Serbian Tribology Society

SERBIATRIB '19

16th International Conference on Tribology

Faculty of Engineering
University of Kragujevac

Kragujevac, Serbia, 15 – 17 May 2019

TRIBOLOGICAL BEHAVIOR OF COARSE RAPESEED OIL ADDITIVATED WITH NANOPARTICLES OF ZINC OXIDE

Traian Florian IONESCU[1], **Dionis GUGLEA**[1], **Constantin GEORGESCU**[1],
Petrica ALEXANDRU[1], **Lorena DELEANU**[1,*]
[1]"Dunărea de Jos" University of Galati, Faculty of Faculty of Engineering, Galati, Romania
*Corresponding author: lorena.deleanu@ugal.ro

Abstract: *This paper presents the influence of ZnO as additive in refined rapeseed oil in a mass concentration of 1%wt on the tribological parameters. Tests are done on a four-ball machine from the laboratory LubriTest, at "Dunarea de Jos" University of Galati. The test parameters were load: 100 N, 200 N and 300 N and the rotational speed 1000 rpm, 1400 rpm and 1800 rpm, corresponding to the following sliding speeds, 0.38 m/s, 0.53 m/s and 0.69 m/s, respectively. Particles of ZnO have 14±5 nm. The rapeseed oil was supplied by Expur SA Bucharest. For the tested ranges of the parameters, the additivation of rapeseed oil with ZnO does not improve the friction coefficient, but the wear rate of WSD seems to be less sensitive for the more severe regimes when the vegetal oil is additivated. The additivation of rapeseed oil with ZnO is still efficient for the tested ranges of load and speed as compared to the neat rapeseed oil, but there is visible that friction coefficient and analysed wear parameter are less influenced by the regime for the concentration of 1% ZnO in rapeseed oil.*

Keywords: *rapeseed oil, additive, ZnO, four ball test, friction coefficient, wear rate*

1. INTRODUCTION

The rapeseed oil is in the focus of the researchers for replacing lubricants that are not friendly with the environment.

Metal oxides as additives in lubricants improve especially the wear parameters, protecting the initial texture of the contacting surfaces. Based on experimental results on four ball tribotester, Asrul [1] concluded that the higher concentrate of CuO (3%), the better the tribological behavior.

In a recent review, Shahnazar [2] mentioned ZnO as having good characteristic for improving the tribological behavior of a lubricant due to large surface area, high surface energy, good adsorption on metallic surfaces, good diffusion, easy sintering and a low melting point [3]. Due to the low solubility of ZnO in oil, their dispersion in the base oil or even in water-based fluids could be a challenge [4].

In 2011, Qian et al. [5] prepared ZnO (average size 125 nm) by a homogeneous precipitation method using lauryl sodium sulphate as the surfactant and studied the oil solubility, anti-corrosion, and tribological properties of ZnO used as an additive, but they did not mentioned the base oil. Taking into account the solubility, the addition of 1.0%, 2.0%, 3.0%, and 4.0% mass concentration of ZnO improve the tribological behavior of this type of lubricant (friction reduction and anti-wear properties).

Using the ball-on-disk tests, Gara and Zou [6] investigated the friction and wear properties of ZnO and Al_2O_3 in waterbased nanofluids. The combination of these nanoparticles reduces friction for smooth surfaces, but nanoparticles acted as abrasive wear particles.

Tang and Li [22] considered the nanoparticles a class of additives that have particular mechanisms of reducing friction and wear: rolling effect as in a third-body friction, protective spacers against directly rubbing the solid bodies, mending process if the particle size is smaller than texture parameters and polishing due to their mild abrasive process till the surfaces accommodate.

In a very recent review, Uflyand [7] mentioned the following metal oxides used as additives: TiO_2, CuO, Fe_3O_4, ZnO, Co_3O_4 and Al_2O_3, and results are also reported in [8], [9], [10], [11], [12], [16], [18], [28], [30]. Their mechanisms during lubrication are similar to those of metal nanoparticles, and the authors including the formation of tribo-film or adsorption film, the rolling effect, and the sintering or repair effect. The friction reduction can be due to the effect of viscosity at lower temperature and the rolling effect at higher temperature. The wear reducing mechanism is associated with the deposition of nanoparticles into the texture of the friction surfaces.

The use of ZnO and CuO nanoparticles as lubricant additives [19], [27], [15], [13] in vegetal oils (soybean, rapeseed oil and sunflower) are biodegradable and have better tribological behavior in boundary lubrication.

