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Lubricant Performance and Reliability in Ammonia-Fueled Internal Combustion Engines

Lubricants

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ABSTRACT

In order to achieve greenhouse gas reduction targets set by IMO, the maritime industry is intensively developing new propulsion solutions and innovative energy management technologies for future ships. One of the most effective levers is the use of low-carbon footprint fuels. The combustion of ammonia is widely studied and the first commercial ships will come into operation within the next 2 years. To ensure optimal and sustainable operation of future 2-stroke and 4-stroke engines, the impact of ammonia combustion on the lubricant must be analyzed to evaluate specific constraints and performance requirements.

This study investigates the effects of ammonia combustion on engine lubrication, drawing on specialized engine tests.

Key contributions of this study include:

- Lubricant behavior during durability tests with an ammonia dual-fuel engine
- Observation of wear and corrosion on engine parts and mitigation solutions through lubricant formulation
- Application of analytical techniques to ascertain both the chemical alteration of the lubricant and engine parts conditions after endurance testing.
- Execution of an innovative tribology test in an ammonia atmosphere to gauge the impact of this aggressive gas on oil film integrity and wear phenomena.

The findings offer new insights into the reliability of ammonia powered engines and the sensitivity of engine oil composition to ammonia compatibility.

INTRODUCTION

Ammonia has been studied as a fuel since the mid-20th century and has recently gained interest for decarbonizing large powertrains. The maritime sector plans to introduce its first commercial applications within the next two years to meet IMO and European Council decarbonization goals [1], [2]. Ammonia combustion has many advantages including no direct carbon emissions. It can also be stored as a liquid at around 15 bar at ambient temperature, and benefits from established global supply and storage infrastructure. However, challenges include safety due to ammonia toxicity and combustion management for emission control, stability, and engine durability.

TotalEnergies is studying the impact of ammonia combustion on lubricant performance and aging to provide sustainable technical solutions. This research, conducted in collaboration with Liebherr Machine Bulle, includes a bench test on a large offroad engine and laboratory bench test comparing tribological behavior in air and ammonia atmospheres.

MATERIALS AND METHODS

1. Durability engine test

The aim of this engine test is to comprehensively analyze the aging characteristics of a lubricant and evaluate its subsequent effects on the durability and performance of an ammonia-fueled combustion engine.

1.1. Test engine specification and setup

Liebherr Machine Bulle's pre-development teams adapted a series Diesel engine to run on Dual Fuel ammonia combustion, where the air-ammonia mixture is ignited by a Diesel pilot injection. This prototype retains the standard Diesel engine configuration, including the turbocharging system and combustion chamber, with no changes to component materials.

The characteristics of the prototype engine are described in the table 1.

Table 1: Test engine specification

	9 1
Cylinders	4
Displacement	9 dm3
Bore	135 mm
Stroke	157 mm
Rated Power	300 kW @ 1700-2100 rpm
Max. Torque	1739 Nm

The injection setup is presented in figure 1.

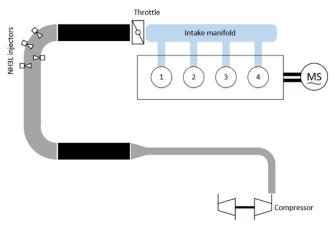


Figure 1: Ammonia injection setup

The injection parameters in dual fuel mode were adjusted to match the maximum cylinder pressure of the series engine under Diesel combustion. And the ammonia/Diesel fuel energy ratio was optimized to maximize lubricant exposure to ammonia while ensuring stable combustion during the endurance run. After calibration, this energy ratio was set at 90%. Table 2 summarizes the engine operating characteristics.

