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TRIBOLOGICAL EVALUATION OF NAPHTHENIC BASE OILS USING FOUR BALL TESTER

Denilson Santos Monteiro[1]
[1] Universidade Estadual do Maranhão, Departamento de Engenharia Mecânica, Cidade Universitária Paulo VI – Avenida Lourenço Vieira da Silva 1.000 – São Luís/MA.
denilsonmonteiro1@aluno.uema.br

Adilto Pereira Andrade Cunha[1]
[1] Universidade Estadual do Maranhão, Departamento de Engenharia Mecânica, Cidade Universitária Paulo VI – Avenida Lourenço Vieira da Silva 1.000 – São Luís/MA.
adiltocunha@professor.uema.br

Lourival Matos de Sousa Filho[1]
[1] Universidade Estadual do Maranhão, Departamento de Engenharia Mecânica, Cidade Universitária Paulo VI – Avenida Lourenço Vieira da Silva 1.000 – São Luís/MA.
lourivalfilho@professor.uema.br

Paulo Roberto Campos Flexa Ribeiro Filho
[1] Universidade Estadual do Maranhão, Departamento de Engenharia Mecânica, Cidade Universitária Paulo VI – Avenida Lourenço Vieira da Silva 1.000 – São Luís/MA.
paulofilho@professor.uema.br

Abstract. *Base oils are the major components in the formulation of lubricants, representing 90% of the sample volume. Bases of mineral origin are classified according to the molecular structure of the hydrocarbon bonds in paraffinic, naphthenic and aromatic. Naphthenic oils are molecular structures of hydrogen and carbon atoms linked in a circular pattern. These oils are used as a basis for obtaining some mineral lubricants due to their good ability to solubilize additives and their low production cost. In addition, these bases have relevant physicochemical properties, with low pour points and high flash and combustion points, enabling them to be used as lubricants in a wide range of temperatures. Today, due to their improved thermal stability, these oils are used in the formulation of cutting oils, compressor oils and insulating oils. Despite all the advantages of physicochemical properties, the antifriction and antiwear capabilities have been little studied and in this way the study aims to investigate the tribological behavior of these samples. These capabilities are evaluated using tribological tests that simulate the operating conditions of lubricants, where analyzing the proper performance of the lubricant through high energy efficiency, low coefficients of friction (COF) and small wear scar diameter (WSD) are fundamental to certify safely the possibility of use in mechanical systems and equipment. In this study, the naphthenic-based lubricants NH-10 and NH-20 were evaluated through tribological tests in a tribometer in the configuration of four balls according to the ASTM D 4172 standard. The NH-10 and NH-20 samples reached values of COF of 0.154 ± 0.012 and 0.143 ± 0.019 and WSD of 0.761 ± 0.010 mm and 0.842 ± 0.075 mm, respectively. Visual evaluations of the morphologies of wear scar lubricated with NH-10 and NH-20 indicate the presence of abrasive and adhesive wear mechanisms. According to the friction traces theory, which classifies the behavior of COF's under steady-state conditions, the curves obtained for NH-10 and NH-20 show type B behavior, where the COF gradually increases during the test. From a tribological point of view, this behavior enables the use of these naphthenic bases for the development of new lubricants.*

Keywords: *Naphthenic oils, Four ball tester, Tribology, ASTM D 4172*

1. INTRODUCTION

Naphthenic oils are used as a base for producing lubricants and process oils that have low levels of polycyclic aromatic hydrocarbons (PAHs < 3.0% by mass) (Petrobras, 2022; Cunha et al., 2022; Barros et al., 2022). Due to their lower production cost compared to paraffinic oils and high thermal stability, naphthenic oils are used in the production of industrial lubricants, as well as in the formulation of machining oils and refrigeration compressor oils (Cadium, 2023). In addition, naphthenic oils have the advantage of better solubilizing additives, which helps to improve their low and high temperature properties, as well as their friction and wear reduction properties (Cadium, 2023; Fofana, 2013).

Despite the wide applicability of naphthenic oils, Brazilian refineries that produce basic oils only meet 34% of the country's demand, necessitating the importation of a significant percentage. This importation raises the costs for producing commercial naphthenic lubricants (Portal Lubes, 2021). Therefore, conducting studies that highlight the applicability and usability of these lubricants can contribute to increased investments in re-refining industries, which may reduce the production costs of these lubricants and the dependence on the international market.

