UNIVERSITI TEKNIKAL MALAYSIA MELAKA

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TRIBOLOGICAL PROPERTIES MODIFICATION OF ZINC DIPRIMARY OCTYL INDUCED PALM OIL BIO-LUBRICANT USING MOLYBDENUM DITHIOPHOSPHATE

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

by

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TAJUK: **TRIBOLOGICAL PROPERTIES MODIFICATION OF ZINC DIPRIMARY OCTYL INDUCED PALM OIL BIO-LUBRICANT USING MOLYBDENUM DITHIOPHOSPHATE**

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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 (Automotive) with Honours. The member of the supervisory is as follow:

....

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ABSTRAK

Kajian ini adalah untuk membangunkan pelincir yang baru untuk menangani pengurangan minyak mentah, kenaikan harga minyak dan pencemaran alam sekitar yang disebabkan oleh minyak berasaskan mineral. Pelincir berasaskan minyak sayuran telah dijumpai sebagai pelincir alternatif kerana sifat-sifat biodegradasi, boleh diperbaharui, mesra alam dan tidak mengandungi toksik. Pelincir yang baru dirumuskan menggunakan 2 wt% konsentrasi Zinc Diprimary oktyl dithiophosphate (ZnODDP) dengan tambahan Molybdenum Dithiophospate (MoDTP) pada kepekatan 0.05 wt% , 0.10 wt%, 0.15 wt% dan 0.20 wt% . Sampel telah diuji mengikut kaedah *American Society for Testing and Material (ASTM)*. ASTM D6595 digunakan dalam sampel ujian untuk menentukan kandungan logam sampel yang dikumpulkan oleh *Rotating Disc Electrode Atomic Emission Spectroscopy (RDE-AES)*. ASTM D4712 digunakan dalam pencirian sampel untuk mencirikan geseran pekali dan diameter parut haus oleh empat penguji bola dan mikroskop laser mengikut ujian masing-masing. Pemalar geseran paling rendah direkodkan pada 0.074 manakala diameter parut haus terendah didapati pada 76.07 μm. Keputusan mendapati keputusan yang diingini adalah pada kepekatan 2 wt% ZnODPP dan 0.05 wt% MoDTP. Kesimpulannya, gabungan ZnODDP dan MoDTP yang ditambah ke dalam minyak kelapa sawit berjaya dibangunkan dan dirumuskan sebagai pelincir-bio yang baru.

ABSTRACT

This study is to develop a new formulated bio-lubricant to address the depletion of crude oil, oil prices increment and the environmental pollution imposed by mineral based oil. Vegetable oil based lubricant has been discovered to be the alternative lubricant due to the properties of biodegradable, renewable, environmental friendly and non-toxic. The new formulated bio-lubricant will use 2 wt% concentration of Zinc Diprimary octyl dithiophosphate (ZnODDP) induced palm oil with addition of Molybdenum Dithiophospate (MoDTP) at concentration of 0.05 wt%, 0.10 wt%, 0.15 wt% and 0.20 wt% respectively. The samples were tested in accordance to the American Society for Testing and Material (ASTM) method. ASTM D6595 was used in sample testing in determining the metal content of samples collected by Rotating Disc Electrode Atomic Emission Spectroscopy (RDE-AES). ASTM D4712 was used in sample characterization to characterize the coefficient friction and wear scar diameter by four ball tester and upright laser microscope respectively. The lowest coefficient of friction was recorded at 0.074 while the lowest wear scar diameter obtained at 76.07 μm. Result found the desirable results recorded was at concentration of 2 wt% of ZnODPP and 0.05 wt% of MoDTP. In conclusion, the combination of ZnODDP and MoDTP induced into palm oil was successfully developed as newly formulated bio-lubricant.

DEDICATION

Special dedication to my beloved family members, especially to my father Otsman Bin Omar and my mother Zaiton Binti Ujang who always supported and encouraged me with motivation and love through my whole journey.

To my respected and professional supervisor, Mohd Faruq Bin Abdul Latif for endless guidance and support from bottom to the top.

