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TRIBOLOGICAL PERFORMANCE AND THERMAL CONDUCTIVITY OF LUBRICANT CONTAINING CUO NANOPARTICLES

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Abstract. *Nanofluids can be described as biphasic mixtures that consists of solid nanometric sized particles dispersed in a base fluid. According to the literature, a variety of nanoparticles have been used to investigate the ability to improve the tribological and thermal properties of lubricants by many authors. This work has as main objective the preparation of an oil-based nanofluid made from copper oxide (CuO) nanoparticles with 0.05; 0.1 and 0.2 wt% concentration dispersed in commercial polyolester synthetic oil. The samples were subjected to ultrasonic bath for 60 minutes and their stability was verified by observing sedimentation. 6.7 ml samples of nanofluids were used to perform dynamic viscosity test under 10 to 60°C temperature range. Tribological performance was evaluated using the High Frequency Reciprocating Rig (HFRR) ball (AISI 52100) on disc (cast iron FC-200) test at 50°C, obtaining values for coefficient of friction (COF), lubricating film formation and wear scar diameter (WSD) of the ball. The coefficient of thermal conductivity (k) was measured using the KD2 PRO equipment by transient line heat source method at 25°C. In comparison with the pure base oil, there was minimal variation in the dynamic viscosity with an increasing tendency for higher concentrations of nanoparticles, reduction of up to 14.5% in WSD and 7.6% in COF as well as a small increase of up to 1.3% for k.*

Keywords: *nanolubricant, tribological performance, thermal conductivity, viscosity*

1. INTRODUCTION

It is well known that the biggest cause of energy loss in mechanical systems is motivated by the friction between its components, however it can be minimized through lubrication. Akbulut (2012) found that the technology associated with lubricants has not kept up with the advances that occur in other branches of engineering, making the study of solutions for tribological limitations one of the greatest scientific challenges today through the development of new lubricants to satisfy their increasingly increasingly stringent applications.

In view of this need, the scope of modern tribology was expanded with the trial of lubrication systems based on nanofluids, whose development was facilitated by the study of nanotechnology in recent years. Nanofluids, in a generic way, consist of a biphasic mixture of solid particles of nanometric dimensions dispersed in a base fluid with or without the presence of surfactants.

According to the literature, a variety of nanoparticles have been used to investigate the effect of their addition on friction and wear properties, obtaining potentially interesting results, as published by Gulzar et al. (2016). Some types of particles have demonstrated the ability to reduce friction in the boundary condition, when added to base oils from different experimental studies as well as improve thermal conductivity coefficient and it is important once, according to Jwo et al. (2008) and Wrenick et al. (2005), in motors and refrigeration compressors, the lubricant has, besides the friction reduction function, participation in the heat dissipation process generated by the interaction between the moving parts.

The viscosity property of a fluid can be understood as a measure of its resistance to deformation. Viscosity is the result of the internal frictional force that develops between the different layers of fluids, as they are forced to displace each other when under the influence of a force. In nanofluids it is desirable that the viscosity remains as close as possible to the base fluid since too much increase can impair the pumping capacity of the oil while a large reduction can compromise the formation of lubricating film making it inefficient.

Kedzierski (2013) studied the effect of adding Al₂O₃ nanoparticles in polyolester base oil on the value of its kinematic viscosity for the temperature range of 15 to 25 °C. The author varied the concentration and the average diameter of the particles and pointed out in his results that, in general, the higher the concentration, the greater the positive difference between the viscosity value measured compared to the pure base oil, considering the concentrations of 5.6 to 39.6%.

Using the same Al_2O_3 nanoparticles and different polyethylene glycol (PEG) base oil, Sharif et al. (2016) came to the same conclusion that the higher the concentration of nanoparticles, the greater the positive difference in the viscosity of the nanofluid to the base fluid, even if in small concentrations (from 0.05 to 0.4% by volume).

