lubricants

Article

The Impact of Ammonia Fuel on Marine Engine Lubrication: An Artificial Lubricant Ageing Approach

Adam Agocs [1,*], Maria Rappo [2], Nicolas Obrecht [2], Christoph Schneidhofer [1], Marcella Frauscher [1] and Charlotte Besser [1]

[1] AC2T Research GmbH, 2700 Wiener Neustadt, Austria
[2] TotalEnergies, 64018 Courbevoie, France
[*] Correspondence: adam.agocs@ac2t.at

Abstract: Ammonia is a prospective zero-carbon-emission fuel for use in large marine diesel engines. Current research focuses on several technical aspects, such as injection strategies or exhaust gas aftertreatment options, but investigations regarding the impact of ammonia on engine oil degradation are largely absent from the literature. This study provides a methodology with which to evaluate this phenomenon via artificial oil alteration. By using an admixture of various contaminations to air, such as ammonia and its partial combustion product nitrogen dioxide, their respective impacts on chemical oil degradation were assessed. Subsequently, the lubricating performance of altered oils was investigated, with a focus on corrosion properties, deposit formation, and load-bearing capability. Although the application of a stoichiometric ammonia–air mixture resulted in less pronounced thermo-oxidative degradation compared to alteration with neat air, static and dynamic deposit formation as well as corrosion properties and load-bearing capability were severely impacted by the presence of ammonia. On the contrary, nitrogen dioxide contamination resulted in higher oxidation and acidification of the oil, but altered samples performed considerably better than ammonia-altered aliquots in terms of coking tendencies, corrosivity, and load bearing.

Keywords: ammonia; engine oil degradation; internal combustion engine; combustion; corrosion; deposit formation; extreme pressure; oil ageing

Citation: Agocs, A.; Rappo, M.; Obrecht, N.; Schneidhofer, C.; Frauscher, M.; Besser, C. The Impact of Ammonia Fuel on Marine Engine Lubrication: An Artificial Lubricant Ageing Approach. *Lubricants* **2023**, *11*, 165. https://doi.org/10.3390/lubricants11040165

Received: 8 March 2023
Revised: 3 April 2023
Accepted: 5 April 2023
Published: 6 April 2023

1. Introduction

In April 2018, the International Maritime Organization (IMO) adopted its strategy to reduce carbon emissions by 40% by 2030 and by 70% by 2050 for individual vessels, and to reduce all greenhouse gas (GHG) emissions by 50% across the shipping industry by 2050 [1]. The use of zero-carbon fuels on a tank-to-wake basis is being strongly considered to achieve these goals.

From that perspective, ammonia has emerged as one of the zero- or near-zero-emission fuels of the future in line with global decarbonization objectives [2–4]. It offers great potential to power large oceangoing ships, as ammonia is composed of three hydrogen atoms connected to one nitrogen atom (NH_3) and hence is carbon-free. Accordingly, it represents one of the few chemical compounds whose combustion produces zero carbon emissions when used as a fuel in an internal combustion engine [4]. Ammonia possesses characteristics which make it one of the most promising solutions to the question of powering large vessels: its worldwide commercial availability [5], mainly driven by the fertilizer industry [2]; the possibility to produce it in a green way [6–8]; its acceptable energy density, which is slightly lower than that of methanol and higher than that of hydrogen [3,9]; and the relative ease of managing it [5].

Equation (1) shows the combustion process of ammonia and the corresponding reaction enthalpy (ΔH^0) for standard state reactants and products.

Equation (1). Combustion of ammonia.

$$2NH_3(g) + \frac{3}{2}O_2(g) \rightarrow N_2(g) + 3H_2O(g)(\Delta H^0_{\text{reaction}} = -316.8\frac{\text{kJ}}{\text{mol}}) \tag{1}$$

NH_3 combusts through NH_2, NH, HNO, NO, NNH and N_2O intermediates into N_2 and H_2O [10]. The kinetics of ammonia-rich mixtures are generally dominated by NH_X—NH_X bonding reactions (H-transfer) [10]. NO mainly forms from HNO, OH, and N radicals [11]. Rich conditions can lead to a significant reduction in NOx emissions [11], as N_2 can form through the intermediary NNH where NO generation is not involved [10]. Ammonia has a comparatively low linear burning velocity [12], which provides challenges during combustion; however, these issues can be overcome by adding secondary fuels, such as hydrogen or methane [10].

Although ammonia is toxic (permissible exposure limits (PEL) of ~50 ppm; immediate danger to life or health (IDLH) limit of 300 ppm) and environmentally harmful, it is assumed that health, safety, and environmental issues can be properly controlled [2].

The method of handling ammonia has been known for decades within the chemical industry. However, little is known about the application of ammonia as a fuel; hence, this issue must be properly addressed [2]. Current research mainly focuses on injection strategies and ignition behavior as well as exhaust gas aftertreatment requirements [3,5,13]. In particular, nitrogen oxides (NO_X) are problematic compounds which are produced in enlarged amounts when ammonia is combusted, making a proper exhaust gas purification via selective catalytic reduction (SCR) highly recommendable [3]. As an alternative to high-cost catalyst systems, scientific work is ongoing to reduce NO_X emissions by preheating the ammonia for a partial decomposition before combustion [14,15].

Investigations into the interaction between engine lubricants and ammonia are largely absent from the literature as ammonia-fueled marine engines are not yet commonly utilized. Studies on that topic are deemed necessary since conventional engine oils are formulated to use hydrocarbon-based fuels and their respective combustion byproducts. The utilization of a different fuel, i.e., ammonia, might open completely new chemical degradation pathways, an issue which has to be addressed via an analysis of lubricant composition, especially by the applied additives. More specifically, in a marine internal combustion engine (ICE) of the 4-stroke, or even more commonly, the 2-stroke type, the impact of ammonia as a fuel towards the lubrication system must be investigated to enable the provision of long-life, reliable lubricants for use in such powertrain systems. Additionally, the detailed analysis of lubrication performance, e.g., in a piston ring–cylinder liner contact, has to be thoroughly assessed in the future if ammonia is going to be used as a fuel.

Lubricants perform several key functions in an ICE, such as friction and wear reduction, cooling and removal of contaminants. To be able to perform according to the OEM specifications, base oils and additives must be selected carefully in a way which corresponds to the respective application. Furthermore, lubrication performance and oil condition are strongly interrelated, e.g., additive depletion or the presence of degradation products [16]. The degradation processes of lubricants in conventionally fueled ICEs is well understood and documented [16–19]. Radicals are formed due to thermo-oxidative stress (high temperature and the presence of oxygen). Consequently, antioxidants are depleted as they react with the radical species. Engine oils often make use of the synergy between sterically hindered phenols and alkylated diphenylamines as antioxidants. Aminic antioxidants are more reactive but form less stable radicals. Phenolic antioxidants “regenerate” the used-up aminic antioxidants via H-radical transfer, by which they form stable phenoxy radicals [17]. Parallel to the depletion of antioxidants, oxidation products form. Oxidation products are mostly acidic in nature [16,17], which leads to an increase in acidity. The base reserve additive, which is usually calcium carbonate suspended in detergent micelles [17], partially neutralizes the organic acids originating from oxidation, which are accordingly depleted. The degradation of antiwear additives, e.g., zinc–dialkyldithiophosphate (ZDDP), happens both through oxidation and tribofilm formation [16]. ZDDP forms a glassy zinc–polyphosphate film on exposed metal surfaces [16], and this protects against wear. ZDDP oxidatively degrades through the rapid formation of dialkyl thiophosphates, which is followed by their depletion and the subsequent formation of dialkyl phosphates [16,17]. Once only dialkyl phosphates remain in the engine oil, the composition of the tribofilm changes [16]: less calcium, phosphor and zinc can be detected, and the wear rate increases [16].

