UNIVERSITI TEKNIKAL MALAYSIA MELAKA

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EFFECT OF ZDDP ADDITION IN CANOLA OIL AS ANTIOXIDIZING AGENT FOR LUBRICATION APPLICATION

This report submitted in accordance with requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor's Degree in Mechanical Engineering Technology (Maintenance Technology) (Hons.)

by

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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's Degree in Mechanical Engineering Technology (Maintenance Technology) (Hons.). The member of the supervisory is as follow:

....

(Muhamad Azwar bin Azhari)

ABSTRAK

Minyak mineral memiliki bidang pelinciran yang tersendiri dan hari ini masalah mula timbul kerana minyak mineral dan minyak sintetik tidak mesra alam. Selain itu, pelupusan minyak amat kompleks untuk dilupuskan. Alam sekitar telah meletakkan minyak mineral adalah yang paling banyak digunakan sebagai pelincir cecair. Tujuan utama kajian ini adalah untuk mewujudkan minyak pelincir alternatif dengan penambahan agen antioksida ke dalam minyak sayuran. Minyak masak canola dipilih sebagai minyak asas pelincir . Walau bagaimanapun, masalah utama minyak sayuran ialah memiliki kestabilan termo- oksidatif yang lemah. Minyak sayuran mempunyai struktur trigliserida yang datang dari tepu dan tak tepu. Struktur trigliserida kurang upaya yang mempunyai ikatan dua dalam wujud di tak tepu dalam asid lemak yang aktif dan memberi kesan pengoksidaan dan menurunkan kestabilan pengoksidaan. Oleh itu, pengenalan kepada Zink Dialkyldithiophosphate (ZDDP) yang dikenali sebagai antiwear yang berkesan dan bahan tambahan antioksidan dalam mencegah degradasi minyak pelincir dicampur di dalam minyak canola dan menggunakan mandi ultrasonik untuk menghasilkan minyak pelincir yang baru. Terdapat empat Persatuan Amerika untuk Ujian dan Bahan (ASTM) kaedah akan dijalankan yang dalam ujian sampel dan peringkat ini adalah penting kerana untuk mencirikan sifat-sifat minyak baru dan mengujinya untuk aplikasi enjin.

ABSTRACT

Minerals oils own completely outclassed lubrications as well as these days environmentally friendly problems begin to arise since the mineral oil and synthetic oil is not eco-friendly. Besides, the disposal of the mineral oil is generally complex. Recent environmental awareness has put mineral oils as the most widely used lubricant base fluid into consideration by the use of biodegradable fluid like vegetable oils and other synthetic fluids into new grease formulation. The main purpose of this study is to create alternative lubricant oil with the addition of the antioxidizing agent into the vegetable oil. Which commercialized cooking canola oil is chosen to be the base oil of the lubricant. However, the major problem of vegetable oil is has poor thermo-oxidative stability. Vegetable oils have triglyceride structures that come from saturated and unsaturated. The triglyceride structures have disabilities which unsaturated double bonds in the fatty acids are active and affect the oxidation and lowering the oxidation stability. Thus, introduction of Zinc Dialkyldithiophosphate (ZDDP) that known as the effective antiwear and antioxidant additive in preventing the degradation of lubricating oil dissolved in commercialized cooking canola oil using ultrasonic bath to produce the newly developed lubricant oil There are four American Society for Testing and Materials (ASTM) methods will be conducted which in a sample testing and characterization stage and it is important because to characterize the properties of the new oil and test it to engine application.

DEDICATION

This thesis dedicate to my parents and my entire friend for supporting me all the way.

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TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

API	-	American Petroleum Institute
ASTM	-	American Society for Testing and Materials
CO	-	Canola oil
EVA	-	Ethylene–vinylacetate copolymer
EC	-	Ethylcellulose
ME	-	Molybdenum ester
PTFE	-	Polytetrafluorethylene
PS	-	Pentasulfide
PAO	-	Polyalphaolefin oil
PO	-	Palm olein
PFAD	-	Palm fatty acid distillate
POV	-	Peroxide values
RDE/AES	-	Rotating disc electrode atomic emission spectroscopy
SEM	-	Scanning electron microscope
SFM	-	Scanning force microscopy
SMCO	-	Sulfide-modified corn oil
TAN	-	Total acid number
TBN	-	Total base number
VI	-	Viscosity index
WSD	-	Wear scar diameter
ZDDP	-	Zinc Dialkyldithiophosphate
TBHQ		Tert-Butylhydroquinone
cSt	-	Centistokes

