Keywords: ammonia, engine, combustion, lubricant, oil, marine, off-road, tribology

Impact of ammonia combustion on lubricant performance and engine durability

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Abstract

Ammonia as a fuel has been studied since the middle of the twentieth century. This technology has found renewed interest in recent years as a way to decarbonize large powertrain applications. The maritime sector will reveal its first commercial applications within the next 2 years in order to provide practical solutions to decarbonize large energy consumers (especially maritime transportation) in compliance with different legislations and greenhouse gas reduction objectives from IMO and European Council. Ammonia does not produce any direct carbon emissions during its combustion; it can be stored in liquid phase at a pressure of approximately 15 bar at ambient temperature; and it benefits from mature supply and storage infrastructures across the globe. Nevertheless, its use involves challenges such as safety linked to ammonia toxicity and combustion management, particularly for emission control, stability and engine durability. TotalEnergies, as a lubricant manufacturer, aims at identifying the ammonia combustion impacts on lubricant performance and aging, with the objective to provide technical solutions that meet the requirements of ammonia applications in a sustainable manner.

This study investigates the influence of ammonia combustion on lubricant performance, particularly its role on engine durability. The results are based on experimental studies carried out on large an off-road engine in collaboration with Liebherr Machine Bulle and a laboratory bench test comparing tribological behavior under air and ammonia atmosphere. The results of these investigations provide lessons on:

- The evolution of lubricant behavior during a durability test using an ammonia Dual Fuel combustion engine
- wear and corrosion phenomena observed on disassembled engines parts and solutions to mitigate them through lubricant formulation
- The relationship between metal surfaces alteration and the tribofilm structure in the presence of ammonia.

1. Lubricant aging during ammonia combustion endurance test

A durability engine test has been developed to study the lubricant behavior under severe ammonia combustion conditions along an extended period of time. The goal of this test is to evaluate the capacity of the engine oil to maintain its performance and the ageing intensity. The test was carried out on a prototype engine whose characteristics are described in the table 1.

Table 1: Test engine specification

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

Liebherr Machine Bulle pre-development teams modified a series Diesel engine in order to operate in Dual Fuel ammonia combustion, i.e. the combustion of the air-ammonia mixture is ignited by a Diesel pilot injection. This prototype engine uses the standard configuration of the Diesel engine in terms of turbocharging system and combustion chamber. No specific change in components material was done on this prototype engine.

1.1. Engine setup and operating conditions

Prior to the endurance test, Liebherr Machine Bulle pre-development teams investigated different strategies and hardware configurations of ammonia injection: gas or liquid phase injection, single-point or multi-point injection, adaptations of the intake line for mixture optimization. For this endurance test, the authors jointly selected a single-point liquid phase ammonia injection to ensure homogeneous air-ammonia mixture cylinder-to-cylinder and a good combustion stability over long duration tests. The injection setup is presented in figure 1.

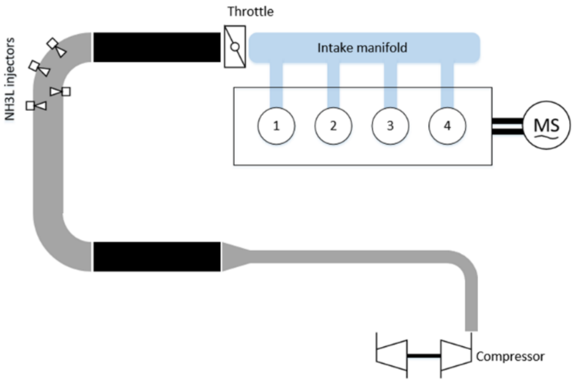

Figure 1: ammonia injection setup for endurance test

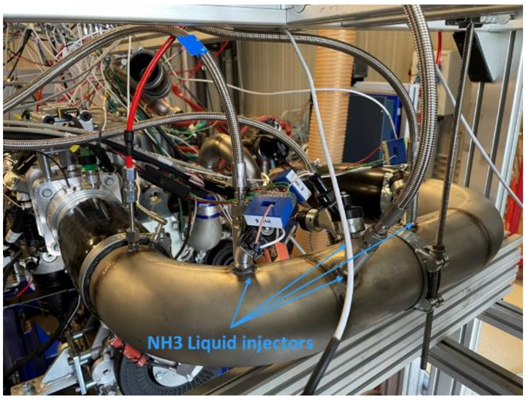

Figure 2: ammonia injectors location

The concept of the durability test was designed on a on a single operating point run for a period of 250 hours. To ensure sufficient severity and stress on the lubricant, several requirements were considered for the calibration of the operating point. A low rotational speed and high load generates high thermal and blow-by gas stress in the oil film around the piston – liner assembly on lubricated contacts. The engine calibration allowed to reach 22.5 bar of BMEP at 1100 rpm which was considered sufficiently representative of high load conditions in field applications. The injection parameters in dual fuel mode were set to operate at the maximum cylinder pressure used by the series engine under Diesel combustion as illustrated in Figure 3. Finally, the ammonia / Diesel fuel energy ratio was optimized to maximize the exposure of the lubricant to ammonia, while allowing a stable combustion throughout the endurance run. That energy ratio was set at 90% after calibration. The summary of engine operating characteristics is presented in Table 2.

