



UNIVERSITI TEKNIKAL MALAYSIA MELAKA

**ADDITION OF MOLYBDENUM DITHIOPHOSPHATE
(MoDTP) INTO ZINC DIAMYL DITHIOCARBAMATE (ZDDC)
INDUCED CORN OIL AS BIO-BASED LUBRICANT
SUBSTITUTION**

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

by

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**TAJUK: ADDITION OF MOLYBDENUM DIITHIOPHOSPHATE (MoDTP) INTO
ZINC DIAMLYDITHIOCARBAMATE (ZDDC) INDUCED CORN OIL AS
BIO-BASED LUBRICANT SUBSTITUTION**

SESI PENGAJIAN: 2015/16 Semester 2

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(Muhamad Azwar bin Azhari)

ABSTRACT

This study reports the development of a new bio-lubricant by using corn oil induced with Zinc Diamyldithiocarbamate (ZDDC) added with Molybdenum Dithiophosphate (MoDTP). The needs of having an alternative lubricant is essential as the existing mineral based lubricant is non-environmental friendly and imposed a threat to the environment. Six samples were prepared with constant concentration of Zinc Diamyldithiocarbamate (ZDDC) at 2 wt% and varied concentration of Molybdenum Dithiophosphate (MoDTP) at 0.05 wt%, 0.10 wt%, 0.15 wt% and 0.20 wt%. The prepared samples were tested using a Kinematic Viscometer to investigate the kinematic viscosity and Rotating Disc Electrode-Atomic Emission Spectroscopy (RDE-AES) to check for dilution of additive in the samples. Characterization process of investigating the coefficient of friction and wear scar diameter uses a four ball tester. Samples with 2 wt% Zinc Diamyldithiocarbamate (ZDDC) and 0.05 wt% of Molybdenum Dithiophosphate (MoDTP) displayed the most desirable concentration of additive added when it exhibited a coefficient of friction of 0.079 and a very small wear scar diameter at 104 μm . This newly developed bio-lubricant showed a reduction on coefficient of friction when only added with 0.05 wt% of Molybdenum Dithiophosphate (MoDTP) into corn oil with constant concentration of Zinc Diamyldithiocarbamate (ZDDC) at 2 wt% exhibited the desirable tribological characteristics and showed the similar trending on wear scar diameter. As a conclusion, with the evidence based on result obtained this bio-lubricant is capable to fulfil the demand to overcome the problem as a bio-based lubricant substitution which were rarely being studied by others.

ABSTRAK

Kajian ini melaporkan pembangunan bio-pelincir yang baru menggunakan minyak jagung terdorong Zink Diamildithiokarbamat (ZDDC) dengan menambahkan Molibdenum Dithiofosfat (MoDTP). Keperluan untuk mempunyai pelincir alternatif amatlah diperlukan kerana pelincir mineral sedia ada ini tidak mesra alam dan mengancam alam sekitar. Enam sampel telah disediakan dengan menggunakan kepekatan malar untuk Zink Diamyldithiocarbamate (ZDDC) pada 2% berat dan dipelbagaikan kepekatan untuk Molibdenum Dithiofosfat (MoDTP) iaitu 0.05% berat, 0.10% berat, 0.15% berat dan 0.20% berat. Sampel yang telah disediakan diuji menggunakan Meter Kelikatan Terpanas untuk mengkaji kelikatan kinematik minyak dan Electrode Cakera Berputar-Spektroskopi Atom Terpancar (RDE-AES) untuk menguji pelarutan bahan tambahan di dalam sampel. Proses pencirian untuk mengkaji pekali geseran dan diameter parut kehausan menggunakan Penguji Empat Bola. Sampel dengan campuran 2% berat Zink Diamildithiokarbamat (ZDDC) dan 0.05% berat Molibdenum Dithiofosfat (MoDTP) menunjukkan kepekatan bahan campur yang diingini apabila ia menunjukkan pekali geseran sebanyak 0.079 dan diameter parut kehausan yang kecil iaitu 104 μm . Minyak bio-pelincir yang baru dengan menambah 0.05% berat Molibdenum Dithiofosfat (MoDTP) ke dalam minyak jagung dengan kuantiti kepekatan yang sama digunakan daripada Zink Diamildithiokarbamat (ZDDC) iaitu 2% berat mencapai ciri-ciri tribologi yang diingini dan menunjukkan trend yang sama pada diameter parut kehausan. Sebagai kesimpulan, dengan adanya bukti berdasarkan hasil kajian yang diperolehi bio-pelincir ini berupaya untuk memenuhi permintaan bagi meyelesaikan masalah sebagai pengganti minyak bio-pelincir di mana ianya jarang dikaji oleh orang lain.

