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Alumina-based nanolubricants: stability and rheological behavior at high shear rates

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O presente trabalho em nível de mestrado foi avaliado e aprovado por banca examinadora composta pelos seguintes membros:

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Este trabalho é dedicado aos meus pais, Ângelo e Rosalina,
e às minhas irmãs Jaquelini e Fernanda.

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The only way to "find out if it will work out" is to do it.

(Simon Sinek)

RESUMO

O desenvolvimento de lubrificantes contendo nanopartículas, denominados nanolubrificantes, tem atraído a atenção de inúmeros grupos de pesquisa tanto do ponto de vista científico como tecnológico. Nanolubrificantes podem ser aplicados em diversos equipamentos e sistemas mecânicos para fins tribológicos, incluindo mancais de compressores utilizados em refrigeradores. Entretanto, uma ampla aplicação dos nanofluidos é dificultada pela tendência das nanopartículas em se aglomerarem e sedimentarem. Com base nesse contexto, o presente estudo tem como principal objetivo avaliar o comportamento reológico e a estabilidade de nanopartículas de alumina em óleo lubrificante. Os nanolubrificantes foram preparados por meio da abordagem de duas etapas, no qual consistiu na dispersão das nanopartículas de alumina não modificadas (A) e modificadas a superfície com ácido oleico (AS), nas frações volumétricas de 0,5 e 1 vol%. A estabilidade dos nanolubrificantes foi avaliada através do método de inspeção visual e do método de estabilidade acelerada. O comportamento reológico dos lubrificantes foi estudado nas temperaturas de 25, 50 e 75 °C em taxas de cisalhamento de até 70.000 s^{-1}. Após atingir o cisalhamento máximo, foi aplicada a taxa de cisalhamento descendente do sistema até 700 s^{-1} para avaliar os possíveis efeitos do tempo e do cisalhamento na viscosidade. Os resultados reológicos foram comparados com o modelo teórico de Lei de Potência. Também foi avaliado o ângulo de contato entre os lubrificantes e a placa inferior do reômetro utilizado neste estudo. Os resultados revelaram que a funcionalização na superfície das nanopartículas de alumina contribuiu para a estabilidade dos nanolubrificantes. Esse fato pode ser atribuído às afinidades químicas do ácido oleico com o meio oleoso. A simulação do armazenamento por 15 dias mostrou que, para os nanolubrificantes A 0,5 e 1 vol%, os valores de transmitância foram acima de 85%, enquanto para os nanolubrificantes AS 0,5 e 1 vol% foram de aproximadamente 50 e 30%, respectivamente. Para as temperaturas de 25 e 50 ºC, o comportamento reológico do óleo lubrificante e das amostras AS foram newtonianos, entretanto os nanolubrificantes A apresentaram comportamento levemente pseudoplástico. Para os experimentos reológicos a 75 °C, foi possível observar que houve tixotropia para todos os fluidos, contudo, o nanolubrificante A 1 vol% apresentou maior área de histerese. Uma análise estatística demonstrou significância na interação entre os fatores fração volumétrica e temperatura na viscosidade dinâmica dos fluidos. De modo geral, a fração volumétrica mostrou-se proporcional à viscosidade, enquanto que a temperatura foi inversamente proporcional. Por fim, concluiu-se que a presença de nanopartículas de alumina no óleo lubrificante não altera o molhamento do óleo base.

Palavras-chave: Al_2O_3. Nanolubrificantes. Reologia. Estabilidade. Funcionalização.

RESUMO EXPANDIDO

Introdução

A eficiência dos equipamentos e a redução do consumo de energia continuam a ser um dos principais desafios da atualidade. Estima-se que aproximadamente 23% do consumo total de energia mundial seja proveniente de contatos tribológicos, nos quais essas perdas são devidas ao atrito e ao desgaste (HOLMBERG; ERDEMIR, 2017). Uma solução para reduzir esse problema é a utilização de óleos lubrificantes que reduzem ou eliminam o contato direto entre os componentes (LOU; ZHANG; WANG, 2015). Nos últimos anos, muitos pesquisadores têm usado nanopartículas de carbono (BORDIGNON *et al.*, 2018), metais (KUMARA *et al.*, 2017, 2018), sulfetos (SAIDI *et al.*, 2020), e óxidos (PEÑA-PARÁS *et al.*, 2015) como aditivos em óleos lubrificantes para melhorar a qualidade tribológica e o desempenho de diferentes sistemas mecânicos. A alumina (Al_2O_3) é um óxido utilizado na indústria química, metalúrgica, cerâmica, dentre outras, devido à sua morfologia e propriedades, incluindo características polares e hidrofílicas (NUGROHO *et al.*, 2021). De acordo com a literatura, as nanopartículas de Al_2O_3 são consideradas uma das partículas mais comuns utilizadas na preparação de nanofluidos (HEMMAT ESFE *et al.*, 2016), devido à sua produção em larga escala e menor custo, além de serem ecologicamente amigáveis (SALEEMI *et al.*, 2015). A dispersão de nanopartículas em óleos é uma abordagem promissora para melhorar as propriedades reológicas, térmicas e tribológicas (ALI; XIANJUN, 2020; SANUKRISHNA; JOSE PRAKASH, 2018). Um dos maiores desafios na comercialização desses produtos é a preparação de nanolubrificantes homogêneos e estáveis (GHIASI *et al.*, 2019). A estabilidade da dispersão está associada ao tempo de estabilidade da suspensão das nanopartículas no óleo lubrificante sem sedimentação. Os principais problemas associados à estabilidade da dispersão das nanopartículas são a aglomeração e a sedimentação. A aglomeração depende das forças de interação entre as partículas (como forças repulsivas eletrostáticas e forças atrativas de Van der Waals), movimento browniano e coesão durante sua colisão (AZMAN; SAMION, 2019). Para melhorar a estabilidade de nanolubrificantes, têm sido aplicados métodos físicos (FONTES; RIBATSKI; BANDARRA FILHO, 2015), químicos como modificação de superfície (JIAO *et al.*, 2011) além do uso de surfactantes como dispersantes (ALI *et al.*, 2016; VAISMAN; WAGNER; MAROM, 2006). O comportamento reológico é uma das propriedades mais importantes para a aplicação de nanolubrificantes, pois permite o entendimento da estrutura fluídica. As propriedades reológicas determinam diretamente a resistência ao fluxo do fluido. Em geral, o comportamento reológico de nanofluido pode ser afetado por fatores como concentração, formato e tamanho de partículas, temperatura, valor de pH, tipo de fluido base, método de preparação, entre outros (HU *et al.*, 2020). Sistemas que empregam compressores para de refrigeração consomem uma quantidade relevante de energia no mundo. A lubrificação a óleo desempenha um papel crucial no bom desempenho e alta confiabilidade desses sistemas (WANG *et al.*, 2020). A lubrificação de mancais em compressores do tipo herméticos é afetada pela viscosidade do óleo, que pode ser determinada pelo tipo de óleo e pela condição de operação do compressor do refrigerador (ZHU *et al.*, 2020). Diante desse contexto, são necessárias soluções alternativas para melhorar a eficiência desses equipamentos mecânicos, como por exemplo o uso de nanofluidos. No entanto, os trabalhos na literatura sobre nanopartículas inorgânicas em óleo não analisam o comportamento reológico sob altas taxas de cisalhamento, limitando-se a 5.000 s^{-1}. Assim, neste trabalho foram aplicadas taxas de cisalhamento de até 70.000 s^{-1}. Essa faixa é relevante para aplicações tribológicas de nanolubrificantes usados em mancais de compressores herméticos, pois esses sistemas operam sob taxas de cisalhamento na faixa entre 10^5 e 10^6 s^{-1}. Além disso, nanopartículas de alumina foram utilizadas como aditivos ao óleo devido ao seu melhor desempenho dielétrico como isolantes, quando comparadas a outras nanopartículas

Objetivos

O objetivo principal deste estudo é avaliar o comportamento reológico e a estabilidade de nanopartículas de alumina em óleo lubrificante utilizado em compressores herméticos de geladeira.

Os objetivos específicos são:

- Avaliar a estabilidade da dispersão de nanolubrificantes à base de alumina nas frações volumétricas de 0,5 e 1 vol% por meio de inspeção visual e métodos de estabilidade acelerada.
- Avaliar o comportamento reológico de nanopartículas de alumina a 0,5 e 1 vol% como aditivos em óleo lubrificante em temperaturas ambiente (25 °C), intermediárias (50 °C) e temperaturas de aplicação reais (75 °C) para taxas de cisalhamento de até 70.000 s^{-1}.
- Comparar os resultados reológicos de nanolubrificantes contendo alumina com óleo puro, avaliando a viscosidade como variável dependente.
- Investigar as influências na estabilidade e reologia de nanolubrificantes contendo alumina modificada superficialmente com ácido oleico, e indicar a melhor condição experimental para aplicação.

Metodologia

Nanopartículas de alumina (99,99%; fase gama, Inframat) utilizadas para desenvolver este estudo têm um tamanho médio de partícula de 20-50 nm e foram adquiridas da empresa. Óleo sintético à base de alquilbenzeno (Zerol AB, Shrieve), de baixa viscosidade com propriedades antiespumantes, foi utilizado e é comumente empregado em sistemas de compressores específicos. Inicialmente, foram caracterizados nanopós de alumina como recebidos (A) e após modificação em superfície com ácido oleico (AS) através da técnica de espectroscopia no infravermelho por transformada de Fourier (FTIR). Posteriormente, os nanolubrificantes foram preparados pelo método de duas etapas, no qual consistiu na dispersão de nanopartículas de A e AS em óleo lubrificante, usando concentrações de 0,5 e 1 vol%. A estabilidade dos nanolubrificantes foi avaliada através do método de inspeção visual, que consistiu em fotografar as amostras por um período de 192 h, e do método de estabilidade acelerada, para simular o período de 15 dias. O comportamento reológico dos lubrificantes foi realizado em um reômetro rotacional com placas paralelas (diâmetro de 35 mm) e gap de 35 μm. A análise consistiu em avaliar a viscosidade de óleo puro e nanolubrificantes A e AS nas temperaturas de 25, 50 e 75 °C por 600 s, com taxa de cisalhamento de 700 a 70.000 s^{-1}. Após atingir o cisalhamento máximo, a taxa descendente foi aplicada ao sistema até 700 s^{-1}. Essa configuração foi escolhida devido às condições reais de aplicação em compressores do tipo hermético utilizados em sistemas de refrigeração.

Resultados e Discussão

Através da análise de FTIR, concluiu-se que houve funcionalização na superfície das nanopartículas. A estabilidade dos nanolubrificantes foi avaliada por meio de inspeção visual e da análise de estabilidade acelerada, logo as amostras contendo AS permaneceram estáveis por um tempo relativamente maior do que as amostras contendo A. Com base na análise de estabilidade acelerada, simulando vida útil de 15 dias, foi possível observar que nos primeiros 100 s, os nanolubrificantes A, 0,5 e 1 vol% apresentam um índice de instabilidade de 100% e 82% respectivamente, ou seja, as nanopartículas sedimentaram. Por outro lado, para AS 0,5 e 1 vol%, os índices de instabilidade são relativamente menores, 20% e 8%, respectivamente. O comportamento reológico dos lubrificantes foi avaliado a 25, 50 e 75 °C e comparado com o modelo da lei de potência. A 25 e 50 ºC, o óleo puro e os nanolubrificantes AS apresentaram comportamento newtoniano, enquanto os nanolubrificantes A foram levemente pseudoplásticos. No entanto, para taxas de cisalhamento >10^4 s^{-1}, todos os lubrificantes apresentaram comportamento newtoniano. A 75°C, foi possível observar que todos os nanofluidos apresentam tixotropia, ou seja, a viscosidade muda com o aumento e diminuição da taxa de cisalhamento durante o tempo dos experimentos. Nesse caso, o nanolubrificante A 1 vol% apresentou a maior tixotropia, 277 ± 55 $\text{kPa}\cdot\text{s}^{-1}$. O efeito da temperatura (50 e 75 °C) na reologia de A e AS a 70.000 s^{-1}, revelou que as viscosidades dos nanofluidos foram maiores quando comparadas ao óleo puro. De acordo com a literatura, esse efeito favorece maior eficiência no sistema de lubrificação entre superfícies. Também foi possível verificar que, em geral, a viscosidade dos lubrificantes aumenta com o aumento da fração volumétrica, enquanto a viscosidade diminui com o aumento da temperatura.

Considerações Finais

O uso de nanopartículas como aditivos em óleos lubrificantes é amplamente estudado a fim de propor soluções tribológicas. Porém, existem ainda lacunas referentes ao comportamento reológico e a estabilidade, que são propriedades fundamentais na comercialização desses produtos. Neste estudo, os testes confirmaram que ocorreu a funcionalização da superfície das nanopartículas de alumina com ácido oleico. Os resultados reológicos mostraram que o óleo lubrificante e os nanolubrificantes A e AS apresentaram comportamento newtoniano nas temperaturas de 25 e 50 °C, para taxa de cisalhamento superior a 10^4 s^{-1}. Entretanto, a 75 °C, todos os fluidos apresentaram tixotropia. De modo geral, observou-se que a viscosidade dos lubrificantes aumentou com o aumento da fração volumétrica, e diminuiu com o aumento da temperatura. Por fim, conclui-se que as melhores condições experimentais relativas à estabilidade foram com os nanolubrificantes AS. Em relação às análises reológicas, os mais adequados foram os nanofluidos com maior concentração de nanopartículas de alumina.

Por fim, este trabalho oferece a oportunidade para o desenvolvimento de outros estudos, tais como:

- Utilização de métodos alternativos que promovam a estabilidade das nanopartículas, incluindo funcionalização e adição de tensoativos diretamente ao óleo base.
- Verificação da influência da adição de nanopartículas de alumina ao óleo nas propriedades térmicas, principalmente na condutividade térmica e capacidade calorífica.
- Avaliação tribológica dos lubrificantes.
- Utilização de outras nanopartículas para gerar maior efeito dilatante, que contribui positivamente para a lubrificação dos mancais do compressor hermético.

Palavras-chave: Al_2O_3. Nanolubrificantes. Reologia. Estabilidade. Funcionalização.

ABSTRACT

The development of lubricants containing nanoparticles, called nanolubricants, has attracted the attention of numerous research groups, both from a scientific and technological point of view. Nanolubricants can be applied to various equipment and mechanical systems for tribological purposes, including compressor bearings used in refrigerators. However, a wide application of nanofluids is hampered by the tendency of nanoparticles to agglomerate and sediment. Based on this context, this study aims to evaluate alumina nanoparticles' rheological behavior and stability in lubricating oil. The nanolubricants were prepared using a two-step approach, which consisted of dispersing unmodified alumina nanoparticles (A) and surface-modified with oleic acid (AS), in the volume fractions of 0.5 and 1 vol%. The stability of nanolubricants was evaluated using the visual inspection method and the accelerated stability method. The rheological behavior of lubricants was studied at temperatures of 25, 50, and 75 °C at shear rates up to 70,000 s^{-1}. After reaching the maximum shear, the downward shear rate of the system up to 700 s^{-1} was applied to evaluate the possible effects of time and shear on viscosity. The rheological results were compared with the Power-Law theoretical model. The contact angle between the lubricants and the lower plate of the rheometer used in this study was also evaluated. The results revealed that the surface functionalization of alumina nanoparticles contributed to the stability of the nanolubricants, which can be attributed to the chemical affinities of oleic acid with the oily medium. The 15-day shelf-life simulation showed that for the nanolubricants A 0.5 and 1 vol% the transmittance values were above 85%, while for the nanolubricants AS 0.5 and 1 vol% they were approximately 50% and 30%, respectively. For temperatures of 25 and 50 ºC, the rheological behavior of the lubricating oil and AS samples was Newtonian, however, the nanolubricants A presented a slightly pseudoplastic behavior. For the rheological experiments at 75 °C, it was possible to observe thixotropy for all fluids. However, the nanolubricant A 1 vol% presented the largest hysteresis area. Statistical analysis showed significance in the interaction between the factors volumetric fraction and temperature in the dynamic viscosity of fluids. In general, the volume fraction was shown to be proportional to viscosity, while the temperature was inversely proportional. Finally, it was concluded that the presence of alumina nanoparticles in the lubricating oil does not change the wettability of the base oil.

