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HIGH PERFORMANCE LUBRICANT FROM MODIFIED VEGETABLE OIL*

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Abstract

The future lubricants must be more environmentally adapted, with a higher level of performance lower total life cycle, cost than currently used lubricants. Environmental friendly, the biodegradable alternatives are available for a large variety of mineral oil based lubricants. Vegetable oils are the major source of these base fluids, although they have lower thermal and oxidation stability and even worse low-temperature behavior than mineral oil. These physical and chemical properties can be improved by chemical modification. The aim of this study was to evaluate physicochemical properties and film formation from modified vegetable oils. The vegetable oil was chemically modified by epoxidation reaction with acetic and formic acid using sunflower oils. Viscosity, iodine value, density, acidity value and thermal stability were determined for epoxidized oils. The film formation was analyzed using a HFRR tribometer. The results showed that epoxidized vegetable oils had excellent properties to be used as lubricant, and their tribological performance is higher than mineral oil.

Keywords: Epoxidation reaction; Biolubricant; Tribological performance.

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1 INTRODUCTION

Development and application of biocompatible lubricants are increasing daily as a result of strict government regulation and increased public awareness for a pollution free environment imposed on mineral oil-based lubricants with their non-biodegradable toxic wastes [1]. The mineral oils consist predominantly of hydrocarbons but also contain some sulfur and nitrogen compounds with traces of a number of metals. Due to their inherent toxicity and non-biodegradable nature they pose a constant threat to ecology and vast ground water reserves [2].
In this context, vegetable oils (VO) constitute a suitable alternative for replacing 'mineral oils', because they are biodegradable and non-toxic [3]. Indeed, VOs have most of the desirable lubricity properties, such as good action lubrication, high viscosity, high flash-point and low volatility. However, a high degree of multiple C–C unsaturations in the fatty acid (FA) chain of many vegetable oils causes low thermal and oxidative stability and confines their use as lubricants to a modest range of temperature [1,4]
An improvement of the thermal, oxidative and hydrolytic stability of vegetable oils can be achieved by a chemical modification. These reactions transform alkene groups present in a vegetable oil in other stable functional groups that can improve the oxidative stability, whereas reducing structural uniformity of the oil by attaching alkyl side chains would improve low-temperature performance. Attempts have been made to improve the stability of vegetable oils by transesterification, selective hydrogenation and epoxidation reactions [5]. Epoxidation is one of the most important reactions of the C–C double bond to improve plant oils oxidative stability [6].
Arumugam et al [7] studied chemical modification of rapeseed oil by epoxidation and hydroxylation process. Epoxidized rapessed oil showed upper oxidative stability, lower flow point and friction reducing ability compared to base oil. Other work developed by Arumugam et al. [8] investigated the tribological characteristics of a diesel engine cylinder liner and piston ring combination under chemically modified biolubricants and commercial synthetic lubricant by using a high-frequency reciprocating Tribometer test rig. The chemically modified biolubricants exhibited good oxidative stability, improved cold flow property, and better performance in terms of frictional force and coefficient of friction than the commercial synthetic lubricant. The coefficient of friction of the chemically modified biolubricants was 23% less than the commercial synthetic lubricant because of the formation of a stable polymeric film on the metal surface during boundary lubrication. Approximately 12% more wear was observed with the chemically modified biolubricant than with the commercial synthetic lubricant because of the anti-wear additives in the latter. Ting et al. [9] analyzed the viscosity and working efficiency of soybean oil-based biolubricants to compare with lubricants for engine. This work used mixtures of original soybean oil, epoxidized soybean oil and hydrogenated soybean oil as base oils. The result showed that the epoxidized soybean oil has a significantly larger viscosity than the engine lubricants and the original soybean oil, while the hydrogenated soybean oil clearly presents opposite results.
The main purpose of this study is to develop biolubricants from renewable sources by epoxidation reaction, comparing the influence of two different peracids in the epoxidation on biolubricants properties and tribological performance.

