ZURICH, MAY 19 – 23, 2025

2025 | 001

Lubricants enabling alternative fuels for maritime decarbonization

Lubricants

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ABSTRACT

Environmental standards are becoming increasingly stringent and the regulatory focus on maritime decarbonization is rapidly growing. These factors are driving infrastructural developments and technological advancements for alternative fuels, engine designs, and operating practices. However, the transition to alternative fuels is highly complex and requires close coordination among multiple stakeholders across the value chain.

For several decades, heavy fuel oil (HFO) had been the dominant marine fuel for the shipping industry primarily because of its low cost, widespread availability, and developed infrastructure. The International Maritime Organization (IMO) has enacted progressively stricter regulations that limit marine fuel sulfur content and nitrogen oxides emissions, and its latest greenhouse gas (GHG) strategy includes an enhanced common objective to reach net-zero GHG emissions from international shipping by 2050, a commitment to ensure an uptake of alternative zero and near-zero GHG fuels by 2030, as well as indicative checkpoints for 2030 and 2040. These regulatory targets are pushing ship owners and operators to change their operational practices, install onboard air pollution control devices, and diversify their fuel portfolios to incorporate alternative fuels. Ammonia is increasingly seen as an attractive future marine fuel for several reasons, one of which is its low carbon and emissions profile. Ammonia emits no carbon dioxide during combustion, making it a zero-carbon fuel when produced from renewable sources such as green hydrogen. This characteristic aligns with global efforts to reduce GHG emissions from the maritime sector.

Lubricant technology plays a crucial role in ensuring that the use of these alternative fuels will not have detrimental impact on engine operability. Gulf Marine is conducting extensive studies to understand how ammonia as a marine fuel affects the performance of lubricants. This paper presents the key findings from Gulf Marine’s investigations related to determining the impact of ammonia on marine cylinder oils and system oils via artificial ageing, and subsequent chemical analysis as well as performance tests. Amidst bunkering uncertainty and complexity, Gulf Marine is fully committed to providing optimal lubricant solutions to enable the use of alternative fuels such as ammonia for maritime decarbonization.

1 INTRODUCTION

In July 2023, the International Maritime Organization (IMO) Member States adopted the 2023 IMO Strategy on Reduction of GHG Emissions from Ships, setting more ambitious targets to address harmful emissions. The revised IMO GHG Strategy, approved at the Marine Environment Protection Committee, establishes a shared goal of achieving net-zero GHG emissions from international shipping by or around 2050. It also includes a commitment to increasing the use of alternative zero and near-zero GHG fuels by 2030. The strategy sets indicative milestones for international shipping to reduce GHG emissions by at least 20% (striving for 30%) by 2030 and by at least 70% (striving for 80%) by 2040. [1].

To achieve these goals, the use of zero- or low-carbon alternative fuels are being strongly considered. Among the alternative fuels, ammonia has emerged as a promising candidate for powering marine engines. Ammonia (NH3) is a carbon-free compound that can be produced using renewable energy sources such as wind, solar, or hydroelectric power [2]. Ammonia can be considered a potential replacement for gasoline, diesel, and kerosene. It can also be considered for all combustion systems, ranging from engines to gas turbines [3]. When utilized as a fuel in an internal combustion engine, ammonia generates zero carbon emissions, making it one of the few chemical compounds with this capability [4].

Ammonia's potential as a fuel for large vessels is attributed to several key characteristics: its global commercial availability [5], largely driven by the fertilizer industry; the potential for green production methods; its adequate energy density; and the relative ease of handling it [6].

The chemical industry has handled ammonia for decades, but its effects as a marine engine fuel on lubricants are not well understood. The literature largely lacks investigations into the interaction between engine lubricants and ammonia, as ammonia-fueled marine engines are not yet widely used. Research in this area is crucial since conventional engine oils are formulated for hydrocarbon-based fuels and their combustion byproducts. Using ammonia as a fuel could introduce entirely new chemical degradation pathways, necessitating an analysis of lubricant formulation. Specifically, the impact of ammonia as a fuel on the lubrication system in a marine internal combustion engine must be studied to develop long-life, reliable lubricants for such applications.

This study aims to develop a methodology capable of testing novel oil formulations which are intended for utilization in ammonia-fueled large marine engines using artificial alteration. Assessing the utility of multiple concentrations of ammonia as well as contamination with nitrogen dioxide, the prevailing combustion byproducts were utilized to better understand the differences in oil degradation and the resulting lubrication performance.

Thus, we focused on chemical degradation and key performance characteristics, such as oil corrosiveness, deposit formation tendencies and tribological properties in terms of friction and wear protection, to enable the establishment of a connecting link between ammonia combustion and engine lubrication.

2 MATERIALS AND METHODS

2.1 Engine Oils

The lubricants used in this study are an approved MAN Energy Solutions (MAN ES) Category II (Cat. II) 40 Base Number (BN) SAE 50 cylinder oil and a 6 BN SAE 30 system oil. Both lubricants are commercially available.