Keywords: Al_2O_3. Nanolubricants. Rheology. Stability. Functionalization.

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A	Alumina nanoparticles
ANOVA	Analysis of variance
AS	Surface-modified alumina nanoparticles
COF	Coefficient of friction
COP	Coefficient of performance
DLVO	Derjaguin and Landau, Verwey and Overbeek´s Theory
FTIR	Fourier-Transform Infrared
CMC	Critical Micellar Concentration
NIR	Near-Infrared
PAG	Polyalkylene glycol
PAO	Polyalphaolefin oil
POE	Polyol ester oil
RCF	Relative Centrifugal Force
SAE	Society of Automotive Engineers
SEM	Scanning Electron Microscopy
STEP	Space-and time-resolved extinction profiles
VCR	Vapor compression refrigeration
vol%	Volume fraction
wt%	Weight fraction
vdw	Van der Waals

LIST OF SYMBOLS AND UNITS

C	Hamaker constant	[-]
g	Acceleration of gravity	[m/s²]
K	Consistency coefficient	[mPa·s]
K_b	Boltzmann constant	[J/mol]
n	Flow behavior index	[-]
R	Particle radius	[µm] or [nm]
T	Temperature	[K] or [ºC]
$t_{requerido}$	duration of the experiment	[s]
Z	Distance between the centers of two particles	[nm]
η	Dynamic viscosity of the fluid	[mPa·s]
ρ	Density of the nanoparticles	[g/cm³]
ρ'	Density of the liquid	[g/cm³]
$\dot{\gamma}$	Shear rate	[s^{-1}]
τ	Shear stress	[Pa]
v	sedimentation speed	[µm/s]

SUMMARY

1 INTRODUCTION

The efficiency of equipment and the reduction of energy consumption remains one of the main challenges today. It is estimated that approximately 23% of the world's total energy consumption comes from tribological contacts, and these losses are due to friction and wear (HOLMBERG; ERDEMIR, 2017).

A solution to reduce this problem to increase the sustainability, durability, and reliability of the equipment, is lubricating oils that reduce or eliminate direct contact between the components (LOU; ZHANG; WANG, 2015). In recent years, many researchers have used carbon (BORDIGNON *et al.*, 2018), metal (KUMARA *et al.*, 2017, 2018), sulfide (KANG *et al.*, 2008; SAIDI *et al.*, 2020), and oxide (CHOUHAN *et al.*, 2020; PEÑA-PARÁS *et al.*, 2015) nanoparticles as additives in lubricating oils to improve the tribological performance of different mechanical systems.

Alumina (Al_2O_3) is an oxide used in the chemical industry, metallurgy, and other industrial applications due to its performance, morphology, and thermal properties, it also presents polar and hydrophilic characteristics (ILYAS *et al.*, 2017; NUGROHO *et al.*, 2021). According to the literature, Al_2O_3 nanoparticles are considered one of the most common particles used in fluid preparation (HEMMAT ESFE *et al.*, 2016), due to their large-scale production and lower cost, in addition to being ecologically correct. (SALEEMI *et al.*, 2015).

Luo *et al.*, (2014) added nanoparticles of Al_2O_3 at a concentration of 0.1 vol% in lubricating oil and reported a 17.61% decrease in the coefficient of friction (COF). The use of Al_2O_3 nanoparticles in a nanolubricant formed a self-laminated protective film on the friction surfaces, capable of converting sliding friction into rolling friction.

The dispersion of nanoparticles in oils is a promising approach to improve rheological, thermal, and tribological properties (ALI; XIANJUN, 2020; SANUKRISHNA; JOSE PRAKASH, 2018). One of the biggest challenges in the commercialization of these products is the preparation of homogeneous and stable nanolubricants (GHIASI *et al.*, 2019). Dispersion stability is associated with the stability time of the suspension of nanoparticles in the lubricating oil without sedimentation or settling down of the nanoparticles due to a downward body force of the cumulative weight. The main problems associated with the stability of nanoparticles dispersion are agglomeration and sedimentation. Agglomeration depends on the interaction forces between particles (such as electrostatic repulsive forces and Van der Waals attractive forces), Brownian motion, and cohesion during their collision (AZMAN; SAMION, 2019). To improve the stability of nanolubricants, physical methods (FONTES; RIBATSKI;

BANDARRA FILHO, 2015), and chemical methods as surface modification of nanoparticles (JIAO *et al.*, 2011) and the use of surfactants as dispersants (ALI *et al.*, 2016; VAISMAN; WAGNER; MAROM, 2006) have been applied.

Luo *et al.*, (2014) used Al_2O_3 nanoparticles (0.05, 0.1, 0.5, and 1 wt%) as an additive in lubricating oil. The nanoparticles were prepared using a hydrothermal method and modified by a silane coupling agent (KH-560), which increased the stability of the nanoparticles in the oil. Other researchers, Choi *et al.*, (2008), prepared and evaluated dispersions of Al_2O_3 nanoparticles and AlN powder in transformer oil using oleic acid as a dispersant. They concluded that excess oleic acid in suspensions can have detrimental effects on thermal and viscous properties.

The rheological behavior is one of the most important properties for the application of nanolubricants, as it allows an understanding of the fluidic structure. For example, rheological properties directly determine fluid flow resistance. In general, nanofluid rheological properties can be affected by factors such as particle concentration, temperature, pH value, type of base fluid, preparation method, and particle shape and size, among others (HU *et al.*, 2020).

Kotia *et al.*, (2018) reported a 10.5% increase in relative viscosity with a 0.5% volume fraction of Al_2O_3 nanoparticles in gear oil (SAE EP90). The viscosity-increasing effect of the addition of nanoparticles is attributed to the agglomeration of nanoparticles in lubricants, which prevents the easy movement of adjacent oil layers.

The area involving compressors for refrigeration systems consumes a relevant amount of energy in the world and oil lubrication plays a crucial role in the good performance and high reliability of these systems (WANG *et al.*, 2020). In this way, the lubricating condition of the journal bearing is affected by the viscosity in the oil sump, which can be determined by the type of oil and the operating condition of the refrigerator compressor (ZHU *et al.*, 2020). Given this context, alternative solutions are needed to improve the efficiency of this mechanical equipment, such as the use of nanofluids.

Nevertheless, the works in the literature regarding inorganic nanoparticles in oil do not analyze the rheological behavior under high shear rates, being limited to 5,000 s^{-1}. In our work, shear rates up to 70,000 s^{-1} were applied, in the range that is relevant for tribological applications of nanolubricants used in bearings such as hermetic compressors, as these systems operate under shear rates in the range between 10^5 and 10^6 s^{-1}. Moreover, alumina nanoparticles were used as additives to oil due to their better dielectric performance as insulators, when compared to other nanoparticles. The present study aims to evaluate the rheological behavior and stability of nanolubricants containing 0.5 and 1 vol% alumina either surface-modified or not modified with oleic acid.

1.1 OBJECTIVES

1.1.1 Main objective

The main objective of this study is to evaluate the rheological behavior and stability of alumina nanoparticles in lubricating oil used in hermetic refrigerator compressors.

1.1.2 Specific objectives

- Evaluate stability of the dispersion of alumina-based nanolubricants in the volume fractions of 0.5 and 1 vol% through visual inspection and accelerated stability methods.
- Assess the rheological behavior of 0.5 and 1 vol% alumina nanoparticles as additives in lubricating oil at ambient temperatures (25 °C), intermediate (50 °C) and actual application temperatures (75 °C) for shear rates up to 70,000 s^{-1}.
- Compare the rheological results of nanolubricants containing alumina with pure oil, evaluating viscosity as a dependent variable.
- Investigate the influences on the stability and rheology of nanolubricants containing surface-modified alumina with oleic acid, and indicate the best experimental condition for application.

2 THEORETICAL BACKGROUND

2.1 FLUID LUBRICATION

The relative movements between surfaces in contact are responsible for the increased friction and wear in materials. An alternative to reduce these losses and consequently increase the sustainability, durability, and reliability of equipment, is the use of solid or fluid lubricants that reduce or eliminate direct contact between the components (BORDIGNON, 2018).

Fluid lubrication consists of the existence of a liquid lubricant film that has the function of preventing contact between components, promoting the partial or total support of a load on tribological surfaces (HUTCHINGS; SHIPWAY, 2017). A common example of liquid lubricant is oil, which in turn can be of mineral, synthetic or biological origin. Oils have different assets and are suitable for different a tribological applications (SHAHNAZAR; BAGHERI; ABD HAMID, 2016).

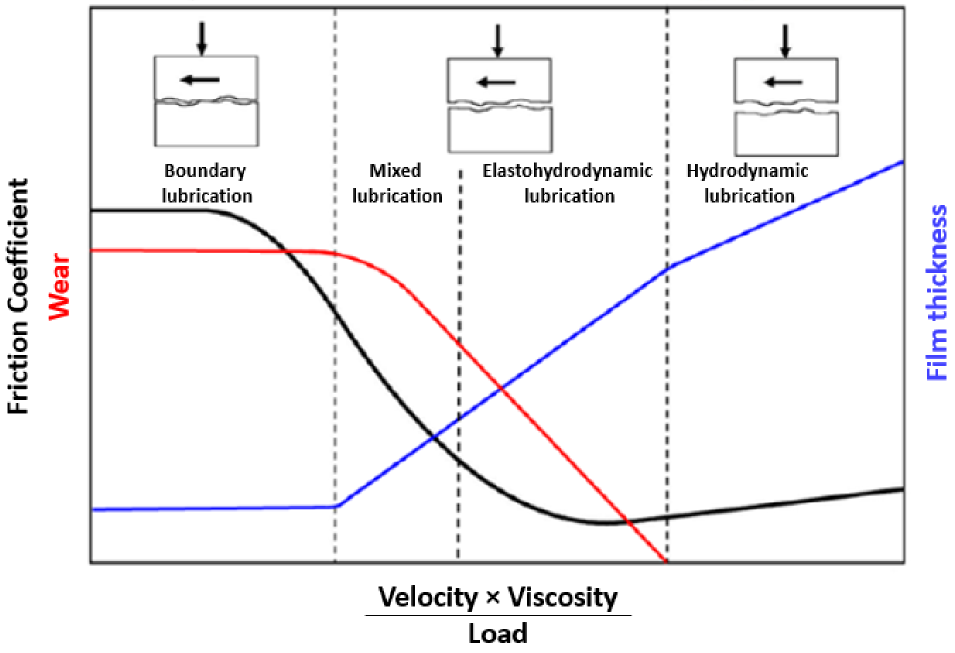
One of the most important properties to be observed in a lubricant is viscosity, as it indicates the ability of the lubricant to keep moving surfaces relatively separate, even under high loads. In this way, viscosity is defined as the resistance to the flow of a fluid deformed by shear forces (EINSTEIN, 1906). According to the classic Reynolds theory for lubrication, for the same sliding speed, higher viscosities provide thicker lubricant films between surfaces in relative motion, while lower viscosities lead to thinner films. The dynamic tribological behavior of lubricated systems is conventionally described by a Stribeck curve, which correlates the frictional forces to the thickness of the fluid film that is relative to the surface roughness, as illustrated in Figure 1, these parameters characterize the lubrication regimes, which in turn have a direct influence on the attrition and wear of tribosystems (SALVARO, 2015; XU; STOKES, 2020).

In the hydrodynamic lubrication regime, the lubricant film is thick and there is no contact between tribological surfaces, thus the entire load is supported by the pressure generated hydrodynamically on the fluid, so there is no wear. In the elastohydrodynamic regime, the thickness of the lubricating film presents the same order of magnitude as the roughness of the surfaces involved, so the elastic deformations are transferred between them. In the limit lubrication regime, wear is more severe, because the thickness of the lubricating film is less than the roughness of the surfaces, thus, contact occurs between the surfaces, which in this case impose elastoplastic deformations. In the mixed lubrication regime, part of the load applied to the system is supported by the higher roughness of the surfaces that are in contact with the Boundary lubrication, while the rest is supported by the hydrodynamic component of the lubrication (BORDIGNON, 2018).

In the case of alternating sliding bearings in compressors, mixed lubrication occurs, as in the points of inversion of the movement, the limit lubrication prevails due to the low speed between the surfaces. As the movement moves away from the extremes, prevails elastohydrodynamic lubrication and sometimes hydrodynamic (DAVIM, 2011; HAMROCK; SCHMID; JACOBSON, 2004).

In lubricating oils for tribological purposes, it is common to use additives to maintain the overall performance of the lubricant, such as film-forming, coagulation, viscosity stabilizer, anti-corrosion, anti-wear, and anti-friction. Such chemical additives as chlorine, sulfur, phosphorus, etc. are considered to improve lubrication performance, forming a sacrificial chemical layer, however, these additives have harmful effects on the environment (KOTIA *et al.*, 2018).

Figure 1 – Stribeck diagram with the main fluid lubrication regimes.



Source: Adapted from Salvaro (2015).

1.1.3 Nanolubricants

Nanofluids are colloidal suspensions of nanoparticles (materials between 1 to 100 nm in at least one dimension) dispersed in a base fluid, which can be water, ethylene glycol, oil, among others (BABITA; SHARMA; GUPTA, 2016; TAYLOR *et al.*, 2013). When the base fluid is oil, the term nano-oil or nanolubricants is often seen in the scientific field.

In recent years, there has been a significant increase in the number of researches involving the application of carbon (BORDIGNON *et al.*, 2018; CHOUHAN; MUNGSE; KHATRI, 2020), metal (KUMARA *et al.*, 2017, 2018), sulfide (KANG *et al.*, 2008; SAIDI *et al.*, 2020) and oxide (CHOUHAN *et al.*, 2020; PEÑA-PARÁS *et al.*, 2015) nanoparticles as additives in lubricants for tribological purposes in different mechanical systems. These, in turn, can offer solutions to problems associated with traditional lubricants that contain phosphorus and sulfur (AZMAN; SAMION, 2019). According to Lee *et al.*, (2009) nanolubricants can function as friction modifiers, with four possible mechanisms: rolling effect, formation of protective films, repair effect, and polishing effect.

Lou, Zhang, and Wang (2015) disclose that the use of graphite nanoparticles as an additive in a domestic refrigerator compressor lubricant, whose weight fractions of 0, 0.05, 0.1, 0.2, and 0.5% with dimension average of 50 nm, showed significant reductions in the temperatures and pressures of the equipment components. In addition, the refrigerator's energy consumption decreased by 4.55% using graphite nanolubricant with 0.1 wt%.

Alumina is an oxide that has polar and hydrophilic characteristics and is commonly used in the chemical industry, metallurgy, and other industrial applications due to its performance, morphology, and thermal properties (ILYAS *et al.*, 2017; NUGROHO *et al.*, 2021). According to the literature, Al_2O_3 nanoparticles are considered one of the most used particles in the preparation of fluids (HEMMAT ESFE *et al.*, 2016), due to their large-scale production and lower cost, in addition to being ecologically correct (SALEEMI *et al.*, 2015).

