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THE EFFECT OF OXIDATION ON THE TRIBOLOGICAL PERFORMANCE OF FEW VEGETABLE OILS[1]

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Abstracts

Lubricants based on mineral oil are in use for various application but they are not environmental friendly. Vegetable oils are increasingly used as lubricant base oils, in the context of environmental regulations and conservation of nature as they are biodegradable and environmental friendly. The one major disadvantage with them is their limited oxidative stability. In the present investigation, the effect of oxidation on the tribological performance of groundnut and palm oils were evaluated by subjecting these oils to accelerated ageing in a dark oven at elevated temperature. The samples were collected at regular intervals and were analyzed for the changes in the properties of viscosity, percentage of free fatty acid and peroxide number and were compared to fresh oils samples and further tibological properties of these samples were evaluated using four ball tester. Observed changes in the wear scar diameter and other physicochemical properties were linked to destruction of triglyceride and subsequent formation of peroxides due to the oxidation of the test oils during the ageing. The difference in the wear properties of groundnut oil to palm oil was accounted for relatively its high content of polyunsaturated fatty acids and its susceptibility to undergo oxidation in comparison to the latter.

Keywords: Vegetable oils; Biodegradable lubricants; Oxidation; Four ball tester.

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INTRODUCTION

Lubricants and greases based on vegetable oils were in use science ancient times.[1] The discovery of petroleum resulted in the various kinds of mineral oil based lubricants having superior quality at affordable price. Over the years, a great deal of effort has been made to develop lubricants with optimum qualities to meet the ever-increasing demands of the industry all over the world.[2] Lubricants based on mineral oil can cause damage to the environment as they are not biodegradable and are very toxic in nature and it is well known that biodegradability and toxicity are the most extensive concerns for environment-friendly lubricants.[3-5] In the past two decades the concern over the usage of petroleum based lubricants and their impact on the environment has created awareness resulting in the various biodegradable oils from agricultural feed stocks.[6,7] Today vegetable oils are used not only as food stuff, but also as a raw material for various industrial applications as well. Notable among the uses are lubricants, polymers, paints and varnishes.[8] The use of vegetable oils for lubricant applications is very significant in terms of conserving environment.

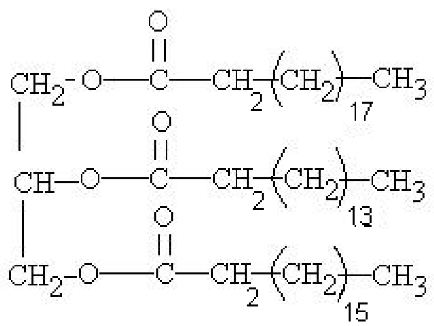

Figure 1. Schematic structure of vegetable oil.

In general, properties of vegetable oils are functions of the composition of their fatty acid constituents. The carbon chain lengths and the saturated or unsaturated nature of their hydrocarbon chains have significant effect on the properties of vegetable oils. In general most of the vegetable oils are very similar in structure, with long chain fatty acids. A typical structure of vegetable oil is shown in the Figure 1. The polar group in vegetable oils ($–COO^-$) is bonded to the triglyceride structure by ester linkage. In principle fatty acids exists in the form of triglycerides in vegetable oils. The primary difference in various vegetable oils are in the amount of saturated or unsaturated fatty acids present in the structure and in the degree of unsaturation in the molecule.[9,10] This unsaturation affects the oxidation stability and the low temperature properties of the vegetable oils. Fatty acids are primarily released from the triglyceride structure by hydrolysis reaction which is catalyzed by oxidation process. It is important to notice that hydrolysis reaction is not an oxidation reaction but usually occur with oxidation as another degradation process resulting in formation of Free Fatty Acids (FFA). The higher the concentration of unsaturation poorer is its oxidation stability, leading to the formation of FFAs.[11,12] Majority of vegetable oils have rapid break down at temperatures above 150^0C. This will have great influence on the product quality and shelf life of the vegetable oil based lubricants. Thus understanding the effect of vegetable oil oxidation will be very useful while formulating biodegradable lubricants.[13,14] In the present study we have used commercially available groundnut and Palm oil for experimental investigation without further purification. The composition of these oils in terms of fatty acids is shown in

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Table1**.** In this study palm and groundnut oils were stored at an elevated temperature in an oven under dark condition to avoid the influence of photo oxidation. The oxidized oil samples were collected periodically and subjected to various physical and chemical tests, further tribological properties were evaluated by using a standard four ball tester machine. The results of these tests were used to judge what influence of chemical changes on the tribological properties of selected base oils.

