UNIVERSITI TEKNIKAL MALAYSIA MELAKA

DEVELOPMENT OF NEW BIO-LUBRICANT USING BLENDED ZDDC AND ZDDP AS TRIBOLOGICAL PROPERTIES IMPROVER IN PALM OIL

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

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DECLARATION

I hereby, declared this report entitled “Development of New Bio-Lubricant Using Blended ZDDC and ZDDP as Tribological Properties Improver in Palm Oil” is the results of my own research except as cited in references.

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APPROVAL

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

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ABSTRAK

Minyak pelincir merupakan sesuatu bahan yang mencelah di antara permukaan bergelongsor untuk mengurangkan geseran dan kehausan. Peningkatan kesedaran terhadap alam sekitar menyebabkan peningkatan keperluan minyak pelincir yang mesra alam sekitar. Hal ini disebabkan majoriti minyak pelincir adalah berasal daripada bahan petroleum yang tidak terbiodegradasi dan toksik kepada persekitaran. Oleh itu, penghasilan minyak pelincir yang tidak toksik dan terbiodegradasi telah digalakkan untuk mengatasi masalah alam sekitar yang berkaitan dengan minyak pelincir mineral. Di dalam kajian ini, objektif utamanya adalah untuk menghasilkan bio-pelincir baru dengan pretasi pelinciran yang memuaskan. Untuk menghasilkan bio-pelincir yang baru, minyak masak kelapa sawit komersial telah dicampur dengan bahan tambah baik minyak pelincir, zink diamildithiokarbamat (ZDDC) dan zink dialkildithiofosfat (ZDDP) dengan menggunakan kaedah pengenalan langsung. 6 kepekatan ZDDC dan ZDDP yang berbeza telah digunakan dalam penyediaan sampel, iaitu 0% berat + 0% berat, 2.0% berat + 0% berat, 1.5% berat + 0.5% berat, 1.0% berat + 1.0% berat, 0.5% berat + 1.5% berat, dan 0% berat + 2.0% berat. Sampel minyak sawit telah diuji untuk pelarutan bahan tambahan dengan mengikut kaedah ujian ASTM dan dicirikan untuk sifat tribologikal dengan menggunakan meter kelikatan terpanas, penguji empat bola dan mikroskop optik. Ciri-ciri tribologikal sampel juga dibandingkan dengan minyak pelincir mineral SAE 15W-40. Daripada keputusan kajian, ianya terbukti bahawa minyak kelapa sawit dengan penambahan 2% berat ZDDP menunjukkan ciri-ciri tribologi yang paling diingini di antara sampel-sampel yang telah disediakan. Ia menunjukkan pekali geseran terendah pada 0.075 dan diameter parut kehausan terkecil pada 80.8μm dan keputusan ini adalah secara relatifnya lebih rendah berbanding dengan minyak pelincir mineral SAE 15W-40. Pada perakhiran kajian ini,

bio-pelincir yang baru dan mempunyai ciri-ciri tribologikal yang unggul telah berjaya dihasilkan dengan menambahkan 2% berat ZDDP ke dalam minyak masak kelapa sawit komersial.

ABSTRACT

Lubricant is a substance that interposes between the sliding surfaces to reduce friction and wear. The growing environmental concerns resulted in the increasing of demand of an environmental friendly lubricant. This is due to the majority of the current lubricants are mineral based lubricants which are non-biodegradable and toxic to the environment. Hence, the development of non-toxic and biodegradable lubricant has been encouraged to overcome the environmental problems that related with mineral based lubricant. In this study, the main objective is to develop a new bio-lubricant with satisfactory lubricating performance. For developing a new bio-lubricant, commercialized cooking palm oil was blended with lubricant additives, ZDDC and ZDDP by using direct introduction method. Six different concentrations of ZDDC and ZDDP were used in the sample preparation which are 0wt% + 0wt%, 2.0wt% + 0wt%, 1.5wt% + 0.5wt%, 1.0wt% + 1.0wt%, 0.5wt% + 1.5wt%, and 0wt% + 2.0wt%. The samples of palm oil were tested for the additive dilution in accordance with ASTM test method and characterized for tribological properties by using heated viscometer, four-ball tester and optical microscope. The samples were also compared with mineral based lubricant SAE 15W-40 in term of tribological performance. From the results, it is evident that palm oil with the addition of 2wt% ZDDP exhibited the most desirable tribological characteristics among the prepared samples. It showed the lowest coefficient of friction at 0.075 and the smallest wear scar diameter at 80.8μm and these results are relatively lower compared to the mineral oil SAE 15W-40. In the end of this study, the new bio-lubricant with superior tribological properties was successfully developed by blending 2wt% ZDDP into commercialized cooking palm oil.