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2 MATERIAL AND METHODS

2.1 Biolubricants Synthesis

The epoxidized Soybean and Sunflower oil was prepared by reaction of each vegetable oil (VO) with peracetic or performic acid generated in situ. This reaction was catalyzed with 2% sulfuric acid. The chosen molar ratio of hydrogen peroxide/acetic acid/ oils was 11/5/1, this last based in to double bonds. The VOs, acetic or formic acid and sulfuric acid were jointly placed into a well-stirred, round bottom glass reactor kept at 50 ◦C. After 30 min, the dilute H_2O_2 (35 wt.%) was added drop by drop to reaction mixture. After the complete addition of hydrogen peroxide, the reaction was continued for 5 h with rapid stirring. The mixtures were then washed with distilled water until the complete removal of acids from the organic phase was achieved, and then treated with $NaHCO_3$ (10 wt%).

2.2 Biolubricants Characterization

2.2.1 Viscosity and Viscosity index

Viscosity index (VI) is an arbitrary measure for the change of kinematic viscosity with temperature. It is used to characterize the lubricating oil in the automotive industry. Viscosity measurements were performed at 40 and 100 ºC using a controlled rheometer, PAVISTEST (Contenco instrument). The viscosity and viscosity index were calculated using ASTM methods D 445-12 and ASTM D 2270-10, respectively. Triplicate measurements were made and the average values were reported.

2.2.2 Density

Density measurements were made at 24 ◦C in agreement with ASTM D1298-99.

2.2.3 Chemical Characterization

Fourier transform infrared (FTIR) equipment used in the tests was Spectrometer Shimadzu, model IRAffinity - 1; coupled with a module HATR Miracle with ZnSe prism, made by PIKE technologies. The spectra were obtained under the following conditions: Number of scans: 32; Range: 700 - 4000cm^{-1} and Resolution: 4 cm^{-1}.

2.2.4 Acidity

The acidity value was measure according to the standard D664, ASTM D 974/08e1 and NBR 14248/2009

2.2.5 Iodine Index

Iodine value (IV) was obtained using the Wij_s method according to AOCS Cd 1-25. Conversion of IV (x), conversion of double bonds as related to IV_0, calculated as:

$x = [(IV_0 - IV)/IV_0]$.

2.2.6 Thermal Analysis

The weight loss of the sample with respect to temperature was measured using a PerkinElmer thermo gravimetric differential thermal analyzer (TG/DTA) under a flow of argon (flow rate of 50 ml/min) at a constant heating rate of 10 ◦C/min, starting at 25°C.

ISSN 2179-3956

2.3 Tribological Perfomance of Biolubricants

Tribological performance tests were evaluated in HFRR (High Frequency Reciprocating Rig) equipment (Figure 1). This test consists of a ball-on-disk contact to measure the friction and wear under boundary lubrication conditions using a highly stressed ball-on-disk contact. A hard steel ball (570–750 HV) of 6.0 mm diameter slides in reciprocates movement on a softer steel disk (190–210HV) of 10 mm diameter under the fully submerged oil condition. During the friction test, coefficient was measured by a piezoelectric force transducer and the formation of electrically insulating films at the sliding contact was measured by the ECR (Electrical Contact Resistance) technique. The parameters used were shown in Table 1.

