DEVELOPMENT OF A NEW HYBRID NANOLUBRICANT (Al_2O_3-MWCNTs/POE) FOR REFRIGERATION COMPRESSORS AND LUBRICITY ANALYSIS WITH HFRR TRIBOMETER

Cleiton Rubens Formiga Barbosa Júnior – cleitonformiga@gmail.com
Universidade Federal do Rio Grande do Norte, Departamento de Engenharia Mecânica, www.dem.ufrn.br
Thiago da Silva André – thiagoandreengmec@hotmail.com
Instituto Federal de Educação Tecnológica do Rio Grande do Norte, www.ifrn.edu.br
Matheus Antônio Pereira da Silva – matheus.silva.110@ufrn.edu.br
Wertson da Silva Resende – wertson.resende.012@ufrn.edu.br
Francisco de Assis Oliveira Fontes – franciscofontes@uol.com.br
Cleiton Rubens Formiga Barbosa – crfb2019@gmail.com
Ângelo Roncalli Oliveira Guerra – angelo.roncalli@ufrn.br
Universidade Federal do Rio Grande do Norte, Departamento de Engenharia Mecânica, www.dem.ufrn.br

F1- Princípios – Termodinâmica, Mecânica dos Fluidos e Transferência de Calor

Abstract. *The development of solid nanoparticles and their dispersion in a base-fluid to improve thermomechanical properties and intensification of heat transfer processes have aroused much interest from the scientific community and boosted several industry segments in recent decades. In this context, it is proposed to investigate a new hybrid nanolubricant from the addition of nanoparticles of alumina (Al_20_3) and multi-walled carbon nanotubes (MWCNTs) to a polyether-lubricating oil (POE), originally developed for application in refrigeration compressors. The nanoparticles of Al_20_3 and MWCNTs were dispersed in 50/50 ratio in POE oil at concentrations of 0,10 g/L, 0,25 g/L, 0,50 g/L and 1,00 g/L. The hybrid nanolubricant Al_2O_3-MWCNTs/POE was subjected to ultrasonic sonication by immersion probe and rotating magnetic stirring to improve stability. The thermophysical properties were measured in the temperature of 50 ^{0}C. The coefficient of friction of hybrid nanolubricant Al_2O_3-MWCNTs/POE at the concentration of 1,00 g/L was slightly lower compared to the base fluid. However, the HFRR lubricity of the hybrid nanolubricant measured by the WSD was slightly lower than the POE oil.*
Keywords: *hybrid nanolubricant, Al_20_3, MWCNTs, coefficient of friction, lubricity.*

1. INTRODUCTION

Friction is one of the main causes of loss of energy efficiency in mechanical systems. Typically, the machine elements fail due to excessive wear. Therefore, more efficient lubrication is essential to increase the efficiency of energy use and the reliability of mechanical systems. HUTCHINGS (1992)

In this context, the addition of nanoparticles to lubricants may enhance the quality of their tribological properties, especially in the boundary and mixed lubrication regimes. The literature has reported numerous examples of improved anti-friction and anti-wear characteristics of a variety of nanoparticles used as lubricating additives including metals, metal oxides, non-metals, and so on.

Most studies show that adding nanoparticles to lubricants can significantly improve lubrication performance, reducing both friction and wear, thus enabling increased load capacity. Mechanisms including surface adsorption, penetration into asperities, and tribo-chemical reaction to reduce wear, as well as size effect, colloidal effect, exfoliation, protective film, and third-body effect to reduce friction, have been proposed to explain the superior performance of lubricants with nanoparticle additives.

BONU et al. (2016) report that nanofluid lubrication is a novel approach to improving the energy efficiency of sliding interfaces, which is useful for reducing friction and wear of machine elements. They studied the addition of POE oil with nanoparticles of 25nm oxide (SnO2) and concentration of 0.03 mg/mL, which showed a significant reduction in the coefficient of friction and wear of up to 38 and 42%, respectively, in comparison with pure POE oil. These researchers are still categorical in stating that the efficiency of lubrication depends on the size of the NPs, the stability of the dispersion and the concentration.

VAKIS et al. (2018) published a review of the latest developments in the field of tribology involving various physical, chemical, and mechanical phenomena at different scales. They investigated the multiphysical nature of the interactions in the tribo-system where the following types of phenomena may occur at the tribological interface or in its immediate vicinity: mechanical (solid and fluid), thermal, electromagnetic, metallurgical, quantum others.

