FORMULATION OF GREASE FROM INDUSTRIAL WASTE

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ABSTRACT

Grease is a semisolid lubricant which helps in reducing the friction between two surfaces. Lubricating grease can be applied to mechanical parts which runs intermittently or being stored for a long period or in contact with the moisture that will cause corrosion to happen. The growing demand on lubricating grease has increased the attention on quality of the grease. A better performance and more environmental friendly bio-grease is preferable. Mixture of Spent Bleaching Earth and Waste Cooking Oil are the base grease for the research. To enhance the rheological properties of the grease, three types of cellulose are added to the grease which are Methyl Cellulose (MC), Carboxymethyl Cellulose (CMC) and Hydroxyethyl Cellulose (HEC). Three types of test were carried out to test the consistency, contamination and also the oil bleed of the formulated grease. The test method for consistency of grease is accordance to ISO 2137 and NLGI (National Lubricating Grease Institute) Number was obtained. The result showed that 75% to 80% of SBE and 20% to 25% of WCO were needed to produce grease with NLGI Number 2 and 3. Addition of less than 10% of additive decreased the amount of SBE needed to about 25%. Among three types of cellulose added, Hydroxyethyl Cellulose has the most improvement to the consistency of the formulated grease. While for oil bleeding test, Methyl Cellulose showed the best performance which is about 35% in reducing the oil separation condition

ABSTRAK

Gris merupakan sejenis pepejal separa yang digunakan untuk mengurangakn geseran antara dua permukaan. Biasanya ia disapukan atas bahagian mesin yang beroperasi secara bersela ataupun bahagian mesin yang perlu disimpan terbuka secara masa panjang yang mana penggunaan gris akan mengurangkan kemungkinan kakisan untuk berlaku. Pada masa kini, pengguna gris semakin prihatin bukan sahaja terhadap kuantiti mahupun kualiti gris. Permintaan pengguna gris lebih kepada gris yang bermesra alam. Dalam kajian ini, gris baru telah dirumuskan dengan menggunakan sisa minyak masak (WCO) sebagai *base oil*, *spent bleaching earth* (SBE) sebagai pemekat dan tiga jenis selulosa yang berbeza sebagai a*dditive*. Selulosa yang ditambah secara berasingan iaitu *Methyl Cellulose* (MC), *Carboxymethyl Cellulose* (CMC) and *Hydroxyethyl Cellulose* (HEC). Gris telah dirumuskan dengan memanipulasi peratusan (w / w) WCO, SBE dan selulosa. Ujian telah dijalankan dengan mengukur penembusan gris mengikut standard ISO 212, *contamination* dan pengasingan minyak gris. Keputusan menunjukkan kira-kira 75% kepada 80% SBE dan 20% kepada 25% WCO diperlukan untuk menghasilkan gris NLGI bergred 2 dan 3. Penambahan *additive* mengurangkan jumlah SBE yang perlu untuk menghasilkan gris NLGI bergred 2 dan 3 kepada kira-kira 25%. Dalam kalangan tiga selulosa yang berbeza, HEC menunjukkan prestasi yang terbaik dalam meningkatkan NLGI nombor gris. Manakala, dalam ujian pengasingan minyak gris, MC pula yang menunjukkan prestasi terbaik yang mana ia dapat mengurangkan pengasingan minyak sebanyak 35%.

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LIST OF ABBREVIATIONS

°C	Celsius
d	diameter
$d_{average}$	average diameter
h	hours
wt/wt%	weight percentage

LIST OF ABBREVIATIONS

ASTM	American Standard Testing and Materials
AW	Anti-wear
CMC	Carboxymethyl Cellulose
EP	Extreme Pressure
HEC	Hydroxyethyl Cellulose
ISO	International Organization for Standardization
MC	Methyl Cellulose
NLGI	National Lubricating Grease Institute
SBE	Spent Bleaching Earth
WCO	Waste Cooking Oil

CHAPTER 1

INTRODUCTION

1.1 Motivation and statement of problem

One of the significant disposal problems on many countries is the waste cooking oil. According to Energy Information Administration in the United States, around 100 million gallons of waste cooking oil is produced per day in USA, where the average per capita waste cooking oil was reported to be 9 pounds. The estimated amount of waste cooking oil collected in Europe is about 700,000–100,000 tons/year. Hence, the government of USA has been encouraging the expertise on waste treatment to solve this problem since decades ago.

