PRODUCTION OF HIGH TEMPERATURE GREASE USING SPENT BLEACHING EARTH (SBE)

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PRODUCTION OF HIGH TEMPERATURE GREASE USING SPENT BLEACHING EARTH (SBE)

NOR AZLINA BT MOHD ALI

A thesis submitted in fulfillment of the
requirement for the award of the degree of
Bachelor of Chemical Engineering

Faculty of Chemical and Natural Resources Engineering
University Malaysia Pahang

DECEMBER 2010

"I hereby declare that I have read this thesis and in my
opinion this thesis is sufficient in terms of scope and quality for the
award of the degree of Bachelor of Chemical Engineering"

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Date : 3 DECEMBER 2010

I declare that this thesis entitled *'Production of High Temperature Using Spent Bleaching Earth (SBE)'* is the result of my own research except as cited in references. The thesis has not been accepted for any degree and it is not concurrently submitted in candidature of any degree.

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With the name of Allah,

The most gracious, The most merciful...

“

Allah! There is no God but Him;
The living, the Self-subsisting, the Eternal.
No slumber can seize Him, nor sleep.
All things in heaven and earth are His.
Who could intercede in His presence without His permission?
He knows what appears in front of and behind His creatures.
Nor can they encompass any knowledge of Him except what he will.
His throne extends over the heavens and the earth,
and He feels no fatigue in guarding and preserving them,
for He is the Highest and Most Exalted.
”

(Surah Al-Baqarah: 255)

To my beloved parents:

Mr. Mohd Ali bin Mohd Nor and Mdm. Norasikin bt Che Abu Bakar

Who gave me everlasting inspiration, never-ending encouragements and priceless support towards the success of this study.

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ABSTRACT

Nowadays, the disposal problem of Spent Bleaching Earth (SBE) from oil palm industry has become a serious environmental issue. Therefore, attempt was made in this research to utilize the SBE as raw material in the production of high temperature grease. The scope of this research includes preparation of calcium fluoride as thermal resistance additives, grease preparation and analysis on the grease produced. The parameters studied for grease preparation are effect of different ratio of SBE and fumed silica as thickener and effect of mixing time. The ratios of SBE used in grease formulation were varied from 100 wt. % to 60 wt. % of thickener weight. The best ratio chosen from grease formulation is based on the dropping point test before it was further used for second parameter. As a second parameter, the mixing time of grease preparation was varied at 1, 2, 3, 4 and 5 hours. The grease produced was analyzed for dropping point, worked penetration, copper corrosion, organic content using FTIR and metal content using AAS. The results obtained were compared to the National Lubricating Grease Institute (NLGI) Guide to classify the grease. Results indicate that the best ratio for grease formulation is 90% of SBE and 10% of fumed silica. Therefore, the usage of fumed silica which is very expensive can be reduced. Results also shows that the consistency of grease decreased as the mixing time increased. With refer to NLGI standard, the consistency of all grease at mixing time 1 to 5 hour is in the range of 2 to 4 grade number and can be classified as high temperature grease since its dropping point is higher than 260^{o}C. As a conclusion, the findings from this research has the high potential to help in solving the environmental problem on SBE disposal which is in line with the government campaign to reduce waste in daily life and indirectly can reduce the production cost with this SBE based grease.

ABSTRAK

Pada masa ini, masalah pembuangan tanah liat pemutih terpakai (SBE) dari industri kelapa sawit menjadi isu alam sekitar yang serius. Oleh kerana itu, usaha dilakukan dalam kajian ini untuk menggunakan SBE sebagai bahan mentah dalam penghasilan gris bersuhu tinggi. Kajian ini merangkumi penyediaan kalsium fluorida sebagai penambah tahan panas, penghasilan gris dan analisis terhadap gris yang dihasilkan. Pembolehubah yang dikaji ialah kesan daripada perbezaan nisbah SBE dan silika kesal sebagai pemekat dan kesan masa campuran. Nisbah SBE digunakan dalam formulasi gris berbeza-beza dari 100 *wt.* % hingga 60 *wt.* % daripada jumlah berat pemekat. Nisbah terbaik dipilih daripada formulasi gris berdasarkan pada ujian titik pertukaran menjadi cecair sebelum nisbah itu diguna pakai untuk pembolehubah kedua. Untuk pembolehubah kedua, terdapat lima waktu pencampuran yang berbeza ketika penghasilan gris telah dikaji iaitu pada 1, 2, 3, 4 dan 5 jam. Gris yang dihasilkan telah menjalani ujian titik pertukaran menjadi cecair, ujian penembusan, ujian hakisan ke atas kuprum, ujian kandungan organik menggunakan FTIR dan ujian kandungan besi menggunakan AAS. Keputusan yang diperolehi dibandingkan dengan panduan daripada *National Lubricating Grease Institute* (NLGI) untuk menetapkan kelas gris. Keputusan kajian menunjukkan bahawa nisbah terbaik untuk perumusan gris adalah 90% SBE dan 10% kesal silika. Oleh itu, penggunaan silika kesal yang sangat mahal dapat dikurangkan. Selain itu, konsistensi gris menurun dengan peningkatan masa pencampuran. Merujuk kepada panduan NLGI, konsistensi gris adalah dalam julat nombor 2 hingga 4 dan boleh digolongkan sebagai gris pada suhu tinggi apabila titik pertukaran menjadi cecair lebih tinggi daripada 260^{o}C. Sebagai kesimpulan, penemuan daripada kajian ini berpotensi tinggi untuk membantu dalam menyelesaikan masalah persekitaran iaitu pembuangan SBE dan ini selaras dengan kempen kerajaan untuk mengurangkan sisa dalam kehidupan seharian, secara tidak langsung dapat mengurangkan kos penghasilan gris dengan terhasilnya formulasi gris daripada SBE.

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LIST OF ABBREVIATIONS

AAS	-	Atomic Absorption Spectroscopy
ASTM	-	American Standard Testing Materials
AW	-	Anti- wear
EP	-	Extreme Pressure
FTIR	-	Fourier Transform Infrared
MDF	-	Medium Density Fibreboard
NLGI	-	National Lubricating Grease Institute
SBE	-	Spent Bleaching Earth

LIST OF SYMBOLS

^{o}C	-	Degree Celcius
”	-	Inch
%	-	Percentage
wt. %	-	Weight percentage
ppm	-	part per million

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Grease is a semi-solid lubricant possessing higher viscosity than oil formed by three composition which are base fluid (60-95%), thickener (5-25%) and additives (0-10%) (Adhvaryu *et al.,* 2005). The function of base fluid is giving the lubricating properties to the grease itself. Mineral oil, synthetic oil and vegetable oil are usually used as grease base fluid to substitute the animal fat that use in yesteryears. Thickener on the other hand is used to thicken the grease and hold the matrix together to avoid mobilizes of grease structure. It is also function as a gelling agent. Basically, fatty acids soap of alkali metals is used as a thickener such as lithium soap, sodium soap and calcium soap or inorganic thickeners, such as bentone or silica are considered are to be not harmful to the environment (Kragujevac *et al.*, 2005). Additives can be classified regarding different aspects to enhance the grease properties base on their applications. Antioxidant, antifoam, antiwear, extreme pressure and high temperature agent are usually used as an additive in grease production. Base fluid generally cannot satisfy the requirements of high performance grease without using the advantage of additives.

High temperature grease and oil is often a synthetic lubricant as the temperature range of conventional grease and oils is easily exceeded by the demands of modern machinery and equipment. Plastic extrusion machinery, glass manufacture, chipboard and MDF plants all need high temperature grease and oil. As the marketing requirement of high temperature grease is increasing and widely used, other method to produce grease should be explored.

Spent bleaching earth (SBE) is a solid waste material generated from the bleaching process of oils and fats. It is generated from pre-treatment of crude palm-oil in refinery in which involves degumming and bleaching. SBE is recycled using solvent extraction process to remove residual oil before reactivation by heat treatment. Regenerated SBE still has adsorptive capabilities and can be reused in the bleaching of crude palm oil.

The disposal of by-products, spent material and industrial waste is one of the major problems face by oils industry today. Regulations for disposal are become stricter. The disposal method must be carefully chosen according to special regulation as directed by environmental department. In Europe, oil and fat industry as well as their by-product and spent material received huge concerned and special enforcement on reuse and regeneration as much as possible for chemical or technical purposes are made (Svensson, 1976).

Malaysia, as the second largest oil palm producer in the world generate large amount of SBE. So, everyday there are a large amount of SBE released from the industry as waste based on worldwide oil production. SBE is commonly disposed at landfills nowadays. However, disposal of untreated spent bleaching earth from crude palm oil industry into landfill is increasingly unacceptable because it is s hazardous to environment due to the substantial oil content in the earth. The SBE has a strong odor, and spontaneous ignition easily occurs if contact with air.

Therefore, a new formula of producing grease should be investigated to solve these two main problems. In that case SBE from oil palm industrial waste respectively will play an important role as a continuous source of raw material for grease production.

1.2 Problem Statements

It is estimated that about, 600000 metric tons or more of bleaching earth are utilized worldwide in the refining process based on the worldwide production of more than 60 million tones of oils (Kheang *et al*., 2006). The similarity of physical properties of regenerated SBE compared to the fresh clay opens for more applications as industrial adsorbents. Pollards *et al.* (1990) reported that SBE was effective in the stabilization or solidification of mixed streams organic matters.

In the oil refining industry, SBE served as by-product and it is containing high percentage of oil. Typically, SBE from oil palm industries contains 17-35% residual oil, metallic purities, fatty acids and gum. The SBE or this solid waste clay is disposed directly to the landfills without treatment causing severe water and air pollution problems (Fletto *et al.,* 2002). However, the dumping of spent clay directly in landfills and public disposal site has been prohibited in most country nowadays. The waste management concerning about the disposal of residues from refineries industry.

Recovery of oil and the reuse of spent bleaching clay are the areas where great opportunity exists for cost saving in the oil processing industry (Fletto *et al.,* 2002). Besides that, the characteristics and lubrication properties of the residual oil and composition of the resulting methyl esters during bleaching shows that the oil has good lubricity such as suitable viscosity range and high viscosity index for use as a lubricant base. SBE can also be used as raw material for high performance grease so that it can maintain a thin film over the metal parts of machines and the oil contact surface to smoothen and lubricate them. Therefore, an economic alternative to solve the disposal problem and current treatment of SBE is by re-used the SBE to produce other oil product such as high temperature grease.