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List of Abbreviations and Symbols

A.D	-	Anno Domini
ASTM	-	American Society for Testing and Materials
B.C	-	Before Christ
C	-	Carbon
C_nH_{2n+2}	-	Saturated hydrocarbon general formula
$C_{15}H_{31}COOH$	-	Palmitic Acid
g	-	Gram
H	-	Hydrogen
H•	-	Hydrogen ion
HEAR	-	High Erucic Acid Rapeseed
KOH	-	Potassium Hydroxide
Mo	-	Molybdenum
MoDTP	-	Molybdenum Dialkyl Dithiophosphate
MoS_2	-	Molybdenum disulfide
mm	-	Millimeter
mm^2/s	-	Kinematic Viscosity (millimetre square per second)
mg	-	Milligram
ml	-	Milliliter
nD20	-	Refractive index
OH	-	Hydroxide
PAOs	-	Polyalphaolefins
PTFE	-	Polytetrafluoroethylene
R	-	Radical
R•	-	Radical Ion
RBD	-	Refined Bleached Deodorized
RDE-AES	-	Rotating Disc Electrode Atomic Emission Spectroscopy
ROO•	-	Peroxide Radical
ROOH	-	Organic Acid
S	-	Sulphur

SAE	-	Society of Automotive Engineers
W	-	Winter
wt%	-	Weight percent
ZDDP	-	Zinc Dialkyldithiophosphate
ZnODDP	-	Zinc Octyl Dialkyl Dithiophosphate
%	-	Percent
°C	-	Degree Celcius
μ	-	Coefficient of friction
μm	-	micrometer

CHAPTER 1

INTRODUCTION

1.1 Introduction to Lubricant

For many decades, axles and oxen carts are lubricated by the farmers using animal fats (Ahmed and Nassar, 2011). In early 1400 B.C., the traces of grease were found from the tomb of Yuaa and Thuiu which is made from the combination of calcium and fat, then was used to lubricate chariot wheels (Davison, 1957).

During 1650 B.C., natural oil was used as a lubricant derived from olive, rapeseed, castor bean, palm oil, and the fat from the sperm whale, animal lard, and wool grease from the time of A.D. 50 until the early of the 19th century (Gawrillow, 2004). During the 16th century, the form of a lubricant used are varied from vegetable oils, animal oils, or mixture of two. One of the earliest crude oil was introduced as lubricant in 1845 from a cotton spinning mill in Pittsburgh, Pennsylvania (Anderson, 1991). In 1769, transportation based on steam engine was introduced to the industry. Proportional to the growing technology and demands, the search of lubricants was improved. Mineral oils were the first substance used which obtained from plants and animal oils (Pirro et al., 2016).

Late in the 18th century, every industrial machines have transformed through the development of technology to improve an economic and cultural conditions of time. The century was known as the Industrial Revolution (Suhane et al., 2012). The lubricants based on petroleum dominated the field due to the rise of the petroleum industry in this era. Petroleum has been well known for a long time since the ancient Assyrians and Egyptians, particularly in lighting and embalming process while the American Indians used crude petroleum for medical purposes. On the other hand, petroleum was discovered by the American colonies by drilling for salt unfortunately has been dispensed as waste. This makes mineral oil started to be used widely and the price is reasonable while turn out the price of natural oil to be more expensive compared to mineral oil as the mineral oil gives an advantages in terms of stability and availability. Synthetic lubricant provides excellent viscosity properties thus retaining their viscosity over wide temperature range. For example, silicone polymer has superior viscosity temperature properties and it is used for lubrication at high temperature. Since the 1950s, synthetic liquid lubricants with a lower volatility, better high thermal performance, and greater resistance have been developed for larger machine with greater speed and higher specifications. For these synthetic neutral substances prepared consists of raw material such as plasticizers, resin polymers, and organic solvents (Anderson, 1991).

Lubricant is a substance that separates between two relative motions of solid surface from contact to each other and also act as a friction reducer, reducing wear agent and dissipating friction heat (Azhari et al., 2015b). According to Hamrock et al., (2004), any substance that reduces friction, wear, provides smooth running and perform as elements of satisfactory life for machines can be called lubricant. This was also supported by Ghosh and Karmakar, (2014) stated that the lubricant is also considered as a third body performed between the interacting surfaces to avoid direct contact between the surfaces with the purpose of reducing friction. Apart from that, significant functions of lubricant encompassed liquid sealing and corrosion protection, heat transfer and prevent overheating (Jain and Suhane, 2012). Lubricant can be drawn by hydraulic motion between two contact surfaces (Anderson, 1991). Hence, help to reduce friction and heat produced, by performing a fluid film between the surfaces (Azhari et al., 2015b).