ALVES et al. (2018) in experimental research with PAO oil added with copper oxide (CuO) nanoparticles show that it is possible to reduce the coefficient of friction or wear at boundary lubrication conditions using these nanomaterials.

There are currently different methods of determining the lubricity of a lubricating oil available on the market. The method of evaluation of the lubricity by means of probe of alternating displacement of high frequency is one of the most used by researchers.

FARIAS et al. (2011) report that lubricity is a qualitative term that describes the ability of a fluid to affect friction between surfaces under load and with relative motion as well as wear on those surfaces. The HFRR (High Frequency Reciprocating Rig) lubricity method simulates the Stribeck curve boundary lubrication regime to assess the ability of the friction reducing lubricating oil and tribological torque wear resulting from dry contact replacement by fluid contact, between two solid surfaces in relative motion.

The present research aimed to investigate the influence of nanoparticle concentration on the coefficient of friction and lubricity of a hybrid nanolubricant composed of polyester synthetic lubricant oil (POE oil) added with alumina (Al_2O_3) and multi-walled carbon nanotubes (MWCNTs).

2. MATERIALS AND METHODS

2.1 Materials of the hybrid nanofluid

The Figure 1 (DANFOSS. (2015)) shows the synthetic oil POE 160PZ used as the base fluid in the formulation of hybrid nanolubricants samples, the subject of this research, is manufactured by Danfoss and has its main application in the lubrication of compressors of refrigeration systems, being compatible with the refrigerating fluids R134a, R404a. R507, R508b, R407c and R410a. BARBOSA JUNIOR (2018) and ALMEIDA (2015).

Property	Specification	Test method
Viscosity at 40 ºC	30 – 33 cSt	ASTM D 445
Viscosity at 100 ºC	5.5 cSt	ASTM D 445
Density at 15.6 ºC	0.989 g/ml	ASTM D 4052
Colour	200	ASTM D 1209
Pour point	-54 ºC	ASTM D 97
Flash point	244 ºC	ASTM D 93
Dielectric strength at 25 ºC	46kV (min)	ASTM D 1816
Acid value (Tan)	0.12 mgK0H/g (max)	ASTM D 974

Figure 1. Characteristics and specifications of synthetic oil POE 160PZ.

According to the literature, the nanoparticles most frequently used in the formulation of simple and hybrid nanofluids are single or multiple-walled carbon nanotubes (MWCNTs, SWCNTs), alumina or aluminum oxides (Al_2O_3) and titanium oxides (TiO_2), because they exhibit excellent thermophysical properties.

The Figure 2 shows the Al_2O_3 nanoparticles used in the formulation of hybrid nanolubricants samples, the subject of this research, are manufactured in the form of dry nano-powder by *Sigma-Aldrich*. The carbon nanotubes of multiple or simple walls are very popular in the application of nanofluids because of the exceptional thermal conductivity, in relation to other existing nanoparticles.

Characteristics	Al_2O_3
Purity (%)	99
Color	Branca
Molecular mass (g/cm^3)	101.96
Average particle diameter (nm)	20
Density (Kg/m^3)	3,89
Thermal conductivity (W/m.K)	36
Specific heat (J/Kg.K)	773
Specific surface área (cm^2/g)	138

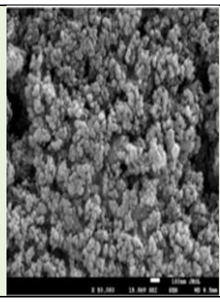

Figure 2. Characteristics and specifications of nanoparticles of the Al_2O_3.

The Figure 3 shows the multiple-walled carbon nanotubes (MWCNTs) used in the formulation of the hybrid nanolubricants samples, object of this research, are manufactured by *Nanostructured & Amorphous Materials* in the form of dry nano-powder through the chemical vapor deposition (CVD). HOLANDA (2018), AZEVEDO et al. (2017)

Characteristics	MWCNTs
Purity (%)	97
Color	Preta
Molecular mass (g/cm^3)	101.96
Average particle diameter (nm)	20-40
Tube length (µm)	50
Density (Kg/m^3)	2,10
Thermal conductivity (W/m.K)	4000
Specific heat (J/Kg.K)	773
Specific surface área (cm^2/g)	223

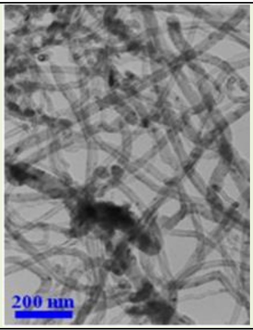

Figure 3. Characteristics and specifications of multiple-walled carbon nanotubes (MWCNTs).