A wide variety of experiments carried out to measure the thermal conductivity of nanofluids is available in the literature. As stated by Cárdenas Contreras (2017), although using the same type of nanoparticle and base fluid, it is possible to identify divergences between the results found in the literature. The great challenge that generates the inconsistencies in the values found is directly associated with the measurement method employed, in addition to the effects caused by the different ways of synthesizing nanoparticles. There are two main techniques used to measure thermal conductivities: transient and steady state.

In general, steady state techniques are useful when there is no variation in the temperature of the material over time. It can be cited as a disadvantage the fact that it is necessary to elaborate a complex experimental configuration. Transient techniques, on the other hand, consist of making a measurement while the material to be tested is heated, the main advantage over the first being the possibility of making measurements in a simpler and consequently faster way, with the hot wire method being most widely found in the literature.

Tawfic (2017) related four fundamental parameters of nanoparticles that affect the thermal conductivity of nanofluids: concentration, size, shape, thermal conductivity, in addition to three others related to the base fluid and its preparation: type of the base fluid and its characteristic thermal conductivity, preparation of the nanofluid and its temperature. Hajjar, Rashidi and Ghoozati (2014) investigated the effect of adding graphene oxide nanoparticles in deionized water at concentrations of 0.05 to 0.25 wt% in the values of coefficient of thermal conductivity. The nanoparticles were produced using the modified Hummers method. The authors concluded that the higher the concentration of nanoparticles, the greater the value measured for the coefficient of thermal conductivity as shown in Figure 9, obtaining a maximum percentage of improvement of 47.5% at 40 °C.

Gulzar et al. (2016) stated that the investigation of lubrication mechanisms is considered a fundamental parameter for the complete understanding of the tribology of NPs. However, the definition of the active mechanisms is the subject of debate in several studies related to lubrication systems based on NPs. Some mechanisms are proposed by the researchers, part of which is the responsibility of the particle itself and the other is caused by the modification of the surface of the tribological pair. The main mechanisms are a) bearing effect, where the NPs act like bearing balls between contact surfaces, b) protective film formation, when NPs adhere to the surfaces forming a tribological film, c) mending effect, that occurs when NPs are deposited in the valleys of surface roughness reducing abrasion and d) polishing effect, that results in reducing the roughness of lubricated surfaces.

To investigate these lubrication mechanisms, surface characterization techniques have been widely used by several authors. Techniques include SEM / EDS, atomic force microscopy (AFM), XRD, XPS and Raman spectroscopy. However, due to the existence of more than one lubrication mechanism acting simultaneously on the surfaces, these analysis techniques are not enough to distinguish one mechanism from the other (LI et al., 2009; GULZAR et al., 2016).

Here, friction and wear behavior of CuO NPs dispersed in POE is investigated. Viscosity and thermal conductivity of nanofluid are also investigated.

2. EXPERIMENTAL

2.1 Preparation of nanofluids

Polyester oil (POE) for R-134a refrigeration systems was used as base fluid for nanolubricants whose chemical/physical features are summarized in Tab. 1. The preparation of the different nano-oils requires the following steps. First, nine samples containing approximately 200ml of POE oil each were numbered and weighed using an electronic analytical balance. Second, quantities of CuO nanoparticles were weighed to obtain the necessary amount to produce samples of 0.05, 0.1 and 0.2 wt% of POE + CuO. Third, each sample was mixed using a 600 RPM magnetic stirrer for 12 hours then subject to ultrasonic bath for 1 hour to promote particles de-agglomeration and finally returned to the magnetic stirrer for another 12 hours period. All samples were left at room temperature to rest for ten days and the stability could be evaluated by observing the separation of phases due to sedimentation as shown in Fig. 1.

