STUDY ON TRIBOLOGICAL PROPERTIES OF VEGETABLE SUNFLOWER OIL USED AS POSSIBLE ECOLOGICAL LUBRICANT

Ioan ŞTEFÂNESCU, Camelia CALOMIR, Constantin GHEORGHIEŞ, Constantin SPÂNU

University “Dunărea de Jos”, Galaţi, Romania
istefanescu@ugal.ro

ABSTRACT

Biodegradable oils have ecological advantages, having comparable or better properties than mineral ones. The paper presents the behaviour two grade sunflower oil (pressing coarse and extraction coarse sunflower oil, respectively) when using them as ecological lubricants. It was monitored the friction coefficient and the structural modifications of sunflower oil grades. The friction coefficient shows that extraction coarse sunflower oils oxidised during 5 hours and additivated with the 2% ascorbic acid has a superior behaviour as compared to a hydraulic oil with a similar viscosity. The X-ray diffractometry may be an instrument for estimating the vegetable oil behaviour as lubricant by evidencing the ordered arrangement of the molecular chains into the oil layers.

KEYWORDS: sunflower oil, ecological lubricants, structural modifications.

1. GENERAL CONSIDERATIONS

The polyglycols, synthetic esteric oils and vegetable oils may be used as basic materials for biodegradable lubricants. The research done in the last 15 years in order to obtain some new products and to use technological processes that have no effect on the environment brought back to present the vegetable oils, practically producing a revival of these lubricants [1, 3, 4, 7]. The greatest advantages of these lubricants are ecological, having reduced toxicity rate and a high biological degradation rate [2, 9, 10]. The biological degradation in aerobic conditions (air) is produced due to gradual hydrolysis and oxidation processes. By oxidation, the oil molecules decompose into CO₂, H₂O and organic biomass.

Chemically, the vegetable oils are triglycerides that contain structural labile elements: ,,double chain”, ,,,β-CH group” and ,,ester group”. The structural elements ,,double chain” and ,,β-CH group” are unstable especially under high thermal and oxidant requests, while the ester group are easily dissociated in water. On the other hand, the ester group is mainly responsible for the rapid biological decomposition of the vegetable oils (fig. 1) [1, 7, 9, 10].

The future accept of the vegetable oils on the lubricant market depends, among others, on the possibility of using an additivation that reduces or removes the undesired great reactivity of these lubricants due to the structural labile elements [1, 7]. The research work for improving the characteristics of these lubricants must be done so that the use of these additives, that are generally non ecological, should not influence the nonpolluting characteristic of the vegetable oils. For some cases the performances of biodegradable oils are comparable or even better than those of mineral oils used in the same applications.

Fig. 1. Composition of some vegetable oils.

2. VEGETABLE OILS THAT MAY BE USED AS LUBRICANTS

In order to obtain an efficient lubrication it is necessary to choose the adequate lubricant according to the tribosystem importance, to the couple of materials in contact, to contact pressure and revolution or sliding speed, taking also into account
the environment conditions (temperature, humidity) [6] they function in.

For ensuring an efficient lubrication, here are the main functions that a lubricant must provide: reduction of friction, reduction of wear, dissipation of heat, softening of noises, vibrations and shocks.

Vegetable oils are attractive as they are easily biodegradable and are applied in tribosystems with acceptable technological losses of oil such as jigsaws and chain transmissions in wood manufacturing, agriculture or food industry. They have a high value of viscosity index (approximately 200), a very good lubricity and protection against wear, acceptable volatility and compatibility with many additives and mineral oils. They are completely biodegrading, the ecotoxicity is very low and the resources are regenerated, yearly. However, conventional vegetable oils (untreated oils) contain a lot of unsaturated hydrocarbons that increase the oxidation tendency and limit their use in higher performance applications. They also have major disadvantages, such as poor behaviour at low temperatures and a low hydrolyzing stability.

They decompose at high temperatures, forming fat acids that attack the friction surfaces. They are siccative, in the presence of air forming a thin, resistant shell that is difficult to remove from surfaces of solid bodies.

Refined vegetable oils have quite a uniform chemical composition, unlike the mineral ones and may be classified according to the fat acids they contain, into the following types [11]:

- saturated acids (without double chain), i.e. palmitic and stearic;
- monounsaturated acids (with only one double chain), i.e. oleic and erucic;
- polyunsaturated acids (with more than double chain), i.e. linoleic and linolenic;
- special acids (containing hydroxy- and epoxy-type radicals).