1.3 Research Objective

The objective of this research is to study the production of high temperature grease using spent bleaching earth (SBE).

1.4 Research Scopes

In order to achieve the objective as stated above, the following scopes of study have been identified:

i. To produce a thermal resistant additive which is Calcium Fluoride (CaF_2) for grease formulation.
ii. To study the effect of different ratio of SBE and fume silica on grease formulation using additive produced from 1.4 (i).
iii. To study the effect of different mixing time on grease formulation at constant ratio from 1.4 (ii).
iv. To characterize the grease produced by dropping point, work penetration, copper strip, AAS and FTIR test.
v. To compare the characteristics of grease produced.

1.5 Rationale and Significance

It is a responsibility as a nation and society to become more concern in handling a large amount of waste generated by industry every day. Waste to wealth is a good approach in order to promote zero waste concepts. As highlighted in the previous section, disposal of SBE has become an environmental issue since the high content of oil in SBE can cause pyrogenic effect. Although attempts have been made by other researcher to recover the oil contains in the SBE, it still does not resolve the main problem which is the disposal of SBE.

Besides that the increasing price of mineral oil due to the high market requirement of petroleum product but with limited mineral sources also becomes an important reason to conduct this research. Utilizing SBE as raw material to produce high temperature grease indirectly saves a lot of money due to conversion of waste into wealth. It is hoped that by utilizing SBE as one of the raw material in grease formulation will able to solve the disposal problem and at the same time reduce grease market price.

CHAPTER 2

LITERATURE REVIEW

2.1 Background of Grease

Lubricating grease is a semisolid product which is generally highly structured colloidal dispersions, consisting of a thickener dispersed in synthetic or mineral oil. Grease is the preferred form of lubrication in hard-to-reach places in a mechanically rubbing or dynamic systems. Lubricating greases has been a need during the ancient times. The Greeks and Roman used animal fat and also vegetable oil as lubrication. They used the animal fat to run machines of various kinds, mills, pulleys, windlasses, chariots and fast carriages. Nowadays, with the modern and advanced technology, the animal fats are not in use as lubricants (Harris *et al.*, 1974).

Grease acts as reservoir for lubricant-based fluids and additive molecules (Adhvaryu *et al.*, 2005) and most of its functional properties depends on their ability to flow under force, shear stability, resistant toward viscosity changes with temperature and pressure, water stable, seal out contaminants, decrease dripping and spattering. The dependability of lubricating grease depends on their physical properties that are most related to the grease structure, which is obtained by the proper selection of ingredients and processing. Additives are usually introduced during the cooling phase of grease making and they remain dispersed in the matrix.

These additives are found to enhance some of the functional properties of the base oil in the grease to achieve high performance requirement such as oxidation, load-bearing, anti-wear, anti-corrosion, and anti-rust. A typical composition of grease as illustrated in Figure 2.1 includes base fluids, thickener, and additives. The base fluid is contained and stabilized in the matrix by the fiber structure of the soap molecules. Metals usually used in the soap composition include lithium, calcium, sodium, aluminum, and titanium as grease thickener (Adhvaryu *et al.*, 2005).

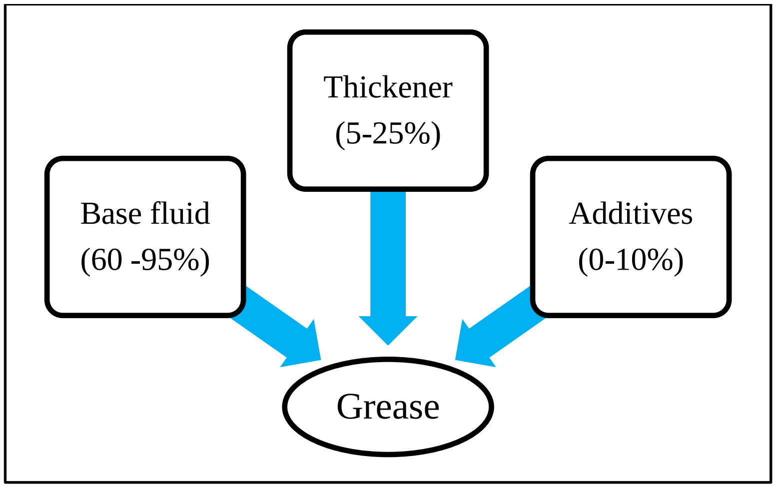


Figure 2.1: Typical composition of grease

Greases fail more rapidly as temperature of operation increases. The most obvious reason for failure lies in the melting point of the thickener or dropping point of the grease. The latter involves a complex of melting and bleed. Evaporation may be significant at high temperatures. Oxidation also increases rapidly as temperature rises. Most mineral-oil-based greases (of adequate dropping point) will operate successfully to about 250 °F (121°C). A smaller number can handle 300 °F (149°C). A few mineral-oil-based greases can operate to about 350°F (177 °C). Around this temperature, synthetic fluids are preferred or required. As service temperature rises, frequency of lubricant addition and relubrication must increase (NLGI, Lubricating Grease Guide, 2006).

The thickening agent commonly used is a metallic soap prepared by saponification of a fatty substance, but can be also a non-soap based such as polyurea or organoclay. The organoclay is widely used in various applications in industry as structure-forming and thickening agents in inks, paints, cosmetics, drilling fluids and lubricating grease formulations due to the ability of swelling and gel formation on organic media cause. Besides that, the use of organoclays as thickening agents in grease formulations confers excellent thermal stability and high performance qualities to the greases (Chtourou *et al.*, 2006). The dispersion of organoclays in lubricating oil is described as the mechanism which separates the individual agglomerated organoclay particles. Dispersion is typically accomplished by the use of polar activators (alcohols, ketones, amides, nitriles) and mechanical shear. The gel structure of the grease is caused by hydrogen bonding between dispersed organoclay particles creating a gel network.

2.1.1 Advantages and Disadvantages of Grease

Grease has their own advantages that make them more suitable to use as lubricant compared to other oil. Some of the reasons are grease has the ability to stay in place or immobilize and does not readily leak from the bearing because it incorporates the use of a thickener matrix. Besides that, it also can seal out the contaminants that can reduce the efficient of the lubricant. Grease also decreases dripping, splattering and leakage due to its high consistency. As its function is to reduce friction, grease can reduce the noise of machine during operation so that the machinery also tends to need less power while operating. In addition, because of its composition which have base oil, thickener and additive which is have their own properties to enhance the grease performance, it can make the greases can work under extreme operating conditions (*MOBIL* Grease).

However, greases may bear some advantages such as it may not reach all places in need of lubrication because it has high viscosity. Besides that, greases do not work as cooling agent because it cannot dissipate heat by convection like circulating oil due to its consistency. Another disadvantage is grease cannot be used at as high speeds as liquids because grease has more resistance to motion at start-up than oil (*MOBIL* Grease).

2.2 Production of Grease

In 1400, animal fat such as mutton or beef fat was sometimes used as grease by mixed the fats with lime to reduce the friction in chariot wheels. With a right condition, lime and oil will be heated to produce grease. However, modern greases were not commercially available until more than 3 300 years later. The first grease produced was a calcium soap grease then it followed by lithium, barium and calcium complex greases which are introduced in 1930s and 1940s. Aluminum complex greases followed in the early 1950s, but modern lithium complex greases did not enter the market until the early 1960s (NLGI Lubricating Grease Guide, 2006).

The grease production data has been collected from manufacturers by the National Lubricating Grease Institute (NLGI) since the early 1960s. The trends can be noted by reviewing the historical data as illustrated in Figure 2.2.

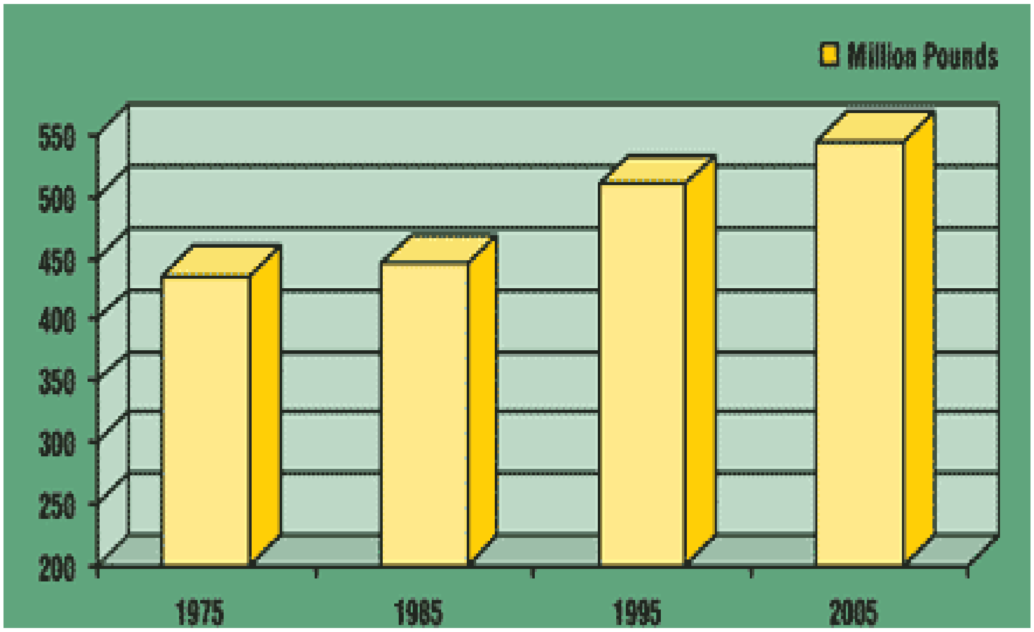


Figure 2.2: Grease production from 1975 till 2005 (NLGI Lubricating Grease Guide, Fifth Edition, 2006)

There are two types of process route in grease manufacturing which is batch process or in-line process. Details descriptions are provided in Section 2.2.1 and 2.2.2.