2.2 Synthesis of the hybrid nanofluid

The simple and low cost "two-step" method was used for the synthesis of the hybrid nanolubricants proposed in the research and has two phases. The first phase comprises only the synthesis of nano-powders of alumina (Al_2O_3) and carbon nanotubes of walls (MWCNTs), that is, the production process of the solid nanoparticles. BARBOSA JUNIOR et al. (2022)

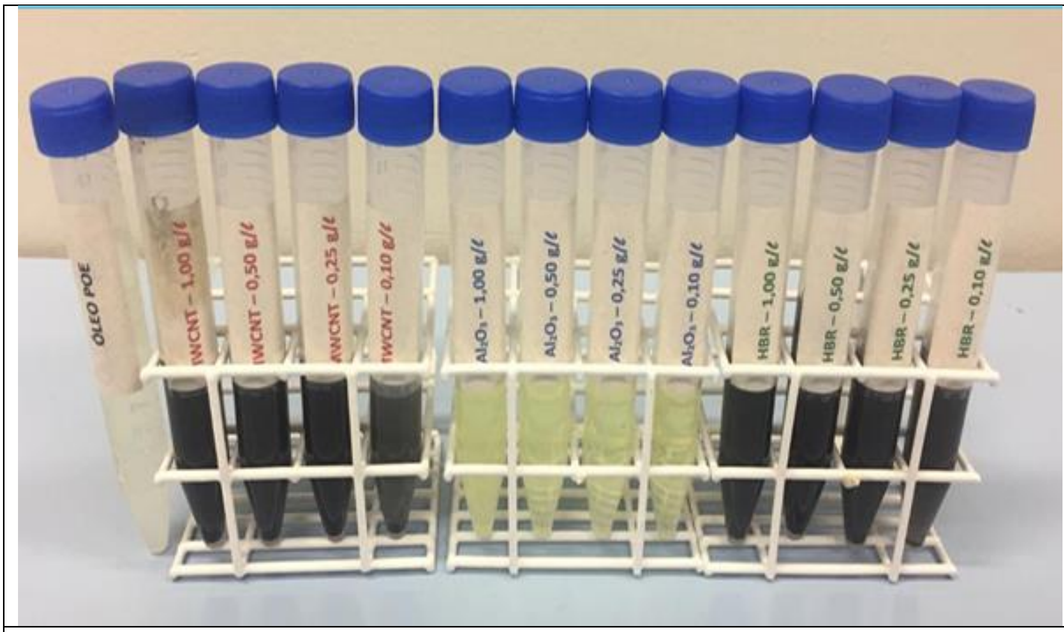

Figure 4. Samples of the base fluid (POE 160PZ oil) and simple/hybrid nanolubricants.

The second phase consisting of the formulation of the hybrid or simple nanolubricants (Figure 4), from their constituents (nanoparticles + base-fluid) purchased in the specialized trade, has the following execution sequence:

1. Measurement of the mass of nano-powders: the amount of mass, for each type of nanoparticle (Al_2O_3 and MWCNTs), corresponding to the concentration in (g/L) of the different nanolubricant samples was measured in analytical balance with resolution of 0.0001 g;
2. Measurement of the base fluid volume: the measurement of the 100 ml volume of the base fluid (POE 160PZ oil) was performed with micropipette and graduated becker.
3. Mixing the solid nanoparticles in the base fluid: After inserting the nanoparticles into the base fluid, the nanoparticles (Al_2O_3 and MWCNTs) are mixed in the liquid medium (POE 160PZ oil) with the help of a glass rod.
4. Nanoparticle defragmentation: to attenuate the agglomerations and to improve the stability of the samples, all the nanolubricants were sonicated by means of immersion ultrasound with a vibration amplitude of 10%, with a duration of 1 hour.
5. Dispersion of the nanoparticles in the base fluid: the final step of nanolubricant synthesis was the dispersion of the nanoparticles in the liquid medium (base-fluid) by means of a rotating magnetic stirrer, with rotation of 450 rpm and duration of 24 hours.

2.3 HFRR lubricity test

The parameters of the HFRR lubricity test and the geometric, dimensional and compositional characteristics of the materials of the sphere/disc tribological pair are established according to ASTM D6079-99 and ISO 12156-1: 1997.

