UNIVERSITI TEKNIKAL MALAYSIA MELAKA

WEAR AND FRICTION PROFILING OF ZINC ION INDUCED CORN OIL BASED BIO-LUBRICANT

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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Date : **16 JANUARY 2017**

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:

……………………………………

(Muhamad Azwar Bin Azhari)

ABSTRAK

Konflik mengenai penggunaan pelincir berasaskan mineral telah mendapat perhatian di kalangan penyelidik semenjak perlindungan alam sekitar terjejas disebabkan oleh pelincir berasaskan mineral sedia ada yang tidak terbiodegradasi, tidak boleh diperbaharui dan sangat bertoksik. Untuk mengatasi masalah ini, kajian ini telah dijalankan dengan tujuan untuk membangunkan sebuah bio-pelincir menggunakan minyak sayur-sayuran dengan penambahan Zinc Dialkyldithiophosphate (ZDDP) bagi meningkatkan sifat pelinciran minyak. Minyak sayuran telah dipilih memandangkan ia boleh terbiodegradasi, boleh diperbaharui, tidak bertoksik dan juga mempunyai ciri-ciri pelinciran yang unggul berbanding minyak mineral. Dalam kajian ini, minyak jagung telah dicampur dengan kepekatan ZDDP yang berbeza sebanyak 1.50% berat, 1.75% berat, 2.00% berat, 2.25% berat dan 2.50% berat ZDDP menggunakan kaedah pengenalan langsung untuk menyiasat kepekatan ZDDP yang paling wajar. Sampel telah diuji dan dicirikan menggunakan kaedah ujian makmal standard untuk menentukan kandungan logam, kelikatan kinematik, pekali geseran dan diameter kehausan parut. Berdasarkan hasil keputusan, ianya didapati bahawa minyak jagung dengan 2.00% berat ZDDP mempunyai kepekatan bahan tambahan yang paling wajar kerana ia menunjukkan pekali geseran dan diameter kehausan parut yang rendah berbanding sampel lain. Minyak jagung dengan 2.00% berat ZDDP mengesan pekali geseran pada 0.073 dan diameter kehausan parut pada 78.87 mikron. Daripada kajian ini, ia juga telah mendapati bahawa prestasi tribologi bio-pelincir yang baru dibangunkan dengan 2.00% berat ZDDP adalah lebih baik daripada pelincir yang dikomersialkan berasaskan mineral di mana minyak jagung dengan 2.00% berat ZDDP mempunyai 0.073 pekali geseran dan 78.87 mikron diameter kehausan parut yang lebih rendah berbanding dengan SAE 15W-40 yang dikesan pekali geseran pada 0.081 dan diameter kehausan parut pada 85.00 mikron. Oleh itu, ianya dapat disimpulkan bahawa minyak jagung dengan kepekatan ZDDP yang paling wajar sebagai pelincir alternatif hijau mempunyai potensi yang tinggi untuk menggantikan SAE 15W-40.

ABSTRACT

Conflict regarding utilization of mineral based lubricant has been in the limelight among researchers since environment protection was affected due to the existing mineral based lubricant which is non-biodegradable, non-renewable and highly toxic. In order to overcome these problems, this study was conducted with purpose to develop a new green bio-lubricant using vegetable oil with addition of Zinc Dialkyldithiophosphate (ZDDP) to improve lubrication properties of the oil. Vegetable oil was chosen since it is biodegradable, renewable, non-toxic and also features superior lubricity than mineral oil. In this study, corn oil had been blended with different concentration of 1.50 wt%, 1.75 wt%, 2.00 wt%, 2.25 wt% and 2.50 wt% of ZDDP using direct introduction method in order to investigate the most desirable concentration of ZDDP. Samples were tested and characterized using standard laboratory test methods for determination of metal content, kinematic viscosity, coefficient of friction and wear scar diameter. From the results, it was found that the corn oil with 2.00 wt% ZDDP possess the most desirable concentration of additive added since it shows lower coefficient of friction and wear scar diameter compared to the other samples. Corn oil with 2.00 wt% ZDDP detected coefficient of friction at 0.073 and wear scar diameter at 78.87 μm. From this study, it was also discovered that the tribological performance of newly developed bio-lubricant with 2.00 wt% ZDDP is better than commercialized mineral based lubricant where corn oil with 2.00 wt% ZDDP possess 0.073 of coefficient of friction and 78.87 μm of wear scar diameter which are lower compared to SAE 15W-40 that detected coefficient of friction at 0.081 and wear scar diameter at 85.00 μm. Hence, it can be concluded that corn oil with most desirable concentration of ZDDP as green alternative lubricant has a high potential to substitute the SAE 15W-40.