Song [24] tested monodispersed spherical zinc aluminate spinel ($ZnAl_2O_4$) nanoparticles, modified by oleic acid in cyclohexanol solution. The dispersion ability of nanoparticles in lubricant oil was good for tested concentrations (0.05, 0.1, 0.5, and 1 wt.%). The tribological properties of the $ZnAl_2O_4$ nanoparticles as an additive in lubricant oil were evaluated with four-ball test and thrust-ring test. For comparison, ZnO and Al_2O_3 nanoparticles as additive in lubricant oil were also tested. The $ZnAl_2O_4$ nanoparticles exhibit better tribology properties in terms of anti-wear and anti-friction than ZnO or Al_2O_3 nanoparticles, separately. The lubricating effect of $ZnAl_2O_4$ nanoparticles can be explained by their rolling effect and sintering process. When the $ZnAl_2O_4$ nanoparticles concentration is 0.1 wt%, there was obtained an optimal effect on reducing both friction and wear.

Magnetic Fe_3O_4 nanoparticles with an average diameter of 11.7 nm were dispersed in alpha-olefin hydrocarbon synthetic lubricating oil with a concentration of 0 to 10 wt% [21], [20]. This resulted in a reduction in COF and the diameter of the wear scar by 45% and 30%, respectively, at the optimal concentration value (4 wt%). The rolling mechanism is responsible for reducing COF and the nanoparticles act as spacers between the asperities and reduce the diameter of the wear scar.

Chan et al. [25] underlined that nano particles as CuO, TiO_2 and ZnO are non-toxic anti-wear additives for lubricants. With their sizes ranging from 2 to several hundreds nanometers, these are able to fill in asperity valleys, creating a thin, smooth and solid lamellar film on contacting surface. The authors of this paper revealed by SEM investigation that there is not a continuous film, but a disperse powder that prevents the two solid bodies to directly contact each other. If the particle size is smaller than the surface roughness, the wear volume decreases with the decrease of additive size. When particle size is larger than the surface texture, grooves are produced due to abrasion. The problem is that small nanoparticles agglomerate and, thus, the particle size in contact becomes a variable during sliding. If particles become larger, they could not be dragged into contact and their beneficial effect is very much reduced. And if they enter into contact they could produce oscillations of friction coefficient and severe wear when they left the contact to be between the solid bodies with wear traces already produced.

A parameter affecting frictional and wear behavior is the concentration of the additive.

The excessive additive particles in the asperities valleys could either give insignificant improvement in tribological performance, or produce abrasive wear (ploughing effects). The latter may be due to the interference of the additive particles causing poor adsorption of base stock at the contact area resulting in inadequate lubrication, as observed in the case of nanoparticles in polar oils such as ester-based oils and vegetal oils.

Bhaumik [27] noticed an increasing trend in viscosity with the increase in concentration of ZnO nanoparticles. The coefficient of friction in case of castor oil samples is found to be less than the commercially available mineral oil, but the coefficient of friction did not decrease further after a certain concentration of ZnO (0.1 wt% ZnO is the optimum in this case). The wear rate is found to be the lowest and it increased with the increase in concentration of ZnO. The formation of tribo-film due to the adsorption of castor oil and the diffusion of zinc oxide in the surface grooves prevented the metal to metal interaction, thus decreasing the coefficient of friction and controlling the surface roughness, but higher percentage of zinc oxide led to deteriorations of the surfaces.

Hernandez Battez et al. [26] studied the anti-wear behaviour of nanoparticle CuO, with a block-on-ring tester, under a load of 165 N, sliding speed of 2 m/s and a total distance of 3,066 m. All formulated lubricants with nanoparticle exhibited reductions in friction and wear compared to the base oil; the lubricants with 0.5% of ZnO and 0.5% ZrO_2 had improved characteristics for wear but the friction coefficient increased.

Sepyani et al. [29] investigated the effect of ZnO nanoparticles on rheological behavior of SAE 50 oil, at different temperatures. Viscosity at different shear rates revealed a Newtonian behavior of the formulated lubricants, having the maximum increase in viscosity of 12% for more concentrated samples, at low temperature.

The aim of this study is to assess the influence of ZnO in coarse rapeseed oil on the tribological characteristics. The authors analysed the friction coefficient and the wear rate of wear scar diameter, but also recorded the temperature in the oil cup, during the tests.

2. THE LUBRICANT AND THE TESTING METHODOLOGY

The additive was supplied by PlasmaChem [32] and has the following characteristics (Fig. 1): average particle size ca. 14 nm, specific surface area: 30±5 m^2/g, purity: >99% and this study presents the results for the neat rapeseed oil (Table 1) and the same vegetal oil additivated with 1% ZnO.

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

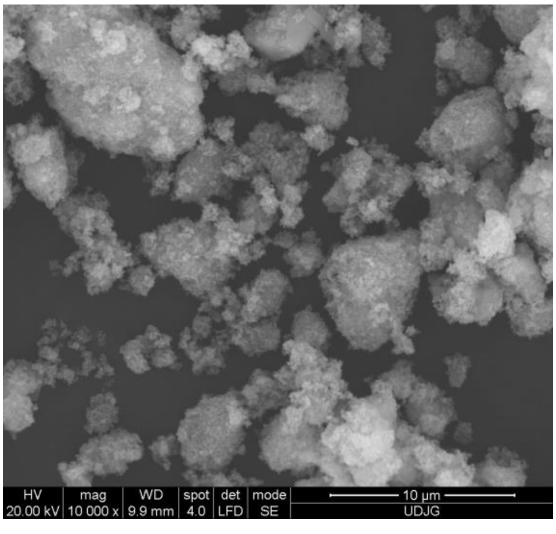


Figure 1. A SEM image of nanoparticles of ZnO

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 [17]:

- mechanical mixing of the additive and an equal mass of dispersing agent (guaiacol, supplied by 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 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 [32].