Table 1. Composition of palm and groundnut oil in terms of their constituent fatty acids

Fattyacid composition (in %)	***C 14:0**	C 16:0	C 18:0	C 22:0	C 24:0	C 18:1	C 22:1	C 18:2
Palm oil	2.5	45.5	2	--	--	44	6	--
Groundnut oil	--	11	2	5	5	46	--	31

**C X:Y is a notation where X indicates No of carbon atoms Y indicates No of double bonds for a given fatty acid chain.*

2 MATERIALS AND METHODS

2.1 Accelerated Ageing of Vegetable Oils

Accelerated ageing of vegetable oil samples were simulated by storing the samples in a dark oven at 60±1^{0}C and was based on the version of AOCS recommended practice.(15) 600 ml of Palm and groundnut oils were taken in one litre beakers and stored in an oven at the specified temperature, the samples were removed at an regular intervals of 14, 28 and 42 days for further analysis and were compared with a fresh oil sample which was used as reference in the present study.

2.2 Kinematic Viscosity of Vegetable Oils

Kinematic Viscosity, an important physical property of base oils, is a measure of oil's flow characteristics. In the present work, kinematic viscosity of fresh and aged oil samples collected from the oven at regular intervals were determined according to the ASTM Standards D445-04 and D 446-04 using U-tube viscometers in a constant temperature bath capable of maintaining the set temperature with an accuracy of ±0.1^{0}C.(16,17)

2.3 Free Fatty Acid and Peroxide Value of Oil Samples

The percent of free fatty(18) acid of fresh and aged oil samples collected at regular interval of 14, 28 and 42 days were evaluated, using the AOCS official method based on the titration of sample against standardized NaOH solution. In addition to that the peroxide values of the aged oil samples were also determined by using the AOCS method.(19)

2.4 Tribological Evaluation of Test Oils

In the present work tribological performance of the fresh and aged palm and groundnut oil samples were carried out using a four-ball tester at 1200 rpm, 400 N, 75 ^{0}C, and 60min. Chrome alloy steel balls, confirming to AISI standard steel no. E-52100, with a diameter of 12.7 mm, Grade 25 EP (extra polish), having Rockwell C hardness of 62(20) were used for the tests. The test balls were thoroughly cleaned,

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along with ball pot and ball holder (top) by first soaking in hexane for one minute and then with sonic agitation for 60 seconds and again rinsed with fresh hexane.

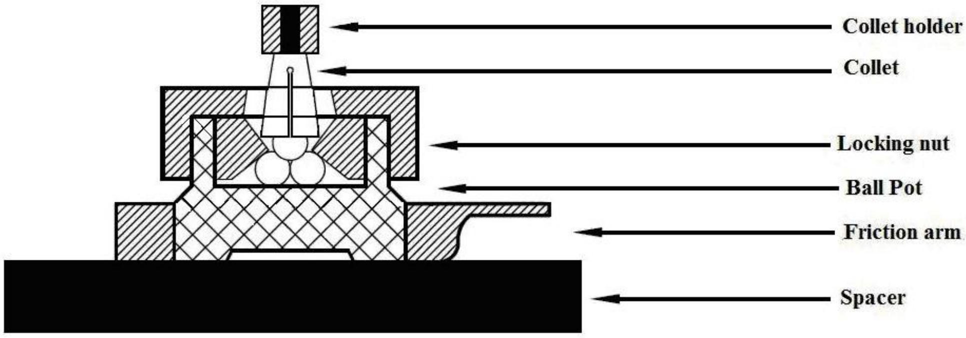

Figure 2. Schematic representation of the ball pot and chuck in a four ball tester.

