The Impact of Nanotechnology on Biolubricants for the Automotive Supply Chain

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ABSTRACT

The environmental problems caused by the use of fossil fuels to sustain the current level of industrialization have sparked worldwide interest in the green economy. New technologies for sustainable additives and lubricants must be environmentally harmless, exhibit biodegradability, non-toxicity and non-bioaccumulative properties, known worldwide as Environmentally Acceptable Lubricant. The technological challenge at the frontier that interposes lubrication performance and biodegradability of lubricants has been crossing a gap in the research and development of formulations using bio-based oils and nanostructured additives. For this article, we focused on formulations of biolubricant using nanoadditives, and efforts were concentrated on analyzing the physicochemical and tribological parameters in industrial and automotive applications. A design of experiments was carried out with 2 factors, being 3 levels of base oils and 5 levels of nanoadditives. The tribological tests of the nanolubricants were performed in a Four Ball equipment (ASTM D4172), in which oxidation, friction and wear values relative to each experiment were obtained. The statistical results showed that the main effects and interactions were attributed to vegetable base oils using hybrid nanostructured additives.

INTRODUCTION

The global demand for oil surpassed pre-pandemic levels in late 2022, according to data published by the Organization of the Petroleum Exporting Countries (OPEC). World energy consumption will grow just 1.3% in 2023, driven by China's economy and amid a slowdown that will push up energy prices.

Statistics show that despite efforts to reduce climate change, even so the petroleum consumption continues to grow. Due to the decrease in gas supply and extreme weather events, which are expected to force many countries to continue to rely on fossil fuels, delaying the transition to green energy.

In this scenario, the automotive industry is currently facing environmental antagonism, strict regulations and a rapid technological transition. Government requirements are increasing, such as those defined by the Kyoto Protocol, which establishes obligations to improve fuel economy and reduce emissions from automotive equipment and vehicles [1].

Since the second half of the 20th century, the market has been seeking more powerful and compact vehicles that increase the load/lubricant ratio in engines, requiring new technologies for lubricating oils and fuels [2]. The main engine failures are related to the interaction of combustion subproducts with lubricating oil, which results in contamination, oxidation and formation of deposits on the contact surfaces, causing corrosion and excessive wear [3].

Since the Industrial Revolution has driven the demand for natural oils, such as lard, olive, canola and peanut oil. Indicates that there are commercially available vegetable-based gear oils that meet most of the requirements of rolling machines and gears operating under high loadings. These gear oils are manufactured from synthetic esters and vegetable oils, mainly of canola [4].

The global biolubricants industry has a demand of less than 350 kt, which represents around 2% of the global market for finished lubricants, with North America (49.17%) and Europe (28.05%) being the largest consumers due to their strict environmental protection policies (EPA, 2011). However, the average growth rate of biolubricants is high compared to finished lubricants, especially for metalworking fluids, mold release agents, chainsaw oils and hydraulic fluids for some applications in transportation, manufacturing, mining and forestry [5].

In recent days, environmental health aspects and increase in pollution have become each and every nation issue to provide better sustainable development for the public. In equipment lubrication sector, the main concern is the loss of lubricants into the environment. Soil and water are directly affected by lubricant system failure whereas the air is polluted by volatile lubricants. Due to increase in environmental awareness, it has become driving force for technology improvement on lubrication. Thus, implementation of biodegradable lubricants has extensively used in environmental sensitive areas [6].

Although vegetable based biodegradable lubricant has better viscosity index, pour point, flash point, good tribology properties and its environmentally friendly for the lubrication systems, but some of its properties are inferior compared to mineral oils [6].

The study explored the replacement of synthetic lubricant SAE20W40 by rapeseed oil-based biolubricant in a four-stroke diesel engine by 150 hour test. The biolubricant was formulated through chemical modifications, such as epoxidation, hydroxylation and esterification. To improve its thermo-oxidative stability and cold flow properties, a CuO based nanoadditive was added [7]

The rapeseed biolubricant reduced the wear of Fe, Al, Cu, soot and ash content, when compared to the SAE20W40 lubricant. Rotary pump oxidation time (min) ASTM D2272 showed similar values for both lubricants, being 35 and 38 min for the biolubricant with CuO and synthetic SAE20W40, respectively [7].

Polycyclic aromatic hydrocarbons (PAHs) and heavy metals are widespread environmental pollutants that are generated by the incomplete combustion of organic materials. PAHs are the important contaminants in used mineral oil (UMO) and likely pose environmental risks and negative effects on human health in the processes of disposal and regeneration.