The test parameters for each test were:

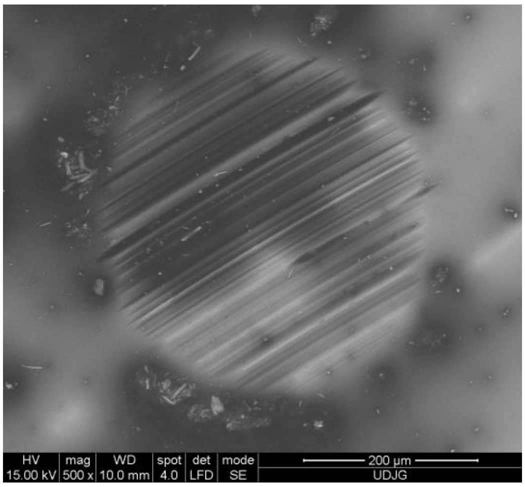
- loading force on the machine spindle - 100 N, 200 N and 300 N (± 5%);
- sliding speeds of 0.38 m/s, 0.53 m/s and 0.69 m/s, corresponding to the spindle speeds of the four-ball machine of 1000 rpm, 1400 rpm and 1800 rpm (± 6 rpm), respectively;
- test time - 60 minutes (± 1%).

3. RESULTS

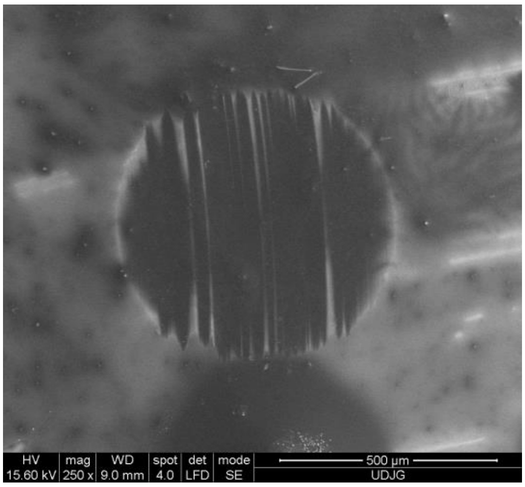
3.1. Friction coefficient

The authors agree with the conclusion of Shahnazar [2] that ZnO nano particles could decrease the wear of direct contact areas by being depositing onto the sliding surfaces, but SEM images do not prove that ZnO forms a lubricating layer on rubbing surfaces as many researches have believed (Fig. 2).

Figure 3 presents the average value of COF as obtained from two tests, for both tested lubricants. It is obvious that the neat oil has lower values, especially for heavy regimes, but the additivated oil has this parameter less sensitive to sliding speed for F=300 N. This is recommended for machines that frequently change their working regime.



a) F=100 N, v=0.38 m/s



b) F=300 N, v=0.69 m/s

Figure 2. SEM images of the wear scars without pulling out the lubricants, at the end of the test

3.2. Wear rate of the wear scar diameter

Measurement of wear trace diameters was performed with the optical microscope, in accordance with the procedure given in SR EN ISO 20623:2018 [31]. Three wear marks were obtained for each test, these being located on the three fixed balls. Two diameters, the first diameter measured along the sliding direction, the second diameter measured perpendicular to the first, were measured for each wear trace.

