LUBRICATION AND TRIBOLOGICAL PROPERTIES OF PALM OIL MIXED WITH ORGANO ZINC COMPOUND

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A thesis submitted
in fulfilment of the requirements for the degree of Master of Science in Mechanical Engineering

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DECLARATION

I declare that this thesis entitled "Lubrication and Tribological Properties of Palm Oil Mixed with Organo Zinc Compound" is the result of my own research except as cited in the references. The thesis has not been accepted for any degree and is not concurrently submitted in candidature of any other degree.

Signature : ....

Name : ....

Date : ....

APPROVAL

I hereby declare that I have read this thesis and in my opinion this thesis is sufficient in terms of scope and quality for the award of Master of Science in Mechanical Engineering.

Signature : ....

Supervisor Name : Prof. Madya Dr. Mohd Fadzli Bin Abdollah

Date : ....

DEDICATION

Dedicated to all my family member and my friend.

ABSTRACT

Friction can be defined as the resistance to motion of one object moving relative to each other. At certain application, frictions are required to be used such as for a brake application. Unnecessary friction creates wear, hence reducing the lifespan of equipment and machinery. One of the solution by using a lubricant to reduce friction and wear to a minimum level. Conventional lubricant which is made of petroleum based is not biodegradable, harmful to the environment and the source not renewable. Hence, the purpose of this study was to investigate the lubrication and tribological properties enhancement by using palm oil as parent base oil mixed with organo zinc compound as additive. Besides that, the predominant wear possess by the worn surface of the ball bearing was identified. The oil samples were prepared by mixing organo zinc compound additive; Zinc Dioctyldithiophosphate (ZnDoDP) or Zinc Diamyldithiocarbamate (ZDDC) between 0 wt. % to 3.0 wt. % concentrations interval with commercialized palm oil and then were homogenized using ultrasonic homogenizer (0 wt. %, 1 wt. %, 1.5 wt. %,2.0 wt.%,2.5 wt. %, 3.0 wt. %) Afterward, the oil sample was tested for their oil properties in accordance to engineering standard in terms of elemental analysis test, viscosity index test, small scale flashpoint test and potentiometric titration acid number test (automatic). Then, the tribological test was performed using a four-ball tribometer in accordance to ASTM D4172. The worn surfaces of the balls were observed using a Scanning Electron Microscope and Energy-dispersive X-ray spectroscopy. The results show that commercialized palm oil with 2.0 wt. % of ZnDoDP had an excellent characteristic in terms of its lubrication and tribological properties than commercialized palm oil with 0 wt. % (ZnDoDP and ZDDC) and commercialized palm oil with the addition of 2.0 wt. % of ZDDC. As a conclusion, palm oil mixed with organo zinc compound as additive enhanced the lubrication properties at 2.0 wt.%, decrease about 20.5% (ZDDC) and 7.9% (ZnDoDP) in their viscosity index and decrease the value of flashpoint about 11.6% (ZDDC) and 15.1% (ZnDoDP) from commercialized palm oil with 0 wt. % additive . Meanwhile, as for their acid number, there are an increased value of about 61% (ZDDC) and 97% (ZnDoDP) from conventional transmission oil. In terms of tribological properties, it shows that at 2.0 wt. %, about 22 % (ZDDC) and 60% (ZnDoDP) value decrease of wear scar diameter from pure palm oil. Meanwhile, the value of the coefficient of friction also decreases if compared to commercialized palm oil with 0 wt. % additive about 36.8% (ZDDC) and 43% (ZnDoDP) resulted in producing an alternative lubricant which can be applied in industry in as substitution to conventional mineral based oil as lubricant.

