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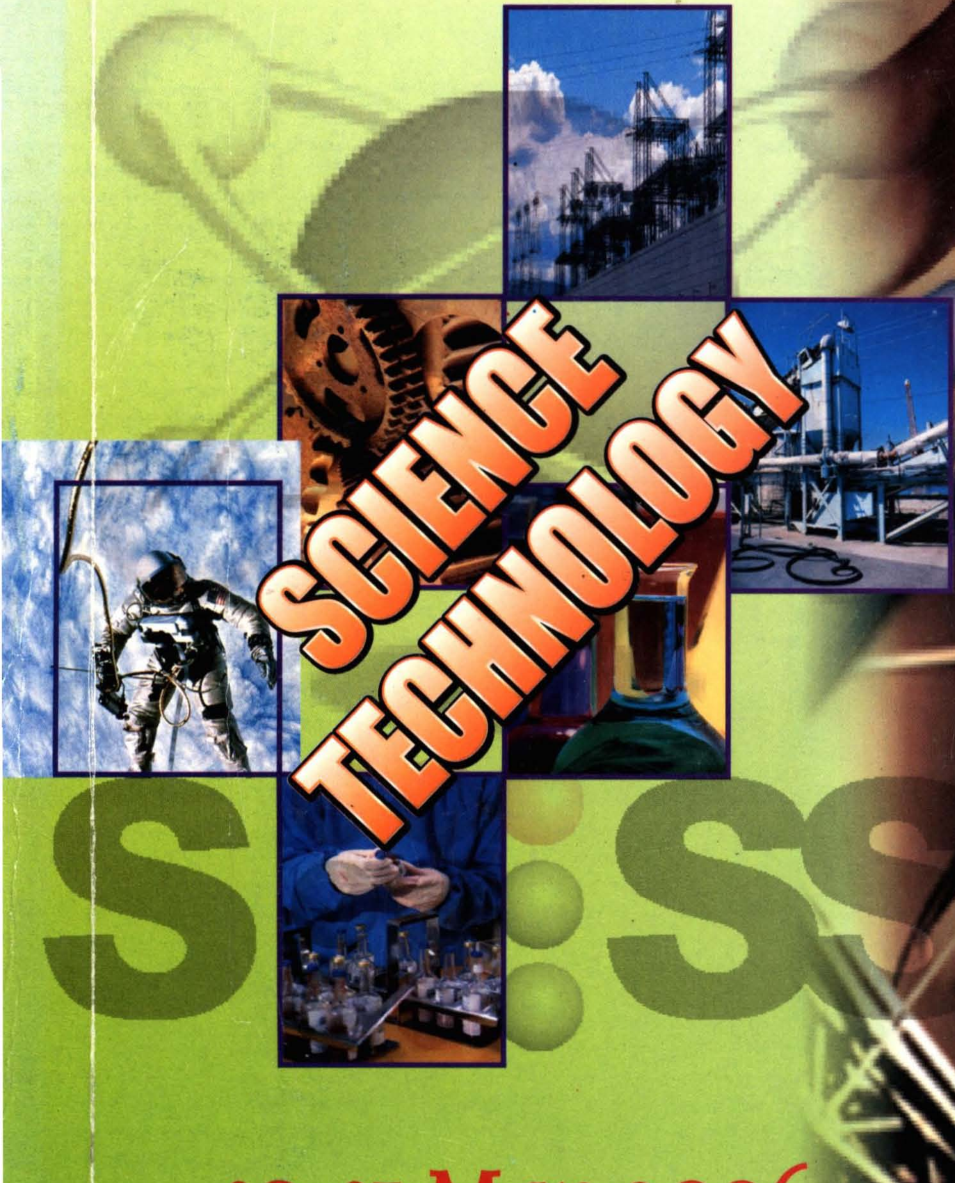

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Oxidation Performance of Plant Oil as Hydraulic Fluid

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ABSTRACT

Although petroleum based oils have been traditionally the most commonly used hydraulic fluid in the fluid power industry, they are being subjected to ever increasing controls particularly due to the increasingly stringent government regulations regarding their use. In response to the stringent controls, non-petroleum based fluid should be used. In this study an experimental evaluation of palm oil as alternative hydraulic fluid has been performed. The effect of additives towards the oxidative and thermal stability of palm oil was evaluated. Two types of commercial additives which are Irgalube F10 and Irganox L135 with different percentages were used during the experiment. Analysis conducted proved that addition of additives which act as antioxidant play an important role in improving thermal and oxidative stability of the palm oil.