Luo *et al.*, (2014) added spherical nanoparticles of Al_2O_3 at a concentration of 0.1 vol% in lubricating oil and reported a 17.61% decrease in the COF. The use of Al_2O_3 nanoparticles in a nanolubricant formed a self-laminated protective film on the friction surfaces, capable of converting sliding friction into rolling friction. Therefore, alumina nanoparticles proved to be potential additives for lubricating oils, as they can reduce friction and wear on surfaces.

Ma *et al.*, (2021) investigated the friction and wear of nanolubricants containing 0.1 wt% of Al_2O_3, SiO_2, TiO_2, and ZrO_2 to commercial motor oil SAE 10W30. Among these four oxide additives, Al_2O_3 had the best performance, with friction reduction by up to 80% and wear relief by 50%, compared to engine oil without the addition of nanoparticles.

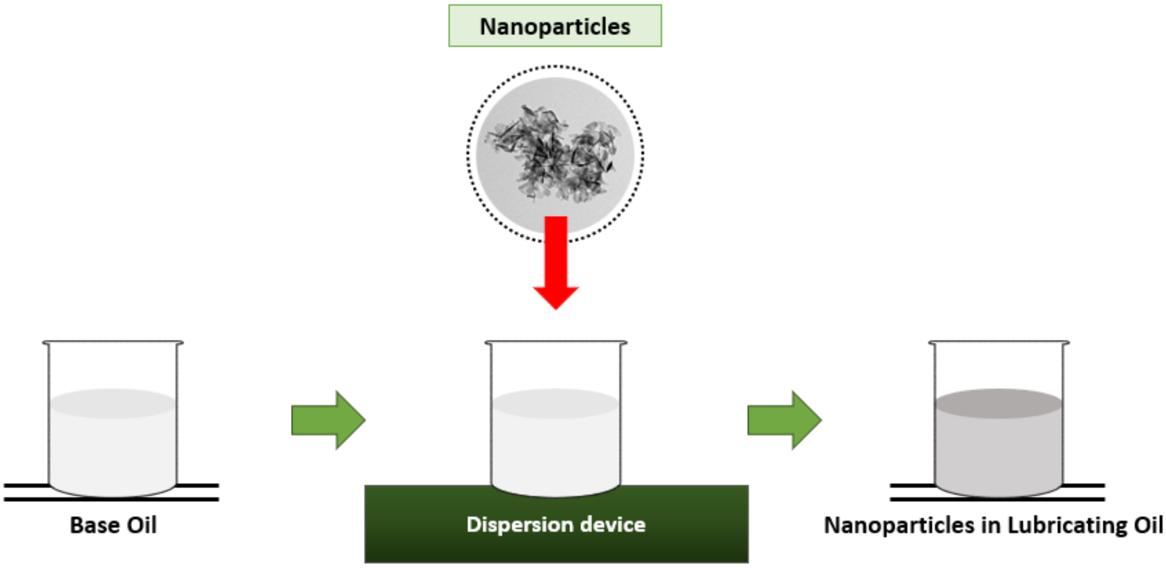
Experimental studies involving a vapor compression refrigeration (VCR) system using Al_2O_3/mineral oil nanolubricant showed that the addition of 0.075 vol% alumina nanoparticles increased the heat absorption capacity in the evaporator section by 35% and reduced the heat. input work for compression at 27%, which shows a 85% increase in the coefficient of performance (COP) of the VCR system (SUBHEDAR; PATEL; RAMANI, 2020).

The advantages of additives in lubricating oil can be summarized in three main categories: economic, operational, and environmental benefits. The reduction of friction and wear will improve the performance of machines and equipment and, consequently, result in lower maintenance investments. The economic gains are attributed to the fact that good lubricity increases the useful life of equipment and/or machinery. Finally, environmental benefits include the use of non-toxic and environmentally friendly nanoparticles (DEEPIKA, 2020). There are two methods of preparing nanofluids: one-step approach and two-step approach (BABITA; SHARMA; GUPTA, 2016).

In the **one-step approach**, the preparation of the nanoparticles and the synthesis of the nanofluid are carried out simultaneously in a single process, that is, it is a combination of the production and dispersion of the nanoparticles in the base fluid in a single step. One of the methodologies for obtaining the nanofluid is to solidify and insert the nanoparticles in the base fluid, which were originally in a gaseous state. The disadvantage of this method is the presence of contaminations that are difficult to eliminate (SEZER; ATIEH; KOÇ, 2019). Sarno *et al.*, (2020) investigated "green" synthesis in their study using the one-step method and the dispersion of quantum dots of carbon/nanocomposites from poly (methyl methacrylate) for tribological applications. The authors obtained promising results in tribological performance tests and the presence of small percentages of nanocomposites in the oil did not show significant changes in the rheological properties of the lubricant.

The **two-step approach** consists of synthesizing nanoparticles in the form of ultrafine dry powder and later dispersing them in the base oil (as illustrated in Figure 2) employing physical processes, such as magnetic stirrers, baths, or ultrasonic probes. This route is used by many researchers to prepare nanolubricants, because it is more economically viable to produce small and large-scale nanolubricants. However, the disadvantage of this method is associated with the probability of oxidation and agglomeration of the nanoparticles that are relatively larger (ALI; TEIXEIRA; ADDALI, 2018).

Figure 2 – Two-step approach to the preparation of nanolubricants.



Source: Author (2022).

One of the main challenges associated with the commercialization of nanolubricants is the instability of the suspension due to the characteristic of the particles in the fluid. This behavior is associated with two competing combinations: Van der Waals and steric interactions (ALI; TEIXEIRA; ADDALI, 2018; AZMAN; SAMION, 2019), which can be studied through the science of colloids.

1.2 COLLOIDS

The dispersion of nanoparticles in oil lubricants can be explained by colloidal theories, which study the behavior of particles between 1 nm and 1000 nm in size, a range that overlaps the size of nanoparticles (CHEN; RENNER; LIANG, 2019; SHAW, 2013). According to colloid science, the tendency of nanoparticles to agglomerate is determined by two factors: thermal agitation and the interaction of nanoparticles (MARTIN; OHMAE, 2008).

Thermal agitation has the energy of K_bT, where K_b is the Boltzmann constant and T is the temperature. It promotes the random movement of particles in the solvent, causing Brownian motion. The interaction between the nanoparticles results in attractive and repulsive forces (DLVO theory), stable dispersions are formed when thermal agitation exceeds the attractive force between nanoparticles (CHEN; RENNER; LIANG, 2019).

The DLVO theory (Derjaguin and Landau 1941, Verwey and Overbeek 1948) explains the interaction between nanoparticles by the attractive forces of Van der Waals and repulsive electrostatic forces. The Van der Waals force is originated through the polarization of nanoparticles, which act as electrical dipoles that can attract and consequently aggregate if there is no repulsive force. In this way, this tendency of aggregation is opposed by the electrostatic force between the nanoparticles. Although this force can be said to be weak in a non-polar solvent, it can be increased through the process of ion selection in a polar solvent (CHEMISTTY, 1992; RUBIO-HERNÁNDEZ, 1999). However, the polarity of the nanolubricants renders electrostatic stabilization difficult in a base oil. Given this context, the dielectric constant can be used to measure polarity. In organic media, for example, where the dielectric constant is less than or equal to 5, the electrostatic interaction is considered weak even when the nanoparticles have a surface charge. This is because most of the lubricant dielectric constants have values of 2.5, that is, lower than the dielectric constants of water or other polar solvents. Thus, the surface charge of the nanoparticles cannot improve the dispersion in the lubricating oil (CHEN; RENNER; LIANG, 2019).

The steric stabilization theory establishes a balance between two forces: Van der Waals and elastic steric. Although the Van der Waals force is complex, a simplified way of representing it prescribed by Hamaker (1937) is expressed in Equation (1) as a potential, which can be used for colloidal systems when it is assumed that the size of the nanoparticles is small compared to the average distance between them (CHEN; RENNER; LIANG, 2019; HAMAKER, 1937) :

$$\boldsymbol{V_{vdw}(z,R) = -\frac{C}{6}\left[\frac{2R^2}{Z^2-R^2}+\frac{2R^2}{Z^2}+ln\left(\frac{z^2-4R^2}{z^2}\right)\right]} \tag{1}$$

where V is the potential, vdw stands for van der Waals, Z is the distance between the centers of two particles, R is the radius of the particle and C is the Hamaker constant, which can be approximated by the particle and medium constant through Equation (2) (HAMAKER, 1937):

$$\boldsymbol{C = (\sqrt{C_{Particle}} - \sqrt{C_{Medium}})} \tag{2}$$

According to Equation (1), it is possible to affirm that the shorter the distance between the nanoparticles, the greater the potential, strongly attracting the nanoparticles, which refers to the need to remove them, which may occur through the adsorption of polymers on their surface, for example.

In addition to the Van der Waals potential, Equation (3) can clarify the movement of particles in a colloidal system through the particle sedimentation speed (MARTIN; OHMAE, 2008):

$$\boldsymbol{v = \frac{2R^2(\rho - \rho')g}{9\eta}} \tag{3}$$

where v is the sedimentation speed, R is the radius of the nanoparticles, ρ is the density of the nanoparticles, ρ' is the density of the liquid, η is the dynamic viscosity of the fluid, and g the acceleration of gravity. Thus, the sedimentation speed of the nanoparticles is dependent on the balance between viscous forces, buoyancy, and gravity (SINGH; SHARMA; MAUSAM, 2020). It is also important to note that the particle size has a quadratic influence on the sedimentation speed, therefore, when the agglomeration process begins, the hydrodynamic particle radius increases, directly interfering with sedimentation.

2.3 DISPERSION METHODS

Dispersion stability is associated with the stability time of the suspension of nanoparticles in the lubricating oil without sedimentation or sedimentation of the nanoparticles due to a downward body force of the cumulative weight. In this way, agglomeration and sedimentation of nanoparticles must be avoided. In this context, dispersion methods are extremely important to ensure the stability of nanolubricants (AZMAN; SAMION, 2019). To disperse nanoparticles, different methods can be used, such as physical (NUGROHO *et al.*, 2021) and surface energy modification methods. The latter can be subdivided into the use of surfactants (COLANGELO *et al.*, 2016) and surface chemical modification (ILYAS *et al.*, 2017).

Based on data from the literature, Table 1 shows some studies using alumina nanoparticles as additives in lubricants and their respective dispersion methods. It is noteworthy that the studies reported different methods to evaluate the stability time of nanolubricants.

Table 1 – Overview of dispersion method and stability of Al_2O_3 nanoparticles reported in previous studies as lubricating additives.

Diameter (nm)	**Volume fraction (vol%)**	**Weight fraction (wt%)**	**Base oil**	**Dispersion method**	**Stability time (h)**	**Reference**
10±2	-	0.05 to 0.5*	5W30 synthetic oil	Surfactant	336	(ALI *et al.*, 2016)
10±2	-	0.1*	5W30 synthetic oil	Surfactant	-	(ALI *et al.*, 2018b)
13	0.02	**-**	POE	Physical	24	(NUGROHO *et al.*, 2021)
13	0.02	**-**	POE	Physical	24	(YUSOF *et al.*, 2015)
13	0.07 to 0.6	**-**	PAG	Physical	120	(SANUKRISHNA and JOSE PRAKASH, 2018)
20	0.05 to 2	-	Mineral oil	Surfactant	168	(SUBHEDAR; PATEL; RAMANI, 2020)
20	-	0.25 to 0.75	SAE 20W40	Physical	36	(MOHAN *et al.*, 2014)

(Continuation)

Diameter (nm)	**Volume fraction (vol%)**	**Weight fraction (wt%)**	**Base oil**	**Dispersion method**	**Stability time (h)**	**Ref.**
40	0.3 to 0.9	-	SAE 15W40	Physical	1200	(KOTIA; BORKAKOTI; GHOSH, 2018)
40	-	0.5 to 3	Thermal oil	Surface modification	720	(ILYAS *et al.*, 2017)
45	0.3 to 1	**-**	Therminol 66	Surfactant	192	(COLANGELO *et al.*, 2016)
60	-	0.005 to 0.02	PAO6	Surfactant	3840	(LIU *et al.*, 2020)
78		0.1	Machine oil	Surface modification	480	(LUO *et al.*, 2014)

*With 50% TiO_2 10 nm nanoparticles.

Source: Author (2022).

2.3.1 Physical methods

There are several techniques for dispersing nanoparticles in the base oil using the physical method, such as ball grinding, ultrasound, and high-pressure homogenization.

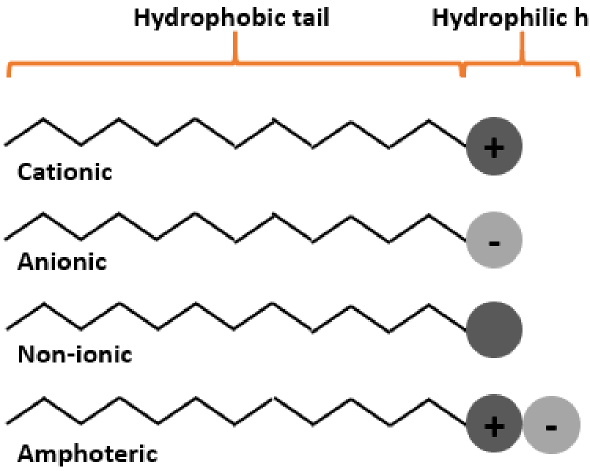
The ultrasound process is the most effective physical method to reduce the agglomeration of nanoparticles. This occurs through the transformation of the energies involved. In this way, sound irradiation causes ultrasonic waves (low and high pressure) in the nanolubricant. In the low-pressure state, cavitation occurs, that is, the formation of thousands of bubbles (unstable cavities), while in the high-pressure state there is the implosive collapse of the bubbles, which results in an enormous dissipation of energy capable of breaking up agglomerates (ILYAS; PENDYALA; NARAHARI, 2017a; LEE; RHEE, 2014).

Hou *et al.*, (2020) had as the main objective in their study to improve the stability of the dispersion of Al_2O_3 nanoparticles in polyalphaolefin oil (PAO6). The results showed that there is an ideal combination between ultrasound power and duration during nanofluid synthesis, which affects dispersion stability. The influence of ultrasound amplitude and duration on all nanofluid samples was characterized by UV spectra. The researchers concluded that nanofluids with concentrations of 0.005 and 0.01 wt% prepared at an ultrasound amplitude of 70% for 5 h showed low sedimentation for more than 160 days, whereas nanofluid 0.02 wt% dispersed with an ultrasound amplitude of 70% for 4 h showed low sedimentation up to 134 days.

2.3.2 Use of surfactants

The use of surfactants to disperse nanoparticles is a very common method, they can be classified as cationic, anionic, non-ionic, and amphoteric (AZMAN; SAMION, 2019; ILYAS; PENDYALA; MARNENI, 2014) as illustrated in Figure 3. The surfactant alters the wetting or adhesion behavior and consequently reduces the tendency for nanoparticles to agglomerate. (NASIRI *et al.*, 2011).

Figure 3 – Classification of surfactants.



Source: Author (2022).

Choi *et al.*, (2008) prepared and evaluated dispersions of Al_2O_3 nanoparticles and AlN powder in transformer oil using oleic acid as surfactant. The researchers concluded in their study that excess oleic acid in suspensions can have detrimental effects on thermal and viscous properties.

The percentage of surfactant used in a nanolubricant is a variable that must be controlled, as its excess can form micelles (which leads to reunion among nanoparticles) whose value exceeds the critical micellar concentration (CMC) (YANG *et al.*, 2011).