Numerous studies have been conducted to improve the physicochemical properties and assess the influence of carboxylic acid content on the toxicity of naphthenic oils (Portal Lubes, 2021; Frank et al., 2009; Wu et al., 2019; Ronai, 2022). However, the anti-wear and anti-friction characteristics in tribological tests have been underexplored. Tribological studies are used to evaluate the ability of lubricants to form a film that reduces friction and wear between surfaces in relative motion (Ribeiro Filho et al., 2022; YANG et al., 2019; Ribeiro Filho et al., 2023). Currently, the main method used to assess the tribological characteristics of lubricants is the four-ball test, which simulates extreme pressure (EP) conditions, where the lubricant is subjected to a loading force of 392 N, at 75°C and 1200 RPM, as established by ASTM D 4172. In this test, the lubricant is evaluated under boundary lubrication conditions, where the viscosity of the sample has little influence on friction reduction. In this regime, the friction between the two contacting surfaces is affected by the sample's ability to adsorb onto the contact surfaces, thus forming a lubricating film (RIBEIRO FILHO et al., 2023; Nguyen et al., 2017; Luo et al., 2019). By examining the morphology of the worn ball surfaces during the four-ball test, it is possible to evaluate the wear mechanisms, indicating the lubricant's ability to withstand high loading forces (Chan et al., 2018). Therefore, using the four-ball method to evaluate lubricant samples becomes an important tool for understanding the tribological behavior of naphthenic samples.

Understanding the tribological properties of these samples can contribute to the development of new lubricant formulations with high anti-friction and anti-wear properties, as well as lower production costs. Hence, this study aims to evaluate the tribological behavior and characterize the main physicochemical properties of two basic naphthenic lubricants to understand their ability to reduce friction and wear when subjected to extreme pressure testing.

2. EXPERIMENTAL SECTION

2.1 Materials

The samples of naphthenic base oils NH-10 and NH-20 were kindly provided by Petrobras (Brazil). Acetone (> w.t 99.5%) used for preparing the spheres for the tribological tests was supplied by Neon (Suzano, Brazil). The balls used in the tribological tests are made of chrome steel alloy (AISI52100) with a hardness of 64 HRC, a diameter of 12.7 mm, and an initial surface roughness of 0.015 µm.

2.2 Physicochemical Characterization

The physicochemical characteristics of density at 20°C and kinematic viscosity at 40 °C and 100 °C of the NH-10 and NH-20 samples were determined following ASTM methods D7042 and D445, respectively, using an Anton Paar SVM 3000 instrument (Graz, Austria). The viscosity index (VI) was determined using ASTM method D2270. The pour point was determined using ASTM standard D97, while the flash point was determined using ASTM standard D92.

2.3 Tribological Evaluation

The tribological evaluation was performed using a four-ball machine according to the parameters established by ASTM D 4172. This test consists of three stationary balls in a fixture immersed in the lubricant sample at 75°C, in contact with a fourth rotating ball under a constant loading force (392 N) and rotation (1200 RPM) for 1 hour. As shown in Figure 1. Before the test, the balls were cleaned with acetone and dried under ambient conditions. At the end of the tests, an optical microscope was used to determine the wear scar diameter and the morphology of the worn surface of the balls.

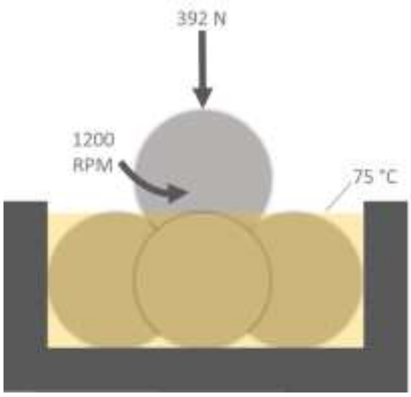


Figure 1. Four-ball tribological test setup.

3. RESULTS AND DISCUSSION

3.1 Physicochemical Characterization

The results of density at 20°C, kinematic viscosity at 40°C and 100°C, viscosity index, pour point, and flash point are presented in Table 1.

Table 1. Physicochemical properties of the NH-10 and NH-20 samples.