2.2 Artificial Alteration

Artificial alteration was conducted in a custom-built alteration reactor system [7], as shown schematically in Figure 1. The reactor, with a net volume of 2000 mL, was heated using an electrical heating jacket and equipped with a magnetic stirrer to continuously mix the oil sample during alteration. The oil samples were maintained at specified temperatures, i.e., 200°C for the cylinder oil and 70°C for the system oil and subjected to a reaction gas mixture at a constant total flow rate of 0.85 L/min for 200 hours. Sampling of the alterations was performed at regular intervals: 25 h, 50 h, 75 h, 100 h, 175 h, and 200 h for the cylinder oil; and 25 h, 100 h, 125 h, 150 h, 175 h, and 200 h for the system oil.

Since ammonia is considered a viable fuel for marine engines, the stoichiometric concentration (21.7 vol% in synthetic air) was used as the reaction gas to simulate practical applications, specifically the complete combustion of ammonia in air. The stoichiometric concentration of 21.7 vol% of ammonia ensures that the amount of ammonia is exactly balanced with the amount of oxygen available from air to achieve complete combustion, producing nitrogen and water without leaving any excess ammonia or oxygen. Additionally, a trace concentration of nitrogen dioxide (1000 ppm in synthetic air) was included to represent a potential combustion byproduct of ammonia [8].

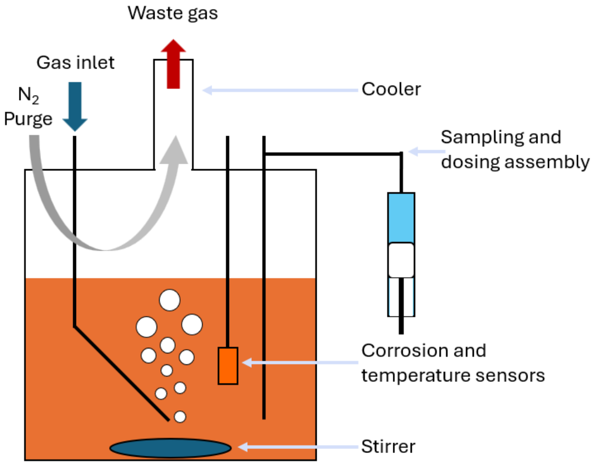


Figure 1. Schematics of the alteration reactor.

2.3 Chemical Analysis and Performance Tests

The intermediary and final altered oil samples were analyzed using conventional oil analytical methods to assess their degradation levels. The analytical approach included:

- Fourier-transform infrared spectroscopy (FT-IR) to determine degradation products, i.e., oxidation, nitration and aminification
- Viscosity, density and viscosity index according to ASTM D7042 via Stabinger viscometer
- Total base number (TBN) according to DIN ISO 3771
- Total acid number (TAN) according to ASTM D664
- Elemental composition via inductively coupled plasma – optical emission spectroscopy (ICP-OES)

To assess the impact of the reaction gas compositions on oil characteristics, the final altered samples underwent performance tests, including:

- Copper corrosion test based on ASTM D130 (modified)
- SRV wear test according to ASTM D6425 and 3D wear determination via confocal-interferometric microscopy
- Micro Coking Test (MCT) according to GFC-Lu-27-T-07
- Komatsu Hot Tube Test (KHT)
- Panel Coker Test (PCT)
- Pressure Differential Scanning Calorimetry (PDSC) according to CEC L 85-99

The modified copper corrosion test (as shown in Figure 2) is based on ASTM D130 but with deviations from the standard method i.e., only half the copper-strip is immersed in the test oil to analyze the effect on both the liquid and gas phases.

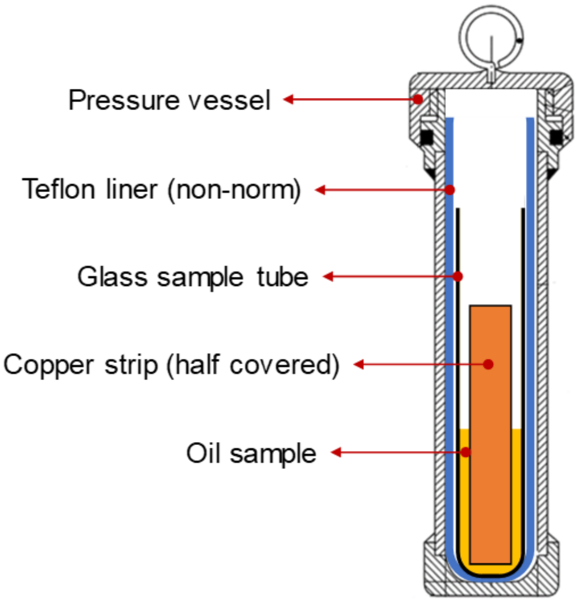


Figure 2. Modified copper corrosion test.

The SRV wear test, performed according to ASTM D6425, involves using a test ball oscillated at a constant frequency and stroke amplitude under a constant load against a test disc moistened with the test oil. The platform to which the test disc is attached is held at a constant temperature. For cylinder oil, the test parameters include a frequency of 50 Hz, a normal force of 300 N, a 1 mm stroke, a temperature of 120°C, double determination, and a duration of 2 hours. For system oil, the parameters are a frequency of 50 Hz, a normal force of 200 N, a 1 mm stroke, a temperature of 80°C, double determination, and a duration of 2 hours. The 3D wear determination is performed via confocal-interferometric microscopy to provide detailed surface topography.