The use of surfactants to stabilize suspensions is not desired due to foaming and degradation when subjected to high temperatures, in addition, when in excessive amounts, surfactants can affect the thermophysical properties of nanofluids, increasing viscosity and reducing thermal conductivity. Therefore, the use of surfactants in solutions should be done with caution (ALI; TEIXEIRA; ADDALI, 2018; JENDRZEJ; GÖKCE; BARCIKOWSKI, 2017). Another problem associated with the use of surfactants is the presence of certain chemical substances in these products, which in turn can have a negative effect on the environment, due to their toxicity (BLASCO; HAMPEL; MORENO-GARRIDO, 2003).

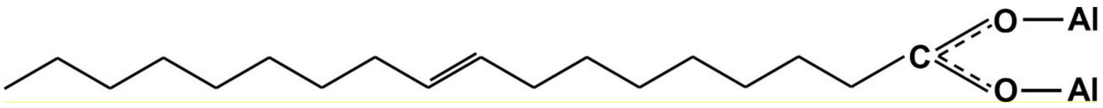
2.3.3 Surface modification of nanoparticles

One of the methods used to achieve the long-term stability of nanofluids is by modifying the surface of nanoparticles through functionalization. This consists of introducing functionalized nanoparticles into the base fluid to obtain a self-stabilized nanofluid. Generally, suitable functional organic groups are selected as they tend to stick to the surface of atoms, allowing the nanoparticles to self-assemble, thus preventing agglomeration (NEOUZE; SCHUBERT, 2008).

In other words, it can be stated that some of the strategies to obtain stable dispersions are through the covalent chemical functionalization of nanoparticles, which occurs through the insertion of functional groups aiming at greater interaction with polar or non-polar media.

Ilyas *et al.*, (2017b) confirmed the functionalization of alumina nanoparticles with oleic acid using Fourier transform infrared (FTIR) analysis. The authors also presented the schematic interaction between the single-bonded COO- group of oleic acid and the aluminum atom, as illustrated in Figure 4.

Figure 4 – Schematic interaction between the oleic acid and the aluminum atom.



Source: Ilyas *et al.*, (2017b).

To guarantee the dispersion and stability of the nanolubricants, Ilyas *et al.*, (2017c) performed the procedure of functionalization of alumina nanoparticles with oleic acid and then added them to the thermal oil. Through the characterization analyses, the researchers concluded that there was a modification on the surface of the nanoparticles with oleic acid and the nanolubricants showed high stability.

2.4 DISPERSION ASSESSMENT METHODS

2.4.1 Visual inspection

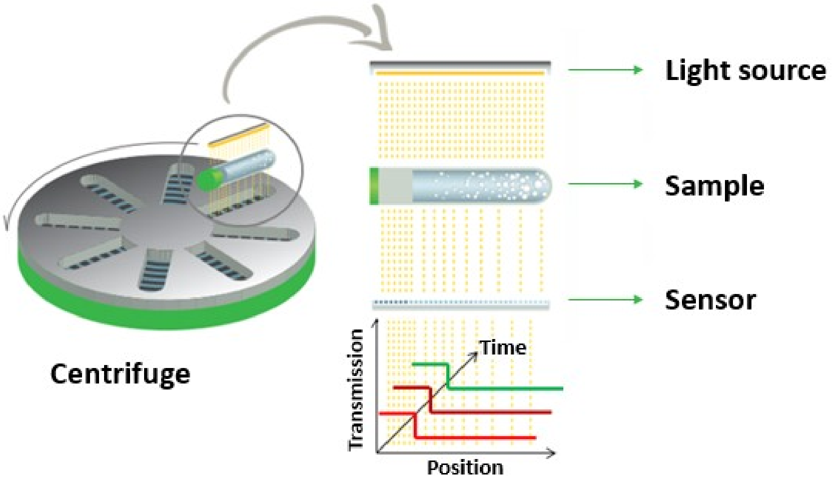
A simple method to assess dispersion stability and widely used in studies on nanofluids is a visual inspection. It is the photographic monitoring of the samples arranged in a transparent container, where it is possible to observe the sedimentation of the nanoparticles over time, categorizing a qualitative assay. In this case, sedimentation is the process of nanoparticles settling down or being deposited as sediment at the bottom of the base lubricant. This process is related to the balance between buoyancy and frictional forces (ALI; TEIXEIRA; ADDALI, 2018).

Yusof *et al.*, (2015) prepared suspensions containing 0.02 vol% alumina with an average diameter of 13 nm in Polyol ester oil (POE). The researchers observed the sedimentation process of the nanoparticles using the visual inspection method for 24 h after preparing the nanolubricants.

2.4.2 Accelerated stability analysis

Space-and-Time-resolved Extinction Profiles (STEP) is a technique used to analyze the accelerated stability of suspensions, where an optical system (transmitter and receiver - near-infrared, NIR) coupled to a centrifuge can record transmission spectra along the entire container used to contain the suspension to be analyzed. The centrifuge performs tests to accelerate sedimentation or flocculation phenomena, to predict the behavior of the suspension as a function of time. In one test, the software measures transmission profiles, particle size, and sedimentation velocity (DAVANZO, 2016; GOTO, 2016). The system described above is illustrated in Figure 5.

Figure 5 – Illustrative system of the analysis performed using the STEP technique.



Source: Adapted from L.U.M. (2019).

Thus, to assimilate the acceleration of nanoparticles sedimentation in the nanolubricant in real-time (without acceleration) it is possible to determine the $Shelf\ life$ (in s) referring to the test conditions used through Equation (4) (L.U.M., 2019):

$$\boldsymbol{Shelf\ life} = (\boldsymbol{t_{required}} \times \boldsymbol{RCF}) \tag{4}$$

where $t_{required}$ is the duration of the experiment in s, and RCF is the relative centrifugal force (value established according to Stokes' Law).

Other authors used the STEP technique to characterize the stability and hydrodynamic size of their nanosuspensions. Silveira (2021) evaluated the stability of suspensions containing carbon nanoparticles. Kessler (2017) also verified the stability of aqueous nanosilver suspensions under centrifugal forces using the same technique.

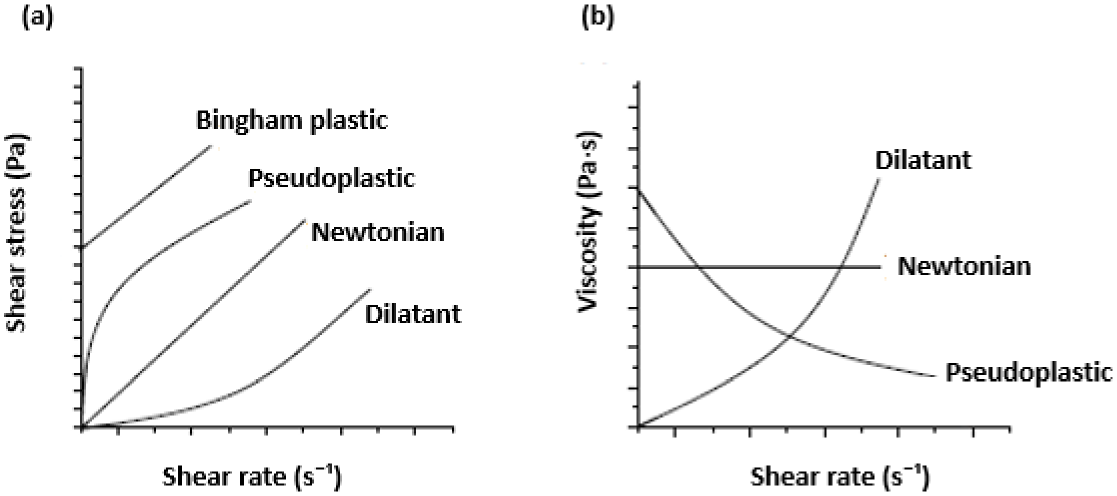
2.5 RHEOLOGICAL PROPERTIES

Rheological behavior has been suggested as a method to assess the dispersion of carbon nanomaterials in different fluids (LITCHFIELD *et al.*, 2006). Viscosity (η) is a property that characterizes the resistance of a given fluid to flow and is associated with the ratio between the shear stress (τ) and the shear rate ($\dot{\gamma}$), as described in Equation (5).

$$\boldsymbol{\tau = \eta\dot{\gamma}} \tag{5}$$

Thus, when the viscosity is constant at different values of the shear rate, the fluid is known as Newtonian.When the viscosity varies as a function of the shear rate, the fluid is known as non-Newtonian (pseudoplastic, Bingham plastic, or dilatant) (DEVENDIRAN; AMIRTHAM, 2016; HEMMAT ESFE; ESFANDEH, 2018; SHARMA; TIWARI; DIXIT, 2016; SURESH *et al.*, 2011) as shown in Figure 6:

Figure 6 – Profiles: (a) shear stress and (b) viscosity as a function of the shear rate.



Source: Adapted from Kessler, (2017).

The Ostwald-de Waele model also known as the Power-Law Model (Equation (6)) is the most generalized model for non-Newtonian fluids. This is described by two parameters consistency coefficient (K) and the flow behavior index (n). The viscosity of fluids that follow the Power-Law is defined by Equation (7). Thus, if the magnitude of $n < 1$, the fluid is known as shear-thinning or pseudoplastic, that is, the apparent viscosity decreases with increasing shear rate. However, when $n > 1$ is shear-thickening or dilating, this means that the apparent viscosity increases with increasing shear rate (SANUKRISHNA *et al.*, 2018).

$$\boldsymbol{\tau = K\,\dot{\gamma}^{n}} \tag{6}$$

$$\boldsymbol{\eta = K\gamma^{\dot{n}-1}} \tag{7}$$

Sanukrishna and Jose Prakash (2018) investigated the thermal and rheological properties of polyalkylene glycol compressor oil with Al_2O_3 nanoparticles. The Ostwald-de Waele rheological model was fitted to predict the behavior of the nanolubricant in relation to temperature and shear rate. Interestingly, pure oil is a Newtonian fluid and was transformed into a non-Newtonian fluid with the addition of alumina nanoparticles. However, the authors did not classify the trends of the experimental curves obtained in the rheological tests.

Viscosity is a function of the concentration of particles in the base oil, shape, size, and interactions of the particles, suspension structure, surface properties, adsorbed species, and the hydrophilic/hydrophobic nature of the particles. Nanoparticles in a suspension are subject to particle-particle forces, particle-fluid interactions, viscous forces under flow, and also Brownian forces. For suspensions of colloidal particles, non-hydrodynamic forces, such as Brownian, electrostatic, and London-Van der Waals forces, become significantly important (CLAYPOLE *et al.*, 2020).

Sharif *et al.*, (2016) investigated the behavior of the viscosity of nanolubricants Al_2O_3/polyalkylene glycol (PAG46) from 0.05 to 1.0 vol% at temperatures from 303.15 to 353.15 K. The results showed that by increasing the volumetric concentration of nanoparticles in the lubricant, the viscosity of nanolubricants also increases. However, the viscosity will decrease with increasing temperature, showing an inversely proportional behavior.

Zawawi *et al.*, (2017) evaluated the rheological behavior of Al_2O_3-SiO_2/PAG46 composite nanolubricants from 0.02 to 0.1 vol% in a temperature range of 303 to 353 K. The researchers concluded that the nanolubricant compound behaves like a Newtonian fluid at all volume concentrations and temperatures analyzed in the study.

Kotia *et al.*, (2018) reported a 10.5% increase in relative viscosity with 0.5 vol% of Al_2O_3 nanoparticles in gear oil (SAE EP90). The viscosity-increasing effect of the addition of nanoparticles is attributed to the agglomeration of nanoparticles in lubricants, which prevents the easy movement of adjacent oil layers.

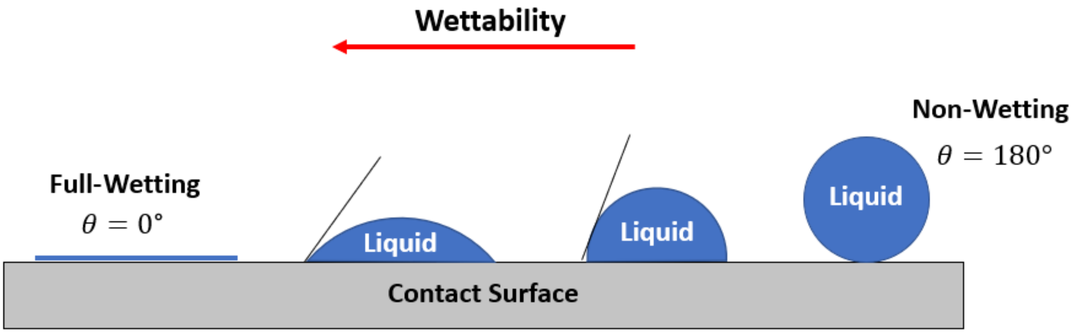
There is a variety of equipment to measure the rheological behavior of nanofluids. However, the most common equipment used for measurements is the rotational rheometer, the piston type rheometer, and the capillary tube viscometer (MEYER *et al.*, 2016).

2.6 WETTABILITY

The tendency for fluid to adhere to spread to a solid surface in the presence of other immiscible fluids is known as wettability (ALI *et al.*, 2018a). This property is crucial not only in nature but also in many applications, such as the development of non-contaminating surfaces, cosmetics, self-cleaning surfaces, moisture collectors, inkjet printers, and lubricants, among many others (KUBIAK *et al.*, 2011).

The degree of wettability is expressed by the magnitude of the contact angle (θ) between the liquid phase and the contact surface. Smaller contact angle values are related to a higher degree of wettability, as there is greater liquid spreading on the contact surface. However, higher values of contact angle have a lower degree of wettability, as illustrated in Figure 7 (BRACCO; HOLST, 2013).

Figure 7 – Relation between surface contact angle and fluids.



Source: Author (2022).

Wettability is associated with the application of fluid lubricants and their spread on slippery surfaces. Thus, it is interesting to know the concept of oleophilic and oleophobic. Surfaces are classified as oleophobic when the contact angle is greater than 90° or as oleophilic when the contact angle is less than 90°. The existence of extreme cases still stands out: when the contact angle is greater than 150°, the surface is called super oleophobic and when this angle is zero, the surface is called super oleophilic. A lubricating oil when deposited on the solid surface tends to spread out due to gravity until, as a liquid cohesion framework (interfacial tension), gravitational frames and as capillary molds (surface tension) are balanced and reach a certain state of equilibrium (WOJCIECHOWSKI; KUBIAK; MATHIA, 2016).

3 MATERIALS AND METHODS

3.1 MATERIALS

Alumina nanoparticles (99.99%; gamma phase, Inframat) used to develop this study have an average particle size of 20-50 nm and were acquired from the company.

The synthetic oil based on alkylbenzene (Zerol AB, Shrieve) is a low viscosity oil with anti-foaming properties, which is used as a lubricant for stationary refrigeration systems. Table 2 provides information regarding the physical and chemical properties of the lubricating oil and alumina nanoparticles.

Other laboratory reactants were used for alumina functionalization, such as oleic acid, o-xylene, and toluene (Sigma-Aldrich).

Table 2 – Data from the synthetic base oil and alumina nanoparticles according to the respective suppliers.

Physical and chemical properties	**Oil**	**Al_2O_3**
Color	Colorless	White powder
BET surface area (SSA)	-	>150 m^2/g
Density, 293 K (20 °C)	0.862 g/cm^3	3.600 g/cm^3
Dielectric Strength	37 kV/cm	-
Dynamic Viscosity, 313 K (40 °C)	1.79 mPa·s	-
Dynamic Viscosity, 373 K (100 °C)	1.07 mPa·s	-
Flash Point	383 K (110 ºC)	-
Pour Point	218 K (-55 ºC)	-
Phosphorus Content	1632 ppm	-
Water by Karl Fischer	46 ppm	-

Source: Adapted from Shrieve and Inframat (2021).