SIFAT PELINCIRAN DAN TRIBOLOGI MINYAK SAWIT DICAMPURKAN DENGAN SEBATIAN ZINK ORGANO

ABSTRAK

Geseran boleh didefinisikan sebagai tindakan daripada menggosok antara satu permukaan ke permukaan yang lain. Selain daripada itu, sesetengah geseran diperlukan untuk sesetengah aplikasi seperti aplikasi dalam penggunaan dalam sistem cengkaman kenderaan. Sebaliknya, geseran yang tidak diperlukan menghasilkan kehausan, seterusnya mengurangkan jangka hayat peralatan dan mesin. Walaubagaimanapun, salah satu penyelesaiannya ialah dengan menggunakan minyak pelincir untuk mengurangkan geseran dan haus hingga ke tahap yang paling minimum. Minyak pelincir yang sedia ada di pasaran adalah diperbuat daripada petroleum adalah sangat merbahaya kepada alam sekitar dan manusia kerana ianya tidak terbiodegradasi, dan sumber asas petroleum itu sendiri tidak boleh diperbaharui. Oleh yang demikian, tujuan kajian ini adalah untuk menyiasat komposisi minyak pelincir dan sifat-sifat tribologi dengan menggunakan minyak sawit sebagai minyak asas dan dicampurkan dengan organo zink majmuk sebagai bahan tambahan. Selain itu, permukaan galas bebola yang terhakis dikaji untuk menentukan jenis kehausan yang utama. Sampel minyak disediakan dengan campuran organo zink sebagai bahan tambahan; Zinc Dioctyldithiophosphate (ZnDoDP) atau Zinc Diamyldithiocarbamate (ZDDC) di antara pada kadar 0 wt. % hingga 3.0 wt. %. dengan minyak masak sawit yang sedia ada di pasaran dan kemudian telah dihomogenasi menggunakan mesin ‘ultrasonic homogenizer’. Selepas itu, sampel minyak telah diuji menggunakan prosedur piawai kejuruteraan dari segi penganalisisan unsur, indeks kelikatan, ujian berskala kecil ‘flashpoint’ dan titrasi automatik nombor keasidan. Kemudian, ujian tribologi telah dijalankan dengan menggunakan mesin ‘Fourball’ tribometer mengikut prosedur ASTM D4172. Permukaan bola yang haus terhasil dari ujian tribologi telah dicerap menggunakan mesin ‘Scanning Electron Microscope’ dan ‘Energy-dispersive X-ray spectroscopy’. Kesimpulannya, minyak sawit yang dicampurkan dengan sebatian zink organo sebagai bahan tambahan meningkatkan sifat pelincir pada kadar 2.0 wt.%, penurunan sekitar 20.5% (ZDDC) dan 7.9% (ZnDoDP) dalam indeks kelikatan dan menurunkan nilai ‘flashpoint’ sekitar 11.6% (ZDDC) dan 15.1% (ZnDoDP) dari minyak sawit tulen. Sementara itu, untuk nilai kandungan asid, terdapat peningkatan nilai sekitar 61% (ZDDC) dan 97% (ZnDoDP) dari minyak transmisi konvensional. Dari segi sifat tribologi, ia menunjukkan bahawa pada 2.0 wt. %, kira-kira 22% (ZDDC) dan 60% (ZnDoDP) penurunan diameter kehausan dari minyak sawit tulen. Sementara itu, nilai pekali geseran juga menurun dari minyak sawit tulen sekitar 36.8% (ZDDC) dan 43% (ZnDoDP), justeru, ia dapat menghasilkan pelincir alternatif yang boleh digunakan untuk industri bagi menggantikan minyak konvensional berasaskan mineral sebagai pelincir.

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LIST OF ABBREVIATIONS

ASTM	-	American society for testing and material
ATF	-	Automatic transmission fluid
B.C	-	Before century
COF	-	Coefficient of friction
cST	-	Centistoke
EDX	-	Energy Dispersive X-Ray
ICP	-	Inductively coupled plasma spectroscopy
MoDTC	-	Molybdenumdithiocarbamate
MoDTP	-	Molybdenumdithiphosphate
PAO	-	Polyalphaolefin
PFAD	-	Palm fatty acid distilled
PIB	-	Polyisobutylene
PIO	-	Polyinternalolefin
RBD	-	Refined, bleached and deodorized
RDE	-	Rotating disc electrode instrument
SEM	-	Scanning Electron Microscope
TAG	-	Triacylglycerol
TAN	-	Total acid number
UTTO	-	Universal Tractor Transmission Oil
WSD	-	Wear Scar Diameter
ZDDC	-	Zinc Diamyldithiocarbamate
ZDDP	-	Zinc Dialkyldithiophosphate
ZEDP	-	Zinc dialkyl(aryl)Ethoxy Dithiophosphates
ZnDTP	-	Zinc Dithiophosphate

LIST OF PUBLICATIONS

Md Alias, M., A., Azhari, M., A., 2016. Preliminary feasibility studies of vegetable oil as substitution to mineral lubricant. *Journal of Mechanical Engineering*, *13(2)*, pp.10-20.

Md Alias, M., A., Abdollah, M., F., Amiruddin, H., 2018. Tribological properties of palm oil blended with zinc dioctyldithiophosphate. *Materials Research Express*, *5(8)*.