The Micro Coking Test (MCT) according to GFC-Lu-27-T-07 (as depicted in Figure 3) assesses the tendency of oils to form coke under high temperatures. In this test, the oil is deposited onto an aluminum alloy plate and subjected to thermal conditions mimicking piston ring zones, with temperatures set at 230°C for the cold spot and 280°C for the hot spot. After a 90-minute test duration, the plate is cooled and conditioned for a visual rating according to a specific grading system.

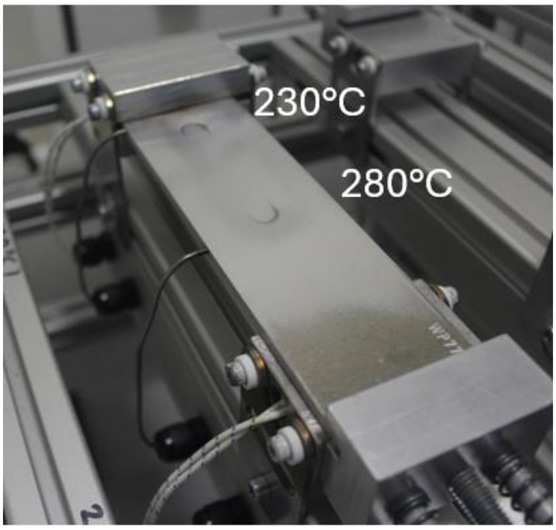


Figure 3. Micro Coking Test (MCT) according to GFC-Lu-27-T-07.

The Komatsu Hot Tube Test (KHT) evaluates the thermal stability and cleanliness of lubricating oils by monitoring deposit buildup in a heated glass tube. During the test, the oil is subjected to high temperatures of 310°C, 320°C, and 330°C for a duration of 70 minutes. The performance of the oil is assessed through the average deposit weight and merit ratings, which are assigned based on the extent of deposit formation. Higher ratings indicate better thermal stability and reduced deposit accumulation. This test is essential for determining the oil's ability to resist thermal degradation and maintain cleanliness under severe operating conditions.

The Panel Coker Test (PCT) is designed to evaluate the performance of lubricating oils under conditions that promote thermal degradation and deposit formation. In this test, the oil is splashed against an aluminum panel at elevated temperatures, specifically 316°C for the panel and 95°C for the sump. The procedure lasts for one hour, during which a 15-second splash of oil is followed by a 45-second bake period. This rigorous testing helps assess the oil's ability to resist oxidation and minimize deposit buildup, providing insights into its suitability for high-temperature applications.

The Pressure Differential Scanning Calorimetry (PDSC) measures the heat flow in lubricants under controlled temperature and pressure conditions. A small quantity of oil is weighed into a sample pan and placed in a test cell, which is heated to a specified temperature and pressurized with oxygen. The cell is maintained at this regulated temperature and pressure until an exothermic reaction occurs, indicating oxidation. The extrapolated onset time of this reaction is recorded as the oxidation induction time (OIT) for the lubricating oil. Conducted at a test temperature of 210°C, this test assesses the heat flow and oxidation induction time of the oil, providing insights into its stability and resistance to oxidation under varying pressure conditions.

3 RESULTS

3.1 Chemical Analyses

The obtained intermediate and final altered oil samples were analyzed using conventional oil analytical methods to characterize their degradation levels. The analytical approach included Fourier transform infrared spectroscopy (FT-IR) to assess the accumulation of key degradation products. Additionally, the total acid number (TAN) was measured according to ASTM D664, and the total base number (TBN) was determined in accordance with DIN ISO 3771 to evaluate acidification and the depletion of base reserves, respectively. Kinematic viscosity was also assessed at 40°C and 100°C following ASTM D7042 to analyze how oil degradation affects the physical properties of the engine oils.

Figure 4a, 4b, and 4c depict the propagation of oxidation, nitration, and aminification, respectively, during the alteration. Aminification refers to the process in which the combustion of ammonia as a fuel produces nitrogen-based compounds. These compounds can react with the lubricant, leading to the formation of amines. The formation of amines can potentially lead to changes in the chemical structure of the lubricant due to chemical reactions between the amines and other components in the lubricant. This process can alter the lubricant’s viscosity, acidity, and overall stability. For the cylinder oil, oxidation increased throughout the alteration, but no nitration was detectable, as nitration products decompose at elevated temperatures [9]. Due to water interference, accurate evaluation of aminification was not possible. For the system oil, no significant oxidation was detectable, but some nitration was visible, along with increasing aminification over time.

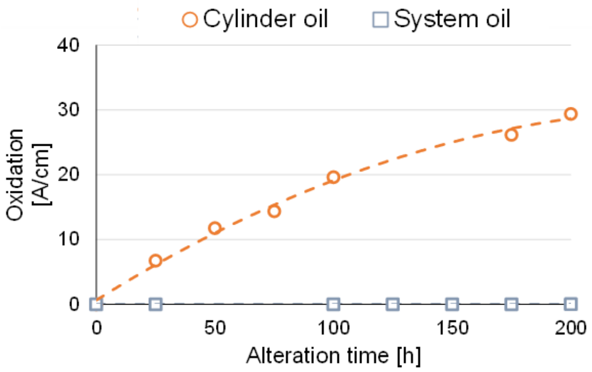


Figure 4a. Propagation of oxidation.