DEDICATION

To my beloved parents and my siblings

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LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

ASTM	-	American Society for Testing and Materials
ADDC	-	Antimony Dialkyldithiocarbamate
BC	-	Before Christ
COF	-	Coefficient of Friction
H_S	-	Hersey number
MoDTC	-	Molybdenum Dialkyldithiocarbamate
PAG	-	Polyalkylene glycols
PAO	-	Polyalphaolefins
RDE-AES	-	Rotating Disc Electron Atomic Emission Spectroscopy
SAE	-	Society of Automotive Engineers
TPPT	-	Triphenyl Phosphorothionate
ZDDC	-	Zinc Diamyldithiocarbamate
ZDDP	-	Zinc Dialkyldithiophosphate
cSt	-	centiStokes
g	-	gram
J	-	Joule
N	-	Newton
m	-	meter
Mg	-	megagram
ml	-	milliliter
mm	-	millimeter
nm	-	nanometer
Pa	-	Pascal
ppm	-	parts per million
rpm	-	revolution per minute

rps	-	revolution per second
s	-	second
wt	-	weight
℃	-	degree of Celcius
μm	-	micrometer
%	-	percent

CHAPTER 1

INTRODUCTION

1.1 Introduction to Lubricant

Lubricant is a substance which is applied to reduce friction and wear between contacting surfaces in relative motion. It can also reduce the heat produced by contacting surfaces. Besides, lubricant acts as an anti-oxidizing agent and prevents corrosion; seals against dust, dirt and water from the surfaces as well as transmits mechanical power in hydraulic fluid power applications (Ahmed and Nassar, 2013). According to Bannister in 1996, a lubricant can perform six basic functions which are reducing friction, reducing wear, absorbing shock, reducing temperature, minimizing corrosion and sealing out contaminants. Therefore, lubricants are extensively used for various applications. The three essential applications of lubricant are automotive, industrial and special purpose. Examples of the lubricants used in automobile and transportation industry are engine oils and transmission fluids; while metal-working fluids and hydraulic oils are common lubricants used for industrial purpose. The lubricants used for specific operations include white oils and instrumental oils (Mobarak et al., 2014).

Lubricants have been widely used all over the world since ancient times. Animal fats and vegetable oils are primary lubricant used by people since 17^{th} Century B.C. Grease made of calcium and fats were used to lubricate chariot axles (Pirro, et al., 2001). In addition, ancient Egyptians used olive oil as a lubricant to move large stones for buildings (Gawrilow, 2003). This is because olive oil can reduce the friction between the stones and floor and make the work became easier. Until the 1920s, the manufacturers started to synthesize the petroleum based lubricants due to the successful development of petroleum and growing lubricant demands (Bhushan, 2001). Since petroleum-based lubricants have been developed, the mineral oil based lubricants have dominated the commercial lubricant market. According to Dowson in 1979, mineral based lubricants have become protuberant due to their excellent quality at a reasonable price. However, the development of advanced machine resulted in the obsolescence of general purpose lubricant as this type of lubricant could not meet the requirements for higher speeds and higher temperatures. In order to produce a better lubricant with higher thermal resistance and lower volatility, the synthetic lubricant has been developed in the 1950s. Dibasic acid esters are the most common materials used for synthetic lubricant and they have low freezing points and excellent viscosity-temperature properties (Anderson, 1991). Nowadays, the scientists still use their expertise to develop new lubricants for each specialized application.

In the 21th century, environmental issues have become important guideline on developing new technologies. Thus, extensive researches on bio-lubricant have been encouraged due to petroleum shortages and environmental concerns and the development of bio-lubricants has become one of the essential elements in the future (Liu et al., 2014). This is due to mineral oil based lubricant are poor biodegradability and toxic. Furthermore, inappropriate disposal of mineral oils will cause serious impacts on the environment. Mineral oil based lubricants will affect the quality of soil and thus result in a great impact towards farming and civil construction. In addition, the high toxicity of mineral oils will contaminate the soil, thereby they will kill the vegetation and the microorganisms when mineral oils contact with the soil (Bartz, 1998; Willing, 2001). Moreover, the use of petroleum-based lubricants and environmental harmful additives have discouraged by environmental legislation by Occupational Safety and Health Administration (OSHA) and other international regulation authorities (Liew, 2015). Therefore, the development of renewable and biodegradable bio-lubricants is an effective solution as a substitution for mineral oils. Vegetable oils are preferred as the promising alternatives to mineral oils because they are biodegradable and available worldwide. Besides that, vegetable oils exhibit both boundary and hydrodynamic lubrications due to the long fatty acid chains and the presence of polar groups in the structure of vegetable oils (Mobarak et al., 2014). However, there are some limitations on the vegetable oils. Thus, lubricant additives play important roles in the oils to strengthen specific properties for the development of better lubricating performance.