CHAPTER 1
INTRODUCTION

1.1 Introduction to Lubricant

Liquid lubricants have been used by mankind for thousands of years. In the beginning, crude lubricants as plain as mud on an inclined plane were used. Modern liquid lubricants consist mainly of mineral and synthetic oils with the addition of additives where special properties are required. The primary function of lubrication oil is to keep up and produce a lubrication film between two moving metal surfaces. This role is very dependent on the viscosity of the oil itself (Harnoy, 2003). In addition to reduce or controlling friction, lubricants are generally expected to reduce wear and frequently to prevent overheating and corrosion. For other common example is in the automotive industry, engine oils are compulsory to perform various tasks, including limiting metal to metal contact thus reducing friction and wear, and cooling the moving parts.

The effect a lubricant has on its surroundings depends on numerous lubricant properties including biodegradability, toxicity and the products on. Synthetic oils have been the major lubricant utilized where environmental concerns are considered (Miller, 2009). Lubricants are divided into four basic classes which are oils, greases, dry lubricants and gases. Base stock is lubricating oil begins with base stock or base oil. Base stocks are mineral which is petroleum or synthetic origin. The base stock provides the basic lubricating requirements of an engine. However, unless it is supported with additives, base oil will degrade very fast in numerous operating conditions. Depending on the type of base stock, petroleum, synthetic or others, different additive chemistries are used. Mineral oils is mineral stocks are developed from petroleum crude oils. The crude oil source and the refining process will verify the base stock characteristics. The crude oils used for diesel engine lubricants are primarily made up of paraffin, napthene, and aromatic compounds. The crude oils with higher paraffin content are most commonly used in blended engine oils.

1.2 Vegetable oil in motor lubricant

Vegetable Oil is usually available everywhere and there at every home and most households dump the waste oil rather than utilizing that. Day by day fuel is getting expensive and increase is hitting new highs across every country across the world. Everyone has started looking for cheap substitutes for everything in the world. Vegetable oils can and have been used as lubricants in their natural forms. They have some advantages and disadvantages when considered for industrial and machinery lubrication. Lubricity is so effective that in some applications, such as tractor transmissions, friction materials need to be added to reduce clutch slippage (Honary, 2009).

Therefore, introduction of vegetable oils as alternative oil is to replace the mineral oils. The advantage of vegetables oils are high viscosity index, high lubricity, high flash point, low evaporative loss, high bio-degradability plus a lower grade of toxicity with regards to their own work as base oil for lubrications. Disadvantage of vegetable oil are small thermal, oxidative, and hydrolytic stabilities and poor low-temperature characteristic. Vegetable oil is a product of huge interest for its environmental characteristics. It is biodegradable and it's renewable and has advantages of significantly reduced sulfate, hydrocarbon emissions and reduces particulate matter. It is nontoxic and does not harm water quality. It runs a diesel engine just as petroleum-based diesel would. Lubricant additives are chemicals that are added to oils in quantities of a few weight percent to improve the lubricating capacity and durability of the oil.

The purposes of lubricant additives are improving the oxidation resistance, improving the wear, control of corrosion, and friction characteristics, control of contamination by reaction products, wear particles and debris, reducing excessive decrease of lubricant viscosity at high temperatures and enhancing lubricant characteristics. Oil additives are critical for the proper lubrication and extended use of motor oil in modern internal combustion engines (Liston, 1992)

1.3 Problem Statement

Demand for transport fuels has risen drastically during the past few decades (IEA, 2008). The demand for transport fuel has been increasing and expectations are that this trend will stay unchanged for the coming decades. In fact, with a worldwide rising number of vehicles and a rising demand of emerging economies, order will probably increase even harder. Transport fuel demand is usually fulfilled by fossil fuel insist. However, resources of these fuels are running out, prices of fossil fuels are predictable to rise and the combustion of fossil fuels has negative effects on the climate. The expected lack of petroleum supplies and the negative environmental consequences of fossil fuels have spurred the search for renewable transportation biofuels (Hill et.al., 2006).

This study is focus about the use of vegetable oil replacing the mineral oil as an alternative way to overcome the issues that have arises. The lubricant made of vegetable oil already is used by human since ancient time. Vegetable oils offer major environmental benefits with value to resource renewability and biodegradability, plus providing satisfactory performance in a wide array of applications. Even though vegetable oil possesses most of the desirable lubricity properties such as good contact lubrication, high viscosity index, high fire point, high flash point, low volatility, non-toxic, good boundary lubrication properties, excellent thin film strength due to adherence to the surface of metals, vegetable oil also have some drawbacks that need to be overcome. However, there are some of disadvantages of using vegetable oil lubricant. The use of it is limited in industrial use due to poor thermal and oxidation stability.