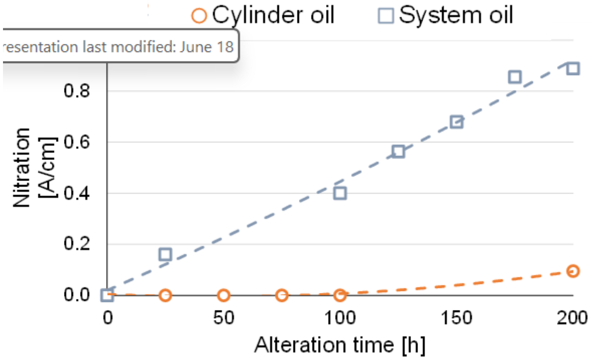


Figure 4b. Propagation of nitration.

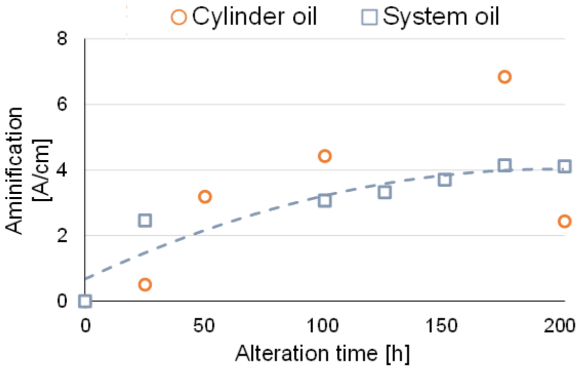


Figure 4c. Propagation of aminification.

Figure 5a and 5b show the propagation of the kinematic viscosity at 40°C and 100°C, respectively. For the cylinder oil, the viscosity increased during the alteration process (due to oxidation). For the system oil, the viscosity was largely unaffected by the alteration.

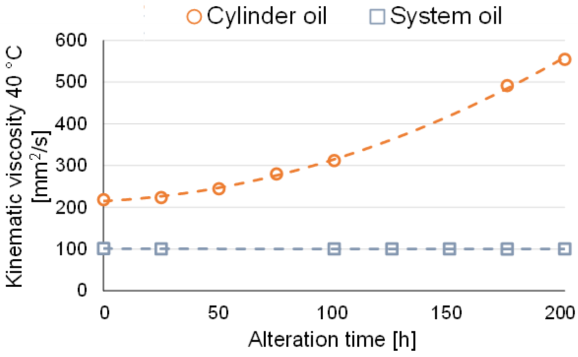


Figure 5a. Propagation of viscosity at 40°C.

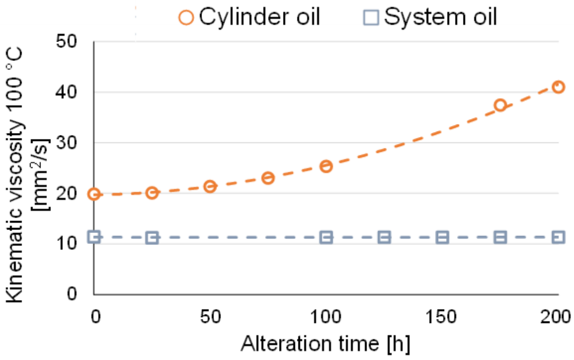


Figure 5b. Propagation of viscosity at 100°C.

Figure 6a and 6b present the propagation of the TBN and TAN, respectively. For TBN, there were very minor changes during the alteration process for both the cylinder oil and system oil. For TAN, there was an increase at the end of the alteration for the cylinder oil (corresponding to oxidation) and for the system oil (possibly due to aminification).

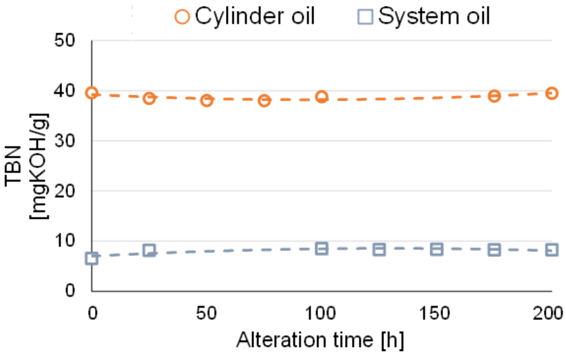


Figure 6a. Propagation of TBN.

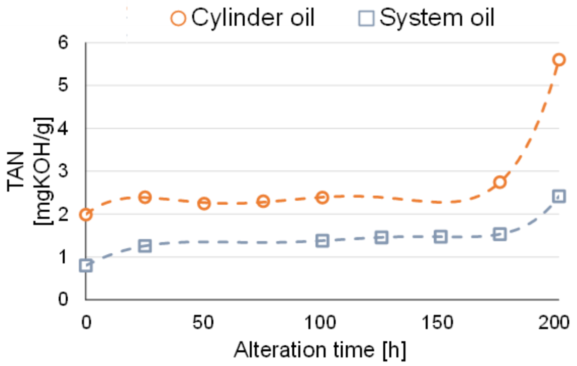


Figure 6b. Propagation of TAN.