Table 2: operating point definition

Engine speed	1100 rpm
BMEP	22,5 bar
Diesel pilot injection energy ratio	10%
Ammonia fuel injection energy ratio	90%
Engine efficiency (delta with reference Diesel engine)	+3%
Max. cylinder pressure vs. Diesel engine max cylinder pressure	1:1

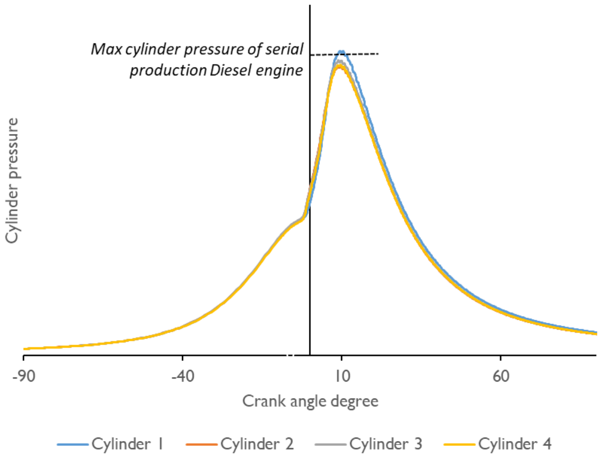

Figure 3: Cylinder pressure measurement on endurance operating point

The entire endurance test lasted 250 hours during which the engine ran on the operating point described above for 8 to 10 hours per day. Throughout the test, the engine lubricant was sampled regularly for analysis to assess its aging. Lubricants technologies were developed by TotalEnergies to ensure proper engine lubrication under ammonia combustion and used in this study. After 150 hours of operation, observing that the analysis showed regular and predictable behavior, a change from Lubricant A to Lubricant B was decided in order to test the impact of engine oil formulation on ageing pattern. Both lubricants used in that study are SAE 40 engine oils sharing the exact same base oil blend technology based on classical API group I, group II base oil slates. Except for the antiwear, different additive technologies were used between lubricant A and lubricant B leading to different total base number (TBN) values as detailed in Table 3.

Table 3: Engine oil characteristics

Name	Base oil blend technology	Antiwear additive	Additive technology	Kinematic Viscosity at 100°C	Kinematic Viscosity at 40°C	VI	TBN
				ASTM D7279	ASTM D7279	ISO 2909	ASTM D2896[1]
Units				mm^2/s	mm^2/s	-	mg KOH/g
Lubricant A	Blend I	AW I	ADD 1	14.44	134.0	107	12,5
Lubricant B	Blend I	AW I	ADD 2	14.33	132.9	107	20.0

At the start, in the middle and at the end of the endurance test, a measurement of NH_3 concentration was carried out in the crankcase ventilation circuit to quantify ammonia concentration to which the lubricant is exposed. Finally, at the end of the endurance test, the engine was disassembled for inspection. The objective was to analyze the condition of the different components to evaluate potential impacts of ammonia combustion on their integrity.

1.2. Lubricant A samples analysis

The following figures present the evolution of lubricant properties when using Lubricant A for the first 150 hours. Figure 4 shows the evolution of the acidity number (TAN) and the basicity number (TBN) of the lubricant. Unlike lubricants in Diesel or gas engines where the TAN increases and the TBN decreases with respect to the neutralization of acids, in this study, both parameters remain stable. Nitrogen oxides remain the main products of ammonia combustion, however, samples analysis does not reveal any trace of nitroxidation within the lubricant.

On the other hand, lubricant kinematic viscosities at 40 °C or 100 °C remains stable throughout the 150 hours hence showing no signs of significant oil ageing. Considering no viscosity increase and quite stable TAN and TBN values over the initial 150 h, it can be assumed that the thermal and chemical conditions do not meet oxidative alteration limits for the lubricant, despite severe operating conditions. It should also be noted that lubricant samples do not reveal presence of soot and no water was detected in the samples either, despite water vapor being a main product of ammonia combustion. This is explained by high load engine operation and therefore continually high engine coolant temperature (87 °C) and high oil temperature (95 °C).

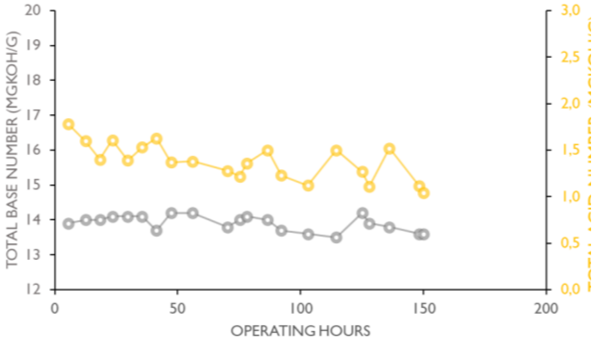

Figure 4: TBN and TAN monitoring of Lubricant A

Figure 5: Relative kinematic viscosities at 40°C and 100°C monitoring of Lubricant A

Figures 6 and 7 show the evolution of metal contents concentrations in lube oil. Interestingly, a clear increase in the concentrations of copper and iron can be observed. The progressions of these concentrations are regular and greater than those found in conventional diesel or gas combustion engines.