Keywords: *Additive, antioxidant, thermal-oxidative stability*

Introduction

Vegetable oils with both applications in food and non-food sectors are getting much attention in future planning. In the past two decades, the concern over the usage of petroleum-based products or mineral oils and their negative impact on environment has created an opportunity to produce lubricants derived from natural esters like vegetable oils (Choi et al. 1997). For the present, vegetable oil are readily available and their prices are depressed but as petrochemical prices continue to increase, greater demands will be made upon vegetable oil for feedstock (Salunkhe et al. 1992).

Thus, alternatives have been reviewed to commercialize vegetable oils in non-food applications such as manufacture of lubricants and hydraulic fluids. However, the major limitations of thermal and oxidative stability need to be addressed. These problems can be overcome by adding additives, genetic modification or chemical modification of the oil.

In Europe, the most common vegetable oil used is canola. Other vegetable oils such as sunflower oil are also used and recently soybean has received a lot of attention in the US. Chemically, all these oils are triglyceride esters. Edible oil consist mainly (95%) of tryacylglycerol and 5% non-tryacylglycerol. These components might be important to its oxidative stability which presence in each oil (Ahmed et al. 2003). They have excellent lubrication and ecotoxicological properties. However their oxidation and thermal stability is limited due to their high level of polyunsaturated fatty acids and the presence of a hydrogen atom in beta position (Bunemann et. al.1998).

The major concern that limits the use of vegetable oil as lubricating fluids is oxidation which leads to polymerization and degradation. Polymerization can increase the viscosity which reduces lubrication functionality while degradation will lead to breakdown products that are volatile, corrosive and diminish the structure and properties of lubricants.

The most common mechanism of oxidation is a free radical chain reaction where autoxidation proceeds in three distinct steps (Kowalski et al. 1997): initiation, propagation and termination. Initiation of the reaction starts with formation of lipid radicals from lipid molecules. Propagation occurs when one lipid radical is converted to a different lipid radical involving abstraction of a hydrogen atom from a lipid molecule or addition of oxygen to an alkyl radical. During termination reaction, free radicals combine to form stable and non-radical compounds with a full complement of electrons. The auto-oxidation process of edible oils is a chain process reaction and can be described by the reaction below (Litwinienko & Kasprzycka-Guttman 1998).

$$\text{Initiation} \quad RH \longrightarrow R^{\bullet} + H^{\bullet}$$

$$\text{Propagation} \quad R^{\bullet} + O_2 \longrightarrow ROO^{\bullet}$$

$$ROO^{\bullet} + RH \longrightarrow ROOH + R^{\bullet}$$

$$\text{Termination} \quad R^{\bullet} + R^{\bullet} \longrightarrow R{-}R$$

$$R^{\bullet} + ROO^{\bullet} \longrightarrow ROOR$$

$$ROO^{\bullet} + ROO^{\bullet} \longrightarrow O_2 + ROOR$$

During oxidation process, alkoxy radicals formed by hydroperoxyde decomposition can decompose to release volatile hydrocarbons, alcohols or aldehydes as secondary products which contribute to increase of acid and peroxide value of the oil.

An additive is a substance added to another substance or material to improve its properties in some way and known able to prevent corrosion, act as antiwear, stabilizing polymer and as an antioxidant. In this study, effect of additive on the oxidative and thermal stability of palm oil was investigated.

Materials and Methods

Materials

The samples that were used are palm super olein (PO). Rapeseed oil (RO) and Mobil EAL 224H were used as references. Palm super olein was blended with additives 1.5% Irgalube F10 (PO + 1.5% F10), 2.0% Irgalube F10 (PO + 2.0% F10) and 1.5% Irganox L135 (PO + 1.5% L135) by using weight to weight ratio. After blending with additives, samples were stirred by magnetic stirrer to ensure homogenous mixture.

Thermo-oxidation Method

This test was conducted by heating the oil samples in an oil bath at 95°C for 792 hours. Samples were collected at 0, 48, 96, 192, 288, 384, 504, 600, 696 and 792 hours.

Acid Value and Iodine Value Test

The acid value was conducted according to standard method AOCS Cd 3a-63. Blank titration is the volume of potassium hydroxide used to neutralize the mixture of 25ml diethyl ether and 25ml ethanol with 1ml of 1% phenolphthalein. An AOCS Te 2a-64 method was used to determine iodine value for each oil sample. Each value was measured in duplicate to ensure precise data were obtained.

Infrared Spectroscopic Analysis

A film of approximately 8μl of sample was deposited on a KBr disc without presence of air. All spectra were recorded from 4000 to 400 cm^{-1} by using a Fourier Transform Infrared (FTIR) spectrophotometer (Spectrum GX).