The cluster analysis showed that samples with high heavy metal and PAH concentrations mainly originated from machine manufacturing and vehicle industries and even 34 to 190 times higher than those in fresh oil [8].

TRIBOLOGICAL CHARACTERISTICS

Tribology is dedicated to the study of wear, friction and, consequently, lubrication, as a traditional way of minimizing the first two phenomena. This science is based on mechanics, physics, chemistry and materials science [9].

The main engine failures are related to the interaction of combustion subproducts in the lubrication system, which results in contamination, oxidation and formation of deposits on the contact surfaces, causing corrosion and excessive wear [10].

The lubrication system plays a vital role in machine components, which prevent wear due to relative movement between contact surfaces, as occurs in bearings, transmissions, pistons, gearboxes, racks and compressors. Friction and wear parameters are controlled by separating of the surfaces by means of a fluid film or by introducing solid lubricants with low shear resistance between the surfaces in contact. In addition, it helps to remove wear fragments and cool the contact surface [11].

The Zinc Dialkyl Dithiophosphate (ZDDP) additive can increase the roughness and consequently the friction during the mixed lubrication regime. The antiwear performance decreases proportionally to the decomposition of ZDDP, and some of its sulfur-containing byproducts promote corrosive wear on the contact surface [12][13].

FORMULATION OF LUBRICANTS

The major challenge for the formulation of biolubricants is the selection of appropriated additives. The additives developed for mineral base oils are generally toxic and not suitable for the environment.

The formulation of biolubricants to meet EAL criteria and the specifications required by the final application still has a large technological frontier, as chemical additives containing chlorine, phosphorus, sulfur and metallic salts continue to be used to improve anti-oxidation, friction reduction and wear resistance properties in conventional lubricants, which signals a concern and the restriction or elimination of these active additives due to their toxicity, low biodegradability and predisposition to bioaccumulation [14].

The lubricating oils and greases are products that come from a difficult formulation, which consists of 70 to 90% base oils and the remainder mixed with active and inert additives to achieve physical, chemical and tribological properties, and meet the performance specifications of equipment and vehicles. The main types of base stocks are mineral, synthetic, re-refined, as well as vegetable oils and esters. Research into green fluids for next-generation biolubricant formulations has been studying vegetable oils, ionic liquids, aqueous solutions and glycerol [15].

The vegetable oils have many inherent qualities compared to mineral oils as a raw material for the manufacture of lubricants. The triacylglycerol structure of vegetable oil indicates that it is an excellent alternative as a base stock. The use of vegetable oils or esters for the formulation of lubricants is being considered in several countries. Biomass-based lubricants are much more attractive in terms of carbon footprint than petroleum-based lubricants due to their relatively low toxicity, high flash point and low emissions of volatile organic compounds (VOCs).

The vegetable base oils generally have excellent physicochemical and tribological properties such as lubricity, high viscosity index, low volatility, high load capacity, lower compressibility and good solubility. However, the use of vegetable base oils in the formulation is still limited for industrial and automotive biolubricants mainly due to low stability against rancidity and thermo-oxidative degradation, which compromises storage due to polymerization and reduces shelf life respectively as a result of degradation, also considering the poor point at low temperatures that increases viscosity and consequently leads to energy loss [16].

Figure 1 shows the molecular structure of vegetable oils have high lubricity, good adhesion to metal surfaces and a high viscosity index. Typically, the triacylglycerol molecule of oils contains glycerol (polar) and long fatty acid chains (non-polar). High levels of unsaturated fatty acids result in low thermal stability. However, the inherent properties, such as surface lubricity through fatty acids that form a compact monolayer with their polar carboxylic.

OXIDATION OF BIOLUBRICANTS

The oxidation of vegetable oil is a natural process of extreme importance for biodegradability. To be considered biodegradable, the lubricating oil must undergo final biodegradation greater than or equal to 60% within 28 days. The presence of oxygen in the composition of vegetable oil contributes to natural oxidation through decomposition by microorganisms and/or enzymes through an aerobic or anaerobic process [20].

The oxidation stability is the resistance of an oil to the formation of oxides. Vegetable oils tend to have lower oxidative stability compared to mineral oils. The oxidation of vegetable oils is due to the unsaturated carbon bonds of fatty acids. The more unsaturated the oil, the lower the oxidative stability, i.e. polyunsaturated oils have lower oxidative stability than monounsaturated oils.

