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The Study of Wear Behaviour of 12-hydroxystearic Acid in Vegetable Oils

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Abstract: Vegetable oils due to high biodegradability, low toxicity, renewability and excellent lubricating performance, have immense potential to replace mineral oils as feedstock for lubricants. Owing to these aspects environmentalists and engineers have made attempts to explore the possibilities of using vegetable oils as environmentally friendly lubricants for range of applications. In this work, the tribological properties of castor oil and sesame oil in the presence of 12-hydroxystearic acid as anti-wear additive were investigated using four-ball tribometer. The viscosity, acid value, peroxide value and iodine value of the selected oils were determined experimentally following AOCS methods. Results revealed that the addition of 12-hydroxystearic acid improved the anti-wear performance of the selected vegetable oils. Moreover, it was noted from the results that 12-hydroxystearic acid was more effective as anti-wear additive in the castor oil as compared to sesame oil under similar experimental conditions. The improved anti-wear performance of the selected vegetable oils in the presence of additive may be attributed to the formation of protective layer as a result of tribochemical reaction on the metal surface.

Key words: Vegetable oils, wear scar diameter, four-ball tribometer, 12-hydroxystearic acid

INTRODUCTION

There is a growing public interest in environmentally friendly lubricants due to new awareness of environmental problems associated with conventional mineral lubricants (Choi *et al*., 1997). Even though the toxicity of lubricants is low, their accumulation in the environment may cause damage in long run. A large proportion of the lubricants pollute the environment either during or after use. In many countries, there are well defined guidelines and legislations for environmentally friendly lubricants (Zeng *et al*., 2007). Several organizations around the world are working to qualify and improve such lubricants by evaluating their potential for environmental harm. Examples include the German “Blue Angel”, European “Daisy” Eco label, Global Eco-Label “GEN mark”, Nordic, “White Swan”, Japanese “Earth friendly mark”, USA “Green Seal”, Canadian “Environmental Choice”, Chinese “Huan”, Singapore “Green Label” and the French “NF Environment mark”. According to the German “Blue Angel” criteria, environmentally friendly lubricating fluids must not carcinogenic/mutagens, chlorides, nitrites, or metals (except potassium and calcium) (Wang and Hadfield, 2003). Moreover, the biodegradability of base stock must be 80%. Similarly, in Europe the CEC (Coordinating European Council contain) developed the CEC L-33-T-82 biodegradability test for two-stroke engine oils which is gaining acceptance for testing other lubricants.

This is a 21 day test in which the disappearance of oil is measured after being inoculated with activated sewage sludge. Lubricants giving results greater than 80% are considered to be readily biodegradable (Booser, 1994; Denis *et al*., 2000). Mineral oil based lubricants, contain many kinds of additives such as antioxidant agents, anti-wear agents, detergents, dispersants, anti-forms, extreme pressure agents, friction modifiers and viscosity improvers. Some of these additives are toxic and harmful to human health, wildlife and environment (Kleinova *et al*., 2008). The environmental and toxicity

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issues of petroleum-based lubricants and their additives as well as their rising cost related to a global shortage have led to renewed interest in the use of vegetable oils, such as soybean oil, canola oil, sunflower oil, coconut oil sesame oil castor oil etc as environmentally friendly lubricants and industrial fluids (Lathi and Mattiasson, 2007; Rudnick, 2009). Vegetable oils generally possess some excellent lubricating properties, for example, good inherent lubricity, low volatility, high viscosity index, excellent solvency for lubricant additives and easy miscibility with other fluids.

Vegetable oils are chemically triglycerides of fatty acids. The long chain fatty acids and the presence of polar groups in the vegetable oils structures make them excellent base stock for environmentally friendly lubricants (Krzan and Vizintin, 2003). They have better anti-corrosion properties as they have strong affinity to adsorb on the metal surface. However, vegetable oils are known for their poor oxidative stability as compared to mineral oils. In addition, environmentally friendly lubricants need to use additives that satisfy biodegradation and bioaccumulation standards (Adhvayu *et al*., 2004). In this study, the tribological properties of vegetable oils are evaluated in the presence of 12-hydroxystearic acid as environmentally friendly lubricants using four-ball machine.

MATERIALS AND METHODS

Base stock and chemicals: Vegetable oils (castor oil and sesame oil) were purchased from local market and were used without any further treatment as base stock. Steel balls used in this investigation were of 12.5 mm. The entire chemicals used were of A.R. grade.

Viscosity measurement: Viscosity of castor oil and sesame oil was measured using Ubbelhode viscometer having viscometer constant of 0.091 cSt sec^{-1} at 30 and 80°C.