Table 2: Operating point definition

Engine speed	I I 00 rpm	
BMEP	22,5 bar	
Diesel pilot injection energy ratio	10%	
Ammonia fuel injection energy ratio	90%	
Engine efficiency	+3%	
(delta with reference Diesel engine)		
Max. cylinder pressure	1:1	
vs. Diesel engine max cylinder pressure		

1.2. Engine lubricants

Two lubricants developed by TotalEnergies to ensure proper engine lubrication under ammonia combustion with different additive technologies were used in this study (Oil A and Oil B). Both lubricants are SAE40 engine oils and containing the same mineral base oils meeting API group II requirements. The main characteristics of the two oils are listed in table 3:

Table 3: Engine oils characteristics

Name	Additives Technology	Base oil Technology	Viscosity grade	Kinematic viscosity at 100°C	Kinematic viscosity at 40°C	VI	TBN
	-	-	SAE J300	ASTM D7042	ASTM D7042	ASTM D2270	ASTM D2896
Unit	-	-	-	mm²/s	mm²/s	-	mg KOH/g
Oil A	Add 1	Blend I	40	14.44	134.0	107	12.5
Oil B	Add 2	Blend I	40	14.33	132.9	107	20

1.3. Oil analysis and performance tests

Throughout the test, the engine lubricant was sampled regularly for analysis to assess its aging. The altered oil samples were characterized by the conventional oil analytical methods listed below:

- Kinematic viscosity and density at 40 °C as well as 100 °C according to ASTM D7042 [3] to evaluate the impact of the alteration on the physical properties of the engine oils (calculation of the viscosity index was performed according to ASTM D2270 [4]).
- Total acid number (TAN) according to ASTM D664 [5] and total base number (TBN) corresponding to ASTM D2896 [6] to determine respectively the acidification and the depletion of base-reserve additives.
- Wear metals analysis according to ASTM D5185.

1.4. Results and Discussion

1.4.1. Analysis of Oil A

The following figures show the evolution of lubricant properties using Oil A over the first 150 hours. Figure 2 depicts the evolution of the acidity number (TAN) and basicity number (TBN). Both parameters remain stable in this study. Nitrogen oxides are the main products of ammonia combustion, but no nitroxidation was detected in the lubricant samples.

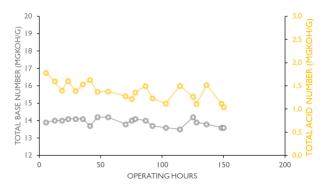


Figure 2: TBN (grey) and TAN (yellow) monitoring of Oil A

As illustrated by figure 3, the kinematic viscosities at 40°C and 100°C remain also stable, indicating no significant oil aging.



Figure 3: Relative kinematic viscosities at 40°C (grey) and 100°C (yellow) monitoring of Oil A

With no viscosity increase and stable TAN and TBN values over 150 hours, it suggests that the thermal and chemical conditions do not cause oxidative alteration of Oil A.

Figures 4 and 5 illustrate the evolution of metal concentrations in Oil A, showing a notable increase in copper and iron levels. These increases are consistent and higher than those in conventional diesel or gas engines.

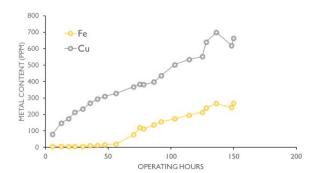


Figure 4: Copper (grey) and iron (yellow) concentrations monitoring of Oil A

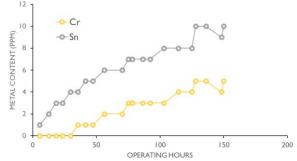


Figure 5: Tin (grey) and Chromium (yellow) concentrations monitoring of Oil A

Copper concentration increases steadily from the start (figure 4). The detection of copper in the oil, as documented by Obrecht et al. in their 2022 study

[7], [8] aligns with expectations due to ammonia's known corrosive effects on copper.

Iron appears after about 50 hours, indicating reduced lubricant protection over time. This may be due to the tribofilm's lack of resilience under ammonia conditions.

Tin and chromium also increase (figure 5), though at moderate levels. Tin rises from the start, suggesting bearing wear. Chromium, found on fire rings, indicates wear at the ring-liner contact. This specific wear may be due to the ammonia accumulation on the ring-liner contact at the topring level.

The initial plan was for the endurance test to last 250 hours. Since metal concentrations increase steadily and aging properties remain constant, extending the test by 100 hours with the same lubricant wouldn't provide new insights. Therefore, we switched to Oil B with the new additive technology ADD 2, designed to better protect against metal attacks.

1.4.2.Lubricant B

Comparing the relative kinematic viscosity of Oil A and Oil B at 40°C (Figure 6) and 100°C (Figure 7), we notice almost no difference.