DEDICATION

To my beloved mother, Siti Faridah Binti Hashim.

To my cherished sibling, Muhammad Shaufiq Bin Ahmad Mokhtar.

To my respected supervisor, Muhamad Azwar Bin Azhari.

To my helpful friends.

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LIST OF SYMBOLS AND ABBREVIATIONS

%	-	Percent
AD	-	Anno Domini
ASTM	-	American Society for Testing and Materials
BC	-	Before Christ
C	-	Carbon
℃	-	Degree Celcius
cSt	-	Centistokes
DBP	-	Dibutyl Phosphite
g	-	Gram
HO•	-	Hydroxy Radical
HP	-	Hindered Phenolic
kg/m^3	-	Kilogram per Cubic Metre
mm	-	Millimetre
MoDTC	-	Molybdenum Dithiocarbamate
MoDTP	-	Molybdenum Dithiophosphate
MoS_2	-	Molybdenum Disulfide
N	-	Newton
PAO	-	Polyalphaolefin
PKO	-	Palm Kernel Oil
PTFE	-	Polytetrafluoroethylene
R•	-	Free Radical
RDE-AES	-	Rotating Disc Electrode Atomic Emission Spectroscopy
RO•	-	Alkoxy Radical
ROO•	-	Peroxy Radical
ROOH	-	Hydroperoxides
RPO	-	Red Palm Oil

SAE	-	Society of Automotive Engineers
TCP	-	Tricresyl Phosphate
UV	-	Ultraviolet
WSD	-	Wear Scar Diameter
wt	-	Weight
ZDDP	-	Zinc Dialkyldithiophosphate
α	-	Alpha
μm	-	Micrometre

CHAPTER 1

INTRODUCTION

1.1 History of Lubricant

Presence of lubricant film between relative moving surfaces that give a physical benefit has been known for several millennia (Mortier et al., 2011). The importance of reducing friction has been started since 1880 BC in ancient Egypt where the Egyptians slaves use branches of trees to reduce the sliding friction for transportation of large stone building blocks (Bhushan, 2013). The usage of branches of trees presumably work as a rolling friction. The large stone building blocks were dragged along the wooden track and it was seen that an amount of liquid most likely water was poured into the immediate path of the block as lubricant to reduce friction. This shows that lubricant has been used since ancient time to provide a smooth sliding contact for material transportation.

Cheenkachorn (2006) claimed that vegetable oils and animal fats have been used for lubrication of rotating components since 1650 BC. At that time, animal tallow was used to lubricate Egyptian chariot wheels while some equipment and machinery were lubricated using whale fat. Then, usage of lubricants from different sources continue to be enhanced where grease was used for lubrication of chariot wheels. The grease was made from combinations of animal fat and calcium that were developed as early as 1400 BC (Pirro and Wessol, 2001).

From the time of AD 50 until the early 19th century, various oil from vegetable and animal were obtained and used for lubrication such as olive, rapeseed, castor beans, palm oil and the fats from sperm whale, animal lard and wool grease. At the late 18th century to 19th century, the Industrial Revolution inspired the need for inexpensive, thermally and oxidative stable lubricants (Gawrillow, 2004). In this century, mineral oil was started to be produced commercially in large quantities. Since mineral oil was available in large quantities, mineral based lubricant began to be developed due to overall performance of mineral oil and low in cost for the production of mineral based lubricant (Suhane et al., 2012).