With the equipment in operation, the steel ball is actuated and describes an alternating movement of limited stroke with high frequency, under the action of a normal load pre-established in the test, and the test disc is fixed in a small vat containing the sample oil lubricant.

Figure 5 shows several photos and the schematic diagram of the HFRR tribometer from the Tribology and Structural Integrity laboratory at Federal University of Rio Grande do Norte (UFRN) in Natal/Brazil, which was used to determine the lubricity of nanolubricants in this research work. FAZAL et al. (2021), ALVES et al. (2016), FARIAS et al. (2014), ALVES et al. (2013), FARIAS et al. (2011)

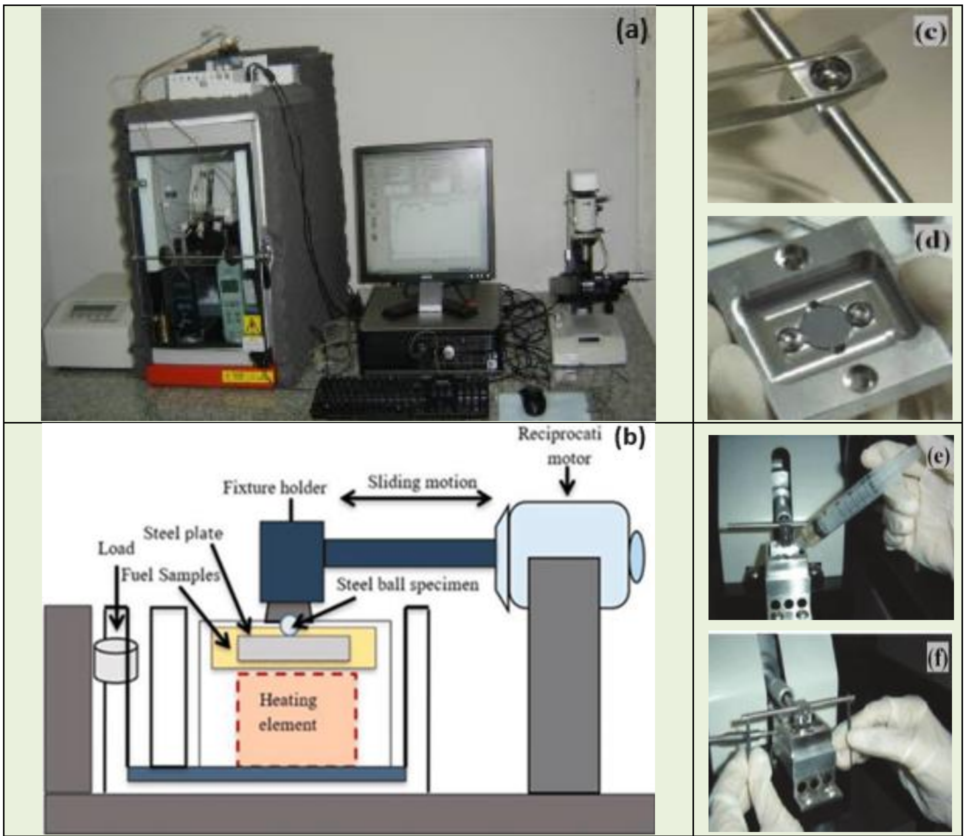

Figure 5. HFRR test: (a) picture of equipment (b) Schematic diagram (c, d) Steel ball/disc pair and supports (e, f) application of nanolubricant and load in HFRR unit.

The hard steel ball slides against the soft steel disc with a 1,00 mm stroke at a frequency of 20Hz and sliding speed of 0,01 m/s for 1 hour.

The ball and disc in contact are fully submerged in 2.0 ml of lubricant at normal load of 2 N. The tests were performance in triplicate. The temperature of lubricant was kept at 50 ^{0}C.

The HFRR lubricity test basically consists of sliding the surface of a spherical test piece onto the flat stationary surface of the test disc. The lubricity performance of each nanolubricant tested was analyzed as a function of the mean values of the friction coefficient and the wear area of the steel sphere (WSD).

The surfaces of the sphere/disc tribological pair were integrally immersed in the test fluid sample (hybrid nanolubricants with different concentrations of solid alumina nanoparticles (Al_2O_3) and multi-walled carbon nanotubes (MWCNTs) or POE oil).

The test develops automatically and the performance parameters of the HFRR such as coefficient of friction, test fluid film thickness and contact temperature are displayed, in real time, on the screen of the computerized data acquisition equipment.