Petrol engines are characterized by faster additive depletion and oxidation [19] since their air-to-fuel ratio (AFR) is lower compared to diesel engines. This leads to further radical formation [18]. The chemically reactive radicals react predominantly with polar additives. Comparatively, diesel engines usually exhibit higher soot loading [18] due to the higher boiling range of the diesel fuel. This can lead to the formation of local, fuel-rich regions next to the injection jet, a phenomenon which promotes soot formation. Soot is generally linked to the existence of higher iron concentration in in-service diesel engine oils [18], which is indicative of higher engine wear.

With additive depletion and the accumulation of contaminants during the service life of an engine oil, increases in wear, corrosiveness, as well as in deposit formation can be expected. For this purpose, lubricant formulations are routinely tested via artificial oil alteration methods in the laboratory in order to uncover degradation pathways and give an estimate about prospective service life as well as performance characteristics. Accordingly, several artificial oil alteration methods are available [20–24]. Standardized methods usually utilize air and focus on oxidation stability [20], while more advanced approaches also consider contamination through fuel [21] or combustion byproducts as well [23], such as nitrogen dioxide (NO_2). Altered engine oils from modern alteration methods show good chemical [22,23] and tribological [24] comparability with the used samples derived from internal combustion engines (field tests). Hence, the development of an alteration method with which to accurately model the impact of ammonia on lubricants is conceivable.

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 load-bearing capability, to enable the establishment of a connecting link between ammonia combustion and engine lubrication.

The presented method offers a time- and cost-saving tool to benchmark novel lubricant formulations intended for the use with ammonia. Thus, it could provide valuable input for oil and additive manufacturers regarding chemical interactions and the resulting lubrication performance, which would allow us to assess potential problems in the early development phase.

2. Materials and Methods

2.1. Engine Oil

The lubricant used in this study is a 4-stroke marine engine oil commonly used in the field in ships powered with regular fossil fuels. It is composed of mineral base oils, thus meeting API group II requirements, and a detergent additive package with which to provide engine cleanliness performance in operation. The main characteristics of the lubricant are listed in Table 1.

2.2. Artificial Alteration

Artificial alteration was performed in a custom-made alteration reactor system. The schematics are shown in Figure 1. The applied reactor had a net volume of 2000 mL and was heated using an electrical heating jacket and a magnetic stirrer. Stirring of the oil sample during alteration was also performed by the magnetic stirrer. During alteration, the oil samples were tempered at 170 °C and were subjected to a reaction gas mixture at a constant total flowrate of 0.85 L/min for 100 h. Both the total alteration time and volumetric flow rate were derived using CEC L-48-A00 [20], which is a well-established and widely used artificial alteration method. The flow rate was scaled up in consideration of the higher sample volume compared to CEC L-48-A00 [20], while the duration of the alteration was intentionally kept very similar (96 h vs. 100 h) to allow a similar utilization and workflow to those of the existing method.

Table 1. Physiochemical characteristics of the applied marine engine oil.

Marine Engine Oil SAE-40	
Kinematic viscosity 40 °C	120 mm^2/s
Kinematic viscosity 100 °C	14 mm^2/s
Viscosity index (VI)	110
Total base number (TBN)	30 mg KOH/g
Total acid number (TAN)	1.5 mg KOH/g

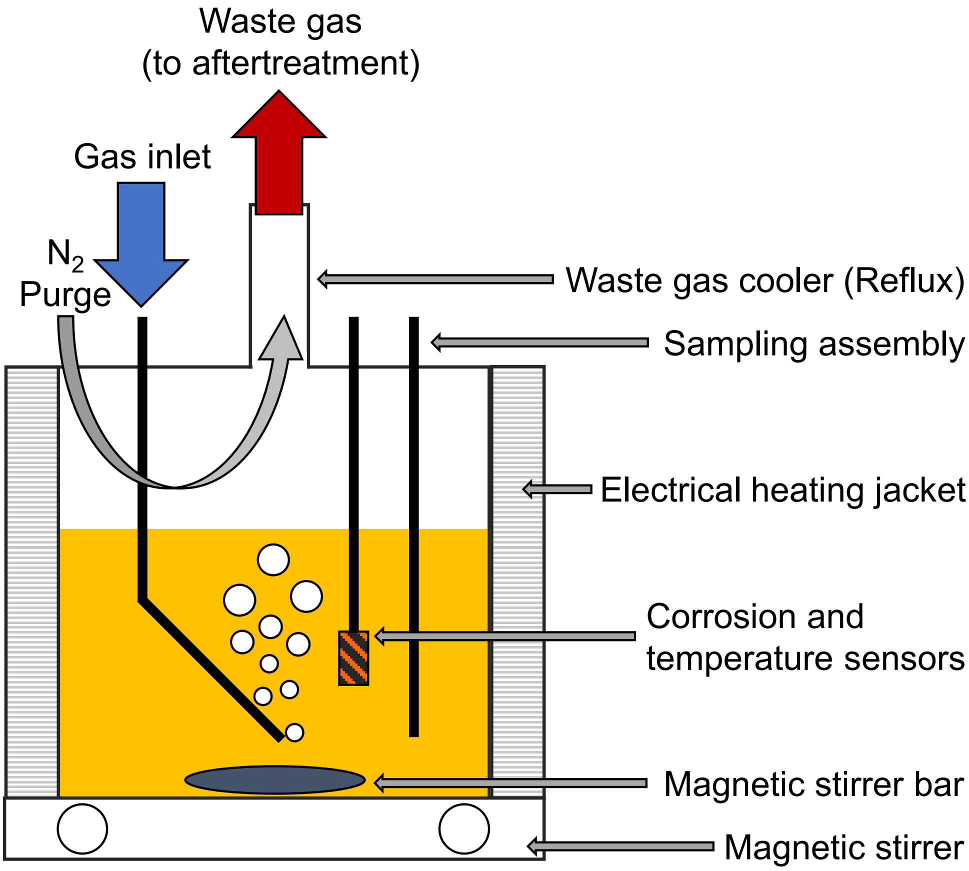


Figure 1. Schematics of the alteration reactor.

In cases of potentially explosive reaction gas mixtures (stoichiometric NH_3), an additional nitrogen purge of the gas phase should be applied to dilute the waste gas under the lower explosion limit. This nitrogen purge is not blown through the oil sample, but is only used to dilute the gas phase above the oil level. The sampling of the alterations was performed at regular intervals, namely at 5 h, 25 h, 50 h, 75 h and finally at 100 h in all cases.

The following reaction gas mixtures were utilized to investigate the influence of NH_3 fueling on the oil alteration, namely:

- Synthetic air
- Synthetic air + 1000 ppm NH_3
- Synthetic air + 21.7 vol% NH_3
- Synthetic air + 1000 ppm NO_2

First, an alteration with synthetic air was performed as the reference reaction gas since air is often used in various established alteration methods, such as occurs in [20,21] or [22]. Since NH_3 is considered to be applicable as a fuel in marine engines, the stoichiometric concentration (21.7 vol% in synthetic air) was subsequently utilized as reaction gas which is representative for practical applications, namely for use in the complete combustion of NH_3 in air. Additionally, a trace concentration (1000 ppm in synthetic air) of NH_3 was also tested to establish an in-depth understanding its influence on the oil aging. Finally, NO_2 was applied as the fourth reaction gas, representing a potential combustion byproduct of NH_3 [6] which was also utilized in the trace concentration of 1000 ppm in synthetic air.

2.3. Online Corrosion Monitoring

In addition to performing conventional oil condition monitoring by sampling and analyzing aliquots, we installed a copper-based corrosion sensor [25] in the alteration reactor to detect the corrosiveness of the engine oils continuously during the individual alterations. Figure 2 shows its schematic setup.