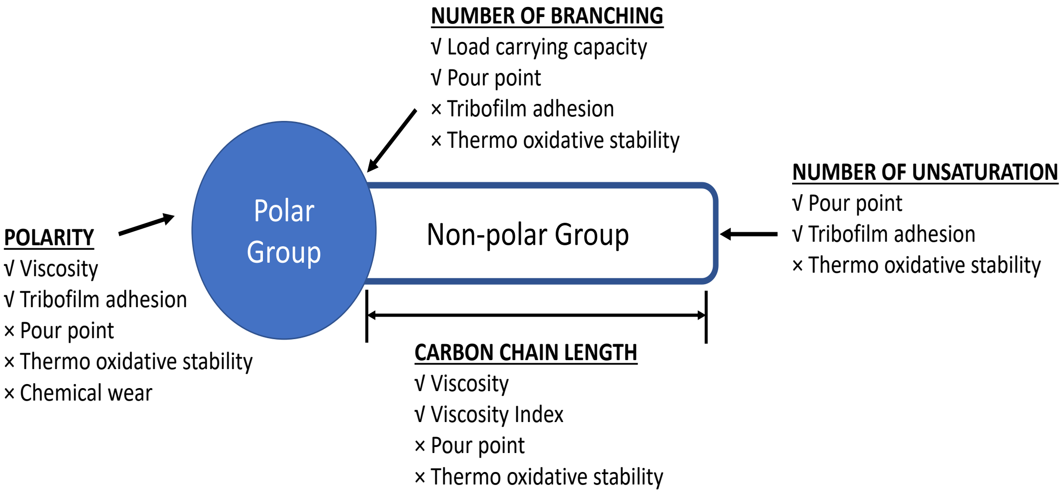

Figure 1. Representation of the molecular structure and physical-chemical properties of vegetable oils [16].

The structure of triglycerides is composed of three hydroxyl groups esterified with the carboxyl groups of fatty acids. Due to their high molecular weight, triglycerides have a high viscosity index. The presence of oxygen in the composition of vegetable oil contributes to natural oxidation [18][19].

groups, which greatly reduces friction and wear, consequently biolubricants can be used in boundary lubrication conditions [17].

This reduction is also attributed to the presence of glycerol in vegetable oils. The oxidation increases through proximity to the contact surface, high temperatures, contaminants, pressure and agitation [21]. These compounds play a prominent role in auto-oxidation when in contact with light, heat, water, or metals. It was also clear that the oxidation changes biodiesel's characteristics, such as increasing acidity and kinematic viscosity, and produces the polymeric compounds [22].

The degradation of biodiesel (fatty acid methyl esters) by oxidation may compromise fuel properties and engine durability due to forming byproducts of fatty acid decomposition. Diesel fuel has oxidation stability 11 times higher than palm-oil biodiesel, analyzed by the RSSOT method (ASTM D7545). These characteristics are closely related to the resistance of the biodiesel and blends to exposure heat and oxygen, which can cause oxidation.

A study compared the effects of adding 35% (by volume) of n-propanol, n-butanol and n-pentanol to diesel and biodiesel on unregulated emissions in a diesel engine. The results obtained showed that the use of high-carbon alcohols in a high blending ratio contributed to the improvement of the fuel properties of biodiesel and to an increase in the blending ratio of alternative fuels, with a reduction in PAH emissions from diesel oil [23].

NANOSTRUCTURED ADDITIVES

The key factors influencing the evolution of engine lubricating oils and additive technologies are fuel economy, environmental conservation and extension of drain intervals. It has long been recognized that the suspension of solid particles in liquid can provide advantages for the fluids industry, which includes heat transfer products, magnetic fluids and lubricants [8].

The tribological characteristics of solid particles in lubricants vary considerably between surfaces, especially in the boundary lubrication regime [24]. The distinct properties related to high surface area, low weight, high hardness, thermal stability and chemical inertness are the differentials of ceramic nanoparticles in relation to other engineering materials, which is why they are considered the main alternatives for use in tribological applications [25].

Research and application of nanoparticles as additives in lubricant oils have been ongoing for over decades, and some tribological improvements are attributed to the following nanomechanisms: nano-rolling due to the almost spherical shape; due to incorporation into the surface, the nanoparticles have a self-repairing effect, and in this case, they act as a third body between the valleys of the asperities, reducing abrasion, and they can react with the surface through tribo-sintering and form a protective film [25][26].