Vegetable oils with a high content of oleic acid may be considered as mixtures of highly monosaturated fat acids, having better rheological properties as compared to other vegetable oils containing saturated fat acids. The vegetable oils containing high quantities of oleic acid (here symbolised with HO) are the most indicated for industrial applications. The technical oleic acid usually contains 65-72% C 18:1, approximately 10% C 18:2 and small amounts of C 18:0 and C 16:0 (where 16 and 18 represent the number of carbon atoms in the acid chain, respectively, and 0, 1, 2 represents the number of double bonds of the molecular chain.). Sometimes natural oil properties may be improved with small quantities of poly-unsaturated fat acids [5].

Therefore, vegetable oils with high content of oleic acid and a small content of unsaturated acid (or even without any) represent the best choice as oiling materials. High oleic materials are more stable than low oleic acid content oils.

The researches [5] were done on rape oil (high oleic), soybean oil (HO) and coconut oil (HO).

The best vegetable oil seems to be the high oleic sunflower oil with a very high content of oleic acid (greater than 90%). The rape and sunflower oil standard quality need a chemical modification of the fat polyunsaturated substances for becoming acceptable lubricants [5].

3. THE SUNFLOWER OIL – AN ECOLOGICAL LUBRICANT

The previous papers [8, 9, 10] on the unadditivated vegetable sunflower oil obtained in different fabrication steps, were studied: after pressing coarse oil, after extracting coarse oil, neutralised and additivated with hydroquinone and ascorbic acid after the first two manufacturing steps. Studying the oxidation resistance of the unadditivated vegetable sunflower oil, it comes out that the oil from the first fabrication steps oxidised less than those used after other fabrication steps (coarse after pressing, coarse after extraction, after degumming and neutralisation, after air-ventilated, dried and refined). Due to this fact, for the additivated vegetable oils there are studied only the first steps. In this experiment the authors used only two antioxidant additives (hydroquinone and ascorbic acid). These antioxidants do not modify the toxicity grade and the biodegradability of the tested vegetable oil. Analysing these two antioxidants the ascorbic acid positively affects the oxidation of the vegetable oil, in a percentage of 2%. The vegetable oil obtained in the first two steps of oil manufacturing (after pressing coarse oil, after extraction coarse oil) presents the most reduced oxidation process as compared to the tested oils obtained after other steps of fabrication (degummed neutralised oil, air-dried and refined) so, first two manufacturing steps present interest for industrial applications of the vegetable oils.

The tribological behaviour of the sunflower oil additivated with ascorbic acid, compared to a hydraulic oil with a similar viscosity, was studied using a sliding tribomodel (fig. 2).

The roller triboelement is made of a steel grade OLC45 according to Romanian standard STAS 880-88 (similar to 1045 SAE steel grade) and a bronze is

![Fig. 2. Sliding tribomodel.](image-url)
1. Hydraulic oil, ISO type class L, family H, ua, uo.

2. Sunflower oil, b, p, ua, uo.

3. Sunflower oil, b, p, ua, ox, 2h

4. Sunflower oil, b, p, ua, ox, 3h

5. Sunflower oil, b, p, ox, 4h

6. Sunflower oil, b, p, ua, ox, 5h

7. Sunflower oil, b, e, ua, uo

8. Sunflower oil, b, e, ox, 2h

9. Sunflower oil, b, e, ox, 3h

10. Sunflower oil, b, e, ox, 4h

11. Sunflower oil, b, e, ox, 5h

12. Sunflower oil, b, p, ua, 3%, Aa

13. Sunflower oil, b, p, Aa, ox, 2h

14. Sunflower oil, b, p, Aa, ox, 3h

15. Sunflower oil, b, p, 3% Aa, ox, 4h

16. Sunflower oil, b, p, 3% Aa, ox, 5h

17. Sunflower oil, b, e, uo, 2% Aa

18. Sunflower oil, b, e, 2% Aa, ox, 2h

19. Sunflower oil, b, e, 2% Aa, ox, 3h

20. Sunflower oil, b, e, 2% Aa, ox, 4h

21. Sunflower oil, b, e, 2% Aa, ox, 5h

b: coarse oil after pressing step;
b, e: coarse oil after extraction step;
ua: unadditivated;
uo: unoxidised;
ox: oxidized;
Aa: ascorbic acid;
2%, 3%: ascorbic acid concentration;
2h, 3h, 4h, 5h: oxidation time, in hours.

