Rapeseed oil with anti-wear additives on the four ball tester

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Abstract. This paper presents a tribological characterization on the four ball tester, for three lubricants: rapeseed oil and this vegetal oil with two anti-wear nano additives (TiO₂ and ZnO, respectively). The lubricants were obtained at laboratory scale by a particular regime of sonication. Each additive was added in: 0.25%, 0.50% and 1% mass concentrations. The tests were done for the following loads and sliding speeds: 100...300 N and 0.38...0.69 m/s. The authors selected three tribological parameters for evaluating the tribological behavior of lubricants formulated based on rapeseed oil and two nano additives (ZnO and TiO₂): average of friction coefficient during 1 h test, wear scar diameter (WSD) and the temperature of lubricant bath at the end of the test.

1. Introduction

Rapeseed oil is a renewable resource that could be used for formulating eco-friendly lubricants. Durak [1] added Turkish rapeseed oil (RSO) in different concentrations, 1, 2, 3, 5, 10, 20, 30, 40, 50 (by %vol), into a base oil to obtain a mixt oil. The study of the effect of adding RSO in mineral oils was done using a specially designed engine journal bearings system. It is known that vegetal oils have a too lower viscosity to face severe regimes. At 40°C, the ratio between the used mineral oil and RSO was 4.499 and at 100°C was 2.226. At 50/50 concentration, these ratios were reduced at 2.637 and 1.743, respectively. The addition of RSO to a mineral-based lubricant decreases the friction coefficient at high journal speeds, even at medium loads. The lubricating oils containing RSO performed a higher reduction in the coefficient of friction at room temperature (25°C) than at higher temperature (100°C). At higher concentration ratio (50%), maximum reduction ratios were obtained with the usage of lubricant with RSO. But analysis of wear parameters was not done.

Lubricants perform better when adding friction modifiers and anti-wear additives, especially in transitory and boundary lubrication regimes [2, 3]. Today, research studies look for additives suitable for vegetal oils. Nano additives could prove new properties, different from properties of bulk materials; due to their size, they can penetrate into the textures of friction surfaces, influencing deformations, local temperature or/and micro cracks generation.

Inorganic and organic additives are added in neat oils for improving their tribological behavior [2, 4-6]. Inorganic compounds include metallic or non-metallic oxides, as CuO [7-9], Al₂O₃ [7], TiO₂ [9-11], ZnO [9], SiO₂ [12, 13], compounds of rare earth metals [14], ZrO₂ [9, 15], metals as Ag [16], Fe, Cu and Co [17], boron compounds, especially hexagonal boron nitride [18-20], WS₂ [21], MoS₂ [12]. Cristea [22] added black carbon, graphite and graphene in soybean oil, improving anti-wear properties, but with low influence on viscosity. Other theories of friction reduction are linked with effects...
including colloidal, rolling, third body friction, mending, polishing and protective film (continuous or partial) [23].

Maliar et al. [24] investigated the tribological behaviour of commercially available SAE 10 mineral and rapeseed oils containing Fe particles synthesized directly in the oil phase. Fe particles (50-340 nm) were synthesized by wet chemical reduction reaction of FeSO$_4$ by sodium borohydride in the rapeseed and mineral oils in the presence of a surfactant. A four-ball tribometer was used to investigate the tribological properties of mineral and rapeseed oil: coefficient of friction (COF), wear scar diameter and wear loss. The presence of Fe particles (0.1% wt) in the rapeseed and mineral oils caused the little change in the COF, but resulted in marked reduction of wear, attributed to the formation of tribofilm and superior load-bearing capability of the modified oil. But findings in [18, 23, 25] pointed out that the rolling, third body effects are responsible for wear reduction, not a continuous protective film.

This paper presents the tribological behavior of rapeseed oil and two nano additivated lubricant having the rapeseed oil as basis and different concentrations of ZnO and TiO$_2$.

2. Lubricants and test plan

Table 1 presents the fat acid composition of the rapeseed oil used in this study, but attention is to be payed to this issue as this vegetal oil could have a large spread of constituents ranges, due to crop origin site, yearly characteristic of the climate etc., as one may see, other researchers reported different concentrations in fat acids.