Then they were wiped with fresh tissue paper and dried with a hot air blower. The ball pot with cleaned balls and test sample was assembled in the testing machine and the test was run at specified conditions mentioned earlier. Schematic representation of ball pot with chuck is shown in Figure.2 once the experiment was over, the test balls were cleaned properly and the wear scar images were captured with digital camera. The diameter was measured later using the software with an accuracy of ±2µm.

3 RESULTS AND DISCUSSION

Kinematic viscosity of fresh and aged oil samples were carried out at 40^0C for fresh and aged oil samples, according the standard procedure given in the previous section. From Figure 3**,** it can be seen that both the Palm and groundnut oil have shown an increase in viscosity with ageing time. The increase in viscosity with ageing is basically due to the oxidation and subsequent release of various primary and secondary products generated during the process. The other possibility for the observed increase in viscosity could be due to the formation of polymeric compounds, because of the reaction between the oxidation products.[21] The formation of free fatty acid is the prominent feature associated with oxidation of vegetable oils. It can be useful tool in predicting the extent of degradation in quantitative terms. The Figure 4 shows the variation of free fatty acids with ageing for palm and groundnut oil samples. It can be seen from the results that the groundnut oil with higher percentage of unsaturated fatty acids in its structure has shown increased volume of free fatty acids (FFA) with time when compared to palm oil.

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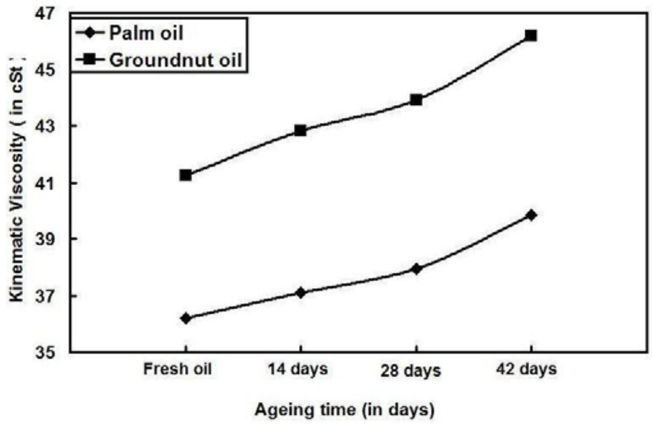

Figure 3. Variation of kinematic viscosity with ageing time for oil samples.

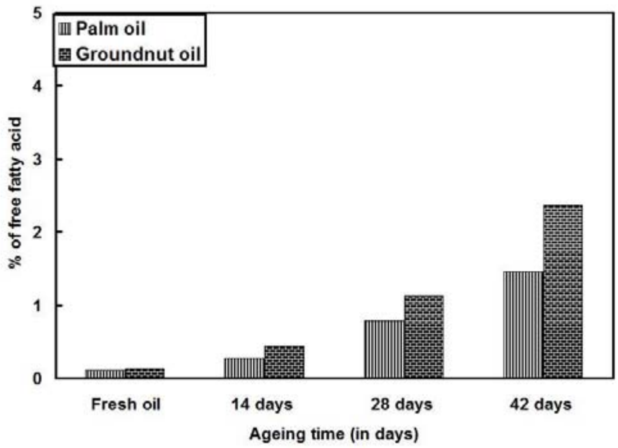

Figure 4. Variation of percentage of free fattyacids with ageing time for oil samples.

The tribological properties of vegetable oils are basically associated with physical adsorption, chemical absorption, and chemical reactions resulting from the interaction of their polar group with the metallic surfaces. It is known fact that the boundary lubrication is primarily affected by adsorbed monolayers. The property of oiliness is attributed the ability of its polar head to adsorb on to a metallic surface and form a firm monolayer on the surface. The variation of wear scar diameter with ageing time for palm and groundnut oils is shown in Figure 5.