DEDICATION

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

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LIST ABBREVIATIONS, SYMBOLS AND NOMENCLATURES

ASTM	-	American Society for Testing and Materials
COF	-	Coefficient of Friction
J	-	Joule
MoDTC	-	Molybdenum Dialkyldithiocarbamates
MoDTP	-	Molybdenum Dialkyldithiophosphate
Mg	-	megagram
N	-	Newton
PTFE	-	Polytetrafluoroethylene
PAO	-	Polyalphaolefins
PAG	-	Polyalkylene glycol
DLC	-	Diamond like Carbon
SAE	-	Society of Automotive Engineers
RDE-AES	-	Rotating Disc Electron Atomic Emission Spectroscopy
ZDDC	-	Zinc Dialkyldithiocarbamate
ZDDP	-	Zinc Dialkyldithiophosphate
MoDTC	-	Molybdenum Dialkyldithiocarbamate
TAGs	-	Triglycerides
SEM	-	Scanning Electron Microscope
Pa	-	Pascal
cSt	-	centiStokes
F	-	Farad

Kgf	-	Kilogram-force
g/Kw h	-	gram/ Kilowatt-hour
KW	-	Kilowatt
cP	-	molar heat capacity at constant pressure
%	-	Percentage
g	-	gram
m	-	meter
ml	-	milliliter
mm	-	millimeter
nm	-	nanometer
ppm	-	parts per million
rpm	-	revolution per second
rev/min	-	revolution per minutes
rps	-	revolution per second
wt	-	weight
°C	-	degree of Celsius

CHAPTER 1

INTRODUCTION

1.1 Introduction

Since the 19th century when the industrial revolution have dominated the production of petroleum as well as the commercial drilling, engineering has advances led to the adoption in different application where machines with high specific power, simple design, light overall weight and low cost was required. Furthermore, engines development which are consist of moving components like pistons, turbine blades or a nozzle over a distance whereby includes the transforming chemical energy into mechanical energy requires effectiveness of lubricant toward moving parts in order a mechanism between two contacting surfaces will slide smoothly over each other. Lubricant has been used since the day machine has invented where insufficient lubrication will affect the machine performance. A study by Suhane et al., (2012) state that lubricants have becoming very common and highly demand by various industrial afterwards since the industrial revolution, which influenced the price and availability of lubricants used from vegetable until animal sources. A study by Mobarak et al., (2014) stated that to achieve reliable and safe operation at desired operating conditions need an effective lubrication toward a moving components to allow the components to slide more smoothly over each other.

Lubricants are substance in a liquid state that applied between two moving part surfaces in order to minimize the friction and wear between two contacting surfaces whereby to minimize the coefficient of friction toward two contacting surfaces, preventing from rust and reducing the oxidation, acting as an insulator in transformer applications, and seal against dirt, prevent from dust and water toward the surfaces

(Mubarak et al., 2014). Apart from that, a study by Suhane et al., 2012 stated that lubricant generally is major of base oil and minor is some additives whereby the additives are able to reduce the friction and wear, increasing viscosity, improving viscosity index, resistance to corrosion and oxidation, aging or contamination. Besides, with different concentration and type of additive used will affect the desirable characteristics.

Specifically, lubricants are described as mineral oil, synthetic or bio-based fluid (Sander et al., 2012). A lubricant characteristics and desired from the performance of view to have include the viscosity, viscosity index, pour point, cloud point, flash point, fire point, oxidation stability, neutralization number and environment compatibility to be a good lubricant. Selecting a proper lubrication is essential to reducing the long-term costs which mean longer life span of the lubricant life, minimized machine wear, minimized incipient power losses and provide safety condition as well (Pantelis et al., 2015). A study by Krzan et al., (2004) state that in the late 19th century, lubricating oils were based mainly on rapeseed, castor and whale oil. However, due to the rapid industrialisation from the ages of industrial revolution era, mineral oil from the petroleum produce has been used as the base stocks of liquid lubricants (Azhari et al., 2015).

A study by Pantelis et al (2015) state that certain bio-based lubricants already attract an attention because of the tribological properties which providing a good friction and wear characteristics, hence it has influenced the scientific world that encourage them to looking for an alternative lubricant that are environmental friendly. Moreover, due to the environmental issues a studies have been conducted to search an alternative lubricant which is more environmental friendly but at the same time possess the same lubricity effect that is required by a lubricant (Azhari et al., 2015).

1.2 Classification of lubricant

According to Mobarak et al., (2014) stated that lubricant can be classified into 3 physical states. The states of lubricants are classified as solid lubricant, semi-solid lubricant and liquid lubricant. The classification of physical states lubricants are

classified based on the physical appearance whereby solid, semi-solid and liquid (Suhane et al., 2012).

1.2.1 Solid lubricant

The film of a solid material is composed of inorganic as well as organic compounds and used in the dry powder form or with binders to make them stick firmly to metal surfaces while in use.