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CHAPTER 1

INTRODUCTION

1.1 Background of the study

To reduce friction, a substance called lubricant was used in between two contacting surfaces. Meanwhile, the principle of supporting the sliding load by forming a film to reduce friction is called lubrication. Every machinery and equipment need lubricants to reduce friction and abstain from the state of wearing. For some equipment, they require lubricants for energy consumption. Lubricants can be in the form of solid, liquid or gas (Bhushan, 2001). Hundreds of years before centuries, workers like farmers used animal fats to reduce friction by applying them on the oxen carts (Ahmed and Nassar, 2011). Besides that, another proof of lubricants' usage several thousands of years before centuries (BC) was the archeology discovery of historical artifacts from various forms of bearings with traces of bituminous substances on them. These were found on the Mesopotamian potter wheel (4000BC), which strengthened the fact of lubricants' (fats and vegetable oils') usage before centuries (Caines et al., 2004).

An Egyptian mural dating to about 2000 B.C illustrated a liquid (either water, natural oil, grease or blood), assumed as lubricant being poured ahead of transporting sledge that was carrying a statue (Caines et al., 2004). Before the industrial revolution, natural oils like animal fats and vegetable oils were widely used. Various types of vegetable oils were derived from many types of seeds like olive oil, rape (colza) and linseed. According to Anderson (1991), during the 16th century, animal oils, vegetable oils or mixtures of the two of them were used as lubricants. Bee wax, animal tallow, and water are examples of natural lubricants that were used to lubricate wooden cartwheels and bearings. Therefore, lubricants and their utilization are not new, since they have been used for thousands of years before, and improvisations have been made from time to time to fulfill the needs of today's world (Azhari et al., 2015). According to Anderson (1991), an ancient tribe that lived in the Middle East used petroleum for lighting purposes, while Egyptian pupils used the same liquid for embalming works. Besides that, American Indians used petroleum for medical purposes. Hence, the use of petroleum is not new. About two hundred years before, demands for petroleum-based products started to increase due to the era of an industrial revolution.

The beginning of the industrial revolution era was discovered in Britain, which started around 1760. The industrial revolution is an era where most manpower is replaced by machinery. The use of mineral oils from the distillation of coals or shales started in this era, to lubricate a large scale of iron and steel-based machinery. In the 1850s, petroleum oil began to be produced in the United States, Canada, Russia and Romania (Caines et al., 2004). In Pittsburgh, Pennsylvania, in 1845, mineral oils was drilled from a salt well and mixed with sperm whale oil, and they were used to lubricate spindles. Fifteen years later, Colonel Edwin L. Drake drilled the first actual oil well, and hence, petroleum lubricants began replacing animal and vegetable oils throughout the industry. From time to time, as technology became more progressive, synthetic lubricants were developed in the 1930s, to be used for larger and high-speed machines, due to their excellent lubricant properties which retain viscosity at varying temperature range (Azhari et al., 2015).

The usages of lubricants and lubrication were discovered since men invented machines. According to Srivastava (2014), a well-formulated lubricant plays a major role in extending the life of the equipment and saving energy, depending on their operating and design parameters. The main functions of lubricants are to reduce friction and to prevent wear and tear. Furthermore, lubricants can also be used as a cooling agent. According to

Caines et al. (2004), the use of lubricants in engines as initial transfer agents between some parts heated by combustion such as piston, but the heat dissipates from the system like a sump, and cooling jacket. Besides, the lubricant itself absorbs the heat generated by friction during the mechanical work performed. Rajab et al. (2004), stated that a lubricant can act as an insulating liquid in the transformer operation. As it is used in the transformer operation, it provides two main purposes namely as a cooling medium and as an insulation material.

In the machinery and production industry, one of the lubricant functions is used as a cooling agent, which is known as 'coolant'. According to Palmer (2009), there is a difference between coolant and lubricant in terms of their functions. Coolant is water or oil-based with other substances like sulphur or chlorine, and some other additives. Coolant is used to control the heat generated by the machining process through quenching, and improve product quality in terms of surface finish (surface roughness). Meanwhile, lubricant helps reduce friction and excessive heat during machine operation, therefore minimizing heat buildup. Excessive heat can damage the microstructure of the metal, either the product itself or the cutting tool, whereby it reduces its life span (Ghani et al., 2015). Other than that, lubricants are also used in agricultural machinery. Universal Tractor Transmission Oil (UTTO) is a functional lubricant used in agricultural machinery such as for tractors. The main function of this lubricant is to lubricate gearbox, rear axle, and gears, power transfer, hydraulic system lubrication, provides adequate cooling and gives friction for wet brakes (Stojilković and Kolb, 2016). Lubricant is one of the various base oil products.