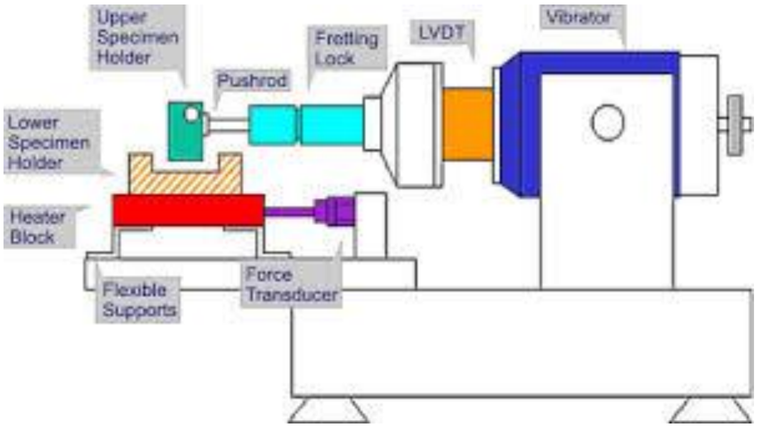

Figure 1: Schematic of the HFRR. Farias, (2011).

Table 1: Parameters used in HFRR test.

Parameters used in the High Frequency Reciprocating Rig Equipment				
Frequency	Load	Displacement	Temperature	Time
20 Hz	10 N	1 mm	50 º C	60 min

The tribological pairs (ball and disc) were cleaned by immersion in toluene for 7 minutes and dried with hot air again immersed for 3 minutes in acetone.

3 RESULTS AND DISCUSSION

3.1 Characterization of Biolubricants

The physicochemical properties are important for assessing the lubricant quality. Table 2 presents some properties of biolubricants synthetized in this research as well of the mineral oils, for effect of comparison.

ISSN 2179-3956

Table 2: Physical and Chemical Properties of epoxidized oils and mineral oil

Biolubricants, Lubricants. PCP*	Acidy (mg KOH/g)	Density (g/cm^3)	Iodine Index (g I_2/100g fat)	TG (ºC)	Viscosity (cSt) at 40 ºC and 100ºC	Viscosity Index
OGEAA	±0.54	0.9197	4.1	330	86.4/25.8	156
OGEAF	±0.18	0.9363	1.3	310	70.23/15.67	155
OM	-	0.8474	-	250	82.2/15.06	146
OGC	±0.08	0.9183	119.77	300	27/5.7	147

* *Physical and Chemical Properties.*

Legend: OGEAA (Epoxidized Sunflower Oil with Acetic Acid); OGEAF (Epoxidized Sunflower Oil with Formic Acid); OM (Mineral Oil); OGC (Commercial Sunflower Oil) TG (Thermal Analysis).

The iodine index is the number of centigrams of iodine absorbed per one gram of fat (unsaturation). The absorption of iodine determines the amount of double bonds in fatty acids. High iodine index shows that more unsaturated bonds are present in the oil or fat analyzed. As in the epoxidation reaction, the unsaturated bonds are replaced by oxirane ring, the iodine index tends to be very low due to the lack of unsaturated bonds. As observed in Table 2, the iodine index for biolubricants were low, indicating some few insaturations in epoxidized oils. Also, it is possible to conclude that epoxidation with performic acid was more effective in breaking the double bonds, once the iodine index reached very low value. The iodine value found after epoxidation (4.1 and 1.3 g I2/100 g fat) indicated a good conversion of double bonds, 96.6 and 98% for peracetic and performic acid, respectively [10].

The biolubricants had acid value higher than sunflower oil, probably this is caused by residual acid from epoxidation reaction. However, these values are adequate to lubricant use. The high acidity in biolubricants is not recommended due to the occurrence of corrosion, which can accelerate wear.

The viscosity for biolubricants showed higher values (Table 2) than those of sunflower oil. It is important to consider that the viscosity is the most important lubrication property. Normally, the vegetable based lubricant shows high viscosity, making it more suitable for boundary lubrication. Also, the epoxidized oil from peracetic epoxidation has viscosity higher than performic epoxidation. Mungroo et al [11] studied epoxidation of canola oil with same peracids and they conclude that epoxidation with performic acid produced more Glycol than epoxidation with peracetic acid. Its formation indicate the instability of oxirane ring and the epoxide yield decreases with glycol formation through the hydrolysis of de oxirane ring. This fact can promote a decrease in viscosity of epoxidized oil. However their viscosity indexes are similar. VI indicates changes in viscosity with variations in temperature. A high VI indicates small changes in viscosity at different temperatures, whereas a low VI indicates high changes in viscosity at different temperatures. According to [12] vegetable oil-based biolubricants have higher VI than mineral oils (around 100), which ensures that biolubricants remain effective even at high temperatures by maintaining the thickness of the oil film. Biolubricants based on epoxidized oils exhibit VI around 155 (Table 2) and they are suitable for a wide temperature range.

