UNIVERSITI TEKNIKAL MALAYSIA MELAKA

ADDITION OF LITHIUM HYDROXYSTEREATE INTO USED COOKING PALM OIL AS BIO-DEGRADABLE GREASE FORMULATION

This report is submitted in accordance with the requirement of Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor of Mechanical Engineering Technology (Maintenance Technology) with Honours

By

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APPROVAL

This report is submitted to the Faculty of Mechanical and Manufacturing Engineering of UTeM as partial fulfilment of the requirement for the degree of Bachelor of Mechanical Engineering Technology (Maintenance Technology) with Honours. The member of the supervisory is as follow:

……

(Qamar Fairuz Bin Zahmani)

ABSTRAK

Di zaman teknologi yang sedang meningkat maju ketika ini, penggunakan petroleum semakin bertambah. Dalam pada masa yang sama kuantitinya juga semakin berkurang. Salah satunya yang turut terjejas akibat konflik ini adalah tentang penghasilan grease. Untuk mengatasi masalah ini, kajian dilakukan dengan menghasilkan grease baru dengan menggunakan sumber mineral asas dari minyak sayuran yang telah dipakai. Dalam kajian ini, untuk menghasilkan grease yang baru menggunakan minyak masak terpakai dengan penambahan Zinc Dialkyldithiophosphate (ZDDP) bagi meningkatkan sifat kelinciran kerana (ZDDP) merupakan bahan yang menggurangkan geseran dan menggurangkan hakisan. Selain dari penggunaan Zinc Dialkyldithiophosphate (ZDDP) dalam penghasilan grease yang baru satu lagi penambah yang digunakan adalah dengan menggunakan Lithium Hydroxystereate. Lithium Hydroxystereate ini adalah sebagai agen pemekat yang mana ianya digunakan bertujuan untuk mengubahkan bentuk struktur minyak menjadi grease. Minyak masak sawit yang telah digunakan dicampurkan dengan nilai yang sama iaitu 2wt% daripada ZDDP dan berbeza nilai daripada agen pemekat yang menggunakan 5wt%, 10wt%, 15wt% dan 20wt% daripada Lithium Hydroxystereate. Kesemua sampel telah diuji dan dicirikan dengan kaedah dari melakukan ujian makmal seperti ASTM D2266 four-ball tester, ASTM D2596 dan tekanan yang melampau, dan Scanning Electron Microscope (SEM). Hasil kajian yang dijalankan, keputusan menunjukkan bahawa gris yang menggunakan 5wt% Lihthium Hydroxystereate mempunyai nilai pekali geseran 0.0646 dan wear scar diameter yang lebih kecil 352.8 μm dan lebih baik berbanding dengan sampel yang lain. Manakala, sampel yang menggunakan 20wt% lithium hydroxystereate mampu menahan tekanan yang melampau sehingga 400 Kg.f yang menujukkan nilai lebih tinggi berbanding sampel -sampel lain.Berdasarkan dari keputusan ujian dapat disimpulkan apabila penambahan nilai lithium kedalam minyak mempengaruhi nilai pekali geseran wear scar diameter dan tekanan yang melampau membuatkan peningkat nilai.

ABSTRACT

In an age of technology are rapidly developing at the moment, the use of petroleum is increasing. In the same time the quantity is also decreased. One of them is also affected by this conflict is about the production of grease. To solve this problem, a study done by generating new grease using mineral resources base of vegetable oils that have been used. In this study, to produce a new grease using used cooking oil with the addition of Zinc Dialkyldithiophosphate (ZDDP) to improve the lubrication properties because (ZDDP) are materials that reduce the friction and reduce the erosion. Apart from the use of Zinc Dialkyldithiophosphate (ZDDP) in the production of another new grease additive used is to use Lithium Hydroxystereate. Lithium Hydroxystereate is a thickening agent which is used to transform the structure of oil into grease. Used palm oil is mixed with the same value of 2wt% of ZDDP and different value of thickening agent using 5wt%, 10wt%, 15wt% and 20wt% of Lithium Hydroxystereate. All samples were tested and characterized using laboratory tests such as ASTM D2266 four-ball tester, ASTM D2596, extreme pressure and Scanning Electron Microscope (SEM). Based on this study, the results show that grease using 5wt% Lithium Hydroxystereate has a coefficient of friction of 0.0646 and wear scar diameter 352.8 μm which is smaller and better compared to other samples. On the other hand, samples using 20wt% lithium hydroxystereate are able to withstand pressures of up to 400 Kg.f which is higher than other samples. Based on the test results it can be concluded that the addition of lithium values to the oil affects the wear coefficient of the wear scar diameter and the extreme pressure causes the value to increase.