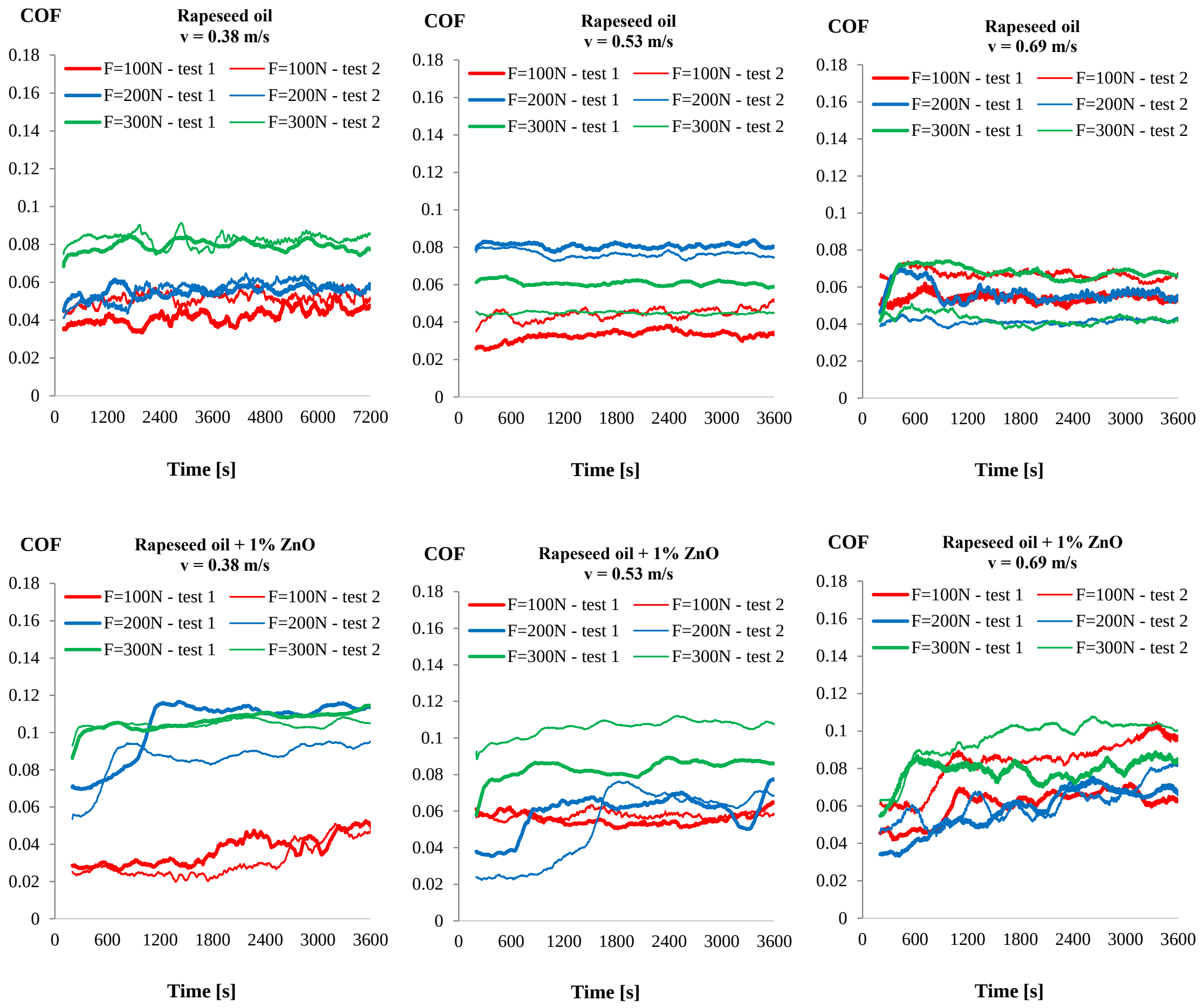


Figure 3. COF evolution in time

(2 sample per second and a moving average on 200 consecutive values)

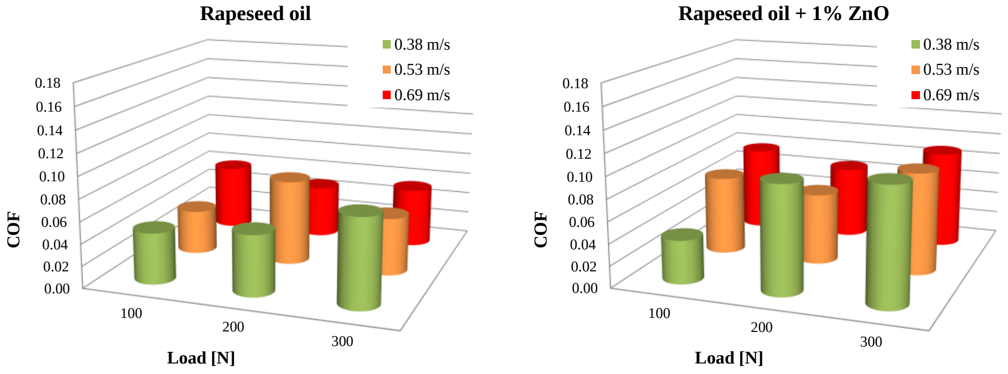


Figure 4. Average of COF for two values (two tests done under the same parameters)

With three traces of wear, six diameters were obtained and their mean value was calculated. This value represents the diameter of the wear scar, reported for each of the tests performed. The same method of obtaining the wear diameter is also given in specialized reports [31].

Figure 5 shows images of the wear scars as obtained with the help of an optical microscope. One may notice that the contact surfaces as resulted after testing with the additivated oil is less damaged.

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:

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

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. The product F×L is the mechanical work done by the tribotester. Thus, the wear rate of WSD reflects the dimensional modification of WSD for the unit of mechanical work.

Figure 6 presents the wear rate of WSD and the values are lower for heavy regimes (F=200...300 N) for all sliding speeds. Only when tested at lowest speed (v=0.38 m/s) this parameter is close for both tested lubricants.