Industrial Revolution was sparked because of human desire to excel and achieve comfort levels aided by the inquisitive approach of human. At that time, presence of machines were used to replace muscle power that changed almost every aspect of human daily life and contribute to the improvement in agriculture, manufacturing, mining and transportation (Suhane et al., 2012). Thus, adequate lubrications are needed during this period to keeps the performance and condition of the machine in good state. In the 20^{th} century, mineral oil has been completely overtook vegetable oil and animal fats as base oil for production of lubricant (Mortier and Orszulik, 2012). Since then, mineral oil has been used widely as lubricant until now.

Todays, vegetable oils have started back to be develop as alternative way to substitute mineral based lubricant. The usage of mineral based lubricants have been considered since mineral based lubricant causes negative impact on the environment. Lubricants are always improve from time to time in order to fulfill the needs of technology and surrounding condition.

1.2 Introduction to Lubricant

Lubricant is any substance used to separate two or more contacting surfaces which provide smooth running between them. The presence of lubricant between the contact surfaces is designed to lower the friction and wear of the contact surfaces especially in rotating machinery (Wan et al., 1998). Generally, lubricant is used for machinery lubrication to maintain the machine performance, minimize wear and prolong the life of machine component (Nicholls et al., 2005). 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).

Acording to Hamrock et al. (2004), typically lubricant are used for lubrication in the form of liquids such as mineral oils, silicone fluids, water and synthetic ester. Lubrication for dry bearings usually uses lubricant in the state of solid such as polytetrafluoroethylene or known as PTFE. Besides that, greases which is a lubricant in the form of semi-solid are used to lubricate rolling-element bearings whereas lubricants in the form of gases such air are used in gas bearings. The various types of lubricant form are select depend on the application to be used in order to provide the machine elements with satisfactory life.

Lubricants commonly contain an additive to enhance or suppress the properties of base oil. The type and amount of additives depend on the type oil base oil and also application of the lubricant to be used. Lubricants typically consist of 90% base oil which is generally mineral oil derived from petroleum resources and less than 10% additive. Sometimes, vegetable oil and synthetic oil such as silicones, esters and polyalphaolefins are used as lubricant base oil. The additives are usually added into the base oil to improve the oxidation stability, reduced friction and wear (Suhane et al., 2012).

Ahmed and Nassar (2013) stated that lubrication are purposely used to reduce friction and wear in bearings or sliding components in order to prevent premature failure. In bearing application, lubricant acts to prevent undesirable material from entering the bearings which keeps the metal surface of the bearing in clean condition and also protects against corrosion and rusting.

There are different roles of lubricant in different lubrication regimes which consist of boundary lubrication, mixed lubrication and hydrodynamic lubrication. In boundary lubrication, the solid surfaces are very close to each other which the contact between the surfaces occur at asperities and their reaction with lubricant (Ahmed and Nassar, 2013). Presence of additive in the lubricant will act to create a film on the surface resulting in reduction of friction and wear. There is a situation where the additive will fail to form a film properly when the operating conditions change and occurrence of severe adhesive wear. In hydrodynamic lubrication, the surfaces are completely separated to each other by lubricant film and thereby no wear should occur. However, wear may happen under certain condition such as during starting and stopping where the wear occur before a sufficient of the formation of thick lubricant film. This means that the wear occur in boundary or mixed lubrication regimes during a short period of time contact (Torbacke et al., 2014).

1.3 Problem Statement

Mineral based lubricant is widely used for lubrication of machinery in industry for a very long time. The production of mineral based lubricant is derived from petroleum which is non-renewable resources. The growing scarcity of petroleum resources in recent years have been serious concern in mineral based lubricant production (Nizam and Bari, 2009). With the shortage of petroleum reserve and the increasing of demand, the petroleum price had increased each year and thereby affect the production of mineral based lubricant.

Besides that, 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., 2015a). As what has been stated by Sapawe et al. (2014), the petrochemical in mineral based lubricant is highly toxic and also flammable which can cause harm to the environment if it is dispose improperly. Thus, the improper management of disposing the waste oil will contribute to the ecological pollution, such as cases occurred in the United States where more than 60% of the lubricants used lost to the environment (Erhan and Sharma, 2006). Therefore, development of bio-lubricant which is biodegradable, non-toxic and renewable resources are desired to replace the mineral based lubricant as an alternative way to overcome the environmental issues that have arisen in order to generate a sustainable future (Siniawski et al., 2007).