DEDICATION

To my beloved Father, Mohd Eza Bin Mohd Ariffin.

To my beloved mother, Maimanah Binti Wahab.

To my cherished sibling, Siti Nurbalqis Binti Mohd Eza.

To my respected supervisor, Qamar Fairuz Bin Zahmani.

To my respected lecture, Muhamad Azwar Bin Azhari.

To my helpful friend.

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TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

%	-	Percent
ADDC	-	Antimony Diakly Dithiocarbamate
ASTM	-	America Society for testing and materials
BC	-	Before Christ
℃	-	Degree Celcius
DBP	-	Dibutyl Phosphite
g	-	Gram
kg/m3	-	Kilogram per Cubic Meter
Kg_f	-	Kilogram-Force
mm	-	Millimeter
MoDTC	-	Molybdenum Dithiocarbamate
MoDTP	-	Molybdenum Dithiophosphate
MoS2	-	Molybdenum Disulfide
N	-	Newton
R•	-	Free Radical
RO•	-	Alkoxy Radical
ROO•	-	Peroxy Radical
ROOH	-	Hydroperoxides
SAE	-	Society of Automotive Engineering
WSD	-	Wear Scar Diameter
Wt	-	Weight
ZDDP	-	Zinc Dialkydithiophosphate
Mm	-	Micrometer

CHAPTER 1

INTRODUCTION

1.1 Introduction Lubricating Grease

In the era of the latest technology, a variety of machines have been used to increase productivity, save time and also to reduce the cost of production. However, to get a low-cost expense it must rely on operating costs and long life of the machine (Wan et al.,1998). From the study by Wilson (1979) stated that Lubrication is wear and friction control by inserting friction reduction film between two contact-moving surfaces. Sometimes, friction reduction and wear prevention functions can be interchangeable. However, friction is a resistance to movement and at the same time wear is the loss of material due to friction, fatigue, and corrosion. Another research by Nicholls et al., (2005) also claimed the lubricants are the main elements used for lubrication of machinery intended to maintain the performance of a machine, as well as to minimize the wear and tear while at the same time it aims to extend the life of the machine components. Lubrication has the function of reducing wear and friction, removing the heat produced during prolonged bearing life, preventing rust and protecting against harmful elements, as well as contact surfaces (Azhari et al.,2014).

Lubricant has long been found by archaeologists and created since 4000 years ago. Lubricant creation occurs when humans create by using the fundamental basis of natural resources coming from the basic form of raw animal fat (Duncan,1998). According to (Cheenkachorn, 2006) since 1650 BC the animal fats have been used as the lubricant for rotating components. At that time, whale fat was used as lubricant to lubricate equipment and machineries. A study by Bhushan (2013) stated that in 1880 BC, the ancient

Egyptians has found the importance of reducing friction when they use the transport of large stone blocks to construct buildings by putting animal fat on the surface of branches of tree as lubricants**.**