Acid value determination: Acid value for castor oil and sesame oil was determined using the AOCS (1997a) standard method (Ca-5a-40). According to this method, about 2 g of the given oil sample was thoroughly mixed with 25 cm^3 ethanol followed by two drops of phenolphthalein indicator in a titration flask and then titrated against 0.01 N aqueous solution of potassium hydroxide [KOH] until pinkish colour appeared. From the titration data acid value was calculated using the following Equation:

$$\text{Acid value} = N \times V \times \text{Eq. Wt} \times 100/W \times 1000 \quad (1)$$

where, N represents the normality of KOH, V is the volume of KOH used for titration, W is the weight of oil sample (g), and Eq. Wt is the equivalent weight of KOH.

Iodine value determination: Iodine value of the selected vegetable oils was determined by following AOCS (1997b) standard method (Cd 1-25). According to this method, 20 g of oil sample under investigation was dissolved in one litre of chloroform. About 10 cm^3 of this solution was mixed carefully with 25 cm^3 0.2 M iodine monochloride solution in acetic acid in a 250 cm^3 titration flask and was kept Stoppered in dark for an hour with gentle stirring. After one hour about 10 cm^3 of 2.5 M potassium iodide aqueous solution was added to this reaction mixture followed by 50 cm^3 of distilled water and then titrated against 0.1 M sodium thiosulfate $Na_2S_2O_3.5H_2O$ aqueous solution till light brown appeared. To this reaction mixture few drops of starch indicator were added and then titrated against 0.1 M sodium thiosulfate $Na_2S_2O_3.5H_2O$ aqueous solution until the bluish colour disappeared. Blank experiment was also performed without containing oil sample under similar experimental conditions. From the titration data, iodine value was calculated according to the following formula:

$$\text{Iodine Value} = (V_b - V_s) \times M \times 127 \times 100/W \times 1000 \quad (2)$$

where, V_b is the volume of $Na_2S_2O_3.5H_2O$ used for blank sample (Oil free mixture), V_s is the volume of $Na_2S_2O_3.5H_2O$ used for oil solution, M is the molarity of $Na_2S_2O_3.5H_2O$ solution, and W is the weight of oil sample (g).

Peroxide value determination: Peroxide value of castor oil and sesame oil was determined according to AOCS (1997c) standard method (Cd 8b-90). About 2.5 g of the given vegetable oils sample was mixed thoroughly with a solution having acetic acid and chloroform at a ratio of 3:2 followed by the addition of 1 cm^3 standard aqueous solution of potassium iodide (KI) and 35 cm^3 distilled water with constant stirring. This reaction mixture containing few drops of starch indicator was then titrated against 0.01N $Na_2S_2O_3.5H_2O$ aqueous solution until yellow colour disappeared. Similar experiment was also carried out under the same experimental conditions without containing oil sample. From the titration data the peroxide value was calculated according to the following formula:

$$\text{Peroxide value} = [(V_s - V_b)\ N \times 1000]/\ W \quad (3)$$

where, V_b represents the volume of $Na_2S_2O_3.5H_2O$ used in the presence of oil sample, V_s is the volume of $Na_2S_2O_3.5H_2O$ used in the absence of oil sample, N is the normality of $Na_2S_2O_3.5H_2O$ solution used for titration and W is the weight of oil sample (g).

Wear measurement: Four-ball machine (ASTM, D2266) was used to investigate the anti-wear properties of the selected vegetable oils under the applied load of 78 N at 80 and 30°C. Anti-wear performance of the vegetable oils under investigation can be estimated from the size of Wear Scar Diameter (WSD) from the lower three stationary balls of four-ball tribometer during the experiment. Before the start of each experiment steel balls and other appropriate parts of four-ball machine were properly washed with toluene and dried in oven at about 50°C. These washed balls were then fitted in four-ball machine where the top ball was held in a special chuck at the lower end of vertical spindle of an electronic motor moving with constant speed.

The upper ball is rotating in the cavity of three identical balls in contact and clamped in a steel cup containing the test fluid. The four ball machine was run for specific time duration at desired load and temperature. After completion of experiments, the steel balls were collected, washed in an ultrasonic bath for about two minutes and dried. The wear scar diameter on each of the three lower balls was measured with optical microscope and recorded in millimetres.