On the other hand, for country like Malaysia who has high production rate of petroleum, disposal of spent bleaching earth is also one of the issues to be concerned. Bleaching earth is known to be very useful in crude oil refining for its high absorption capacity for colored materials. During refining, 40% of vegetable oil is adsorbed on bleaching earth and the waste is called spend bleaching earth (SBE). Every year, Japan discharges more than 80,000 metric tons of SBE to the environment (Seiji Kojima et al., 2004). Rather than dispose this industrial waste to the environment; it can be reused as the material to produce lubricating grease.

The main purpose of this work is to fully reutilize these industrial wastes and turn it into a value-added product. In order to have better consistency grade and friction coefficient product, fumed silica and three different types of cellulose are being chose to be the additive for its higher molecular weight that exhibit substantional shear-thinning or pseudoplastic behavior (Karsheva et al., 2007).

1.2 Objectives

The following are the objectives of this research:

- To formulate multipurpose grease using industrial waste (Waste Cooking Oil & Spent Bleaching Earth).
- To investigate the effect of fumed silica and cellulose on the apparent mechanical properties of the lubricating grease.
- To characterize the formulated grease using ASTM tests.

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1.3 Scope of this research

In this work, waste cooking oil is used as the base oil of the grease whereas the thickener will be spent bleaching earth. Fumed silica and three types of cellulose are used as the additive which is methyl cellulose, hydroxyethyl cellulose and sodium carboxymethyl cellulose. In order to learn the effect of the composition of waste cooking oil and spent bleaching earth on the properties of the grease, weight percent has been varied. Besides, the effect of present of the additive is also being observed by varying the weight percent of the additive ranging from 0.1 wt% to 40 wt%. Analysis to investigate the properties such as the penetration and consistency, drop point, thermal stability, oxidation stability and oil separation includes the penetration test (ASTM D 217), dropping point test (ASTM D 2265), thermal stability test, oxidation stability test (ASTM D 942) and grease oil separation test. Instruments use including penetrometer, drop point apparatus, thermal gravimetric analyzer (TGA), oxygen pressure vessel and cone sieve.

1.4 Main contribution of this work

Environmental issue will be the main contribution of this works. The production of this multipurpose lubricating grease will certainly reduce the amount of disposal of these two industrial wastes to the environment. In other words, the pollution causes by waste cooking oil and spent bleaching earth will be minimized.

Additionally, another score of this work will be the reduction of production cost. Since the materials used to produce this lubricating grease are waste products, hence the production cost will be dramatically reduced and definitely much lower than the lubricating grease in the current market.

1.5 Organisation of this thesis

The structure of the reminder of the thesis is outlined as follow:

Chapter 2 provides description related to the product of this work. General discussions on the history and the types of lubricants are presented. This chapter also provides an overview on the composition of lubricating grease and the types of base oil, thickener and additive in current market are presented. The applications of each type of grease are compared and how the selection of grease was done for specific use. A summary on the previous researches on the material used for grease production and also the rheological properties of the grease produced.

Chapter 3 provides description on the materials used in the formulation of lubricating grease. The source of material and also some general properties are being discussed. In this chapter, the methodologies on investigating the rheology properties of the grease are being discussed in details.

Chapter 4 provides a full description on the results obtain from the experimental work. This chapter also includes analysis on the experimental data and further discussion on the results is also contained. Review and comparison between previous work and the outcome of this study are also presented.

Chapter 7 includes the conclusion and outcome of this study. Recommendations for future study are also being included in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

This chapter will be focusing on the definition of lubricating grease, the history of lubricating grease, the type of lubricating grease, type of base oil, thickener, and additives. Previous study on lubricating grease will also be discussed.