The introduction of the lubricant in contact surfaces prevent in wear, thus extended the life span of the machine. The presence of lubricant in rotating gear will act as 'shock absorber' and absorb the vibration. Lubricant possible transfer the heat produced between the surfaces due to high pressurizing may raise the temperature and act as cooling agent. Lubrication keeps the dirt contaminants out. Dirt is evident in all aspects of surface contact. The contaminants, including wear debris, sludge, soot particles, acids, or peroxide. The contaminants could be wiped away, as in the case of grease, or caught in a filtration medium. Lubricant also acts as a seal against outside dirt indigestion (Bannister, 1996). Hence, prolong bearing life, prevention of rusting and protection from harmful elements (Azhari et al., 2014). This was also supported

1.2 Potential of Vegetable Oil

Various vegetable oils consist of palm, soybean, sunflower, peanut, cottonseed, coconut, castor and corn oils (Azhari et al., 2014). Most of the bio-lubricant contain great proportion of unsaturated free fatty acid which is defined as the ratio and position of carbon-carbon double bond, one two and three double bonds of carbon chain is called as anoleic, linoleic, and linolenic fatty acid mechanisms respectively (Kalam et. al., 2012).

Vegetable based oil can be classified into two type which is edible and non-edible. Edible oil is a liquid fat that completely of being eaten as a food or through food access such as coconut, olive, soybean, sunflower, palm, peanut, rapeseed and corn while non-edible consist of neem, castor, mahua, rice bran, karanja, jatropha and linseed oils (Azhari et al., 2014).

The development of vegetable based oil as alternative lubricant has drawn the concern of Energy Department to curb the environmental pollution imposed by mineral based oil. The characteristics of vegetable oil which are biodegradable, non-toxic and renewable source give strong reason to be the potential for the future lubricant (Azhari et al., 2016a). Vegetable oil also possess the desirable properties such as high viscosity index, high lubricity and high flash point (Mobarak et al., 2014).

Some vegetable oils have been studied by researchers due to its availability (Farhanah and Syahrullail, 2016). A study conducted by Mahipal et al., (2014) showed that positive result in use of ZDDP as additive on karanja oil compared to SAE 20W-40 conventional lubricant oil that provided better anti-wear and anti-friction properties. Unfortunately, the cloud point and pour point have been found higher compared to conventional mineral based oil.

This was also observed by Cheenkachorn, (2013) whereby the introduction of anti-wear additive reduce the friction coefficients of soybean oil. ZDDP can form a thin film layer on surface contact to prevent metal contact. The ZDDP chemical reaction is greater in terms of absorption compared with free additive of the vegetable oil on the metal surface.

Same analysis were carried out by Azhari et al., (2015b), with zinc introduced into corn oil and canola oil has proven in enhancing the tribological properties. ZDDP could improve the oxidation stability in the vegetable oils (Azhari et al., 2014).

Besides, with the right amount concentration, ZDDP will give better performance in reducing the kinematic viscosity and coefficient friction (Azhari et al., 2015b). Thus will give a better opportunity to future development in lubricant industries.

1.3 Problem Statement

Mineral based oil can be harmful due to its toxicity and exposure to environmental may adversely affect health. The assortments of a harmful nature when released into the environment can impact living things and resulting in pollution of both aquatic and terrestrial ecosystems (Ssempebwa and Carpenter, 2009). Mahipal et al., (2014) stated that disposal causes severe environmental hazards particularly through the hydraulic, mining, agriculture and petrochemical industries. In addition, mineral based oil lubricants sources are non-biodegradable and non-renewable (Azhari et al., 2016a). The depletion of reserve crude oil has caused the oil price increases. The issue have to be concerned to develop an alternative lubricant. (Mobarak et al., 2014).