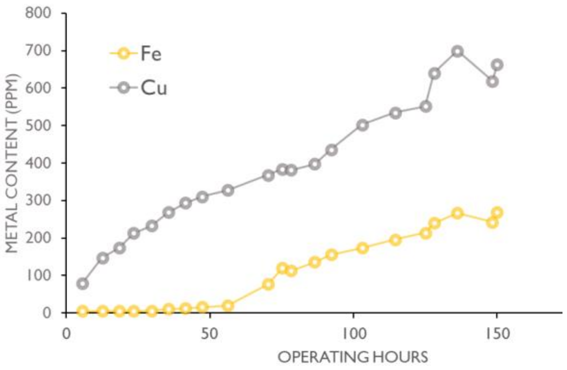

Figure 6: Copper and iron concentrations monitoring of Lubricant A

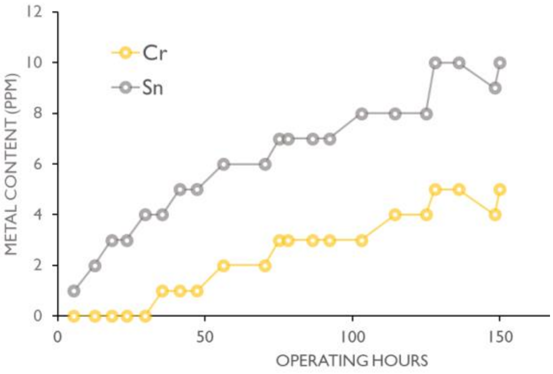

Figure 7: Chromium and tin concentrations monitoring of Lubricant A

In the case of copper, the concentration progresses quite regularly from the start of the tests. The presence of copper in the oil had been observed in a study carried out by Obrecht et al. in 2022 [1] and is expected given the corrosive nature of ammonia towards copper. Iron is present in several engine parts made of different steels. Iron in the lubricant is not immediate but appears after about fifty hours, thereby suggesting a degradation of the lubricating protection performance over time. The lack of resilience of the tribofilm under ammonia operating conditions is a potential hypothesis leading to a lower protection of the lubricated metal surfaces in motion.

Other metals such as tin and chromium also show a significant progression even if the concentrations remain moderate. Like copper, the tin concentration increases from the beginning of the tests, suggesting wear of the bearings. The chromium concentrations are significantly lower but nevertheless higher than a wear threshold considered significant at 3 ppm. Chromium is present on the fire rings. Its presence in the oil suggests wear at the ring-liner contact. In the case of ammonia combustion engines, the greater quenching distance is likely to generate ammonia accumulation area in the top land, without combustion. We can then question the impact of the presence of ammonia on the ring-liner contact at the top-ring level.

Since metal concentration progressions are regular and ageing properties are relatively constant, operating an additional 100 hours with the same lubricant would certainly not provide any new information. A change of lubricant was decided to test the impact of a new additive technology ADD 2 in the formula of lubricant B. The new additive technology ADD 2 aims to protect lubricated surfaces, having noted attacks of several metals.

1.3. Lubricant B samples analysis

Over the remaining 100 h of the endurance test, the lubricant B oil samples show kinematic viscosity profiles quite similar to Lubricant A sample during the initial 150h of the test as illustrated by Figures 8 and 9. This observation confirms that additivation B does not affect its viscosity performance of the engine oil.

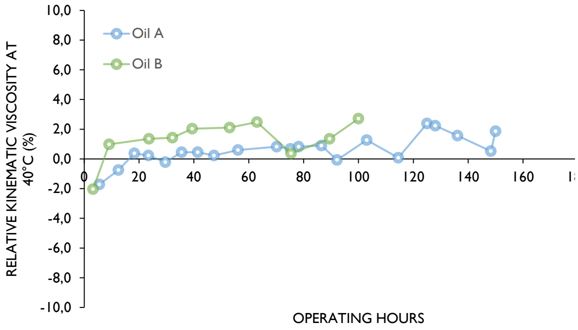

Figure 8: Relative kinematic viscosity at 40 °C of Oil A and Oil B

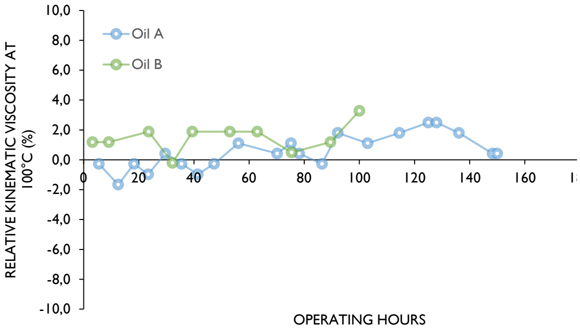

Figure 9: Relative kinematic viscosity at 100 °C of Oil A and Oil B

Figures 10 and 11 compares the evolution of acidity and basicity during the engine test for lubricants A and B. Whereas, no significant evolution of the acidity number is observed on Lubricant B oil samples, a regular decrease in the total based number is observed for Lubricant B. This behavior differs from Lubricant A and can be explained by the difference in the chemical nature of additives technologies used in both lubricants. Considering the higher initial TBN of Lubricant B, the decrease is considered quite reasonable and does not generate any increase in acidity number as emphasized previously. Considering chemical composition of Lubricant B, it is very likely that beyond the first 100 hours the TBN would continue to decrease to stabilize at 14 like lubricant A, maintaining its alkalinity reserve. Nevertheless, this hypothesis shall be verified thank to additional tests.