According to Bhushan (2001), base oil can be classified into two categories, namely petroleum base stocks, that are derived from crude oil. The basic type of hydrocarbon generally consists of eighteen to forty carbon atoms which are paraffin, aromatics, and naphthenes (cycloparaffins). Most of the molecules are mixed-type containing two or more basic hydrocarbon structures. Besides that, the molecule structure of basic hydrocarbon contains here atoms such as sulfur, nitrogen or oxygen into the various hydrocarbon structures. Another basestock is the synthetic basestock, made of vegetable and animal oils, including petrochemical and coal-derived basestock. It consists of long-chain molecules produced by chemical reactions to acquire a specific characteristic. Synthetic base stock can be classified into five major groups, namely synthesized hydrocarbons, esters, ethers, halogenated compounds and silicone polymers (Bhushan, 2001).

Lubrication is a method of applying lubricant on two contacting surfaces with a relative motion to reduce friction and wear of one, or both surfaces (Googelberg, 2012). Rizvi (2009) mentioned that the basic principle of lubrication still prevails in the prevention of metal-to-metal contact by the means of an intervening layer of fluid or fluid-like material. The intervening layer of fluid or fluid-like material can be in three states, namely solid-state, liquid state or semi-solid state (like grease). Based on the three states of lubricants, the usage can be distinguished based on the function or operation process of the machine (Srivastava, 2014). Lubrication is categorized into an assortment of lubrication regimes like hydrodynamic lubrication, elastohydrodynamic lubrication, boundary lubrication, and partial lubrication. Full film lubrication or hydrodynamic lubrication can be defined as the lubrication condition of two contacting surfaces that are completely separated but fully supported by the fluid film, either in static or operating conditions (Reynolds, 1886). Bhushan (2001) stated that in hydrodynamic lubrication regime, the lubrication films are generally thick, hence, they prevent both contact surfaces from coming into contact. This is commonly referred to as ‘the ideal form of lubrication’ condition, due to their properties of high wear resistance and low friction. The example of hydrodynamic lubrication is thrust bearing.

A lubrication condition of fluid film and the asperities of the contacting surface supporting the normal load is usually referred to as elastohydrodynamic lubrication (Dowson and Higginson, 1959). As the contact surface pressure increases, that surpasses the elastohydrodynamic condition, it fosters the contact asperities as shown in Figure 1.1, (unevenness of surface) to deform plastically.

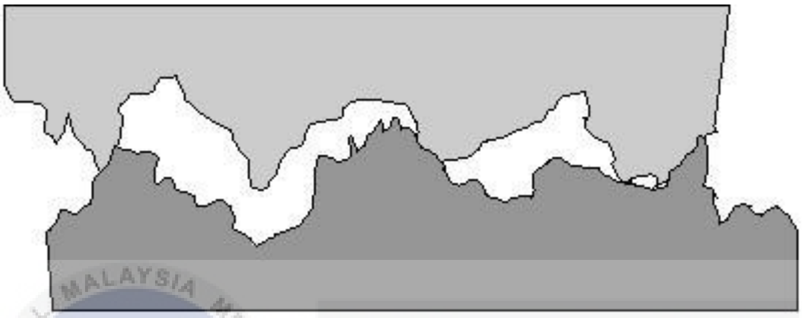

Figure 1.1: Asperities image

Therefore, the fluid film will decrease and the number of contact asperities will increase. According to Bhushan (2001), if the average fluid film thickness is lower than the average relative surface roughness, the load supporting system becomes mostly supported by the surface contact. When the condition continues, lubricant molecules react with the asperity surface which produces boundary chemical film, which can be advantageous or harmful in terms of wear. The coalition between the load sharing by asperities and the occurrence of the chemical reaction is known as the boundary lubrication regime (Bhushan, 2001). The example of elastohydrodynamic lubrication is ball bearings and gears.

Hamrock et al. (2004), claimed that in the boundary lubrication regime, the viscosity of the lubricant is not an influential parameter for contact behavior It is the physical and chemical properties of the thin films of molecular proportions and at which surface that it were attached A boundary lubrication film produce from chemical reaction between lubricant molecules and the asperity surface. Hamrock et al. (2004) reported that there is a little amount of wear or no wear at all in hydrodynamic and elastohydrodynamic lubrication. This is due to the zero interaction of contacting surfaces between asperities. Both regime lubrications of hydrodynamic and elastohydrodynamic are different than boundary lubrication regime. In the boundary lubrication regime, as the load increases, the wear rate and the degree of asperity interaction also increases. All machines need lubrication to extend their lifespan.

1.2 Problem statement

Petroleum, a conservative lubricant, has been widely used in industrial mechanics and engines as a lubricant for a very long time. Pop et al. (2008) stated that about 85% usage of lubricants around the world uses petroleum-based oil. Products like grease, metalworking fluids or insulating lubricants derived from petroleum, are based on non-renewable resources. Year after year, the demand for petroleum continues to increase due to industrialization, modernization, and development. These consequently causes the depletion of oil reserves and an increase in oil prices (Reeves et al., 2015).