Figure 6: Relative kinematic viscosities at 40°C of Oil A (blue) and Oil B (green)

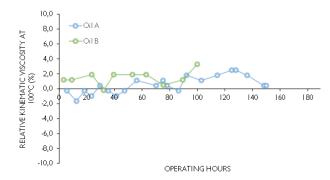


Figure 7: Relative kinematic viscosities at 100°C of Oil A (blue) and Oil B (green)

Considering the evolution of TAN (Figure 8) during the engine test for Oil A and Oil B, no significant change in acidity is observed. On the other hand, the TBN (Figure 9) in Oil B samples decrease regularly compared to Oil A which is quite stable. This behavior can be attributed to the different chemical nature of the additive technologies used in both lubricants.

Given the higher initial TBN of Oil B, the decrease is reasonable and does not lead to an increase in acidity, as previously noted. Considering the chemical composition of Oil B, it is likely that beyond the first 100 hours, the TBN would continue to decrease and stabilize at 14 like Oil A, maintaining its alkalinity reserve. However, this hypothesis needs to be verified through additional tests.

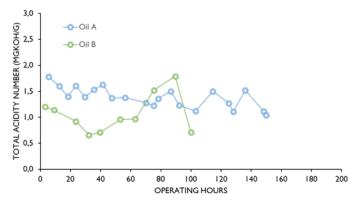


Figure 8: Comparison of the TAN of Oil A (blue) and Oil B (green)

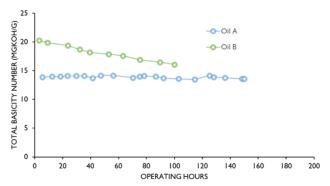


Figure 9: Comparison of the TBN of Oil A (blue) and Oil B (green)

The figures 10a, b, c and d depict the evolution of wear metal element during the engine test comparing Oil A to Oil B.

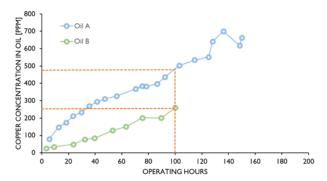


Figure 10a: Copper concentrations comparison of Oil A (blue) and Oil B (green)

We observe a slower increase in copper concentrations with Oil B compared to Oil A.

The same trend is observed with Iron on the Figure 10b below.

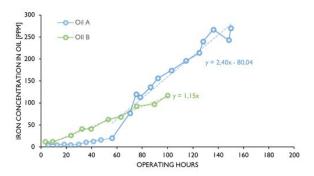


Figure 10b: Iron concentrations comparison of Oil A (blue) and Oil B (green)

Additionally, the chromium concentration also progresses more slowly with Oil B compared to Oil A (Figure 10c), indicating a more resilient tribofilm for ring-liner contact.

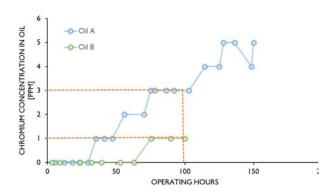


Figure 10c: Chromium concentrations comparison of Oil A (blue) and Oil B (green)

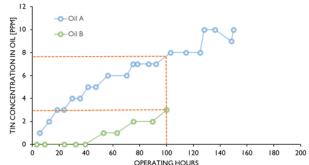


Figure 10d: Tin concentrations comparison of Oil A (blue) and Oil B (green)

After 100 hours of operation, Oil B shows half the tin concentration of Oil A.

These results suggest that the additive technology in Oil B better mitigates wear phenomena compared to the additive system in Oil A by almost 50% considering copper, tin and chromium concentration at 100 hours (orange dash lines on figures 10a, c and d).

1.5. Engine inspection

Finally, at the end of the endurance test, the engine was disassembled by the Liebherr teams and the parts inspected one by one. The engine components did not show significant degradation. In particular, the turbocharger is in perfect condition. The only exceptions are on the moving parts.

The pistons do not show any carbon deposit as we could expect. Carbon deposits are only observed on the intake valves. Therefore, the piston bottoms show a black deposit which suggests significant thermal stress (Figure 11).



Figure 11: Piston bottom of cylinder 1

The connecting rod small end and big end bearings show significant wear areas. The top rings show more wear than expected for this endurance period. Indeed, the polishing height of the top rings which corresponds to the worn surface exceeds half the height of the ring (Figure 12).

