VOL. 10, NO. 15, AUGUST 2015 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

www.arpnjournals.com

PHYSICAL PROPERTY MODIFICATION OF VEGETABLE OIL AS BIO-LUBRICANT USING ZDDP

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ABSTRACT

The need for development of new green lubricant is in the limelight of researchers today. This is due to the fact that, the existing mineral based lubricants are of non-renewable sources and prone to environmental issues. This paper reports the physical property improvement of canola oil and corn oil with the addition of Zinc Dialkyldithiophosphate (ZDDP) as anti-wear agent. Samples with addition of 0wt%, 2 wt% and 5 wt% ZDDP were prepared and tested using RDE-AES spectrometer and a heated viscometer. The samples were then characterized using a pin-on-disc tribometer. Corn oil has a lower kinematic viscosity value compared to canola oil and gives a lower kinematic viscosity value of 36.3 cSt with the addition of 2 wt% ZDDP. The addition of 2 wt% ZDDP in corn oil and canola oil proves to lower the coefficient of friction for both type of oil. The results showed that it is feasible to continue the study on addition of ZDDP in vegetable based oil for substitution to mineral based lubricant oil.

Keywords: Bio-lubricant, corn oil, canola oil, ZDDP.

1. INTRODUCTION

Lubricant is substance that can ensure two or more surfaces in relative motion do not contact each other in form of oil, grease or soap. According to Bannister (1996), lubricant also is a substance that can reduce friction, heat production and wear by forming a fluid film between the surfaces. This will avoid the surfaces in contact each other thus friction and heat production can be reduced. Long time ago, animal fat has been used by farmers to lubricate the axles of their ox (Nehal and Amal, 2011). On other note, studies by Pirro, *et al.* (2001) reported that, as early as 1400 B.C., combination of calcium and fats produce grease which then was used to lubricate chariot wheels. During 16th century, lubricant use is form vegetable oils, animal oils, or mixture of two (Anderson, 1991). There use beeswax, animal tallow and water to lubricated wooden chart wheels and bearing. It is believed that, lubricant already has been used by people thousand years ago and it is upgraded along time to time to fulfill today needs.

During 19th century, every industrial machines changed and it transformed by technology to improve an economic and culture conditions of the time. The century was known as Industrial Revolution (Suhane, *et al.* 2012). In this era, petroleum based lubricants was quickly dominated the field (Anderson, 1991). Grease oil has been upgraded by combinations of petroleum oils with calcium, potassium and sodium soaps (Pirro, *et al.* 2001). This makes mineral oil started to be used widely and the price is reasonable. Thus it makes the price of natural oil more expensive then mineral oil as mineral oil are more stable and easy to get in large quantity. Besides that the development of larger machines used at greater speed led to specialization in lubricating materials. Therefore, in 1930s serious effort was taken to develop synthetic lubricant. This is because synthetic lubricant provides excellent viscosity properties thus retaining their viscosity over wide temperature range. As example silicone polymer which has superior viscosity temperature properties and it is used for lubrication at high temperature (Anderson, 1991).

Mineral oil based lubricant are seen to be one of the contributor to environmental pollution. This problem occur when the wasted oil produced and their subsequent disposal cause serious environmental hazards. These hazards typically are in the hydraulic, agriculture, mining and petrochemical industries (Mahipal, *et al.* 2014). Besides that, Erhan *et al.* (2006) in his studies reported that the existing mineral base oil is not biodegradable. Therefore, this study will involve of use of vegetable oil as a replacement for mineral based oil as alternative to overcome these issues.

Vegetable oil characteristic which are biodegradable and originate from a renewable source makes it a suitable substitute to mineral oil as lubricant. Vegetable oils typically have most of the desirable properties such as high viscosity index, high lubricity, high flash point, bio-degradability and low toxicity with regard to their use as base oils for lubricants (Anand, *et al.* 2014). However, there are some disadvantages of using vegetable oil as lubricant. According to Liu, *et al.* (2014), one of the problems of vegetable oils is their poor oxidation stability. This is the biggest problem carried by vegetable oil because it causes an increase in oil acidity, viscosity, corrosion and volatility in order to make them as lubricant.

A number of researcher found that an antioxidant additive Zinc Dialkyldithiophosphate (ZDDP) can be a solution regard to vegetable oil as lubricant. This is because ZDDP has an outstanding performance as antioxidant agent (Erhan *et al.* 2006). Besides that, ZDDP also has abilities as radical scavenger and hydroperoxide decomposer (Erhan *et al.* 2006). Therefore, these findings can be a modification to form other alternative oil, which

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is an improvement of vegetable oil generally corn oil for this study. On other note, studies by Erhan *et al.* (2006) reported that, mixture of additive ZDDP improved the oxidation stability of vegetable oil. Therefore, the selection of Zinc Dialkyldithiophosphate (ZDDP) as anti-oxidizing agent will be used in this study to blend with commercializes corn oil to overcome the problem and enhance the lubricant properties.

