Influence of ZnO concentration in rapeseed oil on tribological behavior

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Abstract. This paper presents results of testing the coarse rapeseed oil additivated with different concentrations of ZnO (0.25%wt, 0.50%wt and 1%wt, with 14 ± 5 nm in size), on a four-ball machine. The test parameters were load on main shaft of the machine: 100 N, 200 N and 300 N and the rotational speed 1000 rpm, 1400 rpm and 1800 rpm. For the tested range of ZnO concentration, the value of 1%wt does not improve the friction coefficient, but the wear rate of wear scar diameter was lower than that obtained with the neat rapeseed oil and the values are less sensitive with load and sliding speed for the more severe regimes. The additivation of rapeseed oil with ZnO is still efficient for the tested range of load and speed as compared to neat rapeseed oil. The authors formulated lubricants using as dispersant (2-methoxyphenol) in the ratio 1:1 to the additive. The technology is at scale laboratory and implies mechanical stirring and sonication. The tribological behavior was analysed based on obtained results, by mapping the friction coefficient, the wear rate of the wear scar diameter and the final temperature in the oil bath. For the additivated lubricants the following conclusions could be drawn. Friction coefficient tends to reach 0.1 only for low speed and high load (v = 0.38 m/s and F = 300 N), wear rate of wear scar diameter decreases with the increase of load, for each tested speed, probably because of a full fluid film generation. For F = 250...300 N, the map reveals a poor dependence on the additive concentration. The final temperature in the lubricant bath depends on speed, but for the same speed, it depends less on load, having a maximum value for 0.75% nano additive. These conclusions underlined the necessity of testing the new formulated lubricants because additive concentration and regime parameters could have synergic influences on the tribological parameters.

1. Introduction

The rapeseed oil is a plant oil in the focus of tribologists as it has a set of properties that recommends it for applications that do not exceed temperature limit and seizure limit. Additivation of this oil is still at the beginning as, due to their complex composition, the additive response could be unexpected. Metallic oxides are treated in literature [1], [2] [3], [4], [5] as a particular group, including ZnO [6], [7], [8], CuO, Al_2O_3, ZrO_2, TiO_2, even a combination $ZnAl_2O_4$ [9] etc. Shahnazar et al. [1] mentioned vegetal oils as base-stock for formulating additivated lubricants used in food, pharmacological industry, such as bakery ovens or kilns, where the risk of contamination needs to be minimized.

Lubricants having vegetal oils as base oil and ZnO and/or CuO as additives are biodegradable and have better performance in boundary lubrication [5].

Nano-ZnO has good characteristics for being introduced in lubricants: large surface area, high surface energy, strong adsorption (but by mechanical fixing), high diffusion, easy sintering, and a low melting point [10]. Due to the low solubility of ZnO in oil, its dispersion in the base oil could prove to

be a challenge [11]. In 2011, Qian et al. [12] using lauryl sodium sulfate as the surfactant, studied the tribological properties of nano-ZnO as a lubricant additive, the average size of particles reaching 125 nm. The addition of 1.0%, 2.0%, 3.0%, and 4.0% mass fraction of ZnO resulted in oil decreases the wear by creating deposits on the sliding surfaces and forming a lubricating layer on moving surfaces.

Hernandez Battez et al. [13] reported the antiwear behaviour a polyalphaolefin oil (PAO6) with CuO, ZnO and ZrO_2 nanoparticles, respectively, in concentration of 0.5%, 1.0% and 2.0%wt, after testing on block-on-ring tribometer. Tests were done under a load of 165 N, sliding speed of 2 m/s and a total distance of 3.066 m. All formulated lubricants exhibited reductions in friction and wear as compared to the base oil; the suspensions with 0.5% of ZnO and ZrO_2 had the best general tribological behaviour, but with high friction and wear reduction values even at low deposition levels on the wear surface; CuO suspensions showed the highest friction coefficient and the lowest wear at the content of 2%. The antiwear mechanism of nano additive was produced by tribo-sintering. A previous study of Hernandez Battez et al. [14] presented the tribological behaviour of ZnO nanoparticles as an additive in polyalphaolefin (PAO6) and on the influence of dispersing agents (OL100 and OL300), based on tests run on a four-ball machine. OL300 has better dispersant properties than OL100; formation of aggregates was found for 1% and 1.5% of ZnO in PAO6 + 3% OL300, and these non-coated ZnO nanoparticles had an abrasive behaviour in the contact area, despite their lower hardness as compared to steel surfaces; the tribological behaviour improvement of PAO6 + 1% OL300 + ZnO mixtures was related to the increase of ZnO concentration and their surface deposition on the wear scar surfaces.