Table 1. Characteristics of as supplied DANFOSS POE.

| Property | Specification | Test Method |
|--------------------------|---------------|-------------|
| Viscosity at 40°C (cSt) | 31-33 | ASTM D 445 |
| Viscosity at 100°C (cSt) | 5.5 (min) | ASTM D 445 |
| Density at 15.6°C (g/ml) | 0.989 | ASTM D 4052 |
| Pour point (°C) | -54 (max) | ASTM D 97 |
| Flash point (°C) | 244 | ASTM D 93 |

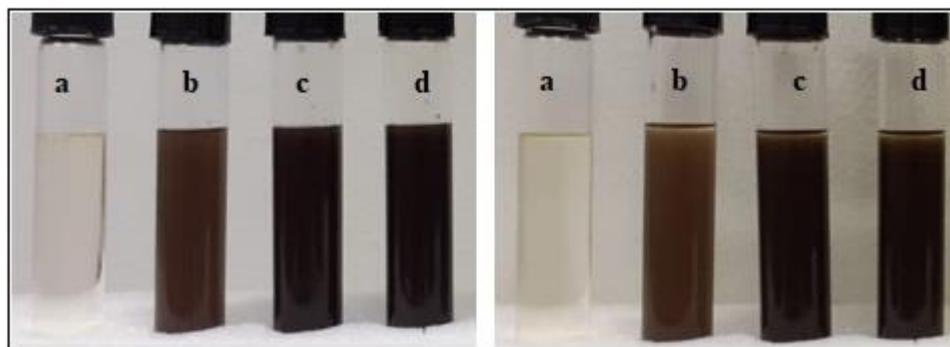


Figure 1. Samples of pure base oil (a) and base oil containing CuO NPs as prepared at 0.05wt% (b); 0.1wt% (c) and 0.2wt% (left) and after ten days (right).

2.2 Tribological tests

The samples were taken to High Frequency Reciprocating Rig (HFRR) test (PCS Instruments) using ball on disc as specimens made of AISI 52100 (6mm diameter) and FC-200 cast iron (10mm diameter vs. 3mm thick) respectively. This method presents many advantages such as less demand on oil, simple operation and good reproducibility. The apparatus required approximately 2ml of lubricant for each test, under the following conditions: 2N load, 50°C constant temperature, oscillation frequency of 20Hz and 60 min of running time. All the supporting parts were subjected to ultrasonic bath immersed in acetone to avoid contamination between each test. The tests of each sample were carried out three times and the mean values were considered.

After HFRR tests each ball was cleaned and taken to optical microscope with 100x magnification where the wear scar was measured in x and y-axis considering the beginning and end of visible scratches. The mean value is considered as the average WSD and comparisons were made between each nanolubricant and pure oil results.

2.3 Dynamic viscosity and Thermal conductivity tests

Dynamic viscosity test is developed in Brookfield DVIII-Ultra (Brookfield) rheometer using a small sample adapter device. A cylindrical container is filled with 6.7ml of lubricant and a spindle is inserted into it. The angular speed was set to 12 RPM. The necessary force to rotate the spindle deflects a standard spring and the viscosity value is determined. The measurements were taken under the range of temperature from 10 to 60°C and to keep it controlled a thermostatic bath (Brookfield TC-550) is programmed.

Using the same apparatus for temperature controlling, the thermal conductivity (k) was determined using KD2 PRO (Decagon) device (KS-1 needle type) by transient line heat source method at 25°C ensuring a 15-minute interval between measurements to minimize errors during heating and cooling of the needle.

3. RESULTS AND DISCUSSION

3.1 Tribological properties

The friction coefficients of the pure oil and nanolubricants as well as the percentage of film formation are displayed in Fig. 2. The average friction coefficient for three times experimental data of pure oil is 0.132 with a maximum standard deviation of only 0.0049.

The results show that the average friction coefficient of all nanolubricants were lower than that of pure oil. The smallest COF was 0.122 found for POE+CuO at 0.2 wt% concentration. This provides the best friction reduction behavior, representing an improvement of 7.6% compared to the pure oil. The 0.05wt% sample provided a 0.124 COF bringing up a 6.1% reduction. Finally, the 0.1 wt% nanolubricant had a 0.130 result, performing a 1.5% reduction in COF.