After the end of the HFRR lubricity test, the steel ball is removed and cleaned for 100 × magnification optical microscope measurement of the steel ball wear scar based on the mean of the diameters in the directions (X and Y).

3. RESULTS AND DISCUSSION

All the lubricity versus time tests were conducted in a totally automatic way and the programming was carried out with the help of the dedicated software of the HFRR tribometer of the PCS instruments brand.

The film coefficient of friction and film thickness were collected at a rate of 1 second through the data acquisition system of the instrument itself and the wear band (WSD) of the sphere was measured with the aid of an optical microscope with a magnification of 100X.

The coefficient of friction and the WSD were the parameters used to evaluate the lubricity. The automation of the HFRR lubricity test enabled the reproduction of the test equally for all nanolubricant samples, without operator interference, allowing to increase the level of reliability and reproducibility of the obtained results.

The Figure 6 shows the coefficient of friction versus time take the form of a "cloud" of points. This cloud aspect is caused by the amount of dots represented in the graph by each nanolubricant sample tested. There were 3600 friction coefficient readings acquired during the 1 hour test (one reading every second).

In Figure 6 it is easily observed that in all HFRR lubricity tests, the coefficient of friction of the nanolubricants showed a tendency to grow over time.

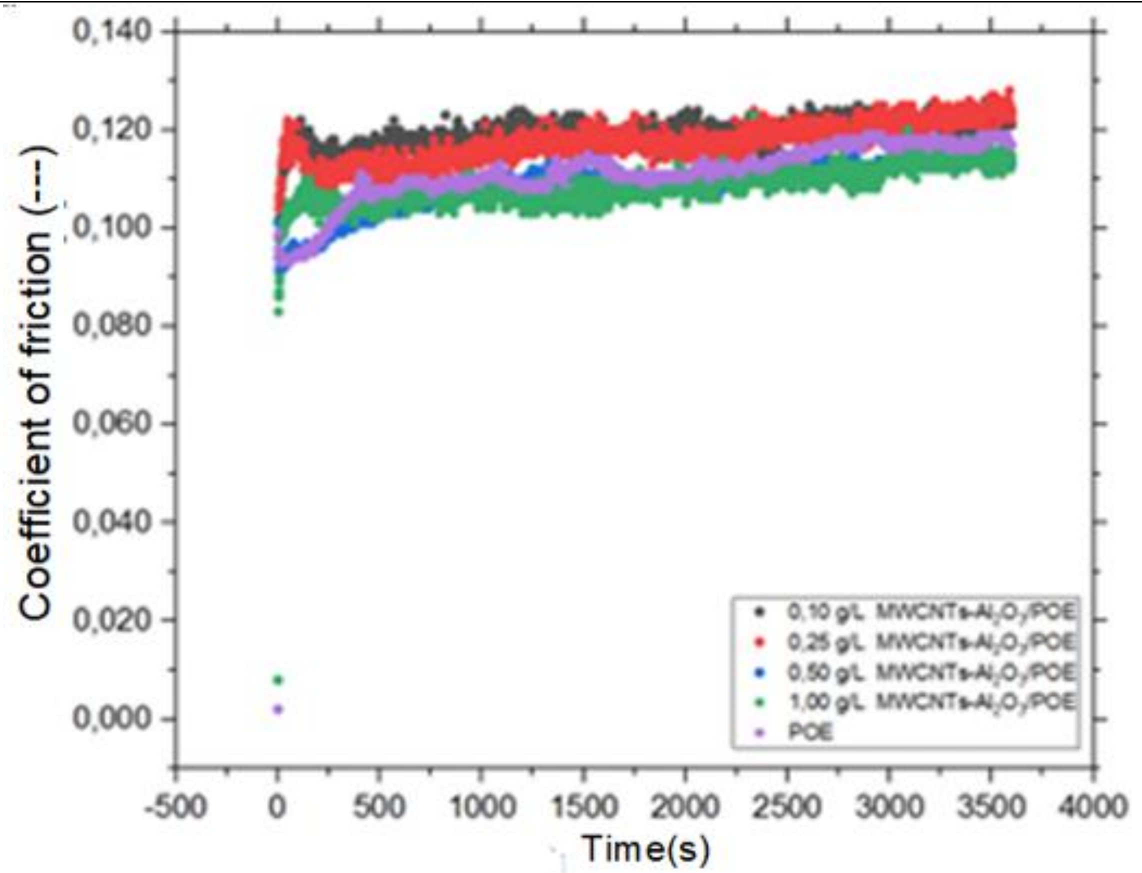

Figure 6. Coefficient of friction of POE oil and hybrid nanolubricants (MWCNTs-Al_2O_3/POE) with concentration of 0,10 g/L, 0,25 g/L, 0,50 g/L, 1,00 g/L versus time

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Also, in the first few seconds of the test, the characteristic of running, in which the values of the coefficient of friction increase from zero and go through an instability phase at the beginning of the test (wider cloud range).