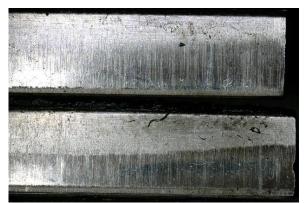


Figure 12: Top rings from cylinders 1 and 2

The top of the liners shows a clear coloration potentially attributable to corrosion (Figure 13).

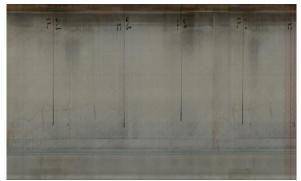


Figure 13: Liner from cylinder 2

These degradations correlate with the lubricant analyses. Based on previous observations, it is likely that most of the degradation occurred during the first 150 hours with Oil A.

2. Friction performance and tribofilm formation

An innovative tribological method is also presented in this paper. The objective is to assess the effect of ammonia in oil friction performance and the impacts on the tribofilm formation.

2.1. Tribometer setup

A conventional ball-on-disk SRV tribometer was modified to measure the coefficient friction under controlled atmosphere including ammonia atmosphere. The advantage of this tribometer is that it allows for the retrieval of the ball and disk after testing, enabling the determination of the tribofilm's composition and thickness using X-ray photoelectron spectroscopy (XPS).

As illustrated in figure 14, the tribometer was placed in a sealed chamber to regulate the surrounding atmosphere.

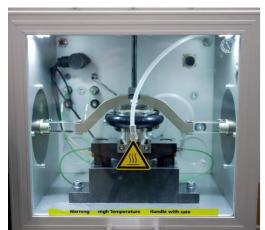


Figure 14: SRV Tribometer with controlled atmosphere

A commercial SAE40 engine oil (Oil C) was tested under two conditions: a 100% air atmosphere and a 100% ammonia atmosphere (NH3).

2.2. Result and Discussion

Figure 15 represents the friction coefficient of Oil C under air atmosphere (blue curve) and ammonia atmosphere (green curve) while Figure 16 illustrates the average friction coefficient for each test without running-in (600-10800s of test sequence). The friction coefficient remains relatively stable, suggesting minimal evolution of the tribofilm during the tests. The test conducted under ammonia atmosphere results in a 20% higher average friction coefficient (excluding the running-in sequence) compared to the test conducted under air. These results prove that replacing air with ammonia affects the friction properties of a lubricated contact.

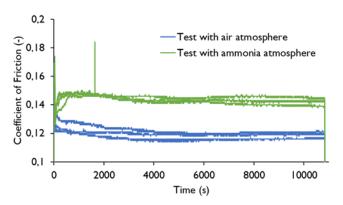


Figure 15: Comparison of the friction coefficient under air (blue) and ammonia (green) atmospheres.

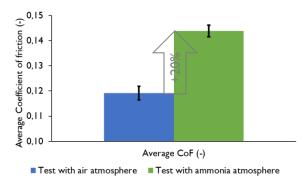


Figure 16: Comparison of the averaged friction coefficient under air (blue) and ammonia (green) atmospheres.

At the conclusion of the test, the disk-ball system is retrieved for each sample. The scar characteristics on both the disk and the ball are measured, in particular, the wear scar diameter and the wear volume. Figures 17a, 17b, and 17c respectively show the wear scar diameter, wear scar area, and wear volume measured on the ball. Similarly, Figures 18a, 18b, and 18c illustrate these measurements on the disk.

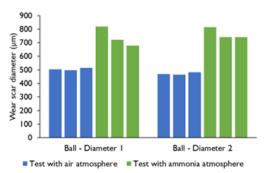


Figure 17a: Ball wear scar diameter under air (blue) and under ammonia (green) atmospheres

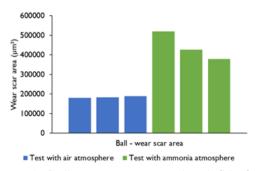


Figure 17b: Ball wear scar area under air (blue) and under ammonia (green) atmospheres

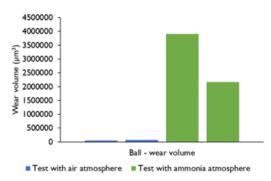


Figure 17c: Ball wear volume under air (blue) and under ammonia (green) atmospheres.