Fig. 3. Value of the friction coefficient or steady state regime.

used for the shoe triboelement, made of CuSn12 according to Romanian standard STAS 197/2-83 or ISO 1338-77. The lubrication was obtained by partially sinking the roller in a bath containing the tested lubricants.

The test rig is designed for different forces applied to the shoe, here of 500, 1000, 1500N, respectively. During the test, the friction moment in the contact area and the shaft rotation speed were measured with a transducer. For the steady state regime, the value of the friction coefficient is presented in figure 3, resulting that, for the pressure of 1MPa, the values of the friction coefficient are almost equal for both pressing coarse and extraction coarse sunflower oil grades. For the other pressures (0.33MPa and 0.66MPa) the friction coefficient is lower for the sunflower oils obtained after-pressing coarse and extraction coarse, oxidised and additivated, as compared to a hydraulic oil with a similar viscosity.

4. STRUCTURAL CHANGES OF OXIDISED VEGETABLE SUNFLOWER OIL, POINTED OUT BY X-RAY DIFFRACTOMETRY

For studying the orientation of the sunflower oil molecules within a given volume, the X-ray diffractometry was used [9, 10]. Oil samples with different additivating grades, before and after test, as shows figure 2, were introduced into a special box made of plastics, as presented in figure 4. The box has a parallelepipedic cavity, covered by a thin celluloid sheet. The cavity contains the oil sample that was irradiated with a X-ray beam, having wave length $\lambda = 1.542\text{Å}$, using a diffractometer DRON 3.

Fig. 4. Special box and the direction of irradiation.

The diffraction spectrum in the angular interval $20 \in [5^\circ, 30^\circ]$ was recorded and diffractograms for each sample of tested oil were obtain. At the beginning it was determined the diffractogram for the thin celluloid sheet. The directions of irradiation, that was 0-20, are presented in the figure 4, too.
Fig. 5. Diffractogram for thin celluloid sheet.

Fig. 6. Diffractogram for sunflower oil (extraction coarse grade) with 2% ascorbic acid, unoxidised.

Fig. 7. Diffractogram for sunflower oil (extraction coarse grade) with 2% ascorbic acid, after 2 hours of oxidation process.

Fig. 8. Diffractogram for sunflower oil (extraction coarse grade) with 2% ascorbic acid, after 3 hours of oxidation process.
Figures 5 and 6 present the diffractogram for the thin celluloid sheet and the unoxidised oil, respectively. The figures 7, 8 and 9 present the diffractograms for the sunflower oil additivated with 2% and oxidised in air for a period 2, 3, 5 hours, respectively. It is noticed that increasing the oxidation time, there is a tendency of ordering the arrangement of some molecular formations within the oil layers that give Bragg reflections in the range \(2\theta \in [9^\circ - 14^\circ]\). This may be correlated to the decreasing of the friction coefficient characterising the tested tribosystem.

5. CONCLUSIONS

At present the biodegradable lubricants based on vegetable oils present a special interest taking into account the protection of the environment.

The characteristics of the biodegradable oils are comparable and, in some cases, they are even better than those of mineral oils used for the same applications.

Tribological behaviour reflected by the friction coefficient shows that extraction coarse sunflower oils, oxidised for 5 hours and additivated with 2% ascorbic acid, has a superior behaviour as compared to a hydraulic oil having similar viscosity. Therefore, coarse sunflower oils with the above-mentioned characteristics may be used as lubricant in industrial applications.

The X-ray diffractometry may be considered an instrument for estimating the vegetable oil lubrication capacity by pointing out the arrangement changes of the molecular chains.

The decrease of the friction coefficient may be connected with the increase in the degree of molecular chain orientation.

REFERENCES

9. Ţeneseacu I., Calomir C., Spână C., Dima St., 2004, Lubrifiante ecologici pe bază de uleiuri vegetale, Seminarul Național de Organe de Mașini, Brașov, pp. 95-100.