Determining the optimal concentration of nanoparticles that have the most positive effect in reducing friction is a very particular task that depends on both the type of nanoparticle and the type of the base fluid, in addition to factors such as shape and size of the particles, in addition to the load applied to the tests that influence the system lubrication regime.

Battez et al. (2010) studied the addition of CuO (30~50 nm) in polyalphaolefin (PAO) with concentrations of 0.5 and 2.0 wt%, varying the load applied in the tribological test. For the case of smaller loads, the lower concentration of nanoparticles proved to be more effective in reducing friction, while in larger loads, the opposite occurred. The authors state that for the first case, there was less contact between the roughness of the surfaces, requiring a smaller amount of nanoparticles to achieve the desired effect, while the opposite occurs in larger loads. Even so, in all cases there was a

reduction in the friction coefficient with the addition of nanoparticles. The authors concluded that the particles served as rolling spheres and, using XPS surface assessment techniques, identified the formation of a protective tribo-film due to the tribo-sinterization mechanism.

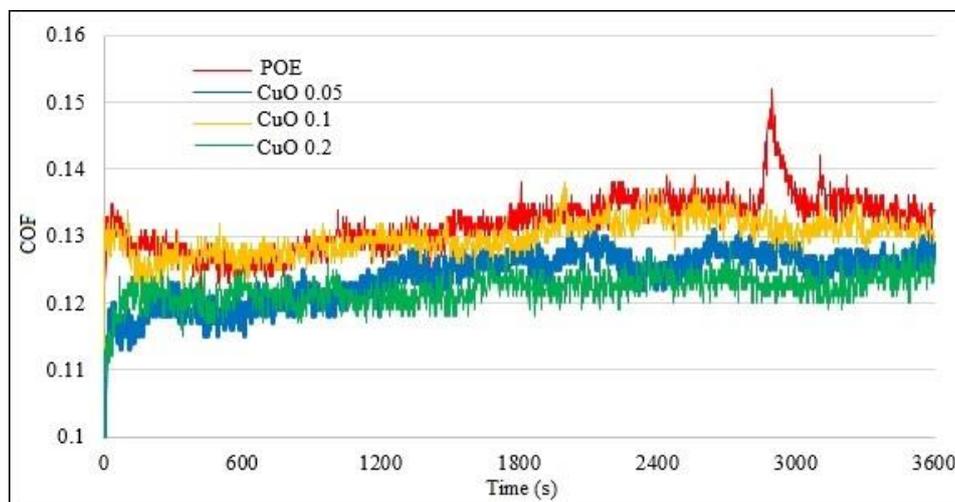


Figure 2. Coefficient of friction for pure oil and nanolubricants in different concentration versus time

After HFRR tests, WSD was measured using optical microscope. The ball wear scar for pure oil and each of the maximum reductions for each nanolubricant is showed in Fig. 3. It can be seen that the scratches in the specimen tested with pure oil are easily seen due to their apparent greater depth which makes them darker. The average WSD for pure oil is 238.5 μm .

Minimum variation in WSD was found for all concentrations of POE+CuO nano-oil. The minimum value was 204 μm , that leads to a 14.5% reduction in wear area for 0.05wt% concentration. The same value of 208.5 μm WSD was found for 0.1 and 0.2 wt% samples considering the beginning and end of visible scratch, representing a 12.6% improvement.