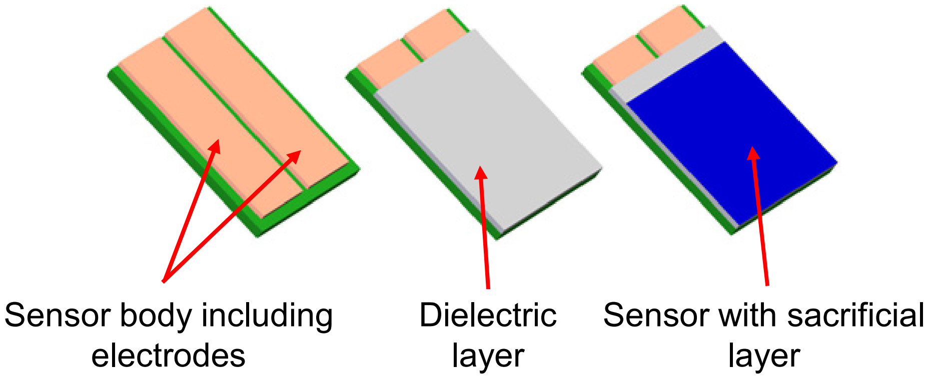


Figure 2. Schematic setup of the corrosion sensor.

The sensor body was a common printed circuit board (PCB) with structured readout electrodes which were covered by a solder resist layer for isolation. A sacrificial layer, as a core piece of this sensor concept, was deposited onto the PCB and exposed to the lubricant during alteration. Consequently, the sacrificial layer was corroded once the lubricant developed significant acidification or corrosiveness, respectively. The associated material loss was monitored by assessing the remaining area using capacitively coupled electrodes. Therefore, the readout electrodes were connected to the electronic device, which consisted of a capacitance to frequency converter. The frequency signal was determined by a microcontroller and transferred to the PC.

For the experiments within the presented study, copper with a thickness of 100 nm was used. Capacity readouts were recorded every 30 s during the alterations (approximately 10,000 data points per experiment are presented)

2.4. Chemical Oil Analysis

The derived intermediary and final altered oil samples were subjected to conventional oil analytical methods in order to characterize their degradation levels. The applied analytical approach consisted of:

- Fourier transform infrared spectroscopy (FT-IR) using a Tensor 27 FT-IR spectrometer (Bruker, Ettlingen, Germany) to determine the accumulation of relevant degradation products, namely

  - oxidation based on the peak height at 1720 cm^{-1} according to [17,18],
  - nitration based on the peak height at 1630 cm^{-1} according to DIN 51453 [26] and
  - aminification based on the maximal peak height between 3086 cm^{-1} and 3586 cm^{-1} (details see Section 3.1).
- Total acid number (TAN) according to ASTM D664 [27] and total base number (TBN) corresponding to DIN ISO 3771 [28] to determine the acidification and the depletion of base-reserve additives, respectively.
- Kinematic viscosity and density at 40 °C as well as 100 °C according to ASTM D7042 [29] to analyze the impact of oil degradation on the physical properties of the engine oils (calculation of the viscosity index was performed according to ASTM D2270 [30]).
- Water content by indirect Karl Fischer titration using an Oven Sample Processor 774 and a KF Coulometer 756 (Metrohm, Herisau, Switzerland) corresponding to DIN 51,777 [31] of the final samples.

2.5. Lubricant Performance Tests

Furthermore, the final altered samples were subjected to performance tests to determine the impact of the various reaction gas compositions on oil characteristics, consisting of

- static deposit control performance using the micro coking test (MCT) according to GFC-LU-27-A-13 [32],
- dynamic deposit control performance by thermo-oxidation engine oil simulation test (TEOST MHT®) corresponding to ASTM D7097 [33] as well as
- extreme pressure properties (EP) according to ASTM D7421 [34] using an Optimol® SRV® 5 tribometer (Optimol Instruments Prüftechnik, Munich, Germany).

The MCT is a static micro-coking test in which the oil is deposited onto an aluminum alloy plate and subjected to thermal conditions similar to those found in the piston ring zone of an internal combustion engine, namely 230 °C at the cold spot and 280 °C at the hot spot. After a 90 min test duration, the plate is cooled and conditioned for visual rating according to a grading system [32] in order to estimate the cleanliness performance of the tested lubricant.

In the TEOST test, the candidate oil is mixed uniformly with a catalyst and subjected to a flow of air to promote oxidation. The sample flows down in a spiral fashion along the metal coil onto the deposition rod which is heated at 285 °C and circulates for a total of 24 h. Weighing the deposition rod before and after test allows us to evaluate the propension of engine oil to form deposits under dynamic, high-temperature oxidative conditions.

The SRV® test method covers a procedure for determining a lubricating oil's coefficient of friction (CoF) and its ability to protect against extreme pressure (EP) when subjected to high-frequency, linear oscillation motion using an SRV® tribometer. The detailed parameters are described in Tables 2 and 3 for the performed EP experiments.

Table 2. Determination of the extreme pressure properties according to ASTM D7421—Test specimen and parameters.

Contact	**Punctual (Ball/Disc)**		
		Ball	Disc
Test specimens	Dimensions	Ø10 mm	Ø24 × 7.9 mm
	Material	steel 100Cr6	steel 100Cr6
	Hardness	60 ± 2 HRC	60 ± 2 HRC
	Final surface quality	Ra = 0.055 ± 0.003 µm	0.035 µm ≤ Ra ≤ 0.065 µm
Movement		Oscillating	
Frequency		50 Hz	
Stroke		2 mm	
Load		100–2500 N	
Time		Max 64 min	
Temperature		80 °C	

Table 3. Determination of the extreme pressure properties according to ASTM D7421—Test protocol.

Test Protocol		Force	Contact Pressure	Temperature	Time
Step 1	Running-in	100 N	2200 MPa	80 °C	15 min
Step 2	Test	+100 N/load stage	Up to 6400 MPa	80 °C	2 min/load stage

3. Results

3.1. Propagation of Alterations

Figure 3a displays the FT-IR difference spectra of the final altered samples (100 h) where the fresh oil spectrum was subtracted. In detail, the values in the region of 3000–3500 cm^{-1} were attributed to aminic degradation products. According to Coates, aliphatic primary amines show absorption bands around 3300–3380 and 3345–3425 cm^{-1}, aliphatic secondary amines show bands in the region of 3360–3310 cm^{-1}, aromatic primary amines show bands between 3415–3380 cm^{-1} as well as 3510–3460 cm^{-1}, aromatic secondary amines show bands of around 3450 cm^{-1} and heterocyclic amines show bands between 3490–3430 cm^{-1} [35]. Thus, the depicted region selected for quantification of the aminification had overlapping signals of various hydrocarbon structures containing aminic functional groups; hence, this parameter was overall considered as belonging to "aminification". Nevertheless, the maxima of the selected absorption bands match up with the literature very well, and consequently, seem to be reliable for use in quantitative analysis.

