UNIVERSITI TEKNIKAL MALAYSIA MELAKA

IMPROVEMENT OF TRIBOLOGICAL PROPERTIES OF ZINC DIALKYLDITHIOPHOSPHATE (ZDDP) INDUCED CORN OIL BIO-LUBRICANT WITH THE ADDITION OF MOLYBDENUM DIALKYLDITHIOPHOSPHATE (MoDTP)

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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TAJUK: **IMPROVEMENT OF TRIBOLOGICAL PROPERTIES OF ZINC DIALKYLDITHIOPHOSPHATE (ZDDP) INDUCED CORN OIL BIO-LUBRICANT WITH THE ADDITION OF MOLYBDENUM DIALKYLDITHIOPHOSPHATE (MoDTP)**

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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 Engineering Technology (Maintenance Techonology) (Hons.). The member of the supervisory is as follow:

…………………………………

(Muhamad Azwar Bin Azhari)

ABSTRAK

Permintaan untuk pelincir alternatif dan kebimbangan kepada isu-isu alam sekitar mendorong kajian ini untuk membangunkan bio-pelincir baru berasaskan minyak sayur-sayuran. Walau bagaimanapun, prestasi minyak sayuran sebagai minyak pelincir tidak berkesan kerana menghasilkan geseran yang tinggi pada permukaan. Dalam kajian ini, minyak jagung komersial dicampurkan dengan bahan tambahan Zink dialkyldithiophosphate (ZDDP) dan Molybdenum dialkyldithiophosphate (MoDTP) untuk meningkatkan sifat-sifat fizikal dan tribologikal minyak. Minyak masak jagung komersial telah dipilih sebagai minyak asas dan dicampur dengan 2% berat ZDDP dan ditambah dengan 0.00% berat, 0.05% berat, 0.10% berat, 0.15% berat dan 0.20% berat MoDTP. Sampel diuji menggunakan Elektrod Cakera Berputar-Spektroskopi Atom Terpancar (RDE-AES) dan Meter Kelikatan Terpanas Kittiwake manakala dicirikan menggunakan Penguji Empat Bola dan Mikroskop Cahaya Sejajar untuk menyiasat pekali geseran dan diameter parut kehausan. Penambahan 2% berat ZDDP dan 0.05% berat MoDTP ke dalam minyak jagung memberikan hasil yang diingini di mana nilai kelikatan kinematik pada 36.20 cSt dan pekali terendah geseran pada 0.074. Campuran ini juga menunjukkan diameter parut kehausan yang rendah pada 74.35 μm berbanding sampel lain. Kesimpulannya, bio-minyak pelincir yang baru telah berjaya dibangunkan dengan menambah ZDDP dan MoDTP ke dalam minyak jagung sebagai pengganti kepada komersial minyak pelincir.

ABSTRACT

The demand for an alternative lubricant and concern to the environmental issues prompted this study to develop a new bio-lubricant based on vegetable oil. However, the performance of vegetable oil as lubricant oil is ineffective because of producing high friction on the surface. In this study, the commercialized corn oil was mixed with additives of Zinc dialkyldithiophosphate (ZDDP) and Molybdenum dialkyldithiophosphate (MoDTP) as to improve the physical and tribological properties of oil. The commercial cooking corn oil was selected as the base oil and mixed with 2wt% ZDDP and added with 0.00wt%, 0.05wt%, 0.10wt%, 0.15wt% and 0.20wt% MoDTP. The samples were tested using Rotating Disc Electrode Atomic Emission Spectroscopy (RDE-AES) and Kittiwake Heated Viscometer while characterize using Four Ball Tester and Upright Light Microscope to investigate the coefficient of friction and wear scar diameter. The addition of 2wt% ZDDP and 0.05wt% MoDTP into corn oil gives the desired result where the kinematic viscosity value at 36.20 cSt and lowest coefficient of friction at 0.074. This mixture also demonstrated lowest wear scar diameter at 74.35 µm compared to the other samples. In conclusion, the newly bio-lubricant has successfully developed by adding ZDDP and MoDTP into corn oil as a substitute for commercial mineral lubricant oil.