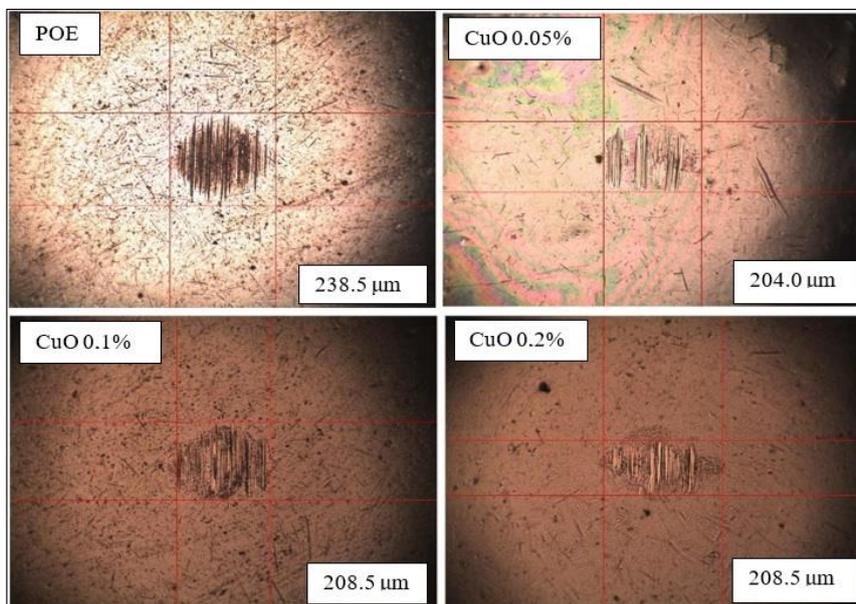


Figure 3. Wear scar for pure oil and nanolubricants in different concentration

The reductions found in the friction coefficients can be explained by the fact that the nanoparticles, depending on their size, can penetrate valleys in the surface roughness according to the mending effect described by Gulzar et al. (2016). This effect can be proven after applying surface analysis techniques such as EDS, SEM, Raman spectroscopy.

Another effect that probably contributed to an improvement in the tribological performance of the tested materials was the bearing effect since the copper oxide nanoparticles have an approximately spherical shape, a characteristic necessary for this type of mechanism to happen.

3.2 Thermal conductivity

Coefficient of thermal conductivity values are displayed in Fig. 4. The measurements were taken at 25°C with 15 min interval between each of them. The average value of k for pure oil was found as 0.147. The higher value detected was 0.149 for POE+CuO at 0.2 wt% and 0.1 wt% concentration, representing a 1.3% of increment. The last result was 0.148 and it can be observed that none nanofluid presented lower values of k compared to pure oil.

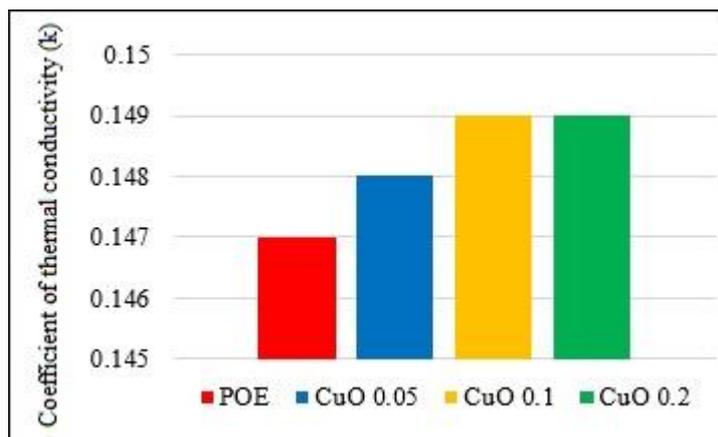


Figure 4. Wear scar for pure oil and nanolubricants in different concentration

Several authors have studied the effect of adding nanoparticles on the thermal conductivity of nanofluids. In general, regardless of the base fluid used, an increase in the thermal conductivity coefficient of the solution is expected since the k value of the nanoparticles, being higher than that of the base fluid, means that, even in small concentrations, the result is improvement in the thermal conductivity coefficient of the final product (WANG, XU and CHOI, 1999).

Using nanoparticles of Al_2O_3 and CuO with dimensions of approximately 20 nm, Wang, Xu and Choi (1999) evaluated the increase in the thermal conductivity of several base fluids (water, ethylene glycol, 10W30 engine oil and vacuum pump fluid). For all fluids, the thermal conductivity of the mixture increases with increasing concentration. However, for a given concentration, the increase in conductivity is different for different base fluids.