2.2.1 Batch Process

For batch process, typical grease kettle with capacity ranged from 2 tons (4000 lbs) to 20 tons (40,000 lbs) is used. This grease kettle are heated with steam or hot oil to temperature approximately at 200°C (395 °F) or higher. In order to improve mixing efficiency, rotating paddle which can force the grease in appropriate directions is installed in the kettle. Besides that, kettles also have recirculation pumps to provide additional vertical mixing action and to transfer the grease to other processing equipment such as a homogenizer. Homogenizer is used to ensure the grease is homogenized mixed by means of milling. It has own purposes such as enables the grease to withstand a shearing action therefore only little changes in consistency during service (Jones, 1968).

2.2.2 In-Line Process

In-line process is differing from batch process because it is a continuous process. The process is begins with saponification followed by dehydration before finishing stage. This process is more flexible, fast and has a better process control. Figure 2.3 shows a comparison between batch and in-line grease manufacturing process. Detail explanations on the stage involve during grease manufacturing process is provided in Section 2.2.3.

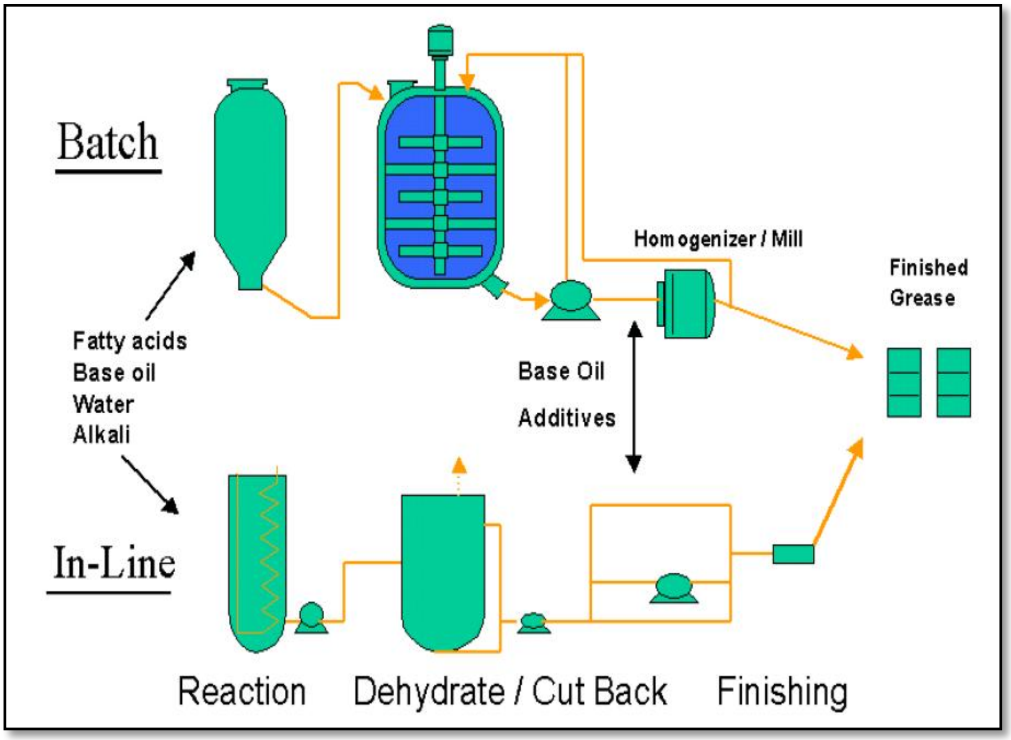


Figure 2.3: Comparison of grease manufacturing process

2.2.3 Stages in Grease Manufacturing

2.2.3.1 Manufacturing of Soap-Based Grease

The production or manufacturing of soap base grease can be divided into four stages. The stages include saponification, forming a solution, soap recrystallization and grease finishing (Jones, 1968). The detail explains are provided following section.

2.2.3.1.1 Saponification

Saponification can be defined as a process when a fatty acid reacts with an alkali and the salt produced is called soap. Most animal and vegetable fats contain glycerin which combined with fatty acids. During saponification process, fat is separated into fatty acids and glycerin by reacting with the alkali. Then, the fatty acid reacts with the alkali to produce soap and water. The reaction carried out in the reaction vessel because it operates at high temperature and needs heat in order to run a quick reaction and water also added in many cases.

There are many types of fats and fatty acids used in grease manufacturing. The cheaper greases usually made up from calcium hydroxide as the alkali and fats such as tallow, bone grease and whale oil products (Jones, 1968c). As time move on, the formulation of grease always improve in order to produce grease with a good quality. Therefore, it is quite common to find specific fats that can be used to enhance grease properties. When the fats with higher concentration are used as raw materials, it is obviously possible to maintain higher standard of product quality and manufacturing control. The soap produced from different alkali will imparts different grease characteristics.

2.2.3.1.2 Forming a Solution

The soap is transfer from reaction vessel into open kettle for structure forming and further cooling stage. Then, it will be continued heating until it dissolved in lubricant. During this process, dehydration may take place. In the previous section, water and glycerin are produced during saponification stage. Some glycerin may be lost during dehydration, but the rest will act as a structure modifier in the finishing stage and it will confer the resistance of heat stability to the grease. Its acts as a modifier of structure and can help grease some measure of heat stability. In order to achieve best result, heat is supply continuously until temperature reaches 250°C (Jones, 1968).

2.2.3.1.3 Soap Recrystallization

This stage is for cooling the soap that already obtained so that the structure is imparted to the grease. In order to produce satisfactory grease, the soap must have a good structure. If the structure is not suitable enough, the hardness of grease will reduces when subjected to a shearing action and the separation of oil or ‘bleed oil’ from grease may occur during storage until it becomes liquefied. The soap will dissolve in hot oil and it is cooled. Before reach ambient temperature the soap will therefore have recrystallized in various forms. Some of these forms take the shape of thick fibres and others short thin fibres when viewed under the electron microscope. The various structure of grease can be produced by controlling the cooling rate during recrystallization (Jones, 1968).

2.2.3.1.4 Finishing

As the last stage of production of grease, it is important to homogenize the grease by milling. At the end of this stage, the required of grease structure that has been formed will achieved except for non-soap thickened product. Milling has several purposes such as can enable the grease to withstand a shearing action and it is carried out by passing the grease through a gap between two surfaces (Jones, 1968). After milling process, it is necessary to filter the grease to remove any impurities or large particles of undispersed soap before final packaging.

2.2.3.2 Manufacturing of Non-soap Based Grease

The preparation of non-soap grease is often a relatively simple process compared to soap thickened grease. In a kettle with agitator, the thickener is gradually added to the base fluid or lubricant so that thickener will disperses in the lubricant by an efficient means of stirring and heating. According to Jones, 1968, the grease is wetted by means of wetting agent such as acetone that possessing polar chemical structure during the preparation of organiclay bentonite grease.

2.3 Types of Grease and Applications

Grease is a semi solid lubricant with viscosity higher than oil. The characteristics make grease suitable for heavy load applications and gearboxes. Machinery operating under very high temperature requires heavy lubrication. Grease provides a thick lubrication film, protecting the machinery from wear and tear. During extreme pressure conditions, the properties of thickener and additive will help to enhance the overall usage. There are many criteria to consider when selecting the grease based on their composition, consistency, application and usage. There are six general categories of grease which are light grease, heavy grease, multipurpose grease, extreme-pressure grease, soap thickened mineral oils and high temperature grease.

2.3.1 Light Grease

One of the main components of this grease is copper. It provides a thin but strong film on movable parts. Light grease oils are also applied on machine parts that are subject to conditions of high temperature such as brake pads and sliding break systems. It is also applied on nuts and bolts.

2.3.2 Heavy Grease

The composition for heavy grease is heavy asphaltic-type oils blended with lighter oils. These types of lubricants are classified as greases but are actually thick, heavy oils used to lubricate open-type gearing and wire rope. The main advantage of these oils is that they form a heavy protective film when heated or painted on surfaces and then allowed to cool. Lighter oil is typically blended with the heavy oils in order to improve the pour point of the oil.

The characteristics of heavy grease are to be thick and waterproof. It can helps to keep machines protect over a longer duration. Shackle pins and leaf springs require heavy grease to function accordingly, because light grease will wear off too fast.

2.3.3 Multipurpose Grease

For multipurpose grease, two types or more specialized grease is combined in their formulation to produce a single type of grease for variety applications. It is possible to replace as many as six specialized greases with single multi-purpose grease and get better results all at the same time. Most of the multi-purpose greases have a soap base of barium, lithium, or calcium complex.

They are not only water-resistant and corrosion inhibiting, but they have very good mechanical and oxidation stability as well. Good multi-purpose lubricating grease can perform well in various applications. Table 2.1 shows the general characteristics for multipurpose grease.

Table 2.1: General characteristics for multipurpose grease (Tribology, 1976)

Characteristic	Specification
NLGI Consistency Grade No.	2
Dropping Point (^oC)	185
Temperature Range (^oC)	-20 to 160

2.3.4 Extreme-Pressure Greases

The extreme-pressure (EP) grease has a unique characteristics which is it contains additives to improve firm strength under various applications. In essence, film strength provides the resistance of the lubricant to being torn apart, thus preventing metal-to-metal contact of the equipment being lubricated. A film is formed by a chemical reaction of the metal to the additives in the grease. The chemical reaction is usually accelerated by pressure exerted on the grease and creating heat. Wear, 1961 stated that using sulfur, chlorine and lead as grease additive will give the EP properties.

2.3.5 Soap Thickened Mineral Oils

Soap Thickened Mineral Oils is the most widely used category of grease in industry today. This type of grease varies by the additive that forms the soap in the lubricants chemical makeup and it is divided into four types soap thickened minerals oil grease. Details description of each type is provided in the following section.

2.3.5.1 Sodium Soap

Sodium soap is general purpose greases because they have a higher dropping point and they are often used to lubricate machine parts operating near heat. Sodium greases made with lighter oils are used for ball and roller bearing lubrications, as are combinations (mixed base) of calcium and sodium grease and the general characteristics for sodium-soap grease is shown in Table 2.2.

Because of their working stability and intermediate melting point, they are used for lubricating wheel bearings (other than disc brakes) and for general-purpose industrial applications. Typical examples include rough, heavy bearings operating at low speeds, as well as skids, track curves and heavy-duty conveyors.