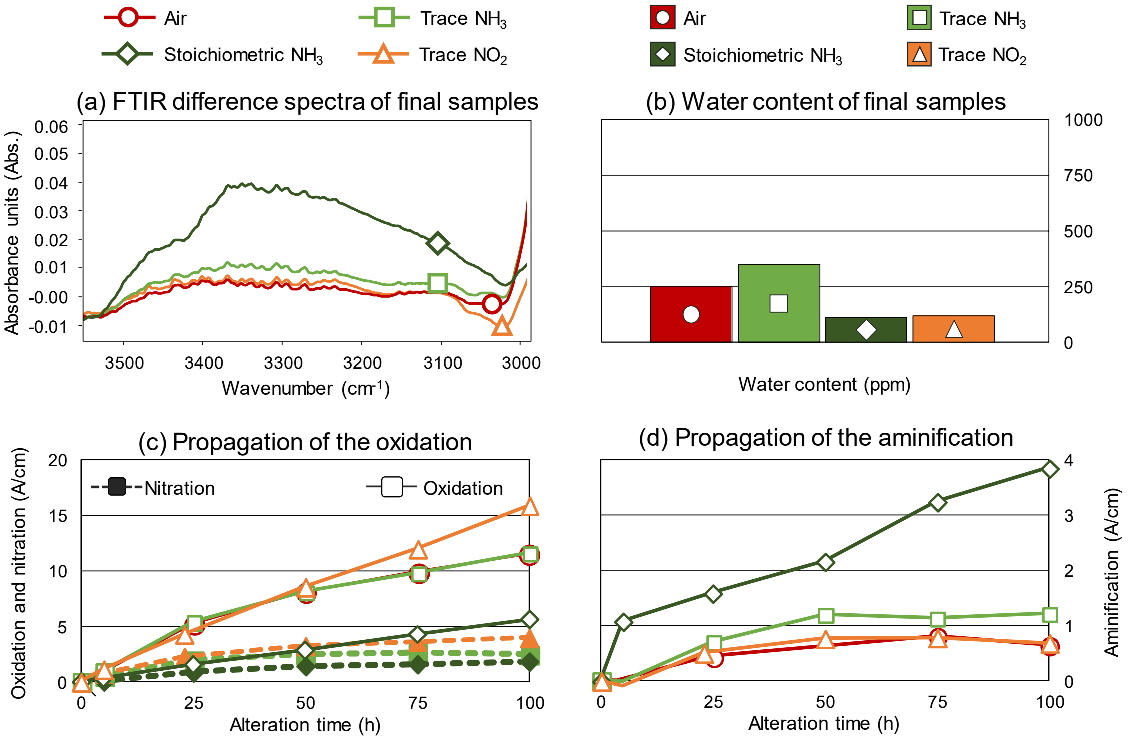


Figure 3. (**a**): FT-IR difference spectra of the final samples; (**b**): water content of the final samples; (**c**): propagation of oxidation and nitration; (**d**): propagation of aminification.

As above mentioned, absorption range might interfere with hydroxyl functional groups, especially water (3570–3200 cm^{-1}) [35]. The water content of the final samples was determined via an indirect Karl Fischer titration. Results thereof are shown in Figure 3b. The water content of the final altered samples was very low, ranging from 110 to 350 ppm, which was expected as the alterations were performed at 170 °C and as such water should evaporate and escape with the waste gas in this temperature range. Accordingly, even if there is a minor interference with water, the presented 4 samples have comparable water content which does not affect the relative comparison.

Figure 3c depicts the propagation of oxidation and nitration during the alterations. Concerning nitration, only minor elevated levels were observed in the case of the trace NO_2 alteration, whereas all other alterations provoked negligible nitration values. Accordingly, nitration does not seem to be a relevant degradation mechanism under the prevailing ageing conditions. This was anticipated, as nitration products in engine oils tend to decompose above 130–140 °C [19,23], hence they were not expected to accumulate at a 170 °C alteration temperature. Oxidation was higher compared to nitration values and significant differences could be observed between the reaction gases. The air and trace NH_3 alterations behaved similarly, reaching almost identical levels after 100 h, while the trace NO_2 showed elevated oxidation at 75 h and 100 h. This was expected, as NO_2 is known to catalyze oxidative reactions. Comparatively, the stoichiometric NH_3 alteration showed a significantly lower oxidation compared with the air alteration. This might be attributed to the fact that the reaction gas contained 21.7 vol% NH_3 in this alteration, resulting accordingly in less oxygen compared to only air as reaction gas. Furthermore, NH_3 acts as a potential reaction partner for oxygen in the system in competition with the engine oil, which might result in a lower oxidation rate as well.

Aminification is shown in Figure 3d. The trace NH_3 alteration showed minimally elevated levels compared to air and trace NO_2, where values below 1 A/cm were detected, which can be considered as no significant formation of aminic compounds. This also indicated the low potential of trace NH_3 to form large quantities of amines during the alteration. In contrast, the stoichiometric NH_3 alteration showed a comparably high abundance of aminic degradation products, proving the occurrence of chemical reactions between the reaction gas and the engine oil when the stoichiometric concentration of NH_3 is applied.

Figure 4a,b show the propagation of the TAN and TBN, respectively. Just as occurring with the oxidation, TAN behaved almost identically in the air and trace NH_3 alterations. The trace NO_2 alteration showed an elevated TAN after 50 h, which once again could be attributed to the higher oxidation level of this alteration. However, the situation was quite different with the stoichiometric NH_3 alteration, which exhibited practically no change in TAN values.

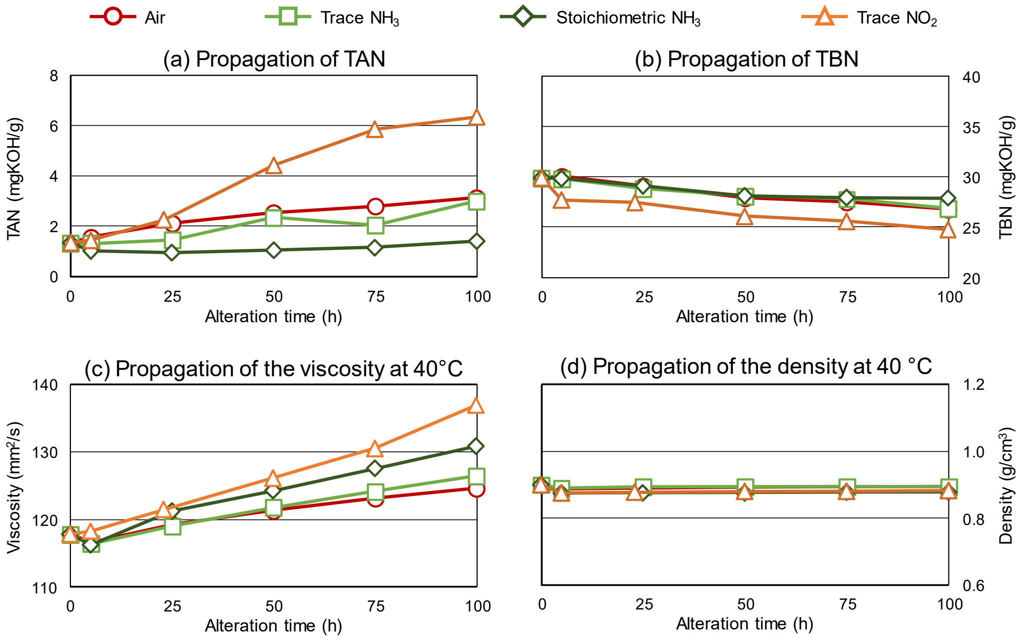


Figure 4. (**a**): Acidification of the oil samples (TAN); (**b**): depletion of the base reserve (TBN); (**c**): kinematic viscosity at 40 °C; (**d**): density at 40 °C.

TBN values generally revealed similar trends for all investigated reaction gases. The base reserve depletion was very well comparable in the air and trace NH_3 alterations, was somewhat accelerated in the trace NO_2 alteration and was slower in the stoichiometric NH_3 alteration. Based on these findings, it can strongly be assumed that the acidification and resulting base reserve depletion was dominated mostly by differences in the oxidation of the oils, resulting in the assumption that oxidation products mainly consist of acidic compounds. A detailed evaluation of the relationship oxidation vs. TAN and TBN is presented in Section 3.3.

Changes in physical properties, namely kinematic viscosity, and density at 40 °C are depicted in Figure 4c,d. The kinematic viscosity showed an increase in all oil samples, which is usually expected in connection with oil oxidation due to the partial polymerization of the base oil matrix [17,22]. Accordingly, the trace NO_2 alteration with the highest oxidation level showed the most significant viscosity increase. However, interesting differences could be observed for alterations with NH_3 contamination. The trace NH_3 alteration showed a higher viscosity compared to the air alteration after 75 h, despite the almost identical oxidation and other parameters. Furthermore, the stoichiometric NH_3 alteration exhibited a significantly elevated viscosity despite displaying the lowest oxidation. If NH_3 was involved in the chemical reactions, this suggests that factors other than oxidation played significant roles in oil thickening. On the contrary, the density of the samples was almost completely unaffected during all artificial alterations and similar to that of the fresh oil even after 100 h alteration time.