DEDICATION

I would like to dedicate my thesis to my beloved parents, siblings and friends.

ACKNOWLEDGMENT

I would like to express my gratitude and appreciation to the most Merciful and Almighty, ALLAH SWT for giving His bless upon completing this final year project report successfully.

In addition, I also want to address my deepest appreciation to Mr. Muhamad Azwar Azhari for his guidance, motivation and full commitment by helping in completing my research and writing of this Final Year Project.

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LIST OF SYMBOLS AND ABBREVIATIONS

+	-	Plus
ASTM	-	American Society for Testing and Materials
℃	-	Degree Celcius
cSt	-	Centistokes
g	-	gram
HO•	-	Hydroxy Radical
HP	-	Hindered Phenolic
mm	-	millimeter
MoDTC	-	Molybdenum DialkylDithiocarbamate
MoDTP	-	Molybdenum DialkylDithiophosphate
MoS_2	-	Molybdenum Disulfide
N	-	Newton
NNDM	-	N, N-*bis* (2-*hydroxyethyl*)-dodecanamide molybdate
PAO	-	Polyalphaolefin
PKO	-	Palm Kernel Oil
PTFE	-	Polytetrafluoroethylene
R•	-	Free Radical
RDE-AES	-	Rotating Disc Electron Atomic Emission Spectroscopy
RO•	-	Alkoxy Radical
ROO•	-	Peroxy Radical
ROOH	-	Hydroperoxides
SAE	-	Society of Automotive Engineers
WSD	-	Wear Scar Diameter
wt	-	Weight
ZDDC	-	Zinc DiamylDithiocarbamate
ZDDP	-	Zinc DialkylDithiophosphate

µm	-	Micrometer
%	-	Percent
nm	-	Nanometer
rpm	-	Revolutions per Minute
psi	-	Pounds per Square Inch
RBD	-	Refined, Bleached and Deodorized

CHAPTER 1

INTRODUCTION

1.1 Introduction to Lubricant

The main purpose of lubrication is to reduce wear, heat loss and the coefficient of friction between two contacting surfaces. Besides, lubrication is used to prevent rust and reduce oxidation process. Lubrication also can act as an insulator in transformer applications and formed a boundary layer against dirt, dust and water (Mobarak et al., 2014). A study by Ahmed and Nassar, (2011) stated that the main function of the engine oil lubricant is to prolong the lifetime of the equipment under different kind of conditions which are speed, pressure and temperature. The lubricant flow sufficiently at low temperature to ensure that the moving parts are not famished of oil and help to minimize the wear by apart the moving parts at high temperature.

Lubrication occurs when two surfaces are separated by a lubricant film and a good lubricant has the characteristics of high viscosity index, thermal stability, high boiling point, low freezing point, corrosion prevention capability and high resistance to oxidation (Mobarak et al., 2014). The automotive engines without effective lubrication will reduce efficiency of fuel and shorten the life of equipment due to high friction and excessive wear. To solve this problem, the proper selected oil with efficient additive must be applied on the interacting metal surface (Komvopoulos and Pernama, 2006). Lubrication generally reduces friction between moving surface by substitute the fluid friction for mechanical friction. Other than that, lubrication functions as liquid sealing, contaminant suspension, corrosion protection and heat transfer. Crucial to know that the wear and heat can be reduced to the acceptable level but they cannot be eliminated completely (Bilal et al., 2013).

Mobarak et al. (2014) stated that lubricants can be classified based on their physical appearances which are solid, semi solid and liquid. Solid is when the composition of inorganic or organic compounds such as molybdenum disulphide forms the film of a solid material. Next, semi solid is the liquid suspended in a thickener or additives of solid matrix, as example is grease. Lastly, the lubricant in liquid form is petroleum oil, vegetable oil, synthetic oil and animal oil.