2. METHODOLOGY

In this study, commercialized cooking corn oil and canola oil are chosen as the parent of the lubricant in order to produce a new bio-lubricant. Zinc dialkyldithiophosphate (ZDDP) is chosen as additive to be blended with corn oil and canola oil to enhance the performance of the present oil. A concentration of 0 wt%, 2 wt% and 5 wt% of ZDDP were added to corn oil and canola oil. The prepared samples were then immersed in a 50°C water bath for 20 minutes to ensure that ZDDP is properly dissolved into the parent base oil. After sample preparation, the samples were tested using rotating disc electrode atomic emission spectroscopy (RDE-AES) which is automatically monitored by spectroil software. This test method determines the concentration of wear metals and contaminants in used lubricating oils. In this study, this method was chosen in order to determine the concentration of zinc and phosphorous added into the parent base oil via addition of ZDDP.

The samples were also tested using a Kittiwake heated viscometer in order to determine the kinematic viscosity at 40°C. Then, the samples were characterized using a pin-on disc friction tribometer. Load at 5N, 10N, 15N and 20N were applied in order to determine the coefficient of friction of the prepared samples. The sliding distance of tribometer was fixed at 1000 meter. Flat ended aluminum pin with a diameter of 4 mm and length of 30 mm were machined and used in determining the coefficient of friction. Wear coefficient for both the pin and samples were calculated from the volume of the material lost during the friction run.

3. RESULTS AND DISCUSSION

a) Concentration of Phosphorous and Zinc

Addition of ZDDP into the parent corn and canola oil was tested for the concentration of Zinc and Phosphorous using an RDE-AES spectroscopy. From Table 1, it is evident that the concentration of Zinc at 0 wt% addition in corn oil stated at < 1 ppm and phosphorous stands at 19 ppm at the same concentration of ZDDP. As the concentration of ZDDP increases to 2 wt%, the concentration of zinc and phosphorous increases to 1246 ppm and 1321 ppm respectively. Further increment of ZDDP concentration to 5 wt% showed a tremendous increment in the concentration of zinc and phosphorous where it increases to 3076 ppm for zinc and 4413 ppm for phosphorous.

On the other hand, the concentration of zinc for canola oil without any addition of ZDDP stands at <1 ppm while showing 14 ppm for phosphorous. With the addition of 2 wt% of ZDDP, the concentration of zinc and phosphorous increases to 1412 ppm and 1399 ppm respectively. The concentrations of zinc and phosphorous increased further to 2816 ppm and 3894 ppm when the concentration of ZDDP was increased to 5 wt% in canola oil.

Zinc Dialkydithiophosphates were originally prepared by reacting various types of alcohols with phosphorus pentasulfide (P_2S_5), then neutralizing the resultant intermediate with zinc oxide to give the product (Johnson, 2013). Henceforth, the two elements which were examined using an RDE spectroscopy which is Phosphorous and Zinc were determined to see the effectiveness of dilution.

From Table-1 it is evident that, with an increasing percentage of ZDDP in the oil, it will eventually give a positive increment of zinc and phosphorous concentration. This could suggest that ZDDP has been completely diluted into the parent corn and canola oil.

b) Effect on kinematic viscosity

The prepared samples were tested using heated viscometer at 40°C to investigate the kinematic viscosity. Figure-1 shows the kinematic viscosity of three different concentrations of both oil tested using heated viscometer. The kinematic viscosity for pure corn oil was observed at 37.3 cSt. However, with the addition of 2 wt% of ZDDP to the oil, the kinematic viscosity of corn oil reduced to 36.3 cST. The value of kinematic viscosity at 40°C of corn oil with 5 wt%

Table-1. Concentrations of Zinc and Phosphorous with addition of 0 wt%, 2 wt% and 5 wt% ZDDP in Corn Oil and Canola Oil.

Properties	Corn			Canola		
	0 wt%	2 wt%	5 wt%	0 wt%	2 wt%	5 wt%
Zinc	<1ppm	1246ppm	3076ppm	< 1ppm	1412ppm	2816ppm
Phosphorous	19ppm	1321ppm	4413ppm	14ppm	1399ppm	3894ppm

on the other hand, increases to 37.9 cST. The same trend of kinematic viscosity was observed on canola oil. Pure canola oil showed a kinematic viscosity value of 4.03 cSt. The value decreases to 38.6 cSt when added with 2 wt% ZDDP while increases tremendously to 43.7 cST when added with 5 wt% ZDDP. It also observed for 2 wt% of

VOL. 10, NO. 15, AUGUST 2015 ISSN 1819-6608
ARPN Journal of Engineering and Applied Sciences

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ZDDP which indicate the lowest kinematic viscosity value which is 38.64 cSt. Corn oil without any ZDDP additive showed 40.33 cSt in kinematic viscosity value. The value of kinematic viscosity at 40ºC of canola oil with 0 wt% of ZDDP was observed at 40.33 cSt. After canola oil was added with 2 wt% of ZDDP, the value of kinematic viscosity was then reduces to 38.63 cSt. Then, with addition of 5 wt% of ZDDP was increased the value of kinematic viscosity to 43.73 cSt. It shows that the lowest value of kinematic viscosity at addition of 2 wt% of ZDDP, produce the newly developed bio-lubricant oil.