3.3. Temperature in the oil bath

The evolution of oil bath temperature during a test of 1 h is given in Figure 8.

The difference among final registration of temperature (at the end of the test) is small for low regimes (v=0.38...0.53 m/s) and its value is kept in the range 43...55°C, but for the highest speed (v=0.69 m/s), the temperature values are spread on a larger interval.

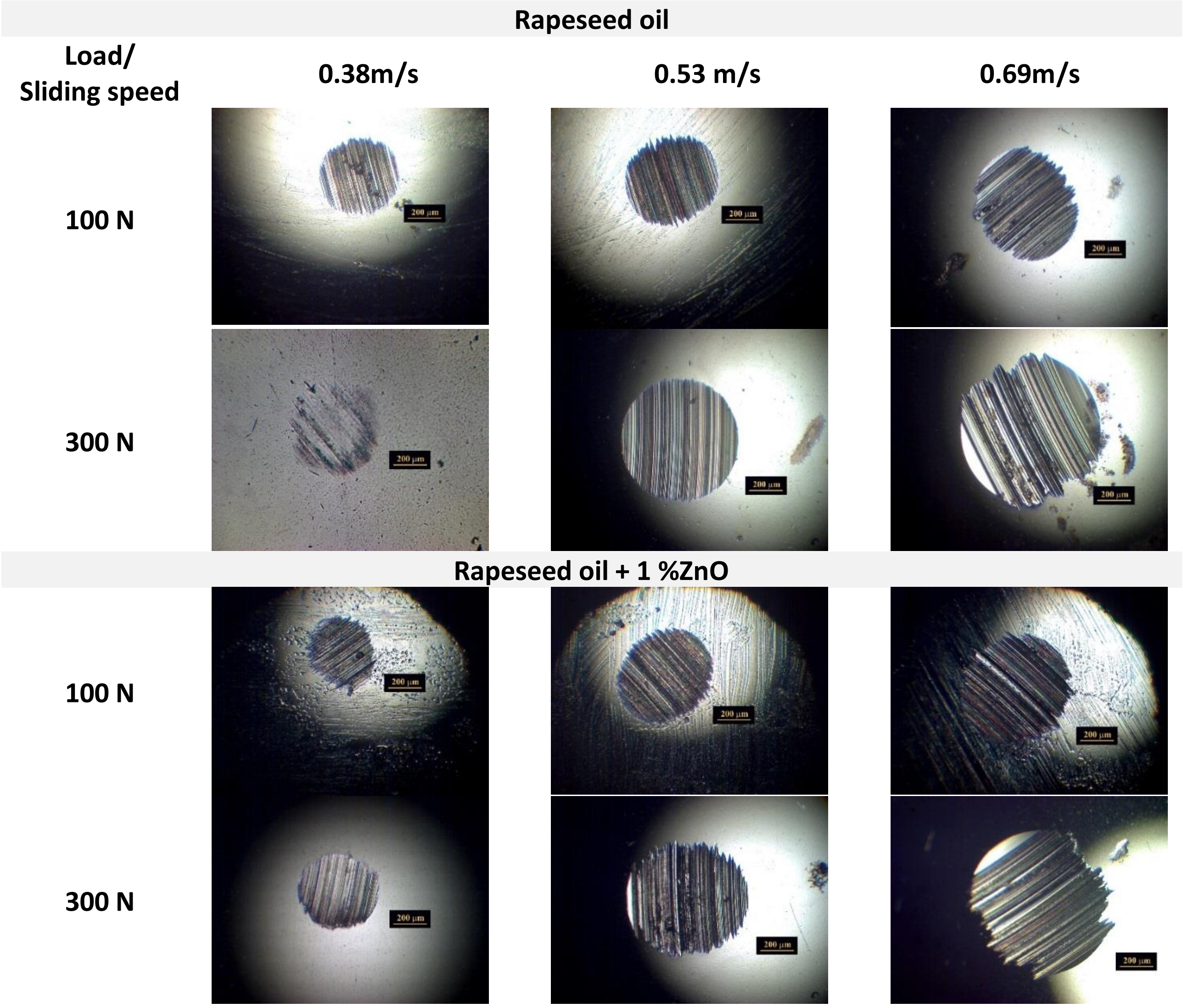


Figure 5 Typical wear scars for different regimes

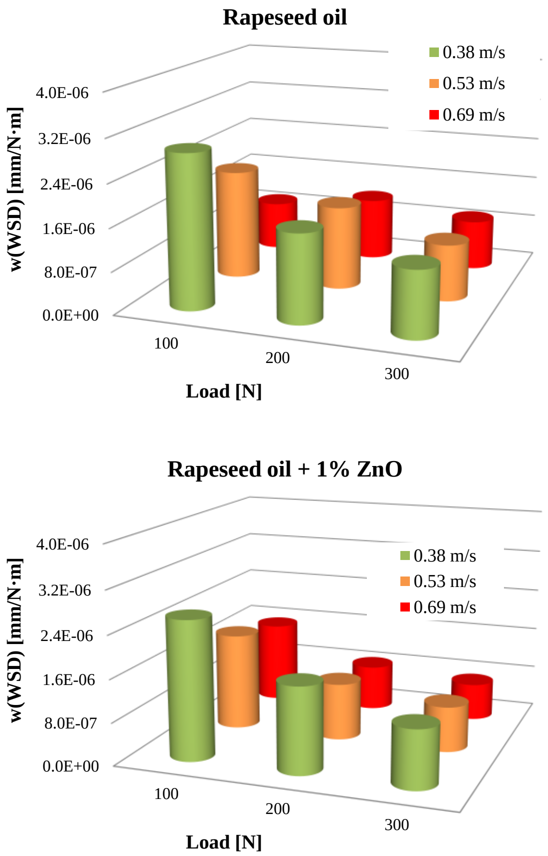


Figure 6. Wear rate of the wear scar diameter for the two tested lubricants, for different regimes