Figure 5 gives an overview of the signals measured by the copper-coated corrosion sensor chip for which an increase in the signal is indicative of corrosion on the surface [25]. Air, trace NH_3, and trace NO_2 showed no significant increase in the sensor signal; this indicated that no severe corrosion took place during the respective alterations. The stoichiometric NH_3 alteration displayed a severe and rapid increase in the sensor signal after approximately 30 h, which is a sign that corrosion took place on the copper surface. A possible explanation for the strong impact of stoichiometric NH_3 on the corrosion properties could be that copper ions were able to form amino complexes in solutions. Nevertheless, further research is needed to accurately characterize the physiochemical reactions taking place on the metal surface. It has to be stated that NH_3 represents a potential hazard for copper-containing engine parts and that engine performance as well as component lifetime might be negatively impacted by NH_3 fueling. Hence, it is recommended that engine oil manufacturers apply selected additives, such as specific corrosion inhibitors, to counteract feasible damage to vital engine components.

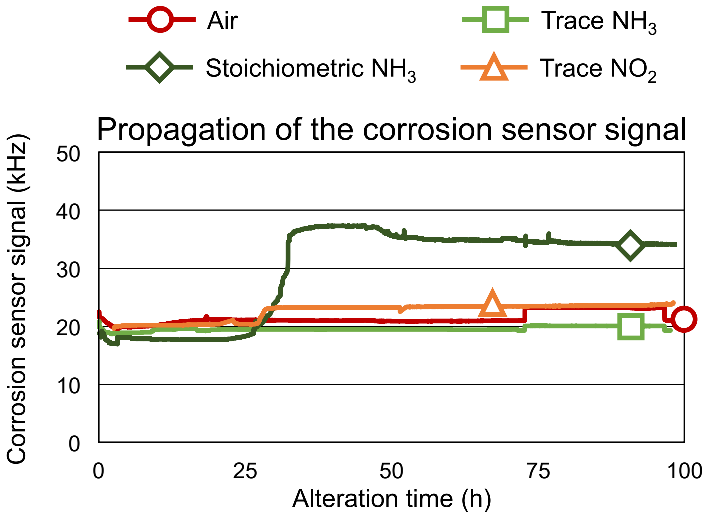


Figure 5. Signal of the copper-based corrosion sensor (the markers only facilitate easier distinction between the individual experiments).

3.2. Repeatability and Extended Alteration Time

The alteration with stoichiometric NH_3 was performed for a second time with an extended runtime to investigate the repeatability of the alteration method as well as to test how oil degradation propagates upon further alteration. Figure 6 compares various chemical and physical parameters until 100 h with the original alteration and continues to show their progress until an alteration duration of 200 h is reached. As shown in Figure 6a, the oxidation and aminification showed a very good reproducibility, with only marginal differences until 100 h between the original alteration and the repetition. Oxidation and aminification seemed to further increase in a close-to-linear manner with prolonged alteration time, which proves the continuation of chemical degradation. TAN and TBN data from both alterations (not displayed) also demonstrated comparable propagation until 100 h and close-to-linear further progress for the prolonged procedure, although the overall changes were minor when stoichiometric NH_3 was used (see Figure 4a,b).

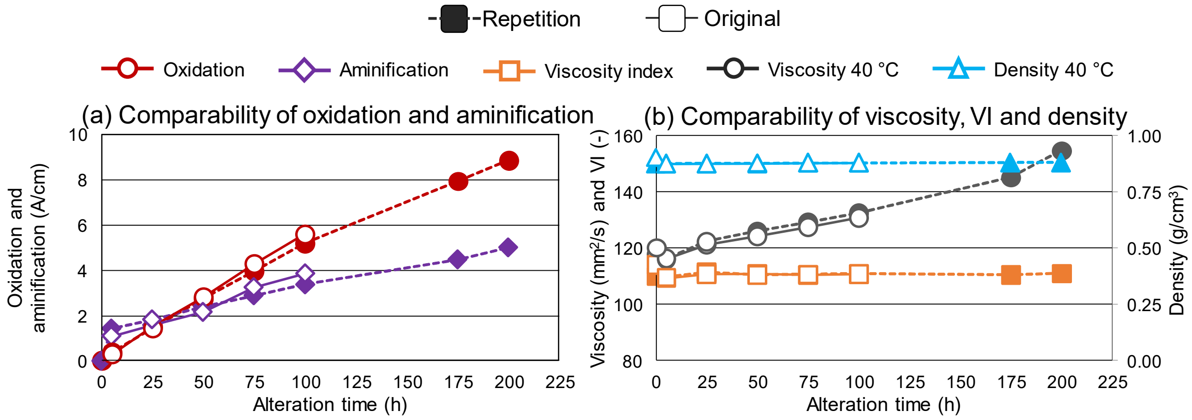


Figure 6. Repeatability of the stoichiometric ammonia alteration and extended alteration time. (**a**): oxidation and aminification; (**b**): physical properties at 40 °C (kinematic viscosity, density, VI).

Regarding the physical parameters of viscometry (Figure 6b), similar conclusions could be drawn. Density and viscosity index remained largely unaffected during the extended alteration, analogous to the results of original alteration. The significant increase in kinematic viscosity was reproduced reliably in the repeated alteration until 100 h. Furthermore, the viscosity also increased in a close-to-linear fashion, slightly increasing manner until 200 h, which corresponds to the further oxidation and aminification of the oil sample.

Overall, a very good reproducibility regarding all measured conventional oil parameters was proved and it could be demonstrated that the degradation of the oil propagated further in a predictable manner if the alteration time is increased.

3.3. Relationship of Degradation Processes and Overall Trends of Oil Degradation

This chapter aims to highlight correlations between various degradation parameters. For this purpose, both stoichiometric NH_3 alterations (original and repetition) were considered. In detail, the impact of the oxidation on TAN, TBN, and kinematic viscosity is displayed in Figure 7a–c, respectively. It can be stated that TAN, TBN, and kinematic viscosity all showed a relationship with the oxidation. Some of these correlations are well understood, especially between oxidation and acidification, as oxidation products are often acidic in nature [17], resulting in a TAN increase and TBN decrease. It is noteworthy that all performed alterations behaved in a very similar manner regarding TAN and TBN. This suggests that NH_3 and, hence, aminification had no effect on these parameters and that oxidation remained the main governing factor in this regard.