Properties	NH-10	NH-20
Density at 20 ºC (g/cm³)	0.8970	0.9017
Kinematic viscosity at 40 ºC (cSt)	10.13	20.38
Kinematic viscosity at 100 ºC (cSt)	2.39	3.59
Viscosity index	23	13
Pour point (ºC)	-39	-33
Flash Point (ºC)	152	160

The values shown in Table 1 show that NH-20 has a higher density than NH-10. This is related to the higher viscosity observed in NH-20, since the density results depend on the viscosity, sample quality and additive content (Ribeiro Filho, 2023; API 1509, 2016; Lin and Kedzierski, 2020; Ewen et al., 2016). Density plays a crucial role in evaluating lubricants in use. An increase in density compared to unused lubricant may suggest the existence of insoluble elements, water, high density substances and oxidized compounds. On the other hand, a decrease in density may be an indication of the presence of low density contaminants and/or fuels (Carreteiro and Belmiro, 2006).

From the kinematic viscosity data in Table 1, it can be concluded that the NH-20 molecule has a structure with stronger intermolecular forces, resulting in a higher kinematic viscosity compared to NH-10. As for the viscosity index, which measures the sensitivity of viscosity to changes in temperature, it was observed that both NH-10 and NH-20 have low viscosity indexes, 23 and 13, respectively. These results indicate that the samples undergo significant viscosity changes in response to temperature variations (Narayana et al., 2022; Verdier et al., 2009; Braga et al., 2014).

Pour point analyzes revealed that both NH-10 and NH-20 have a wide operating range at low temperatures, making them suitable for cold conditions. In addition, the flash point results indicated that the samples have high flash points, which is advantageous for operations at high temperatures, ensuring greater safety in applications with higher temperatures. These characteristics make both lubricants (NH-10 and NH-20) versatile and able to perform well in a variety of thermal conditions (Carreteiro and Belmiro, 2006).

3.2 Tribological evaluation

The results obtained for the friction coefficient and the wear scar diameter (WSD) of NH-10 and NH-20 samples are illustrated in Figure 2.

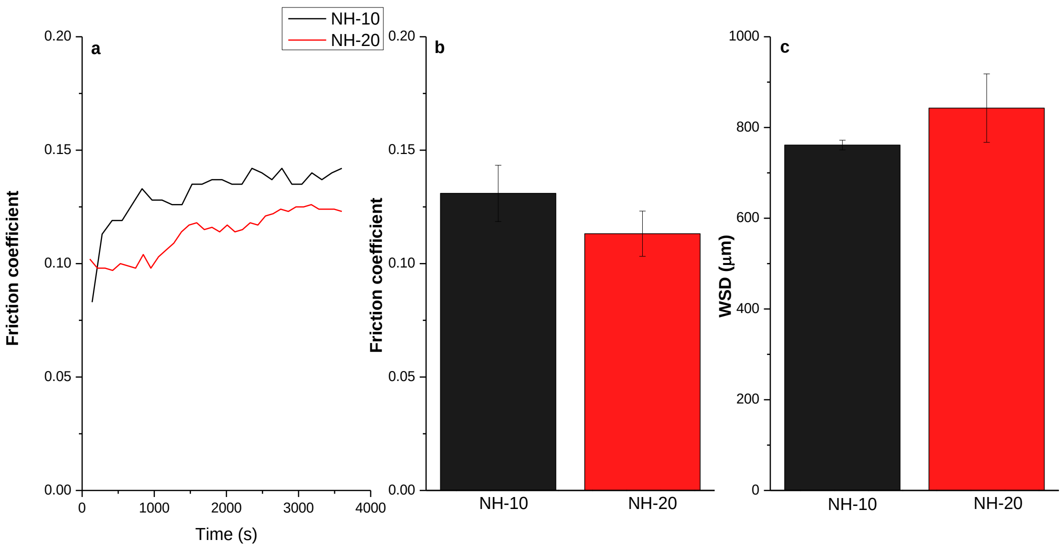


Figura 2. Friction coefficient and WSD curves in tribological tests of NH-10 and NH-20 samples.