Besides, non-renewable resource lubricants have adverse impacts due to their inappropriate use, resulting in contamination and pollution of surface water and groundwater, soil contamination and, subsequently, contamination of agricultural products and foods (Birova et al., 2002). A study conducted by Shashdaran and Jayaram (2010) found that microscopic organisms exist in minerals, which can potentially harm human skin by irritation or allergies. Their study also stated that about 80% of all occupational diseases of operators were due to skin contact with mineral-based cutting fluids. A study conducted by Erhan et al. (2006) stated that the existing mineral-based oil is non-biodegradable. Most industries cannot propose efficient ways to dispose of these non-biodegradable products, which lead to environmental pollution (Bork et al., 2014). Therefore, one of the occurring issues is the problem with waste oil disposal (Azhari et al., 2015). Thus, in this condition, multiple studies were conducted to find an alternative solution to solve the issue by developing a lubricant that is sustainable, and safe for humans and the environment, for a better future (Imran et al., 2013).

The alternative to substitute mineral oil as lubricant is the vegetable oil (Jayadas and Nair, 2005; Mahipal et al., 2014; Azhari et al., 2015: Nuri et al., 2015; Suffian et al., 2015; Padmini et al., 2015 Gurudatt and Nagaraju, 2016; Panchal et al., 2017; Wagh and Mhaske, 2018; Sing et al., 2018)**.** It is suitable to be developed as bio-lubricants since vegetable-based oil lubricants are biodegradable, nontoxic compared to petroleum-based oils, and are made from renewable resources. A large amount of unsaturated fat and polar ester groups in vegetable oil provides good lubricating abilities than petroleum based oil (Petlyuk and Adams, 2004). A strong interaction between lubricated surfaces makes it become an anti-wear additive and anti-friction additive. One characteristic possessed by the vegetable oils is the Amphiphilic Nature - it gives them good film or force relationship, and provides high strength lubricant films that interact strongly with metallic surfaces, reducing both frictions and wear due to long fatty acid chains and the presence of polar groups in the vegetable oil structure (Quinchia et al., 2014). Moreover, Fox and Stachowiak (2007) claimed that vegetable oils are particularly effective as boundary lubricants, as the high polarity of the entire base oil allows strong interactions with the lubricated surfaces. Boundary lubrication performance is affected by the attraction of the lubricant molecules to the surface and the possible reaction with the surface.

In Malaysia, palm oil and palm oil-based products are one of the major export commodity. Therefore, the availability of the palm oil supply is high, added with its sustainable resources. However, an experiment conducted by Syahrullail et al., (2013) showed that palm fatty acid distilled (PFAD) oil has a higher wear scar diameter. It is because oxygen bond in the PFAD chemical chain caused the oxidation at the ball bearing surface, hence made the ball bearing brittle and produced higher wear. It showed that the palm oils alone were not suitable for lubrication purposes. The drawback of vegetable oil caught the attention of researchers to find an alternative solution to enhance the lubrication performance (tribological properties) by introducing an additive into a vegetable base oil.

The adding of zinc ion derivatives into vegetable oil as an additive has captivated many researchers who want to develop a new bio-lubricant. Zinc Diamyl Dithiocarbamate (ZDDC), Zinc dialkyl(aryl)Ethoxy Dithiophosphates (ZEDP), and the most attractive chemical structure that enhances oxidation stability and reduces friction and wear - Zinc Dialkyl Dithiophosphate (ZDDP) are the examples of lubricant additives from zinc ion derivatives. According to Jayadas and Nair (2006), vegetable-based oils have excellent properties such as high viscosity index, high lubricity, high flash point, low evaporative loss, high biodegradability, and low toxicity. However, there are still downsides of the vegetable-based oils, namely their low-temperature flow behavior, and low oxidation stability. Oxidation leads to polymerization and degradation of vegetable oil. It is believed that the polymerization process causes an increase of viscosity, hence reduces lubrication functionality. The increases in viscosity that are seen as a result of oxidation can be explained by pointing to the polymerization of products such as sludge. Meanwhile, the degradation process causes the production of the volatile product and decreases lubricant properties (Kodali, 2002). Therefore, the addition of antioxidant like ZDDP can surpass the performance of conventional lubricants in enhancing oxidation stability, and reducing friction and wear. Based on the previous research, it is believed that the introduction of the zinc compound as an additive in vegetable oil will prevail over this problem. Erhan et al.,