Table 2.2: General characteristics for sodium-soap grease (Tribology, 1968)

Characteristics	**Specification**
Appearance	Usually fibrous Yellow or green in color
Water Resistance	Poor
Dropping Point (^oC)	150^oC

2.3.5.2 Lithium Soap

Lithium-soap grease possesses good water resistance properties together with ability to withstand extremes of temperature quite well, so that makes its highly suitable for both high and low temperature application. It is also suitable at low temperature performance until -50ºC because they are made with oil having a low pour point (Tribology, 1968). It is widely used in automotive application as well as industrial application. The characteristics for lithium-soap grease are provided in the Table 2.3.

Table 2.3: General characteristics for lithium-soap grease (Tribology, 1968)

Characteristics	**Specification**
Appearance	Smooth
Water Resistance	Good
Dropping Point (^oC)	180^oC

2.3.5.3 Calcium Soap

It is also called as lime-soap greases. Depending on the method of manufacture so that this type of grease inexpensive. Calcium-soap grease is not suited to applications where the temperature will get above 70ºC because its water content begins to dry out, and the soap and oil separate. The usages include for axle grease, water pump grease and general machinery applications. Table 2.4 shows the general characteristics for calcium-soap grease.

Table 2.4: General characteristics for calcium-soap grease (Tribology, 1968)

Characteristics	**Specification**
Appearance	Smooth
Water Resistance	Good
Dropping Point (^oC)	95^oC

2.3.6 High Temperature

High temperature grease generally describe as non-soap grease due to the usage of non-soap thickener such as polyurea and clay. Polyurea thickeners are preferred over other types of thickener because it imparts high dropping point up to 260^oC and antioxidant properties (Waynick, 1990). Other general characteristics for high temperature grease are shown in the Table 2.5. This type of grease is designed for high and heavy load for good performance in automotive machineries, electric motor, air craft and plastic extrusion machinery.

Table 2.5: General characteristics for high temperature grease (Tribology, 1968)

Characteristics	Specification
Appearance	Smooth
Water Resistance	Good
Dropping Point (^{o}C)	Higher than 260^{o}C Some grease are not determinable

2.4 Factors Affecting Grease Performance

There are a few factors affecting the grease performance. It can be composition in grease itself, type of thickener used in grease formulation, the mixing time during preparation and process temperature. In terms of grease composition, generally, modern grease formed by based fluids, thickener and additives that can affect on grease performance. The base fluid will stabilized in the matrix by the fiber structure in the molecules of soap. A complex network formed in fiber structures will trap based fluid molecules by direct sorption of the oil by polar ends of soap molecule and penetration of base oil in the interlacing structure of soap fiber. The oil retaining property of grease may be due to the attractive influence of soap fibers extending through many layers of base oil molecule and not to the swelling of the fibers (Browning, 1950). The additive generally used in grease formulation are oxidation inhibitors, corrosion and rust preventives, metal deactivators, extreme-pressure agents, solid lubricants (MoS_2, Graphite) and friction modifiers will give positive effect to grease performance.

In terms of thickener chosen, grease gives different performance based on type of thickener used such as clay, polyurea and silica based grease. As mentioned before, grease non-soap thickener will give great performance such as at high temperature and heavy load application compared to the soap-based that usually used in common application in industry such as at low temperature and pressure. According to Hayder *et* *al.* (2008) the usage of fumed silica as thickener will give higher dropping point due to its elongated, has chain like structure and high oil absorbing properties. Other evident also refer to Chtourou, 2006 which states that the grease properties such as excellent thermal stability and high performance qualities can be created by using organoclays as thickener in grease formulations.

Mixing time during preparation is important parameter because it also will affect the grease characteristics. The increases of mixing time will cause less viscosity of grease and become softer (Hayder *et al.*, 2008). This may be due to wetting of the agglomerate of mixture by fluid with increasing the time until the wetting is completed. After the wetting completed, there is only in a little changes in the texture. This texture of grease can give different characteristics to grease that will impart on grease performance. So, the chosen of composition, types of thickener and mixing time during grease formulation and preparation are very important to get the optimum result of grease.

2.5 Analysis and Test on Grease Characteristics

Analysis and test are usually performed on grease produced to check their properties using standardized method. This is very important for grease grading and classification. The suitable analysis for different characteristics is provided in Table 2.6.

Table 2.6: Test for grease characteristics (NLGI Lubricating Grease Guide, 2006)

Grease Characteristics	Analysis/Test
Consistency	Cone Penetration
Mechanical Stability	Working Stability, Roll Stability
High Temp. Performance	Dropping Point, Bearing Life Tests
Low Temp. Performance	Low Temperature Penetration and Torque, Flow Pressure
EP/AW Performance	TIMKEN and Four Ball Apparatus
Wet Condition Performance	Water Resistance, Water Washout, Water Spray-Off
Pumpability/Dispensability	Apparent Viscosity
Stability	Oil Bleed, Oil Separation
Others	Oxidation Stability, Copper Corrosion, Base Oil Viscosity, Solid Contaminants

2.5.1 Grease Consistency, Worked Penetration and Classification

Consistency is the condition of a material of standing together or remaining fixed in union, its resistance to movement or separation of the constituent parts. Grease consistency is important for both type of application (ability required to stay put, seal and lubricate) and method of application (dispensing method). For lubricating greases the consistency is usually determined by penetration test which is penetration depth of a standard cone under prescribed conditions of weight, temperature and time.

Based on National Lubricating Grease Institute (NLGI), 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 25ºC. 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 used in various industrial applications as shown in Table 2.7.

Table 2.7: Grease classification at different worked penetration (NLGI Lubricating Grease Guide, 2006)

NLGI Consistency (Grade no.)	ASTM Worked Penetration at 25ºC (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

2.5.2 Dropping Point

The dropping point is a material specific temperature, at which conventional greases pass from a semisolid to a liquid state and start flowing. In the laboratory the dropping point is expressed as temperature, at which the first drop of grease/oil is extruded from a sample under prescribed conditions.

Dropping point levels depend mostly on the thickener type, but could also vary considerably due to variations in raw materials and manufacturing process and thus could be used as quality control standard. A dropping point test result may be used as indication of the maximum temperature grease can be exposed to, but in practice operating temperatures should be kept well below it. The ASTM standard dropping point for different type of grease is shown in Table 2.8.

Table 2.8: ASTM Standard for Grease Dropping Point

Types of grease	Dropping Point Range (^oC)
Calcium Base Grease	71– 99
Sodium Base Grease	135 - 177
Lithium Base Grease	177 – 204.5
Bentone Base Grease	Over 260
Silicone Grease	Over 260

CHAPTER 3

METHODOLOGY

3.1 Introduction

This chapter provides explanations on experimental procedures involve in producing high temperature grease. The procedures are divided into three parts which are additive preparation, grease formulation at different ratio of SBE and fumed silica and grease analysis. For additive preparation, calcium fluoride is prepared as anti thermal resistance additive. The method of calcium fluoride preparation is explained in Section 3.3.1. In grease formulation, two parameters were studied which are different ratio of SBE and fumed silica as thickener and mixing time. Finally, grease produced are tested for dropping point, worked penetration, copper strip test, Fourier Transform Infrared Spectroscopy (FTIR) and Atomic Absorption Spectroscopy (AAS) to compare the characteristics of grease. Details procedures involve in grease formulation and analysis are further discussed in Section 3.3.2 and 3.3.3

3.2 Materials and Apparatus

For calcium fluoride preparation, calcium chloride (CaCl) and ammonium fluoride (NH_4F) are needed. The materials for grease preparation are silicone oil, spent bleaching earth(SBE), fumed silica, molybdenum disulfate (MoS_2), and the calcium fluoride (CaF_2) that prepare earlier. In grease analysis, Thermal B oil is used as heat transfer fluid for dropping point test, nitric acid (HNO_3) 65% and hydrogen peroxide (H_2O_2) 35% is used in grease digestion before running for AAS. The purity of all chemicals used are 99.9% to ensure the optimum result obtain except for HNO_3 and H_2O_2 which is 65% and 35% purity respectively as required in standard for grease digestion using microwave extractor. In the grease production, the apparatus used are 1 ml stainless steel beaker, 500ml beaker, vacuum filter and electrical heater with temperature controller. For grease analysis, the apparatus and equipments used are penetrometer, dropping point apparatus, copper strip, Fourier Transform Infrared Spectroscopy (FTIR) and Atomic Absorption Spectroscopy (AAS).

3.3 Experimental Procedures

3.3.1 Part I: Calcium Fluoride (CaF_2) Preparation

Calcium fluoride, CaF_2 prepared in this step is in nanocrystal form. The properties of nanocrystals CaF_2 is expected to give a better performance for grease formulation as compared to powder form. Firstly, 0.01 M $CaCl_2$ and 0.02 M NH_4F was diluted with 100ml distilled water in different flask before it was mixed with vigorous stirring. The mixture was stirred for 2 hours. The gradual transformation of the reaction mixture from transparent solution into opaque white suspension can be seen throughout this process. Then, the solid was separated via centrifugation with rotational speed was limited to 10 000 rpm (Wang *et al.*, 2007). As the last step, the slurry was filtered using vacuum filter to remove the residual chloride and the ammonium ions until white solid of the product collected. Summary of experimental procedure is illustrated in Figure 3.1.