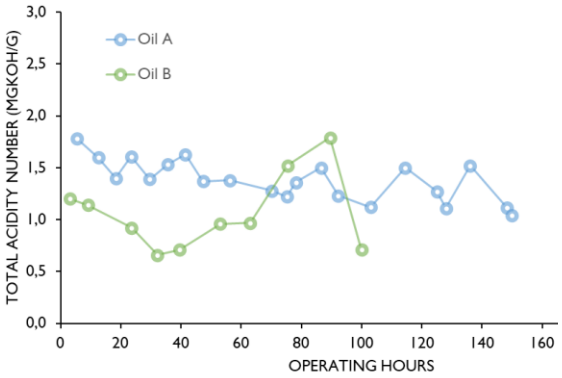

Figure 10: Total acidity number (TAN) comparison of Oil A and Oil B

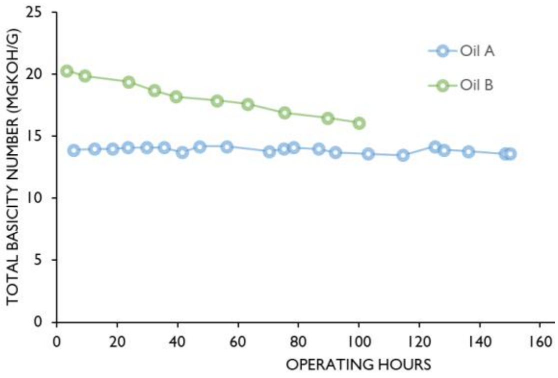

Figure 11: Total basicity number (TBN) comparison of Oil A and Oil B

Wear metal elements measured during the engine test on lubricants A and B oil samples are reported on Figures 12a, b, c and d. We clearly observe a slower progression of copper and iron concentrations with lubricant B compared to lubricant A. Additionally, the progression of the chromium concentration is also lower with lubricant B which therefore seems to ensure a more resistant tribofilm for ring-liner contact. Finally, after 100 h of operation on both oils, lubricant B shows twice as less tin concentration than with lubricant A. This suggests that the additive technology of the lubricant B allows an improved wear phenomena mitigation compared to lubricant A additive system.

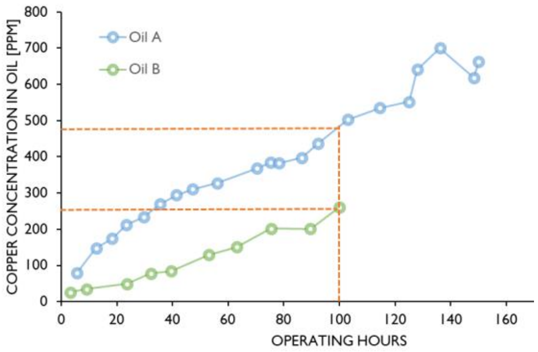

Figure 12a: Copper concentrations comparison of Oil A and Oil B

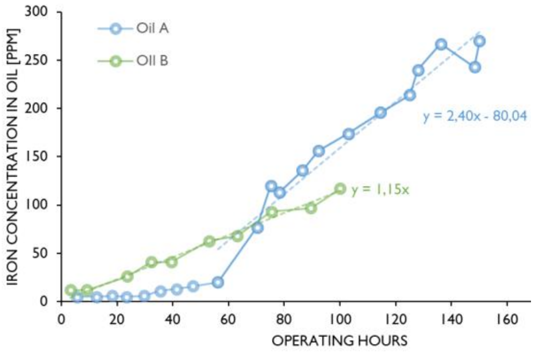

Figure 12b: Iron concentrations comparison of Oil A and Oil B

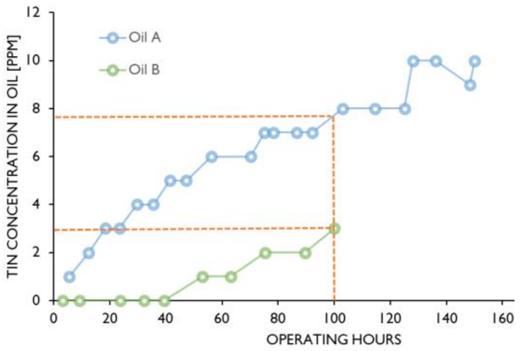

Figure 12c: Tin concentrations comparison of Oil A and Oil B

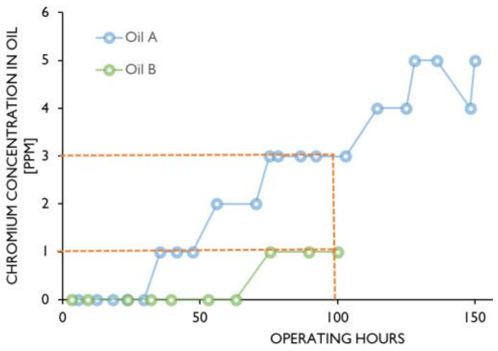

Figure 12d: Chromium concentrations comparison of Oil A and Oil B

1.4. Ammonia concentration measurements of crankcase gases

In order to know what concentration of ammonia the lubricant is exposed to in the crankcase, a specific measurement setup was installed for these tests. The ammonia concentration measurement was carried out at the start of the test, after 125 hours, and at the end of the test. Figure 13 shows the ammonia concentrations measurements for the 3 samples.

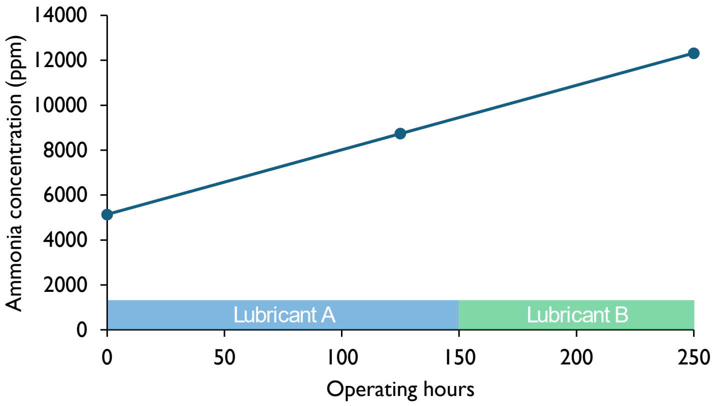

Figure 13: Ammonia concentration measurements in crankcase ventilation gases

The results show a clear increase in the NH_3 concentration throughout the endurance test. The concentration at the end of the test is consistent with the level measured during a study carried out in 2022 [1]. It is difficult to identify the reason for the concentration increase. However, this could be linked to the suggested wear phenomenon in the ring-liner- contact and therefore a degraded sealing of the combustion chamber. As a result, it is confirmed that the lubricant is exposed to high concentrations of ammonia around the liner and in the crankcase. These conditions will subsequently be reproduced in laboratories to study more closely any potential alteration of the lubricant