The research by Syed (2009) has stated in the late 1800s to early 1900s, people started to develop a new type of lubricating grease using petroleum products as precursors. Grease creation is also based on the application and requirements to a machine as well as the progress of the technology used. To create lubricating grease requires three main sources which is base oil, additives, and thickening agent. There are three types of base oil that are commonly used which is mineral, synthetic and vegetable oils and they have their own different characteristics. A research by Ahmed and Nassar (2013) has claimed that mineral oil is a natural source of crude oil from the earth that can be obtained from the oil refining process. For synthetic oil, basically it comes from mineral oil resources. Vegetable oil comes from renewable source. In producing lubricating grease, additives are used to help in stabilizing the oxidation process and act as anti-wear agent (Masabumi et al.,2008). Another addition that is used to develop the grease is thickening agent which is to change the structure of lubricant to become semi-solid lubricant. At that time, they develop the lubricating grease by added the thickening agent such as Calcium soaps, Aluminum soaps, Sodium soaps and Lithium soap to forming the grease. Lubricating grease is a semi-solid structure which is influenced by the mixture of thickening agent and additives that form the structure of production of lubricating grease.

According to In-Sik Rhee (2000), the thickening agent has served to change the characteristic of a solid lubricant to semi-solid structure. The thickener which works to hold the oil within microstructural and has provided varying resistance to flow. Some of the characteristics of grease include water resistant, mechanical stability, temperature properties and others. Another research by Yamaguchi et al., (2016), stated that a thickening agent is used for grease as an endurance agent on grease when subject to high-temperature conditions. According to Kudryavtsev (2016), lithium-based thickening agent are widely used in lubrication industry and the thickening agent commonly used is lithium

hydroxystereate. Lithium hydroxystereate also known as lithium soap. Lithium soaps have a higher degree of stability in oxidation up to about 200°C and the specialty of the lithium is it can adapt in low or high temperature and in at the same time it also has advantages in water resistant.

Lubricating grease depend on the type of based oil used and application. Vegetable oil-based lubricating grease have few limitations in term of oxidation stability. A Research by Azhari et al., (2015) has stated the oxidation stability problem in oil is a major problem factor caused by the high unsaturated fatty acid contained in vegetable oil. Therefore, the way to solve the problem is by adding additives to vegetable oils to overcome oxidation problems. Apart from the thickening agent, there is an additional mixture of other substances known as Zinc Dialkyldithiophosphate. Zinc Dialkyldithiophosphate also was known as ZDDP. ZDDP is an additive agent that is capable of controlling the stability of oxidation present in vegetable oils. According to by Barnes et al., (2001) has stated that their antioxidant properties and their ability by using ZDDP to prevent possible wear. This statement also is supported by Erhan et al., (2006) that has stated ZDDP as an antioxidant agent has high properties in controlling oxidation.

Another important element in producing grease apart from oil and thickening agent is the additives. Additives added into grease will later determine the characteristic of the developed grease. Some example of additives to be incorporated in development of grease includes anti-friction, anti-oxidation agent, detergent and anti-wear. Anti-oxidation agent is added into any grease to increase the durability and endurance of the grease life span. Anti-wear and anti-friction acts as a protective layer to protect the surface of moving when grease is applied.

1.2 Problem Statement

Bannister (1996) has stated that the mineral-based lubricants are widely used over the years as machinery lubrication in the industry. It is also one of the non-renewable sources for using natural mineral resources derived from petroleum. In the coming decades, these mineral resources will fall short because petroleum is the only major mineral commodities which are widely used at this time. As what has been stated by Nizam and Bari (2009), production of mineral oil-based lubricants is increasingly affected each year when petroleum prices are rising because of a lack of reserves and at the same time the growing demand.

Pollution is the entry into the environment of pollutants such as chemicals, noise, heat, light, and energy that cause effects that destroy the environment and threaten the natural resources and ecosystems. Margareth et al., (2010) has stated the increased use of petroleum day to day as a primary energy source provides the main problem in terms of environmental pollution and also disturb the ecosystem of aquatic life. Besides, environmental issues related to the non-biodegradable content of petrochemical in lubricant started to arise due to the difficulties of disposing of the waste oil (Azhari et al., 2015). As another alternative way to resolve issues related environmental problems arising, bio-lubricants using biodegradable resources has been developed due to it characteristics which is renewable and non-toxic (Siniawski et al., 2007).