Sepyani et al. [15] evaluated the addition of nano ZnO in SAE 50 oil and its influence on viscosity. At different shear rates, all lubricants had Newtonian behavior. The results showed that the maximum increase in viscosity was 12% that occurs for more concentrated samples at low temperature. Thus, it is expected that the addition of ZnO in the rapeseed oil to have a minor influence of the dynamic viscosity of the formulated lubricant. In conclusion, the tribological behaviour of this metallic oxide is based on the action as friction and wear modifier and not as viscosity improver of this metallic oxide.

Bhaumik et al. [16] investigated the tribological properties of ZnO nano friction modifiers in castor oil, in different concentrations between steel surfaces, tests being done using a four-ball test rig. Anti-wear properties of the castor oil samples were improved by adding ZnO as nano friction modifier, up to a certain concentration of zinc oxide (0.1%), beyond which not much improvement in the coefficient of friction was noticed, but wear rate increased. The formation of tribo film due to the adsorption and the adherence of this nano friction modifier on the metallic surfaces were responsible in reducing wear. The results show that castor oil can be a good choice as a green lubricant for the replacement of commercial mineral oils, if optimally additivated.

From the available documentation, ZnO was rarely used in rapeseed oil for improving wear and friction characteristics. This research aims to point out the influence of the additive concentration in rapeseed oil, on tribological parameters determined on four-ball tester.

2. Lubricant formulation and test method

The additive was supplied by PlasmaChem [17] and has the following characteristics (see figure 1): average particle size ca. 14 nm, specific surface area 30 ± 5 m^2/g, purity > 99%.
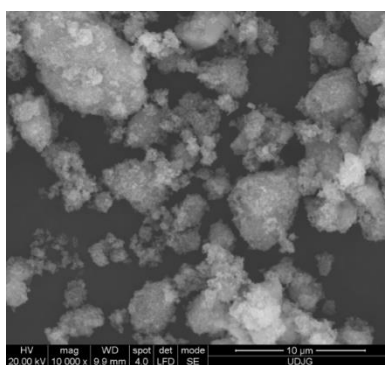

Figure 1. The nanoparticles of ZnO.

This study presents the results for the neat rapeseed oil (see Table 1) and the same vegetal oil additivated with 1% wt ZnO.

The ratio of the root-mean-square roughness of surfaces in contact to the nanoparticles size is essential because the particles have to remain in the lubricated contact in order to protect them against wear, during the system functioning. If their size is too large as compared to surface profiles, the nanoparticles will not deposit on the contact zone, they will be dragged and squeezed in contact, resulting an increase of both friction and wear [5]. The issue related to this type of nano lubricants is that, initially, the nanoparticles remain dispersed, but after an operating time, they are pressed into the solids' texture and agglomerated from nano to macro size. The dispersant and the lubricant have to prevent that, but larger particles are noticed on contact surface and even around it (see figure 2).

Table 1. Typical composition in fatty acids of the rapeseed oil (from Expur Bucharest).

Fat acid	Symbol	Composition, %wt
Myristic acid	C14:0	0.06
Palmitic acid	C16:0	4.60
Palmitoleic acid	C16:1	0.21
Heptadecanoic acid	C17:0	0.07
Heptadecenoic acid	C17:1	0.18
Stearic acid	C18:0	1.49
Oleic acid	C18:1	60.85
Linoleic acid	C18:2	19.90
Linolenic acid	C18:3	7.64
Arachidic acid	C20:0	0.49
Eicosenoic acid	C20:1	1.14
others		3.37

The formulated lubricant was obtained in small amounts of 200 g, each. The steps followed in this laboratory technology were similar to those presented by Cristea [18]:

- mechanical mixing of the additive and an equal mass of dispersing agent (guaiacol, from Fluka Chemica, with the chemical formula $C_6H_4(OH)OCH_3$ (2-methoxyphenol)), for 20 minutes;

- gradually adding rapeseed oil, mixing with a magnetic homogenizer for 1 hour;

- ultrasonication + cooling of formulated lubricant in step of 10 minutes; the fluid is heating to about 70°C during sonication; the cooling time was 1 hour; this technological 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 test balls are lime polished, made of chrome alloyed steel balls, having 12.7 ± 0.0005 mm in diameter, with 64-66 HRC hardness, as delivered by SKF. The oil volume required for each test was 8 ml ± 1 ml. The test method for investigating the lubricating capacity was that from SR EN ISO 20623:2018 [19].

The test parameters for each test 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;

- loading force on the machine spindle - 100 N, 200 N and 300 N (± 5%);

- test time - 60 minutes (± 1%).

The graphs of the wear scar diameters (WSD) as a function of speed could not reflect in a relevant way the influence of testing regimes, because all tests has 1 h (with different sliding distances for each speed), and, thus, the authors studied the influence of additive concentration with the help of wear rate of the scar diameter, noted by w(WSD). The w(WSD) is calculated with the help of the following relationship:

$$w(WSD) = \frac{WSD}{F \cdot L} \left[mm / (N \cdot mm) \right] \tag{1}$$

where WSD is the average value of six measurements of the wear scar diameter, two on each fixed ball (one along the sliding direction and the other perpendicular to it), F is the load applied on the main shaft of the tribotester (carrying the rotating ball) and L is the sliding distance. Thus, the wear rate of WSD reflects the dimensional modification of WSD for the unit of mechanical work, done by the tester system.

3. Results

From SEM investigations, the authors noticed that the nanoparticles of ZnO are spread over the contact scar of the balls. Images in figure 2 were obtained at a scanning electron microscope, after drying the balls as they were taken from their cup to point out the presence of the additive on the contact zone. The additive does not form a continuous layer on the contact and the nanoparticles agglomerate in very different size and shape, especially under low load (F = 100 N). Under higher load, the particles agglomerate less and have a spheroidal shape (figure 2a) also presents how the two scar diameters were measured. Mariani [20], Gulzar et al. [21], Chan et al. [22] and Zulkifli et al. [23] stated that metallic oxide (CuO, ZnO etc.) are able to coalesce in asperity valleys, creating a thin, smooth and solid lamellar film between contacting surfaces. Authors' SEM investigation (figure 2) revealed that this "film" is not continuous, the additive being spread in contact as small rollers or spheroidal particles that prevent wear of the triboelements and reducing friction when acting like micro rolling bearings.
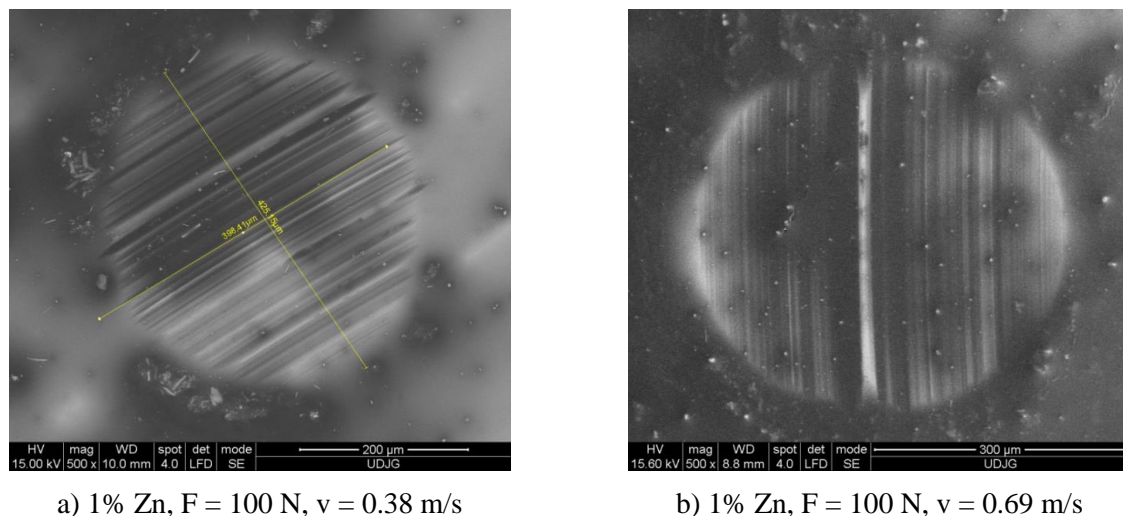

