydroxide

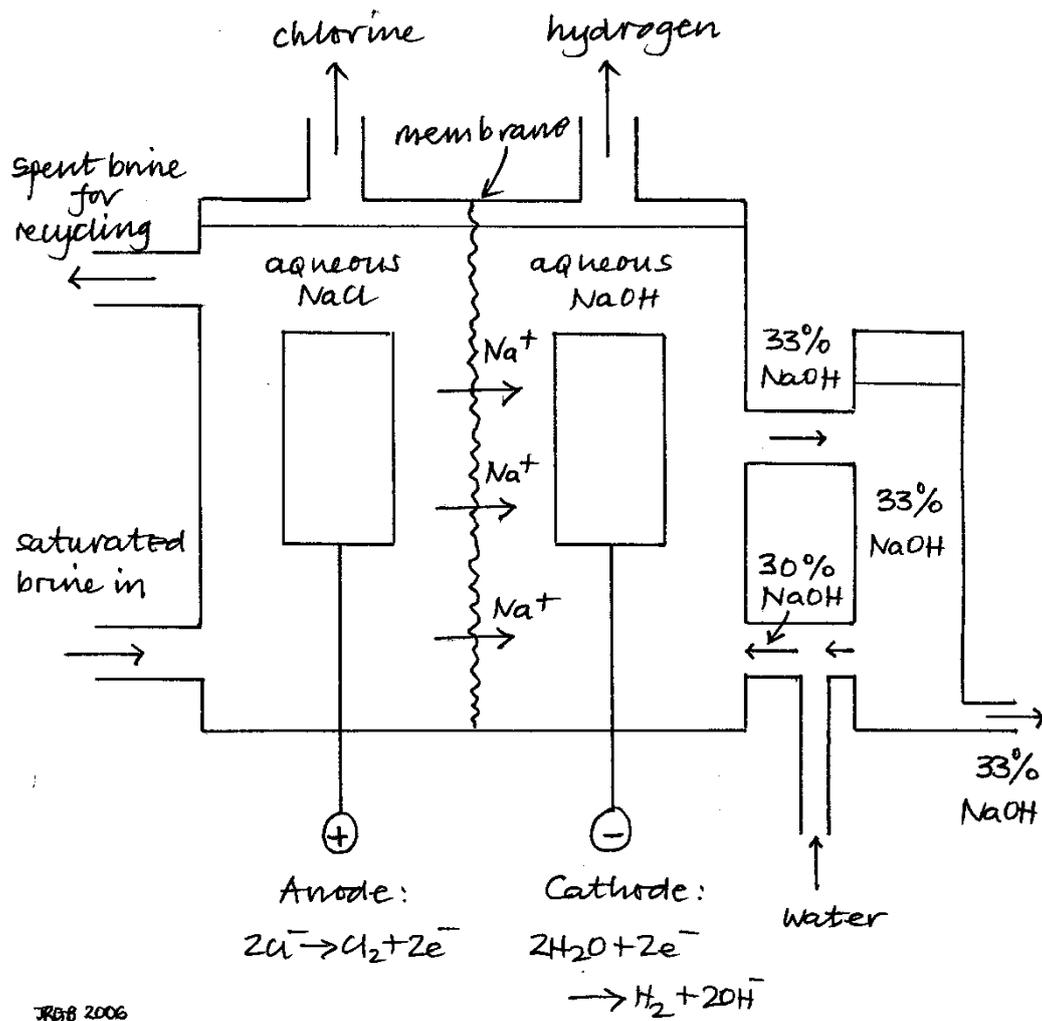


Fig.2.3 The Membrane Cell. (Source: http://www.rod.beavon.clara.net/membrane_cell.htm)

The Electrochemical and chemical reactions occurring in membrane cells can be summarised as follows:

At the Anode (titanium), oxidation reaction takes place thus;

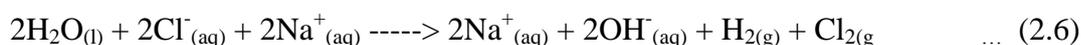


At the Cathode (nickel) reduction reaction takes place thus;



Na^+ migrates across the membrane to cathode compartment combining with OH^- to form NaOH.

Overall cell reaction (showing Na^+ spectator ions):



Side reactions



Product is concentrated sodium hydroxide.

2.7.4 Alkali Metals

The Alkali Metals are the series of elements in Group 1 (IUPAC STYLE) of the periodic table, excluding hydrogen. These are lithium (Li), sodium (Na), potassium (K), rubidium (Rb), caesium (Cs), and francium (Fr). They are highly reactive and are never found in elemental form in nature. See Table.2.4

The Alkali Metals are silver-colored (caesium has a golden tinge), soft, low-density metals, which react readily with halogens to form ionic salts, and with water to form strongly alkaline (basic) hydroxides. These elements all have one electron in their outermost shell, so the

energetically preferred state of achieving a filled electron shell is to lose one electron to form a singly charged positive ion.



Hydrogen, with a solitary electron, is sometimes placed at the top of Group 1, but it is not an alkali metal (except under extreme circumstances as metallic hydrogen); rather, it exists naturally as a diatomic gas. Removal of its single electron requires considerably more energy than removal of the outer electron for the alkali metals. As in the halogens, only one additional electron is required to fill in the outermost shell of the hydrogen atom, so hydrogen can in some circumstances behave like a halogen, forming the negative hydride ion. Binary compounds of hydride with the alkali metals and some transition metals have been prepared.

Under extremely high pressure, such as is found at the core of Jupiter, hydrogen does become metallic and behaves like an alkali metal.

Table 2.6 Elements of Group 1 in the periodic table.

Period	Element	Symbol	Atomic No
2	Lithium	Li	3
3	Sodium	Na	11
4	Potassium	K	19
5	Rubidium	Rb	37
6	Caesium	Cs	55
7	Francium	Fr	87

Source: http://sambal.co.uk/?page_id=57

The first ionization energy is much lower than the second. In the case of Na, it is nine times easier to remove the first electron than the second. The first electron, in an *s*-orbital, can be removed from the element easily, but the second electron must be removed from a noble gas core, which is closer to the nucleus, and therefore requires much energy. Thus, sodium readily forms Na^+ ions, but never forms Na^{2+} ions. This means that sodium and the other elements in Group 1 have only the one oxidation state of + 1 in their compounds.

2.7 Oxidation Numbers and S-Block Elements

Table 2.7 Physical properties of the elements in Group 1

Properties	Elements				
	Li	Na	K	Rb	Cs
Electron Structure	(He) $2s^1$	(Ne) $3s^1$	(Ar) $4s^1$	(Kr) $5s^1$	(Xe) $6s^1$
First ionization Energy/KJ mole ⁻¹	520	500	420	400	380
Second ionization Energy/KJ mole ⁻¹	7300	4600	3100	2700	2400
Atomic radius/nm (metallic radius)	0.15	0.19	0.23	0.25	0.26
Melting point/°C	180	98	64	39	29
Boiling point/°C	1330	892	760	688	690
Density/gcm ⁻³	0.53	0.97	0.86	1.53	1.90
Standard electrode Potential, M^+ (aq) /M(s)/Volts	-3.05	-2.71	-2.93	-2.92	-2.93

Source: http://sambal.co.uk/?page_id=57

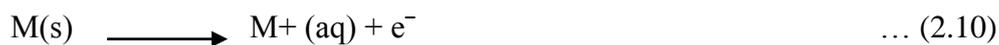
2.7.6 Physical Properties

The atomic radii of alkali metals are included in Table 3.3. The atomic radii increase with atomic number down the groups since each succeeding element has electrons in one more shell than the previous element. The outermost *s*-electrons in these metals are held very weakly by the nucleus. Thus, the outer electrons can drift further from the nucleus than in most other atoms, and the elements have larger atomic radii than those elements which follow them in their respective periods. The large atomic size results in weaker forces between neighboring atoms since there is a reduced attraction of the nuclear charge for the shared mobile outer electrons, as these electrons get further away. Consequently, the metals have lower melting points and lower boiling points than would normally associate with metals. All the Group 1 metals melt below 200°C. In contrast, most of the transition metals melt at temperatures above 1000°C.