2.2 History of Grease Lubrication

The word "Grease" derived from Latin word "Crassus" which means fat. The first grease was created by combining mutton fat or beef fat with lime and it was used to lubricate wood bearing as it was found to be effective in lubricating wooden axles. However, this simple grease was discovered later that the effectiveness decrease as the operating temperature increase. Later on, on year 1859 after the discovery of oil, different type of modern grease such as lime soap and calcium grease were produced (Piet M. Lugt, 2012).

Figure 1-1 Wood Journal Bearing

On 1942, calcium complex grease and lithium grease were patented. These greases are still widely used in the market for their multipurpose application and high mechanical stability (C. E. Earle, 1942). Now, researchers are focusing their study on developing high molecular weight of thickener as they can be used in large variety environment such as wet environment and high operating temperature. In year 1992, thickener compose from high molecular weight of polymer was first invented (D. Meijer et al., 2010)

2.3 Lubricating Grease

The fundamental function of lubricating grease is to prolong the life of mechanical units and reducing friction and wear simultaneously. The subsidiary function will be seal out contaminant, heat dissipation, reduce noise and vibration (George E. Totten et al., 2003). Compared to lubricating oil, grease has its superiority on retention of lubricant. Lubricating oil which is difficult to retain need to be replenished frequently which is a huge drawback for lubricant. Lubricating grease which composes from thickener can retained more steadily with the help of the thickener. Besides, lubricating grease has few more advantages over lubricating oil. For instance, grease is easier to be handled, less expensive and adhere better to the surfaces (George E. Totten et al., 2003).

Grease consistency (NLGI Number) is an important grease parameter to determine the stiffness of the grease and the uses of the grease on certain operating condition such as operating temperature, speed, pressure or load.

Table 1-1 NLGI Grade Standard

NLGI number	ASTM worked (60 strokes) penetration at 25 °C *tenths of a millimeter*	Appearance	Consistency food analog
0	445-475	fluid	cooking oil
0	400-430	semi-fluid	apple sauce
0	355-385	very soft	brown 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

Lubricating grease is mainly composed of base oil, thickener and sometimes it is added with an additive to enhance the lubricating grease properties such as resistance to corrosion, against aging, act as viscosity improver and antioxidant (M. Weigand, 2006). An additive with antioxidant property is important as to inhibit oxidation from happening as oxidation of grease will lead to base oil thickening, sludging and deposition to occur. Base oil that is commonly used is synthetic oil, vegetable oil and mineral oil. Whereas for thickener, it might be soap thickener, complex metallic soap, non-soap thickener and organic thickener. Plenty types of additive have been developed. The latest one for bio-degradable lubricating grease will be cellulose. Previous researches have been done on cellulose such as ethyl cellulose and methyl cellulose (N. Nú˜nez, 2012).

Composition of grease is different depending on the base oil, thickener and additive use. There are two major concerns in formulating grease which are friction-reduction ability and themal oxidation stability (Sharma et al., 2008). Generally, base oil hold around 70 % to 95 % of the grease whereas for thickener is around 3 % to 30 %. Less than 10 % of additive will be used as too much of additive use will become an impact for another property. For instance, too much of corrosion inhibitor can be detrimental where the water resistibility of the grease will be reduced (N. Canter, 2012).

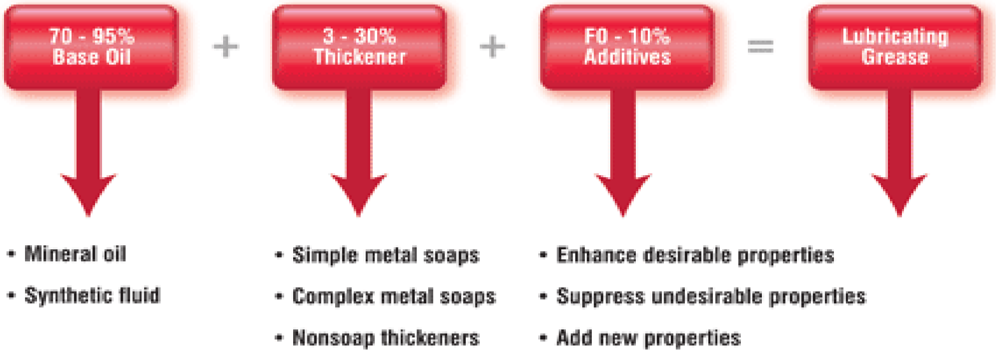

Figure 1-2 Composition of Grease

Standard lubricating grease is able to withstand extreme condition such as extreme temperature and pressure. During the operating time, the thickener release a small amount of base oil to lubricate the surfaces and regain the semi-solid form after the load has been removed or the former ordinary temperature is attained (Ishchuk, 2008).