3.2 SURFACE MODIFICATION OF ALUMINA NANOPARTICLES

In this study, the surface modification of alumina nanoparticles is performed through the functionalization of the carboxylic group on the surface of the nanoparticles using oleic acid. This procedure was adapted from two investigations on oil-based nanofluids, respectively with nanoparticles of zinc oxide and alumina (ILYAS *et al.*, 2019; ILYAS; PENDYALA; NARAHARI, 2017b).

Initially, 3 mL of oleic acid and 100 mL of o-xylene are added, and both are stirred with a magnetic stirrer for 30 min at a constant temperature of approximately 50 °C. Then 2 g of alumina nanoparticles are added to the solution, under conditions of constant agitation reacting for 90 min at 50 ºC. Subsequently, the mixture is sonicated for 30 min (with a pulse and power of 30 and 70%, respectively) in a high-power ultrasound (Misonix, S-4000-010) to coat the surface of the nanoparticles as much as possible. During this dispersion step, an ice bath was used to dissipate heat. The nanoparticles are collected through a centrifuge (Kasvi, K14-4000) at 4000 rpm for 2 h. To remove unreacted components and free ions, the collected functionalized nanoparticles are mixed in toluene, dispersed, and centrifuged twice. After this washing step, the functionalized nanoparticles are dried in a drying oven at 50 ºC for 24 h. Thus, the characterizations were carried out with the nanopowder resulting from the process, to guarantee the presence of functional groups in the nanoparticles.

3.3 PREPARATION OF NANOLUBRICANTS

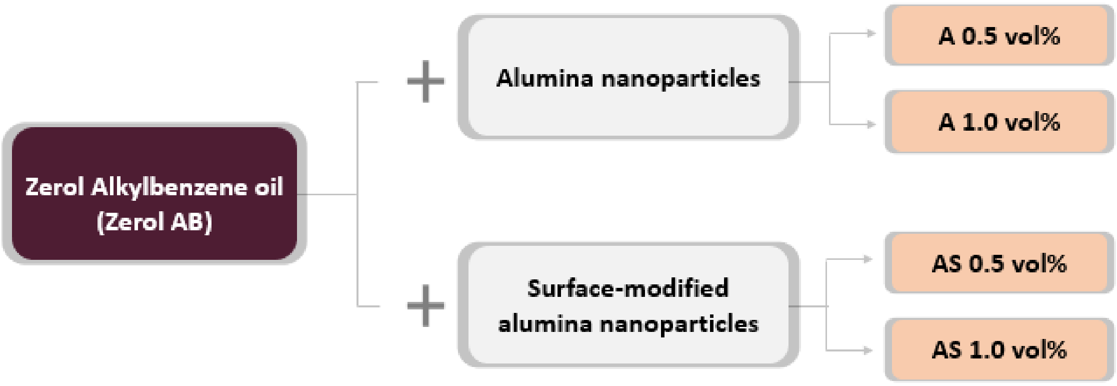
The nanolubricants were prepared using a two-step method, which consists of dispersing nanoparticles in the form of ultra-fine dry powder and then dispersing them in the fluid (BABITA; SHARMA; GUPTA, 2016). Pure alumina nanoparticles and surface-modified alumina nanoparticles with oleic acid were dispersed in different volume fractions of 0.5 and 1 vol% in lubricating oil. Thus, the required masses of nanoparticles corresponding to the volume fractions were determined by Equation (8) and weighed using a high-precision electronic balance.

$$\boldsymbol{vol\%} = \left(\frac{\left(\frac{m}{\rho}\right)_{Al_2O_3}}{\left(\frac{m}{\rho}\right)_{Al_2O_3} + \left(\frac{m}{\rho'}\right)_{oil}} \right) \times \mathbf{100} \tag{8}$$

Subsequently, the nanoparticles were dispersed in the lubricating oil for 5 min (5 sonications of 1 min and rest of 1 min between each sonication) in high power ultrasound (Misonix, S-4000-010), with a frequency of 15 kHz and power of 90 W. To dissipate the heat from the nanolubricants generated during the ultrasonic homogenization, an ice bath was used. Figure 8 presents the abbreviated names used in this study to refer to different combinations of nanolubricants.

After the sonication process, 30 mL lubricating oil samples were subjected to the dehumidification process, which was carried out in a 250 mL Erlenmeyer coupled to a vacuum pump (Edwards, E2M-15), together with a thermal plate with a magnetic stirrer (Dist, DI-03) at 40 ºC (BORDIGNON *et al.*, 2018). This step aims to strongly reduce the concentration of water present in these oil samples since the presence of humidity directly influences the rheological results, increasing the viscosity of the lubricants.

Figure 8 – Identification of nanolubricants and volume fractions used in this study.



Source: Author (2022).

3.4 NANOPARTICLES AND LUBRICANTS CHARACTERIZATION

3.4.1 Scanning electron microscopy

Alumina nanopowders, before and after the surface modification, were covered with gold. Morphological characteristics and particle size were captured on a scanning electron microscope (SEM, Tescan, Vega3 LMU) at magnifications of 150,000×. Then, the particle size distribution curves for alumina were performed in ImageJ software considering the evaluation of the average diameter of ~100 nanoparticles.

3.4.2 Infrared spectrometry

Fourier-Transform Infrared Spectroscopy (FTIR, Shimadzu, IRPrestige-21) was carried out on alumina nanoparticles with spectrum analysis ranging from 400 to 4000 cm^{-1}. The samples were prepared by mixing 0.5 wt% with KBr (99.99%) and then compacted in a digital hydraulic press (Pike, CrushIR) using a load of 24.5 kN for 10 s. Then, the pellet resulting from this process was analyzed in the FTIR equipment in transmittance mode.

3.4.3 Visual inspection

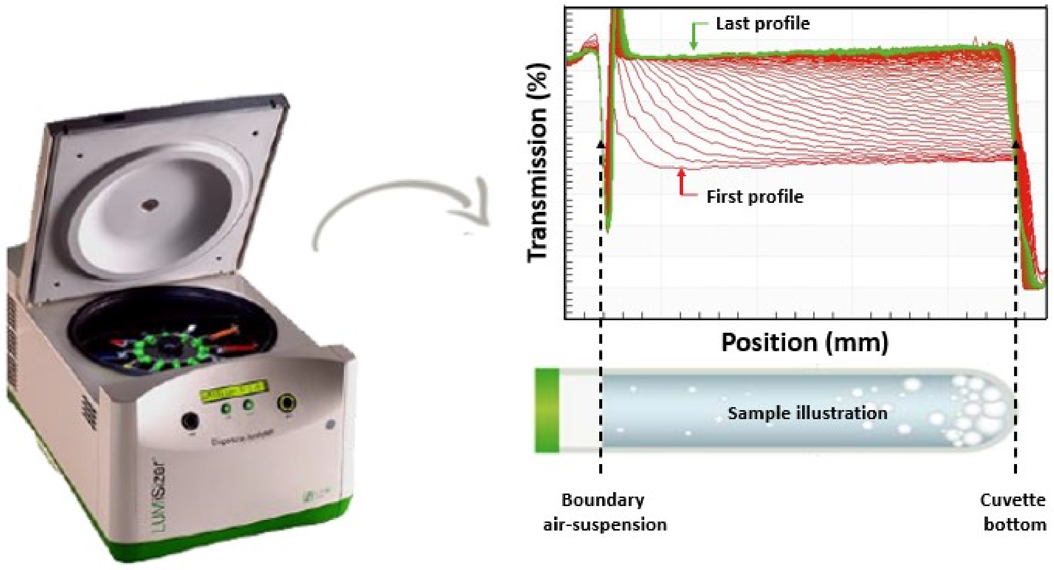
The stability of the nanolubricants was visually evaluated using a camera on a cell phone (iPhone 8), positioned 30 cm from the samples in an environment with humidity and temperature controlled on a stable bench, being subjected only to the action of gravity.

3.4.4 Accelerated stability analysis and particle size distribution

A multi-sample analytical centrifuge was used to simultaneously estimate the hydrodynamic particle size distribution and the stability of dispersions along the time. The equipment (LUMiSizer, 6110-87, LUM) consists of accelerating the dispersion separation process. The hydrodynamic particle size distribution and accelerated stability of the nanolubricants were performed with an analytical centrifuge. Instability indices were calculated with dedicated software (SEPView). The nanofluids were added to polyacrylate cuvettes and then placed horizontally in the equipment and exposed to centrifugal force (constant rotation speed of 3000 rpm). Thus, 199 analysis profiles were used with a 5 s interval between each profile at a temperature of 25 °C, simulating a shelf life of 15 days.

A representation of the accelerated stability analysis is illustrated in Figure 9. LUMiSizer measures the transmitted light intensity as a function of time and position along the entire length of the cuvette, which contains the sample. The shape and progression of the transmission profiles provide information about the kinetics of the separation process and allow for the characterization of the particles, as well as the evaluation of particle-particle interactions (LERCHE; SOBISCH, 2014). The red lines identify the first and other profiles throughout the analysis, while the green lines identify the last profiles.

Figure 9 – Equipment and measurement principle of the accelerated stability analysis performed by LUMiSizer.



Source: Adapted from L.U.M. (2019).

3.4.5 Rheological behavior

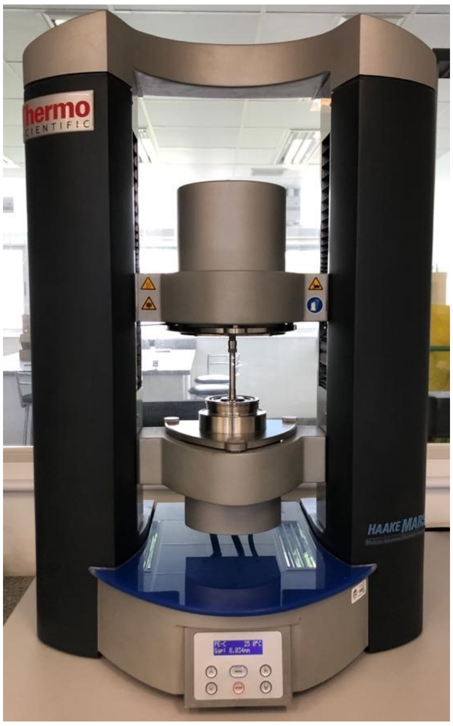
The rheological behavior of the lubricants was analyzed in a rotational rheometer (Haake MARS III, Thermo Fisher Scientific), as shown in Figure 10.

To perform the analysis, the configuration of parallel stainless-steel plates with a diameter of 35 mm and spacing of 35 µm between them was used. The sample volume used for each test was 100 µL, which is experimentally evaluated in preliminary tests.

The experiment consisted of evaluating the viscosity of pure oil and nanolubricants containing alumina (A and AS) at temperatures of 25, 50, and 75 °C for 600 s, whose adopted shear rate was 700 to 70,000 s^{-1}. After reaching the maximum shear, a descending rate was applied to the system up to 700 s^{-1} to evaluate the possible effects of time and shear. This configuration was chosen due to the real working conditions in hermetic type compressors used in refrigeration systems.

Finally, the results obtained from the rheological behavior took into account the average curve of 3 validated tests for each lubricant.

Figure 10 – Rotational rheometer used in rheological behavior tests.



Source: Author (2022).

3.4.6 Wettability of lubricants

The contact angle of base oil and nanolubricants A and AS were measured in a goniometer (Krüss DSA25) as illustrated in Figure 11.

To perform this analysis, approximately 3 µL of each sample were used and deposited on a stainless-steel plate (Sq = 1.00 ± 0.05 µm / Sa = 0.80 ± 0.03 µm), the same material used in the tests rheological. The contact angle was measured from 30 s after drop deposition at a temperature of 25 °C, using DS4 software.

Figure 11 – Goniometer used for contact angle measurements.

Source: Author (2022).

3.5 STATISTICAL ANALYSIS

A factorial design with 2 factors was proposed, evaluated at 3 levels, resulting in 9 runs and 2 more replications, totaling 27 experiments for each type of nanolubricant (A and AS). The objective was to determine the influence of factors and their interactions on the viscosity of the samples, having reached the maximum shear rate equal to 70,000 s^{-1}. Table 3 presents the levels and factors analyzed.

Table 3 – Factors and levels of a 3^2 factorial experimental design.

Volume fraction (vol%)	**Temperature (ºC)**
0	25
0.5	50
1	75

Source: Author (2022).

Rheological data were interpreted in *Statistica 13.5*, software, with a 95% confidence level for Analysis of Variance (ANOVA) and through surface graphs with the interaction between factors.

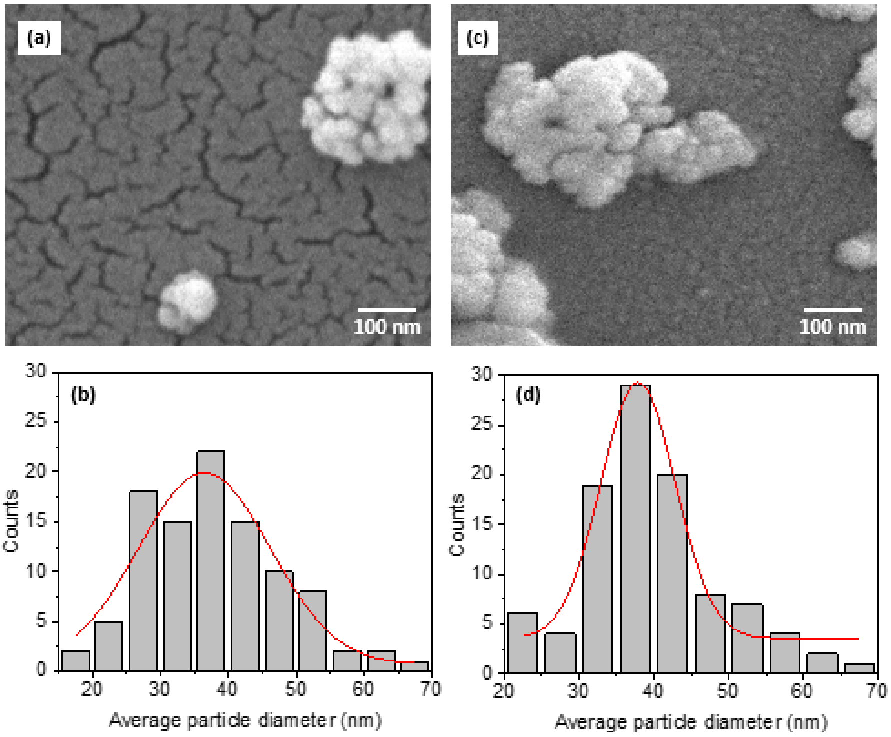
4 RESULTS AND DISCUSSION

4.1 MICROSTRUCTURE ANALYSIS OF NANOPARTICLES

Figure 12 illustrates SEM images and average particle diameter distribution curves for alumina nanopowders before (a and b) and after the surface modification process (c and d).

According to the results, alumina nanopowders present heterogeneous characteristics in their sizes and shapes. The average particle diameter was approximately 38 nm and corresponded to the specification range (20-50 nm) provided by the manufacturer. However, it can also be seen that the nanoparticles are agglomerated.

Figure 12 – SEM image and average particle diameter distribution: pure alumina nanopowders (a and b) and alumina nanopowders with surface modification using oleic acid (c and d).



Source: Author (2022).