Vegetable oil seemly can be a candidate to be the alternative lubricant since the characteristics are biodegradable and renewable source. (Azhari et al., 2015b). According to McNutt, (2016), vegetable oils with high oleic acid content are the preferred replacement for mineral oils in industries. Vegetable oils are also preferred to synthetic fluids because of the economic, eco-friendly and non-toxic properties compared to conventional mineral based oil. Vegetable oils have low volatility due to high molecular weight of the triacylglycerol molecule and have a narrow range of viscosity changes with temperature which is high value of viscosity index (Mahipal et al., 2014). The rapidly biodegradable and non-toxic, offered safety to the environment and operators. The bio-lubricant also exhibits performance benefits in better lubricity, higher flash point, lower volatility, higher viscosity indices, higher shear stability, lower compressibility, higher detergency, higher resistance to humidity, and higher dispersancy (McNutt, 2016).

However, a research done by Tiong et al., (2012) stated that vegetable oil becomes less effective under extreme loads and increasing friction. This was also supported by Syahrullaill et al., (2013) as in the article, the metal oxidation will occur and weaken the structure of the metal thus led the vegetable oils performance decreasing when working at high temperature and pressure.

The vegetable oils also have lower thermal stability and clogged tendency (Aravind et al., 2015). This vital problem will cause to increase in oil acidity, viscosity, corrosion and volatility in order to consume it as lubricant (Liu et al., 2015). This will restrain the capacity of the vegetable oils to become the alternative lubricant thus the chemical modification is the solution to overcome the issues. It is believed that the addition of additives enhance the bio-lubricant properties (Azhari et al., 2015a). Prior studies conducted by various researchers discovered that Zinc dialkyl dithiophosphate (ZDDP) can be the solution additive to overcome the regarding issues. The abilities as radical scavenger and hydroperoxide decomposer has resulted the ZDDP as anti-friction an outstanding performances (Erhan et al., 2006).

ZDDP can react with the asperities to form a boundary layer between the two contacting surface to reduce friction and wear scar diameter. The same concentration with combination of karanja oil bio-lubricant exhibits excellent physical properties (Mahipal et al., 2014). However, Azhari et al., (2015a) stated that the excessive amount of concentration ZDDP will show the varied behaviour. It will decrease the anti-wear qualities and increase the thickness film.

Apart from zinc there is another additive that could be added into lubricant oil to reduce friction and wear. Prior studies had found the combination of Molybdenum dithiophosphate (MoDTP) with ZDDP is capable in improvement of the tribological properties (Azhari et al., 2016a). The use of molybdenum based friction modifiers, organomolybdenum compounds has drawn considerable attention for many years due to excellent exhibited properties such as anti-friction, anti-wear, anti-oxidant, and extreme pressure (Unnikrishnan et al., 2002).

Organomolybdenum compounds content in MoDTP act by forming tiny platelets of the low shear strength, layer-lattice compound molybdenum disulphide (MoS_2) on rubbing asperities, and provided in reduce friction consistent to its properties as friction modifiers. The special lamellar-type structure and low shear strength make it easier in shearing between the two contacting surface that provides superior friction reduction particularly in high-pressure contacts (Tang and Li, 2014).

Both additives give satisfactory performance in enhancing tribological properties respectively. However, the right amount of concentration of ZDDP and

MoDTP combination gives better tribological properties improvement (Komvopoulus et al., 2006). This is also supported by Unnikrishnan et al., (2001), whereby the combination of ZDDP and MoDTP exhibited the superior tribological performance in reducing wear and friction. However, the desirable blending concentration has not been established. Therefore, this study will investigate the desirable concentration of zinc diprimary octyl and MoDTP as additive and friction modifier which is rarely based studied by other researchers.

1.4 Objective

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

1. To develop a new bio-lubricant oil with the addition of friction modifier and anti-wear agent.
2. To test and characterize the newly developed bio-lubricant.
3. To compare the tribological performance of the newly develop bio-lubricant with existing mineral based oil.

1.5 Scope

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

1. Developing a new bio-lubricant oil using zinc diprimary octyl dithiophosphate and molybdenum dialkyl dhithiophosphate (MoDTP) induced palm oil.
2. Testing the newly developed bio-lubricant using Rotating Disc Electrode-Atomic Emission Specstroscopy (RDE-AES) accordance to ASTM D6595.
3. Characterizing the newly developed bio-lubricant by conducting four-ball test accordance to ASTM D4172.
4. Comparing the tribological performance of the newly develop bio-lubricant with existing mineral based oil.