2.4 Base Oil

The liquid phase of lubricating grease is always the base oil where the fluid viscosity properties of the base oil determine the performance of grease. For instance, low viscosity-oil suitable to be applied on surfaces that operates at low temperature, low load and high speed; high viscosity-oil favorable to be applied on machine that work at high-temperature, high load and low speed (Parkash, 2009). Hence, identification of base oil properties is the main step in formulation of grease.

Base oil that is commonly used is synthetic oil, vegetable oil and mineral oil. Mineral oil is a liquid by-product of distillation of petroleum to produce gasoline and other petroleum-based products from crude oil. The main types of mineral oil are paraffinic oil which is based on n-alkanes, naphthenic oil which is based on cycloalkanes and aromatic oil which is based on aromatic hydrocarbon (Takadoum, 2008). Grease compose from mineral oil and solid are heavy lubricant. They are specialized to lubricate rough fitting machine part that work under pressure or load with low speed such as concrete mixer, bearing and roller of conveyer (Ronald L. Hughes, 2012).

Synthetic oil is produced from chemical modified petroleum component or other raw material with predicted molecular structure by combining organic or inorganic base stock oil with polymer. Grease formulated from synthetic oil can work under extreme temperature and pressure with higher viscosity index. Besides, it also possesses properties such as resistance to oxidation and better shear stability (ASTM Fuels & Lubricants Handbook, Hydrocarbon Chemistry, 2003). In market, a widely used lithium complex grease is composed from polyalphaolefin (a type of synthetic oil) and lithium complex soap. This type of grease has high dropping point, excellent resistance to water wash, antiwear, antirust, anticorrosion and is high temperature degradation. This high quality grease is normally used for aircraft wheel bearing. Besides, this grease also provides outstanding protection at operating temperatures from –54 ºC to 177 ºC (George E. Totten, 2003).

A vegetable oil is a triglyceride extracted from a plant and is types of bio-based oil where the grease compose from this type of oil are categorized as bio-grease. Since it is bio-based oil (less harm to the environment), it has been used as the first choice of lubricant for food and pharmaceutical industries. In the lubricant market, common used ones including high oleic canola oil, castor oil, palm oil, sunflower seed oil and rapeseed oil. Natural and unmodified vegetable oil has poor oxidation and low-temperature properties. These inherent problems of vegetable oils can be improved by attaching functional groups at the sites of unsaturation through chemical modifications (S. Z. Erhan, 2013). From Table 1.2, it shows that the best primary biodegraded quantity of lubricant is vegetable oil which is around 70 – 100 %.

Table 1-2 Typical Test Results for Lubricants

TYPICAL TEST RESULTS FOR LUBRICANTS	
LUBRICANT TYPE	**PRIMARY BIODEGRADED QUANTITY**
Vegetable Oils	70 - 100 %
Polyols and Diesters	55 - 100 %
White Oils	25 - 45 %
Mineral	15 - 35 %
PAG	10 - 20 %
PAO	5 - 30 %
Polyether	0 - 25 %

2.5 Thickener

Thickener is an agent added to the base oil in order to increase the viscosity of the liquid form oil and prevent it from flowing (Landsdown, 2004). Grease is classified into two types which are organic thickener and inorganic thicker. For organic thickener, it might be soap or non-soap. Most widely used thickener in the industries goes to the soap based lubricating thickener which is lithium soap especially the bearing industries. According to Landsdown (2004), it is widespread used as it has a wide temperature range from -51 ˚C to 149 ˚C and also of the excellent heat resistant quality. Besides, lithium grease also well-known of its excellent pumpability and good oxidation stability.