The reduced interatomic forces in these metals make them relatively soft. They can be cut with a penknife. As have seen, *s*-block elements have larger atomic radii than transition metals of approximately the same relative atomic mass. Thus, the *s*-block elements will be less dense and have larger molar volumes. Of the elements in table 3.2, their densities vary from approximately 1g cm^{-3} to 1.9g cm^{-3} . Most transition metals have a density greater than 7g cm^{-3} .

2.7.7 Chemical Properties

All the metals are high in the activity (electrochemical) series. The standard electrode potential for the conversion of each metal to its ions is positive and greater than 2.0 volts for all metals except beryllium. Hence, these metals are very good reducing agents. They all react vigorously with water, reducing it to hydrogen.



Excluding lithium, which reacts slower than all the other elements of Group 1, the reactivity of the elements with water closely follows the value of E° , for example, sodium reacts vigorously, fizzing and skating about on the water surface. Potassium reacts even more vigorously giving small cracks and pops as the hydrogen explodes and producing a lilac flame as the hydrogen burns. Rubidium and caesium explode violently in contact with water. Although electrode potentials relate only to aqueous solutions, they also provide a guide to the general reactivity of a substance. All the *s*-block elements are such good reducing agents that they can react with chlorine, bromine, sulphur, hydrogen and oxygen on heating. They, of course, tarnish rapidly in air, forming a layer of oxide, and the reactivity of the metals is such that lithium, sodium and potassium are usually stored under oil.

CHAPTER THREE

3.0 MATERIALS AND METHODS

3.1 Extraction of Alkali from Plantain Peel-Ash

The apparatus and materials used were weighing balances, a large shallow tray called “combustion pan”, a sieve set, laboratory glass wares, hydrometer, plastic buckets and containers. 10 kg of plantain peels were collected from eateries in Lagos, dried by placing them under an industrial gas burner fired grease boiler until dried enough to break with hand. The dry weight was 5kg. The dried peels were burnt inside the combustion pan with industrial gas burner and ash of 1 kg was obtained. This is in contrast to oven drying practiced by (Onyeagbado et al 2002). Ash samples were naturally powdery, but it was sieved with 0.105 mm sieve (US sieve No. 140; Tyler equivalent 150 Mesh) to remove large particles. Kuye and Okorie (1990) had shown that a particle size of 1.06×10^{-4} m gave the highest concentration of potassium hydroxide when the slurry of ashed sample containing 0.15kg of the ashes in 2.5dm³ of distilled water was kept for eight hours at 60°C.

The ashes were allowed to cool down, packed into a 5-liter transparent bucket and boiled water poured into it. The slurry was kept for 24 hours before draining of extract. After draining, the first extract was kept in a separate plastic container before more cold water was poured into the slurry for further extraction. This was repeated the third time and all the extracts kept in different containers. The following extracts were made. 0.5 litres of 1.300 specific gravity Bio-alkali, 0.75 litres of 1.250 specific gravity bio-alkali and 0.75 litres of 1.220 specific gravity. The density of the alkali was measured using a hydrometer and then converted to specific gravity.

3.2 Lubricating Grease Formulation

The apparatus and materials used included a Bunsen burner, spatula, evaporating dish, mercury-in-glass thermometer, weighing balance, laboratory glass wares, stirrer and penetrometer. The raw materials for preparing lubricating grease are the alkali, fatty acid and lubricating oil. The alkali used was the bio-alkali extract, while the lubricating oil is mineral oil. The fatty acid was palm oil. Palm oil was purchased from Agege market while N-500 base oil was from base oil tank farm in Apapa, both in Lagos. N-500 grade has viscosity of between 91 and 101 Cst at 40°C and is good for grease production. Tallow, Stearic acid and Caustic soda (for control experiment) were all bought from Ojota Chemical market, Lagos. The experiments were carried out using Palm oil, animal fat (Tallow) and Stearic acid separately. All experiments and tests were carried out in the laboratory of Mega Lube Industries Ltd, Lagos. Mega Lube Industries Ltd is a Lubricating grease manufacturing company.

A 5x5 factorial experiment in 3 replicates was used for the study. This involved 5 different specific gravities and 5 different volumes of the Bio-Alkali (BA). The first alkali extract was too strong while the last extract was too weak. With the aid of hydrometer, the extracts were compounded and five different specific gravities of the extracts were formulated by diluting stronger extracts with weaker extracts, and kept in 5 different containers from which experiments were carried out. To form a grease base, the volume of the base oil and the fatty acid are usually equal while the alkali is always a fraction (percentage) of the volume of the fatty acid. The mixture was boiled in a stainless pot and stirred. Grease preparation is accomplished in three stages, namely; Stage 1: The mixture was boiled and stirred until saponification takes place with foaming. Stage 2: The saponified mixture was further boiled, stirred to dehydrate. Stage 3: The heater was turned off and melted grease base was stirred

and more base oil added as a finishing procedure. This is required to bring down the temperature of the grease to safe storage range to avoid separation.

3.2.1 Preparation of bio alkali grease

The following procedures were followed in all preparations.

100ml of palm oil was mixed with 100ml of N-500 base oil. Bio-alkali with specific gravity of 1.245 was first experimented upon using the following volumes; 33ml, 36ml, 39ml, 42ml, 45ml. After that, 1.250 SG was used, and then 1.255, 1.260 and 1.265 SG were used respectively. In the preliminary experiments lower and higher values of volumes and specific gravities were used in trial runs but they all gave very bad results that formed no grease at all. It was after several trials that the above volume and specific gravity ranges were selected for analysis because they presented data either close to or within the recommended consistency values of 85 – 475. In each case, the three compounds; alkali, base oil and palm oil were mixed inside a stainless steel pot. Stainless steel pot was used to withstand the corrosive nature of alkali. The mixture was placed on a Bunsen burner and boiled. As the boiling went on, the mixture was stirred continuously. The temperature rose rapidly and at 110°C it started foaming. This was a sign of saponification. Foaming continued for about 10 minutes before there was complete saponification, then dehydration and intimate mixing of the soap and base oil commenced. This continued for the next 10 minutes before complete melting and dehydration was achieved and this time, the temperature was maintained at 150°C. The mixture was a transparent reddish- yellow compound. At this point, the heat was put off and additional 100 ml of base oil gradually poured into the mixture as it was continuously stirred. Additional 100 ml was poured because a good thickener should form a consistent grease in concentration of 25-50wt% for metallic soap (Izuagie,2006) and up to 40% may be acceptable for inorganic thickeners in mineral oil (Graham,1991). By the time all the oil was

poured, the temperature has come down to 70°C. At this temperature, the grease could be stored without the fear of separation. Palm oil was used because Tallow and Stearic acid gave fluidized grease only when mixed with a ratio of palm oil. Hence experimentations with them were discarded and all efforts focused on palm oil.

3.2.2 Preparation of NLGI #0 grease

The materials and methods used to determine the optimum consistency of 361 were used to prepare NLGI #0 grease. Further dilution with lubrication oil can lead to NLGI #00 and NLGI #000. It must be noted that there is a difference between the consistency of grease base and consistency of the grease itself. Consistency of the grease base depends on getting appropriate specific gravity of the alkali and mixing it at correct ratios with equal volume of fatty acid and lubrication oil. When the specific gravity and volume of alkali are wrong, they will affect the best consistency a grease base should have. However, when one has got the best consistency a particular grease base can have, then the variation of the consistency of any grease produced from it can be achieved by varying the quantity of 'finishing' lubrication oil added to the grease base. For the NLGI #0 grease, the ration of bio alkali, palm oil and N-500 base lubricating oil was **1: 2.8:5.6**.

3.2.3 Preparation of control samples

A polymer-base NLGI #0 from ASCON was collected as a control sample for analysis. Another sodium-base NLGI #0 was formulated as a second control sample for analysis. The reason for using the two control samples are as follows. ASCON grease was used because it is commercially available, while sodium-base sample was used to have a similar soap base for comparison since the ASCON NLGI #0 is polymer-base. The materials and methods used for preparing the bio alkali grease is similar to that of sodium base only that sodium

hydroxide was used to replace the bio alkali. The ratio of the reactants is as follows: 1: 3: 15 for Caustic soda, Palm oil and N-500 base oil respectively.