The lowest value of kinematic viscosity present in the oil contains various metals, mainly zinc metal. Zinc created a boundary film which formed on the metal surfaces contacting. This film acts as a friction modification agent showing that ZDDP additives in the right amount are beneficial (Mahipal, *et al.* 2014). However, the kinematic viscosity of corn oil with 5 wt% of ZDDP showed a higher value. At higher concentration, the excess ZDDP effect on the boundary film formation. This problem make more film is formed on metal and this condition may contribute to the increase of the kinematic viscosity due to the excess of the metal present in the oil (Hutchings, 1992).

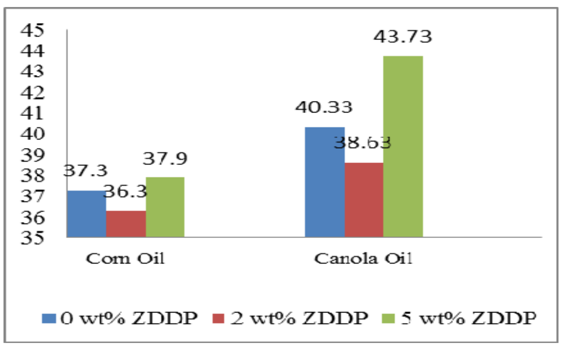

Figure-1. Kinematic Viscosity Value for Corn Oil and Canola Oil with Addition of 0 wt%, 2 wt% and 5 wt% ZDDP.

c) Effect on coefficient of friction

Figure-2 and Figure-3 show the Coefficient of Friction of three different concentrations of oil tested using a pin-on disc friction tribometer for Corn Oil and canola oil. Friction coefficient decreased with increasing applied load was shown in 2 wt% and 5 wt% of ZDDP in corn oil. While on the other hand, the coefficient of friction in 0 wt% of ZDDP increasing with applied load. It can correctly be said that with the existence of ZDDP in the corn oil, will give a good antifriction behavior. The value of coefficient of friction at addition of 2 wt% of ZDDP in corn oil, it is seen to read at 0.42 when 5N load was applied. The value of coefficient of friction fell steadily to 0.38 at 10N while the trending of decrement continues with the increment of applied load which is 0.33 value of coefficient of friction for 15N load applied. The value of coefficient of friction remains constant at 0.33 when 20N of load was applied.

On the other hand, the value of coefficient of friction for addition of 2 wt% of ZDDP in canola oil at 5N load applied reads at 0.41. The value of coefficient of friction increased when 10N of load was applied to 0.43. When addition 15N of load was applied, the coefficient of friction is seen to be decreased to 0.37 while the value remains decreasing to 0.35 when 20N of load was added. This could prove that the addition of ZDDP to both oils increase the effectiveness of anti-friction.

The addition of ZDDP helps to form a reaction film where this film acts as a mechanical protective barrier between the two contacting surfaces. This will help to reduce the frictional torque of the contacting surfaces with the addition of ZDDP at 2 wt%. The reduction of frictional torque will lead to a lower coefficient of friction (Mahipal, 2014). From the results, it is evident that at 5 wt% of ZDDP addition, the coefficient of friction has increased. At higher ZDDP concentration, the boundary film formation is affected. The adverse effect of the boundary layer is due to the fact of the presence of excess zinc adsorption on the contact surfaces. This leads to an increment of frictional torque of the contacting surfaces leading to an increase of coefficient of friction.

Figure-2. Coefficient of Friction for Corn Oil with Addition of 0 wt%, 2 wt% and 5 wt% ZDDP.

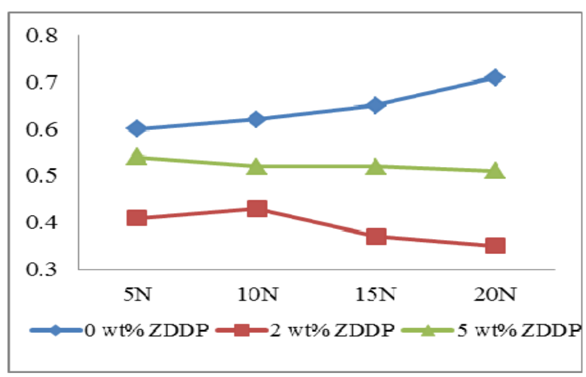

Figure-3: Coefficient of Friction for Canola Oil with Addition of 0 wt%, 2 wt% and 5 wt% ZDDP.

4. CONCLUSIONS

In conclusion, three different concentration of ZDDP were effectively added to corn oil and canola oil and proven by RDE spectroscopy. Corn oil and canola oil

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with 2 wt% ZDDP showed the most effective concentration as it shows the lowest reading of kinematic viscosity at 40ºC of 36.3 and 38.6 respectively. Stable behavior of the friction coefficient was found in 2 wt% of ZDDP in corn oil and canola oil as it shows the smallest value of friction coefficient. The newly found results would encourage further studies on green bio-lubricants.

ACKNOWLEDGEMENTS

The author would like to acknowledge the Ministry of Science Technology and Innovation [FRGS/2013/FTK/TK06/02/3/F00166] and Universiti Teknikal Malaysia Melaka for the support and funding throughout this study.

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