Comparing the studies by Masuda et al. (1993), Wang, Xu and Choi (1999) and Li et al. (1999) it is evident that the smaller the size of the nanoparticle, the greater the gain in heat transfer. Working with Al_2O_3 in water, the first authors identified an increase of 20% in the coefficient of thermal conductivity with nanoparticles with an average size of 13 nm, the next researchers obtained as a result an increase of 12% with nanoparticles of 28 nm while the last ones disclosed the result of 8% increase with nanoparticles with an average size of 38 nm. All used the same concentration, which made this comparison possible.

The gain in thermal conductivity identified in the present study may be related to an increase mechanism described by Wang, Xu and Choi (1999). Due to the small size of the particles dispersed in the fluid, additional transport energy can arise from the collective effect between Brownian movements and the forces between particles, which include Van der Waals forces (the greater the distance between the particles is smaller) and electrostatic force from the double electrical layer on the surface of the particles. These movements cause microconventions that increase the heat transfer inside the nanofluid.

Another mechanism for improving the thermal conductivity of a nanofluid is described in the work by Kumar et al. (2015), who mentions that particle adhesion can form a chain-like structure and that it can increase the heat transfer along these currents when oriented longitudinally to the heat flow. Therefore, an increase in the concentration of nanoparticles can result in the formation of longer chains (currents), contributing to the thermal diffusion mechanism to occur more efficiently.

3.3 Dinamic Viscosity

Based on data collected from studies by different authors with different base oils and nanoparticles, it is understood that, in general, with the increase of the solid phase concentration, the increase in the viscosity of the final product in relation to the pure lubricant should be expected, regardless of the type of oil or nanometric material dispersed in it. The same is observed in aqueous solutions.

Meybodi et al. (2015) developed a method for predicting viscosity in water-based nanofluids with different nanoparticles (SiO_2 , Al_2O_3 , TiO_2 and CuO). His experimental data showed that for all nanofluids there was an increase in viscosity with an increase in volumetric concentration. The authors listed the most popular nanofluid viscosity prediction models used in the literature. The classic models presented by these authors demonstrate that the viscosity of the nanofluid depends on the viscosity of the base fluid and the volumetric concentration of nanoparticles, however, the experimental results of the present work show that there is also temperature dependence in the prediction of viscosity.

An example that can be mentioned to reinforce this statement is the work developed by Harichandran et al. (2019) who studied the same base fluid (polyolester oil) added with hexagonal boron nitride nanoparticles. In their work, the authors concluded that, for each volumetric fraction tested, the greatest increase in the viscosity of the nanofluid occurred for the highest temperature investigated (70°C) based on experimental data.

The result of the present work showed values of dynamic viscosity of the nanolubricants very similar to those of the base oil, mainly for the concentrations of 0.05% and 0.1% of CuO , being these on average 1.5% and 2.5 % higher if compared to pure base oil for the investigated temperature range. It is understood that this similarity is due to the small concentration of nanoparticles that do not offer sufficiently significant resistance to cause significantly large changes in the torque exerted by the equipment to maintain a constant angular velocity, which is why this result was expected.

It was also noted that, for a concentration of 0.2% CuO , the viscosity was slightly higher than the other samples, with a positive average difference of 3.1%. Fig. 5 shows the relative dynamic viscosity data of the POE + CuO nanofluid and the pure base oil.