ISSN 2179-3956

3.2 Chemical Analysis

The Infrared spectrum was used for verifying the disappearance of double bonds and formation of epoxy groups during the reaction by qualitative identification of main signals (Figure 2). Although epoxidized sunflower oil with peracetic acid presented lower transmittance, all epoxidized oils showed similar characteristic bands.
Analyzing the FTIR spectra of epoxidized oils and sunflower oil, it is possible to confirm that the epoxidation has takes place. The appearance of a band at 830 cm-1 which is not seen in raw oil is characteristic of the epoxide and it can be assigned to ring vibrations of epoxy ring in cis-epoxides. These results agree with study of [7]. However, the band at 3014.71 cm-1, that correspond C=C, didn´t disappear totally in epoxidized oil spectra, indicating that the conversion was not complete.

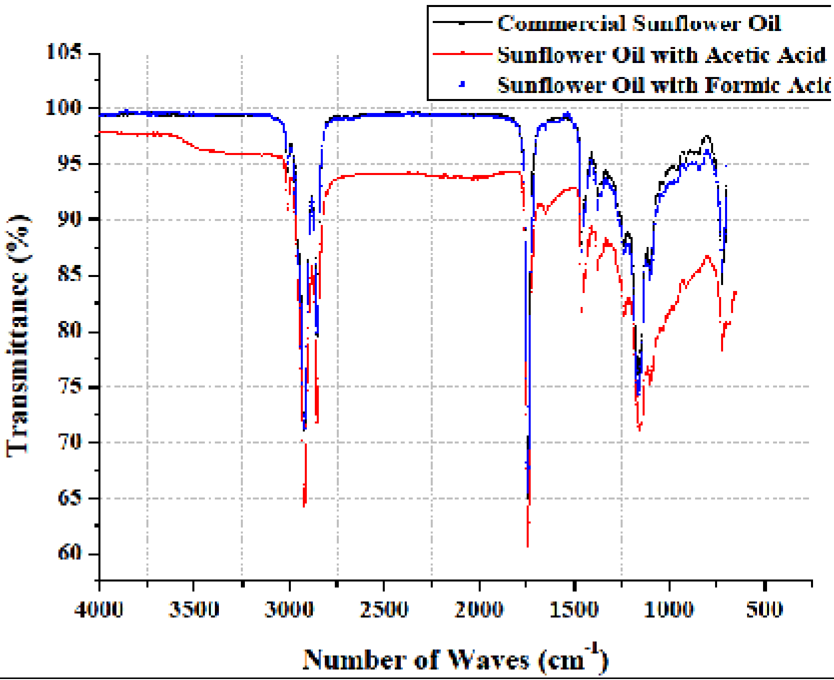

Figure. 2. Comparison of the infrared spectra of the epoxidized sunflower oil and sunflower oil.

Figure 3 shows the thermogram of the epoxidized sunflower oils, sunflower oil and mineral oil. It is clear from the graph that epoxidized oils are thermally stable below the temperature of 330 and 310°C for peracetic and performic epoxidation, respectively. 95% of weight loss was observed for the epoxidized oil in the temperature range of 450 and 600°C, peracetic and performic epoxidation, respectively.
The curves TGA of epoxidized sunflower oil (biolubricants) represents the thermal behavior that occurs in three stages of weight loss attributed to volatilization and / or decomposition of triacylglycerides. For epoxidized sunflower oil from performic epoxidation, the first step (temperature 310ºC) is related to the decomposition of organic matter, probably linoleic acid. The second step of loss occurs between the temperatures 450°C - 600°C. This step is related to the output of chemical residues (ashes).