3.3 Testing

No testing was carried out the same day the grease was blended. They were left till the following day so as to fully cool down.

3.3.1 Consistency test.

The testing was done according to ASTM D217-02 Standard Test Methods for Cone Penetration of Lubricating Grease. The penetration is measured in tenths of a millimetre.

3.3.1.1 Un-Worked Penetration Test

Three samples each of the grease and the controls were subjected to penetration test. They had their different penetration levels measured using penetrometer by filling in a standard grease cup, cylindrical in shape with 50ml capacity with a little disturbance, the surface was smoothed and placed on the penetrometer assembled and pressed for five seconds during which a special grease-cone on the assembly has its tip just touching the level of the grease surface at the start. The distance dropped for each sample was read from the dial indicator of the penetrometer and recorded.

3.3.1.2 Worked Penetration Test

The worked penetration test was carried out in the same manner with that of the Un-worked penetration test but the difference was that the grease samples were worked for 60 double strokes in the standard grease worker cup. In this method, the disturbance of the grease was standardized by the prescribed working process and is more reliable than Un-worked

penetration test because the grease has been subjected to a work load of double strokes over a wide range of temperatures.

The Un-worked and the worked penetration test describe above were used to determine the grease consistency and the grease consistency is its resistance to deformation by an applied force. A significant difference between un-worked and worked penetration can indicate poor shear stability.

3.3.2 Dropping Point test

The dropping point test procedures given in ASTM standards D-566 and D-2265 were followed. The test apparatus consists of a grease cup with a small hole in the bottom, test tube, two thermometers, and an electric heater. The inside surfaces of the grease cup are coated with the grease to be tested. A thermometer is inserted into the cup and held in place so that the thermometer does not touch the grease. This assembly is placed inside a test tube. The test tube is lowered into the container which is filled with oil in D-566 and has an aluminium block in D-2265. Another thermometer is inserted into the oil/block.

To execute the test, the oil/block was heated, while being stirred, at a rate of 4.4 °C to 6.7 °C per minute until the temperature is approximately 100 °C. The heat was reduced until the test tube temperature 95°C. Once the temperature stabilized the sample was inserted and heating continued. The dropping point was the temperature recorded on the test tube thermometer, plus a correction factor for the oil/block temperature, when a drop of grease falls through the hole in the grease cup.

3.4 Design of Experiment

The experiment to discover the optimum specific gravity and volume of the bio alkali extract that gave the best grease consistency will be analyzed as a factorial experiment using Split

Plot in Randomized Complete Block Design. When there are two nested groupings of the observations on the basis of treatment application, it is known as a split plot design (http://support.sas.com/documentation/cdl/en/statug/63033/HTML/default/viewer.htm#statug_anova_sect028.htm). The two treatment factors in this work (specific gravity and volume) are nested, in that each volume carries the specific gravity treatment inside it. This is unlike other factorial experiments in which the factors are independent of each other. For instance, if we intend to test the effect of type of alkali and type of palm oil in the consistency of the grease, then each factor is independent of the other and simple factorial design can be applied. It must be stated that the ANOVA is not just to determine the effect of specific gravity and volume of bio alkali in lubricating grease per se because it is obvious that they do have significant effects, but the essence is to lay a solid foundation to conduct FLSD so as to determine the specific gravity and volume that have least variation within their treatment means. It is these set of data that can be said to be the best ratios in the bio alkali grease production stoichiometry.

Split plot design is characterized by randomizations at two levels. In simple terms, a split-plot experiment is a blocked experiment, where the blocks themselves serve as experimental units for a subset of the factors. Thus, there are two levels of experimental units. The blocks are referred to as whole plots; while the experimental units within blocks are called split plots, split units, or subplots. Corresponding to the two levels of experimental units are two levels of randomization. One randomization is conducted to determine the assignment of block-level treatments to whole plots. Then, as always in a blocked experiment, a randomization of treatments to split-plot experimental units occurs within each block or whole plot.

Facilities for construction of split-plot designs are not as yet generally available in software packages; with SAS/JMP being one exception (Jones and Nachtsheim, 2009). Therefore manual calculations will be done using machine formula shown in the appendix (Anova in

RCBD), since EXCEL and other available software cannot do it properly. Besides, the construction of the ANOVA will be in nested format.

It must also be noted that Factorial experiments could be laid out in different ways such as a Completely Randomized Design(CRD), Randomized Complete Block Design (RCBD), or other layouts, (Kristensen and Halekoh, 2013), but Randomized Complete Block Designs is preferred in this work. Randomized Complete Block Designs differ from the Completely Randomized Designs in that the experimental units are grouped into blocks according to known or suspected variation which is isolated by the blocks. Therefore, within each block, the conditions are as homogeneous as possible, but between blocks, large differences may exist. Recent works, most notably by Lucas and his coworkers (Anbari and Lucas (1994), Ganju and Lucas (1997, 1999, 2005), Ju and Lucas (2002), Webb et al. (2004)) demonstrated that many experiments previously thought to be Completely Randomized experiments also exhibit split-plot structure.

The above explanatory note is to forestall any misunderstanding on the choice of experimental design chosen as any other design will, unlikely produce the correct result.

CHAPTER FOUR

4.0 RESULTS AND ANALYSIS

Experimental work was divided into three stages as follows:

Stage 1

Preliminary experiments were conducted to eliminate various specific gravities and volumes that did not form any type of grease whatsoever. It was after these trials that the ranges that produced results whose consistencies fell within prescribed standard were identified. All the data generated here were of no analytical use and hence discarded.

Stage 2

After eliminating values that did not produce grease, the experiment was expanded to identify the specific gravities and volumes that produced grease whose consistencies either fell within or close to the standard range. This informed the decision to narrow down the specific gravities to 1.245 -1.260 and volume from 33% to 45%. The results of these experiments are presented in Table 4.1 and Table 4.2. The summary of the consistencies with the quality of grease produced is shown in the appendix.

Stage 3

The specific gravity and volume that produced the best consistency was used to formulate NLGI #0 grease. This grease was subjected to various quality tests and compared to two control samples. One of the control samples was grease formulated from Sodium Base while the other was commercially available grease. The results are presented in Tables 4.3, 4.4, and 4.5

4.1 Bio alkali grease Consistency results.

The summary of the Consistency measurements of Lubricating grease produced from bio-alkali of different specific gravities and volumes are presented in presented in Table 4.1

Table 4.1 Consistency measurements of Lubricating grease produced from bio-alkali of different specific gravities and volumes.

	SG	%VOL	REPLICATIONS			TOTAL
			I	II	III	
	1.245	45	500	500	500	1500
		42	475	474	475	1424
		39	470	472	471	1413
		36	475	473	472	1426
		33	500	500	500	1500
TOTAL		ΣV	2420	2419	2418	7257
	1.250	45	500	500	500	1500
		42	500	500	500	1500
		39	430	429	430	1289
		36	365	364	367	1096
		33	370	372	371	1113
TOTAL		ΣV	2165	2165	2168	6498
	1.255	45	500	500	500	1500
		42	500	500	500	1500
		39	400	399	402	1201
		36	361	360	362	1083
		33	369	367	366	1102
TOTAL		ΣV	2130	2126	2130	6386
	1.260	45	500	500	500	1500
		42	500	500	500	1500
		39	480	479	481	1440
		36	465	463	464	1392
		33	410	411	412	1233
TOTAL		ΣV	2355	2353	2357	7065
	1.265	45	500	500	500	1500
		42	500	500	500	1500
		39	480	483	481	1444
		36	470	472	471	1413
		33	472	473	474	1419
TOTAL		ΣV	2422	2428	2426	7276
G/TOTAL		$\Sigma\Sigma V$	11492	11491	11499	34482

4.2 Production of NLGI #0 grease from Bio alkali and Sodium hydroxide

The summary of the grease produced with the various percentage compositions of the base oil, palm, bio alkali and sodium hydroxide is as shown in Table 4.2

Table 4.2: Variation of composition and temperature of the produced grease sample

S/No	Grease Sample	Bio-Alkali	Sodium-base
1	Mass of base oil (B) (g)	280.0	450.0
2	Mass of thickener used (T) (g)	99.2	99.0
3	Saponification temperature ($^{\circ}$ C)	110	120
4	Maximum Reaction temperature ($^{\circ}$ C)	130	150
5	Blending time (minutes)	20	30
6	Percentage (T/B) (%)	35	22
7	Cooling time to storage temp of 50 $^{\circ}$ C	30	60

4.3 Consistency Test (Un-Worked and Worked Penetration)

The summary of the un-worked and worked penetration values of the bio alkali grease, sodium-base grease and Ascon grease is as shown in Table 4.3.