1.5. Aged lubricant composition analysis

In order to provide better insights on the structural degradation of the lubricant, used oils at 150 hours and after 100 hours for lubricants A and B respectively, were studied by mass spectroscopy at TotalEnergies R&D center. The mass measurements were obtained using an Orbitrap Qexactive plus instrument equipped with an electrospray ionization (ESI) source. Acquisitions were carried out on negative detection mode to have a selective ionization of detergent molecules. Prior to analysis, sample were solubilized in a toluene/methanol mixture (50/50, v/v) at 0.1 mg/mL with addition of 2% of ammonium hydroxide dopant to favorize ionization. Orbitrap and source parameters were set as follows: capillary voltage fixed to 3 kV, sheath gas flow rates equal to 10, capillary temperatures equal to 350 °C, AGC target at 1e6 ms with a maximum injection time of 50 ms, and S-lens Rf at the maximum of 100%.

The results are depicted in figures 14a, b, c and d through Kendrick mass defect plots, which serve as molecular maps to align molecular families differing only by alkylation levels on the same horizontal line. Both native lubricants exhibit three distinct families: 2 types of detergent additives, and dithiophosphate (DTP) antiwear additive. Post-aging, Lubricant A shows a complete absence of DTP, indicating their full consumption, aligning with the emergence of polyphosphates undetectable under the current conditions. Aging also reveals the presence of nitro-oxidation products in detergents, hinting at ammonia's impact on these additives. This is further evidenced in figures 15a and 15c with compound class distribution for Lubricant A, which compares the relative abundance of each class pre- and post-aging. The classes O3, O1, and O2P1S2 correspond to detergents, and DTP antiwears, respectively. The absence of native DTP (O2P1S2) post-aging confirms their total consumption. Nitro-oxidation is identifiable with the emergence of O3N1 and O5N1 (detergents nitro-oxidation) classes.

In contrast, Lubricant B Kendrick mass defect plots (Figures 18 and 20) show significant differences, notably the presence of monothiophosphate (MTP) and phosphate, which are consistent with degradation intermediates preceding polyphosphate formation. This suggests that Lubricant B anti-wear additives are less degraded than those in Lubricant A. Figures 16 and 17 underscores this with compound class distributions that show a decrease in native DTP (O2P1S2) and the appearance of MTP (O3P1S1) and phosphate (O4P1). The detergents in Lubricant B also undergo nitro-oxidation, but with a lower relative abundance than in Lubricant A.

Overall, these results strongly evidence that Lubricant B is less degraded than Lubricant A focusing on detergent and antiwear additives. This is corroborated by the lower wear metal content observed in the standard oil analysis discussed previously.