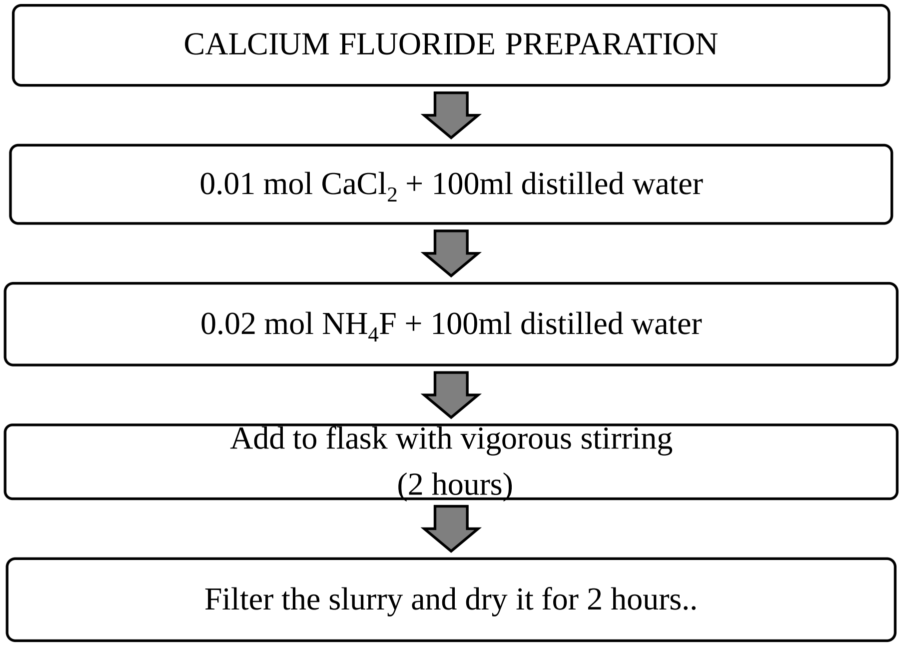


Figure 3.1: Flow chart of additive (CaF_2) preparation

3.3.2 Part II (a): Grease Formulation with Different Ratio of SBE and Fumed Silica

In this part, all the materials which are silicone oil, SBE, fumed silica, molybdenum disulfate and calcium fluoride were weighed. 25g of silicone oil was heated until 80°C in stainless steel beaker. After that, the thickener which is fumed silica was added to the beaker with non-stop stirring at the temperature range of will 100°C to 110°C to ensure the thickener is wetting and dispersed completely in the silicone oil. Then, SBE was added according to the ratio required. After 1 hour, the grease additive which is 5g (2 wt. %) of CaF_2 was added to the mixture followed by 0.05g (0.2 wt. %) of MoS_2. The stirring and heating in the range of 90^oC to 100^oC were continued for one hour. Lastly, the grease was cooled at the room temperature and it was kept in the suitable container. The steps above were repeated for different ratio of SBE and fumed silica as listed in Table 3.1. The flow chart of grease production is illustrated in Figure 3.2. Then the grease produced with different ratio of SBE and fumed silica has been analyzed for dropping point. The best ratio was chosen based on two criteria which are highest dropping point and highest amount of waste (SBE) used in its formulation.

Table 3.1: Ratio of fumed silica and SBE for grease formulation

Sample No.	Fumed Silica		SBE	
	Weight percentage, %	Mass, g	Weight percentage, %	Mass, g
1	0	0.00	100	25.0
2	10	2.50	90	22.50
3	15	3.75	85	16.25
4	25	6.25	75	13.75
5	30	7.50	70	12.50
6	40	10.00	60	15.00

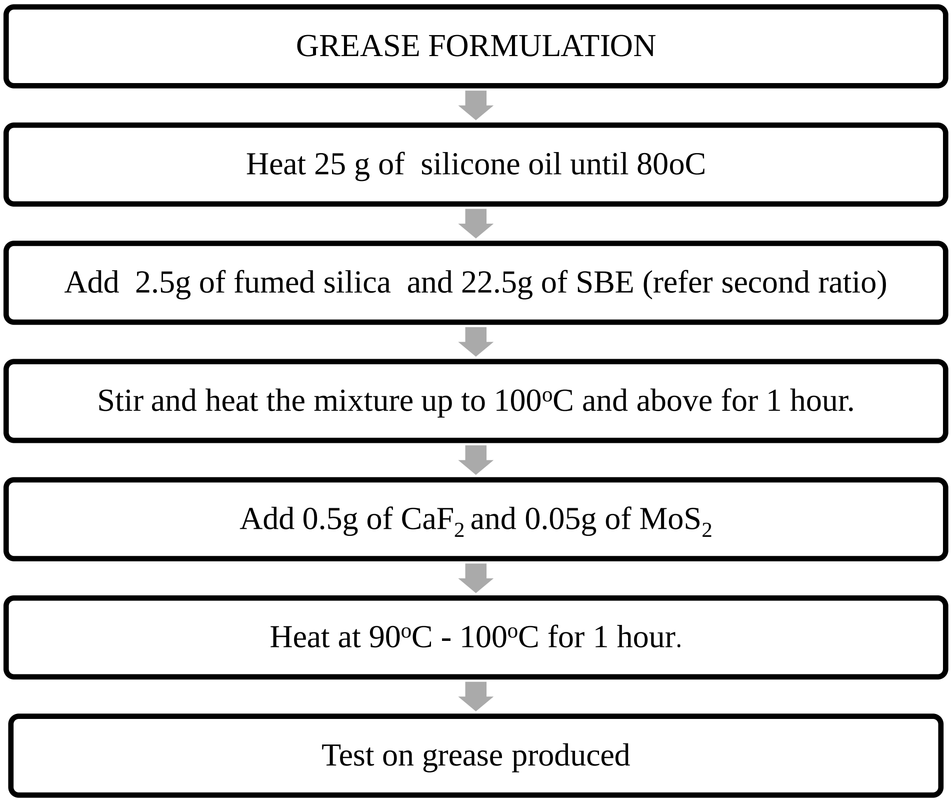


Figure 3.2: Flow chart of grease formulation

3.3.3 Part II (b): Grease Preparation with Different Mixing Time

The characteristics of the grease were tested on the grease based on the different mixing during preparation. The amount of grease required for this is about 500g. The same procedures for grease formulation as described in section 3.3.2 are repeated to produce the required amounts of grease. However, the mixing time was continued at 1,2,3,4 and 5 hours. After that, grease was characterized using few analyses to determine the best mixing time.

3.3.4 Part III: Analysis on Grease Characteristics

As mentioned before, the grease produced was tested for dropping point, work penetration, Copper Strip Test, metal content using Atomic Absorption Spectroscopy (AAS), and organic content using Fourier Transform Infrared Spectroscopy (FTIR). The analyses procedures are explained in details in Section 3.4.1, 3.4.2, 3.4.3, 3.4.4 and 3.4.5.

3.3.4.1 Dropping point

In general, the dropping point is the temperature at which the grease passes from a semisolid to a liquid state under the conditions of test. The dropping point is a qualitative indication of the heat resistance of grease on applications where a semi-solid lubricant is required. The apparatus used are a grease cup, a special test tube, thermometers, 400 ml beaker with Thermia B oil as a heat transfer medium, small metal rod and electrical heater and stirrer. The apparatus is set up as illustrated in Figure 3.3.

For this test, the cork was placed on one of the thermometers so that the tip of the thermometer bulb will be about 1/8” above the bottom of the grease cup when the apparatus is assembled. The other cork is placed equidistant between the lower end of upper cork and the grease cup. This cork used to fit the thermometer inside the test tube. The other thermometer was immersed into the Thermia B oil in the beaker until about the same level as the test thermometer.

The cup was filled with a sample of grease. The metal rod was used to cut a wedge of grease from the cup by revolving the cup against the rod and simultaneously pushing the rod upward. A smooth film of grease remained in the wall of cup. Then, the apparatus were assembled before it was heated and stirred at a rate of 8-12°F per minute until the bath reaches a temperature approximately 30°F below the expected dropping point. Rate of heating was reduced so that the temperature in the test tube will be within 4°F or less of the oil temperature. As the temperature increases the grease will slowly protrude through the orifice of the cup. The temperature at which a drop of grease falls to the bottom of the cup is the dropping point. If the drop has a tailing thread, the test is continued until it breaks completely (ASTM D-566, 2009).

Figure 3.3: Dropping point Apparatus

3.3.4.2 Worked Penetration

The purpose of worked penetration is to determine the consistency of grease which is the hardness or softness the grease. A standard brass cone as illustrated in Figure 3.4 was initially touch the sample of grease surface before it was allowed to drop and penetrate freely for 5 seconds through a grease medium (ASTM D-217, 2009). The penetration value (10^{-1} mm) was digitally display. This procedure was repeated for 3 times to get the average penetration value. The work penetration value was referred to the NLGI guide to check the grease consistency and to classify the grade number of the grease (No. 000 – 6). The equipment used for this process is standard cone and penetrometer as illustrated in Figure 3.4 and Figure 3.5.

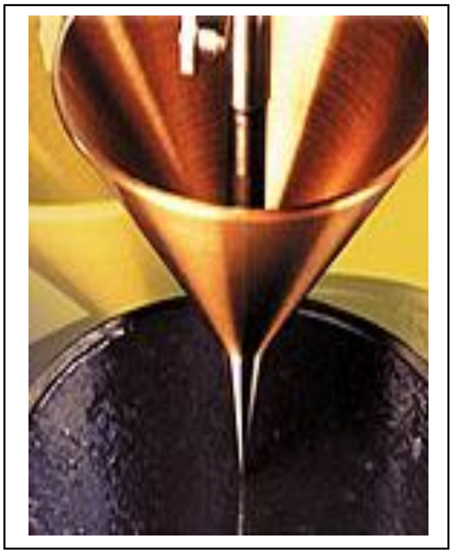


Figure 3.4: Standard cone for penetration test.

Figure 3.5: Penetrometer

3.3.4.3 Copper Corrosion

This test followed the copper corrosion test, ASTM D-4048, which is a qualitative, nonspecific measure of a lubricant’s corrosivity toward copper. It can be used to indicate the presence of relatively active sulfur if the analyst or equipment operator knows that other lube components or contaminants that corrode copper are absent.

A polished copper strip was immersed in 30ml of grease. After that, it was put into oil bath temperature with 100^{o}C for 24 hours. After the test period, the strip was examined for evidence of corrosion and a classification number from 1-4 is assigned based on a comparison with the ASTM Copper Strip Corrosion Standards.

3.3.4.4 Atomic Absorption Spectroscopy (AAS)

Atomic absorption spectroscopy is a technique used to determine the concentration of a specific metal element in a sample. The technique can be used to analyze the concentration of over 70 different metals in a solution. Atomic absorption methods measure the amount of energy (in the form of photons of light, and thus a change in the wavelength) absorbed by the sample.

The process of atomic absorption spectroscopy (AAS) involves two steps which are atomization of the sample and the absorption of radiation from a light source by the free atoms. Upon the absorption of ultraviolet or visible light, the free atoms undergo electronic transitions from the ground state to excited electronic states.