ISSN 2179-3956

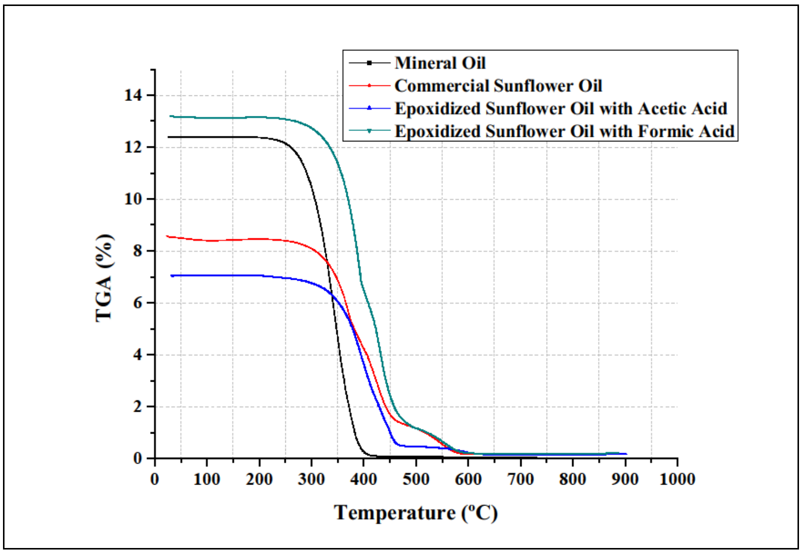

Figure 3. TGA thermogram of the epoxidized sunflower oil, sunflower oil and mineral oil.

Comparing the commercial oils, mineral oil and epoxidized sunflower oils, it observed that epoxidized oils have better thermal stability than mineral. But as the mass loss, the epoxidized oil with formic acid and the mineral oil had the greatest losses.

Mineral oil when heated, in the presence of oxygen, above 250°C can generate water vapor, and above 400°C generate to methane, ethane, ethylene and carbon dioxide in [13]. In their studies, Piluski and Hotza [13] indentified that the loss of water vapor, volatilization and dehydroxylation of the mineral oil was about 16.95%, indicating that the result of this study is consistent with the literature. Mineral oil heated in air showed mass losses in the range of 250-400°C, 16.11% of water loss, volatilization and dehydroxylation of the mineral oil were verified. It was also observed that at 400°C the lost weight was 100%.

Thus, the epoxidized sunflower oil with acetic acid showed better thermal stability and lower mass loss than epoxidized sunflower oil with performic acid.

3.2 Tribological Performance of Biolubricants

The tribological tests were performed on tribometer HFRR (High Frequency Reciprocating Rig). This tribological performance was evaluated based on the friction coefficients and percentage of films formed, Figures 5a and 5b, respectively.

Observing the friction coefficients in Figure 5a, the mineral oil showed the higher value than the epoxidized vegetable oils. The epoxidized oil from peracetic epoxidation reduced the friction coefficient in almost 50% in comparison with mineral oil. This fact is due to its high viscosity, which improves the protection of surface. It is also important to consider the chemistry nature of biolubricants, its polarity promotes the adsorption on metal surface resulting in reduction of friction and wear. They form a thin layer that improves the metal-to-metal separation.