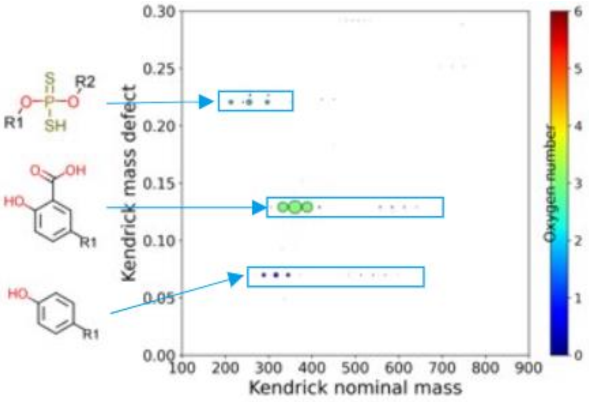

*Figure 14a: Kendrick mass defect of **Lubricant A - fresh***

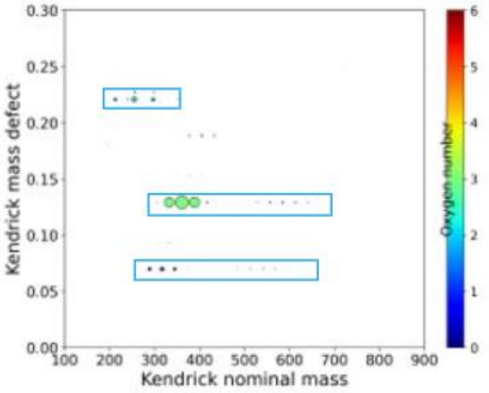

*Figure 14b: Kendrick mass defect of **Lubricant B – fresh***

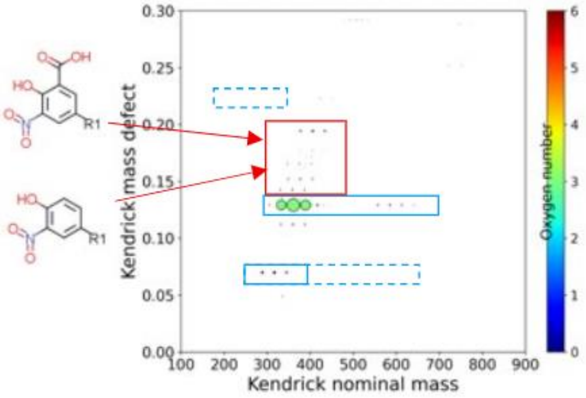

*Figure 14c: Kendrick mass defect of **Lubricant A - aged***

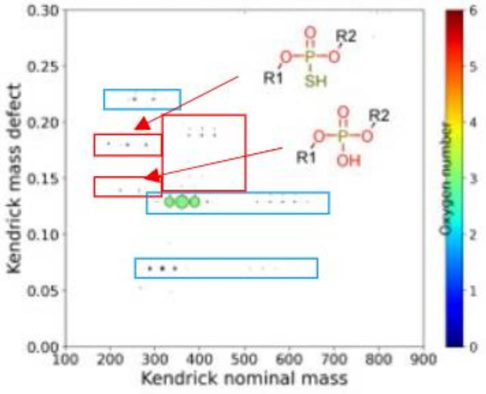

*Figure 14d: Kendrick mass defect of **Lubricant B – aged***

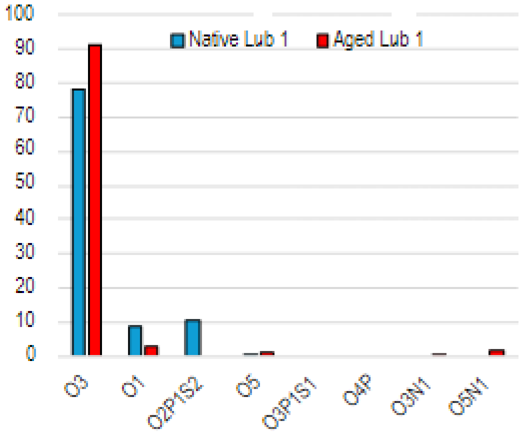

Figure 15: Component class distribution for ***Lubricant A***

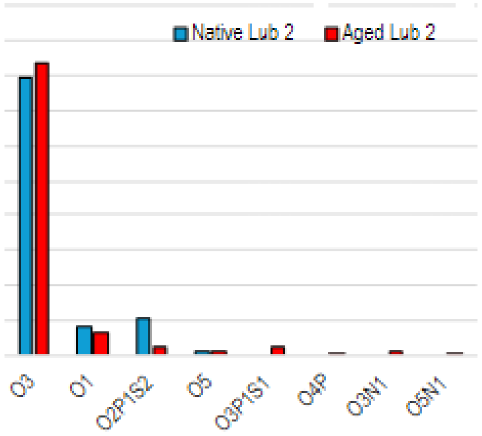

Figure 16: Component class distribution for ***Lubricant B***

1.6. Endurance 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. As a reminder, on this test engine, almost all the components (except the ammonia injection system) come from a series production Diesel engine, both in terms of design and materials.

Regarding air path component, unlike the study carried out in 2022 [1], the turbocharger is in perfect condition. No clearance from the shaft suggests any wear of the bearing. The engine head does not show any particular deterioration with the exception of wear at the head of the valve stems. This can be explained by engine operation on a single point at low speed, on which the expected axial rotation of the valve is limited. Carbon deposits are also observed on the intake valves, most certainly from the lubricant. On base engine components, there is no particular trace of deterioration. The honing of the liners is still visible, without significant wear while the top of the liners shows a clear coloration potentially attributable to corrosion. Moving parts are more altered. 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, as shown by the analysis results. Indeed, the polishing height of the top rings which corresponds to the worn surface exceeds half the height of the ring. The pistons do not show any carbon deposit as we could expect. However, the piston bottoms show a black deposit which suggests significant thermal stress.

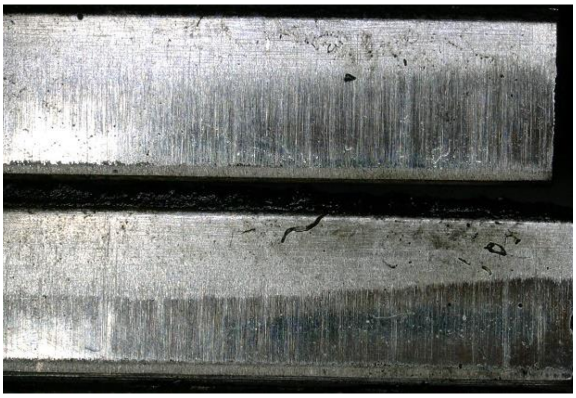

Figure 17a: Top rings from cylinders 1 and 2

Figure 17b: Piston bottom of cylinder 1

Figure 17c: Liner from cylinder 2

Overall, the engine components do not appear to have suffered any significant degradation with the exception of the connecting rod small end and big end bearings and the top rings. These degradations are correlated with the lubricant analyses. Based on the previous observations, it is likely that most of the degradations were performed during the first 150 h with Lubricant A.

2. Impact of ammonia on friction and tribolfilm performance

A first tribological study was therefore conducted by TotalEnergies to study the impact of a controlled ammonia atmosphere on lubricated contacts. The aim of this study is to understand whether the presence of ammonia impacts the friction performance and whether it can affect the tribofilm. A ball-on-disk tribometer was used to control precisely the contact speed and normal force applied on the lubricated contact. As depicted in figure 18, the tribometer is installed in a sealed chamber in order to control the atmosphere around the contact. For these first campaign, the same commercial lubricant is tested with a 100% air atmosphere and a 100% NH_3 atmosphere. These opposite conditions aim to study the impact of ammonia on the lubricated contact.