The following one goes to the calcium based lubricating grease which is highly water resistance and is most suitable to work in the wet environment. Unlike calcium soap based lubricating grease; sodium soap based that has a wide range of temperature up to 149 ˚C may absorb water and is easily washed away with a large amount of water which makes it not suitable for wet environment (Landsdown, 2004).

For complex soap thickener, lithium complex, calcium complex and aluminium complex are widely used in the market. These three complex soap thickeners have good water and heat resistance properties and also have excellent oxidation stability (Kristopher Sonne, 2009).

For non-soap thickener, Benonite, polyurea and polyurea complex are widely used. The properties of Bentonite and polyurea are almost same as complex soap thickener. Unlike these two non-soap thickener, polyurea complex has its superiority in EP (extreme pressure) and AW (anti-wear) properties (Kristopher Sonne, 2009).

The two most notable thickeners are Lithium Complex and Polyurea Complex. These two thickeners have great overall properties and are closest to being a multipurpose grease. Polyurea greases are very popular motor bearing greases due to the extreme pressure and anti-wear properties (Kristopher Sonne, 2009).

2.6 Additive

According to Knotek and Stenerson (2006), the purpose of addition of additive to lubricating grease is to enhance the performance properties of the base oil and also to impart entirely new performance characteristics to the finished oil compound. Besides, additive may also help in reducing the rate of decomposition of grease during its service life. Different type of additives may have their respective specialty.

For equipment that undergoes heavy loaded, extreme pressure (EP) additive may be required. EP additives enhance the load-carrying ability, cushioning the shock load and inhibit the welding of surfaces (Knotek and Stenerson, 2006). Other types of additive including oxidation inhibitors, anti-rusting additives, viscosity index improver and so on. However, too much of additive added might be a drawback for the properties of the grease. For instance, excessive of corrosion inhibitor can be detrimental where the water resistibility of the grease will be reduced (N. Canter, 2012).

Previous researches have been done a new type of additive which is cellulose. Ethyl cellulose and methyl cellulose are the two celluloses that have been investigating since 2011. It was found out that addition of cellulose as the additive enhances the mechanical stability of grease that composes from Castrol oil (N. Nú˜nez et al, 2012). The high molecular weight property of the cellulose provides better lubrication to the mechanical part.

CHAPTER 3

MATERIALS AND METHODS

3.1 Introduction

This paper is focused on the formulation of multi-purpose grease from industrial wastes. The formulations consist of mixing and homogenizing of two base components; waste cooking oil (base oil) and spent bleaching earth (thickener) according to different weight percent. This mixture will be the base grease which acts as the reference in the aspect of tested properties. Three difference types of cellulose; Carboxymethyl Cellulose, Methyl Cellulose and Hydroxyethyl Cellulose are added according to specific weight percent.

Testing on the formulated grease is important to investigate the properties of the grease, but the practical service of the grease in the industries is complicated where lab testing is unable to be exactly the same. However, these results are the primary selection or screening for their specific function and application.

In this study, the grease property is tested using International Organization Standardization (ISO) method.