The unique properties of low weight, high hardness, thermal stability and chemical inertness are what set ceramics nanoparticles apart from other engineering materials, and they are being considered as the main candidate for use in tribological applications [27][28].

Nanoparticles are highly active at high temperatures, which in turn increases the dielectric strength of insulating oil samples. Nanoparticles react with free radicals, delaying the formation of peroxides that are susceptible to the onset of chain oxidation. Under these conditions, nanofluids remain stable at high temperatures and consequently have high thermal resistance during operation [29].

The tribological properties of 15W40 lubricating oil with SiO_2, WS_2, Cu, CuO and graphite nanoparticles were mixed into the lubricant homogeneously by means of magnetic stirring and ultrasonication. The tribological test of the nanolubricant was carried out in a four-ball tester, according to ASTM-D4172 standard for lubricant wear prevention characteristics and ASTM-DIN 51350-02 standard for extreme pressure test. The experimental analysis showed that the coefficient of friction and wear scar diameter were reduced with the use of both nanoparticles in the 15W40 lubricant [30].

Biomass-derived biolubricants can reduce the carbon footprint of production, lubrication and power generation. When nanoadditives are used, the performance improvement of biolubricants is more pronounced. The characteristics of current biolubricants can be produced from agricultural feedstock, with the potential to replace conventional mineral oil products [31].

MATERIALS AND METHODS

The materials used in the functionalization of the nanostructured additives were simple and hybrid nanoparticles, oleic acid as surfactant in a [1:1] ratio then added to the base oils. Tables I and II present the information on these materials (predictor variables) that will be used in the design of experiments (DoE). The tribological tests were performed in four ball equipment using the ASTM D4172-94 method to evaluate the performance of the 18 experiments (Table III), that indicates in the multilevel factorial and relationship between response variables. Figure 2 illustrates the assembly diagram and the operating conditions of the four Ball tribometer.

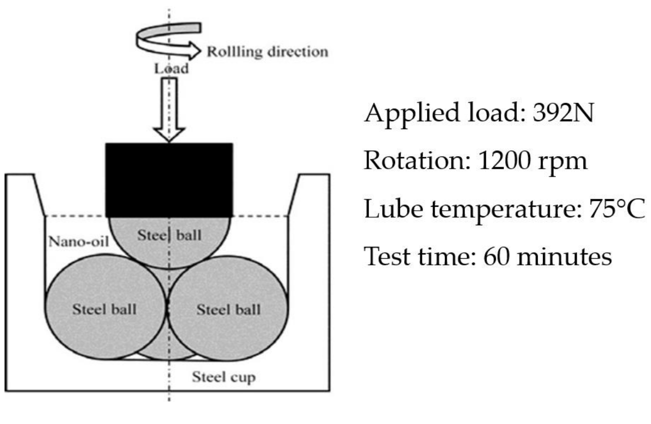

Figure 2 - Representation of the four ball Tribometer and ASTM D4172 Standard Test Method.

Table I - Base Stocks Properties

Conditions	Vegetable	Synthetic	Mineral	Surfactant
Identification	BV4	BS1	BM3	AO
Trade name	Canola	PAO-6	Paraffinic	Oleic acid
API group	G-V	G-IV	G-III	G-V
Chemical Composition	Triesters and fatty acids	Poli α olefins (alkenes)	Alkanes	Fatty acids
Carbon chain	$C_3H_8O_3$ + RCO_2H	CnHn	CnH_2n+2	$C_{18}H_{34}O$
HC Saturation	10% saturated 70%mono in* 10% poli in	HC controlled 100%	HC ≥ 90% saturated S ≤ 0,03%	100% mono
Kinematic Viscosity (40°C)	33 cSt	50 cSt	41 cSt	-
Biodegradability ASTM D5864	75 – 85%	15 – 65%	25 – 30%	55 – 65%

Table III - Nanoparticles Properties

Nanoparticles Condition	NS1	NS2	NH1	NH2	NH3
	Simple (inert)	Simple (inert)	Hybrid (inert)	Hybrid (inert)	Hybrid (ative)*
Morphology	Hexagonal	Orthorhombic	Hexagonal & Orthorhombic	Hexagonal & Amorphous	Spherical and Lamelar
Mohs scale	5 to 6	6	5 to 6	-	-
Surface area (m^2/g)	8 to 62	16 to 78	8 to 78	31 - 156	155