Table 4.3 Consistencies of NLGI #0 test samples and control (0.1mm)

S/No	Samples	Un-worked	Worked	Balance
1	Bio alkali grease	360	363	1
2	Sodium-Base grease	360	362	2
3	Ascon	363	365	2

4.4 Dropping Point Test

The summary for the dropping point test values of the grease and the controls in degree Celsius ($^{\circ}\text{C}$), and the cost in N/kg are as shown in the Table 4.4

Table 4.4: Dropping point values and Cost of Production

S/No	Grease sample	Dropping Point ($^{\circ}\text{C}$)	Cost (N/kg)
1.	Bio Alkali base	143	135
2.	Control 1(Sodium base)	145	256
3.	Control 2 (Ascon)	150	300

CHAPTER FIVE

5.0 DISCUSSIONS

5.1 Mean of the consistencies

The summary of the mean of the consistencies from Table 4.1 is presented in Table 5.1

Table 5.1 Mean of the Consistencies.

*9	MEAN SPECIFIC GRAVITY					MEAN OF MEANS
	1.245	1.250	1.255	1.260	1.265	
45	500.0	500.0	500.0	500.0	500.0	500
42	474.7	500.0	500.0	500.0	500.0	494.94
39	471.0	429.7	400.3	480.0	481.3	452.46
36	475.3	365.3	361.0	364.0	421.0	407.32
33	500.0	371.0	367.3	411.0	473.0	424.46
MEAN OF MEANS	484.2	433.2	425.72	451	485.06	

The result of the preliminary consistency test shows that the consistency was bad at both lower specific gravity and volume. As both factors increased, the consistency improved to a point where it started going bad again. The set of data that produced the best grease consistency was specific gravity of 1.255 and volume of 36%. From Table 5.1 a plot of the mean consistencies at various specific gravities and volumes was carried out with scilab software and shown in Fig (5.1). The scilab code that produced Fig (5.1) is shown below:

```

C= [500.0    500.0    500.0    500.0    500.0
    474.7    500.0    500.0    500.0    500.0
    471.0    429.7    400.3    480.0    481.3
    475.3    365.3    361.0    364.0    421.0
    500.0    371.0    367.3    411.0    473.0];

```

```
//x : volume ([45 42 39 36 33]) and y : matrix (C)
```

```
x=[45 42 39 36 33];
```

```
plot(x,C);
```

```
plot(x',C); // idem, x is automatically transposed to match C (here the columns)
```

```
xlabel('Volume'); ylabel('Consistency');
```

Fig 5.1 is a chart which can be used to determine the grease consistency given any specific gravity and volume of choice. The graph is also used to develop the consistency equation shown in equation (5.12) From graph, it is obvious that best mean specific gravity and volume of the alkali that gave the best consistency of 361 are SG1.255 and Volume 36%.

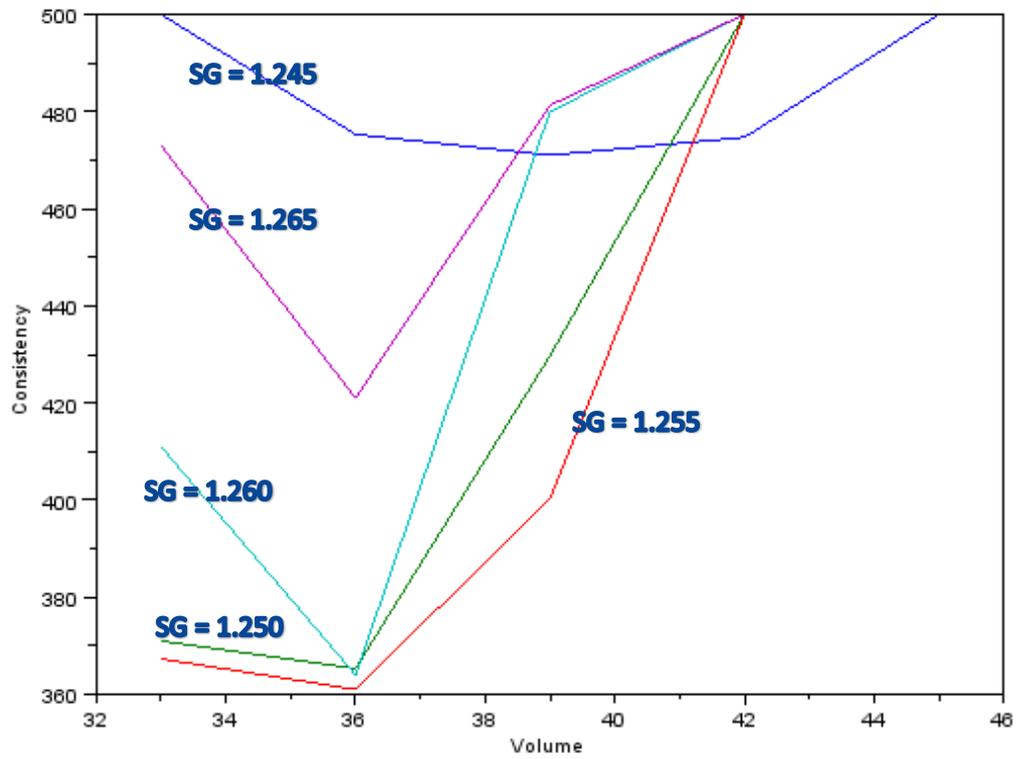


Fig. 5.1 Graph of Grease Consistency at different Specific gravities and Volumes

5.2 Analysis of variance (ANOVA)

Analysis of Variance (ANOVA) was carried out to determine the effect of Specific gravity (SG) and Volume (V) of Bio-alkali on the Consistency of the lubricating grease produced. The ANOVA is shown in Table 5.2. Analysis of variance (ANOVA) is a collection of statistical models used to analyze the differences between group means and their associated procedures (such as "variation" among and between groups), in which the observed variance in a particular variable is partitioned into components attributable to different sources of variation.

Table 5.2 ANOVA showing the effect of Specific gravity and Volume of Bio-alkali on the consistency of lubricating grease.

SOURCES OF VARIATION	D.F	S.S	M.S	OBS.F	EXPECTED F 1%
MAIN PLOT ANALYSIS					
μ	1	158344.32	-	-	8.65 7.01
Block	2	1.52	0.76	0.82 ^{N.S}	
Factor A	4	48119.13	12029.78	12935.25**	
Error(a)	8	7.43	0.93		
Total	14	48128.08			
SUB-PLOT ANALYSIS					
Factor B	4	78526.75	19631.69	24850.24**	3.83
Interaction AB	16	52831.13	3301.95	4179.68**	2.49
Error(b)	40	31.72	0.79		
Total	60	131389.60			
Grand Total	74	179517.68			

NB: N.S = Not Significant, ** = highly significant.

Null hypothesis $H_0: \mu_A = \mu_B$... (51)

Alternative hypothesis $H_1: \mu_A \neq \mu_B$... (5.2)

Where H_0 = null hypothesis, μ_A = factor A treatment means, μ_B = factor b treatment means

In analysis of variance, an F-test is used to test group variance against a null hypothesis, and is often used to determine whether any group of trials differs significantly from an expected value. If F-calculated is greater than the F-tabular, then there is a significant treatment effect, and that at least one of the treatments is different. F-LSD or LSD can be done to find which Mean(s) is (are) different.