With this issue, this study aims to be the new purpose in developing new lubricating grease by using renewable and biodegradable source which is vegetable oils as the base oil. This statement is also supported by Campanella et al., (2010) where vegetable oil biodegradable has features environmentally friendly renewable and non-toxic compared to mineral-based lubricants. Besides that, the research by Fox and Stachowiak (2007) has claimed that vegetable oils have good lubricants because they have a polar ester group composition. Due to the structure of long-chain fatty acids in vegetable oils poles, the high-strength lubricating film that interacts strongly with metal surfaces can

reduce wear and friction. However, the performance of vegetable oil in reducing wear and friction is not capable of rivaling the performance of mineral-based lubricants. Therefore, to improve the performance of vegetable oils by introducing additives into the base oil for the purpose of transforming the structure and improving the performance of vegetable oils as equivalent or better lubricants from mineral-based lubricant performance (Azhari et al., 2015).

In order to improve the properties of new develop lubricant Zinc dialkyldithiophosphates (ZDDP) additives will be added to the composition. As what has been claimed by Ludema (1996) in the 1930s and 1940s invention anti-wear chemicals have been found to be known as Zinc dialkyldithiophosphates (ZDDP). This is to ensure that new grease production has the essential characteristics as a lubricant such as anti-oxidizing, anti-wear, and anti-friction. Research by Mahipal et al., (2014) claimed the wear scar diameter become smaller after adding Zinc dialkyldithiophosphates (ZDDP). To develop a new biodegradable grease, lithium hydroxystereate also will be added into the vegetable oil to increase the viscosity and remain the vegetable oil in semi-solid structure (In-Sik Rhee, 2000). Thickening agent that are commonly used are soap based, such as calcium salts, sodium, lithium because they have long chain fatty acids. According to Sukirno et al., (2009) lithium thickening agent is important in the creation lubricating of grease due to its excellent properties such as smooth appearance and high drop points.

Therefore, this study is focuses in using used vegetable oils that can be recycled as a major source of new grease production by adding thickening agents such as lithium hydroxystearate and additional agents such as zinc dialkyldithiophosphates in producing new greases to address the problem of the use of natural mineral resources from petroleum.

1.3 Objective

The aim of this study is based on the problem statement is listed as follows:

i. To develop a new biodegradable grease using used palm oil.
ii. To test the develop new biodegradable grease for its lubricity performance.

1.4 Scopes

In order to achieve the objective, several scopes have been stated:

i. Developing new biodegradable grease using used cooking palm oil, ZDDP and Lithium Hydroxystereate.
ii. Testing the lubricity performance of biodegradable grease using ASTM D2266 Four Ball Tester and ASTM D2596 Extreme Pressure Test.

CHAPTER 2

LITERATURE REVIEW

2.1 Lubricant

Lubricant is a substance used between moving two surfaces to reduce friction and wear (Wilson, 1979). A film is constructed between the surface when a lubricant is applied and it acts as a control agent for friction. As friction is reduced, wear will then be reduced as well. Cheenkachorn (2006) stated that animal fats have been used as lubricants for rotating component since 1050 B.C.

A research by Azhari et al., (2014) has claimed that lubricant has the function to reduce the friction and wear, produces at the contact surface, protection against harmful element, prevention of rust and can transfer away the heat produces at the contact surface. Friction needs to be reduced as it contributes to the generation of heat as well as wear. This statement also be supported by Nicholls et al., (2005) has stated that lubricant is main element used for lubrication of machinery to maintain the performance of machine and minimize the wear and tear. At the same time that can also extend the life of mechanic component. Lubricant helps reduce friction which ultimately reduces the generation of heat and wear caused by the formation of liquid films between surfaces (Bannister 1996). Another research by Lubricant also plays an important role to flush away contaminant and debris presence in the engine and to transfer away the heat produces at the contact surfaces (Torbacke et al., 2014). As the mention by Mang et al., (2007), the lubricants have been used as a basic thing to facilitate to provide a smooth sliding contact the material transportation in their daily lives.