The alternative way to substitute the mineral based lubricant with more eco-friendly resources is by using vegetable oil. As what has been claimed by Kučera and Rousek (2011), high oleic content in vegetable oil making it suitable to replace mineral based lubricant and synthetic esters. Furthermore, vegetable oil possess environmentally friendly properties such as biodegradable, renewable and non-toxic compared to mineral based lubricant (Campanella et al., 2010). Moreover, vegetable oil possess good lubricity due to its composition of polar ester groups. The structure of long polar fatty acid chains in vegetable oil offer high strength lubricant films that interact strongly with metallic surfaces and thereby reducing both friction and wear (Fox and Stachowiak, 2007). However, performance of vegetable oil in reducing friction and wear is incapable to rival the performance of mineral based lubricant. This problem has attracted the attention of researchers to improve the performance of vegetable oil by introducing an additive into the base oil.

Development of a new bio-lubricant using vegetable oil with addition of additive such as Zinc Dialkyldithiophosphate (ZDDP) has attracted many researchers due to its performance in reducing friction and wear. The vegetable oil is famous with their properties of high viscosity and viscosity index, excellent lubricity, high flash point and low volatility (Hsien, 2015) whereas the addition of ZDDP into vegetable oil usually acts as anti-wear and antioxidant agents (Farhanah and Sytahrullail, 2015). It is believed that through combination of vegetable oil and ZDDP is capable to produce a new bio-lubricant which can surpass the performance of mineral based lubricant in reducing friction and wear.

There are various types of experiments that have been conducted by many researchers through a combination of vegetable oil with different concentrations of ZDDP to analyze the behavior of the wear and friction generated. A research of developing a new bio-lubricant conducted by Mahipal et al. (2014) on the performance of karanja oil as lubricant with addition of different concentration of ZDDP as additives showed that the coefficient of friction and wear scar diameter of karanja oil with right amount of ZDDP had a better results compared to mineral based lubricant SAE 20W-40. However, karanja oil with excessive concentration of ZDDP resulted in increment of the coefficient of friction which is exceeds the coefficient of friction of the mineral based lubricant. This research proves that the right quantity of ZDDP added into vegetable oil are desired in order to produce a bio-lubricant with lowest coefficient of friction and wear scar diameter compared to mineral based lubricant.

A research conducted by Azhari et al. (2015b) on development of bio-lubricant using corn oil with addition of ZDDP as lubricant physical property improver found that the coefficient of friction at right amount of ZDDP presences in the corn oil are decreasing with increment of applied load on the pin-on-disc test. However, the presence of excessive ZDDP in the corn oil showed that an increasing trend of coefficient of friction with increment of applied load. The research by Azhari et al. (2015b) also verifies that only right amount of ZDDP in the vegetable oil is beneficial in order to produce a new bio-lubricant with a lowest coefficient of friction to substitute the mineral based lubricant.

Another research by Azhari et al. (2015c) on the comparison between canola oil with addition of ZDDP and SAE 40 lubricant in terms of tribological properties found that performance of canola oil with desirable addition of ZDDP producing a better results compared to mineral based lubricant SAE 40. The result shows that the presences of ZDDP at desirable quantity in the canola oil produces the lowest coefficient of friction and wear scar diameter among the samples. This research indicates that the vegetable oil with most desirable concentration of ZDDP gives a better tribological properties compared to mineral based lubricant SAE 40.

Researchers had been conducting numerous experiments to develop desirable bio-lubricant by introducing different concentration of ZDDP into different type of vegetable oil such as Mahipal et al. (2014) had induced karanja oil with different concentration of ZDDP, Azhari et al. (2015b) had induced corn oil with different concentration of ZDDP and Azhari et al. (2015c) had induced canola oil with different concentration of ZDDP. The results from their researches showed that there are pros and cons of the combination between vegetable oil and ZDDP which depends on the quantity of ZDDP added into base oil. Addition of ZDDP up to certain threshold limit showed decrement trend of wear scar diameter and coefficient of friction. In contrary, the coefficient of friction and wear scar diameter of vegetable started to growth when addition of ZDDP exceeds the threshold limit of the concentration. Thus, the amount of ZDDP added into base oil affect the tribological performance that will be generated.