Comparing the friction coefficient of the hybrid nanolubricants and the POE oil, in the graphs of Figure 6, it can be observed practically throughout the test that the hybrid nanolubricant with a concentration of 1.00 g/L presents values slightly smaller than those of the base fluid.

The HRFF lubricity tests of POE oil and nanolubricants were done in triplicate to increase reliability of the results. The Figure 7 show the smaller wear scars (WSD) of the spheres obtained in the HFRR lubricity tests of each nanolubricant and of the base fluid.

The hybrid nanolubricant presented the lowest WSD of 172 μm at a concentration of 0.25 g/L. The POE oil showed the WSD 128 μm. This WSD was the best wear value of the sphere and was not surpassed by any nanolubricant subjected to the lubricity test under the same conditions.

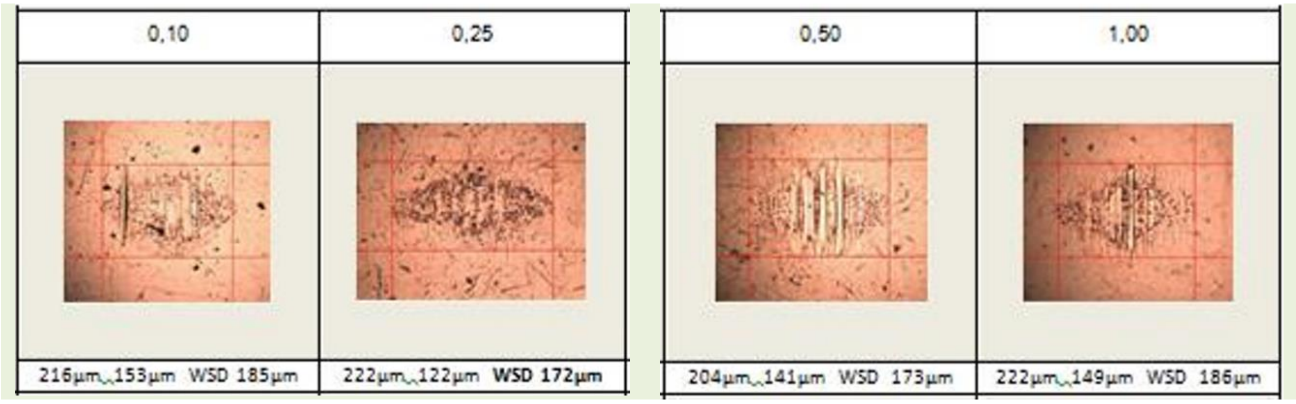

Figure 7. Wear scar diameter of the HFRR lubricity test of hybrid nanolubricants at different concentrations of nanoparticles.

4. CONCLUSIONS

At the end of this research on the development of a new hybrid nanolubricant for application in refrigeration compressors and evaluation of lubricity using a HFRR tribometer, it can be concluded that:

1. The preparation of hybrid nanolubricant proposed by the "two-step" method using ultrasonic sonication techniques of immersion and magnetic stirring of suspended particles gave good stability characteristics, delaying agglomeration and reduced sedimentation of the nanoparticles in the base fluid, as can be observed through the sedimentation method by visual inspection.

2. The lubricity test on the HFRR tribometer is carried out completely automatically, without operator interference, ensuring a higher level of reliability and reproducibility of the results obtained.

3. In the HFRR lubricity test, the hybrid nanolubricant with a concentration of 1.0 g/L presented lower coefficient of friction and wear-rate diameter (WSD) of the larger sphere compared to the POE synthetic oil.

4. Under similar lubricity test conditions in an HFRR tribometer, the POE 160PZ synthetic oil (base fluid) showed a smaller ball wear diameter (WSD) than all hybrid nanolubricants tested.

5. Under similar lubricity test conditions in an HFRR tribometer, the hybrid nanolubricant (Al_2O_3-MWCNTs/POE) with a concentration of 1.00 g/L showed a slightly lower coefficient of friction when compared to the synthetic oil POE 160PZ

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