CHAPTER 2

LITERATURE REVIEW

2.1 K-Chart

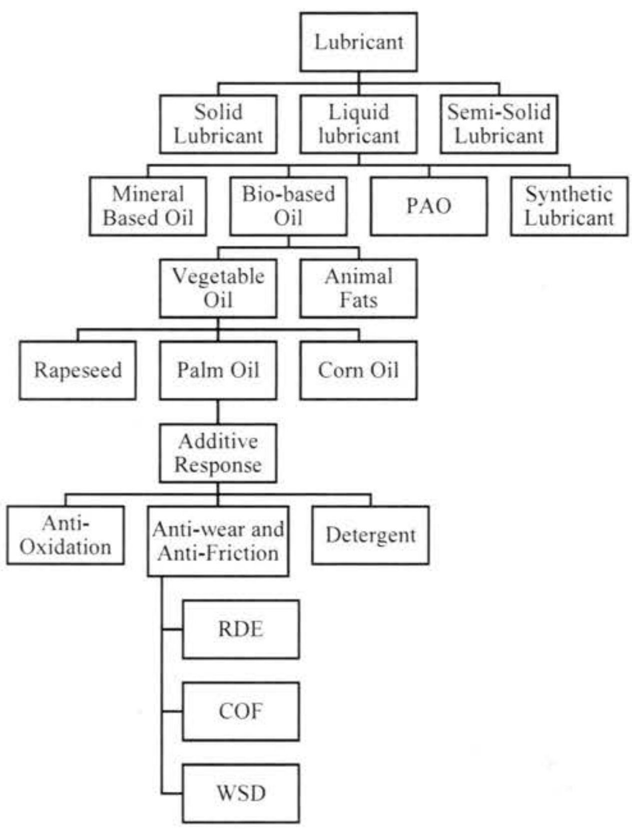

Figure 2.1: Structure of K-chart research flow.

K-chart is a tool for systematically organizing research which consist scopes of issues under study, methodology, results and a timelines in the form of a tree diagram as shown in Figure 2.1. However, it depends on the researcher how to develop the structure of K-chart according to relevant chapter to discuss in the study. In this study, K-chart was developed for research to organize, planning and monitoring the relevant chapter and issues in order to reach the objective of this study.

2.2 Classification of Lubricant

Lubricant has been used widely in machinery particularly in sliding and rolling motion (Zhou and Vincent, 1999). Lubricant is a substance that is present between the two relative motion contact surfaces in term of reducing friction and wear (Hamrock et al., 2004). The lubricant influence the performance by its different appearances. According to Zhou and Vincent (1999), lubricants can be classified as solid lubricants, semi-solid lubricants, and liquid lubricants.

2.2.1 Solid Lubricant

Solid lubricants are commonly required on equipment with inadequate lubrication and difficult component to lubricate with fluid lubricant. This is also supported by Miyoshi (2001) stating that, solid lubricant is necessary when the liquid lubricant does not meet the requirement of modern technology. Various event discovered the presence of solid lubricant could prolong the lifespan of components of machinery (Campbell, 1966). Solid lubricant is a material which appears between two contact solid motions to separate each other to decrease the amount of friction and wear in dry condition (Miyoshi, 2001). According to Bhushan (2013), solid lubricant is used in high load and low speed operating machinery particularly with component such as bearing. Solid lubricant presence in form of powder or thin film to prevent damage during the relative motion. On the other hand, dust, sand and gravel could also act as solid lubricant and cause the vehicle to skid as the friction between the tire and surface road decreased (Lansdown, 1982). However, it is undesirable thing that should be avoid. The application of solid lubricant is shown as in Table 2.1.

Table 2.1: Application of solid lubricant (Miyoshi 2001)

Requirement	Applications
Avoid contaminating product or environment	Food-processing machines Space telescopes Optical, metalworking, surface-mount, medical and dental equipment Tape recorders Microscopes and cameras Paper-processing and business machines Automobiles Spectroscopes
Maintain servicing or lubrication in inaccessible or unlikely areas	Aircraft Space vehicles Satellites Aerospace mechanisms Nuclear reactors Consumer durables
Resist abrasion in dirt-laden environments	Space vehicles (rovers) Automobiles Agricultural and mining, off-road vehicles, construction and textile equipment
Provide prolong storage or stationary service.	Aircraft and Railway equipment Missile components Nuclear reactors Telescope mounts Heavy plants, buildings and bridge, furnace