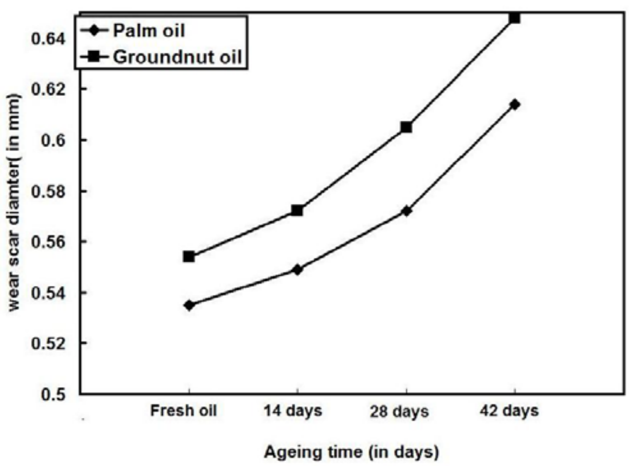

Figure 5. Variation of wear scar diameter with ageing time for oil samples.

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Since saturated fatty acids have no double bonds they can align in a straight chain and is closely packed on the surface providing a stronger protective layer. However the unsaturated fatty acids which have at least one double bond result in a weaker protective layer, consequently resulting in the observed difference.(22) Oxidation of vegetable oils results in changes with respect to various physical and chemical properties of the test samples and is likely to have a negative impact on the tribological performance of these oils. A schematic representation of these reactions is shown in Figure 6.

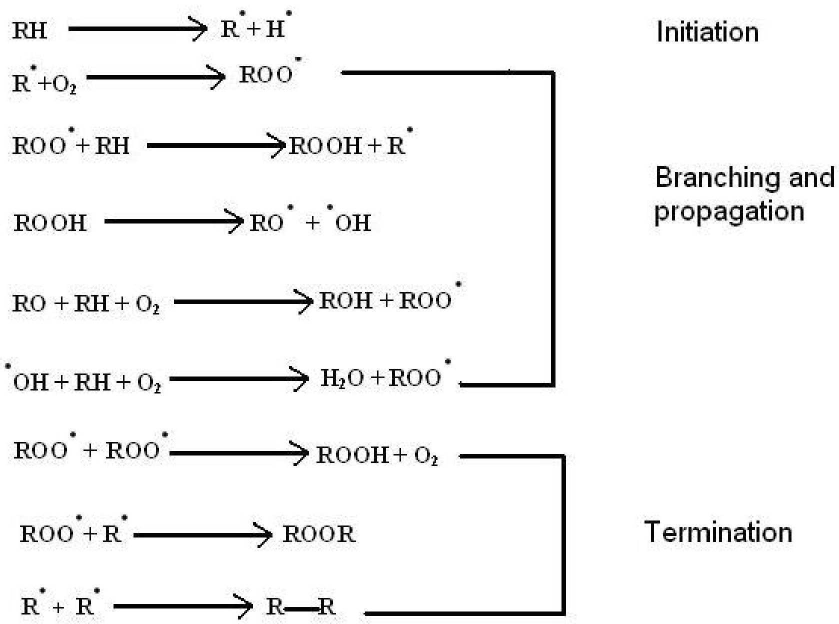

Figure 6. Schematic representation of oxidation reactions

This is generally initiated with formation of free radical compound resulting in forming peroxides and hydroperoxides as major products, which consequently plays a major role in formation of free fatty acids during the degradation process.(23,24) Figure 7 shows the variation of the peroxide number with ageing for palm and groundnut oil.

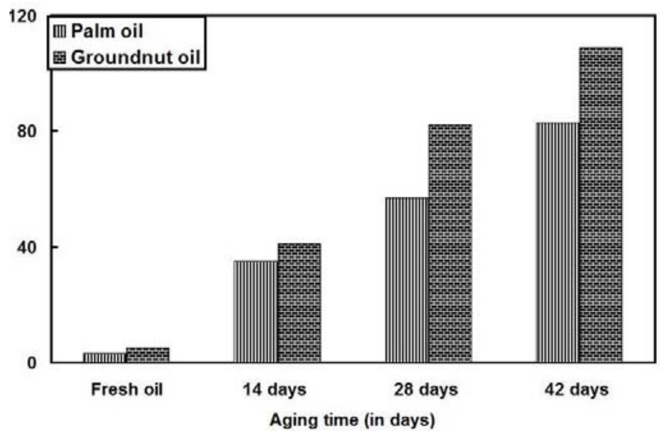

Figure 7. Variation of peroxide level with ageing time for the two oils.