RESULTS AND DISCUSSION

Additive free vegetable oils: Four-ball tribometer was used to evaluate the tribological properties of vegetable oils. The anti-wear performance of the selected vegetable oils was assessed by measuring the WearScar Diameter (WSD) at the three lower stationary balls of tribometer. The variations of WSD for selected oils with sliding distance at 30 and 80°C are shown in Fig. 1 and 2. It can be seen that castor oil without containing any additive showed better anti-wear performance at 30 and at 80°C as compared to sesame oil under similar experimental conditions. The improved anti-wear behaviour of castor oil at different temperatures may be attributed to its chemical composition. It has been found that castor oil contains high percentage of triglyceride of ricinoleic acid containing double bond and hydroxyl group in its structure as shown in the Fig. 3. The presence of hydroxyl group and double bond in the castor oil give it preference over other vegetable oils to use as base stock for lubricants. Moreover, the presence of hydroxyl group in castor oil structure makes it polar and therefore, shows greater affinity to adsorb at the metal surface. As a result thick layer of oil molecules is formed at the metal surface reducing wear and friction. Also, it is well known, that oils having high acid value, low iodine value, high viscosity, and high peroxide value show better anti-wear performance (Haq and Ahtaram, 2007). So far, castor oil under investigation meets all these requirements as shown in the Table 1. Therefore, castor oil showed improved antiwear performance as compared to sesame oil under similar experimental conditions.

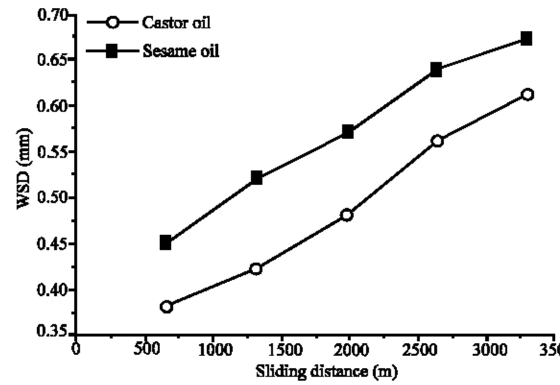

Fig. 1: Variation of WSD with sliding distance at 30°C for selected vegetable oil

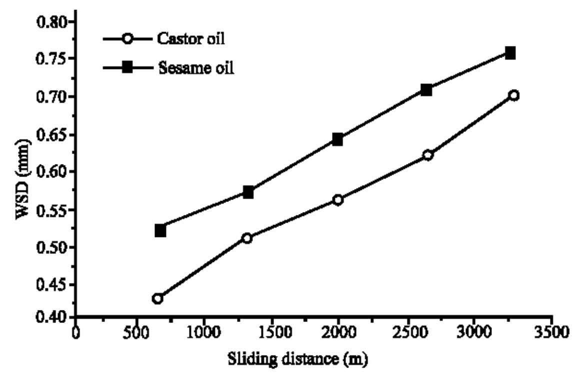

Fig. 2: Variation of WSD with sliding distance at 80°C for selected vegetable oils

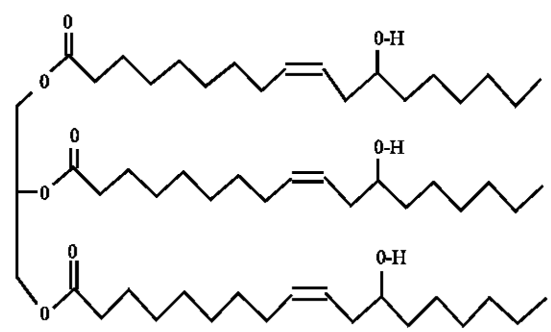

Fig. 3: Structure of the major component (90%) of castor oil

Table 1: Some important parameters of the tested vegetable oil

Oil parameters	Castor oil	Sesame oil
Viscosity (cSt S^{-1} at 30°C)	60	43.35
Viscosity (cSt S^{-1} at 80°C)	45	32
Acid value (mg KOH g^{-1})	1.12	1.03
Iodine value	87	112
Peroxide value (meq kg^{-1})	7.2	6

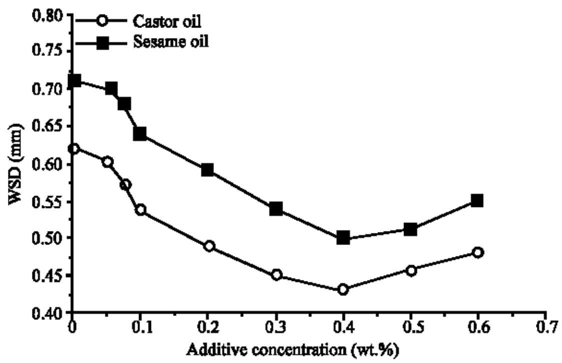

Fig. 4: Variation of WSD with additive concentration at 30°C for selected vegetable oils