The null hypothesis for this work is as follows

1. All the blocks have the same effect on the consistency of the bio alkali grease
2. All the levels of specific gravity (factor A) have the same effect on the consistency of the grease
3. All the levels of volume (factor B) have the same effect on the consistency of the grease
4. All the combinations of specific gravities and volumes have the same effect on the consistency of the grease

This null hypothesis simply means that there are no significant differences in the effects of the blocking, the specific gravity levels, the different volumes and the interaction between the different levels of specific gravity and the volumes. If null hypothesis is accepted, then no stoichiometry can be generated from the experiment. This will mean that either more work needs be carried out or that bio alkali cannot be used to produce grease.

5.3 Standard Errors of the Experiments

Formula for calculating standard errors for the experiment can be seen in the appendix.

(a) Standard error of the difference between two factor A means or between two main plot

(Whole plot) treatment means is 0.99532

(b) Standard error of the difference between two factor B means, that is, two sub-plot

Treatment means is 2.055

(c) Standard error of the difference between two factor B means (i.e. sub-plot treatment

Means) for the same level of factor A i.e. $a_1b_1 - a_2b_2$ is 4.599

(d) Standard error of the difference between two factor A means of the same or different levels of B is 4.173

Looking at the ANOVA Table, the observed $F < \text{Expected } F$ for blocks at 1% levels of probability. Hence null hypothesis is accepted. However for factors A, B and Interactions AB, observed $F > \text{Expected } F$, hence null hypothesis is rejected. Then alternative hypothesis $H_1: \mu_A \neq \mu_B$ is accepted.

The summary of the ANOVA table is as follows

1. The effect of blocking on the consistency of the grease is not significant at 1% level of probability. This result is obvious since the experimental material is homogenous.
2. The effect of specific gravity of the bio-alkali on the consistency of lubricating grease produced with it is significant 1% levels of probability.
3. The effect of the volume (quantity) of bio-alkali used in saponification of palm oil for the production of lubricating grease on the consistency of grease produced is also significant at 1% level of probability
4. The combined effect of both the specific gravity and the quantity of bio-alkali used in Lubricating grease production is equally significant at 1% level of probability.

Having concluded that both factors, volume and specific gravity, have significant effects statistically, it is necessary to determine the particular treatment means that contributed to these differences. This was done by FLSD

The decision rule for FLSD =LSD at any α -level is as follows:

If the difference between any two means is greater than their LSD (least significant difference), then those two means are statistically different at that α -level. Conversely, if the difference between any two means is less than their LSD or FLSD, then those two means are statistically equal. The aim here is determine those treatments that are statistically different and observe their levels of contributions to the effects observed in ANOVA. The treatment means that have least variations within its effects when the means are separated will be used as the appropriate ratio that will form the stoichiometry of bio alkali grease.

To separate the means by the means of FLSD = LSD at 1% level of probability, a two way test was done in order to ignore the sign convention. The calculations are shown in the appendix

1. For factor A, specific gravity,

$$\text{FLSD} = \text{LSD} = t_{\alpha/2, \text{Error (a) d.f}} \times S_d = 3.343$$

Then table of mean difference for the mean of means from Table 5.1 is shown in Table 5.3 below for specific gravity effect on consistency.

Table 5.3 Table of mean difference for the mean of means of consistency due to the effect of Specific gravity as factor A

SPECIFIC GRAVITY	SG1.265 = 485.06	SG1.260 = 451	SG1.255 = 425.72	SG1.250 = 433.2	SG1.245 = 484.2
SG1.245 = 484.20	0.86	33.2	58.48	51	0
SG1.250 = 433.20	51.86	17.8	7.48	0	
SG1.255 = 425.72	59.34	25.28	0		
SG1.260 = 451	34.06	0			
SG1.265 = 485.06	0				

From Table 5.2, it is obvious that FLSD is only greater than the difference between the mean of means of consistency reading under SG1.245 and SG1.265. Hence null hypothesis is accepted that:

$$\mathbf{H_0: \mu_{SG1.245} = \mu_{SG1.265}. \quad \dots (5.3)}$$

That means that statistically speaking, both SGs have the same consistencies. Null hypothesis is however rejected for all other means, and alternative hypothesis is accepted indicating that the mean of means of other SGs presented statistically significant differences in consistencies and the relationship from Table 5.3 is as follows:

$$\mathbf{H_A : \mu_{SG1.265} > \mu_{SG1.260} > \mu_{SG1.250} > \mu_{SG1.255} \quad \dots (5.4)}$$

It is instructive to notice that SG1.255 has the minimum variation within its consistency means and hence presents the best option as an ideal specific gravity for the bio-alkali. Again, this information from FLSD not only confirms that of ANOVA that differences in the SGs have high significant effect on the consistency of the grease produced, it has gone further to show the relationship between the effects in equations (5.3) and (5.4)

2. Secondly FLSD for factor B, the volume of bio-alkali = 4.15

The table of mean difference for the mean of means from Table 5.1 is shown below for volume effect on consistency in Table 5.4

Table 5.4 Table of mean difference for the mean of means of consistency due to the effect of volume as factor B

% VOLUME	33%=424.4	36%=407.32	39%=452.46	42%=494.94	45%=500
45%=500	75.54	92.68	47.54	5.06	0
42%=494.94	70.48	87.62	42.48	0	
39%= 452.32	28.0	45.14	0		
36%=407.32	17.08	0			
33%=424.40	0				

Judging from the FLSD of 4.15, and Table 5.4, null hypothesis was rejected for all means and alternative hypothesis accepted as:

$$\mathbf{H_A : \mu_{45} > \mu_{42} > \mu_{39} > \mu_{33} > \mu_{36} \quad \dots (5.5)}$$

It is equally instructive to notice that VOL₃₆ has the minimum variation within its consistency means and hence presents the best option as an ideal volume for the bio-alkali. Again, this information from FLSD not only confirms that of ANOVA that differences in the volume of the bio-alkali used have high significant effect on the consistency of grease produced, it has equally gone further to show the relationship between the effects in equation (5.5)

5.4 Consistency Empirical formulation

Obviously there is a relationship between the interactive effect of the volume of alkali used in grease production and its specific gravity on the consistency of lubricating grease produced as shown in Fig. 5.1. This relationship, however, has not been captured mathematically in literature. The analysis of variance indicated that the effects of both volume and specific gravity on the lubricating grease consistency are very significant, so also is the effect of the

interactions of both factors. To express these effects mathematically, using the experimental results in Table 5.1, various mathematical equations were examined to determine whether a model could be developed to define this relationship as captured in Fig 5.1. They were then modeled into an empirical formula.

Mathematical relationship between specific gravity and volume of bio alkali in lubricating grease production are given below

1. Linear equation

A linear equation is an algebraic equation in which each term is either a constant or the product of a constant and (the first power of) a single variable. A common form of a linear equation in the two variables x and y is

$$y = mx + b, \quad \dots (5.6)$$

where m and b designate constants (parameters), the constant m determines the slope or gradient and b determines the point at which the line crosses the y -axis, otherwise known as the y -intercept.

The general (or standard) form linear equation considered is written as:

$$Ax + By = C, \quad \dots (5.7)$$

where A and B are constants, C is consistency while x and y are volume and specific gravity respectively. It is obvious that the data of Table 6.1 cannot give a straight line graph. Hence linear equation was discarded.

2. Exponential Function

The exponential function considered was

$$C = e^{(x+y)} \quad \dots (5.8)$$

Where C is the consistency; x and y are volume and specific gravity respectively.

It is equally obvious that this function cannot be used to describe the data in Table 5.1

3. Logarithmic Function

The Logarithmic function considered is given in equation (5.9)

$$\text{Log}(xy) = \text{Log}(x) + \text{Log}(y) \quad \dots (5.4)$$

Where x is volume and y is specific gravity; xy is a combination of x and y. The data again did not fit well to the function and was therefore discarded.