3.2 Performance Tests

For the modified copper corrosion test, the copper strip visual ratings were similar for the fresh and aged cylinder oils, and the fresh system oil. For the aged system oil, corrosion was visible in the gas phase i.e., top half of the strip that was not immersed in the test oil. The visual appearance of the copper strips is shown in Figure 7 and the visual ratings are summarized in Table 1. These observations are in line with the trace elements found in the oils. Figure 8 shows the copper content in the oils before and after alteration. For the system oil, the increase in copper content after alteration indicates copper corrosion. It corresponds to deteriorating visual rating in the gas phase with altered system oil.

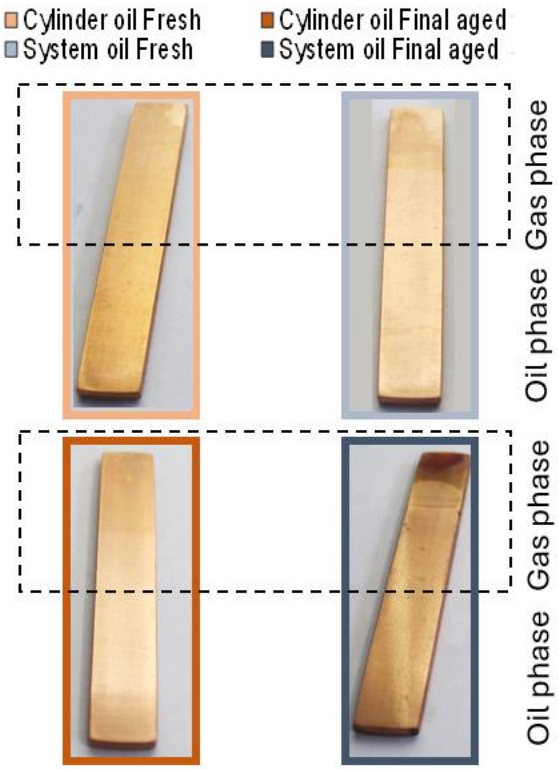


Figure 7. Copper strip visual appearance.

Table 1. Copper strip visual ratings

Sample	Phase	Visual Rating
Cylinder Oil (Fresh)	Oil Phase	1B
	Gas Phase	1B
Cylinder Oil (Final Aged)	Oil Phase	1A
	Gas Phase	1B
System Oil (Fresh)	Oil Phase	1A
	Gas Phase	1B
System Oil (Final Aged)	Oil Phase	1B
	Gas Phase	3A

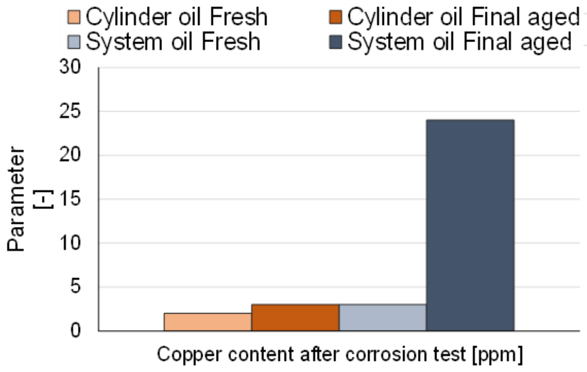


Figure 8. Copper content in oils before and after alteration.

The friction and wear properties of the oils were evaluated using the SRV tribometer. The friction curves for the fresh and final-aged cylinder oils were largely comparable, as shown in Figure 9a. Similarly, as depicted in Figure 9b, the friction curves for the fresh and final-aged system oils were mostly comparable, except for some instability visible with the final-aged oil in the later stages of the test.

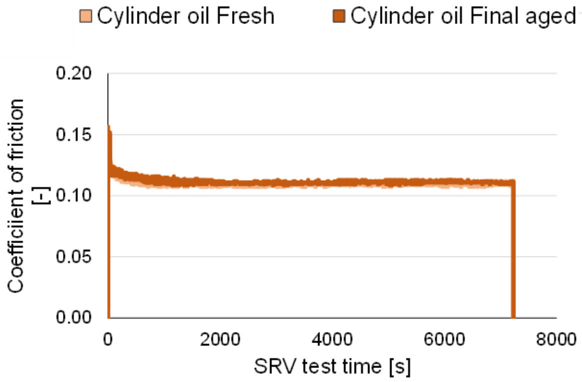


Figure 9a. Friction curves for cylinder oils.

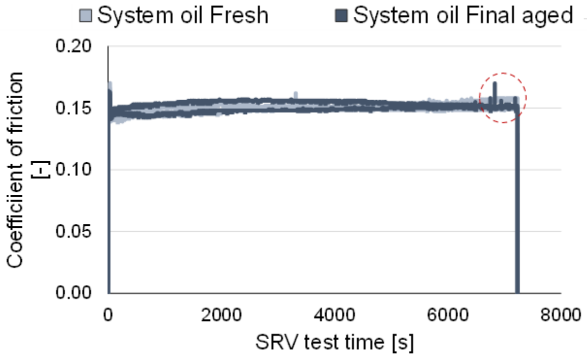


Figure 9b. Friction curves for system oils.