2.2 Classification of lubricant

Lubricants can be produced when surfaces are touched which produce smoothness in any of the different physical conditions. In the industry, lubricants are selected according to the requirements in the machining or motoring industry according to the performance and characteristics of the specifications found in the lubricant type. According to Suhane et al., (2012) lubricant can be classified with three different physical structure which is liquid, semi-solid and solid. These types of lubricant structure have distinctive characteristics which can be applied according to the suitability and effectiveness of a situation.

2.2.1 Liquid Lubricant

In industry any part of the liquid that is used to reduce the friction or moving part is has known as the liquid lubricant. According to Bhushan (2013) first liquid lubricant that has use from animal tallow and olive to reduce friction. Lubricant is applied to a rotating part component to prolong the service life of the component. For the lubricant category that can be divided two main categories based that is natural organic oils and synthetic organic oils. For natural organic oils commonly used of the lubricant in machinery they use vegetable oil and animal fats like rape seed oils, castor, shark oil and whale oil. Synthetic organic oils are the combination of some material that can make the good boundary lubricant. This type of oil has the good boundary lubricant and give the smooth sliding contact to reduce the friction at that time.

According to Gawrillow (2004) in 19^{th} century, by transformation of industry machine the lubricant by using vegetable oil and animal fats become limited because technology required about inexpensive, thermally and oxidative stable lubricant.

Lubricant by using vegetable oil and animal fat unable to maintain their performance to reduce friction for long period because there has presence of oxygen which can make the high temperature. Oils are less cooperative in oxidative stability and thermal stability tend to produce sticky deposits result from the breakdown (Bhushan, 2013).

Since the discovery of petroleum, dramatic changes occur in the lubricant industry in the mid-19th century at the time of production of mineral oil gained much commercial demand due to the then price of petroleum mineral resources and cheap (Suhane et al., 2012). According to Miyoshi (2001) has stated the development of machinery industry who have advanced that involve high speed, high temperature pressure, and high power has led to the development of produced syntenic lubricants intended to deal with each situation that occurs to maintain engine performance and prolong the life of the machine. In order to produce a good quality of lubricants that use petroleum, the improvement is made by adding additives in synthetic lubricants for the purpose to improve the oxidation stability, high lubricating properties, as protection from corrosive and able to withstand the pressure of carrying the load. Without the addition of lubricant additives are not able to withstand the pressure applied under extreme conditions. A research by Bhushan (2013) has claimed synthetic lubricating properties are able to survive in conditions of high temperature and pressure, high humidity, high vacuum and low fire danger.

According to Bhushan (2013) has stated improvement of lubricant can be obtained by the addition of lubricant additives and base oil types use appropriate circumstances. In industrial, lubricating fluids often used are oil-based foundation of natural organic matter and synthetic. Basically, liquid lubricant is used to transfer either force or energy like hydraulic system and other than also can control wear, friction, surface damage (Menezes et al., 2013). Another research by Bhushan (2013) has claimed that another ability can get in liquid lubricant are absorb heat that can minimize operating system temperature. Table 2.1 displays the various types of liquid lubricant that are currently used in lubricating industry.

Table 2.1 Types of Liquid Lubricant and Principle Attribute (Bruce, 2010)

Type	Principal attribute
Mineral oil of fractions	Low cost
Synthetic hydrocarbons	Low temperature fluidity
Organic esters	Low temperature fluidity
Polyglycol ether	Good viscosity-temperature properties
Water base lubricants	Less flammable
Oil-water emulsions	Less flammable
Phosphate esters	Less flammable
Silicones	Excellent viscosity-temperature properties
Polyphenylethers	Thermal stability
Perfluoropolyethers	Oxidation resistant
Halocarbons	Non-flammable

2.2.2 Semi Solid Lubricant

According to Speight and Exall (2014) stated that semi-solid lubricant is the result of a mixture of lubricating fluid with a thickening agent. Semi-solid lubricant acts as a protective film on the surface of moving mechanical parts. This statement has been supported by Stachowick and Batchelor, (2013) which states that the thickening agent mixture is intended to produce a gel that can protect its surface steadily. Some examples of semi-solid lubricants often used in the industry is grease. In the production of grease, it