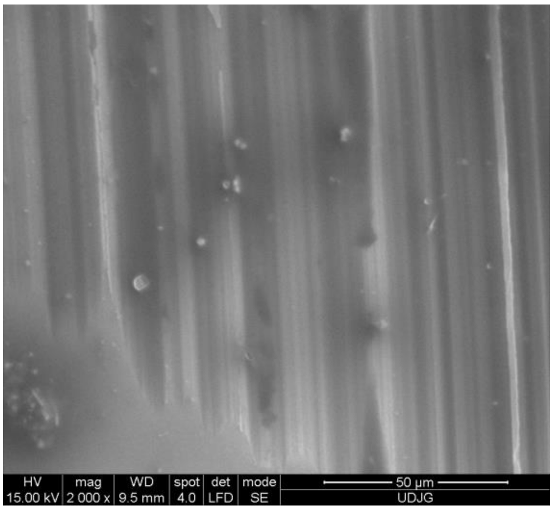


Figure 7. A detail of the wear scar without cleaning the lubricant

For the most severe regime the final recorded temperature for the rapeseed oil is about 70°C. The rapeseed oil additivated with ZnO has these temperatures higher, in the range of 50...60°C for v=0.38...0.53 m/s and for the highest speed the interval is larger (60...77°C). The supplementary heat generation could be explained by the friction of intermediate particles of Zn, rolling or being dragged in contact.