As presented in Figure 10, the coefficient of friction values for the fresh and final-aged cylinder oils were largely comparable. Likewise, the coefficient of friction values for the fresh and final-aged system oils were mostly comparable. The coefficient of friction values for the cylinder oil and the system oil were not directly comparable due to different normal forces.

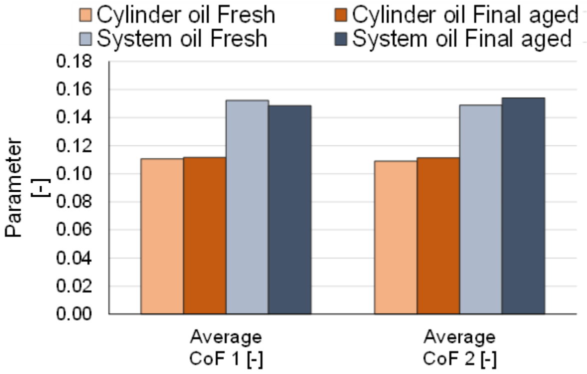


Figure 10. Average coefficients of friction.

As shown in Figure 11a, the wear scar areas on the SRV ball for the fresh and final aged cylinder oils were comparable. As depicted in Figure 11b, a slight increase in the wear scar area on the SRV disc was visible with the final-aged cylinder oil.

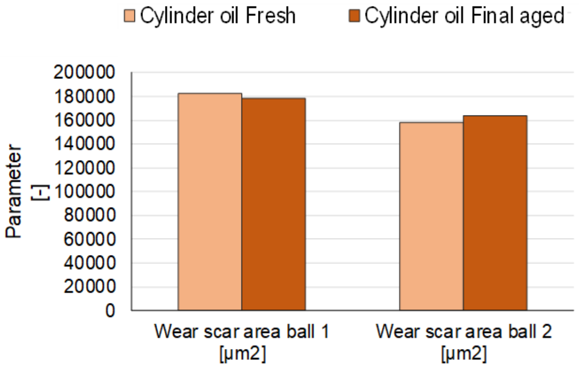


Figure 11a. Wear scar area on SRV ball for cylinder oils.

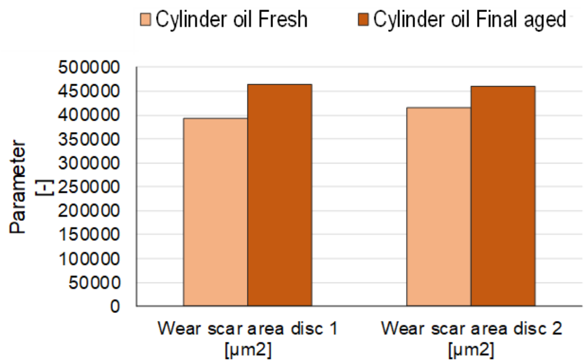


Figure 11b. Wear scar area on SRV disc for cylinder oils.

As shown in Figure 12a, a slight increase in the wear scar area on the SRV ball was visible with the final-aged system oil. As depicted in Figure 12b, the wear scar areas on the SRV disc for the fresh and final-aged system oils were similar.

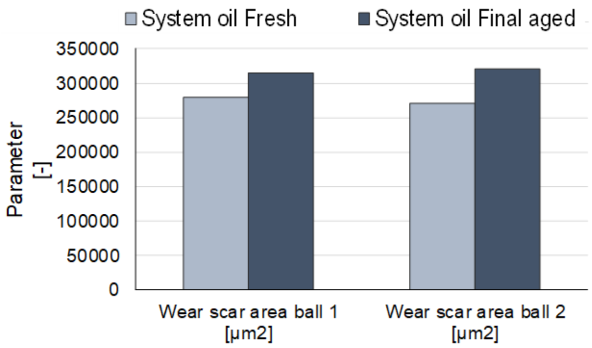
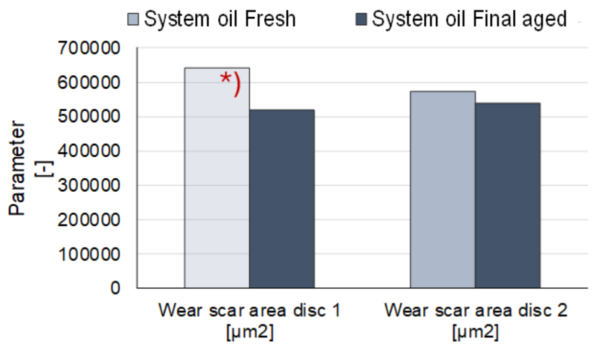


Figure 12a. Wear scar area on SRV ball for system oils.



*) Disc of System oil fresh / determination 1 is less reliable for wear determination due to deep scratches

Figure 12b. Wear scar area on SRV disc for system oils.

Figure 13a and 13b show the deposit formation properties of the cylinder oils based on the Micro-Coking Test (MCT). The lacquer merit ratings of the final-aged oil were slightly reduced compared to the fresh oil. The deposit formation was slightly lower in the final-aged sample compared to the fresh oil.