Thermogravimetry Analysis (TGA)

Thermogravimetric analysis (TGA) provides a quantitative measurement of any weight change with thermally induced transitions. TGA was performed using Perkin Elmer Pyris 6 TGA at a heating rate of 5°C/min. Sample of approximately 15mg was heated from 30°C to 52°C. The instrument was purged with nitrogen flow at a rate of 20.00 ml/min.

Viscosity Test

Viscosity was measured by using Brookfield DV-1+ viscometer.

Results and Discussion

Acid and Iodine Value Analysis

Acid value (AV) test was conducted to indicate relative changes that occur in oil during oxidation process. AV test showed that the total acid number (TAN) for all oil samples increased after heating in oil bath at 95°C. It has been shown that the increase in TAN is correlated with the hours of heating. Reaction rate at early stage was very slow as oxidation depends on the amount of free radical form at reaction environment. Compared to pure palm oil, rapeseed oil showed a lower acid values, but TAN of rapeseed oil increased rapidly after 600 hours of heating. This sudden increase can be contributed by the rapid formation of hydroperoxides and its secondary products such as alcohols, ketones, aldehydes and carboxylic acids due to thermo-oxidation process. Palm oil blended with additives showed lower acid value compared to pure palm oil and rapeseed oil. This proved that additives are able to act as antioxidant when added to palm oil.

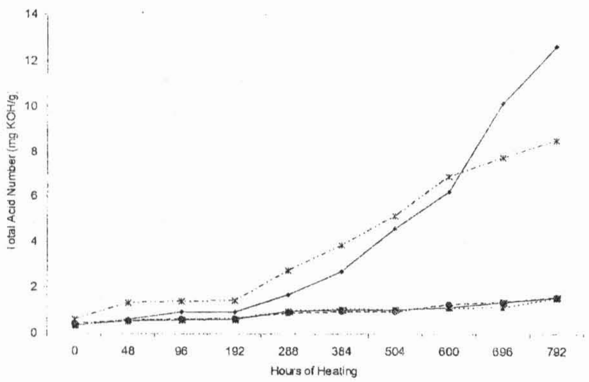

Fig. 1: Variation of Total Acid Number (TAN) with Hours of Heating for Palm Oil (-♦-), Rapeseed Oil (-x-) and Palm Oil with Additives; 1.5% F10 (-■-), 2.0% F10 (-▲-) and 1.5% L135 (-●-)

Iodine value (IV) test shows that iodine value decreased after heating in oil bath at 95°C for 792 hours (Table 1). A decrease in iodine value is due to the destruction of double bonds by oxidation. Heating process will provide energy to excite the molecules of oil giving molecules enough energy to break down the double bond in the chain. This mostly happened at unsaturated bond forming the saturated structure. The tendency of hydrogen allylic to oxidize will enable formation of peroxide in cyclic form. This will cause the decrease of double bond in oil sample.

Table 1: Iodine value for palm oil with and without additives and rapeseed oil

Samples	0 hour	792 hour
SO	59.44	42.97
SO + 1.5% F10	61.64	57.65
SO + 2.0% F10	59.03	58.03
SO + 1.5% L135	60.41	55.80
RO	87.66	71.51

Infrared Spectroscopic Analysis

This analysis was conducted to determine the main functional groups presents in oil samples before and after heating. Overall, palm oil blended with additives showed better stability against thermal-oxidation with less expansion of the overtone region and less decrease of the intensity of C-H stretching. There is an expansion of the overtone region of C=O stretching due to the formation of hydroperoxides after heating process which can undergo further oxidation process forming aldehyde, ketone, alcohol and acids. There is decreasing intensity of C-H stretching (C=C-H) at 3006 cm^{-1} and the peak is shorter and weaker due to the changes of atom which attached to the C=C from hydrogen to alkyl, carbonyl, or hydroxyl after heating process. The infrared spectrum near 3006 cm^{-1} appears the band of cis double bonds CH groups. The frequency of this band is related to the composition of the oils. Oils with high polyunsaturated acyl group have higher frequency values than those with high monounsaturated or saturated acyl group. During the oxidation process, cis double bonds disappear as well as isomerization of cis to trans group along with hydroperoxide generation. Thus decrease the frequency of this band. Changes during the themo-oxidation process also observed in the region between 1620 cm^{-1} and 1670 cm^{-1} for rapeseed oil