It is clear from the graph that initially the peroxide level is very small and comparable for both oils used in the present investigation. With ageing, an increase in the content of peroxide level is observed. The increased level of peroxides indicates faster

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degradation of vegetable oil.(25,26) This quantitative difference in the properties of palm and groundnut oils is explained in terms of their composition. Palm oil having more saturated fatty ester has a relatively better oxidation stability compared to groundnut oil, which has significant amounts of polyunsaturated fatty acids. These polyunsaturated fatty acids are highly susceptible to oxidation, leading to the destruction of triglyceride structure and formation of various oxidation products. These products are unstable and as their level builds up a part of them decompose forming various secondary products.(27-29) There is a continuous reaction between these peroxides and its derivatives with the surface causing increased wear with ageing for both palm and groundnut oils.
The presence of moisture, which is generated as a by product during the oxidation, promote the formation of iron soaps of fatty acids under sliding conditions. It is expected that iron soap formed during the process expected to protect against the wear, but the high stress exerted by the test configuration possibly hinders the anti wear action, at the same time on the other hand the iron soap having low shear strength, offer less resistance to shear and which possibly explains the reduced coefficient of friction with aging in the present investigation(30) as evident from the Figure 8.The other research studies have also noted similar observation.(31) It was also observed that the relative difference in the observed in coefficient of friction was closely related to the percentage of unsaturated fatty acid present in the given vegetable oil. It can be seen that decrease in coefficient friction was more with groundnut oil when compared to palm oil. Since ground nut oil has, relatively, a higher content of unsaturated fatty acids, when compared to palm oils, it is prone to oxidation easily resulting in the observed difference in the properties.

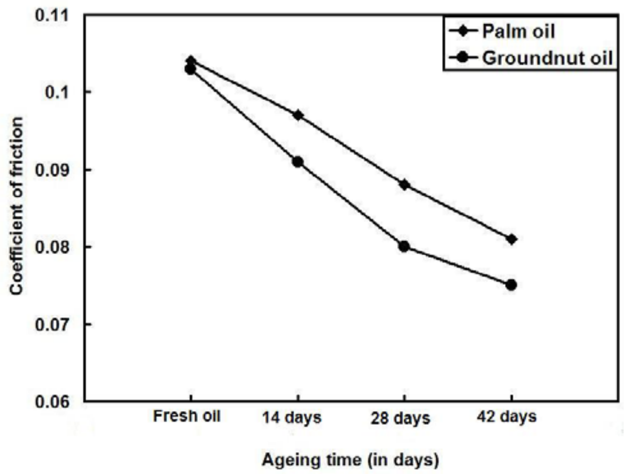

Figure 8. Variation of coefficient of friction with ageing time for different oils.

4 CONCLUSIONS

The present study was focused on effects of oxidation on Tribological properties of palm and groundnut oil using a four ball apparatus to focus on the effects of oxidation. The following conclusions were drawn. Increase in wear, observed with oxidised oil samples is linked to the destruction of triglyceride Structure.

1. Increase in the kinematic viscosity, peroxide level and percentage of free free fatty acid were observed for both palm and groundnut oil with ageing. The increase in the kinematic viscosity was possibly because of polymeric compounds formation due to oxidation. Further the reaction between the

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hydroperoxides formed during the oxidation and metal surface is responsible for the increased wear with ageing of palm and groundnut oil.

2. The free fatty acids formed during the oxidation process, resulted in forming soft iron soap by reacting with the metal surface, which offer low resistance to shear, resulting in low coefficient of friction.
3. The relative difference in fatty acid content, peroxide level and viscosity was basically due to the higher percentage of polyunsaturated fatty acid in groundnut oil.

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