Therefore, this study proposes to develop a bio-lubricant with most desirable concentration of ZDDP added into the vegetable oil to acquire an excellent profiling of wear and coefficient of friction in order to develop a new bio-lubricant which is comparable with mineral based lubricant SAE 15W-40.

1.4 Objectives

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

i. To develop a new bio-lubricant with addition of anti-wear additive.
ii. To test and characterize the newly developed bio-lubricant with standard laboratory test methods.
iii. To compare the performance of the new bio-lubricant with commercialized mineral based lubricant.

1.5 Scopes

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

i. Developing bio-lubricant using corn oil with addition of Zinc Dialkyldithiophosphate (ZDDP).
ii. Testing of metal content of the new bio-lubricant using RDE-AES (ASTM D6595) and kinematic viscosity using kinematic viscometer.
iii. Characterizing wear and friction of the new bio-lubricant using Four-Ball Tester (ASTM D4172).
iv. Comparing the tribological properties of the new bio-lubricant with SAE 15W-40.

CHAPTER 2

LITERATURE REVIEW

2.1 Classification of Lubricant

Any substance which has an ability to separate two or more surfaces from direct contact to each other and resulting in reducing friction and wear, it can be considered as lubricant (Hamrock et al., 2004). The friction between the contacting surfaces is reduced due to formation of protective film by lubricant which acts separating two contacting surfaces (Suhane et al., 2012). Lubricant can exist in any physical state as long as it provides smooth running between contacting surfaces. Each physical state of lubricant has different specific function to be performed. In industry, lubricant selection is determined based on their specific function and type of application will be exposed to the lubricant. Suhane et al. (2012) stated that lubricant can be classified into three physical appearances which is solid, semi-solid and liquid lubricant. These physical appearances will be discussed in next sections for more detail.

2.1.1 Solid Lubricant

Any solid material that has an ability to reduce friction and mechanical interactions between surfaces in relative motion against the action of a load can be considered as solid lubricant (Rudnick, 2009). Solid lubricant also known as dry lubricant that was developed to meet low friction and wear demands of various applications. It was developed with the function to reduce friction and wear between relative contacting surfaces motion under various environmental and operational conditions. These are because various applications have been specialized and oriented towards conditions of extreme environments such as high or low temperatures, radiation, vacuum and high contact pressures (Menezes et al., 2013).

As stated by Bhushan (2013), application under extreme condition such as operation of bearing at high loads and low speeds and a hydrodynamically lubricated bearing requiring start or stop operations typically used solid lubricant to interpose between the contacting movements. Solid lubricant is very useful in operational conditions under high load, low speed or vibration due to the capability of solid lubricant in maintaining lubricant film under these conditions. According to Lansdown (1982), utilization of solid lubricant has an assortment of advantages compared to conventional liquid or grease-type lubricants in applications involving extreme temperature, cryogenic temperature, vacuum and high-pressure environments.

Generally, solid lubricant is required when the liquid lubricant is unable to keep its performance and function properly in the system at high contact pressure or temperature (Torbacke et al., 2014). For an example, in the condition of high-temperature lubrication, the liquid lubricant will certainly oxidized and decompose at faster rate which resulting in lubrication failure (Bhushan, 2001). In this situation, solid lubricant is essential as alternative to meet the service parameters when the liquid lubricant performance is affected by operation under extreme condition (Rudnick, 2009).

According to Rudnick (2009), in the application which involves sliding surface with a rough texture, solid lubricant is a preferred substance to react with the rough surface. This is due to the capability of solid lubricant under this circumstance to cover the surface asperity of the mating surfaces which is more effective than liquid lubricant. Besides that, Menezes et al. (2013) stated that solid lubricant capable to provide lubrication at high temperature up to 350℃ which is higher than many liquid oil-based lubricants capability. These characteristics make solid lubricant suitable to be used for processes involving extreme temperatures or extreme contact pressures.

Solid materials such as graphite and molybdenum disulfide (MoS_2) are the most widely used as solid lubricant (Mang and Dresel, 2007). These materials consist of layered lattice structures which resulting a satisfactory lubricating properties. According to Rudnick (2009), it was stated that lamellar structure of graphite and