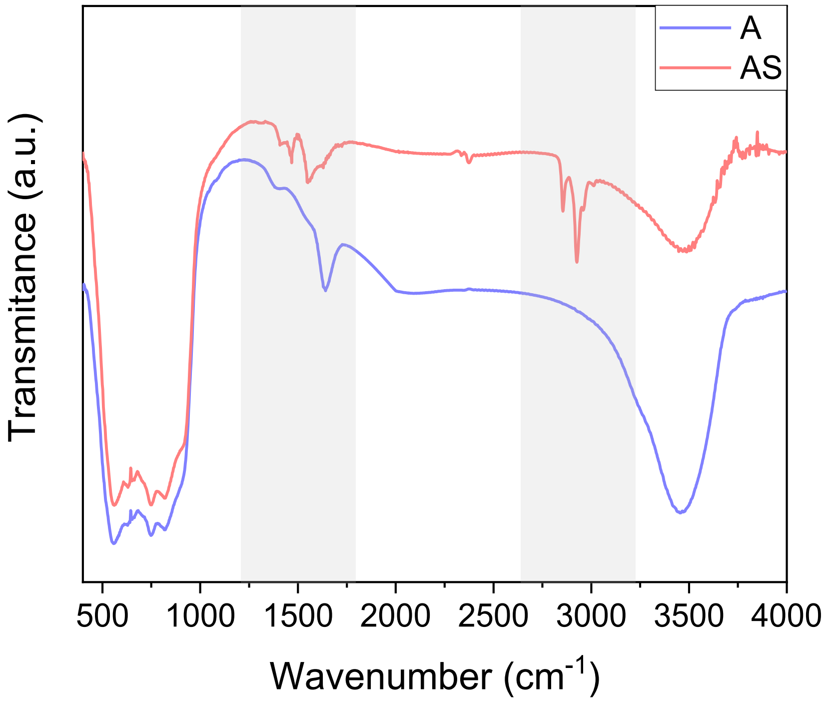
4.2 STRUCTURAL ANALYSIS OF NANOPARTICLES

FTIR analysis was performed to confirm the adsorption of the oleic acid group on the surface of alumina nanoparticles. Figure 13 shows the comparison of infrared spectra of pure alumina (A) and surface-modified alumina (AS) nanoparticles using oleic acid.

The presence of the carboxylic group on the alumina surface is indicated by two bands detected at 2922.2 cm^{-1} and 2852.7 cm^{-1}, which are accredited for the asymmetrical and symmetrical CH_2 stretch, respectively. The CH_2 stretch is considered one of the main pieces of evidence for the presentation of acid groups on the nanopowders' surface. Similar results are found in the literature using FTIR analysis for nanoparticles functionalized with oleic acid. The O–H band of the carboxylic acid can be seen at 1458.2 cm^{-1}. In general, the stretch band peaks of the C=O functional group of oleic acid are detected in the range of 1700 - 1730 cm^{-1}, which are absent in AS. However, it is observed that a new band is displayed in the AS spectrum at 1585.3 cm^{-1} and 1643.7 cm^{-1}, which are attributed to the asymmetric and symmetric C=O stretch, in which it can be explained that the carboxylic acid groups functions are attached symmetrically and at an angle to the surface of the alumina nanoparticles (ILYAS *et al.*, 2017).

Thus, the FTIR analysis confirmed that the carboxylic acid was adsorbed on the surface of alumina nanoparticles as carboxylates. Finally, it is possible to visualize the O–H elongation bands at 3435.5 and 3442.9 cm^{-1} for respective AS and A samples. This is attributed to the adsorbed humidity as the FTIR analysis is performed in air. Thus, the consequent size and surface area of the nanoparticles are a result of moisture (DAMAYANTI, 2010).

Figure 13 – FTIR spectra of pure alumina nanoparticles (A) and alumina nanoparticles with surface modification (AS) using oleic acid.



Source: Author (2022).

4.3 STABILITY ANALYSIS OF NANODISPERSIONS

Figure 14 shows the photographs of dispersions as a function of time. To qualitatively evaluate the nanolubricants, visual analysis was performed after preparation: 0 h (a) 1 h (b), 48 h (c), and 192 h (d) in an environment with controlled temperature and humidity.

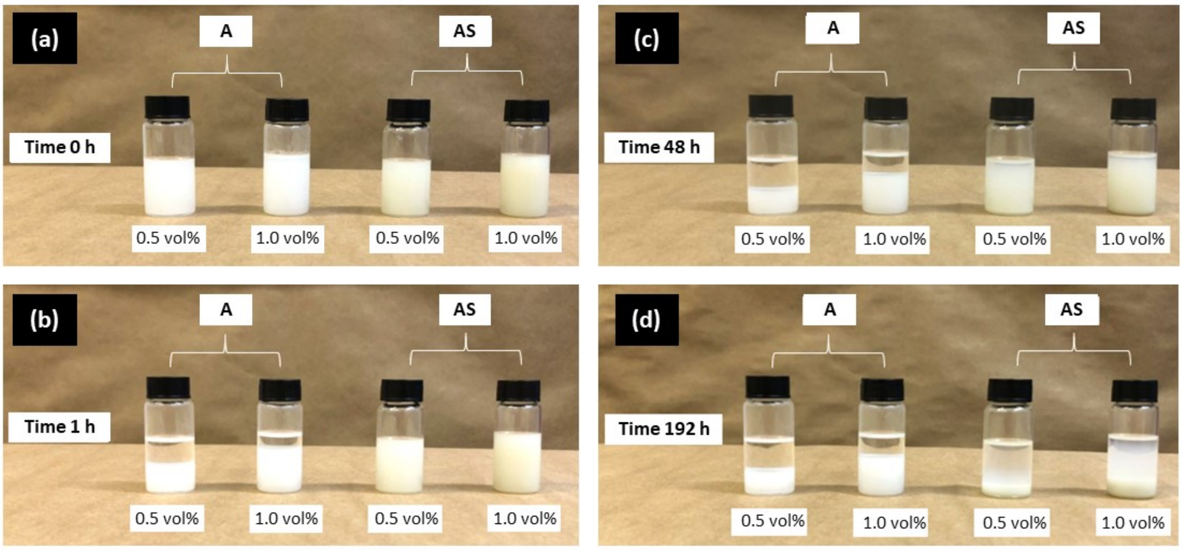
It can be seen in Figure 14 (a) that at first all nanolubricants are dispersed, indicating that visually there is no evidence of sedimentation at that moment. After 1 h of dispersion of the nanolubricants (Figure 14 (b)), the pure alumina nanoparticles settle, while the AS nanolubricants remain stable. After 48 h (Figure 14 (c)), a phase separation begins in AS nanolubricants, which shows the sedimentation process. This is more visible 192 h after the dispersion of nanoparticles in the base oil as shown in Figure 14 (d). This fact can be explained by the chemical affinities of oleic acid with the nanolubricant system.

The stability of colloidal suspensions is related to several factors, including nanoparticle properties (volume fractions, particle shape, and size) and lubricant properties (density, viscosity, polarity, and pH) (AZMAN; SAMION, 2019).

The ideal stability time for nanofluids can be defined as the maximum time that the suspension remains completely dispersed. Thus, colloid chemistry indicates that when a particle size reaches a critical size, the particle remains stable and no sedimentation occurs. However, high surface energies and subsequent nanoparticle interactions cause agglomeration, clustering, and faster settlement in fluids (SEZER; ATIEH; KOC, 2018).

The presence of carboxylates on the surface of functionalized nanoparticles changed their polarity, so the stability of AS nanolubricants can be explained through the non-polar behavior of both alumina and lubricating oil.

Figure 14 – Visual inspection of nanolubricants containing pure alumina (A) and surface-modified alumina (AS) with oleic acid soon after preparation 0 h (a), 1 h (b), 48 h (c), and 192 h (d).



Source: Author (2022).

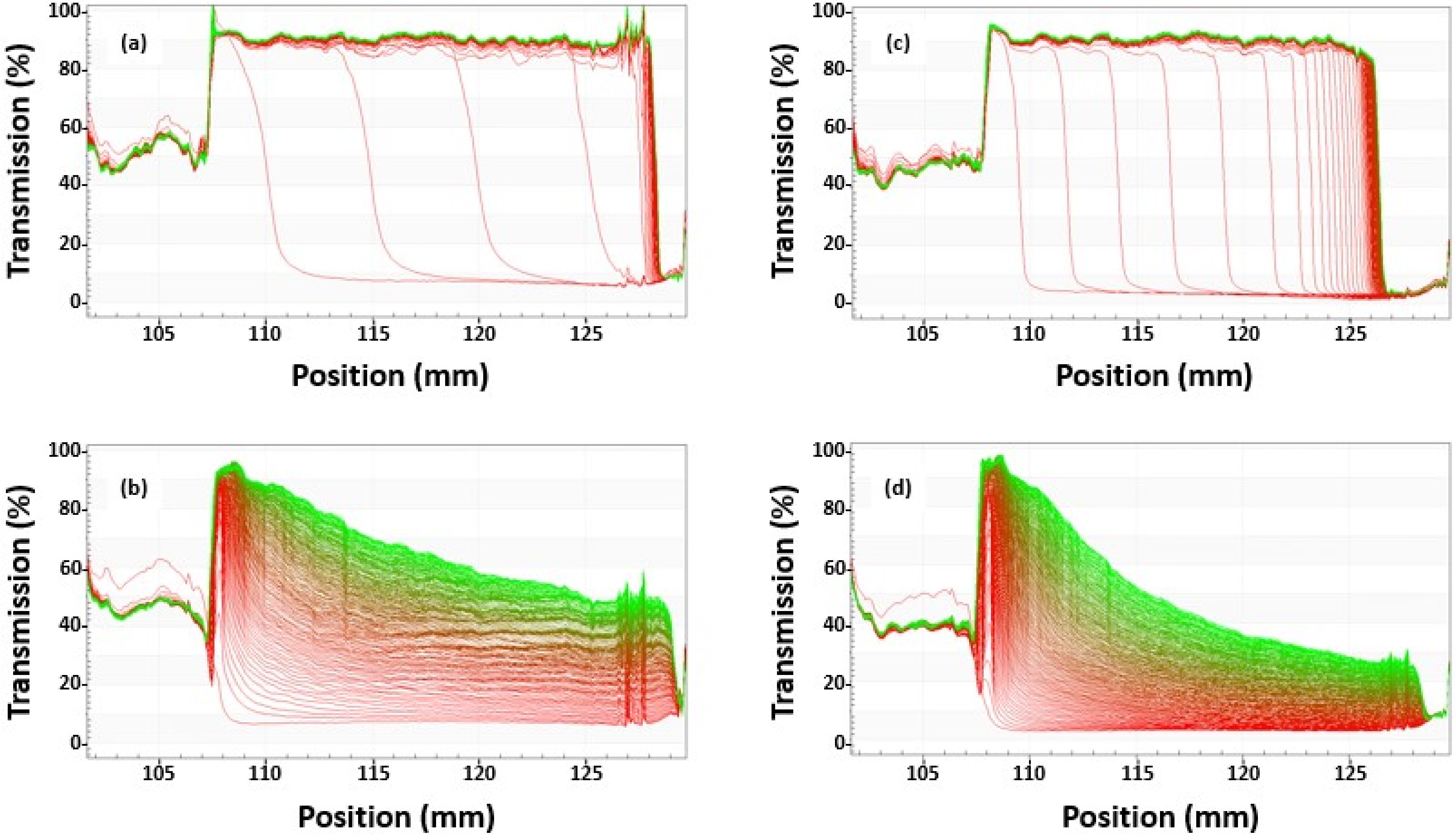
The visual stability analysis proved that the functionalization of the alumina surface was effective. Thus, the accelerated stability test was carried out, simulating the shelf life of 15 days.

The study of the stability of nanolubricants was carried out in the LUMiSizer equipment, where it is possible to obtain a primary measurement from the optical system coupled to it, which are the light transmission profiles as a function of time and position throughout its entire length of the cuvette.

There were 199 profiles, with an interval of 5 s between each one, which showed an increase in the percentage of transmittance of the nanolubricants over approximately 1230 s of analysis (Figure 15). The closer to 0% transmittance, the more stable the suspension. As the test time progresses and the transmittance of the sample approaches 100%, it means that sedimentation of the suspensions has occurred. Thus, it is possible to observe that at the 125 mm position, close to the bottom of the cuvette, the nanolubricants containing pure alumina (Figure 15 (a) e (c)) presented transmittance values above 85%, indicating the sedimentation of the nanoparticles in the suspension. For AS 0.5 vol% (Figure 15 (b)), the transmittance values were 50%, while AS 1 vol% (Figure 15 (d)) presented a percentage of approximately 30% of transmittance, which in turn was significantly lower than the other nanolubricants.

This statement can be corroborated by Figure 16, where the stability index of the sample over time is presented. The instability index, defined by the clarification of the fluid in a given separation time, is divided by the maximum clarification, which represents the separation of phases of the samples over time (SILVEIRA, 2021). Thus, it is possible to observe in Figure 16 that in the first 100 s of analysis, the instability index of nanolubricants A, 0.5 and 1 vol%, present an instability index of 100 and 82% respectively, i.e., the sedimentation of the nanoparticles has already occurred. On the other hand, for AS 0.5 and 1 vol%, the instability indexes are relatively lower, 20 and 8%, respectively.

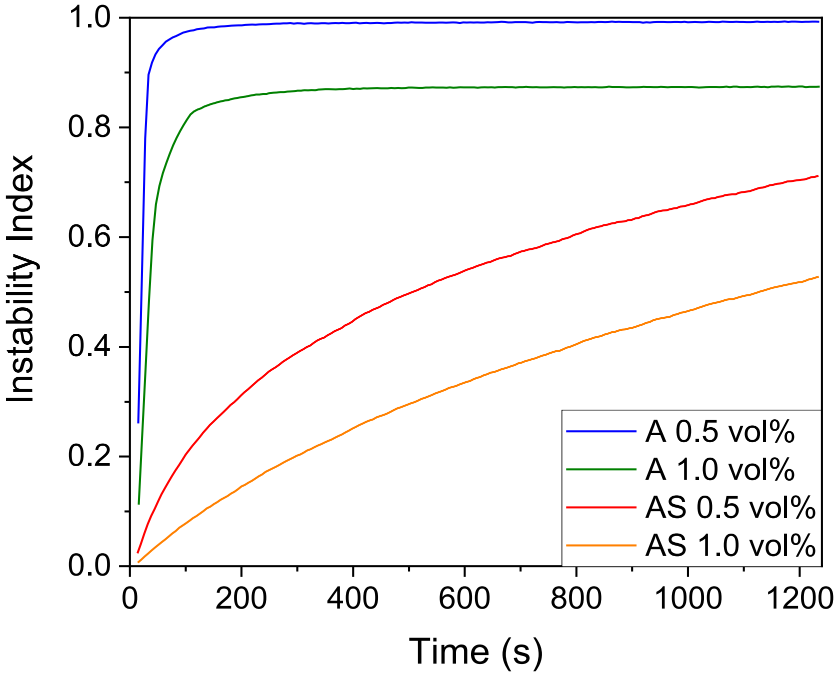
Figure 15 – Profiles of nanolubricant samples: A 0.5 vol% (a), AS 0.5 vol% (b), A 1 vol% (c) and AS 1 vol% (d).



Source: Author (2022).

The 15-day simulated shelf life performed in the accelerated stability analysis showed that the nanolubricants containing pure alumina settle in the first minutes after the dispersion of the nanoparticles in the lubricant oil. However, the AS 0.5 vol% nanolubricants presented an instability index of 70%, and the AS 1 vol% nanolubricants presented an instability index of 50% at the end of the experiment. Therefore, based on the results, it is concluded that the stability of the nanolubricants when compared to each other is proportional to the increase in the volume fraction of the nanoparticles in the oil.

Figure 16 – Instability index as a function of time of nanolubricants containing pure alumina (A) and surface-modified alumina (AS) with oleic acid.