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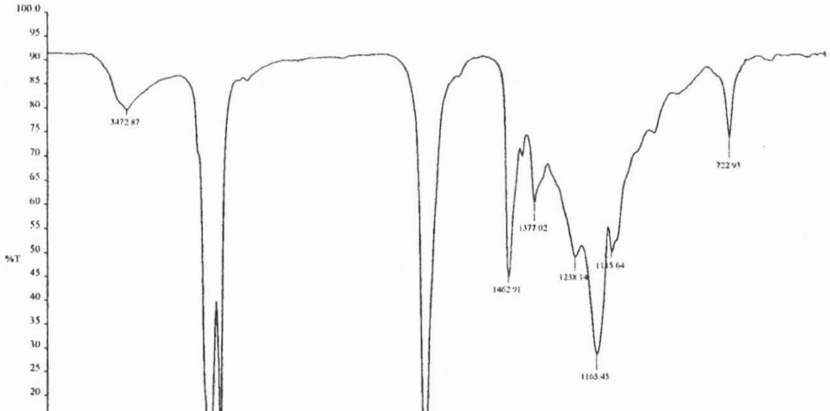

Fig. 2: Infrared Spectra of Palm Oil after 792 Hours of Heating.

Thermogravimetry Analysis

Activation energy is defined as the minimum energy that the molecules have to overcome before a reaction can take place. It was found that the onset temperature for palm olein blended with additives was higher compared to the oil itself. This indicates that with the addition of additives to the oil increases the onset temperature and its ability to act as an antioxidant.

Table 2. Maximum Degradation Temperature for all Samples

Samples	0 hour	792 hours
SO	412.21	408.85
SO + 1.5% F10	415.98	411.19
SO + 2.0% F10	411.64	411.49
SO + 1.5% L135	410.66	410.24
RO	411.85	404.44

Referring to Table 2, palm oil has a slight change of maximum degradation temperature from 412.21°C to 408.85°C. Rapeseed oil showed higher decrease in maximum degradation temperature. This changes show that palm oil is more thermal-oxidatively stable compared to rapeseed oil. This is due to long triglyceride structures and natural antioxidant in palm oil that help to maintain its thermal stability. In this study, palm oil with additives has higher activation energy compared to pure palm oil while the rapeseed oil showed the lowest activation energy after 792 hours of heating. Palm oil with 2.0% F10 showed the highest activation energy after heating compared to all other oil samples. It is obvious that palm oil blended with additives are more thermal oxidatively stable followed by pure palm oil and rapeseed oil.

Viscosity Test

In a liquid, the molecules have limited mobility with large cohesive forces present between the molecules. Changes in chemical condition of oils after heating results in viscosity increase (Figure 3). It was due to the formation of free radicals and the formation of more complex structures. Palm oil super olein showed lower viscosity value compared to rapeseed oil and the palm oil blended with additives showed lower viscosity value than pure palm oil. Viscosity analysis showed that palm oil is more thermal-oxidatively stable compared to rapeseed oil after heating and palm oil blended with additives have the best stability against thermal-oxidative degradation. The lowest viscosity value was obtained by palm oil with 2.0% F10 thus the most effective to maintain the thermal oxidative stability of palm oil.

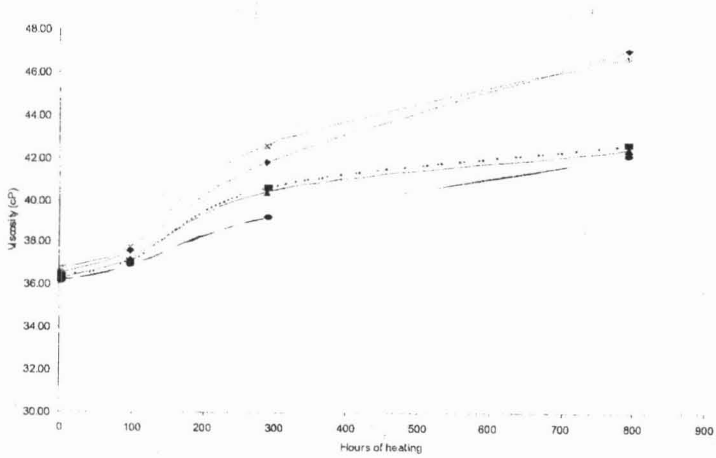

Fig. 3: Viscosity of different samples versus hours of heating. Palm oil (-♦-), rapeseed oil (-x-), palm oil with additives; 1.5% F10 (-▲-), 2.0% F10 (-●-) and 1.5% L135 (-■-)

Conclusion

During the test, it was found that the percentage of additives added to palm oil was able to help maintain the thermal-oxidative stability of Super Olein. 2.0 % F10 was the most suitable amount of additive to help maintain the thermal-oxidative stability of palm oil. The analytical results proved that the oil after heating is more thermal-oxidatively unstable. Physical changes of the oil samples after heating brought to an increase in viscosity values and therefore change the chemical condition of the oil. As a conclusion, presence of additives as antioxidants in the oil samples able to provide better stability against thermal-oxidative degradation, hence improving the thermal-oxidative stability of the oils.

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