Table II - Table III - Multilevel factorial experiment (Minitab 19 software)

TESTS	Factor A BaseStock	Factor B NanoAddit
1	BV4	SN1
2		NS1
3		NS2
4		NH1
5		NH2
6		NH3
7	BS1	SN1
8		NS1
9		NS2
10		NH1
11		NH2
12		NH3
13	BM3	SN1
14		NS1
15		NS2
16		NH1
17		NH2
18		NH3

Number of replicates: 5

Total tests: 90

Response variables:

- Viscosity Index
- Coefficient of Friction
- Wear Diameter
- Oxidation Index

RESULTS E DISCUSSION

The results represented through regression analysis with values obtained for each response variable of the experiments with vegetable (BV4), synthetic (BS1) and mineral (BM3) base stock in natura and with the addition 0.5% by weight of simple (NS1 and NS2) and (NH1, NH2 and NH3) nanoadditives or additive nanostructured are presented as follows. Initially, a preliminary analysis of the stability of the nanolubricant (NS2) was carried out, and then tests were performed in the four ball tribosystem in a mixed lubrication condition based on the ASTM D4172-94 method. A reduced fraction of oleic acid in the surface modification (functionalization) of nanoparticles that not was used, which did change the physical-chemical and tribological results.

FRICTION COEFFICIENT

Figures 3 e 4 show the regression graph with values variation and averages of friction coefficients for base stocks and simple and hybrid nanoadditives respectively, between of 6 to 54 minutes. Based on the degradation rate (bathtub curve) 10% of the time related to the transient period (premature failure) and 10% of the degradation period (end of life) were discarded for each experiment.

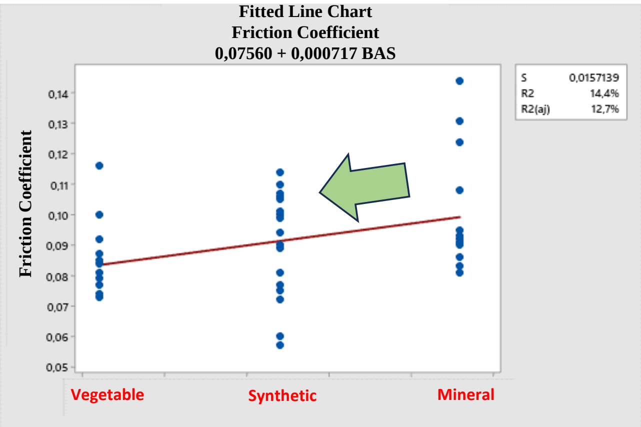

Figure 3. Comparative values and average friction coefficients of base stocks with and without nanoadditives.

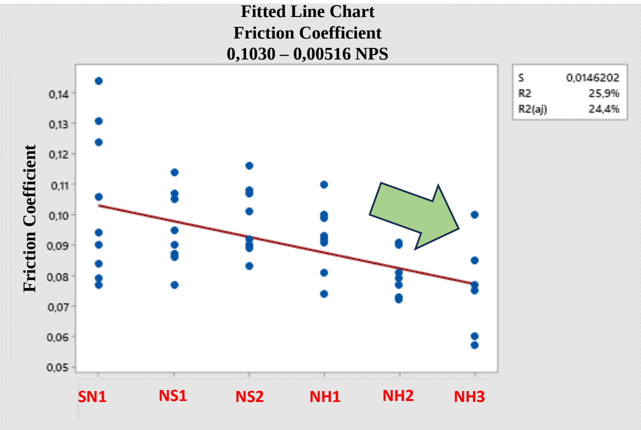

Figure 4. Comparative values and averages of friction coefficient related to the use of nanoadditives in both base oils.

Based on the results above, a large oscillation (standard deviation) in the coefficient of friction values is observed. Most nanoadditives reduced the coefficient of friction of nanolubricants, but it was more pronounced in mineral-based nanolubricants. Vegetable oil (Canola) and its respective oxide-based nanolubricants (NH1 and NH2) presented the lowest coefficient of friction values (0.076-0.077), which may be related to the high levels of fatty acids.

Among the nanoadditives, the greatest reduction in friction (0.064) occurred using NH3 in synthetic oil, probably due to the presence of the metallic salt in the composition of NH3. The addition of 0.5% oleic acid (OA) in synthetic base stock did not present a significant change in relation to the coefficient of friction.