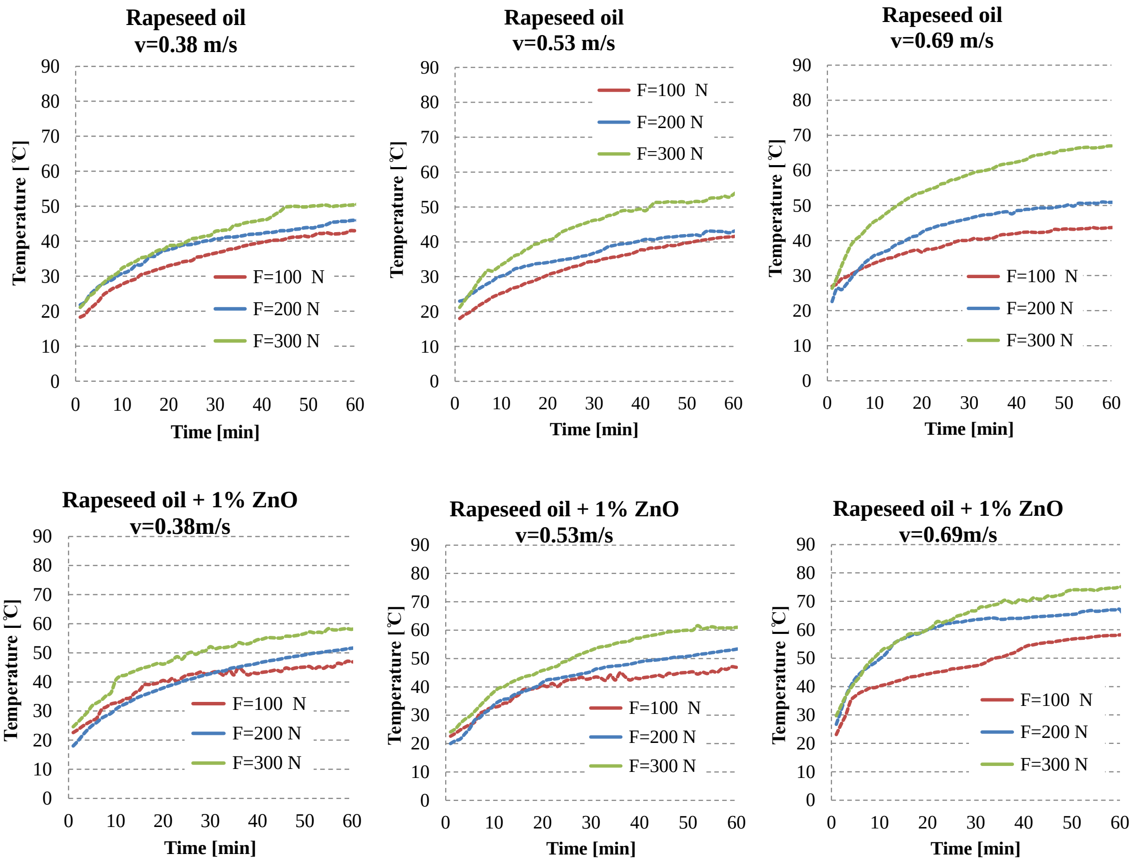


Figure 8. Temperature evolution

4. CONCLUSIONS

At least for the tested ranges of the parameters (v=0.38...0.69 m/s and F=100...300 N), the additivation of rapeseed oil with nanoparticles of ZnO does not improve the friction coefficient. But this additive was efficient for wear reduction, the authors pointed this out by comparing the values of the wear rate of wear scar diameter.

ACKNOWLEDGEMENT

This paper was supported by Doctoral School for Mechanical and Industrial Engineering of "Dunarea de Jos" University of Galati.

REFERENCES

[1] T.M. Asrul, N.W.M. Zulkifli, H. H. Masjuki, M.A. Kalam: Tribological properties and lubricant mechanism of nanoparticle in engine oil, Procedia Engineering, Vol. 68, pp. 320–325, 2013.

[2] S. Shahnazar, S. Bagheri, S. B. Abd Hamid: Enhancing lubricant properties by nanoparticle additives, International Journal of Hydrogen Energy, Vol. 41, pp. 3153-3170, 2016.

[3] J.W. Soares, J.E. Whitten, D.W. Oblas, D.M. Steeves: Novel photoluminescence properties of surface-modified nanocrystalline zinc oxide: toward a reactive scaffold, Langmuir, Vol. 24, No. 2, pp. 371-374, 2007.

[4] E. Tang, G. Cheng, X. Ma, X. Pang, Q. Zhao: Surface modification of zinc oxide nanoparticle by PMAA and its dispersion in aqueous system, Applied Surface Science, Vol. 252, No. 14, pp. 5227-5232, 2006.

[5] J. Qian, Y. Zhang, L. Wang, J. Xing: China Petroleum Processing and Petrochemical Technology, Vol. 13, No. 3, pp. 69-73, 2011.

[6] L. Gara, Q. Zou: Friction and wear characteristics of waterbased ZnO and Al_2O_3 nanofluids. Tribology Transactions, Vol. 55, No.3, pp. 345-350, 2012.

[7] I. E. Uflyand, V. A. Zhinzhilo, V. E. Burlakova: Metal-containing nanomaterials as lubricant additives: State-of-the-art and future development, Friction, Vol. 7, No. 2, pp. 93–116, 2019.

[8] I.E. Uflyand, V.A. Zhinzhilo, L.S. Lapshina, A.A. Novikova, V.E. Burlakova, G.I. Dzhardimalieva: Conjugated thermolysis of metal chelate monomers based on cobalt acrylate complexes with polypyridyl ligands and tribological performance of nanomaterials obtained, Chemistry Select, Vol. 3, pp. 8998–9007, 2018.

[9] S.S. Sanukrishna, S. Vishnu, T.S. Krishnakumar, M.J. Prakash: Effect of oxide nanoparticles on the thermal, rheological and tribological behaviours of refrigerant compressor oil: An experimental investigation, International Journal of Refrigeration, Vol. 90, pp. 32–45 2018.

[10] G.C. Cristea, D. Cazamir, D. Dima, C. Georgescu, L. Deleanu: Influence of TiO_2 as nano additive in rapeseed oil, ACME 2018, The 8th International Conference on Advanced Concepts in Mechanical Engineering, June 07-08, Iasi, IOP Conference Series: Materials Science and Engineering, 444, Machine Design. Tribology, 022011

[11] S. Ingole, A. Charanpahari, A. Kakade, S. Umare, D.V. Bhatt, J. Menghani: Tribological behavior of nano TiO_2 as an additive in base oil, Wear, Vol. 301, pp. 776–785, 2013.

[12] P. Zulhanafi, S. Syahrullail, M.M. Faridzuan: Tribological performance of palm kernel oil added with nanoparticlecopper oxide using fourball tribotester, Jurnal Teknologi, Vol. 79, pp. 53–59, 2017.

[13] M.F. Trajano, E.I.F. Moura, K.S.B. Ribeiro, S.M. Alves: Study of oxide nanoparticles as additives for vegetable lubricants, Materials Research, Vol. 17, pp. 1124–1128, 2014.