Other than that are shorter life, storage time, low cold flow behavior and also poor seal compatibility. This problem can rectified through modification of other alternative oil, which is an innovation from vegetable oil mainly canola oil for this study. The addition of suitable anti-oxidant will enhance the stability of vegetable oil. Oxidation determines the service life of a lubricant. Oxidation resistance and operating temperature will measure the oxidation resistance of the oil (Landsdown, 2004). Therefore, the selection of Zinc Dialkyldithiophosphates (ZDDP) as anti oxidizing agent will be used in this study to blend with commercialize canola oil to overcome the problem and enhance the lubricant.

1.4 Objective of Research

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

(i) To prepare an alternative lubricant oil with the addition of antioxidizing agent.

(ii) To test and characterize the newly developed lubricant oil.

1.5 Scope of Research

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

(i) Prepare alternative lubricant oil using commercialized cooking canola oil with the addition of ZDDP as an antioxidizing agent.

(ii) Determine the cooperating action between the vegetable base oil, canola oil and the antioxidizing agent, ZDDP using the direct method.

(iii) Conducting a few sample tests upon new developed oil using laboratory machines to test and characterize the oil.

(iv) Conducting the application test upon the new developed oil in engine application.

CHAPTER 2
LITERATURE REVIEW

2.1 Lubricant

The modern history of lubricant additives began in the early 20th century with the use of fatty oils and sulfur in mineral oils to improve lubrication under high loads. World War II provided a major momentum to the development of lubricant additives as the military, engine builders, and machine manufacturers demanded more public production of their equipment (O'Brien, 1983).Liquid lubricants have been practiced by humans for thousands of years. Initially, crude lubricants as simple as mud on an inclined plane were used. Art from ancient Egypt shows the Egyptians pouring a lubricant in front of a sled that is being perpetrated (Williams, 1994).Worldwide consumption of lubricants in 2005 was around 40 million metric tonnesand approximately 30% of the lubricants consumed ended up in ecosystem (Bartz, 2006). Present production of biodegradable lubricant is only 1% of the total production (Bartz,2006). A lubricant consists of a base oil (>90%) and an additive package (<10%). The base oil used for the formulation of most lubricants is environmentally hostile mineral oil. The impact of lubricant upon to the natural enviroment is dependent with several lubricant attributes which includes the level of toxicity, biodegradability and the products of biodegradation (Mansfield, 2009). Synthetic oils have already been the main lubricant implemented where the environmental problems tend to be considered (Miller, 2009). The most recent research projects have reviewed the view of applying a vegetable oil based lubricant.

2.2 Vegetable Oil

Vegetable oils have been used as lubricating oils from ancient days (Dowson, 1998). They are easily obtained from natural sources. The requirement of lubricants became very high cause of rapid industrialisation, putting pressure on the price and availability of lubrication from vegetable and animal sources.

Vegetable oils are perceived to be alternatives to mineral oils for lubricant base oils because of certain inherent technical properties and their ability for biodegradability. Compared to mineral oils, vegetable oils in general possess high flash point, high viscosity index, high lubricity and low evaporative loss (Erhan and Asadauskas, S., 2000; Adhvaryu and Erhan, 2002; Mercurio, et al., 2004).

Poor oxidative and hydrolytic stability, high temperature sensitivity of tribological behaviour and poor cold flow properties are reckoned to be the limitations of vegetable oils for their use as base oils for industrial lubricants (Erhan and Asadaukas, 2000; Adhvaryu et al., 2005). Recently, demand for environmentally friendly lubricants are increasing because of the high concern for environmental protection. Vegetable oils are natural products and they are recognized as a fast biodegradable fluid. Therefore, they are promising candidates for the base oils of the environmentally friendly lubricating oils (Asadauskas et al., 1996).

Lubricity or oiliness of vegetable oils is attributed to their ability to adsorb to the metallic surfaces and to form a tenacious monolayer, with the polar head adhering to the metallic surfaces and the hydrocarbon chains orienting in near normal directions to the surface (Weijiu et al., 2003) as depicted in Figure. 2.1.