The concentration of surfactants or adsorbent agents, such as fatty acids, influences the reduction of friction. Fatty acids in natural oils are desirable for boundary lubrication due to their ability to adhere to metal surfaces [17]. This behavior is due to the polar carboxyl group that establishes an effective monolayer to reduce friction [30].

The properties of nanomaterials in lubricating fluids indicate improvements through the addition of nanoparticles to reduce the coefficient of friction and protect the tribosystem, reducing the size of fragments resulting from wear, attenuating heat and promoting better cooling, and consequently increasing energy savings and reducing gas emissions. [29].

OXIDATION CONTENT

The oxidation percentage is indicated by the difference between the values of the FTIR analyses (ASTM E2412), relative to carbonyl (C=O) which is indicated in the band of 1680 to 1800 cm^{-1} of the absorbance spectrum, before and after the four ball tribological tests (ASTM D4172-94) one hour long, starting from 75°C reaching approx. 90°C at the end of the benchtest.

Figures 5 e 6 show the regression graph with values variation and averages of oxidation content for base stocks and simple and hybrid nanoadditives respectively.

The results below show that the nanoadditives reduced the oxidation content of the vegetable-based nanolubricants, being more pronounced for NH2.

While for the synthetic and mineral base oils, small reductions of this parameter are observed in the presence of nanoadditives, which contributes to reducing lubricant degradation and consequently extending the oil change interval.

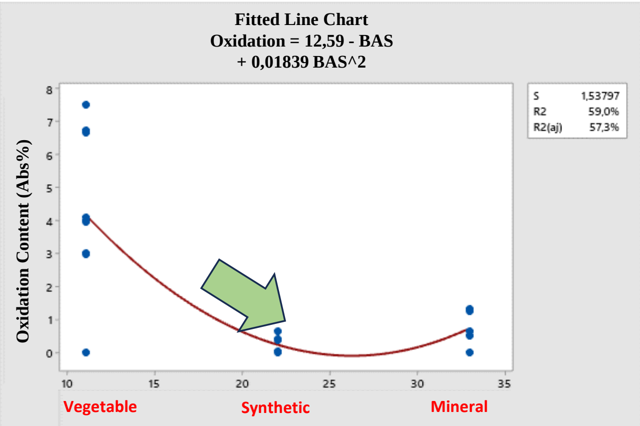

Figure 5. Comparative values and average oxidation content of base stocks.

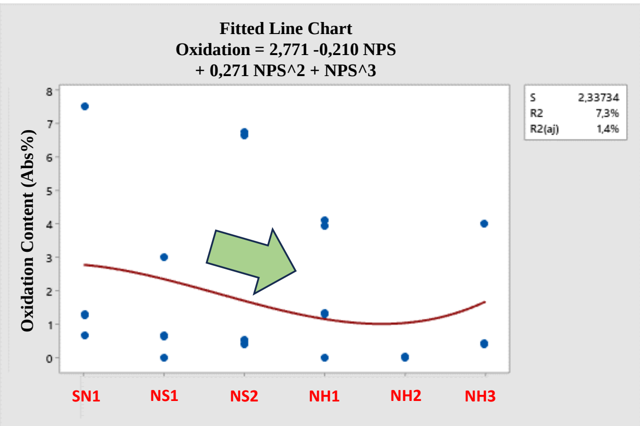

Figure 6. Comparative values and averages of oxidation content related to the use of nanoadditives in both base oils.

The results above show that the lowest oxidation content values were for mineral and synthetic oils, i.e., those with more saturated hydrocarbons and, therefore, more stable to oxidation. The nanoadditives reduced the oxidation index of vegetable-based nanolubricants by up to 50%, being more effective using NS1, NH1 and NH2 nanoadditives, incredibly the latter completely preventing the oxidation of synthetic and mineral oils.

The NH2 hybrid nanoadditive with high surface areas (sizes of 30 to 140 nm), i.e., high surface energy that is probably attracted by free radicals originating from the cracking of unsaturated double bonds (C=O) of hydrocarbons. The metallic salt (NH3) may also be contributing to the secondary oxidation process, through the catalysis of metallic ions that increases the concentration of hydroperoxides, and in the case of vegetable oil, it is accelerated by the presence of fatty acids.

The nanoparticles react with free radicals, delaying the formation of peroxides that are susceptible to the onset of chain oxidation [29]. Under these conditions, the nanofluids remain stable at high temperatures, consequently increasing thermal resistance during operation. This oxidation reduction will also contribute to the remediation of polyaromatic hydrocarbon compounds (PAHs)[36].