[14] S. Bhaumik, R. Maggirwar, S. Datta, S.D. Pathak: Analyses of anti-wear and extreme pressure properties of castor oil with zinc oxide nano friction modifiers, Applied Surface Science, Vol. 449, pp. 277-286, 2018.

[15] F.A. Essa, Q. Zhang, X. Huang, A.M.M. Ibrahim, M.K.A. Ali, M.A.A. Abdelkareem, A. Elagouz: Improved friction and wear of M50 steel composites incorporated with ZnO as a solid lubricant with different concentrations under different load, Journal of Materials Engineering Performance, Vol. 26, pp. 4855-4866, 2017.

[16] V.P. Suresh Kumar, N. Manikandan, C. Subakaran, Y.G. Sterbin Jeso: An experimental effect of ZnO nanoparticles in SAE 20W50 oil, International Research Journal of Engineering Technology (IRJET), Vol. 5, pp. 1069–1073, 2018.

[17] G.C. Cristea: *Tribological characterization of soybean oil additivated with nano materials based on carbon (black carbon, graphite and graphene*, PhD thesis: "Dunarea de Jos" University of Galati, Romania, 2017.

[18] X. Ran, X. Yu, Q. Zou: Effect of particle concentration on tribological properties of ZnO nanofluids, Tribology Transactions, Vol. 60, pp. 154-158, 2017.

[19] S. Arumugam, G. Sriram: Synthesis and characterization of rapeseed oil bio-lubricant dispersed with nano copper oxide: its effect on wear and frictional behavior of piston ring–cylinder liner combination, Proceedings of the Institution of Mechanical Engineers, Part J: Journal of Engineering Tribology, Vol. 228, p. 1308, 2014.

[20] G. Zhou, Y. Zhu, X. Wang, M. Xia, Y. Zhang, H. Ding: Sliding tribological properties of 0.45% carbon steel lubricated with Fe3O4 magnetic nanoparticle additives in base oil, Wear, Vol. 301, pp. 753–757, 2013.

[21] K. Trivedi, K. Parekh, R.V. Upadhyay: Nanolubricant: magnetic nanoparticle based, Material Research Express, Vol. 4, 114003, 2017.

[22] Z. Tang, S. Li S: A review of recent developments of friction modifiers for liquid lubricants (2007–present) Current Opinion in Solid State and Materials Science, Vol. 18, pp 119–139, 2014.

[23] E. Tang, G. Cheng, X. Ma, X. Pang, Q. Zhao: Surface modification of zinc oxide nanoparticle by PMAA and its dispersion in aqueous system, Applied Surface Science, Vol. 252, No. 14, pp. 5227-5232, 2006.

[24] X. Song, S. Zheng, J. Zhang, W. Li, Q. Chen, B. Cao: Synthesis of monodispersed $ZnAl_2O_4$ nanoparticles and their tribology properties as lubricant additives, Material Research Bulletin, Vol. 47 No. 12, pp. 4305-4310, 2012.

[25] C.H. Chan, S.W. Tang, K. Noor, Mohd, W.H. Lim, S.K. Yeong, Z. Idris: Tribological behavior of biolubricant base stocks and additives, Renewable and Sustainable Energy Reviews, Vol. 93, pp. 145-157, 2018.

[26] A. Hernandez Battez, R. Gonzalez, J.L. Viesca, J.E. Fernandez, J.M. Dıaz Fernandez, A. Machado, R. Chou, J. Riba: CuO, ZrO_2 and ZnO nanoparticles as antiwear additive in oil lubricants, Wear, Vol. 265, pp. 422-428, 2008.

[27] S. Bhaumik, R. Maggirwar, S. Datta, S.D. Pathak: Analyses of anti-wear and extreme pressure properties of castor oil with zinc oxide nano friction modifiers, Applied Surface Science, Vol. 449, pp. 277–286, 2018.

[28] M.V. Thottackkad, P.K. Rajendrakumar, N.K. Prabhakaran: Experimental studies on the tribological behaviour of engine oil (SAE15W40) with the addition of CuO nanoparticles, Industrial Lubrication and Tribology, Vol. 66, pp. 289-297, 2014.

[29] K. Sepyani, M. Afrand, M.H. Esfe: An experimental evaluation of the effect on ZnO nanoparticles on the rheological behavior of engine oil, Journal of Molecular Liquids, Vol. 236, pp. 198-204, 2017.

[30] P. Yang, X. Zhao, Y. Liu, X. Lai: Preparation and tribological properties of dual-coated CuO nanoparticles as water based lubricant additives, Journal of Nanoscience and Nanotechnology, Vol. 16, p. 9683, 2016.

[31] SR EN ISO 20623 Petroleum and related products. Determination of the extreme-pressure and anti-wear properties of lubricants. Four-ball method (European conditions), 2018.

[32] Nanomaterials and related products, 2016, PlasmaChem, available at: http://www.plasmachem.com/download/PlasmaChem-General_Catalogue_Nanomaterials.pdf, accessed 20.02.2016.