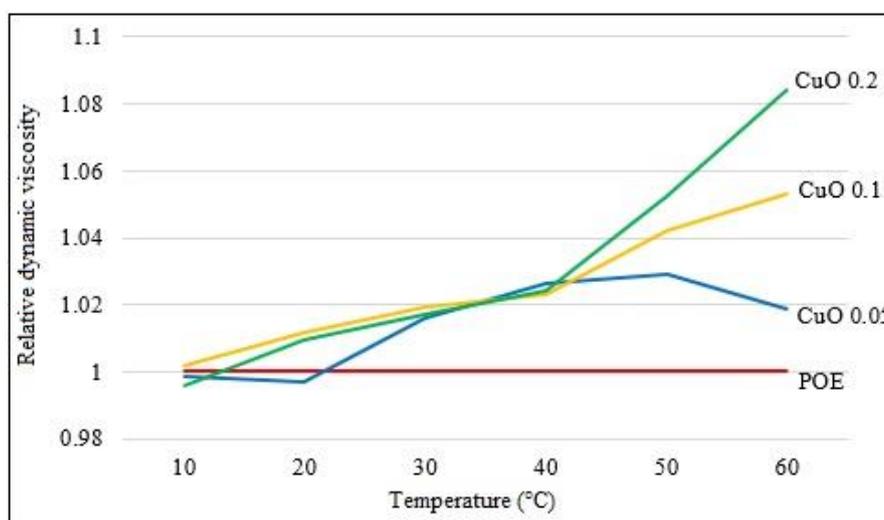


Figure 5. Relative dynamic viscosity between pure oil and nanolubricants at different temperatures

As in this work, Kedzierski (2012) studied the effect of the addition of CuO nanoparticles on the viscosity of polyolester oil in different concentrations. The author identified that for concentrations of up to 5.6 wt% (having tested concentrations of 2.9%, 5.6% and 39.2%) there was an increase of up to 20% in the viscosity of the nanolubricant in relation to oil pure. Additionally, the researcher stated that the increase in viscosity is proportional to the increase in concentration when they are less than 5.6%.

Using these same nanoparticles, Pastoriza-Gallego et al. (2011) investigated the variation in the viscosity of the nanofluid water + CuO as a function of the concentration of nanoparticles and temperature. The authors used commercially acquired CuO samples and synthesized in the laboratory (average size 23~37 nm and approx. 11 nm, respectively) and concluded that for both samples the relative viscosity increased with increasing nanoparticle concentration and with increasing temperature although the one with dispersed nanoparticles of smaller average size showed significantly higher viscosity values.

In the present study, the behavior of greater positive differences was observed with the increase in temperature between the viscosity of the nanofluid and the base fluid, the same behavior was identified by Harichandran et al. (2019) when studying the same oil added with hexagonal boron nitride nanoparticles. This phenomenon can be explained by the fact that, at the end of the tests, there was formation of sedimentation at the bottom of the rheometer container due to the great reduction in viscosity above room temperature, which favors the precipitation of nanoparticles, once they pass to face less resistance and the action of gravity is increased occurring that the accumulation of particles can interfere in the results

4. CONCLUSIONS

The tribological performance and thermal conductivity of nanolubricants prepared from polyolester based oil added with CuO nanoparticles in different concentrations were investigated. In conclusion, we can see that a suitable nano-oil can substantially reduce the friction coefficient with respect to pure oil and the optimum concentration must be defined for each type of nanoparticles as well as the reduction in wear could be evidenced through measurement of wear scar diameter. The explanation can be in the mechanisms of friction reduction such as rolling, sliding and exfoliation of nanoparticles. It is still possible to observe an improvement in thermal conductivity coefficient although on a smaller scale. It was identified that the coefficient of thermal conductivity increases with increasing concentration of nanoparticles proving what has been published in the literature. This is possible due to the additional transport energy generated in the system from the nanoparticles movements that cause microconvections, increasing the heat transfer and by the formation of chain-like structures that facilitates the heat flux along these structures when aligned to the heat flow. The rheological study showed a slight tendency to increase the dynamic viscosity with the increase in the concentration of nanoparticles as predicted in studies available in the literature. Thus, it is understood that the addition of nanoparticles should not exceed the concentration of 0.2% so that there is no damage to the pumping capacity of the lubricant.

5. ACKNOWLEDGEMENTS

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