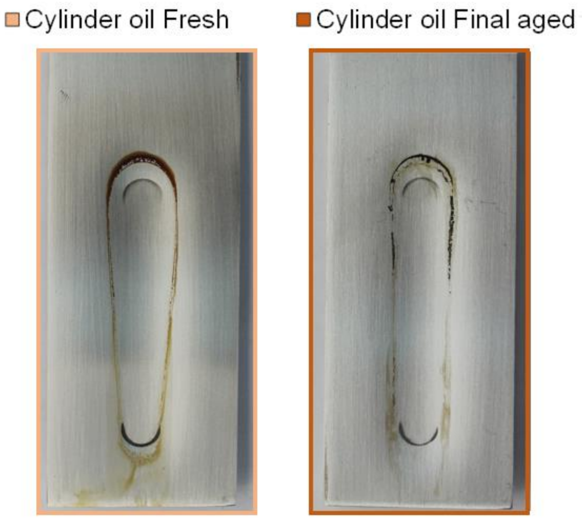


Figure 13a. Images of deposit formation in MCT.

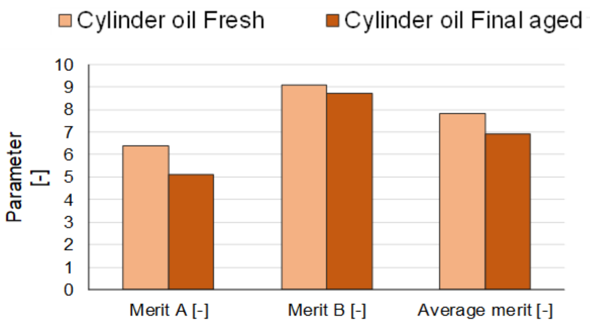


Figure 13b. Lacquer merit ratings in MCT.

For the Komatsu hot tube test (KHT), there was an increased average deposit weight with the final-aged cylinder oil compared to the fresh cylinder oil for temperatures above 310°C, as shown in Figure 14. Both fresh and final-aged cylinder oils generally showed similar merit ratings at each temperature, i.e., 310°C, 320°C, and 330°C, as displayed in Figures 15a, 15b, and 15c.

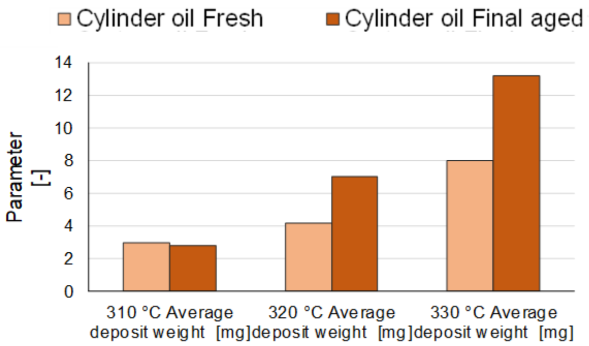


Figure 14. Average deposit weight in KHT.

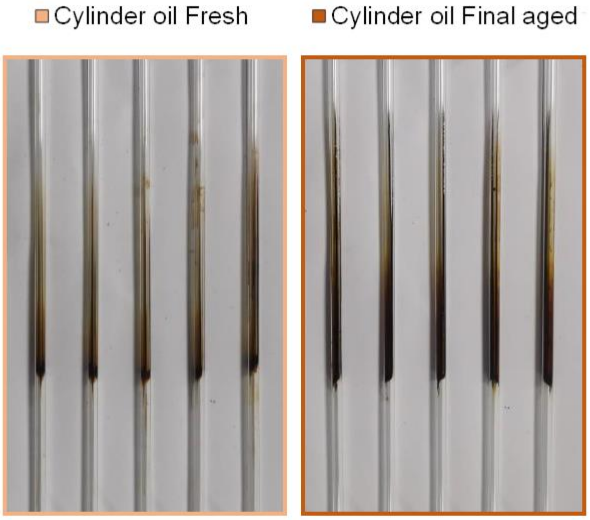


Figure 15a. Images for cylinder oil at 310°C in KHT.

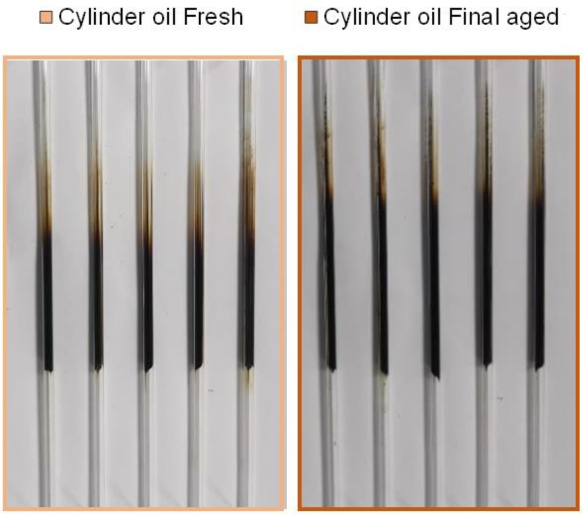


Figure 15b. Images for cylinder oil at 320°C in KHT.

