Oxidation Stability Comparison between Zinc Dialkyldithiophosphate and Zinc Diamyldithiocarbarmate Induced Palm Oil Bio-lubricants

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ABSTRACT

The environmental impact imposed by mineral based lubricant and the threat of petroleum depletion has triggered this study to search for an alternative lubricant using commercialized palm oil. The low oxidation stability of vegetable oil limits the performance of palm oil as a lubricant. This study introduces Zinc Dialkyldithiophosphate (ZDDP) and Zinc Diamlydithiocarbamate (ZDDC) into commercialized palm oil at different concentrations to investigate the effect of oxidation stability using a Rotating Pressure Vessel Oxidation Test. This study discovered that ZDDP displayed a better performance compared to ZDDC in terms of oxidation stability where it exhibited a longer oxidation time of 128 minutes at a concentration of 2 wt%. It can be concluded that the addition of organo zinc compound had improved the oxidation stability of commercialized palm oil as lubricant.

Keywords: *Palm oil, ZDDP, ZDDC, Bio-lubricant*

Introduction

Lubricant is a substance that is applied between two contacting surfaces to reduce friction, minimize wear and reduce heat [1]. At present, most of the lubricant used either domestically or in the industry is derived from petroleum sources. With the current scenario of unstable petroleum crude

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prices due to the depletion of sources, added with the adverse environmental effect that the mineral based lubricant imposed on the environment, several studies have been done in order to search for an alternative substitute to petroleum based lubricant [2].

To date, numerous studies have been conducted by researchers to replace petroleum based lubricant. The most suitable candidate as base stock is seen to be oils derived from vegetable sources. Vegetable oil based lubricant are non-toxic and biodegradable compared to conventional petroleum based lubricant [3]. Vegetable oil also exhibits good properties, such as excellent lubricity, high viscosity index and high flash point that makes vegetable oil a suitable candidate to replace petroleum as base stock for lubricant production [4]. Lubricant derived from vegetable and animal fats have been used since 1650 BC where the Egyptians used animal fats to lubricate wheels of chariots and whale fats were used to lubricate equipment and other machinery [5]. However, these superior characteristics that vegetable oil possess has a weakness as vegetable consist of mono and poly unsaturated fats. According to Azhari et al., the high substance of unsaturated fats in vegetable oils makes the oil less cooperative to stabilize any oxidation process [6]. Heat and oxygen from lubrication process will accelerate the oxidation process of vegetable oil based lubricant. In general, oxidation starts with an initiation process when an external force separating the hydrogen from the chain producing free radicals. The free radicals will then react with oxygen to produce peroxy radicals. Following the next steps of oxidation process is propagation process. In this process, peroxide radicals will form more radicals through reaction with more components in the lubricants. The completion of branching and termination process in oxidation will result in a longer chain of carbon molecules [7]. The steps of oxidation are displayed as in Table 1.

Oxidation needs to be delayed if not suppressed as oxidation will reduce the function of lubricant in lubrication process. The process of oxidation will cause the kinematic viscosity of oil to increase and this will contribute the increment of friction and wear on the internal surfaces of the machine.

This oxidation process may be suppressed by using anti-oxidant additives. Organo zinc compounds such as Zinc dialkyldithiophosphate (ZDDP) and Zinc diamyldithiocarbarmate (ZDDC) can be used as an anti-oxidizing agents and it also improves anti-oxidation performance in lubricating oil [8]. Antioxidants are added into lubricant base stocks in order to decrease the rate of oxidation in lubricating oil which is particularly important at elevated temperature [9]. Apart from that antioxidants end these chain responsed by most likely uprooting free radical intermediates, or by being oxidizing themselves. Consequently, most cell reinforcements are frequently decreasing agents [10].

Table 1: Lubricating oil oxidation process

Steps	**Equation**
Initiation	RH → R● + H●
	R● + O_2 → ROO●
Propagation	ROO● + RH → ROOH + R●
	ROOH → RO● +●OH
Branching	RO● + RH → ROH + R●
	●OH + RH → H_2O + R●
Termination	R● + R● → R-R

While adding anti-oxidation agent is seem necessary to reduce the oxidation process upon lubricants, concentrations of the anti-oxidants added shall be controlled. Azhari et al., and Mahipal et al., studied the desirable concentrations of zinc additives in vegetable oil to investigate the improvement of tribological properties with the addition of ZDDP [11, 3]. From the studies, it is evident that the most desirable concentrations of ZDDP to be added into any type of vegetable oil shall be at 2 wt% or below. Therefore this study investigated the effect of different organo zinc substance which is ZDDP and ZDDC on the suppression of oxidation in vegetable oil based lubricant with addition of additive not more than 2 wt%.