| Fat acid           | Symbol | Composition, %wt$^1$ | Composition, %wt$^{[1]}$ | Composition, %wt$^{[26]}$ | Composition, %wt$^{[27]}$ |
|--------------------|--------|----------------------|--------------------------|---------------------------|--------------------------|
| Myristic acid      | C14:0  | 0.06                 |                          |                           |                          |
| Palmitic acid      | C16:0  | 4.60                 | 4.44                     | 5.1                       | 4.5                      |
| Palmitoleic acid   | C16:1  | 0.21                 | 0.3                      | 0.3                       |                          |
| Heptadecanoic acid | C17:0  | 0.07                 |                          |                           |                          |
| Heptadecenoic acid | C17:1  | 0.18                 |                          |                           | 0.1                      |
| Stearic acid       | C18:0  | 1.49                 | 2.72                     | 2.0                       | 1.8                      |
| Oleic acid         | C18:1  | 60.85                | 74.15                    | 55.0                      | 60.7                     |
| Linoleic acid      | C18:2  | 19.90                | 13.23                    | 25.9                      | 19.9                     |
| Linolenic acid     | C18:3  | 7.64                 |                          |                           | 9.1                      |
| Arachidic acid     | C20:0  | 0.49                 |                          | 0.5                       | 0.6                      |
| Eicosenoic acid    | C20:1  | 1.14                 |                          |                           | 1.5                      |
| others             |        | 3.37                 |                          |                           |                          |

The formulated lubricants were processed in amounts of 200 g, each. The steps of this laboratory technology were similar to those presented by Cristea [22]:
- mixing of the additive and an equal mass of dispersing agent (guaiacol, with the chemical formula C$_6$H$_4$(OH)OCH$_3$ (2-methoxyphenol)), for 20 minutes;
- gradually adding the vegetal oil, mixing again with a magnetic homogenizer for 1 hour;
- ultrasonication + cooling of the additivated lubricant in step of 10 minutes; the fluid is heating to about 70...75 °C during sonication; the cooling time was about 1 hour; this step is repeated 5 times to have a total sonication time of 60 minutes. The parameters of ultrasonic regime are power 100 W, frequency 20 kHz ± 500 Hz, continuous mode.
The balls are lime polished, made of chrome alloyed steel balls (100Cr6), having 12.7 ± 0.0005 mm in diameter, with 64-66 HRC hardness, as delivered by SKF. A volume of 8 ml ± 1 ml lubricant is introduced in the ball cup, for each test. The test method for investigating the lubricating capacity was that from SR EN ISO 20623:2018 [28].

The test parameters were: sliding speeds of 0.38 m/s, 0.53 m/s and 0.69 m/s, corresponding to the spindle speeds of the four-ball machine of 1000 rpm, 1400 rpm and 1800 rpm (± 6 rpm), respectively, load on the machine shaft - 100 N, 200 N and 300 N (± 5%), test time - 60 minutes (± 1%). Each test (load, velocity, lubricant) was repeated twice.

The two nano additives were supplied by PlasmaChem [29] and have the following characteristics (figure 1). Particles of ZnO (figure 1.a) have average particle size ca. 14 nm, specific surface area 30 ± 5 m²/g, purity > 99% and TiO₂ (figure 1.b) is a mixed rutile/anatase phases and was obtained by photocatalytic process, the average size of particles being 21 ± 5 nm, specific surface 50 ± 10 m²/g, purity after ignition > 99.5%, ignition loss < 2%, humidity < 1.5%, other elements: Al₂O₃ < 0.3 wt%; SiO₂ < 0.2 wt%, density approx. 130 g/l. For obtaining the images in figure 1, each powder was pressed on a black carbon ribbon in order to protect the microscope vacuum pump. There were formulated lubricants with 0.25%, 0.5% and 1.0 %wt nano additive.

![Figure 1](image1.png)

**Figure 1.** SEM images of the nano additive before being added in the rapeseed oil.

3. Results

Here, tribological behavior was evaluated by three parameters: average value of friction coefficient for 1 h test, the wear scar diameter (WSD) and the temperature of the bath oil at the end of the test. Values given in figures 2, 5 and 6 are calculated from two tests under the same conditions and with the same lubricant. For a test, each value of WSD is the average of six measurements, two on each of the fixed balls. A measurement is done on the sliding direction, the other one is done perpendicular to that.