a) 1% Zn, F = 100 N, v = 0.38 m/s　　　　　　b) 1% Zn, F = 100 N, v = 0.69 m/s

Figure 2. Worn scars, dried in calm air with the lubricant on.

The obtained experimental data were included in maps that could emphasis the synergic effect of two variables, here, the load and the additive concentration, each map being drawn for the same sliding speed. The maps were done with the help of Matlab R2016a, using a spline interpolation and the surfaces are "forced" to include the experimental values. A point on these maps represents the average of two tests, with the same set of parameters (F [N], c [%wt.], v [m/s]), where F is the load on the spindle of the four ball tester and c is the mass concentration of the nano additive (0%, 0.25%, 0.5%, 1.0%), and v is the sliding speed.

Figure 3 presents the maps for the friction coefficient (COF). The qualitative modification could be allocated to change in the lubrication regime. For instance, at v = 0.38 m/s, COF has the lowest values (blue colour) for the neat oil till 200 N and for 0.75...1% additive concentration, for F = 100...150 N. The values that characterize a mixt or boundary regime (around 0.1) were obtained for concentration of 0.75...1% and for loads F = 200...300 N. Under high load the neat oil has for this tribological parameter a better (lower) value. For the additivated oil, COF decreases when the additive is towards

1% due to its rolling effect in contact, but under higher loads, the particles do not roll, being dragged in contact. They protect the surface but increase the friction. Increasing the sliding speed at v = 0.53 m/s, COF has a band of low values (blue colour and light green) for concentrations 0.6...1%. And the parameter seems to be almost insensitive to load, meaning a friction almost constant even if the contact has the load variable in the tasted range. At lower concentration (0.15...0.35%), COF increased toward 0.1, meaning that this concentration interval makes COF to increase. Probably, the presence of ZnO particles disturb the generation of the EHL film. At highest speed (v = 0.69 m/s), COF has only a small region (F,c) with values around 0.1, meaning the speed increase is beneficial for not losing power by friction. As it is given in Dowson et al. [24], speed has a more powerful influence on generating a fluid film than load and, here, additive concentration. The lowest values of COF were also obtained for the neat vegetal oil.