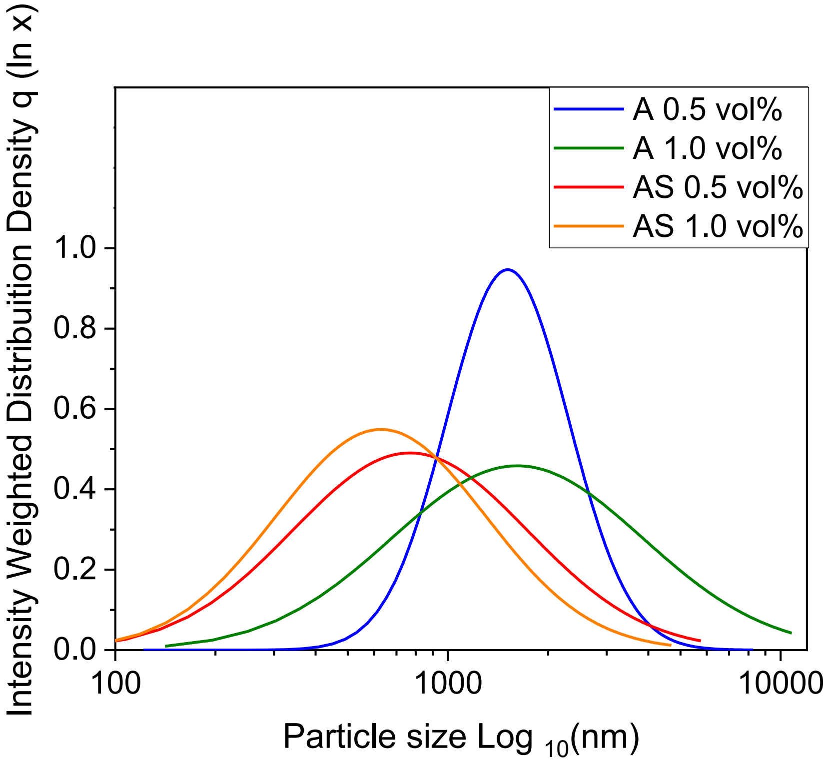
Source: Author (2022).

4.4 NANOPARTICLE SIZE DISTRIBUTION IN BASE OIL

Based on the parameters used in the accelerated stability analysis, the particle size distribution was performed simultaneously with the same equipment, referring to the hydrodynamic diameter of the nanolubricants in this study.

Figure 17 and Table 4 show the results obtained from the distribution of the alumina particle size in the base oil. It is observed that the presence of oleic acid in nanolubricants directly influences the average hydrodynamic size of the particles (≤ 50%), since AS 0.5 and 1 vol% presented values of 759.2 and 607.7 nm, respectively, while for samples A 0.5 and 1 vol% values were higher at 1545 and 1834 nm. However, it is concluded that in both cases there were agglomerations of alumina nanoparticles in the lubricating oil.

Figure 17 – Particle size distribution of the stabilized alumina-containing nanolubricant.



Source: Author (2022).

As shown in Table 4, it is noted that there is a trend regarding the concentration of samples. In general, it is observed that nanolubricants whose concentrations of 0.5 vol% in the size range ≤ 10% and ≤ 16% presented higher values than nanolubricants of 1 vol%. It is also possible to verify that the presence of oleic acid reduced the size of the hydrodynamic diameter of the AS samples, showing once again the importance of using strategies such as the surface modification method for the stability of nanofluids.

Table 4 – Particle size distribution of the stabilized alumina-containing nanolubricant.

Nanolubricant	**10% ≤ (nm)**	**16% ≤ (nm)**	**50% ≤ (nm)**	**84% ≤ (nm)**	**90% ≤ (nm)**
A 0.5 vol%	935.0	1007	1545	2884	3146
A 1.0 vol%	711.8	739.0	1834	3634	4039
AS 0.5 vol%	300.6	357.7	759.2	1763	2193
AS 1.0 vol%	286.1	333.5	607.7	1363	1754

Source: Author (2022).

4.5 RHEOLOGICAL BEHAVIOR OF NANOLUBRICANTS

Figure 18 illustrates the results obtained through 3 rheological tests, for the dynamic viscosity as a function of the shear rate at the temperatures of 25 (a), 50 (b), and 75 ° C (c) for lubricating oil and nanolubricants A and AS at concentrations of 0.5 and 1 vol%. Note that the scales of the graphics were adjusted to better visualize the behavior of the curves.

According to Figure 18 (a), the addition of alumina nanoparticles to the oil, for both AS and A nanolubricants in the volume fraction of 0.5 vol%, reduced the dynamic viscosity when compared to pure oil at 25 °C. This behavior was not expected because in general, the viscosity of nanofluids is proportional to the volume fraction and size of the nanoparticles, and an inverse trend is observed with increasing temperature. However, the rheological behavior of nanofluids is quite different from each other, so a specific behavior cannot be established for all nanofluids (SANUKRISHNA; JOSE PRAKASH, 2018). Although for a temperature of 25 °C (Figure 18 (a)), nanolubricants A and AS at 1 vol% and the other nanolubricants tested at temperatures 50 and 75 °C (Figure 18 (b) and (c), respectively) showed viscosity values higher than those in pure oil, indicating the most common behavior in systems involving the addition of nanoparticles to fluids.

Regarding nanolubricants containing surface-modified alumina, it is possible to verify that the viscosity is relatively lower than that of nanolubricants containing alumina without functionalization, at temperatures of 25 and 50 °C, this fact can be attributed to the deagglomeration of the nanoparticles in the oily medium, showing the influence of sample stability in rheological tests.

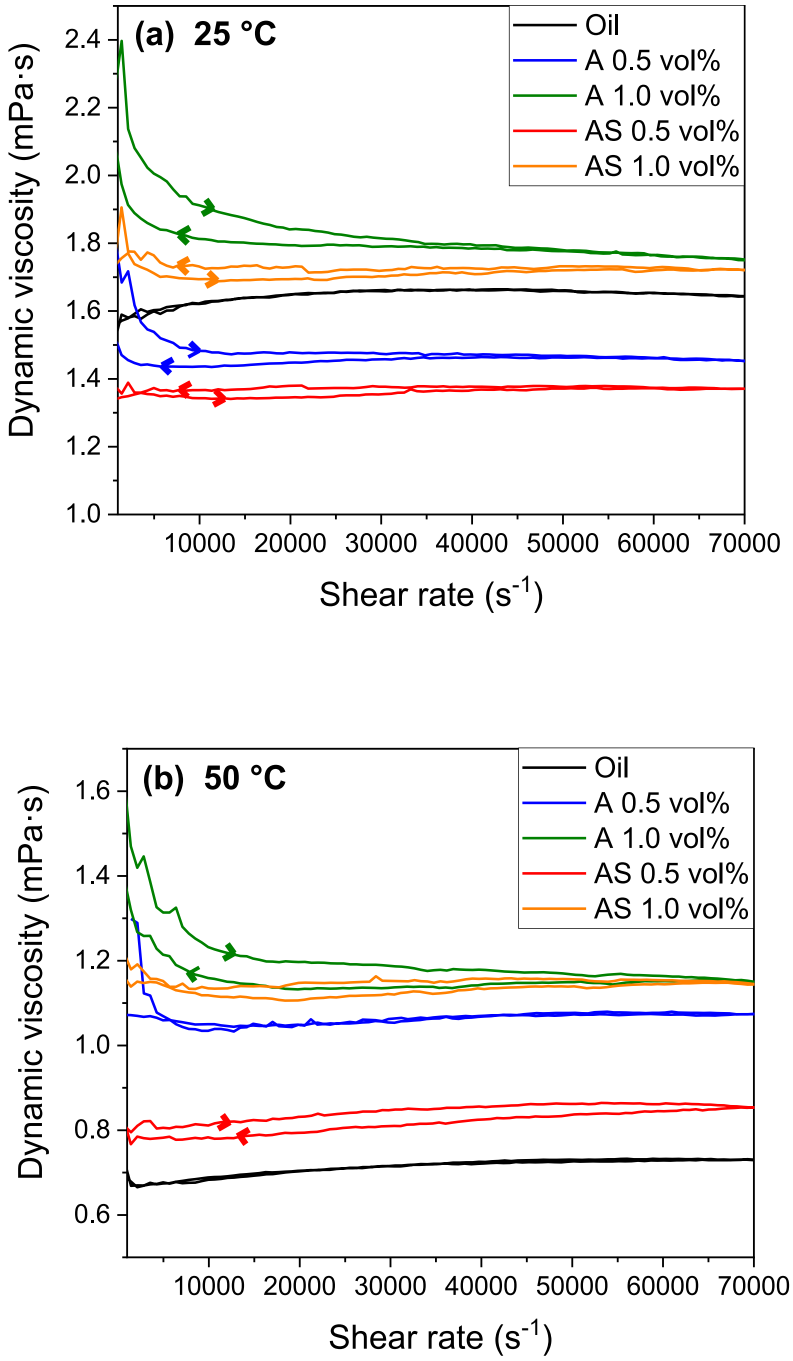
Another point observed is when comparing the oil viscosity measurements with the data from the supplier (1.79 mPa·s (40 °C) and 1.07 mPa·s (100 °C) reported in Table 2), it is observed that the measured viscosity was lower. This might have occurred because the rheological tests were performed after demoisturing. Thus, the presence of water (46 ppm, Table 2) might have increased the viscosity of this specific lubricant.

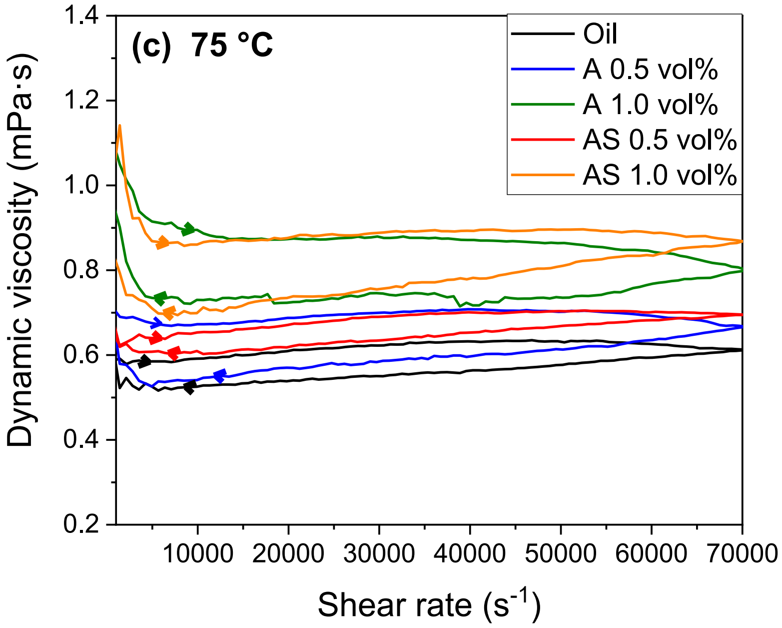
A fluid is considered Newtonian when its viscosity remains constant with the shear rate and when the relationship between shear rate and shear stress is linear (ZAWAWI *et al.*, 2019). As can be seen in the results, the lubricating oil exhibits Newtonian behavior at temperatures of 25 and 50 °C (Figure 18 (a) e (b)), whose viscosity is approximately constant at 1.65 and 0.72 mPa·s respectively.

According to temperatures of 25 and 50 °C, nanolubricants A containing 0.5 and 1 vol% of alumina nanoparticles have a slight tendency to decrease viscosity with increasing shear rate. This behavior is characteristic of pseudoplastic fluids. Sanukrishna and Jose Prakash, (2018), also investigated the rheological behavior of alumina-containing nanolubricants and found that the oil was no longer Newtonian after the addition of the nanoparticles.

As for nanolubricants AS 0.5 and 1 vol% under the same conditions mentioned above (25 and 50 ºC), it was possible to verify that there were no significant changes and they behaved like Newtonian fluids, from shear rates > 10^4 s^{-1}. For a temperature of 75 °C (Figure 18 (c)), it is possible to observe that all lubricants present thixotropy, that is, the viscosity changes with the increase and the reduction of the shear rate during the time of the experiments. The fluid hysteresis area is represented in Figure 19, where it is possible to verify that the nanolubricant A, whose concentration of 1 vol% presented the highest thixotropy in the order of 277 ± 55 kPa·s^{-1}.

Figure 18 – Dynamic viscosity as a function of shear rate for pure oil, A 0.5 and 1 vol%, AS 0.5 and 1 vol% at temperatures of 25 °C (a), 50 °C (b) and 75 °C (c).





Source: Author (2022).

Thus, to investigate the rheological behavior of the lubricants involved, it was decided to compare the results obtained with the theoretical Power-Law model, Equation (6).

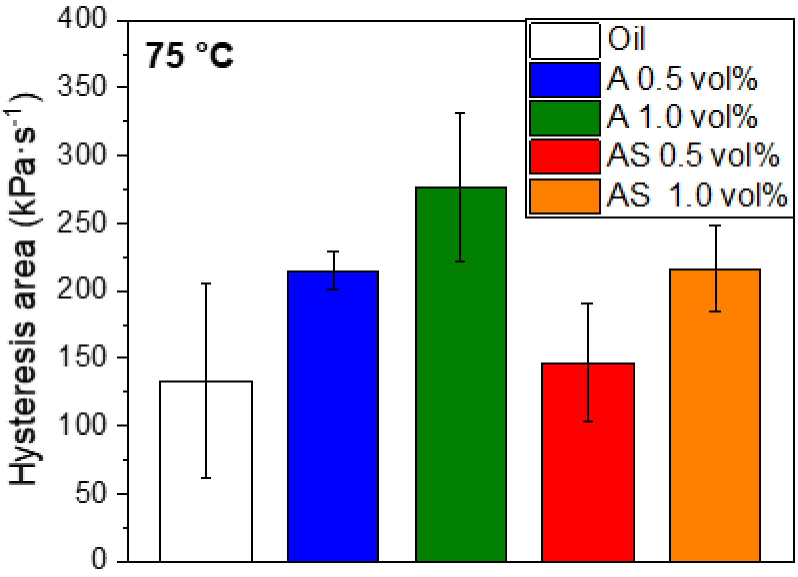
Table 5 shows the rheological parameters of theoretical models for each fluid evaluated in this study. It is observed that R^2 values are greater than 99% for all lubricants, confirming the similarity between experimental and theoretical values. According to the values obtained in the flow behavior index, it can be stated that all lubricants resemble Newtonian fluids, especially for high shear rates.

Table 5 – Rheological parameters of the Power-Law theoretical model for each fluid.

Fluid	Temperature (°C)	K (mPa·s)	n	R²
Lubricant oil	25	1.709	0.9970	0.9999
	50	0.556	1.0255	0.9999
	75	0.349	1.0517	0.9960
A 0.5 vol%	25	1.565	0.9939	0.9999
	50	0.900	1.0160	0.9998
	75	0.414	1.0433	0.9931
A 1.0 vol%	25	2.492	0.9687	0.9999
	50	1.317	0.9881	0.9961
	75	0.843	0.9952	0.9901
AS 0.5 vol%	25	1.278	1.0067	0.9999
	50	0.664	1.0260	0.9999
	75	0.372	1.0563	0.9984
AS 1.0 vol%	25	1.621	1.0057	0.9961
	50	1.014	1.0120	0.9990
	75	0.440	1.0613	0.9938

Source: Author (2022).

Figure 19 – Lubricants hysteresis area at a temperature of 75 °C.



Source: Author (2022).