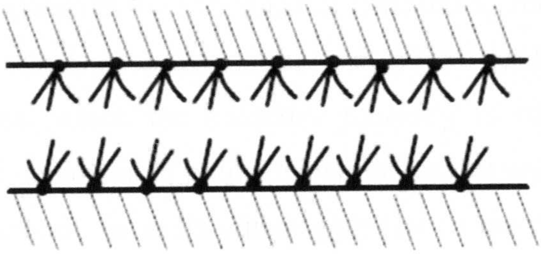

Figure 2.1: Monolayer of vegetable oil molecules adsorbed on metallic surfaces

Many countries including Austria, Canada, Hungary, Japan, Poland, Scandinavia,Switzerland, the USA, and EU are either in the process of formulating or have already passed.

Legislation to regulate the use of mineral oil based lubricants in environmentally sensitive areas (Bartz, 1998; Bartz, 2006). The U.S. market for all lubricants is 8,250,000 tons/year and only 25,000 tons per year were based on vegetable oils (Whitby, 2004). Vegetable products as well as modified vegetable oil esters can be used as a base stock for preparation of environment friendly, rapidly biodegradable lubricants.

According to (Emmanuel and Mudiakeoghene, 2008), auto oxidation of vegetable oil occurs due to lipid oxidation presence in the vegetable oil. Auto oxidation denotes to a difficult set of reactions which cause in the incorporation of oxygen in lipid structures. For oil that contain unsaturated fatty acid, with the presence of light, metal ions, oxygen, moisture content, temperature and antioxidant additive will experience auto oxidation more rapidly. Auto oxidation reactions happen at an increasing rate after the initial induction period. This behavior can be explained by assuming that oxidation proceeds by a sequential free radical chain reaction mechanism.

According to (Syahrullaila, et al. 2013), vegetable oils consist of a high friction coefficient than mineral oil. Besides, vegetable oil's wear scars are smaller than those formed by mineral oil. Hence, vegetable oils have potential as lubricants. In their study, the performance of vegetable oils as a lubricant was tested using a four ball tribometer under extreme pressure conditions, using the method of ASTM D2783.

The role of peroxides is important in order to monitor oxidative degradation by measuring peroxide values (POV) (Mochida & Nakamura, 2006). In general, when heat, metals or other catalysts cause unsaturated oil molecules to convert to free radicals is the moment where the oxidative rancidity in oils arises. These free radicals are effortlessly oxidized to produce hydroperoxides and organic compounds, such as aldehydes, ketones, or acids which give rise to the undesirable odors and flavors characteristic of rancid fats (Emmanuel & Mudiakeoghene, 2008).

2.2.1 Palm Oil

Palm oil has the possibility to be used as an industrial lubricating oil. Palm oil is vegetable oil, which is biodegradable, and has a high production rate, which could fulfill the demand for vegetable-based lubricating oil in the future. One hectare of palm trees can produce almost 10 times as much oil compared to other sources of vegetable oil (Ming & Chandramohan, 2002). Thus, palm oil has the potential to fulfill the supply volume in the demand for vegetable-based lubricants.

Palm oil is obviously reddish colored due to the fact of a substantial beta-carotene content material. Tend not to be baffled with oil pressed out from the center of the same fruit, or coconut oil extracted from the center of the coco palm. The dissimilarities are in color, including saturated fat content which palm mesocarp oil is 41% saturated, whereas palm kernel oil as good as coconut oil are 81% and 86% saturated equally (Fauzi & Sarmidi, 2010).

Palm oil is consumable vegetable oil pressed out through the mesocarp of the fruit within oil palms (van der Vossen & Mkamilo, 2007). Most of palm oil origin came from the African oil palm Elaeis guineensis, and to a lesser extent from the American oil palm Elaeis oleifera and the maripa palm Attalea maripa.

2.2.2 Corn Oil

Throughout the United State, the common of the crude corn oil is at present developed by four wet milling firms and refined corn oil is generated by merely three of these. It had been predicted that in 1996 approximately 90% of commercial corn oil in the US was coming from wet milled germ and also the remainder from dry milled germ. (Gunstone, 2002).

In contrast to most different vegetable oils, corn oil is acquired from seeds (kernels) which consist of solely 3-5% oil. Extraction of oil directly through the kernels is theoretically possible, yet 'corn kernel oil' would certainly cost a lot to generate because of due to the low levels of oil inside the kernels. Generally because corn kernels possess high levels of starch (60-75%), a process of 'wet milling' originated to segregate genuine starch effectively from corn kernels. The initial corn wet mill within the US began to generate corn starch in 1842 through 1860 various corn wet mills had been in operation (Gunstone, 2002).