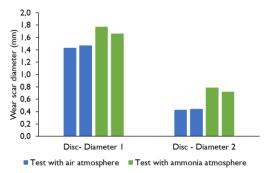


Figure 18a: Disk wear scar diameter under air (blue) and under ammonia (green) atmospheres

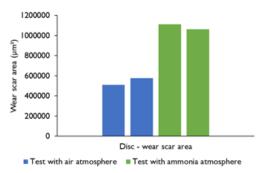


Figure 18b: Disk wear scar area under air (blue) and under ammonia (green) atmospheres

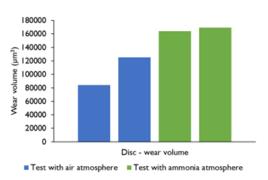


Figure 18c: Disk wear volume under air (blue) and under ammonia (green) atmospheres

The results indicate a significant difference, especially on the ball (figures 17a, b and c), highlighting the behaviour of the ammonia atmosphere to provide higher wear than air. These findings are consistent with engine test results.

Figure 19 compares the nitrogen concentration in the tribofilm for both tests using XPS technique. Despite the high nitrogen content in the air, no nitrogen is absorbed into the tribofilm. Conversely, in an ammonia atmosphere, nitrogen atoms are detected, suggesting that ammonia is absorbed into the tribofilm and potentially reacts with the lubricant constituents.

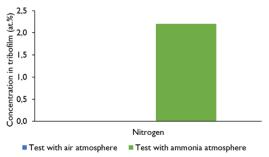


Figure 19: Nitrogen concentration in tribofilm measured with XPS

By analyzing the iron concentration at various depths starting from the surface of the disk (depth = 0 nm), the thickness of the tribofilm can be estimated. The iron concentration steadily increases within the tribofilm and stabilizes at a high level once the bulk material is reached, indicating the boundary of the tribofilm.

Figure 20 illustrates the results obtained for both air and ammonia atmospheres. Based on these two curves, the thickness of the tribofilm is estimated to be approximately 30 nm in the ammonia atmosphere. while for the air atmosphere test, the tribofilm thickness appears to exceed 70 nm. For the latter, the curve does not stabilize because it reaches the detection limit of the XPS technique.

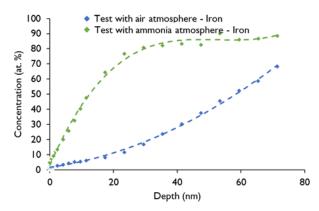


Figure 20: Iron concentration in tribofilm measured with XPS

These findings reveal the significant impact of ammonia on the wear sensitivity of lubricated moving parts. The tribofilm appears to be compromised in both thickness and structural integrity, indicating diminished lubricating efficacy. Consequently, ensuring effective engine wear protection in the presence of ammonia poses a substantial challenge for the development of appropriate ammonia-compatible engine lubricants.

CONCLUSIONS

A 250-hour durability test was conducted on a 4stroke 4-cylinder Diesel engine retrofitted for dualfuel ammonia combustion mode. The use of two different engine lubricant technologies demonstrated the potential to mitigate wear and through corrosion oil formulation. These phenomena were significantly reduced with Lubricant B, which contains a new additive technology that decreases wear and corrosion by more than 50% in the endurance test.

Additionally, a new tribological test conducted under ammonia conditions revealed the impact of ammonia on lubricated contacts, showing degradation in the tribofilm's thickness and composition.

To continue our investigation, new tribological tests will be done with atmospheres more representative of combustion gases and new formulations in order to provide enhanced tribofilm's resistance.

As experienced in this study, fostering close collaboration between oil manufacturers and engine designers is crucial. Such partnerships will enable the development of integrated technical solutions that optimize the durability and performance of ammonia combustion engines. By working together, these stakeholders can address the unique challenges posed by ammonia as a fuel, ensuring that engines are both efficient and long-lasting.

ACRONYMS, ABBREVIATIONS

TAN: Total Acid Number

TBN: Total Base Number

VI: Viscosity index

BMEP: Brake Mean Effective Pressure

SRV: Schwingung (Oscillation), Reibung (Friction),

Verschleiß (Wear)

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