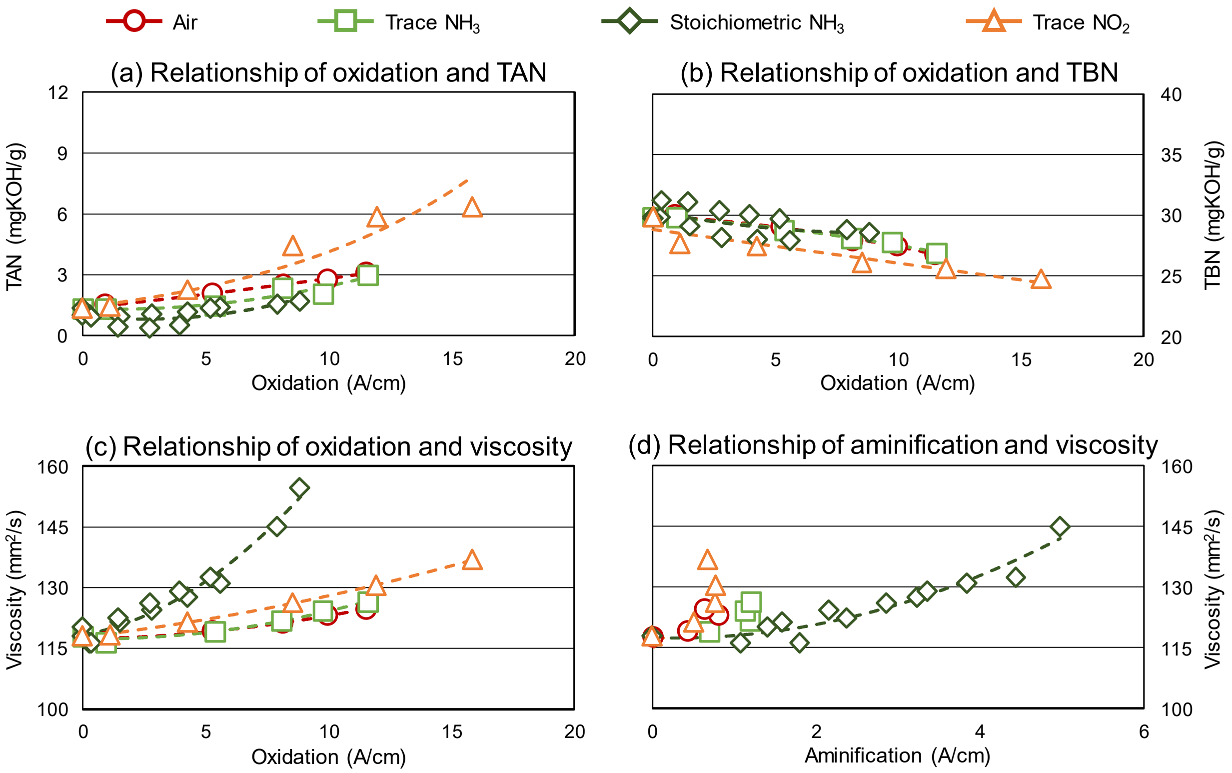
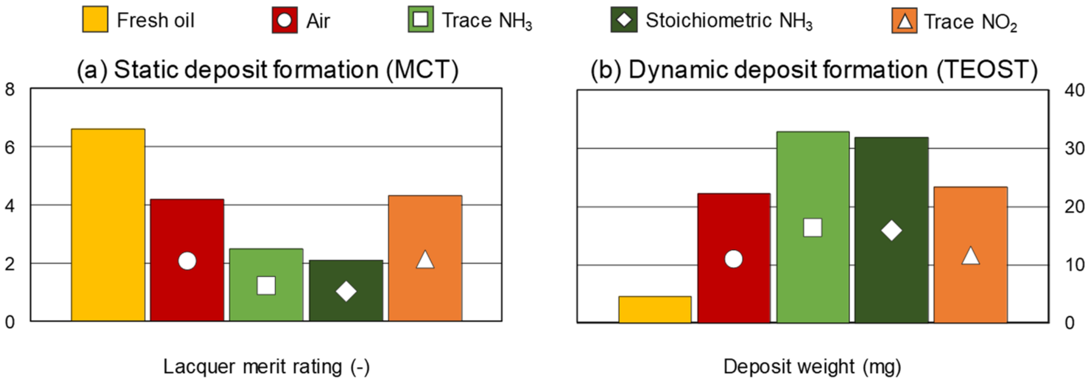


Figure 7. Correlations between degradation parameters. (**a**): oxidation and TAN; (**b**): oxidation and TBN; (**c**): oxidation and kinematic viscosity at 40 °C; (**d**): aminification and kinematic viscosity at 40 °C. The displayed lines only facilitate the better visualization of the trends.

However, different results were found for kinematic viscosity at 40 °C (see Figure 7c). Air, trace NO_2, and trace NH_3 once again behaved very similarly; the viscosity increased with the oxidation, which was possibly due to partial polymerization of the oil samples [17,22]. On the contrary, the viscosity of the stoichiometric NH_3 alteration also showed a correlation with the oxidation. However, the increase was more rapid and intensive. This can be explained when the relationship between aminification and kinematic viscosity is considered (Figure 7d). The kinematic viscosity exhibited a direct proportional correlation with the aminification, whereas no connection could be observed in the case of the air, trace NO_2 and trace NH_3 alterations. This was because no significant aminification took place. Accordingly, the deviation of kinematic viscosity for the stoichiometric NH_3 alteration displayed in Figure 7c can be explained as the kinematic viscosity increased both with oxidation and aminification simultaneously, resulting in significantly higher values at similar oxidation levels.

3.4. Performance Results

Figure 8 shows the deposit formation properties of the fresh and final altered engine oil samples. Deposit formation is especially important during long-range engine operation. Accordingly, both static (MCT—Figure 8a) and dynamic (TEOST—Figure 8b) conditions were investigated. The former was indicative of, e.g., the oil sump, the latter of, e.g., the piston ring area in an internal combustion engine.



(c) Static deposit formation (MCT) - Images of deposits after test

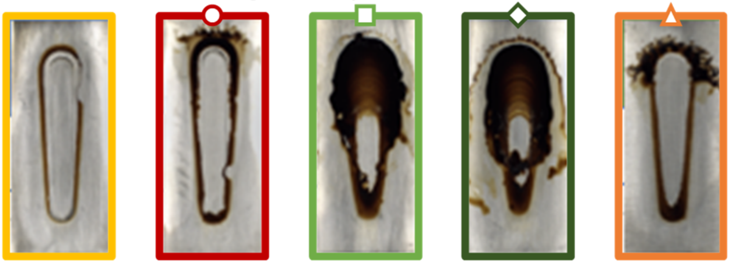


Figure 8. Deposit formation of the fresh and final altered engine oil samples. (**a**): static deposit formation (MCT); (**b**): dynamic deposit formation (TEOST); (**c**): static deposit formation (MCT)—images.

The fresh oil performed well in both cases. All alterations provoked a decrease in lacquer merit rating under static conditions and an increase in deposit weight when dynamic conditions were applied. The trace NH_3 and stoichiometric NH_3 alterations significantly underperformed every other altered oil sample under both static and dynamic conditions. This is especially interesting considering that the stoichiometric NH_3 alteration showed the lowest oxidation amongst the oil samples, despite having some of the worst deposit formation properties. Additionally, the trace NH_3 alteration exhibited comparably severe deposit formation despite it being performed almost identically with the air alteration in every conventional regard. The air and trace NO_2 alterations also demonstrated increased deposit amounts compared to the fresh oil. However, the increase was not as severe as that observed in case alterations with NH_3, despite the relatively high oxidation. This shows that NH_3 impacted the oil condition in ways that were not immediately obvious through conventional oil condition analysis. The presence of NH_3 in even the trace concentration (1000 ppm) resulted in severe deposit formation, comparable to that of oils after alteration with stoichiometric concentration, despite having low oxidation and TAN values. The images of the MCT test plates are displayed in Figure 8c to give a visual overview of the deposit formation.

Figure 9 presents the tribological properties of the fresh and final altered engine oil samples in terms of failure load and CoF during the EP tests. The alteration with air and with trace NH_3 addition demonstrated a slight decrease in failure load compared to the fresh oil. The trace NO_2 alteration gave a more pronounced drop, whereas the stoichiometric NH_3 alteration resulted in a comparatively large (approximately 55%) decrease and, overall, the worst EP performance among the altered oil samples. The propagation of the CoF was similar for all investigated oil samples with comparable values until the respective failure loads, and the friction curves were smooth without fluctuations (one determination displayed in Figure 9b). Accordingly, the selected alteration conditions seemed to have no influence on the CoF, but had significant impacts on the load-bearing capability (EP performance). This was most pronounced in case of the stoichiometric NH_3 alteration. This result once again corroborates the findings obtained on deposit formation regarding the impact of NH_3 on the engine oil alteration. In particular: the stoichiometric NH_3 alteration showed the least degradation according to conventional oil parameters (e.g., oxidation and TAN), but the worst EP performance. In addition, the trace NO_2 alteration also showed diminished EP performance, which correlates with the high oxidative degradation observed in this case. However, the effect of the stoichiometric NH_3 seems to be stronger.

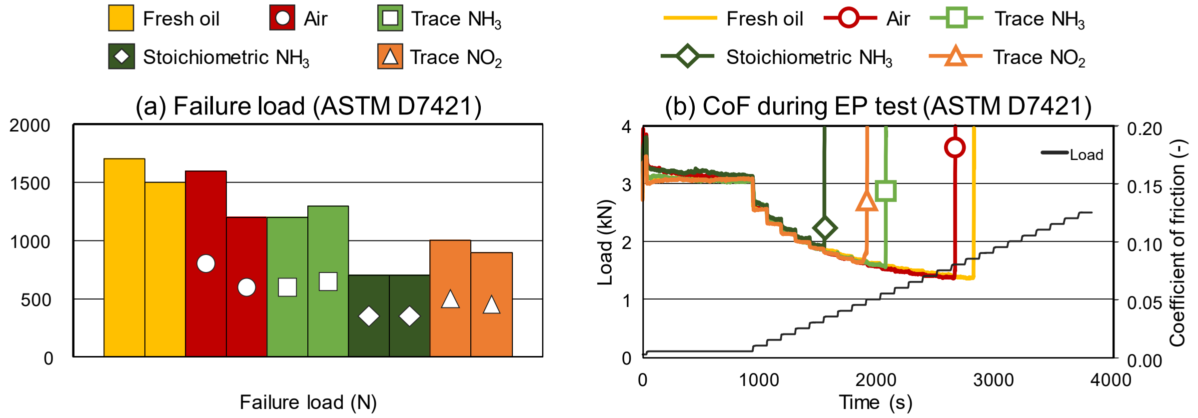


Figure 9. Tribological properties of the fresh and final altered engine oil samples. (**a**): EP failure load; (**b**): CoF during EP experiments (one of two determinations shown).