Methodology

Commercial palm oil was purchased from local store and used as is. ZDDP and ZDDC was purchased and used without any prior modification. Seven samples were prepared with variation of zinc additives and concentration. ZDDP was added into commercialized palm oil at 1.2 wt%, 1.6 wt% and 2 wt% concentration. ZDDC was also introduced to the commercialized palm oil at the same concentration. A control sample with 0 wt% addition of additive was also prepared using the same commercialized palm oil. Upon introduction of additives, the samples were immersed in a heated water bath at 50°C for 20 minutes to ensure dilution.

After sample preparation, the samples were then tested for oxidation properties using a Rotating Pressure Vessel Oxidation Test in accordance to ASTM D2272. The samples were pressurized to 90 psi with oxygen and thermally heated to 150°C using steel pressure of water and copper coil catalysts reached a pressure drop of 25 psi was seen.

Result and Discussion

The samples were tested using a rotating pressure vessel oxidation test to investigate the oxidation stability of the lubricant oil added with ZDDP and ZDDC additives. The result of each oxidation test is per tabulated in Table 2 and depicted as in Figure 1.

Table 2: Rotating Pressure Vessel Oxidation Test

Sample	Time Taken (minutes)
Pure Palm Oil	32
1.2wt% ZDDC	52
1.6wt% ZDDC	59
2.0wt% ZDDC	62
1.2wt% ZDDP	111
1.6wt% ZDDP	124
2.0wt% ZDDP	128

From the experiments, it is evident that the oxidation time for pure palm oil reads at 32 minutes. This is clear that the pure palm oil takes a very short time to completely oxidize during the oxidation test. However, with the addition of ZDDC, the time taken for palm oil to oxidize gradually increase. At a concentration of 1.2 wt% ZDDC, the time taken for the sample to completely oxidize was recorded at 52 minutes. However, at 1.6 wt% and 2.0 wt%, the oxidizing time for the samples continue to increase to 56 and 62 minutes respectively. This shows that the oxidation stability of the samples added with ZDDC are improved with the presence of Anti-oxidizing agent ZDDC. The additive ZDDC is known to mutually function as a radical scavenger and hydroperoxide decomposer. It transforms the hydroperoxide formed throughout the oxidation process to non-radical products, thus avoiding chain propagation. The mechanism of oxidation inhibition by ZDDC consists of complex reactions between alkylperoxy radicals, organic hydroperoxides and intermediate decomposition products of initial compounds [13].

The bio-lubricant recorded a longer time to fully oxidize when induced with ZDDP additives. When the palm oil bio-lubricants were added with 1.2wt% concentration of ZDDP additives, the sample showed an increment of oxidation time to 111 minutes. Through further addition of ZDDP additives at 1.6wt% concentration, the palm oil bio-lubricant completely oxidized at 124 minutes. With the addition of ZDDP additives at

2.0wt% concentration, the samples of newly developed bio-lubricant shows an increment of time which was found to be oxidized at 128 minutes. It can be observed that the ZDDP samples are more effective in slowing down the oxidation reaction as it took longer time for the samples to be fully oxidized comparing with the samples added with ZDDC. This is because ZDDP has a presence of sulphides, where these sulphides decelerated the initiation of new radical chain. When hydroperoxides react with hyroperoxide decomposer with sulfides, it will produce alcohols and sulfoxides. This enables the sulfoxides to react much further and eliminate additional equivalents of hydroperoxides in complex chain of reaction. Therefore the oxidation process can be slowed down [14]. The oxidation stability of vegetable oils are improved with the presence of additives. The introduction of antioxidant is capable to resolve the oxidative stability drawbacks in vegetable based oil [7]. This also supported by Hu et al., that ZDDP is an effective anti-oxidant additives [15].

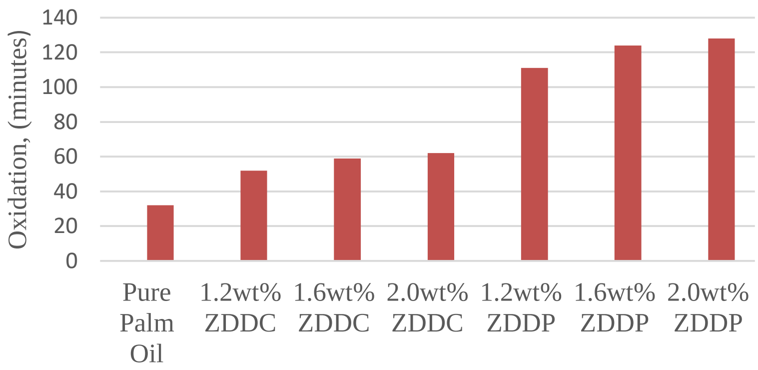

Figure1: Oxidation Time of New Bio-Lubricant

Conclusions

Oxidation in lubricant oil shall be suppressed in order to increase the performance of a lubricant. In this study the addition of ZDDP and ZDDC has increased the oxidation time of palm oil based bio-lubricant. However, this study discovered that the addition of ZDDP at 2 wt% displayed a better oxidation time compared to other concentrations of additives added to the commercialized palm oil.

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