1.2.2 Semi-solid lubricant

Liquid is formation of a solid matrix of thickener and additives like grease and usually semi-solid lubricant obtained by combining oil with thickening agent. The improvement of grease oil has been made through a combinations of petroleum oils with calcium, potassium and sodium soaps where this make the mineral oil based lubricant started to be used widely and the market price is reasonable (Azhari et al., 2015).

1.2.3 Liquid lubricant

The example of oils such as petroleum, vegetable, animal and synthetic oils. Basically contain hydrocarbon with 12 to 50 carbon atoms and cheap and stable under service conditions therefore it is widely used. A study Azhari et al., (2015) stated that petroleum is the main source in producing mineral based oil lubricants for many years.

1.3 Problem statement

Most lubricants oil are formulated from mineral oil and frequently using various types of additives which is not environmentally friendly and the production process already produced some environmentally hazardous chemical component (Pantelis et al., 2015). A study by Adhvaryu et al., (2003) stated that most of lubricants come from petroleum stock, whereby it is toxic to environmental and difficult to dispose as well. Moreover, mineral oil based lubricant is one of the contributor toward the environmental pollution when the waste oil produced and their subsequent disposal cause serious environmental hazards which increase concern on environmental issues includes the toxicity, biodegradability and renewability of mineral based lubricants (Azhari et al., 2015). Apart from that, fresh lubricants and used lubricants can affect considerable damage toward the environment mainly due to the high potential of serious soil and water pollution as well as the additives contained in lubricant can be toxic to flora and fauna (Suhane et al., 2012). A study by Mahipal et al., (2014) stated when the waste oil produced, it will cause a serious environmental hazards because the existing mineral based lubricant are non-biodegradable and non-renewable. However, vegetable oils are renewable resources for the industrial and also transportation application lubricants (Bergstra, 2004). Therefore, vegetable oils have become a suitable candidate to replace the mineral oil based lubricant for solving the environment problem as well as the base oil storage.

Regarding to the stated issues, creating a new renewable and bio-degradable lubricant are studied by various researchers. Vegetable oil have turned the attention of the world toward using vegetable oil the base stock in lubrication production due to the most esters are bio-degradable compared to mineral oils. A study by Castro et al., (2006) stated that vegetable oils can gives significantly environmental advantages because vegetable oils is biodegradability and renewability. It also it gives satisfaction lubricity performance in difference of applications. The use of vegetable oil as lubricant oils in local and industrial processes has increase the life span of machinery and vegetable oils are naturally occurring the substances that can protect the environment as a biodegradable fluid. A study by Khan et al., (2012) stated that vegetable oils having tribology characteristics similar or superior to those mineral

based oils due to the high load carrying abilities, high viscosity index, excellent friction coefficient and harmless to the aquatic organisms also vegetation surrounding. Apart from that, 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 contacting surfaces.

In contrast, the biggest problem occurs in vegetable oil are poor hydrolytic, oxidation stability and poor low-temperature characteristics (Adhyaru and Erhan, 2002; Zeman et al., 1995). Furthermore, this tribological properties of pure vegetable oils do not meet the requirements of commercial lubricant. Pure vegetable oil exhibits a significantly higher coefficient of friction and wear scar diameter compared to the commercial lubricant which is SAE 40 (Azhari et al., 2015). There are numerous researches that proves that the capability of pure vegetable oil is limited. According to Azhari et al., (2015) the coefficient of friction of pure corn oil is increasing with the increment of the load that was applied and the value of CoF shows higher than the CoF of the corn oil with the addition of additive. Moreover, this is also proven by the study of Azhari et al., (2015) where the value of kinematic viscosity and coefficient of friction for pure canola and corn oil are significantly higher than the canola and corn oil with the addition of 2 wt% of Zinc Dialkyl Dithiophosphate. From the results, these researchers indicate the pure vegetable oils cannot be used for commercial lubrication purposes due to their tribological properties and the tribological properties should be enhanced for further development in order to be used as a lubricant. Apart from that, the lubricating performance of vegetable oils with the addition of ZDDC are barely satisfactory and they do not achieve the conventional mineral based lubricant standard.

In order to produce a better performance of bio-lubricant, additives should be blended with the vegetable oils because the additives of friction modifier and anti-wear agent can be added to improve the tribological characteristic of vegetable oils as well as to ensure them to function as a commercial lubricant. A study by Nizam et al., (2009) stated that when added zinc diamylidithiocarbamate (ZDDC) and zinc dialkyldithiophosphate (ZDDP) into vegetable oil, the newly developed vegetable based lubricant exhibited a desirable tribological characteristics which the selective addition of additives is crucial to increase its stability and provide the vegetable oils to work under wider range of temperature and pressure. A study by Azhari et al., (2015)