4. Discussion

The impact of ammonia on a commercially available marine diesel engine oil was studied. Artificial alterations were performed with air, trace ammonia (1000 ppm), and stoichiometric ammonia (21.7 vol%), as well as trace nitrogen dioxide (1000 ppm) as a potential combustion byproduct. Conventional chemical analyses showed that the air and trace ammonia alterations had similar properties. The trace nitrogen dioxide alteration displayed an accelerated thermo-oxidative degradation, whereas the stoichiometric ammonia alteration displayed a less pronounced thermo-oxidative degradation than the air alteration in terms of oxidation values, TAN increase, and TBN decrease. Additionally, the presence of aminic compounds was detected via FT-IR during the alteration with the addition of trace ammonia and to a greater extent during the stoichiometric ammonia alterations, indicating the progress of chemical reactions between the oil and ammonia.

An increase in kinematic viscosity was observed during all alterations. It was once again similar for air and trace ammonia. However, it was higher for trace nitrogen dioxide due to the relatively high oxidation, as well as for stoichiometric ammonia despite the relatively low oxidation. This suggests that the present aminic compounds are additionally resulting in viscosity increases. Further data evaluation revealed that oxidation is the main governing factor behind the TAN increase and TBN decrease, while the increase in kinematic viscosity correlates with both oxidation and aminification of the engine oils. This explains the intensive viscosity increase in the case of the stoichiometric ammonia alteration. Although oxidation is relatively low, the aminification is high, proving that both degradation processes result in a viscosity increase simultaneously.

The applied online copper-based corrosion sensor indicated corrosion after 30 h in the case of the stoichiometric ammonia alteration, while the other reaction gas mixtures did not affect the copper surface until 100 h. These findings emphasize that ammonia fueling also influences the corrosiveness against copper, a quality which is commonly utilized in ICEs. Hence, the application of specific corrosion inhibitors is highly recommended to counteract feasible damage to vital engine components.

Performance results revealed that trace and stoichiometric ammonia alterations are severely harmed considering deposit formation characteristics, both under static as well as dynamic conditions, despite the relatively advantageous results in terms of conventional oil parameters. This suggests that the present aminic compounds result in the more pronounced coking tendencies of the engine oil samples. Similarly, the stoichiometric ammonia alteration showed the worst tribological performance, namely regarding EP performance in terms of failure load, while showing the least pronounced thermo-oxidative degradation.

These results highlight that ammonia—besides offering several advantages—poses challenges as fuel for use in an internal combustion engine. Even a trace concentration of ammonia was found to severely impact the deposit formation characteristics, the stoichiometric concentration, and also corrosiveness against copper and extreme pressure performance, despite exhibiting comparatively low oxidation and acidification. Accordingly, the conventional oil condition monitoring techniques did not demonstrate the oil damage to the full amount, i.e., regarding degradation in lubrication and coking performance, which poses potential risks to a reliable engine operation. Thus, oil manufacturers need to consider the impact of ammonia during the development of new additive packages. Moreover, the presented study emphasizes the need for suitable chemical analytical procedures when ammonia is utilized as fuel.

5. Conclusions

The presented methodology can be considered to be suitable for use to investigate the impact of ammonia on marine engine lubricants as a clear differentiation in the oil performance was enabled with various ageing gases.

- Oxidation was low when utilizing stoichiometric NH_3 as a reaction gas mixture compared to air.
- The presence of aminic degradation products was indicated in the oils altered with trace and stoichiometric NH_3 reaction gas.
- An increase in kinematic viscosity can be attributed to the aminic species.
- Corrosiveness against copper was shown when stoichiometric NH_3 was used as a reaction gas.
- Both trace and stoichiometric NH_3 concentration impacted the deposit control performance severely compared to air or NO_2.
- Lubricants altered with stoichiometric NH_3 reached the lowest failure load (EP performance) amongst the samples.
- Furthermore, the repeatability of the novel methodology was demonstrated, including the possibility of achieving more pronounced oil degradation by extending the alteration time.

Nevertheless, a refinement of the presented method is conceivable, i.e., considering the further application parameters and other contaminants. Moreover, in-depth investigation of the chemical reactions between engine oil and ammonia is also necessary, and advanced techniques such as mass spectrometry should be used to accurately describe the involved structures and give a possible explanation of the increased deposit formation and diminished tribological performance.

Author Contributions: Conceptualization, A.A., M.R., N.O. and C.B.; methodology, A.A., M.R., N.O. and C.B.; software, C.S.; validation, A.A., M.R., N.O. and C.B.; formal analysis, A.A., C.B. and C.S.; investigation, A.A., M.R., N.O., C.S. and C.B.; resources, M.R., N.O. and C.B.; data curation, A.A., M.R. and C.B.; writing—original draft preparation, A.A., M.R., N.O. and C.S.; writing—review and editing, M.R., N.O., M.F. and C.B.; visualization, A.A.; supervision, M.F. and C.B.; project administration, M.F. and C.B.; funding acquisition, M.F. and C.B. All authors have read and agreed to the published version of the manuscript.

Funding: Presented results were realized in research projects with financial support from the participating project partners and the Austrian COMET program (Project InTribology, No. 872176). The COMET program is funded by the Austrian Federal Government and concerning InTribology by the provinces of Lower Austria and Vorarlberg.

Data Availability Statement: Data are contained within the article.

Conflicts of Interest: The authors declare no conflict of interest.

Abbreviations

AFR	air-to-fuel ratio
ΔH^0	standard enthalpy
EP	extreme pressure
FT-IR	Fourier-transform infrared spectroscopy
GHG	greenhouse gas
ICE	internal combustion engine
IDLH	immediate danger to life or health
MCT	micro-coking test
NH_3	ammonia
NO_2	nitrogen dioxide
NO_X	nitrogen oxides
OEM	original equipment manufacturer
PCB	printed circuit board
PEL	permissible exposure limits
SCR	selective catalytic reduction
TAN	total acid number
TBN	total base number
TEOST	thermo-oxidation engine oil simulation test
VI	viscosity index
ZDDP	zinc-dialkyldithiophosphate