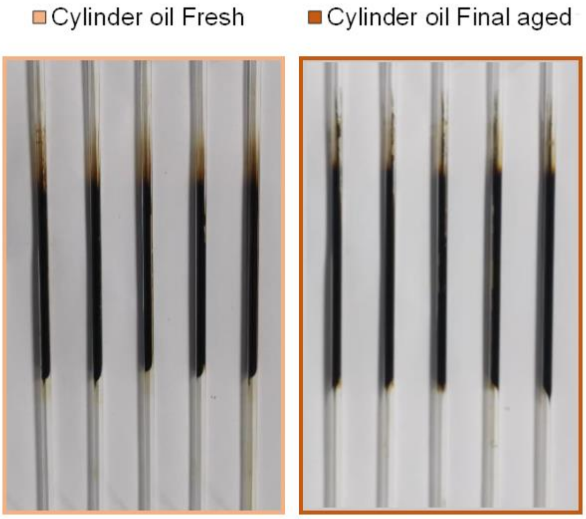


Figure 15c. Images for cylinder oil at 330°C in KHT.

As depicted in Figure 16, the Panel Coker Test (PCT) showed an increase in the coking value with the final-aged cylinder oil compared to the fresh cylinder oil. The tendency for deposit formation was higher in the final-aged cylinder oil than in the fresh cylinder oil.

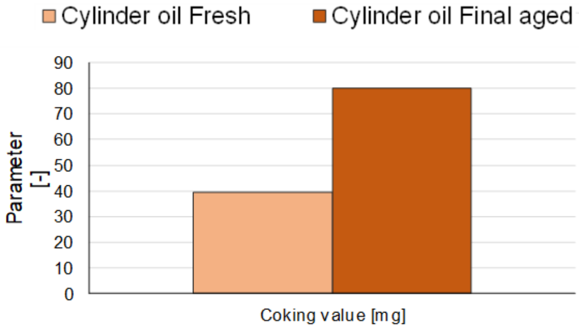


Figure 16. Coking value in PCT.

As presented in Figure 17, the Pressure Differential Scanning Calorimetry (PDSC) test showed a decreased oxidation induction time for the final-aged cylinder oil sample compared to the fresh cylinder oil. The oxidation stability was reduced in the final-aged sample compared to the fresh oil.

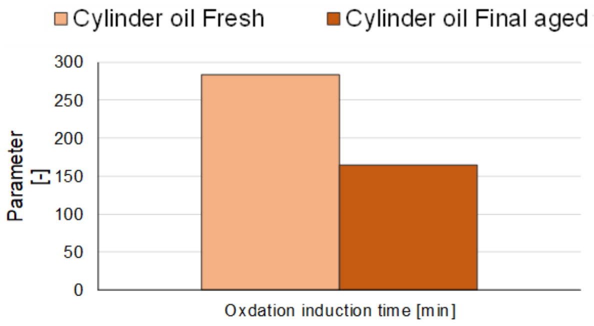


Figure 17. Oxidation induction time.

4 CONCLUSIONS

The FT-IR analysis of the cylinder oil revealed high oxidation, some aminification, and the presence of nitrogen compounds. Additionally, physical properties showed the presence of water and an increase in viscosity. In contrast, the system oil's FT-IR analysis indicated no oxidation but elevated aminification and some nitration, with no water detected. The physical properties of the system oil showed that its viscosity remained unchanged.

For the cylinder oil, the Total Base Number (TBN) showed a slight decrease despite oxidation, as this decrease was counteracted by ammonia, making TBN an unreliable indicator of oil condition alone. The Total Acid Number (TAN) indicated oxidation, with an increasing TAN at later stages of alteration. In contrast, the system oil exhibited a slight overall increase in TBN, with no oxidation observed and only the effects of ammonia being visible, which also renders TBN an unreliable indicator of oil condition. The TAN for the system oil showed no oxidation and only a slight increase in TAN at later stages of alteration.

The copper strip test results indicated that the final-aged cylinder oil was similar to the fresh oil, demonstrating that copper corrosion protection was not impacted. In contrast, the system oil showed signs of copper corrosion after artificial aging, particularly in the gas phase, indicating that copper corrosion protection was negatively affected.

In terms of friction, the cylinder oil was largely unaffected by artificial aging, while wear showed a slight elevation on both balls and discs following the aging process. In contrast, the system oil also exhibited friction that was largely unaffected by artificial aging, but wear was elevated on the balls and remained unchanged on the discs after the same process.

Deposit formation in the cylinder oil was elevated after artificial aging, a finding confirmed by all methods used, including MCT, the Oil Chute, Panel Coker, and KHT. The KHT specifically indicated elevated deposit formation at temperatures above 310°C. All methods demonstrated an increase in deposit weight. Additionally, the oxidation stability analysis using PDSC showed a decreased oxidation induction time, indicating an increased oxidation tendency in the final-aged sample compared to the fresh oil.

While not all bench tests indicate a performance detriment, certain tests do show some performance degradation for the final-aged oils. However, these results are not totally unexpected and are considered acceptable given the severe test conditions and extended alteration time, and they are consistent with findings from other sources. Overall, the laboratory bench tests did not reveal any severe impairment of the oils' performance. Although laboratory bench tests do not fully replicate real-world engine conditions, they provide valuable insights into key performance parameters that should be monitored.

5 ACKNOWLEDGMENTS

The authors of this paper would like to extend their sincere gratitude to the Austrian Center of Competence for Tribology (AC2T research GmbH) for their invaluable support and participation in this study.

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