AAS is very sensitive and high cost maintenance equipment, so it is very important to conduct it carefully to avoid any damage or error in result. The standard solution of each metal element was prepared at 1ppm, 5ppm, 10ppm and 20ppm. Since the grease properties itself is high viscosity, so it needs a few steps to be done before it can be run using AAS. The phase of the grease was changed as the AAS only can analyze the sample in liquid form. A few steps involved are digestion of grease using microwave extractor, filtration and dilution. The grease was digest using microwave extractor and about 10 minutes was taken to complete this stage. The solvent used are nitric acid and hydrogen peroxide. Precaution must be taken when handling the high concentration of nitric acid as it is a corrosive chemical and be dangerous to the consumer. After the digestion process, the grease solution was filtered using syringe filter before it has been diluted with ultra pure water. Once again, the solution was filtered using pump filter and added with a few drops of nitric acid to acidify the solution as the last step before further AAS analysis. These four stages are very important in order to remove all the contaminant in the solution to avoid any damage to the AAS system.

3.3.4.5 Fourier Transform Infrared Spectroscopy (FTIR)

Fourier transform infrared spectroscopy (FTIR) is a nondestructive, instrumental analytical technique that can be used to detect individual components in lube oil quantitatively or semi quantitatively. It is also used in “fingerprint” analysis to compare an unknown lubricant with a known product or to identify contaminants in a finished lube. FTIR replaces more expensive tests to rapidly trend build up of soot, fuel dilution and oxidation products in oil.

When conducting this analysis, the grease was analyzed using FTIR without dilution. But, it must be run with Potasium Bromide, KBr because the FTIR cannot detect the organic compound in the grease if it is just put on the solid or liquid plate. Since the grease is a semi-solid component so the KBr was used in order to support the analysis.

CHAPTER 4

RESULT AND DISCUSSION

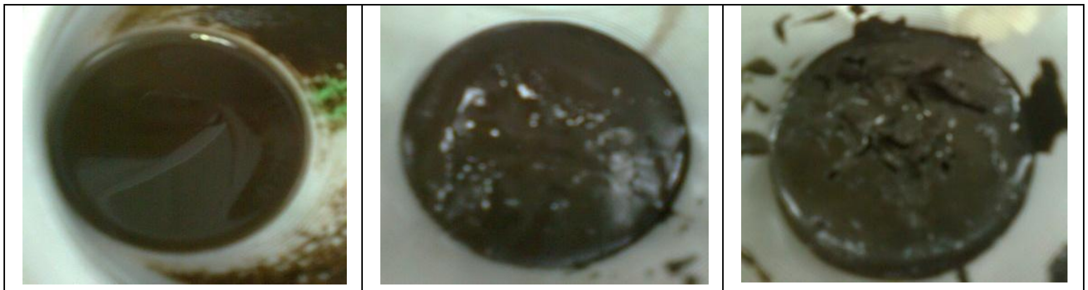
4.1 Introduction

This chapter discussed the overall result obtained in this research. The two parameters studied as mentioned in Chapter 1 are effect of different ratio of SBE and fumed silica in grease formulation and effect of the mixing time on grease characteristics. For the first parameter, the grease produced was tested for dropping point in order to choose the best formulation before proceed to the second parameter. The grease sample obtained from the second parameter is analyzed using dropping point, worked penetration, copper corrosion, Fourier Transform Infrared Spectroscopy (FTIR) and Atomic Absorption Spectroscopy (AAS). Further explanation is provided in the following section.

4.2 Effect of Different Ratio of SBE and Fumed Silica to Grease Characteristics

4.2.1 Grease Appearance

The effect of different ratio of thickener which is SBE and fumed silica used in grease formulation were investigated and discussed in this section. Six samples of grease have been prepared with different ratio of thickener in order to identify the best ratio for formulation of high temperature grease. From the observation, the texture of the grease is different when different quantity of fumed silica and SBE used in its formulation. As shown in Figure 4.1, the appearance of grease that used more fumed silica is harder compared the less fumed silica used. Grease formulation with 100% of SBE used as thickener is less viscous and liquid-like form compared to other samples which contain fumed silica in its formulation. This observation is in line with the role of fumed silica itself to hold the grease matrix together and the combining of SBE and fumed silica as thickener can prevent loss of lubricant under operating condition and evidently, this of implies the considerably resistance to flow of grease itself (Delgado *et al.*, 2005).



Sample 1 Sample 2 Sample 3

Sample 4 Sample 5 Sample 6

Figure 4.1: Appearance of grease for different ratio of SBE and fumed silica

4.2.2 Dropping Point

Dropping point test was conducted to choose the best grease formulation. Grease was tested for dropping point based on ASTM method to determine the temperature at which the grease turn into liquid form. This method also can identify the temperature of the grease can stand with. Results obtained from this analysis are tabulated in Table 4.2.

As shown in the Table 4.1, the dropping point for grease formulation with 100% of SBE is 188^{o}C and this is very low compared to others which are exceeding 300^{o}C. As mentioned previously in Chapter 2, grease can be classified as high temperature grease if the dropping point is higher than 260^{o}C (National Lubricating Grease Institute, NLGI, ASTM D-566). Therefore, the ratio of SBE and fumed silica used for grease sample 2,3,4,5 and 6 as stated in Table 4.1 can be used for high temperature grease formulation. Fumed silica plays an important role to thicken the grease so it has been proven in this first parameter experiment when all samples achieve the standard for high temperature grease except sample 1 which is using 100% of SBE without fumed silica as grease thickener. This is because fume silica provides gallants that form greases having dropping point about 260°C and the increase of fumed silica concentration will tend to increase the stiffness of grease (Hayder *et al.*, 2008). The present of fumed silica even in a small amount in the formulation can help the grease against the effects of heat. However, the usage of fumed silica can be minimized by combining it with the SBE as thickener in grease formulation.

Table 4.1: Dropping Point at different ratio of fumed silica and SBE.

Sample	Weight Percentage (%) of thickener		Dropping Point (°C)
	Fumed Silica	SBE	
1	0	100	188
2	10	90	>300
3	15	85	>300
4	25	75	>300
5	30	70	>300
6	40	60	>300

Based on the result, the best ratio for grease formulation is 90% of SBE and 10% of fumed silica which is sample 2. Sample 2 was chosen because it fulfilled the criteria as stated in previous chapter which are having the viscous texture, over 260°C of dropping point and highest waste (SBE) used in the formulation so that the usage of fumed silica can be minimize in order to reduce the manufacturing cost.

4.3 Effect of Mixing Time of Grease Characteristics

4.3.1 Grease Appearance

Five samples at mixing time of 1, 2, 3, 4 and 5 hours were prepared respectively with thickener ratio of 90% of SBE and 10% of fumed silica. The grease prepared was analyzed physical appearance, worked penetration, dropping point, copper corrosion, FTIR and AAS.

Figure 4.2 shows the appearance of grease obtained from the second parameter. In terms of texture, the grease becomes less viscous when the period of stirring is increased. The texture of grease with one hour mixing time is harder than other mixing time and for sample with five hour mixing time, the texture is liquid-like form. The grease obtained is also darker as compare to the others. This result is in good agreement with those reported Hayder *et al*., (2008). This is because the wetting of agglomerate of the SBE and fume silica particles with the base oil increased when the mixing time is increased. Thus, the grease obtained become less viscous.

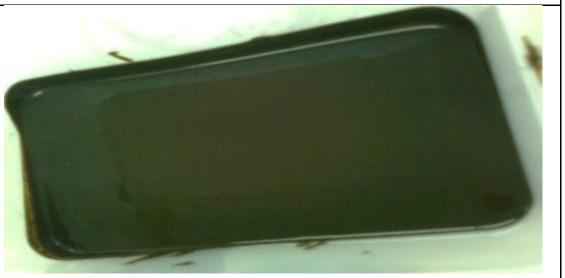
Duration of Mixing Time, (hour)	Grease Appearance
1	
2	
3	
4	
5	

Figure 4.2: Grease appearance at different mixing time

4.3.2 Dropping Point

The most important thing in this test is to investigate the effect mixing time to the dropping point of grease. Results obtained show that all samples can stand with the high temperature and did not melt at all even it was heated up to 300°C for more than 1 hour. From observation, the color of Thermia B oil turns darker after one hour of heating. However, still no dropping point was obtained even though temperature reached 300°C. Thermia B oil is a mineral oil supply by SHELL and it is used as a heat transfer fluid. The heating was stopped after temperature reached 300°C as the boiling point of Thermia B oil is 320°C. This action is a must to avoid any explosion or burning. In addition, the color of Thermia B oil was changed after no more heat capacity in the oil to be transferred to the grease in cup for heating purpose. Figure 4.3 shows that the change of Thermia B oil color at initial and at the end of analysis. All samples comply with the ASTM dropping point standard for high temperature grease which is more than 260°C as mentioned in previous section 4.2.2.

(a) (b)

Figure 4.3: The color change of Thermia B Oil (a) initial and (b) end of analysis.

4.3.3 Worked Penetration

Different mixing time will give different consistency of grease. Based on the NLGI Standard, the consistency of industrial greases is classified by the distance in tenths of a millimeter, that a standard cone penetrates a sample of the grease under standard conditions at 25ºC. For this analysis, about 500g of each sample is required to be tested so that the cone will not touch the base of grease container if the work penetration reaches maxima value. The result of the penetration test has been plotted and illustrated in Figure 4.4. From the graph, it shows that the increase of mixing time gradually increases the worked penetration. However, the grease structure becomes harder as the mixing time increase. This means that the grease consistency is reduced once the grease have been heated and stirred for a longer time (Hayder *et al*., 2008). The worked penetration is 190mm and 275 mm for duration of mixing time 1 and 5 hour respectively. The worked penetration measurement is in inverse scales of consistency that is, the softer the grease consistency, the higher worked penetration number.