In contrast, lubricants also can be classified into two categories regarding to their sources which are mineral oil lubricant and the bio-lubricant. The major concern is the using of petroleum based lubricants in industries that can causes to environment pollution (Mahipal et al., 2014). Mineral oil based lubricant is produce from crude oil sources and it can be harmful to the environment (Bilal et al., 2013). Other than that, the depletion of crude oil, the increasing of oil prices and the pollution defects the environment have led the interest to develop and using alternative lubricants (Mobarak et al., 2014). Due to concern of environment, lubricants are synthesized from plant oils and other environmentally friendly sources known as bio-lubricant which is derived from plants and animals (Bilal et al., 2013).

A research by Mobarak et al., (2014) stated that bio-lubricants have high flash point, high lubricity, high viscosity index, and low evaporative losses. The popular bio-lubricant is from various parent oil such as soybean, cottonseed, sunflower, peanut, palm, coconut, castor and corn oils (Azhari et al., 2014). Vegetable oil is believed to play an important role to substitute the mineral based oil because it has many advantages over base lubricant which are renewability, biodegradability and less toxicity (Shahabuddin et al., 2013).

1.2 Problem Statement

The reserve crude oil in the world is undergoing depletion, while the oil prices increasing and the demand to protect environment from pollution have led to develop and using alternative lubricant (Mobarak et al., 2014). Most of the available lubricants are based on mineral oil derived from petroleum oil but it is not adaptable to the environment because containing toxicity and non-biodegradable sources

(Shahabuddin et al., 2013). According to Bilal et al. (2013) lubricant based mineral oil gained from crude oil can be harmful to the environment laterally with human life extended. Mineral oil based lubricant are used in industries always be a concern to the environmental pollution (Mahipal et al., 2013).

Several environmental hazards occur from the wasted oil produced and subsequent disposal which are found in the hydraulic, agriculture, mining and petrochemical industries (Mahipal et al., 2013). Besides, Srivastava and Sahai (2013) reported that lubricant losses to the environment by the action of evaporation, spills and leakages have become the major concerns to the issue of pollution and environmental health. Annually, there are 12 million tons of lubricant waste was released to the environment (Shahabuddin et al., 2013). According to Srivastava and Sahai (2013) reported that every year about 5 to 10 million tons of petroleum products was released to the environment and 40% of them are from the urban runoff, industrial and municipal waste, refinery processes and condensation from marine engine exhaust. Moreover, the wasted of mineral oil based lubricants are not easy to dispose due to its non-biodegradable nature (Shahabuddin et al., 2013). This problem can be overcome by using the sources from vegetable oil because of its renewability and biodegradability characteristics.

Vegetable oil is one of sources for producing alternative lubricant because it has advantages of renewable sources, environmentally friendly, less toxicity, biodegradability and more (Shahabuddin et al., 2013). However, a study by Bilal et al. (2013) stated that vegetable oil based lubricant has some disadvantages which are high viscosity at low temperature and poor oxidative stability at high temperature makes it easily to oxidize. Without additive, vegetable oil based lubricant cannot reduce friction and wear effectively. To overcome these problems, additives are designed specifically for plant based lubricants to eliminate the problem related to low and high temperatures. A research by Azhari et al. (2015a) proved that Zinc Dialkyldithiophosphate (ZDDP) is the solution to overcome the oxidation problem in the vegetable oil based lubricants. The addition of ZDDP into vegetable oil shows that it can improve the physical properties compared to vegetable oil without ZDDP and give a better performance in kinematic viscosity, wear scar diameter and coefficient of friction.

Basically, ZDDP reacted to the asperities and formed a thin oil film to separate between two surfaces and reduce contact (Rudnick, 2009). In contrast, from the prior study by Azhari et al., (2015a) shows that the different wear behaviour will occur if the concentration is too much. The higher concentration will lead to the increases the thickness of film and decreasing the antiwear qualities. The 2wt% concentration of ZDDP into canola, karanja and corn oil provided the better performance based on coefficient of friction, wear scar diameter and kinematic viscosity compare than the others concentration. The blending of ZDDP into corn oil has proved to be a good bio-lubricant according to excellent performance in reducing coefficient of friction and wear (Azhari et al., 2015a). The 2wt% concentration of ZDDP also provided an excellent performance by combining with the karanja oil (Mahipal et al., 2014). Further investigation will be developing by adding molybdenum organic metallic compound which is Molybdenum Dialkyldithiophosphate (MoDTP) into ZDDP induced corn oil bio-lubricant for improving the tribological properties.