1.2 Classification of Lubricant

Lubricant can be classified into three categories which are solid lubricant, semi-solid lubricant and liquid lubricant. Solid lubricant is a solid material that has layered crystalline structure which minimizes friction between contacting surfaces. A common method to apply solid lubricants is to blend certain solid lubricants in an aerosol carrier and spray directly onto the surfaces to be lubricated. Adhesives and epoxy resins will make the powder of solid lubricants strongly bond to a surface for longer wear life (Gresham, 1997). Examples of solid lubricant are graphite, hexagonal boron nitride and transition metal dichalcogenides. Semi-solid lubricant is a substance that consists of base oils and thickening agents. Semi-solid lubricant can stay in contact and it can be used for sealing purposes of protecting the surfaces from contamination by corrosive environment or moisture. One of the most common used semi-lubricants is calcium based soap grease and it can be used for low speed applications. Liquid lubricant is a substance in liquid state which reduces friction and heat when applied as a surface to moving parts. It can be categorized into two main groups: first group is natural organics that consist of mineral oils, vegetable oils and animal fat; another group is synthetic organics that are mixtures of two or more of these materials (Bhushan, 2013).

There are three main sources for a variety of liquid lubricants which are mineral oils, synthetic oils and vegetable oils. Mineral oil based lubricant are refined and manufactured from crude oil which is originated from fossil fuel. Crude oil has a complex structure and it can be separated into a number of fractions by distillation process which was also known as fractional distillation. Mineral oils have become the most commonly used lubricant in the industry due to their excellent boundary lubrication properties. However, pollution in both aquatic and terrestrial ecosystems will be initiated after disposal of mineral oil (Ssempebwa and Carpenter, 2009). Synthetic lubricant is a lubricant that produced by chemical synthesis of petroleum and other raw material. Synthetic oils are developed for specialized applications and better performance. The most beneficial properties of synthetic lubricant are that they can withstand extreme environments, such as high temperatures and pressures, high humidity and vacuum condition (Bhushan, 2013). Examples of synthetic oils are polyalphaolefins (PAO), phosphate esters, polyalkylene glycols (PAG) and silicone polymers. However, PAO and PAG have a major disadvantage that is poor soluble to lubricant additives, thus this limits the types of additives which can be used to develop effective lubricants (Srivastava and Sahai, 2013). Vegetable oils are refined from a renewable resource which is plants or crops, such as oil palm, soybean, corn, canola, coconut, sunflower and peanut. Vegetable oils have high oleic content which helps them to use as lubricants. Vegetable oil based lubricants have high viscosity index and high flash points. Moreover, vegetable oils are renewable, biodegradable and low toxic products (Torbacke et al., 2014). Thus, vegetable oils are environmentally preferred compared to the mineral oils. However, the major drawback of vegetable oils is the presence of double bond in the structure which causes the problem of poor oxidation stability.

1.3 Problem Statement

The technological advances in green technology have become prominent in the different fields. This resulted in a problem of demanding on the lubricants which are environmental friendly become a major concern in today's industries. Continued growing environmental concerns are the main factor that increased the demand and usage of vegetable oil utilization in lubricants for many applicants (Gawrilow, 2003). The characteristics of mineral oil are non-biodegradable, non-renewable and toxic will cause environmental pollution. The majority of the current lubricants are mineral based lubricants which are difficult to dispose and toxic to the environment (Kucera and Rousek, 2011). According to Bergstra (2004), vegetable oils are renewable resources for the industrial and transportation applications lubricants. Hence, vegetable oil has become a suitable candidate to replace the mineral oil based lubricant for solving the environmental problem and base oil shortage.

Vegetable oil based lubricants are non-toxic and biodegradable compared to conventional petroleum based lubricants (Mahipal et al. 2014). This will minimize the damage to the environment. Moreover, vegetable oils are sustainable energy and cheaper base oils for lubricants compared to synthetic fluids. This is because the resource of vegetable oils is renewable and it can be found in abundance. Vegetable oils also show good properties, such as excellent lubricity, high viscosity index and high flash point (Mobarak et al., 2014). The triglycerides of vegetable oils provide lubricant films which interact with the metallic surfaces and they will also reduce the friction and wear between the contact surfaces. This is one of the reasons why the vegetable oils can be used as lubricants. Furthermore, vegetable oils also exhibit high solubilizing power for polar contaminants and additives molecules (Erhan et al., 2006). This property will help the lubricant additives to dissolve into the base oils for the future development of lubricant.