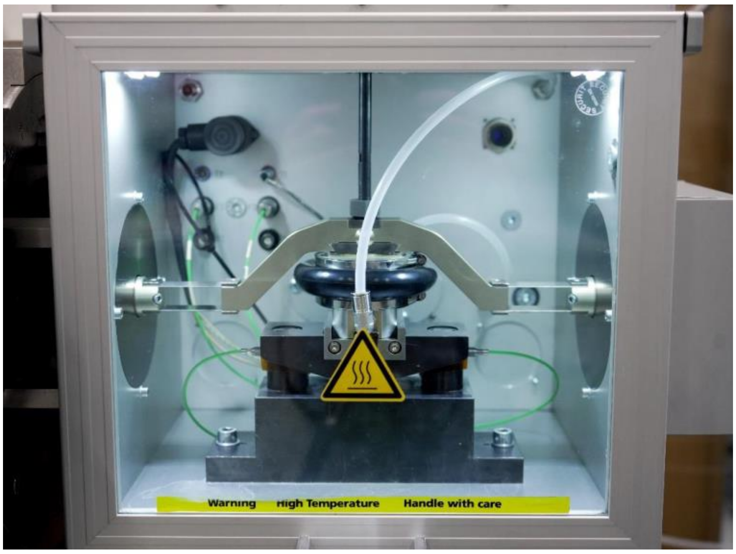

Figure 18: Tribometer with controlled atmosphere

The friction coefficient recordings along the two tests are shown in Figure 19. Figure 20 illustrates the average friction coefficient over each test. We observe a relatively flat evolution of the friction coefficient suggesting a limited evolution of the tribofilm during the test. The test performed under ammonia atmosphere leads to a 20% higher friction coefficient on average (running-in sequence excluded) compared to the test performed under air. This observation indicates that replacing air by ammonia, impacts the friction properties of a lubricated contact.

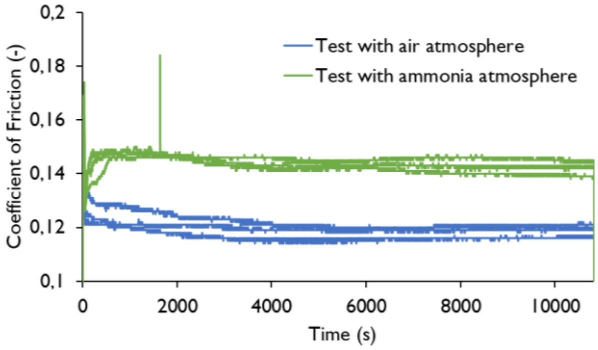

Figure 19: Friction coefficient calculation during the tests

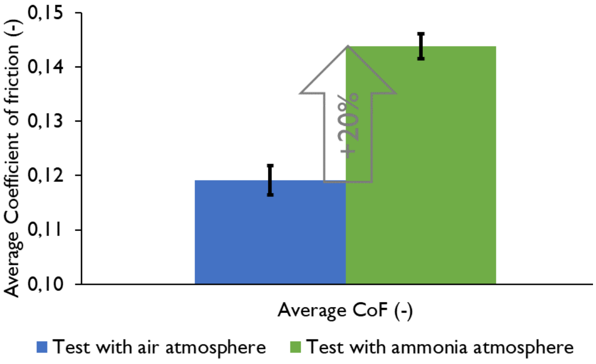

Figure 20: Averaged friction coefficient ; 600-10800 s of test sequence (without running-in)

At the end of the tests, the wear on the test parts is measured. The wear scar diameter is measured in 2 directions orthogonal to each other of the scar (diameter 1 and 2) for the 3 balls used in the tribometer. The results are presented in Figure 21a, b and c. All measurements (wear scar diameter, wear scar area and wear volume) are consistent with high wear in the presence of ammonia compared to the presence of air.

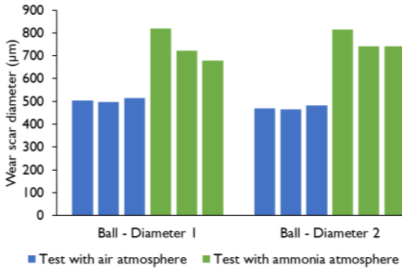

Figure 21a: Ball wear scar diameter measurements

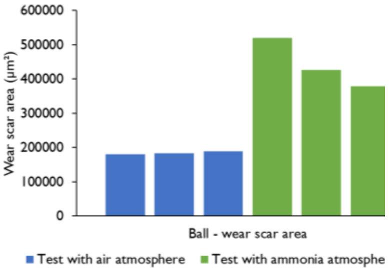

Figure 21b: Ball wear scar area measurements

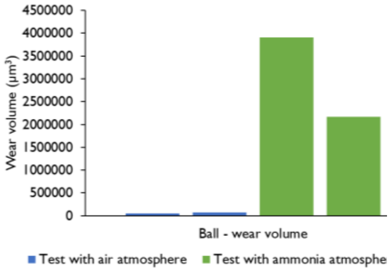

Figure 21c: Ball wear volume measurements

The disk is also analyzed after testing. The diameter of the wear scar, the surface and the wear volume are presented in Figures 22a,b and c. The differences in wear between the test parts in air atmosphere and in ammonia atmosphere are less significant but confirm greater wear in ammonia atmosphere.

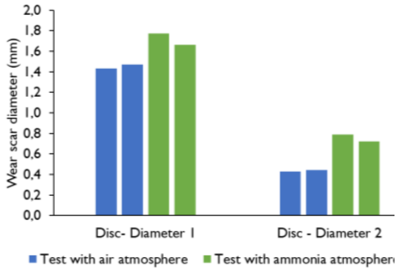

Figure 22a: Disk wear scar diameter measurements

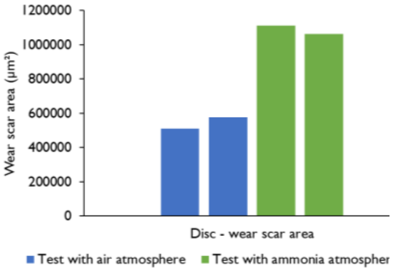

Figure 22b: Disk wear scar area measurements

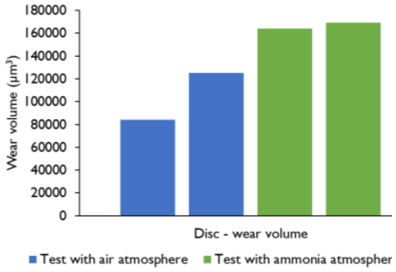

Figure 22c: Disk wear volume measurements

In order to better understand the behavior of the tribofilm for the two controlled atmospheres, the composition of the tribofilm was studied using the X-ray photoelectron spectroscopy technique (XPS). Figure 23 shows the comparison of the nitrogen concentration in the tribofilm for the two tests. Despite the high nitrogen content in the air, no nitrogen is absorbed in the tribofilm. On the contrary, in ammonia atmosphere, nitrogen atoms are detected, suggesting the absorption of ammonia in the tribofilm and a potential reaction with the lubricant constituents.