In the group of metal dithiocarbamates, Molybdenum metallic compounds have the most interest in the engine crankcase lubricants (Rudnick, 2009). Molybdenum compound has been proved as friction modifiers for several decades because the properties of antifriction, antioxidant, antiwear and extreme temperature (Unnikrishnan et al., 2002). On the other note, it has been proven as friction modifier additive for engine oil by formulated Molybdenum disulfide (MoS_2) through complex tribochemical reactions which is known to reduce friction (Komvopoulos and Pernama, 2006). The decomposition of molybdenum compound are weakly linked by Van Der Waals forces and it is easily broke its bond to be excellent friction performance (Liskiewicz et al., 2013). However, molybdenum compound cannot be used as an additive alone because its solubility in base oil is low. This problem causes the preventing of using molybdenum compound in many commercial formulations.

The solution to overcome this problem is by combination with the antiwear agent such as ZDDP into molybdenum compound (Unnikrishnan et al., 2002). It is because ZDDP can act as a catalyst to the formation of MoS_2 embedded in the short chain zinc polyphosphate. Moreover, ZDDP play a role to supply excess sulfur provided complete sulfuration of the molybdenum containing compound. The existence of the layer of MoS_2 under the surface of the molybdenum and ZDDP is believed as the factor the decreasing of coefficient of friction of sliding metal surfaces. Other than that, if molybdenum compound cannot adsorbs on the metal surfaces faster than ZDDP. ZDDP will dominate the near surface region and causes the increasing the coefficient of friction but the compound has become more stable. The effect of molybdenum compound and ZDDP on friction and wear behaviour depends on which of them are faster to be adsorbs on the sliding surface (Komvopoulos and Pernama, 2006). From the result, new research ought to be done to determine the desirable concentration of both additives as to develop a new bio-lubricant. Throughout the study, the information on the blending of the molybdenum and ZDDP are scarce due to lack of research based on the molybdenum organic metallic compound. Therefore, this study is mainly about the research to determine desirable concentration of additives by addition of MoDTP into ZDDP induced corn oil bio-lubricant as tribological properties improver.

1.3 Objective of Research

Based on the problem statement discussed above, the objectives of this study are listed below:

1. To develop a new biodegradable lubricant with the addition of tribological property improver additive.
2. To test and characterize the newly developed bio-lubricant.

1.4 Scope of Research

In order to achieve the objectives, the scopes are prepared as shown below:

1. Developing new bio-lubricant oil using commercialized cooking corn oil with addition of MoDTP into ZDDP induced corn oil bio-lubricant as tribological property improver additive agent.
2. Testing newly developed bio-lubricant oil using RDE-AES (ASTM D6595).
3. Characterizing of newly developed bio-lubricant using four ball testers (ASTM D4172).

CHAPTER 2

LITERATURE REVIEW

2.1 Lubrication

Lubrication is used to minimize the wear and friction of the relative motion surfaces by using the ability of oil or another liquid (Rudnick, 2009). A study by Mobarak et al., (2014) stated that a protective film layer was formed by lubricant between two moving surfaces and it is the reason how friction and wear were reduced. The primary objective of lubrication despite of reducing wear and friction is to reduce the normal and shear stress in solid surface contact (Ludema, 1996). On the other perspective, according to (Hamrock and Schmid, 2004) stated that the primary purpose of lubricant is to control wear and friction and the secondary properties of lubricant are listed below:

1. Lubricant can be drawn between the moving parts by hydraulic action.
2. Lubricant has the ability of high heat-sink capacity which is to cool the contacting parts.
3. Lubricant easily reacting or mixing with chemical for variety properties of corrosion resistance, protective layer or detergency.
4. Efficiently to remove wear particles.