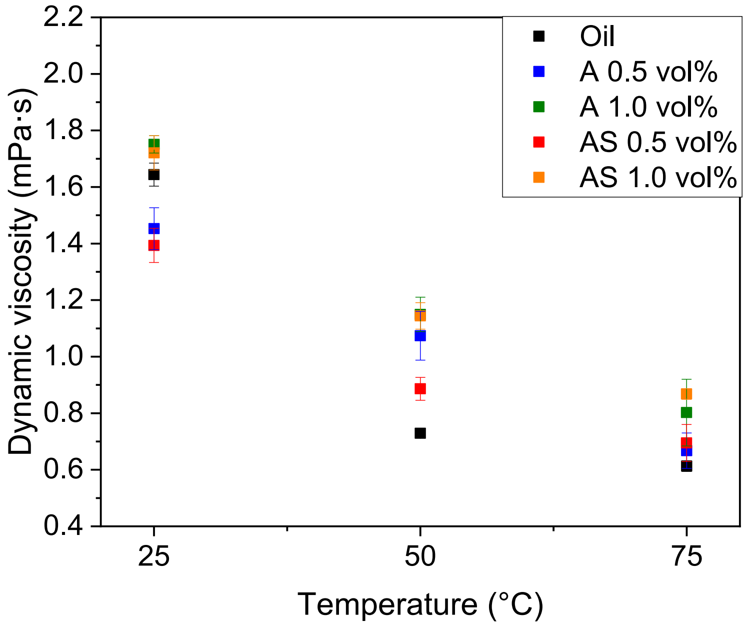
The strategy of carrying out the rheological tests at 3 different temperatures took into account some aspects such as the commercialization of lubricant products at room temperature (25 °C), a median temperature at which tests involving physical and chemical properties (50 °C) are carried out and a working temperature of hermetic type compressors (75 °C).

Figure 20 shows the dynamic viscosity as a function of temperature for the shear rate of 70,000 s^{-1}. It is observed that all lubricants decrease viscosity with increasing temperature. It is believed that the high temperature of nanolubricants intensifies the Brownian movement, causing this effect (SHARIF *et al.*, 2016). Note also that there is a tendency to increase the dynamic viscosity of nanolubricants A when compared to nanolubricants AS, this fact is related to stability, as the more agglomerated nanoparticles, the higher the viscosity.

The increase in temperature helps the particles to overcome the Van der Waals attraction forces which can disintegrate the nanoparticle agglomerates suspended in the base lubricant and, therefore, the intermolecular interactions between the molecules become weak and this phenomenon leads to a decrease in viscosity. Specifically, due to the increase in temperature, the Brownian movement will be intensified, which can cause increased chaos and this will consequently decrease the viscosity of the nanolubricant (SANUKRISHNA; JOSE PRAKASH, 2018).

Another relevant observation in Figure 20 is associated with the behavior of nanolubricants A and AS in presenting higher viscosity values compared to pure oil for temperatures of 50 and mainly 75 °C (as mentioned above, real working conditions of bearings in compressors of the hermetic type). This is an important point, because according to the Stribeck Diagram (illustrated in Figure 1), higher viscosities provide thicker lubricating films between the surfaces in relative motion, thus favoring greater efficiency in the lubrication system (BORDIGNON, 2018).

Figure 20 – Effect of temperature on dynamic viscosity for the shear rate of 70,000 s^{-1}.



Source: Author (2022).

4.6 STATISTICAL ANALYSIS

An analysis of variance (ANOVA) to assess the individual or combined effect of temperature and volume fraction on dynamic viscosity is presented in Table 6 for nanolubricants containing pure alumina nanoparticles (A) and Table 7 for nanolubricants containing surface-modified alumina nanoparticles (AS).

The smaller the P-value, the greater the statistical relevance of the factor. According to the results from the 3^2 factorial design, it is possible to verify that both for the statistical analysis of nanolubricants containing pure alumina nanoparticles and for the statistical analysis of nanolubricants AS, temperature and volume fraction were significant, as they presented value-P less than 0.05. However, the interaction of temperature with the volume fraction was not significant with a P-value greater than 0.05.

In both cases, the quality of the model fit was evaluated by the coefficient R^2 adjust with a value greater than 92%, indicating a good agreement between the experimental and predicted values.

Table 6 – Analysis of Variance (ANOVA) to assess factors capable of changing the viscosity of nanolubricant A.

	Coefficients	**P-value**
Intersection	1.098062	0.000000
Temperature (x_1)	-0.921531	0.000000
Volume fraction (x_2)	0.238924	0.000331
$x_1 \cdot x_2$	0.041213	0.313595
$R^2 = 0.93558$; Adjust $R^2 = 0.92024$		

Source: Author (2022).

Table 7 – Analysis of Variance (ANOVA) to assess factors capable of changing the viscosity of nanolubricant AS.

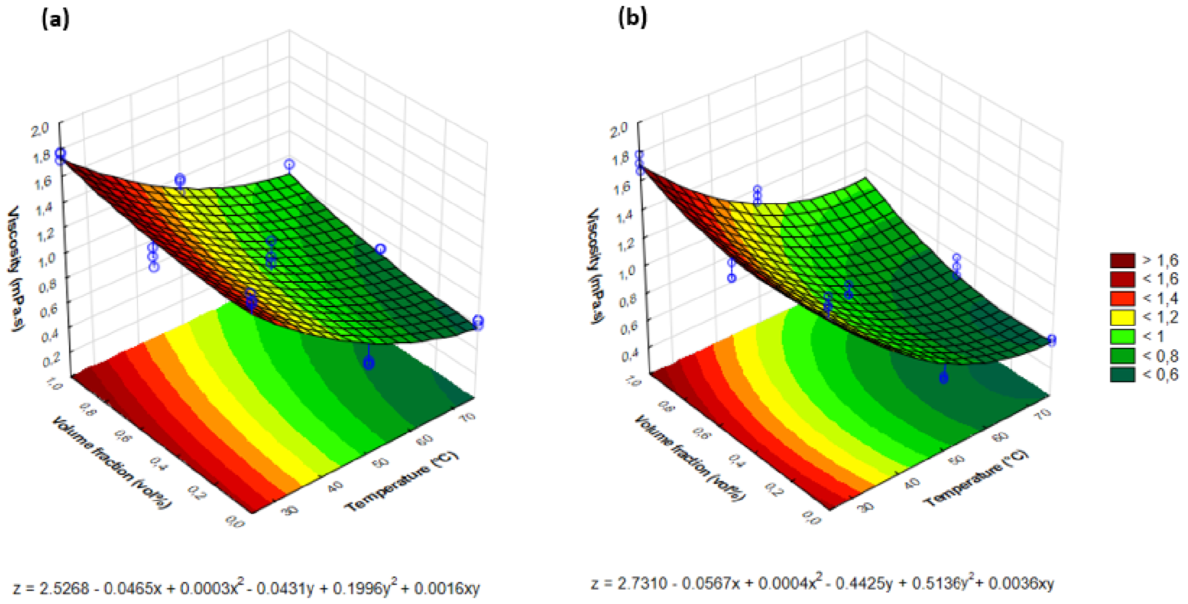
	Coefficients	**P-value**
Intersection	1.076989	0.000000
Temperature (x_1)	-0.860744	0.000000
Volume fraction (x_2)	0.249111	0.000010
$x_1 \cdot x_2$	0.088983	0.106674
$R^2 = 0.95864$; Adjust $R^2 = 0.9488$		

Source: Author (2022).

The results already discussed are also observed in the surface graphs generated for viscosity as a function of temperature and the volume fraction of nanoparticles.

Figure 21 presents three-dimensional response surface plots for the viscosity of nanolubricants A (a) and AS (b). It is possible to verify as the temperature increases, the viscosity of the nanolubricant decreases, indicating that the variables are inversely proportional, corroborating the results obtained earlier in this study. However, as the volume fraction of nanoparticles in the oil increases, it is possible to observe that the viscosity of the medium also increases, showing that both variables are proportional.

Figure 21 – Response surface plots for the viscosity of nanolubricants A (a) and AS (b).



$z = 2.5268 - 0.0465x + 0.0003x^2 - 0.0431y + 0.1996y^2 + 0.0016xy$

$z = 2.7310 - 0.0567x + 0.0004x^2 - 0.4425y + 0.5136y^2 + 0.0036xy$

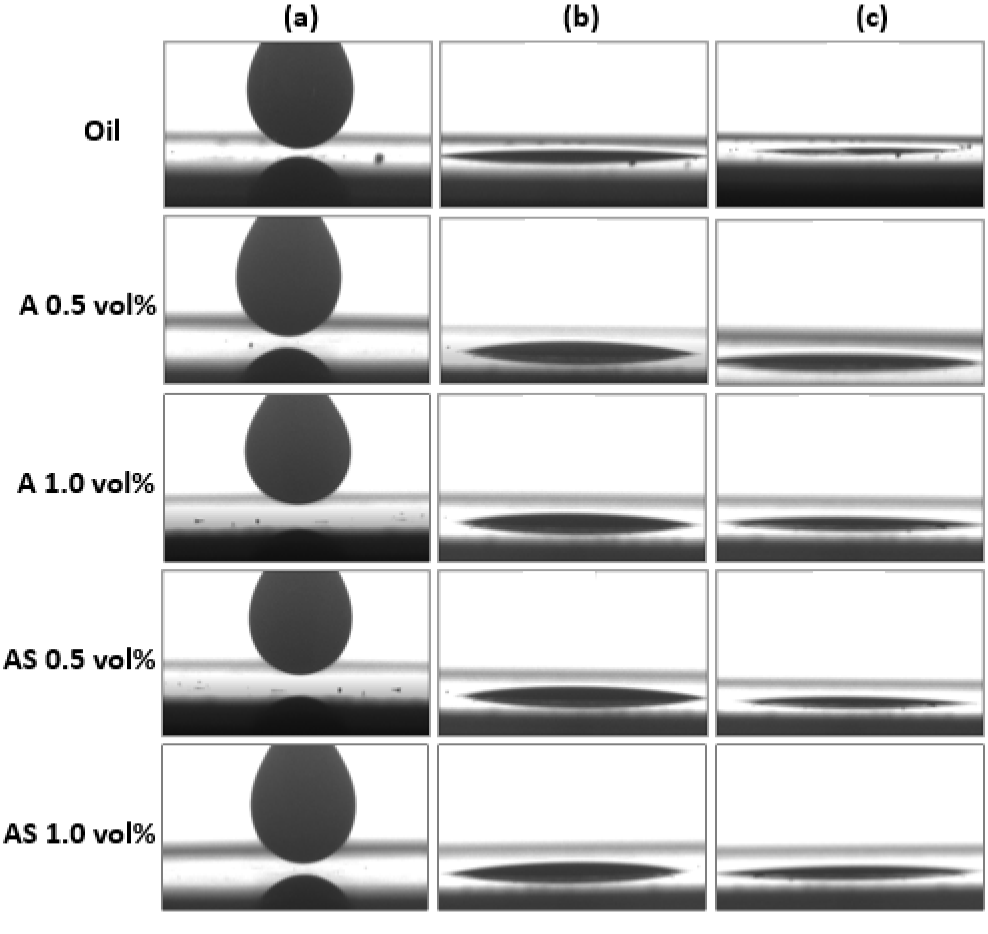
Source: Author (2022).

Finally, the results showed that the influences of the variables temperature and volume fraction are significant, as both affect the dynamic viscosity of nanolubricants A and AS. It is worth mentioning that viscosity is cited as an important parameter in the fluid lubrication regimes of the Stribeck curve (Figure 1).

4.7 CONTACT ANGLE AND WETTABILITY

The wettability analysis consisted of measuring the contact angle between the study lubricants and the flat surface of the lower plate used in rheological tests. Figure 22 shows the images obtained before (a), after 5 s (b) and 30 s (c) of applying 3 μL of pure oil and nanolubricants A and AS (0.5 and 1 vol%) on the surface.

Figure 22 – Contact angle of pure oil, nanolubricants A 0.5 and 1 vol%, AS 0.5 and 1 vol% in the substrate before (a), after 5 s (b) and 30 s (c).



Source: Author (2022).

It is possible to observe a similar behavior for all lubricants involved in this study. Therefore, the surface wettability property is associated with the tendency of a liquid to spread or not on a solid surface. While the presence of functional groups in nanoparticles can significantly improve the stability of suspensions, studies show that it can also change the wettability property of substrates (KUBIAK *et al.*, 2011).

However, in this study, according to the results obtained, the presence of alumina nanoparticles in the lubricating oil does not change the wettability, since it maintains a total substrate wetting (approximately 0º). Metallic surfaces must have good wettability to provide better penetration of the lubricant and allow the formation of a homogeneous oil layer even in difficult-to-reach regions (WOJCIECHOWSKI; KUBIAK; MATHIA, 2016). In this case, from a rheological and tribological point of view, in general, the greater the wettability of the fluid on a surface, the better the lubrication between the components of the system.

5 CONCLUSIONS AND PERSPECTIVES

5.1 CONCLUSIONS

The application of nanoadditives in lubricants is considered a potential alternative to reduce friction and wear, avoid wasting energy, reduce emissions and protect the environment. This study presents a review of the literature on nanolubricants, including preparation methods, stability, dispersion methods, and rheological behavior.

Initially, alumina (A) and surface-modified alumina with oleic acid (AS) nanopowders were characterized. Through the analysis of FTIR, it was concluded that there was a functionalization on the surface of the nanoparticles. Thus, later the nanolubricants were prepared through the two-step method, which consisted of dispersing A and AS nanoparticles in lubricating oil, whose concentrations used were 0.5 and 1 vol%.

In this study, the stability of nanolubricants was evaluated through visual inspection and the STEP technique, which showed that samples containing AS remained stable for a relatively longer time than samples containing A. Based on the accelerated stability analysis, simulating shelf life of 15 days, it was possible to observe that in the first 100 s of analysis, the instability index of the nanolubricants A, 0.5 and 1 vol%, present an instability index of 100% and 82% respectively, i.e., the sedimentation of the nanoparticles has already occurred. On the other hand, for AS 0.5 and 1 vol%, the instability indexes are relatively lower, 20% and 8%, respectively.

The rheological behavior of the lubricants was evaluated at temperatures of 25, 50 and 75 °C and compared with the theoretical Power-Law model. At temperatures of 25 and 50 ºC Pure oil and AS nanolubricants showed Newtonian behavior, while A nanolubricants showed a slight pseudoplastic behavior. However, all lubricants showed Newtonian behavior for shear rates $>10^4$ s^{-1}. At 75 °C it was observed that all lubricants exhibit thixotropy, that is, the viscosity changes with the increase and decrease of the shear rate during the time of the experiments. In this case, the nanolubricant A whose concentration of 1 vol% presented the highest thixotropy in the order of 277 ± 55 $kPa \cdot s^{-1}$.

The effect of temperature (50 and 75 °C) on the viscosity of nanolubricants A and AS for the shear rate of 70,000 s^{-1}, revealed that the viscosities of the nanolubricants were higher when compared to pure oil. According to the literature, this effect favors greater efficiency in the lubrication system between relative surfaces.

It was also possible to verify that, in general, the viscosity of lubricants increases with the increase of the volumetric fraction, while the viscosity decreases with the increase of temperature, corroborating the results obtained in the statistical analysis.

Finally, it is concluded that the best experimental conditions of this study for application in the stability analyzes were the AS nanolubricants, while in the rheological analyzes were the nanolubricants with the highest volume fraction of alumina nanoparticles.

5.2 SUGGESTIONS FOR FUTURE STUDIES

This dissertation provides the opportunity for the development of further studies, such as:

- Use of other methods that promote the stability of nanoparticles, such as other means of functionalization and the addition of surfactants directly to the base oil.
- Verification of the influence of adding alumina nanoparticles to oil on thermal properties, especially thermal conductivity and specific heat capacity.
- Tribological evaluation of the lubricants.
- Use of other nanoparticles to generate a greater dilating effect in the oil, which positively contributes to the lubrication of hermetic compressor bearings.

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