References

1. DVN Group. IMO GHG Strategy. Available online: https://www.dnv.com/maritime/hub/decarbonize-shipping/key-drivers/regulations/imo-regulations/ghg-vision.html (accessed on 8 March 2023).
2. European Maritime Safety Agency. Update on Potential of Biofuels in Shipping. Available online: https://www.emsa.europa.eu/newsroom/latest-news/item/4834-update-on-potential-of-biofuels-for-shipping.html (accessed on 8 March 2023).
3. Chiong, M.C.; Kang, H.S.; Shaharuddin, N.M.R.; Mat, S.; Quen, L.K.; Ten, K.H.; Ong, M.C. Challenges and opportunities of marine propulsion with alternative fuels. *Renew Sustain. Energy Rev.* **2021**, *149*, 111397. [CrossRef]
4. Al-Aboosi, F.Y.; El-Halwagi, M.M.; Moore, M.; Nielsen, R.B. Renewable ammonia as an alternative fuel for the shipping industry. *Curr. Opin. Chem. Eng.* **2021**, *31*, 100670. [CrossRef]
5. Dimitriou, P.; Javaid, R. A review of ammonia as a compression ignition engine fuel. *Int. J. Hydrogen Energy* **2020**, *45*, 7098–7118. [CrossRef]
6. Chehade, G.; Dincer, I. Progress in green ammonia production as potential carbon-free fuel. *Fuel* **2021**, *299*, 120845. [CrossRef]
7. Zhang, H.; Wang, L.; Van Herle, J.; Maréchal, F.; Desideri, U. Techno-economic comparison of green ammonia production processes. *Appl. Energy* **2020**, *259*, 114135. [CrossRef]
8. Sánchez, A.; Martín, M. Optimal renewable production of ammonia from water and air. *J. Clean. Prod.* **2018**, *178*, 325–342. [CrossRef]
9. Zamfirescu, C.; Dincer, I. Using ammonia as a sustainable fuel. *J. Power Sources* **2008**, *185*, 459–465. [CrossRef]
10. Chai, W.S.; Bao, Y.; Jin, P.; Tang, G.; Zhou, L. A review on ammonia, ammonia-hydrogen and ammonia-methane fuels. *Renew Sustain. Energy Rev.* **2021**, *147*, 111254. [CrossRef]
11. Berwal, P.; Kumar, S.; Khandelwal, B. A comprehensive review on synthesis, chemical kinetics, and practical application of ammonia as future fuel for combustion. *J. Energy Inst.* **2023**, *99*, 273–298. [CrossRef]
12. Kobayashi, H.; Hayakawa, A.; Kunkuma, K.D.; Somarathne, A.; Okafor, E.C. Science and technology of ammonia combustion. *Proc. Combust. Inst.* **2019**, *37*, 109–133. [CrossRef]
13. Zhou, X.; Li, T.; Wang, N.; Wang, X.; Chen, R.; Li, S. Pilot diesel-ignited ammonia dual fuel low-speed marine engines: A comparative analysis of ammonia premixed and high-pressure spray combustion modes with CFD simulation. *Renew Sustain. Energy Rev.* **2023**, *173*, 113108. [CrossRef]
14. Ezzat, M.F.; Dincer, I. Comparative assessments of two integrated systems with/without fuel cells utilizing liquefied ammonia as a fuel for vehicular applications. *Int. J. Hydrogen Energy* **2018**, *43*, 4597–4608. [CrossRef]
15. Gill, S.S.; Chatha, G.S.; Tsolakis, A.; Golunski, S.E.; York, A.P.E. Assessing the effects of partially decarbonising a diesel engine by co-fuelling with dissociated ammonia. *Int. J. Hydrogen Energy* **2012**, *37*, 6074–6083. [CrossRef]
16. Agocs, A.; Besser, C.; Brenner, J.; Budnyk, S.; Frauscher, M.; Dörr, N. Engine Oils in the Field: A Comprehensive Tribological Assessment of Engine Oil Degradation in a Passenger Car. *Tribol. Lett.* **2022**, *70*, 28. [CrossRef]
17. Dörr, N.; Agocs, A.; Besser, C.; Ristic, A.; Frauscher, M. Engine Oils in the Field: A Comprehensive Chemical Assessment of Engine Oil Degradation in a Passenger Car. *Tribol. Lett.* **2019**, *67*, 68. [CrossRef]

18. Agocs, A.; Nagy, A.L.; Tabakov, Z.; Perger, J.; Rohde-Brandenburger, J.; Schandl, M.; Besser, C.; Dörr, N. Comprehensive assessment of oil degradation patterns in petrol and diesel engines observed in a field test with passenger cars—Conventional oil analysis and fuel dilution. *Tribol. Int.* **2021**, *161*, 107079. [CrossRef]
19. Agocs, A.; Budnyk, S.; Frauscher, M.; Ronai, B.; Besser, C.; Dörr, N. Comparing oil condition in diesel and gasoline engines. *Ind. Lubr. Tribol.* **2020**, *72*, 1033–1039. [CrossRef]
20. CEC, L. *48-A00: Oxidation Stability of Lubricating Oils Used in Automotive Transmissions by Artificial Ageing*; Coordinating European Council for the Development of Performance Tests for Fuels, Lubricants and Other Fluids: Brussels, Belgium, 2014.
21. Besser, C.; Schneidhofer, C.; Dörr, N.; Novotny-Farkas, F.; Allmaier, G. Investigation of long-term engine oil performance using lab-based artificial ageing illustrated by the impact of ethanol as fuel component. *Tribol. Int.* **2012**, *46*, 174–182. [CrossRef]
22. Besser, C.; Agocs, A.; Ronai, B.; Ristic, A.; Repka, M.; Jankes, E.; McAleese, C.; Dörr, N. Generation of engine oils with defined degree of degradation by means of a large scale artificial alteration method. *Tribol. Int.* **2019**, *132*, 39–49. [CrossRef]
23. Besser, C.; Agocs, A.; Ristic, A.; Frauscher, M. Implementation of Nitration Processes in Artificial Ageing for Closer-to-Reality Simulation of Engine Oil Degradation. *Lubricants* **2022**, *10*, 298. [CrossRef]
24. Agocs, A.; Budnyk, S.; Besser, C.; Ristic, A.; Frauscher, M.; Ronai, B.; Dörr, N. Production of Used Engine Oils with Defined Degree of Degradation in a Large-scale Device: Correlation of Artificially Altered Oils with Field Samples. *ACTA Tech. Jaurinensis* **2020**, *13*, 131–150. [CrossRef]
25. Schneidhofer, C.; Sen, S.; Dörr, N. Determination of the Impact of Biogas on the Engine Oil Condition Using a Sensor Based on Corrosiveness. In *Biofuel Production—Recent Developments and Prospects*; Bernardes, D.S., Ed.; InTech: London, UK, 2011; pp. 577–596.
26. *DIN 51453:2004-10*; Testing of Lubricants—Determination of Oxidation and Nitration of Used Motor Oils—Infrared Spectrometric Method. Deutsches Institut für Normung: Berlin, Germany, 2004. [CrossRef]
27. *ASTM D664-18e2*; Standard Test Method for Acid Number of Petroleum Products by Potentiometric Titration. ASTM International: West Conshohocken, PA, USA, 2018. [CrossRef]
28. *DIN ISO 3771:1985–04*; Petroleum Products; Total Base Number; Perchloric Acid Potentiometric Titration Method. Deutsches Institut für Normung: Berlin, Germany, 1985.
29. *ASTM D7042–21*; Standard Test Method for Dynamic Viscosity and Density of Liquids by Stabinger Viscometer (and the Calculation of Kinematic Viscosity). ASTM International: West Conshohocken, PA, USA, 2021. [CrossRef]
30. *ASTM D2270–10*; Standard Practice for Calculating Viscosity Index from Kinematic Viscosity at 40 °C and 100 °C. ASTM International: West Conshohocken, PA, USA, 2016. [CrossRef]
31. *DIN 51777:2020–04*; Petroleum Products—Determination of Water Content Using Titration According to Karl Fischer. Deutsches Institut für Normung: Berlin, Germany, 2020. [CrossRef]
32. *GFC-LU-27-A-13*; Microcoking Test for Automotive Lubricants. Carburants, Lubrifiants & Fluides pour le Transport: Paris, France, 2018.
33. *ASTM D7097–19*; Standard Test Method for Determination of Moderately High Temperature Piston Deposits by Thermo-Oxidation Engine Oil Simulation Test—TEOST MHT. ASTM International: West Conshohocken, PA, USA, 2020. [CrossRef]
34. *ASTM D7421–19*; Standard Test Method for Determining Extreme Pressure Properties of Lubricating Oils Using High-Frequency, Linear-Oscillation (SRV) Test Machine. ASTM International: West Conshohocken, PA, USA, 2020. [CrossRef]
35. Coates, J. Interpretation of Infrared Spectra, A Practical Approach. In *Encyclopedia of Analytical Chemistry*; Meyers, R.A., Ed.; John Wiley & Sons Ltd.: Chichester, UK, 2000; pp. 10815–10837.