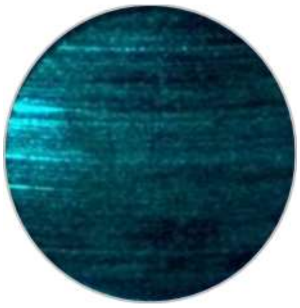
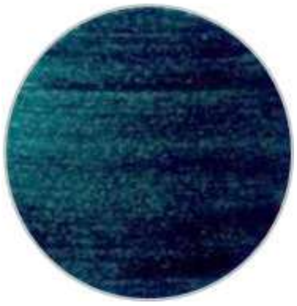
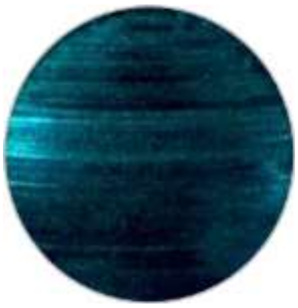
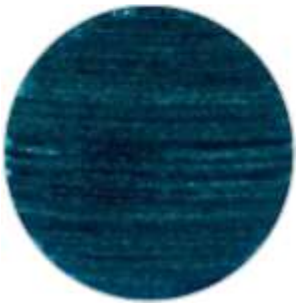
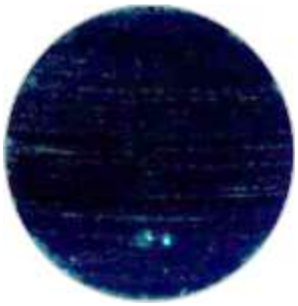
The curves representing the friction coefficient of NH-10 and NH-20 samples exhibit a gradual increase throughout the test, as shown in Figure 2.a e 2.b. Based on the concept of friction traces, it is possible to classify the friction coefficients in steady-state conditions into four distinct types: Type A, where the coefficient remains constant during steady-state; Type B, characterized by a gradual increase in the coefficient during the test; Type C, where the coefficient decreases gradually during the test; and Type D, in which the friction coefficient fluctuates throughout the test (Ribeiro Filho et al, 2023; Minami et al., 1999; Gates and Hsu, 1991; Fox et al., 2004).

Typically, Type A is associated with low wear rates, which is advantageous in terms of performance. Types B and C may be acceptable for lubricants since they exhibit an increase in the friction coefficient, but still maintain tolerable levels of wear. However, Type D is considered unacceptable as it is often related to high wear levels, which can impair the system's performance (Ribeiro Filho et al., 2023).

Analyzing the NH-10 and NH-20 samples, we observe that their friction curves fall into the characteristics of Type B. The NH-10 sample has a Wear Scar Diameter (WSD) value of 761.33 µm, while NH-20 has a WSD of 842.66 µm (Figure 2.c). These values indicate that, although the friction coefficients increased during the test, they still remain at a level that can be considered acceptable for lubricants ((Ribeiro Filho et al., 2023; Minami et al., 1999).

The morphologies of the wear surfaces of the balls in the tribological tests using NH-10 and NH-20 samples are presented in Table 2.

Table 2. Wear morphology of the balls lubricated with the NH-10 and NH-20 samples, after tribological tests.

Item	1st ball	2nd ball	3rd ball
NH-20	 872 µm	 757 µm	 899 µm
NH-10	 759 µm	 773 µm	 752 µm

The grooves observed in the direction of application are a result of abrasion and adhesion wear mechanisms (Ribeiro Filho et al., 2022; Noorawzi and Samion, 2016; Afifah et al., 2019). Among the NH-10 and NH-20 samples, NH-10 demonstrated the highest resistance to lubricant film wear, showcasing its superior absorption characteristics on the metallic surfaces of the balls. This highlights NH-10's enhanced performance in mitigating wear and promoting better surface protection in comparison to NH-20.

4. CONCLUSION

In the present study, we investigated samples of naphthenic base oils (NH-10 and NH-20) and conducted a detailed analysis of their main physicochemical characteristics. Subsequently, these samples were subjected to tests in the Four Ball machine to evaluate their tribological performance. The NH-10 and NH-20 samples exhibited viscosity indexes of 23 and 13, respectively, indicating that their viscosities vary significantly with temperature changes. Furthermore, we observed that the samples showed a wide range of pour and flash points, maintaining fluidity at both low and high temperatures. This is a valuable attribute as it ensures that these lubricants remain effective even under extreme temperature conditions.

Regarding the tribological tests, it became evident that the NH-10 sample produced higher friction coefficients compared to NH-20. However, the NH-10 sample also demonstrated the highest wear reduction capacity, resulting in lower Wear Scar Diameter (WSD) values when compared to those obtained by NH-20. This can be attributed to a combination of factors, including the specific properties of the lubricant and its interaction with the metal surfaces during the test. The NH-10 sample seems to provide a more robust and resistant lubricating film, allowing better protection against wear and groove formation under extreme pressure and friction conditions of the Four Ball test. These results are relevant for industrial applications, where the appropriate choice of lubricant can have a significant impact on the lifespan and performance of equipment. Despite presenting higher friction coefficients, the NH-10 sample demonstrated greater efficiency in wear prevention, making it a potentially more advantageous option in high-pressure and load scenarios.

5. ACKNOWLEDGEMENTS

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