Similar tests done by Bhaumik et al. [16], with speed 1200 rpm (0.48 m/s), load 392 N, 1 h, at 75°C and room temperature, using balls with close characteristics and dimension, give the lowest value of COF (0.06) for castor oil + 0.1% ZnO and between 0.062...0.07 for the other additive concentrations (0.5...2%).
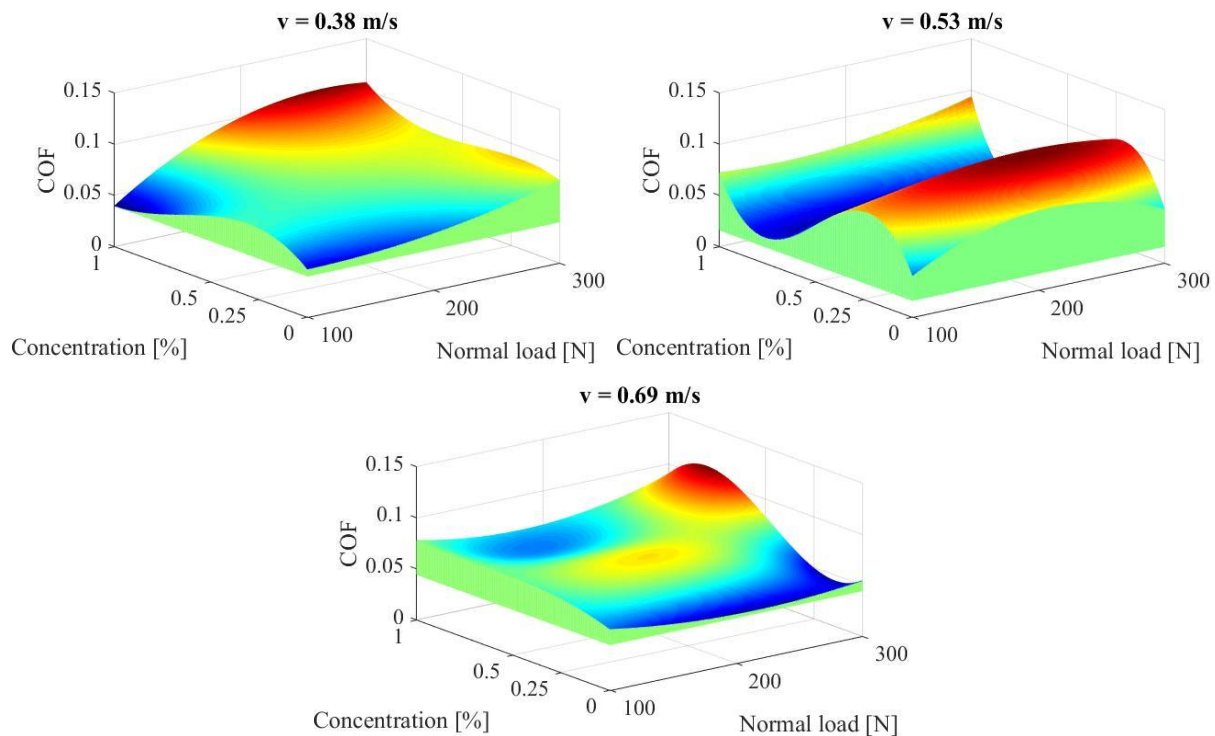

Figure 3. Maps for the friction coefficient (average value for each test).

Bhaumik et al. [16] reported a decrease of the WSD for 0.1% ZnO in castor oil, at 0.42 mm, as compared to 1 mm for castor oil + 0.5% ZnO, for intermediate test parameters as compared to authors' tests (0.48 m/s and F = 392 N). For the same concentration, the authors obtained 0.56...0.72 mm for F = 300 N, for v = 0.38 m/s and v = 0.53 m/s, respectively (Table 2).

Table 2. WSD, calculated as average of six measurements of diameters of the fixed ball

Load (N)	v = 0.38 m/s ZnO concentration (wt%)				v = 0.53 m/s ZnO concentration (wt%)				v = 0.69 m/s ZnO concentration (wt%)			
	0	0.25	0.5	1	0	0.25	0.5	1	0	0.25	0.5	1
100	0.37	0.386	0.438	0.379	0.351	0.3922	0.399	0.351	0.438	0.399	0.438	0.438
200	0.476	0.528	0.603	0.476	0.45	0.487	0.606	0.454	0.603	0.606	0.603	0.603
300	0.560	0.656	0.724	0.560	0.527	0.620	0.722	0.527	0.724	0.722	0.724	0.724