On the other hand, the oxidation of vegetable oil is a natural process of extreme importance for biodegradability. According to ANP Resolution Nº 22/2014 [30], in order to be considered biodegradable, the lubricating oil must undergo final biodegradation greater than or equal to 60% within 28 days. The presence of oxygen in the composition of vegetable oil contributes to natural oxidation through decomposition by microorganisms and/or enzymes through an aerobic or anaerobic process [19].

WEAR DIAMETER

Figures 7 e 8 show the regression graph with values variation and averages of wear diameters for base stocks and simple and hybrid nanoadditives respectively.

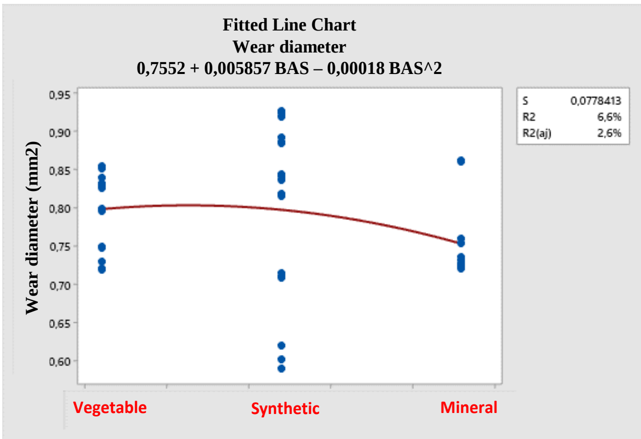

Figure 7. Comparative values and average wear diameters of base stocks.

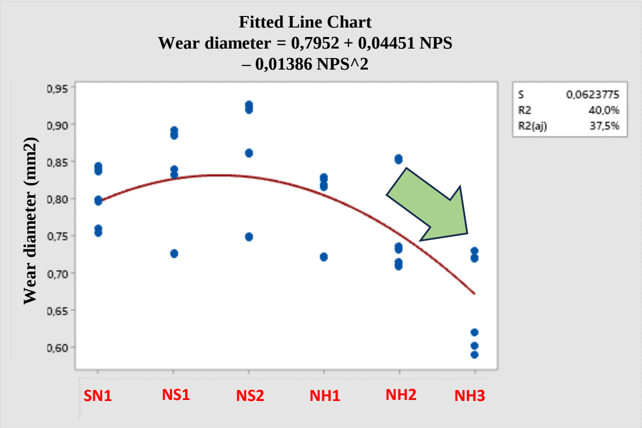

Figure 8. Comparative values and averages of wear diameter related to the use of nanoadditives in both base oils.

The results above show that, as was the case with the friction coefficient, the hybrid nanoadditives also contributed to the reduction of wear for most nanolubricants. In this parameter, it was more pronounced with the use of hybrid nanoadditives in synthetic-based (0.60 and 0.82 mm) and mineral-based (0.73 mm) nanolubricants; once again, the NH3 nanoadditive stood out, presenting the lowest wear values.

The antiwear benefits of hybrid nanoparticles derive from their ability to deposit on wear (abrasion) scratches and reinforce the interface between surfaces that approach each other under high sliding speed [31].

Film formation is strongly influenced by the base oil and EP (extreme pressure) additive, just as the antiwear behavior of oxide nanoparticles depends on the base oil. The nanolubricant does not present good antiwear capacity when combined with sunflower and soybean vegetable oil, due to the chemical nature of the polar groups that favor the formation of a lubricating film [35].

Probably during the elastohydrodynamic lubrication (EHD) regime, the incorporation of nanoparticles occurred through mechanical retention at low speed, considering that the diameter of the nanoparticle is greater than the thickness of the lubricant film. However, the boundary lubricant film incorporated with nanoparticles does not alter the contact surface at high speeds, since in this condition the thickness of the film may be smaller than the diameter of the particle [29][36].

SUPPLEMENTING THE LUBRICANT WITH NANOADDITIVE

A tribological comparison was performed with the nanoadditives NH1 and NH2 added to an industrial synthetic lubricant (DIN 51517 part 3) used in gear and reducer applications, considering the response variables friction coefficient and wear cap diameter. Figures 9 to 11 present the comparative graphs of friction coefficient, oxidation content and wear diameter values between an industrial synthetic lubricating oil (original) and those supplemented with the addition 0.5% by weight of hybrid nanoadditives NH1 and NH2.