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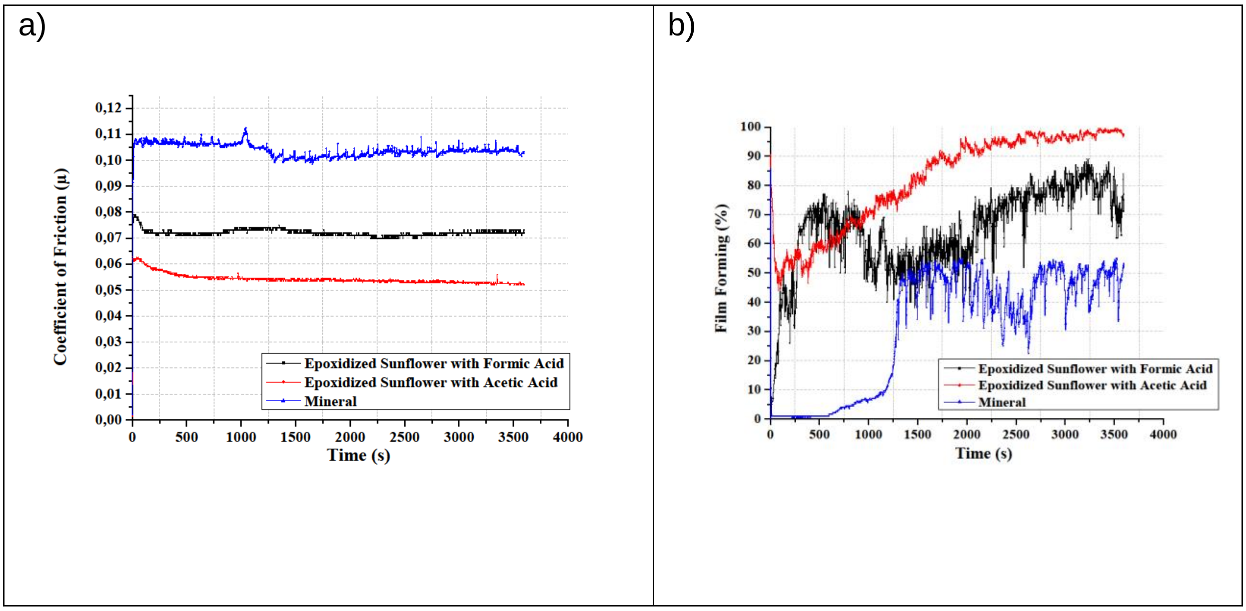

Figure 4: Coefficients of Friction and Film Formation

Figure 4b shows the film formation ability for epoxidized lubricants and mineral oil, and friction coefficient results. The best performance was observed to epoxidized oil from peracetic acid, after 2000 seconds the percentage of film formation reached almost 100%. Also, for this biolubricant few fluctuations was observed to film formation. The mineral oil showed lower ability to form the film, and this film is more instable. Probably, this fact has occurred because of adhesion of layer lubricant has not been strong and it was removed because of the motion of the ball [14].
According to Havet et al [15] the better film formation of epoxidized vegetable oils is assigned to the presence of ester groups. The atom of the oxygen from ester adsorbs on the surfaces: it can be safely assumed that these atoms adsorb on metallic hydroxides. Also, an increase in the length of the fatty acid chains tends to increase the adsorbed film thickness, which improves the surface protection.

4 CONCLUSIONS

This current work has focused on the synthesis of biolubricant from epoxidized vegetable oil and the effect of peracid used in epoxidation on biolubricant properties. Thus, the following conclusions can be drawn from the results presented above:

- The epoxidation reaction was effective in breaking of double bonds as indicated by very low iodine index.
- The epoxidized sunflower oils have properties suitable for the formulation of lubricants, especially for applications operating over a wide temperature range, because of its excellent viscosity index.
- The epoxidation reaction with peracetic acid shows great improvement in oil viscosity and, consequently, in the lubricity. Also, they have a good thermal stability.
- These biolubricants showed good performance in boundary conditions, decreasing friction coefficient and improving film formation on metal surface. However, better performance was observed for epoxidized sunflower oil from epoxidation with peracetic acid.
- In comparison with traditional lubricant (mineral oil), the epoxidized sunflower oils exhibit high performance, with very low friction coefficients.

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