4. Quadratic Function

Another mathematical function considered was the quadratic function in the form given in equation (5.10)

$$f(x) = ax^2 + bx + c, \quad a \neq 0. \quad \dots (5.10)$$

This was inappropriate because it has a single variable specific gravity, then a bivariate quadratic function of the second-degree polynomial was also considered. The bivariate quadratic function is given in equation (5.11).

$$\mathbf{Cst = Ax^2 + By^2 + Cx + Dy + Exy + F} \quad \dots (5.11)$$

Where Cst is consistency, x is specific gravity, and y is volume. A,B,C,D,E and F are constants. This equation can faithfully simulate the behaviour of the data in Table 5.1 and Fig. 5.1 with due considerations.

General considerations

The following empirical formula was developed using the data range that falls in between specific gravity of 1.250 – 1.260, and volume of 33% and 36% taking cognizance of equation (6.10) The enclosed data gave a less erratic behavior and can be assumed to represent the consistency response to variation in specific gravity and volume of the bio alkali. To faithfully simulate the data empirically, the parameters in equation (10) are defined as follows:

$$A = 4.4, B = 2(10^5), C = -11, D = -100, E = 1 \text{ and } F = 361 \text{ (the best consistency)}$$

$$V_B = (v - v_i), SG_B = (Sg - sg_j)$$

Cst_{ij} = Grease consistency at ith column and jth row

v = the volume of bio alkali that gave the best consistency = 36

v_i = The volume of bio alkali at ith column

sg = the specific gravity of the bio alkali that gave the best consistency = 1.255

sg_j = the specific gravity of the bio alkali at the jth row

F = the best consistency got for the bio alkali grease at $v = 36$ and $sg = 1.255$

Hence equation (5.11) can be reduced to

$$Cst = 4.4V_B^2 + 160000 SG_B^2 - 11V_B - 100 SG_B + V_B .SG_B + 361 \quad \dots \quad (5.12)$$

5.5 Regression Analysis

As stated earlier, just like in every other stoichiometric development, parabolic data are always generated. To obtain a linear regression one has to apply the principle of single jeopardy by dividing the data into two with the best reading as terminal; either in ascending or descending order. Whichever of the data that presents the cheapest option is chosen as data of single jeopardy while the other is a data of double jeopardy. The jeopardy is bad part of the data while single jeopardy occurs when little was spent in getting the bad result, but additional jeopardy is incurred if much is spent and yet bad result was got. Based on this theory, linear regression can be computed for the data.

From the table of means (Table 5.1) it is obvious that at 36% volume all the grease produced were consistent and that the best overall consistency was got at SG of 1.255 and 36% volume. Hence 36% volume was chosen as the volume upon which different specific gravities and the resulting consistencies would be used for the regression equation. Specific gravity is treated as independent variable while consistency is treated as dependent variable.

Linear regression equation is given as

$$Y = a + bX \quad \dots (5.13)$$

Where Y = dependent variable

a = the interception (the value of y when x =0)

b = the gradient of the line

X = independent or explanatory variable.

To solve the regression equation, one has to solve for 'a' and 'b'

$$b = \frac{\sum[(x_i - \mu_x)(y_i - \mu_y)]}{\sum[(x_i - \mu_x)^2]} \quad \dots(5.14)$$

$$a = \mu_y - b\mu_x \quad \dots (5.15)$$

where x_i = the x value for observation i. $i = 1$ to n, n being the number of data

μ_x = mean value of x

y_i = value of y for observation i,

μ_y = mean value of y

From Table 5.1, values of x and y were generated for specific gravity, X = 1.245 to 1.255, and consistency, Y = 475.3 to 361.0 as shown in Table 5.4.

NB Dividing the parabolic data of Table 5.1 into two gives SG 1.245 to 1.255 and SG 1.255 to 1.265. The first half, SG 1.245 to 1.265 is cheaper than the second half of SG 1.255 to SG 1.265 because it is cheaper to produce lower value SGs. Hence the first half of the data and their corresponding consistencies were used.

Table 5.5 Regression analysis data

	X	Y
	1.245	475.3
	1.250	365.3
	1.255	361.0
TOTAL	3.75	1201.6
MEAN	1.25	400.5

From equation (5.14), $b = -11830$,

From equation (5.15), $a = 15188$.

Hence regression equation

$$Y = 15188 - 11830X \quad \dots (5.16)$$

5.6 Coefficient of Determination

This is used to determine how well the regression equation fits the data and is given as,

$$R^2 = \left\{ \frac{1}{n} \sum [(x_i - \mu_x) * (y_i - \mu_y)] / (\sigma_x * \sigma_y) \right\}^2 \quad \dots(5.17)$$

Where R is correlation, n is the number of observations used to fit the model, \sum is the summation symbol, σ_x is the standard deviation of x, and σ_y is the standard deviation of y.

$$\sigma_x = \sqrt{[\sum (x_i - \mu_x)^2/n]} \quad \dots (5.18)$$

$$= 0.00409$$

$$\sigma_y = \sqrt{[\sum (y_i - \mu_y)^2/n]} \quad \dots (5.19)$$

$$= 54.80$$

Therefore, Coefficient of determination

$$R^2 = 0.88$$

The coefficient of determination of 0.88 indicates that about 88% of the variation in the consistency of the grease produced when bio alkali used in production is 36% volume of the Palm oil used can be explained by the relation to the specific gravity of the bio-alkali. This is a good fit for the data.

5.7 Optimization

Mathematically speaking, optimization is the maximizing or minimizing of a given function possibly subject to some type of constraints. An optimization problem can be represented in the following way

Given: a function $f: A \rightarrow \mathbf{R}$ from some set A to the real numbers

Sought: an element x_0 in A such that $f(x_0) \leq f(x)$ for all x in A ("minimization") or such that $f(x_0) \geq f(x)$ for all x in A ("maximization").

Typically, A is some subset of the Euclidean space \mathbf{R}^n , often specified by a set of constraints, equalities or inequalities that the members of A have to satisfy. The domain A of f is called

the 'search space' or the 'choice set', while the elements of A are called 'candidate solutions' or 'feasible solutions'. The function f is called, variously, an **objective function**, **cost function**, etc.

The objective function for the experiments and hence the entire project is "consistency". Several thickeners, both soap and non soap base are available for lubricating grease production. Soap base thickeners are product of chemical reaction between fatty acid and alkali. Consistency of lubricating grease is a measure of its stiffness, and before any product is called grease, the consistency must fall within those given by ASTM and NLGI, as presented in Table 2.1

In systems engineering, optimization has to do with the efforts and processes of making a decision, a design, or a system as perfect, effective, or functional as possible. It can involve the specific methodology, techniques, and procedures used to decide on the one specific solution in a defined set of possible alternatives that will best satisfy a selected criterion. This is also known as system optimization and that is our concern in this project

The objective function of this project is the grease consistency but consistency has no empirical formula; hence in optimizing this project the objective is to minimize the cost of producing grease with the consistency of NLGI # 0 to 000 with plantain peel ash as the source of alkali.

Three major ingredients are required for grease production, but only two can be manipulated to optimize the profit. This can be achieved by minimizing their costs. The three ingredients are Alkali, Palm Oil and Lubricating Oil. However the two variables whose costs can be minimized are alkali and lubricating oil. There is little option in palm oil since there is only one palm oil type in the world. Cheap sourcing is the only option for it.

5.7.1. Bio-alkali production Optimization

To minimize the cost of production of bio-alkali, the following procedures are recommended

- (a) Location of plantain chips manufacturers and other eateries that deal on lots of plantain menu. These people will have lots of plantain peels.
- (b) Drying will not be carried out in oven as practiced by (Onyeagbado et al, 2002). Collected peels should be kept under any industrial heat source like boilers or burners as was practiced in this project. The waste heats from the burner will dry the plantain peels.
- (c) Very dried plantain peels should be set on fire either in open chamber or specially constructed incinerator. By this no fuel is wasted in the combustion process.
- (d) Any type of water, especially bore-hole water should be used in extracting the alkali since foamability of the soap base is not desirable.

This procedure was followed and the bio alkali produced was =N=50/litre when compared to its industrial equivalent of =N=150/litre.

5.7.2 Optimizing lubricating oil selection

Grease of NLGI#0 to 000 consistencies are mainly used in gear box applications that are either noisy, worn out or is leaking. Incidentally most gear oils are dark in colour. So instead of using a lighter coloured N-500 base oil whose cost is =N=250/litre, one should go for HPFO(high pour fuel oil) which is very thick and yet cost about =N=85/ litre. The grease will be darkish but not different from the colour of regular gear oil but much cheaper.