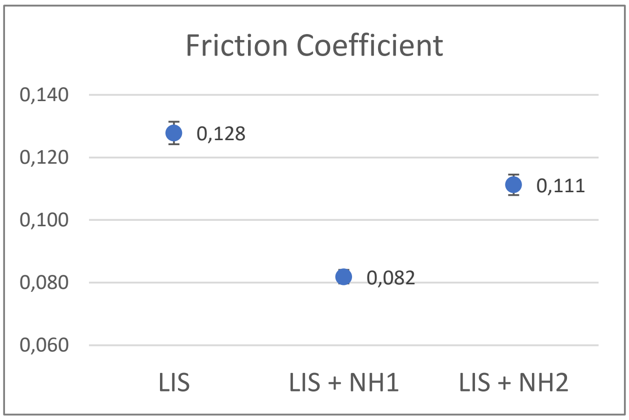

Figure 9. Comparative values of friction coefficient of synthetic industrial lubricant (LIS) with and without nanoadditives.

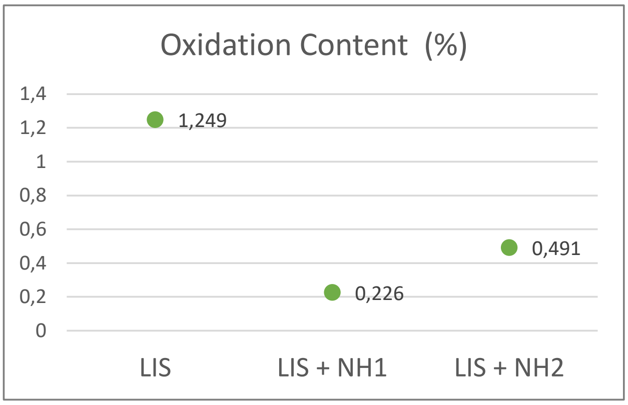

Figure 10. Comparative values of oxidation content of synthetic industrial lubricant (LIS) with and without nanoadditives.

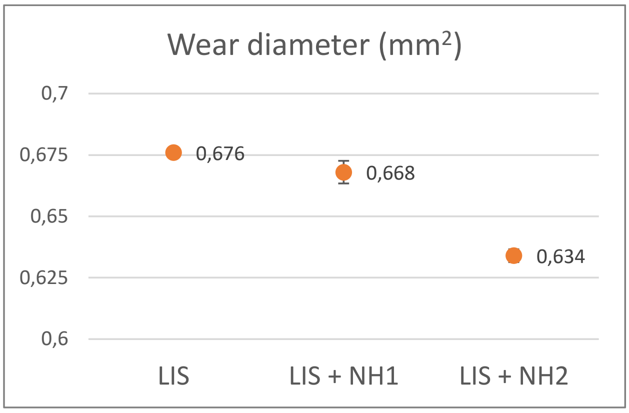

Figure 11. Comparative values of wear diameter of synthetic industrial lubricant (LIS) with and without nanoadditives.

The results of the comparison between industrial lubricants supplemented with hybrid nanoadditives show that the lowest friction coefficient value was for the NH1 nanoadditive, which also contributed to the reduction of the oxidation content. Regarding wear reduction, the lowest value was obtained using the NH2 nanoadditive.

CONCLUSIONS

The physicochemical and tribological parameters in the combinations from the experiments (DoE) of vegetable, synthetic and mineral base oils, with simple nanoadditives NS1, NS2 and hybrids NH1, NH2 and NH3 are presented below:

- The simple and hybrid nanoadditives reduced the oxidation content for all nanolubricants;
- Between base stocks the vegetable-based oil presented the lower friction coefficient values;
- The hybrid nanoadditives reduced the friction coefficient for all nanolubricants;
- Between base oils there is no significant change in wear diameter;
- The NH3 nanoadditive based on metallic salts presented the smallest wear diameter for mineral based nanolubricants.
- The industrial synthetic lubricant (gears and reducers) showed a reduction in friction and oxidation values with the supplementation of NH1 nanoadditive, as well as a reduction in wear using the NH2 nanoadditive.

The frontier between lubrication performance and lubricant biodegradability will continue to seek new additive technologies that are more efficient and soluble in bio-based stocks, considering mainly the omnipresent oxidation and friction parameters that contribute to lubricant degradation and energy efficiency respectively, these being the main requirements for the future development of high-performance biolubricants and their respective applications.

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