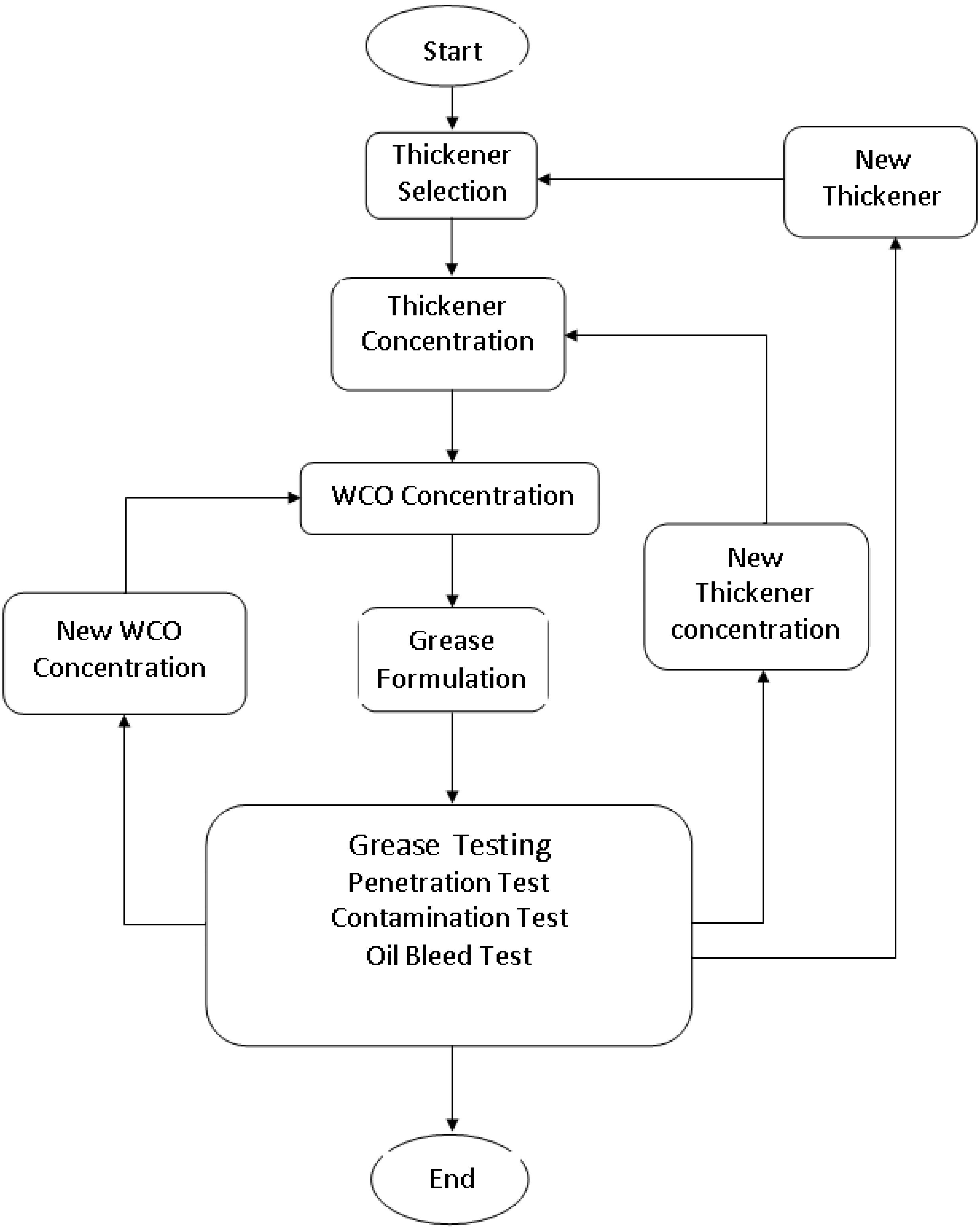

Figure 3-1 Experiment Flow Diagram

3.2 Materials

3.2.1 Waste Cooking Oil (WCO)

Waste cooking oil which was collected from various food stall at Pasar Besar Kuantan, Pahang underwent pre-treatment to remove the solid and unwanted sediment to make sure there was no solid form impurity during the formulation of the bio-grease. Simple filtration was done using filter paper and simple sedimentation was carried out on the WCO at room temperature.

Figure 3-2 Waste Cooking Oil

3.2.2 Spent Bleaching Earth (SBE)

Spent bleaching earth (SBE) was collected from FELDA Vegetable Oil Product Sdn Bhd located in Kuantan Port Industrial Area, Kuantan, Pahang. The collected SBE underwent sieve tray filtration to make sure the fineness of the solid SBE and also even particles size distribution.

Figure 3-3 Spent Bleaching Earth

3.2.3 Cellulose

Three types of synthetic cellulose (MC, HEC and CMC) were purchased from Sigma-Aldrich and no pre-treatment is needed. The average molecular weights are 88,000 for MC, 250,000 for HEC and 90,000 for CMC.

Figure 3-4 (From left to right) Methyl Cellulose, Carboxymethyl Cellulose and Hydroxyethyl Cellulose

3.3 Grease Formulation

The formulation of grease required vigorous mixing to homogenize the base oil (WCO), thickener (SBE) and additives (Cellulose). The weight percent of thickener, base oil and additives is important in grease formulation as it is greatly influenced the stability and