Analysing the values in figure 2, COF has a tendency to increase with load, with one exception that should be verified (rapeseed oil + 1% TiO₂, 300 N, 0.38 m/s). When taking into account the nature of the additive, its influence depends also on sliding speed. TiO₂ makes COF to be reduced more notably as compared to the value obtained with neat vegetal oil under low speed of 0.38 m/s and 0.53 m/s. At higher speed, this additive has lower values only for low load (100 N). Small concentration of ZnO increases COF. The conclusion will be that neat oil generally offers a better value of COF, at least for the tested loads and speeds.
Figures 3 and 4 present WSDs for tests done with the three lubricants, under extreme values of sliding speeds and for 1% wt concentration of the additive. In a qualitative way, the best behavior could be pointed for the neat vegetal oil and the lubricant additivated with +1% ZnO. Areas of wear scars are smaller, wear seems to be uniform, without deep traces, especially at \( F = 300 \text{ N}, v = 0.69 \text{ m/s} \). Under low load, the neat oil has the aspect of wear scars similar to that of lubricant with 1% ZnO.
At low speed, WSD is less influenced by the nature of lubricant, except for high load (F = 300 N) for high concentration of the nano additive (1% wt). It is interesting to notice that at 0.25% and 0.50% ZnO, the load produces the same average value of WSD. At v = 0.53 m/s, WSD is increasing with load for all tests, higher values being obtained for additivation with TiO$_2$ with low and high
concentration (0.25% and 1%). But for ZnO, the values of WSD seem not to be influenced by load. Same tendency is kept for \( v = 0.9 \) m/s.

At the most severe regime (higher velocity, greater load), the qualitative appreciation is the same: better behavior is noticed for the rapeseed oil and the lubricants with 1% ZnO (figure 5).

The influence of additive on wear is beneficial especially at \( v = 0.38 \) m/s, meaning that under this speed, the particles remain in contact and protect, as suspension or particles deposited on both contact surfaces.

**Figure 5.** Average values of WSD after tests during 1 h.
At lower velocity and load \( (v = 0.39 \text{ m/s}, F = 100 \text{ N}) \), meaning light regime, the lowest temperatures \( (43^\circ\text{C}) \) at the end of test were obtained for the neat vegetal oil and low concentrations \( (0.25\%) \). The increase in temperature of the nano additivated lubricants could be explained by friction of particles with both contacting surfaces (third body friction), in agreement with a slight increase of the friction coefficient. The neat oil produces the lowest temperature in the lubricant bath.

**Figure 6.** Temperature in the lubricant bath, at the end of the test.
After doing this test plan, the authors concluded that adding separately these additives (TiO₂ and ZnO) the improvement in tribological behavior is quite poor, except some punctual results for WSD. It seems that the weakness of vegetal oils remains a low viscosity and that nano additives are not forming a protective film, but nano to micro lamps that increase COF and do not have a visible effect on wear. Even if the initial dispersion was at nano level, the particles in contact tens to agglomerate to micro level (several microns) and also the formed particles tends to be deposited at the end of the contact (the lubricant run the particles out of the contact). SEM images reveal that the additive does not form a continuous protection and the friction is “a third body” friction: the non-uniformity of the particles distribution in contact is also a cause of non-uniform evolution of coefficient friction and wear (wear scars in figure 7 are obtained after drying the ball in calm hot air, without cleaning the balls).

![SEM images of wear scars, after testing rapeseed oil +1% ZnO.](image)

**Figure 7.** SEM images of wear scars, after testing rapeseed oil +1% ZnO.

4. Conclusions

The authors selected three tribological parameters for evaluating the tribological behavior of lubricants formulated based on rapeseed oil and two nano additives (ZnO and TiO₂), in concentration of 0.25%, 0.50% and 1.0%, respectively. These are the average of friction coefficient during 1 h test, the wear scar diameter (WSD) and the temperature of lubricant bath at the end of the test.

From tests repeated twice for the same set of parameters, the additivation of rapeseed oil produces an increase of the average value of friction coefficient. If considering a threshold of COF ≈ 0.09...0.1 that is reasonable for boundary and/or mixt lubrication, this value is overdue only for additivated lubricants at different concentrations, but especially under higher load of F = 300 N.

At light regime (v = 0.38 m/s, 100 N), only for the lubricant with 1% TiO₂, it was obtained a WSD greater than that of the neat rapeseed oil. The conclusion will be that, at light regime, the nano additive reduces the WSD. This tendency is almost kept for F = 200 N, but for F = 300 N, WSD is greater than that get by neat vegetal oil for higher concentration of the additive. Comparing the results on the nature of the additive, better results were obtained for ZnO, but differences are quite small.

For the other two speeds, WSD is ranked in an increase tendency with the load increase, meaning there is a similar lubrication regime (totally or partially fluid film) that relates strongly the WSD to the load, this being more visible for higher speed (v = 0.69 m/s).

For all tests, temperature of the lubricant bath, at the end of the test, is higher for formulated additivated lubricants. The only exception was obtained for the most severe regime (v = 0.69 m/s and F = 300 N) and for a concentration of 1% TiO₂.
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