Equally opposed to those oilseeds, wherever solvent extraction alone may be used in order to acquire oils, extraction after flaking of wet milled corn germ generates significant amounts of 'fines' which conflict along with the productivity of the extraction procedure. Normally, oil is extracted through the wet milled germ by applying a conditioning (heating) technique, followed out by mechanical expelling (prepress) and also hexane extraction. Recently, extrusion had been applied as signifies of germ preparing for solvent extraction, building up a crude corn oil in term of finest tone and high output. (Maza, 2001). Others have demonstrated the fact that corn seed are usually, productively extracted via supercritical fluid extraction. (Rónyai, et al., 1998).

2.2.3 Canola Oil

Canola oil contains the least amount of saturated fat of any common edible oil with just 7% saturated fat, Canola oil is 93% healthy monounsaturated and polyunsaturated fats. Canola oil is made by crushing the seeds of canola plants, which are grown in the Canada, United States and other parts of the world. Canola was developed in Canada in the 1970's. The name "canola" is a contraction of "Canadian oil, low acid" saturated fat and minimal trans fat intake (Saeidnia & Gohari, 2012).

Canola was initially produced via traditional plant reproduction by rapeseed, which specifically an oilseed plant already have been implemented during historic civilization as the fuel. The phrase "rape" in rapeseed derives from the Latin word "rapum" indicating turnip (Saeidnia & Gohari, 2012).

Canola oil is grown in a producing center by marginally heating and next crushing the seed will be performed. Almost all commercially produced standard canola oil is then purified through the use of hexane (Khattab, et al., 2012).

The crude oil is polished by implementing water precipitation as well as organic acid, "bleaching" with clay, and deodorizing via steam distillation. About 43% of a seed are oil component. The remnant is a rapeseed meal which makes function as high quality animal feed (Saeidnia & Gohari, 2012). Canola oil is considered as an important ingredient in numerous food industries. Its track record as a healthy oil has produced an important request in market segments all over the globe (Gunstone, 2004). Canola oil is more promising source for manufacturing biodiesel than the natural oil as a renewable alternative to fossil fuels because of the lower levels of the toxic and irritating properties of genetically modified rapeseed oil (Khattab, et al., 2012)

2.3 Factors Affecting the Selection of Lubricant

2.3.1 Oxidation Stability

The better immunity of lubricant towards oxidation, the tendency it to develop into sludge, deposits, as well as corrosive byproducts in grease, engine oil plus industrial oil applications can be downplayed (Bart, et al., 2013).

The majority of vegetable oils are normally triglyceride esters (triacylglycerols) of diverse fatty acids together with a small number of exclusions like jojoba oil (Jayadas & Nair, 2006). Unsaturated oils interact with oxygen via a free radical approach to produce product of hydro peroxides, which subsequently decompose thereafter crosslink to produce polymeric gels. This system is called autoxidation (Dugmore & Stark, 2014).

Vegetable oil oxidation has been adverted to in terminology of primary as well as secondary points (Rudnick & Erhan, 2006). The primary stage consists of the free-radical development of hydro peroxides within the fatty acid portions in the molecule. In the secondary stage, after adequate accumulation of the hydro peroxide concentration, the decomposition to form alcohols, aldehydes, and ketones along with volatile decomposition byproducts (Rudnick & Erhan, 2006).

Oxidation characteristics considered experimentally have a tendency to be used to predict lubricant life span within excessive temperature including different excessive applications (Rudnick & Erhan, 2006).

2.3.2 Viscosity

The amphiphilic properties that result from the fatty acid composition of vegetable oils contribute to a better lubricity and effectiveness as anti-wear compounds than mineral or synthetic lubricant oils (Quinchia, et al., 2014).

For thicker fluid films, a combination of higher viscosity and higher pressure–viscosity coefficient are desirable. Both these properties are affected by the molecular structure of the lubricant. Linear and flexible structures provide better viscosity–temperature characteristics compared to the branched and rigid structures. The branched and rigid structures have higher pressure, viscosity coefficients at a given temperature (Quinchia, et al., 2014).

Whenever indicating an oil for any certain application, the viscosity concerning to lubricating oils is sure one of the most important attributes. The chemical composition in the vegetable oil influences the current properties of the petroleum. For instance, in case a fluid oil, which is drawn up to a considerable amount of oleic, linoleic, or linoleic acids or other unsaturated elements is hydrogenated in order to get a saturated variation, the brand new substance would possess the traits of grease (Rudnick & Erhan, 2006).