However, there are some drawbacks on the vegetable oils, such as poor hydrolytic, thermal and oxidation stability and poor low-temperature characteristics (Adhvaryu and Erhan, 2002; Zeman et al., 1995). Moreover, tribological properties of pure vegetable oils do not meet the requirements of commercial lubricant. In the research of Azhari et al. (2016b), pure vegetable oil exhibits a significantly higher coefficient of friction and wear scar diameter compared to the commercial lubricant SAE 40. Furthermore, there are numerous researches that have implied the capability of pure vegetable oil is limited. The coefficient of friction for pure corn oil is increasing with the increment of the load applied and the value of COF is higher than the COF of the corn oil with the addition of additive (Azhari et al., 2015a). This statement also was proven by the study of Azhari et al. (2015b), the value of kinematic viscosity and coefficient of friction for pure canola and corn oils are significantly higher than the canola oil and corn oil with 2wt% of zinc dialkyldithiophosphate. These researches indicate that the pure vegetable oils cannot be used for commercial lubrication purpose and their tribological properties should be enhanced for further development.

In order to produce better performance bio-lubricant, the additives should be blended with the vegetable oils. The additives of friction modifier and anti-wear agent can be added to improve the tribological properties of vegetable oils and make sure them to function as a commercial lubricant. Zinc diamyldithiocarbamate (ZDDC) is one of the common lubricant additives that can improve the tribological properties of vegetable oils. ZDDC was added into corn oil as friction modifier and anti-wear agent for reducing the coefficient of friction and wear scar diameter of pure corn oil (Tamar, 2015). In the study of Zakaria (2015), the canola oil which added with ZDDC has a lower kinematic viscosity, lower coefficient of friction and lower wear scar diameter compared to pure canola oil. Zinc dialkyldithiophosphate (ZDDP) is a common and useful additive for lubricant because ZDDP exhibits antioxidant and anti-wear properties. According to Azhari et al. (2015a), zinc dialkyldithiophosphate (ZDDP) was added into the vegetable oil as physical property modifier for development of a more stable bio-lubricant. Moreover, ZDDP can decrease the coefficient of friction and kinematic viscosity value of corn oil (Azhari et al., 2015c).

Nonetheless, the lubricating performances of vegetable oils with the addition of ZDDC are barely satisfactory and they do not achieve the conventional mineral based lubricant standard. According to Tamar in 2015, corn oil with 2wt% ZDDC has relatively higher wear scar diameter of 65.02μm compared to the mineral based lubricant SAE40 of 41.9μm. Besides that, the wear scar diameter for the addition of 2wt% ZDDC in canola oil is 65.2μm which is noticeably higher than the canola oil with 2wt% ZDDP of 34.72μm (Azhari et al., 2016b; Zakaria, 2015). These experimental results show ZDDC has some deficiencies on the performance and it could not improve the tribological properties of vegetable oils to the optimum level. In order to strengthen the capability of ZDDC in vegetable oils, another lubricant additive in vegetable oils should be added into vegetable oils. A synergistic effect will be provided when ZDDC as an antioxidant is combined with antimony dialkyldithiocarbamate (ADDC) as anti-wear agent. This combination of additives reduces the friction and increase the oxidation stability of vegetable oil (Erhan et al., 2006). This implies that the blending of lubricant additives into vegetable oils can improve the lubricating properties. Therefore, blended zinc diamyldithiocarbamate and zinc dialkyldithiophosphate will be added into palm oil to overcome the problems and enhance the tribological properties of bio-lubricant.

1.4 Objectives

Based on the problem statement, the objectives of this study are:

i. To develop a new lubricant formulation with the addition of lubricant additives.
ii. To test and characterize the newly formulated bio-lubricant using appropriate test methods.
iii. To compare the newly formulated bio-lubricant with the commercialized mineral based lubricant.

1.5 Scopes

In order to reach the objectives, a few scopes have been drawn:

i. Developing new bio-lubricant formulation using palm oil with friction modifier and anti-wear agent.
ii. Testing the newly formulated bio-lubricant for additive dilution through Rotating Disc Electron Atomic Emission Spectroscopy in accordance with ASTM D6595.
iii. Characterizing the newly formulated bio-lubricant using heated viscometer and four-ball tester in accordance with ASTM D4172.
iv. Comparing the tribological properties of the newly formulated bio-lubricant with commercialized mineral based lubricant SAE 15W-40.

CHAPTER 2

LITERATURE REVIEW

2.1 Lubrication Regimes

Lubrication is a process that used to reduce friction and wear between the surfaces to extend the life of machine elements. The lubrication regimes have different characteristics and conditions. Stribeck curve is the important concept for the understanding of the properties of different lubrication regimes. Stribeck curve is generally a curve in the graph of the coefficient of friction against Hersey number. The Hersey number is the dimensionless number which obtained from the product of the absolute viscosity and rotational speed that divided by the pressure. In the Stribeck curve as Figure 2.1, there are 3 main categories of lubrication regimes which are hydrodynamic lubrication, mixed lubrication and boundary lubrication.

$$Hs = \frac{\eta\omega}{p} \qquad \text{(Eq 2.1)}$$

where η = absolute viscosity, Pa·s

ω = rotational speed, rps

p = pressure, Pa