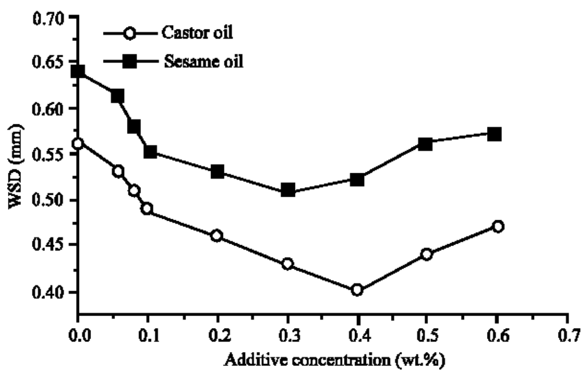

Fig. 5: Variation of WSD with additive concentration at 80°C for selected vegetable oils

Effect of additive on the anti-wear properties of vegetable oils: The anti-wear properties of selected vegetable oils were assessed by measuring the wear scar diameter which indicates the amount of wear produced during the rubbing process in the presence of lubricating oils for specific time duration. 12-hydroxystearic acid was used as anti-wear additive under applied load of 78 N and two different temperatures, i.e., 30 and 80°C. The relationship between the additive concentration and anti-wear performance in terms of wear scar diameter are shown in Fig. 4 and 5. The results shown indicate that 12-hydroxystearic acid considerably reduced the wear scare diameter, thereby improved the anti-wear properties of vegetable oils as environmentally friendly lubricants. The improved anti-wear performance of 12-hydroxystearic acid can be attributed to its chemical structure containing carboxyl group as well as hydroxyl group. The presence of these functional groups in 12-hydroxystearic acid makes it polar, thus showing greater affinity to adsorb on the steel surface. This interaction of hydroxycarboxyl acid molecules with the steel surface results in the formation of chemically polymerized molecules which play an important role in the friction and wear reduction during sliding distance (Jahanmir, 1985; Bowden *et al.*, 1945). Moreover, in the case of 12-hydroxystearic acid and hydroxyl groups are far apart from each other in the molecule which results in greater affinity to adsorb on the metal surface at both the functional groups producing a carboxyl thick layer as a result of tribochemical reaction on the metal surface.

Furthermore, 12-hydroxystearic acid showed better anti-wear performance while blended with castor oil as compared to sesame oil under the same experimental conditions. The improved anti-wear behaviour of castor oil blended with 12-hydroxystearic acid may be attributed to its unusual polar nature and unique chemical composition. castor oil contains high percentage of triglyceride of ricinoleic acid containing carboxyl group and hydroxyl group in its structure and therefore remains polar. As a result of polar mass of castor oil, 12-hydroxystearic acid molecules show strong affinity to adsorb on the metal surface providing a strong protective layer against wear and friction as compared to sesame oil. It is also evident from Fig. 4 and 5 that both castor oil and sesame oil show better anti-wear performance at 30°C as compared to 80°C. This may be explained as that at high temperature the acid molecules might not be able to stay at the surface due to high energy contents of these molecules and therefore unstable protective layer is formed at the surface. Figure 4 and 5 reveal that at 30 and 80°C, WSD decreased as the concentration of acid increased in the oil blend and passed through minima corresponding to 12-hydroxy stearic acid concentration of 0.3 and 0.4wt.%. This trend of minima of WSD with respect to additive concentration agreed with those reported elsewhere (Zhu *et al.*, 2009; Fox and Stachowiak, 2007). These Fig. 4 and 5 how that as the concentration of additive increases in the oil blend, adsorption of the dissolved acid molecules increased on the steel surfaces providing a protective layer at the surface during rubbing. However, it is also appeared from Fig. 4 and 5 that as the concentration of additive in the oil blend increases than that corresponding to the minima in WSD, there is increase in the WSD, thereby shows that the adsorbed layer of 12-hydroxystearic acid molecules start to desorb above these critical concentrations.

CONCLUSION

Vegetable oils can be used as environmentally friendly lubricants using proper additives. Castor oil blended with additive and without additive displayed better anti-wear properties both at room temperature (30°C) as well as at high temperature (80°C) as compared to sesame oil at the same sliding distance and load. The improved anti-wear properties of castor oil blended with 12-hydroxystearic acid may be attributed to unique the structure of castor oil and additive which allow their molecules to show strong affinity to be adsorbed on the metal surface, thereby providing strong protective layer reducing wear and friction along the sliding distance.

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