To formulate NLGI # 0 grease during this project work the following ratio was used

Grease = 36ml alkali: 100ml Palm oil: 200ml Lube Oil = 302g grease.

The cost of the grease will be N74 based on the prevailing cost of raw materials and the optimized bio-alkali grease will cost N40.8

Producing similar grease with regular caustic soda and N-500 base oil will cost N77.4

This makes production of Bio alkali grease very profitable for consistency of NLGI#0.

5.8 Comparative analysis of the grease samples

From Table 5.2, it obvious that the ratio of thickener of bio alkali soap to the base oil is 35% while it is 22% for sodium base control sample. This is not unexpected because the nature and structure of soap will determine the quantity of its soap that will thicken the grease formed. Oluremi, (2012) et al stated that soaps produced from the ash-derived alkalis were not solid; they were soft and jelly-like. This is expected as the percentage concentration of potassium in plantain peel is higher than that of sodium in the extract. The "softness" of the soap made from the extract could therefore be attributable to its large content of potassium hydroxide as potassium hydroxide soaps are known to be softer than the ones made from sodium hydroxide and have found uses in such areas as liquid soaps; as shampoos; shaving creams; cleaning of dirty floors and kitchen utensils; in emulsion polymerization processes used in rubber and plastic industries and in such other similar uses. However the percentage soap content of the grease is within the acceptable standards of 40%. Sodium base soap has lower soap percentage for the obvious reasons that it sodium hydroxide produces stronger soap than potassium hydroxide. From economic point of view, the higher percentage of bio alkali soap thickener present in the bio alkali grease is desirable since it is very cost effective.

5.9 Grease production parameters

Production of bio alkali grease presented better application of lower temperatures both for saponification and reaction than that of sodium base grease. While the grease has saponification and reaction temperatures of between 110 - 130 °C, sodium base grease production temperature ranged between 120-150 °C. This could be explained in two ways. One, bio alkali contains more of potassium hydroxide which is more reactive that sodium

hydroxide, hence saponification takes place at lower temperature than that of sodium soap. Also from Table 3.3, it is obvious that potassium has both lower melting and boiling point than sodium. The other reason why the maximum production temperature is higher in sodium grease could be attributed to stronger soap formed by sodium hydroxide and consequently, higher temperatures are needed to melt the soap base for intimate mixing with the lubricating base oil. This difference in temperature can be entirely attributed to differences in soap base since the same base oil was used. According to Olisakwe, (2011) grease formulations are mainly due to the composition and chemo-physical properties of the base oil with particular reference to viscosity especially in relation to temperature

After grease is produced, it is allowed to cool enough before use. The cooling time of bio alkali grease to storage temperature of 50 °C (from industry experience) was also shorter than that of the sodium base and the reason can be attributed to the sodium being a heavier alkali metal than potassium with the density of 0.97gcm⁻³ compared to 0.87 gcm⁻³ and also due to the higher reaction temperature achieved in producing sodium base grease. It took bio alkali 30 minutes to cool down from 130 °C to 50 degrees but took sodium one hour to cool down to 50°C from 150°C.

Blending time to produce bio alkali grease is shorter than that of sodium base but the reasons can be deduced from the factors mentioned above as regards reactivity and temperature requirements that favour bio alkali grease. This development should not be confused with the position of Awoyale et al, (2011) that the higher the quantities of the thickener or close to the amount of the base oil, the more difficult will be the formation of grease. This is because different soap bases are used in this work and his assertion could be true if the same soap base is used.

5.10 Grease consistency analysis

For the grease consistency test, both the prepared one and that of the controls (Sodium-base and Ascon NLGI#0 grease) were measured using the parameters of the un-worked and the worked penetration test and there were not much differences between them. A significant difference between un-worked and worked penetration if any indicates poor shear stability. Grease consistency is the resistance to deformation by an applied force; this depends on the type and amount of thickener used and the viscosity of the base oil. This is confirmable in Table 5.3 which shows the values (in mm) obtained from the un-worked and worked penetration tests.

5.11 Dropping point analysis

Dropping point test is of importance for grease properties because it gives a general indication of the temperature at which lubricating grease changes from semi – solid to liquid state under specific test conditions. The dropping point of the bio alkali grease was 123 °C and is lower than that of the sodium base (130 °C) and Ascon (127 °C) . This behaviour can be attributed to the fact that the bio alkali soap base has lower melting point than that of sodium soap, however the cost of producing bio alkali grease is the cheapest amongst the three samples. Ascon NLGI #0 grease is polymer-base and hence what was measured cannot be called dropping point technically because dropping points are specifically used for soap-base lubricating grease. With gearboxes, the acceptable operating temperature range can be up to 50°C more than the ambient temperature (maximum 45°C) because of the compactness and the lower quantity of oil contained in modern gearboxes. With a standard gearbox, the maximum allowable inside temperature is 80°C. Higher temperature could damage the oil seals (www.rotomotive.com/support_operating_temperature.html). This shows that all the three samples can withstand the maximum temperatures a gear box can generate. This further

makes the bio alkali grease suitable for gear box applications. While the other samples had better performances indices, bio alkali performances are within the acceptable standard and the grease is much cheaper than the other samples. This makes the prospect of producing bio alkali grease attractive.

CHAPTER SIX

6.0 CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

From the result of this study, it was concluded that:

- (1) Alkali from plantain peel was discovered to form a good grease base but only in the range of consistency number NLGI#0 to 000.
- (2) The cost of bio-alkali produced was N50/litre as against N150/litre of its industrial equivalent. This will help producers cut down the cost of their production by exploring vast quantities of bio-wastes that can be converted to bio-alkali.
- (3) The bio-alkali produced was good when compared to both the sodium-base and commercial grease used as controls.
- (4) The combination of specific gravity and percentage volume of the bio-alkali that gave the best consistency of 361 are 1.255 and 36% respectively.
- (5) The consistency of the bio-alkali grease is within the ASTM standards and the dropping point can comfortably accommodate temperatures generated with gear boxes for which the consistency is suitable for applications.

The overall benefit of this study is that the knowledge gap of appropriate stoichiometry for producing grease from ashes of plantain peel has been provided, and dumping of plantain peels in heaps in farms which is considered adverse to soil fertility will stop.

6.2 Recommendations

It is recommended that further researches should be carried out on using composite mixture of bio-alkali and pure sodium hydroxide to produce grease. This is necessary because since sodium-base can produce very hard grease, the composite mixture of bio-alkali and pure

sodium hydroxide will definitely produce grease that has better consistency than that of ordinary pure bio-alkali and at the same time cheaper in price than those produced from pure sodium hydroxide. These mixed-base greases will definitely have wider applications than those of bio-alkali and more affordable than their commercially available equivalents.

APPENDIX

ANOVA IN SPLIT-PLOT RANDOMIZED COMPLETE BLOCK DESIGN

The Experimental Design is a factorial experiment in a Split-Plot Randomized Complete Block Design (RCBD). Data was used from Table A1 shown below while Table A2 is for a sub-plot analysis. Analysis of Variance (ANOVA) was carried out to determine the effect of Specific gravity (SG) and Volume (V) of Bio-alkali on the Consistency of the lubricating grease produced. Facilities for construction of split-plot designs are not as yet generally available in software packages; with SAS/JMP being one exception (Jones and Nachtsheim, 2009). Therefore manual calculations will be done using machine formula shown in the appendix (Anova in RCBD), since EXCEL and other available software cannot do it properly. Besides, the construction of the ANOVA will be in nested format.

The ANOVA is shown in Table A3.

To construct the ANOVA table, it is necessary relevant information and formula be stated.