When analysing the wear parameter (Figure 4), two distinct zones are visible on the maps, one of high values (red and yellow colours), characteristic for low load and the other one, with low values (light to dark blue) for F = 200...300 N, less dependent on additive concentration. Speed makes the wear rate of wear scar diameter to be under 1×10^{-6} mm/N×m, a good value as comparing to other results obtained on four-ball tribotester. Higher speed produces a fluid film that is in the favour of reducing wear by keeping the separation of the solid bodies in contact.
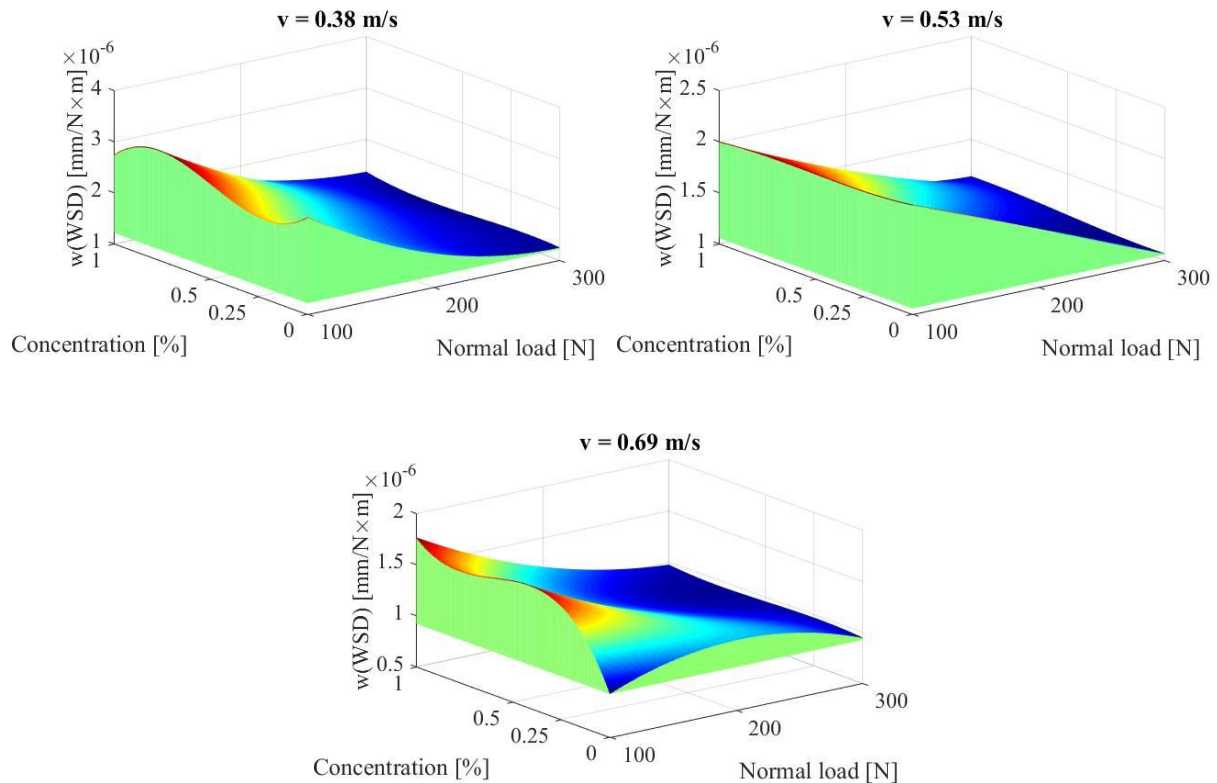

Figure 4. Wear rate of WSD.

Qian et al. [12] obtained smaller WSD for 3% ZnO in base oil, tested on four-ball tester, at 1450 rpm (0.54 m/s) at room temperature, for 30 min. For instance, the WSD for F = 300 N is 0.4 mm, but for 1%, WSD was 0.6 mm. The authors obtained 0.722 mm but for test of 1 h, meaning that continuous running is favourable to keep wear at low level.