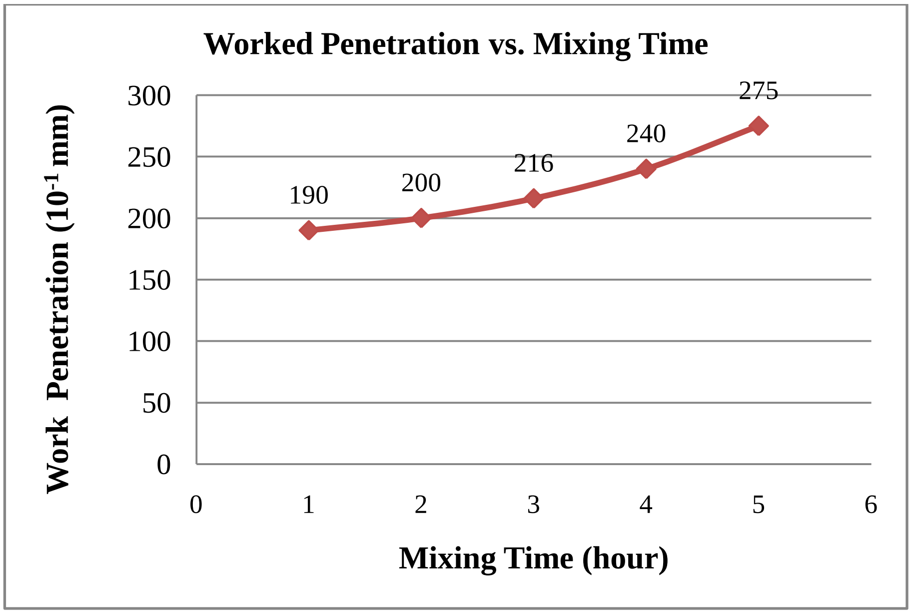


Figure 4.4: Worked penetration (10^{-1} mm) at various mixing time (hour).

The number of worked penetration test of each sample is further referred to the NLGI Standard to classify the consistency and for grading purpose of grease. This grade number is very important in order to know the appearance and the suitable condition of grease should have. Grease consistency depends on the amount and type of thickener(s) used as well as the viscosity of the base oil. The NLGI has established a scale of 000 to 6 representing very low to very high viscosity as stated in Table 2.7 in Chapter 2. Based on that information, the grade number of each sample at different mixing time were identified and tabulated in Table 4.2. The consistency of sample 1 and 2 are classify as grade 4 (hard), sample 3 and 4 is grade 3 (semi hard) and only sample 5 is classify as grade 2 (normal) which is in the common grease range.

The different NLGI grade number will give its own suitable application. Grease in grade 2 is the most common used in various applications and can be considered as multi-purpose grease. The typical applications for grease with grade 3 are for heavily loaded automotive and industrial bearing. For grade 4, its application is quite similar with grade 3 but more suitable for heavier loaded automotive and industrial bearing than in grade 3.

Table 4.2: NLGI Grade Number for grease at different mixing time

Duration of Mixing Time (hr)	NLGI Grade No.
1	4
2	4
3	3
4	3
5	2

4.3.4 Copper Corrosion

As mentioned before in previous chapter, this test method is follow ASTM D-4048 Standard which is to check whether the grease produced from SBE is corrosive toward copper or not. The result was observed after 24 hour a polished copper strip is immersed in grease sample in the beaker before put it into oil bath for at 99.9^{o}C as shown in Figure 4.5. From this analysis, observation was done and there is no corrosion occurred to the copper strip and there are no changes on the copper strip. This observation is in good agreement with the result of Hayder *et al.,* (2008) which is the formulated grease have no negative effect on the metal surface. Therefore, the grease produced from SBE is not corrosive if the proper and recommended ratio used when applies to the system.

(a) (b)

Figure 4.5: Copper Strip Test (a) before and (b) after 24 hour

4.3.5 Metal Content Analysis using AAS

Instead of organic compound content, the grease sample also was analyzed using AAS to determine the concentration of specific metal element content. This technique can be used to analyze the concentration over 70 different metals in solution. The metal element that be analyzed are Lead (Pb). Nikel (Ni), Zinc (Zn), Cadmium (Cd), Chromium (Cr) and Copper (Cu) due to common metal content in the grease.

For this analysis, standard solution at different ppm for each metal (Pb, Ni, Cd, Cu, Cr and Zc) must be prepared to trace the metal element in the solution. Details steps for grease digestion are attached in the Appendix A. The graphs for standard calibration curve and results on the metal concentration obtained from analysis are attached in Appendix A. The result obtained from this analysis shows that the concentration of metal element is negative which means the concentration of metal in the sample is too low as tabulated in Table 4.3. This is because the standard solution prepared still high concentration (1 ppm, 5ppm, 10ppm and 20 ppm) so that the AAS not able to trace metal element content in the grease which is too low in concentration. Besides that, the concentration of the same metal element is quite similar in grease for all mixing time. In order to improve the result, the concentration of standard solution must prepare with lower than 1 ppm, 5ppm, 10ppm and 20 ppm that used before. Therefore, the grease is safe to be used because the metal concentration is too low. From the AAS results obtained, it shows that non-soap based grease contains low concentration is compared to soap-based grease which is used metal soap in its formulation (Moreno *et al.*, 2008).

Table 4.3: Metal concentration in grease at different mixing time

Mixing Time / Metal element	1	2	3	4	5
Lead (Pb)	-2.07	-2.17	-2.62	-2.62	-2.62
Nickel (Ni)	-6.79	-6.81	-6.85	-6.86	-6.89
Cadmium(Cd)	-5.85	-5.85	-5.85	-5.87	-5.87
Copper (Cu)	-1.59	-1.58	-1.59	-1.59	-1.58
Chromium (Cr)	-6.25	-6.22	-6.25	-6.27	-6.28
Zinc (Zn)	-0.65	-0.67	-0.67	-0.68	-0.66

4.3.6 Organic Compound Content Analysis using FTIR

The grease was also tested using Fourier Transform Infrared Spectroscopy (FTIR) to determine the organic compound in that each sample. The organic compound in the sample is determined based on the wavelength number. Since grease is in semi solid phase, FTIR cannot detect the wavelength when use plate that commonly use to test liquid or solid sample. Therefore, Potassium Bromide, Kbr was used to support the analysis as alternative method.

The FTIR spectrum obtained for sample 1 is illustrated in Figure 4.6. Other spectrums are attached in Appendix B. The entire spectrum shows fluctuation at different wavelength. However the trend is quite similar for all the samples. From the observation, the wavenumber (cm^{-1}) of all samples is in the same range which is 402.32 to 3900 cm^{-1}. The average modern infrared instrument records spectra from an upper limit of around 4000 cm^{-1} (by convention) down to 400 cm^{-1} as defined by the optics of the instrument commonly based on potassium bromide, KBr (John, 2000).

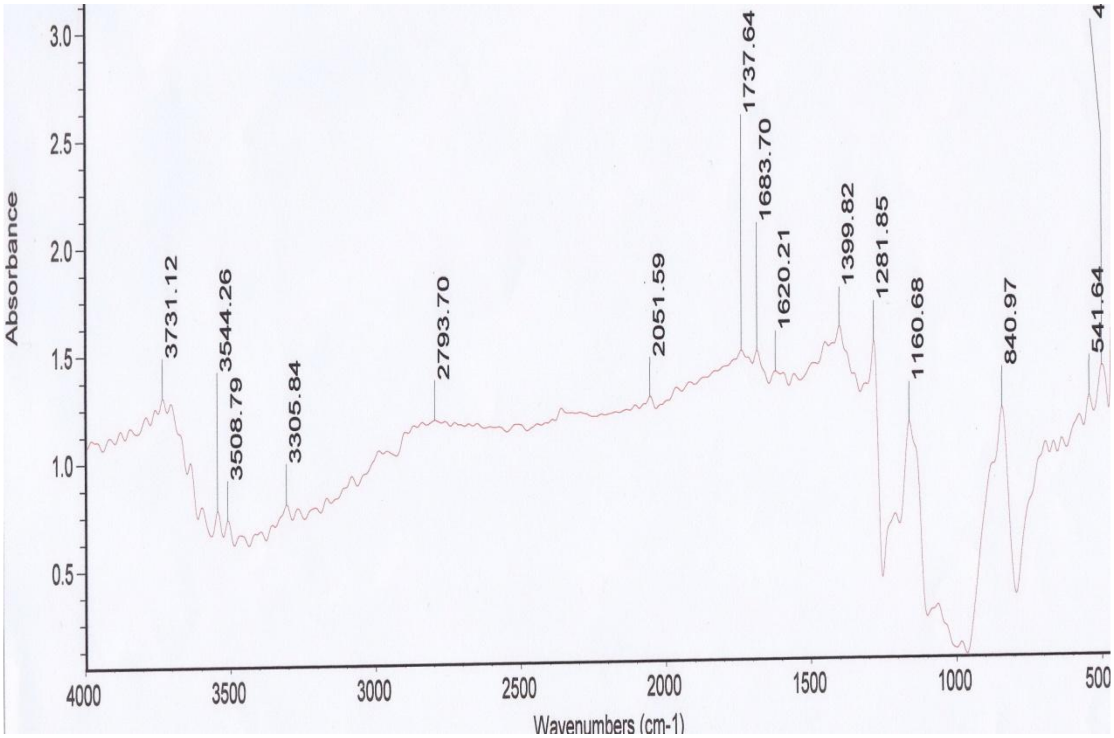


Figure 4.6: FTIR analysis of grease at 1 hour mixing time.

As shown in Figure 4.6, there are several of functional group presences in grease mixture. According to John Coates (2000), bands related to Si-O-Si vibrations appear in the range of 1110-1080 cm^{-1} and the graph shows the wavelength at 1160.68 which is the nearest wavenumber of organic silicone that presence in grease which is use silicone oil as base oil and 10% of fume silica. Peaks of 3544.26 and 3508.79cm^{-1} wavenumber in grease falls in the region 3550–3450 cm^{-1} and conform that the O-H stretch functional group was present in clay which is in SBE as grease thickener. For wavenumber 3305.64 cm^{-1} the compound contains the normal "polumeric" O-H stretch and dimeric O-H stretch bend, often an alcohol or phenol with a sterically hindered O-H group (Neetyu *et al.,* 2009). This spectral feature is also exhibited by certain inorganics and minerals, and is indicative of a "free" OH group, either on the surface, or embedded within a crystal lattice which is contain in SBE and additive, CaF_2 nanocrytals. Peaks of C-H group 840.97 cm-1 and 541.64 cm-1 were present in SBE clay. The gel structure of the grease is caused by hydrogen bonding between dispersed organoclay particles creating a gel network (Chtourou *et al.*, 2006).