Factor A is specific gravity, $a=5$, Factor B is Volume, $b=5$, Replications, $r=3$

Table A1. Consistency measurements

	SG	%VOL	REPLICATIONS			
			I	II	III	
	1.245	45	500	500	500	1500
		42	475	474	475	1424
		39	470	472	471	1413
		36	475	473	472	1426
		33	500	500	500	1500
TOTAL		ΣV	2420	2419	2418	7257
	1.250	45	500	500	500	1500
		42	500	500	500	1500
		39	430	429	430	1289
		36	365	364	367	1096
		33	370	372	371	1113
TOTAL		ΣV	2165	2165	2168	6498
	1.255	45	500	500	500	1500
		42	500	500	500	1500
		39	400	399	402	1201
		36	361	360	362	1083
		33	369	367	366	1102
TOTAL		ΣV	2130	2126	2130	6386
	1.260	45	500	500	500	1500
		42	500	500	500	1500
		39	480	479	481	1440
		36	465	463	464	1392
		33	410	411	412	1233
TOTAL		ΣV	2355	2353	2357	7065
	1.265	45	500	500	500	1500
		42	500	500	500	1500
		39	480	483	481	1444
		36	470	472	471	1413
		33	472	473	474	1419
TOTAL		ΣV	2422	2428	2426	7276
G/TOTAL		$\Sigma\Sigma V$	11492	11491	11499	34482

Table A2. Block total readings for total sum of squares for Sub-Plot Analysis

	FACTOR B					TOTAL
	b1	b2	b3	b4	b5	
a1	1500	1424	1413	1420	1500	7257
a2	1500	1500	1289	1096	1113	6498
FACTOR A a3	1500	1500	1201	1083	1102	6386
a4	1500	1500	1440	1392	1233	7065
a5	1500	1500	1444	1413	1419	7276
TOTAL	7500	7424	6787	6410	6362	34482

NB

N.S means not significant

* means Significant

** means highly significant

Mean square MS = SS/d.f

Error = Total – treatment

Observed F = MS_{tr}/MS_e

Expected F, from Table.

Table A3. ANOVA showing the effect of Specific gravity and Volume of Bio-alkali on the consistency of lubricating grease.

SOURCES OF VARIATION	D.F	S.S	M.S	OBS.F	EXPECTED F	
					5%	1%
MAIN PLOT ANALYSIS						
μ	1	158344.32	-	-	-	-
Block	2	1.52	0.76	0.82 ^{N.S}	4.46	8.65
Factor A	4	48119.13	12029.78	12935.25**	3.84	7.01
Error(a)	8	7.43	0.93			
Total	14	48128.08				
SUB-PLOT ANALYSIS						
Factor B	4	78526.75	19631.69	24850.24**	2.61	3.83
Interaction AB	16	52831.13	3301.95	4179.68**	1.90	2.49
Error(b)	40	31.72	0.79			
Total	60	131389.60				
Grand Total	74	179517.68				

Main Plot analysis

(i). Correction For the Mean

$$CFM = (\sum X^2 \dots) / abr = (\sum \sum \sum X_{ijk}^2) / abr \dots \dots (1)$$

$$= (500+475+\dots+474+471)^2 / 5 \times 5 \times 3 = 1583444.32$$

(ii). Total Sum of Squares

$$TSS = \sum \sum \sum X_{ijk}^2 - CFM \dots (2)$$

$$[(500)^2 + (475)^2 + \dots + (474)^2 + (471)^2] - 1583444.32 = 179517.68$$

(iii) Block Sum of Squares

$$\begin{aligned} \text{BSS} &= (\sum X^2_{i..})/ab - \text{CFM} && \dots (3) \\ &= [(11492)^2 + (11491)^2 + (11499)^2]/5 \times 5 - 1583444.32 = 1.52 \end{aligned}$$

(iv) Factor A Sum of Squares

$$\begin{aligned} \text{FASS} &= (\sum X^2_{.j.})/rb - \text{CFM} && \dots (4) \\ &= [(7257)^2 + (6498)^2 + \dots + (7276)^2]/3 \times 5 - 1583444.32 = 48119.13 \end{aligned}$$

(v) Error_(a) Sum of Squares

$$E_{(a)}\text{SS} = \text{Whole plot SS} - \text{BSS} - \text{FASS} \quad \dots (5)$$

$$\begin{aligned} \text{Whole plot SS} &= (\sum \sum X_{ij.})/b - \text{CFM} && \dots (6) \\ &= [(2420)^2 + (2419)^2 + \dots + (2426)^2]/5 - 1583444.32 = 48128.08 \end{aligned}$$

$$E_{(a)}\text{SS} = 7.43$$

(vi). Factor B Sum of Squares

$$\text{FBSS} = (\sum X^2_{..k})/ar - \text{CFM} \quad \dots (7)$$

From Table 7,

$$\text{FBSS} = [(7500)^2 + (7424)^2 + \dots + (6361)^2]/5 \times 3 - 1583444.32 = 78526.75$$

(vii) Interaction AB Sum of Squares

$$\begin{aligned} \text{ABSS} &= (\sum X^2_{.jk})/r - \text{CFM} - \text{FASS} - \text{FBSS} && \dots (8) \\ &= [(1500)^2 + (1500)^2 + \dots + (1419)^2]/3 - \text{CFM} - \text{FASS} - \text{FBSS} = 52831.13 \end{aligned}$$

(viii) Error_(b)SS Sum of Squares

$$\begin{aligned} E_{(b)}\text{SS} &= \text{TSS} - \text{Whole Plot SS} - \text{FBSS} - \text{ABSS} && \dots (9) \\ &= 31.72. \end{aligned}$$

Standard Errors of the Experiments

(a) Standard error of the difference between two factor A means or between two main plot

(whole plot) treatment means is as follows:

$$\begin{aligned} S_d &= \sqrt{(2E_{(a)}/rb)} && \dots (10) \\ &= \sqrt{[(2 \times 7.43)/3 \times 5]} = 0.99532 \end{aligned}$$

(b) Standard error of the difference between two factor B means, that is, two sub-plot

Treatment means is given as

$$S_d = \sqrt{(2E_{(a)}/rb)} \quad \dots (11)$$

$$= \sqrt{[(2 \times 31.72)/3 \times 5]} = 2.055$$

(c) Standard error of the difference between two factor B means (i.e. sub-plot treatment

Means) for the same level of factor A i.e. $a_1b_1 - a_2b_2$ is given as

$$S_d = \sqrt{(2E_{(b)}/r)} \quad \dots (12)$$

$$= \sqrt{[(2 \times 31.72)/3]} = 4.599$$

(d) Standard error of the difference between two factor A means of the same or different

levels of B i.e. $b_1a_1 - b_2a_1$ or $b_1a_1 - b_2a_1$ is given as

$$S_d = \sqrt{\{[2(b-1)E_{(b)} + E_{(a)}]/rb\}} \quad \dots (13)$$

$$= \sqrt{[(2 \times 4 \times 31.72 + 7.43)/3 \times 5]} = 4.173$$

FLSD CALCULATIONS

1. For factor A, specific gravity,

$$FLSD = LSD = t_{\alpha/2, \text{Error (a) d.f}} \times S_d \quad \dots (14)$$

From ANOVA table, Error (a) d.f = 8, and from eqn(10), S_d for A = 0.99532

From the student t-distribution table, $(t_{\alpha/2}, 8) = 3.36$

Then $FLSD_{0.05} = 3.36 \times 0.995 = 3.343$

2. Secondly FLSD was done for factor B, the volume of bio-alkali.

From equation (11), S_d for factor B is 2.055. From ANOVA Table 8 Error(b) d.f = 40.

From student t-test table, $(t_{0.025}, 40) = 2.02$

$FLSD = 2.055 \times 2.02 = 4.$

Table A4. Summary of measured parameters of the plantain peel ash grease

Specific Gravity	% Volume of ash extract				
	33%	36%	39%	42%	45%
1.245	500 (fluid)	475 (fluid)	471 (fluid)	475 (fluid)	500 (fluid)
1.250	371 (very soft)	365 (very soft)	430 (semi fluid)	500 (fluid)	500 (fluid)
1.255	367 (very soft)	361 (very soft)	400 (semi fluid)	500 (fluid)	500 (fluid)
1.260	411 (semi fluid)	464 (fluid)	480 (fluid)	500 (fluid)	500 (fluid)
1.265	473 (fluid)	471 (fluid)	481 (fluid)	500 (fluid)	500 (fluid)

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