The discussion on temperature recorded at the end of the test is important as a vegetal oil has a narrower temperature range of functioning, higher temperature inducing oxidation and other chemical changes in the components of the oil. The addition of nanoparticles increases this temperature value, especially at higher loads for v = 0.53...0.69 m/s. Observing the evolution of end test temperature for the neat rapeseed oil, the lowest values were obtained and the increase of final temperature with load is almost linear (see figure 5). For F = 300 N and v = 0.38...0.53 m/s, the temperature has just a little increase of several degrees, but for v = 0.69 m/s, this increase is of 10...14°C. For the additivated lubricant, the maximum final temperature was obtained for the additive concentration of 0.5...0.8%. A slight decrease of final temperature was obtained for 1% ZnO, meaning that this concentration (the highest tested in this study) helps to evacuate the heat generated in contact.
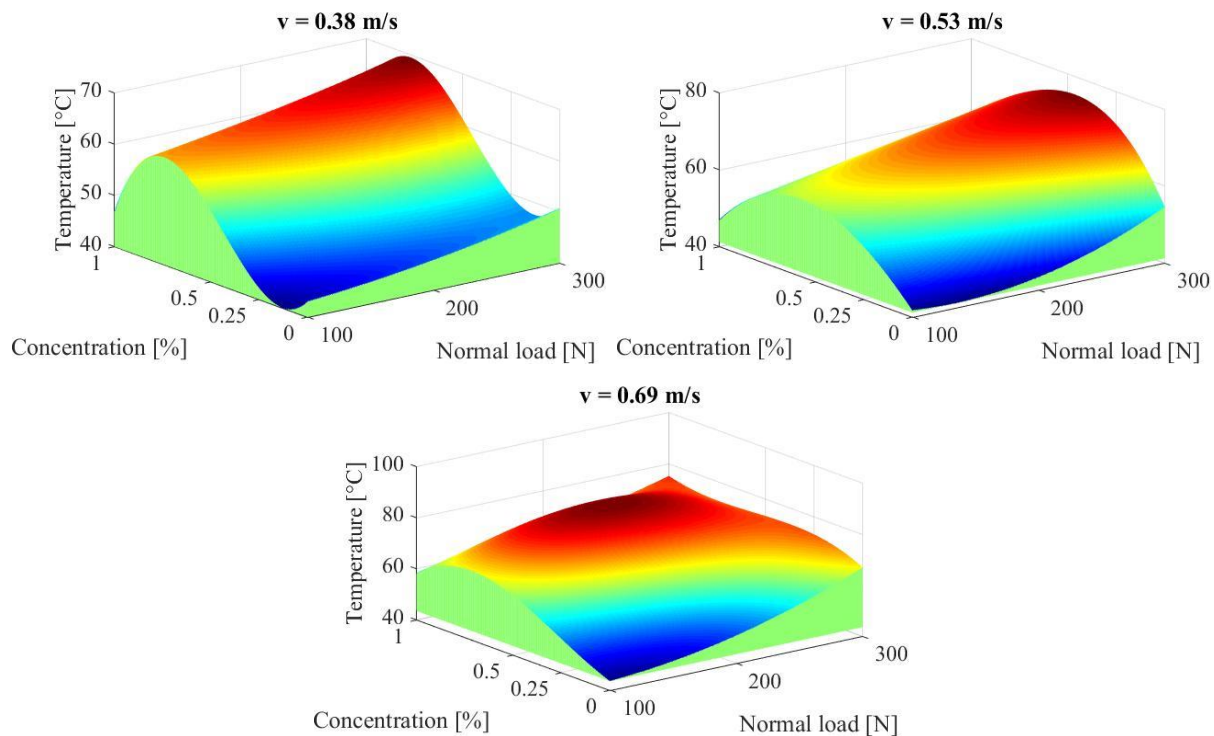
Figure 5. Final temperature in the lubricant bath, recorded at the end of 1 h test.

4. Conclusions

The authors of this research study formulated lubricants based on rapeseed oil, with addition of nanoparticles of ZnO, in different mass concentration (0.25%, 0.5% and 1%, respectively), using as dispersant 2-methoxyphenol in the ratio 1:1 to the additive. The technology is at scale laboratory and implies mechanical stirring and sonication.

The tribological behavior was analysed based on results obtained on a four-ball machine, by mapping the friction coefficient, the wear ate of the wear scar diameter and the final temperature in the lubricant bath.

For the additivated lubricants the following conclusions could be drawn only for the tested regimes:
- friction coefficient tends to reach 0.1 only for low speed and high load (v = 0.38 m/s and F = 300 N),
- wear rate of wear scar diameter decreases with the increase of load, for each tested speed, probably because of a fluid film generation; for F = 250...300 N, the map of this parameter reveals a poor dependence on the additive concentration,
- the final temperature in the lubricant bath depends on speed, but for the same speed, it depends less on load, having maximum values for 0.75% nano additive.

These conclusions underlined the necessity of testing the new formulated lubricants because additive concentration and regime parameters do not have similar influences on the tribological parameters. Thus, the designer and the operator have to make a compromise and select the lubricant and the functioning regime that less affect the entirely system exploitation and adding also some constraints concerning the environment protection and security regulations.

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