A study by Torbacke et al. (2014) showed that lubricant has many functions in tribological contacts. Lubricant played the main role to transfer heat away from the contact due to presence of friction causes by the contacting of two or more surfaces has raised the temperature. Without lubricant, the temperature could be rising high enough to melting the material. Furthermore, contaminant will accumulate in engine during operation and producing wear debris, sludges, acids, soot particles or peroxides. The important function of lubricant is to prevent the action of contaminant from damaging the engine (Nehal and Nassar, 2011). Effective lubricants have an excellent viscosity to maintain the lubricating film under any operating conditions. Other than that, it should be in liquid state as possible to remove heat and prevent power loss because of viscous drag (Hamrock and Schmid, 2004). Besides, the application like hydraulic systems was used lubricant to transfer the power from one point to another (Torbacke et al., 2014).

2.2 Classification of Lubricant

Lubrication has the limitation in technologies and economic because of the physical and chemical degradation due to factors such as temperature and acids, vacuum, radiation and weightlessness (Ludema, 1996). The physical appearance of lubricant influences the application of lubricants in certain operation. Lubricant has been identified existed in three physical appearances and been use in different application due the characteristic and potential.

2.2.1 Solid Lubricant

Solid lubricant is any solid materials that are used to reduce friction and mechanical interactions between relative motions of surfaces against the action of applied load (Rudnick, 2009). It is a form of powder or thin solid film to provide protection between two moving surfaces for reducing wear and friction (Bhushan, 2013). It has been introduced after the fall of performance of traditional liquid lubricants additive (Rudnick, 2009). Moreover, they have been used in small amount in 1800s and further research were started from 1950 to 1965 for the investigation on loose powders, metals, tungstates, oxides and molybdates and layer-lattice salts by the aerospace industry (Ludema, 1996). Solid lubricants usually used when there is problem to keep liquid lubricant in the contact in some applications (Torbacke et al., 2014).

Solid lubricants are typically as a dry film or an additive in liquid to provide effective lubricant for different types of applications (Rudnick, 2009). Besides, it also being used in application involving sliding contact such as operating bearing at high loads and low speeds (Bhushan, 2013). Furthermore, another application that used solid lubricant is when the surfaces are not chemically active with lubricant additives such as polymers or ceramics (Rudnick, 2009). The most popular of solid lubricants are graphite and molybdenum disulfide. Figure 2.1 displays the difference between liquid lubricant and solid lubricant.

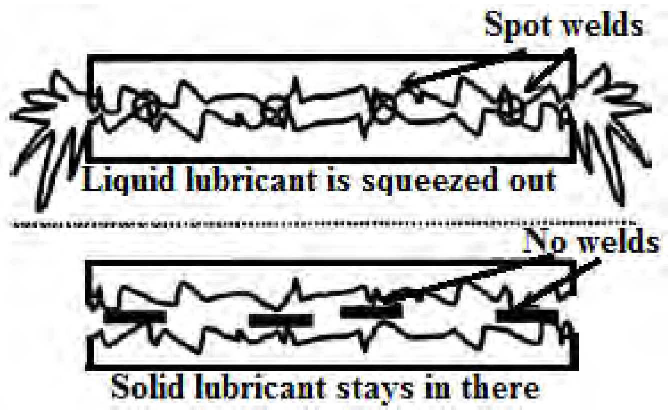

Figure 2.1: Differences between liquid lubricant and solid lubricant (Rudnick, 2009).

Graphite is a form of carbon and it is one of solid lubricant materials that can act as lubricant. It has the same characteristic as molybdenum disulfide which is the decomposition of sheets in hexagonal array. The strong bonding in the sheet of graphite with the weak bonding of van der Waals between sheets has provided low shear strength between sheets. Molybdenum disulfide usually used in powder form because it has possibility to electroplate the surface with molybdenum then treats with sulphur containing gas to gain bonded molybdenum disulfide (Ludema,1996). Graphite and molybdenum disulfide can be useable in high temperature and oxidation atmosphere environments while the liquid lubricants are opposed. In the condition of extreme temperature and extreme contact pressure, graphite and molybdenum disulfide is the great choice to be used as lubricant. Other than graphite and molybdenum disulfide, another compound that can be useful for solid lubricants are boron nitride, talc, calcium fluoride, cerium fluoride, polytetrafluoroethylene (PTFE) and tungsten disulfide (Rudnick, 2009).