Molecules containing NO_2 groups, such as nitro compounds, nitrates, and nitramines, commonly exhibit asymmetric and symmetric stretching vibrations of the NO_2 group at 1660 to 1500 cm^{-1} region (Neetyu *et al.*, 2009). Peaks of 1683.70 and 1620.21 cm^{-1} are the nearest wavenumber which conform the presence of NO_2 group in bentonite base grease. Corresponding to 1399.82 and 1281.85cm^{-1} wavenumber, no group was detected in grease sample. Frequency and functional group present in grease sample are tabulated in Table 4.5.

Table 4.4: Presence of functional group in grease using FTIR Analysis

Peak found (Wavelength, cm^{-1})	Group(s) present
1160.68	Si-O-C
1734.64	Si-O-Si
3731.12	- COO-C-
3544.26	O-H
3508.79	O-H
3305.84	O-H
2793.70	C-H
2051.59	Not found
1683.70	Asymmetric and symmetric stretching vibrations of the NO2 group
1620.21	Asymmetric and symmetric stretching vibrations of the NO2 group
1399.82	Not found
1281.85	Not found
840.97	C-H
541.64	C-H

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Greases with different ratio of SBE and fume silica as well as mixing time were prepared and characterized. The best ratio of SBE to fume silica for grease formulation is 90% to10%. This is because, at this ratio the highest amount of SBE was used and the dropping point achieved was beyond 260^{o}C. The usage of fumed silica which is very expensive is less as compared to other formulation. Other than that, the consistency of the grease prepared is decreased as the mixing time increased. With refer to NLGI standard, the consistency of grease is in the range of 2 to 4 grade number and can be classified as high temperature grease when its dropping point is higher than 260^{o}C. As a conclusion, the findings from this research has the high potential to help in solving the environmental problem on SBE disposal which is in line with the government campaign to reduce waste in daily life and indirectly can reduce the production cost with this SBE based grease.

5.2 Recommendations

Based on the results and conclusions obtained through this study, a few recommendations are proposed in order to improve the result obtained. For characterization the grease, more test or analysis needs to be done such as viscosity test, oxidation stability and four ball bearing test so that the performance of grease produced will be more guaranteed and high quality. These tests are very important to investigate the grease structure and composition undergoes significant modification while working by shearing and oxidation condition (Adhvaryu *et al*., 2004). Problem faced during research is spindle of viscometer equipment is not suitable so that the viscosity of grease cannot be done and only visual checking done on grease texture and appearance. So, lab should provide more equipment for grease testing and a complete set spindle of viscometer so that grease viscosity either high or low can be conduct. For AAS result, the result is negative due to the concentration of standard solution is not really low so the concentration of metal element cannot be detected. To improve this result, the standard solution should be prepared at lower concentration therefore the metal element can be detected even at low concentration.

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APPENDIX A

AAS analysis

1. Preparation of standard solution

- Dilute stock solution of each metal (Pb, Ni, Cr, Cd, Cu and Zn) with ultra pure water to get 1 ppm, 5 ppm, 10ppm and 20ppm concentration.
- Using equation: $m_1v_1 = m_2v_2$

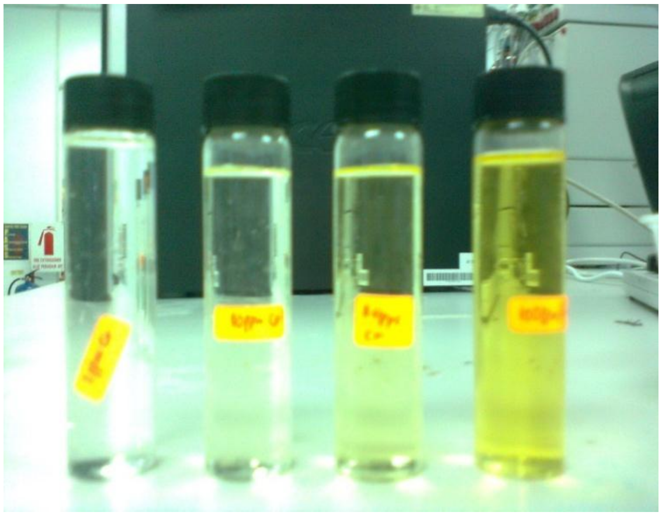


Figure A1: Standard solution of Cu

2. Grease Digestion

- Since AAS is too sensitive equipment, sample of grease has been digested and must be in liquid phase before run it with AAS. So a few methods were done such as:
    - i. Digestion using microwave extractor
    - ii. Dilution of sample
    - iii. Filtration using vacuum filter

- Microwave extractor
    1. Contains of 6 vessels. 1 vessel contain solvent only, the other 5 vessels contain solvent with different sample.
    2. Program Setting:

	Time (min)	Temperature (^{o}C)	*Power (Watt)
1	10	200	1000
2	10	200	1000

*If vessel less than 3: 500 watt

If vessel more than 3: 1000 watt

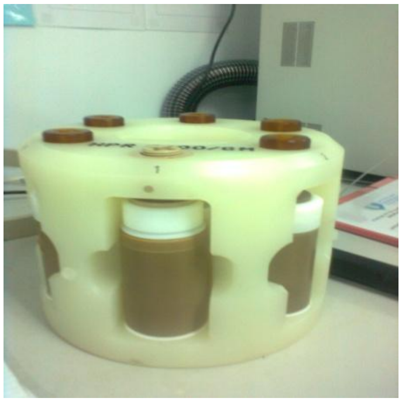
    3. Sample: 0.1 g of grease

Reagent: 9ml of Nitric Acid (HNO_3) 90%
1ml of Hydrogen Peroxide (H_2O_2) 30%.

Add 9ml of HNO_3 65%

Add 1ml of H_2O_2

Add 0.1g of grease



Put the vessel into its place

Put into microwave extractor,
setting the program and run.

Figure A2: Flow diagram for digestion method

- Sample dilution
    i. Sample is taken out from microwave extractor and was filtered using syringe filter before dilution.
    ii. Calculation:

       0.1 g of sample

       10 ml of solvent ($HNO_3 + H_2O_2$)

       = (0.1 g/ 10ml) (1000mg/1g) (1000ml/1L)

       = 10 000 mg/l or 10 000ppm

       $$= \frac{required\ \ ppm\ x\ required\ volume}{10\ 000\ ppm}$$

       $$= \frac{50\ ppm\ x\ 50\ ml}{10\ 000\ ppm} = 0.25\ ml$$
    iii. So, to get 50 ppm of solution, it needs 0.25 ml of 10000ppm sample with 50ml of ultra pure water.

- Filtration
    i. Sample from dilution (50 ppm) was filtered using vacuum filter to remove any impurities.

Figure A3: Filtration using vacuum filter

3. After filtration, a few drop of HNO_3 was added to sample to acidy the solution.
4. Run with AAS

Figure A4: Atomic Absorption Spectroscopy (AAS)

5. Results from AAS analysis were printed out

   *refer attachment

APPENDIX B

FTIR analysis

1. Clean the KBr plate with acetone
2. Put KBr and grease into the plate

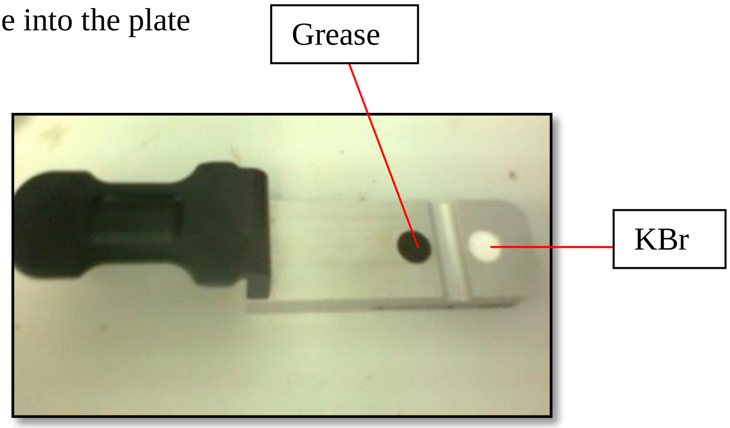


Figure B1: KBr plate

3. Run with FTIR

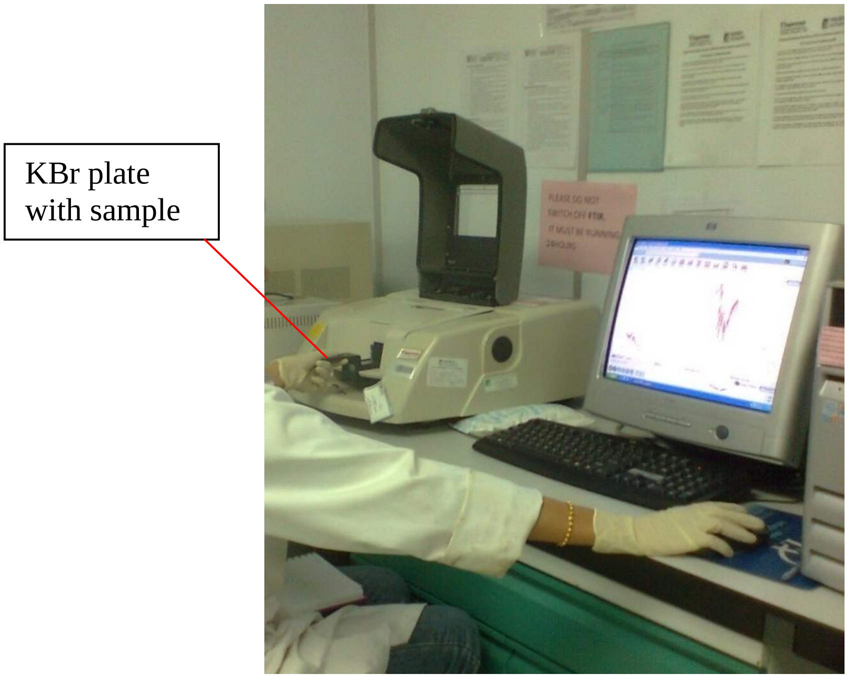


Figure B2: Fourier Transform Infrared Spectroscopy (FTIR)

4. Results from FTIR analysis were printed out

   *refer attachment