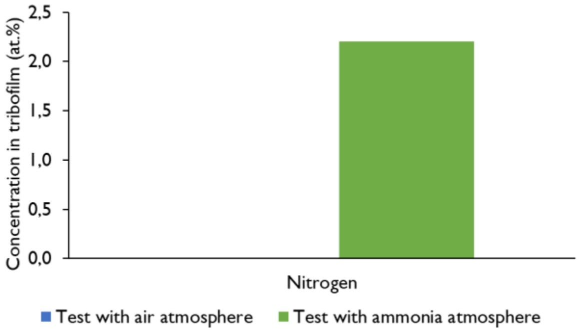

Figure 23: Nitrogen concentration in tribofilm measured with XPS

XPS analysis also makes it possible to measure the iron concentration at different depths. Thus, the thickness of the tribofilm can be estimated by identifying the depth at which the iron concentration stabilizes at a high concentration. In the case of the ammonia atmosphere test, the thickness of the tribofilm is therefore estimated at approximately 30 µm, while for the air atmosphere test, the thickness of the tribofilm seems to exceed 70 µm as illustrated on Figure 24. Thus, ammonia seems to have a significant influence on the tribofilm thickness.

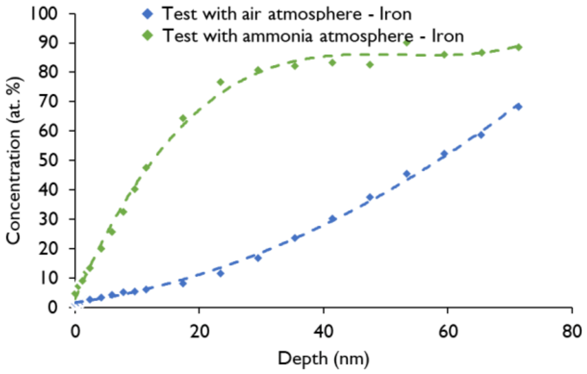

Figure 24: Iron concentration in tribofilm measured with XPS

Phosphorus and sulfur are constituents of the anti-wear additive that generally end up in the tribofilm. Figure 25 shows the phosphorus and sulfur concentrations for each tested atmosphere measured by XPS. In the case of the ammonia atmosphere, the concentration of phosphorus and sulfur decrease rapidly while the analysis is performed deeper. On the surface, the concentration can be higher compared to the reference test in air atmosphere. These results suggest an interaction of ammonia with the molecules present in the tribofilm.

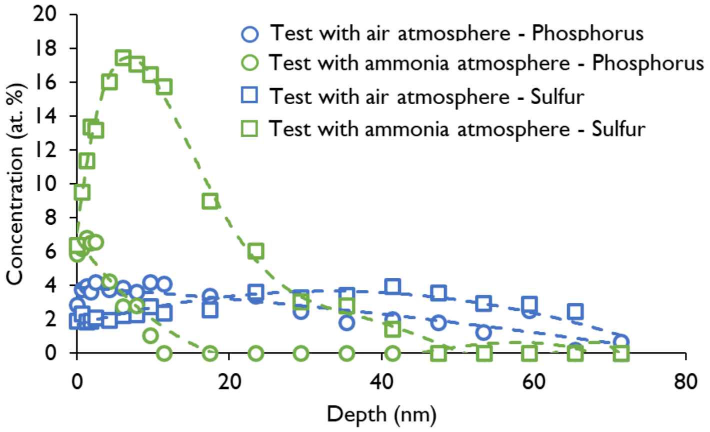

Figure 25: Phosphorus and sulfur concentrations in tribofilm measured with XPS

These results reveal an influence of ammonia on the wear sensitivity in the contacts of lubricated moving parts. The tribofilm seems to be altered, both in thickness and in its structure, suggesting a lower lubricating performance. As a consequence, engine wear protection in the presence of ammonia can set a challenge for the development of adequate ammonia engine lubricants.

3. Conclusions

The ageing of engine lubricant and engine wear protection performance were studied using a durability engine test, tribological testing and analytical techniques. A 250 h durability was developed on a 4-

cylinder Diesel engine retrofitted in dual fuel ammonia combustion mode. The use of 2 different engine lubricant technologies confirmed the possibility to mitigate wear phenomena through oil formulation. Standard oil analysis performed during the engine test did not reveal any significant ageing of the 2 lubricant technologies used. However, in-depth analytical techniques showed a total disappearance of the anti-wear additive and nitro-oxidation markers on the detergent molecules were observed. These phenomena are clearly limited with the lubricant B containing a new additive technology which also reduces wear and corrosion by more than 50% on the endurance test.

Furthermore, a new tribological test conducted under ammonia demonstrate the influence of ammonia on lubricated contacts, showing a degradation in the thickness and composition of the tribofilm.

Further studies will assess the degradation in composition and performance of the same lubricant when subjected to ammonia combustion as compared to Diesel combustion.

The new tribological test will be refined to consider atmospheres representative of the combustion gases and to evaluate molecules that enhance the tribofilm's resistance.

As experienced in this study, close collaborations between oil manufacturer and engine designer will allow concerted technical solutions to optimize the durability and performance of ammonia combustion engines.

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