

2025 | 509

Ammonia combustion engine exhaust gas aftertreatment

Basic research & advanced engineering - new concepts

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This paper has been presented and published at the 31st CIMAC World Congress 2025 in Zürich, Switzerland. The CIMAC Congress is held every three years, each time in a different member country. The Congress program centres around the presentation of Technical Papers on engine research and development, application engineering on the original equipment side and engine operation and maintenance on the end-user side. The themes of the 2025 event included Digitalization & Connectivity for different applications, System Integration & Hybridization, Electrification & Fuel Cells Development, Emission Reduction Technologies, Conventional and New Fuels, Dual Fuel Engines, Lubricants, Product Development of Gas and Diesel Engines, Components & Tribology, Turbochargers, Controls & Automation, Engine Thermondynamis, Simulation Technologies as well as Basic Research & Advanced Engineering. The copyright of this paper is with CIMAC. For further information please visit https://www.cimac.com.

ABSTRACT

Ammonia (NH3) is regarded as a promising future fuel for large engines, especially for international shipping, due to its lack of CO2 emissions during combustion and its ease of storage in liquid state either slightly cooled to approx. -33°C or at moderate pressures of about 9 bar. However, its use can result in high concentrations of pollutants such as NOX, NH3 and N2O, strongly depending on the combustion principle and on the engine's operation. Hereby, special focus must be laid on N2O as its high global warming potential (100y-GWP) of 298 can nullify the reduction in CO2 emissions by switching from fossil fuels to NH3. Additionally, if a diesel-like fuel is used as a pilot, fuel typical diesel exhaust gas components can also be present in the exhaust gas.

Existing data for ammonia engines show high levels of NO and unburnt NH3 in the exhaust gas, along with N2O concentrations up to around 100 ppm. NOx levels can exceed 5000 ppm under lean conditions, while exhaust NH3 concentrations can range from 8000 ppm in lean, hydrogen-enriched conditions to 18.000 ppm in rich conditions. These elevated levels of NO, NH3 and N2O, which exceed typical emissions in current mobile and stationary applications, necessitate aftertreatment measures to control exhaust gas emissions.

While NOx and NH3 can react on commercially available SCR catalysts at NH3:NOx ratios of up to 1 forming dominantly N2, excessive NH3 slip from the engine requires a dedicated ammonia slip catalyst (ASC). Due to the high levels of NH3, high selectivity towards N2 to avoid side product formation (NOx or N2O) is important. For the decomposition of N2O, novel catalyst designs need to be evaluated as currently no N2O catalyst is commercially available for engine exhaust gas conditions.

Laboratory experiments with synthetic exhaust gas are presented, the composition and concentrations of exhaust compounds are set to mimic the expected NH3 combustion engines emissions. Individual catalysts specifically designed to target for instance high NH3 slip or N2O in the exhaust, are tested under these conditions, highlighting the chances and limitations of current and future catalyst technologies. Also, a full exhaust gas aftertreatment system is being presented enabling a high CO2 emission reduction by switching from fossil fuels to NH3.

Overall, achieving lower greenhouse impact by switching to alternative fuels such as ammonia also requires careful consideration of the requirements for exhaust gas aftertreatment systems. Close collaboration on this topic between engine development and exhaust gas aftertreatment ensures to meet legal pollutant requirements while maintaining low emissions of undesired, currently non-regulated substances.

1 INTRODUCTION

Ammonia (NH₃) is regarded a promising future fuel for large engines, especially for international shipping, due to the absence of CO₂ emissions during combustion and its ease of storage in liquid state either slightly cooled to approx. -33°C or at moderate pressures of about 9 bar. However, its use can result in high concentrations of pollutants such as NOx, NH3 and N2O, strongly depending on the combustion principle and on the engine's operation. Hereby, special focus must be laid on N₂O as its high global warming potential (100y-GWP) of 273 [1] can nullify the reduction in CO2 emissions by switching from fossil fuels to NH₃. Ammonia emissions, besides being toxic at high concentrations, when released to the ambient are one of the major sources of global PM 2.5 pollution, already causing a major drop in air quality in East Asia and the Mediterranean area [2]. Additionally, if a diesel-like fuel is used as a pilot fuel typical diesel exhaust gas components can also be present in the exhaust gas.

Laboratory experiments on diesel exhaust gas are presented, the composition and concentrations of exhaust compounds are set to mimic the expected NH $_3$ combustion engines emissions. Individual catalysts specifically designed to target for instance high NH $_3$ slip or N $_2$ O in the exhaust, are combined in two EAT systems and tested under these conditions, highlighting the chances and limitations of current and future catalyst technologies.

1.1 Engine exhaust gas composition

Currently, different combustion concepts for NH₃ are under development. compression ignition (CI) engines [3] offer the option for dual-fuel operation using conventional diesel as a back-up fuel are an attractive option for marine transportation, spark ignition (SI) engines [4] [5] are also investigated. Even though there are high uncertainties with regard to pollutant emissions due to the experimental nature of the engines reported, high levels of NO_x and NH₃ are expected as fuel-born pollutants. Existing data for dual-fuel operated CI engines using Diesel as the pilot fuel shows 1'000 - 3'000 ppm NH₃ at NO_x levels below 1500 ppm. However, more than 10'000 ppm NH₃ in low load conditions, strongly exceeding the NO_x emissions were also observed. [6] For spark-ignited NH₃-ICE using hydrogen as an ignition facilitation fuel, NH3 emissions of up to 10'000 ppm with NO_x levels between 3'000 -10'000 ppm were reported under lean conditions. When lowering the air-fuel-ratio, even higher NH₃ concentrations up to 15'000 ppm with minimal NO_x were observed. Exhaust temperatures were reported at approx. 375 -550°C. [7] A different study on a SI NH₃ engine

using hydrogen as secondary fuel reported similar NH₃ concentrations up to 10'000 ppm with NO_x levels ranging from 1'000 - 4'000 ppm under lean conditions. Ammonia-NO_x-Ratios (ANR) equal to 1 were achievable by engine tuning but limited to a narrow air-to-fuel ratio around 1.2 and only with significant hydrogen contents (20 vol.%) in the combustion chamber. Also, N2O concentrations independent of air-to-fuel ratio of up to 100 ppm were reported. [8] Hydrocarbon (HC) and carbon monoxide (CO) emissions are expected to be significantly lower due to the carbon-free nature of ammonia. First reports indicate HC levels of approx. 80 ppm and CO concentrations of up to 100 ppm for spark-ignited combustion engines [5]. Further information on the expected emissions from NH₃-ICE and their estimated local and global impact can be found elsewhere [2] [9] [10] [11].

The elevated levels of NO, NH₃ and N₂O, which are almost definitely set to exceed typical emissions in current mobile and stationary applications, necessitate aftertreatment measures to control exhaust gas emissions. From the emission data published, estimated representative exhaust gas characteristics are derived as shown in Table 1 below. Four different engine emission characteristics are defined (Case 1 - 4) differing in the NH₃ to NO_x ratio which is the crucial aspect from an aftertreatment point of view. The ANR ranges from 0.8 - 2 covering the entire scope of relevant ratios while keeping other exhaust gas components (H₂O, N₂O, CO, HC) constant.

Table 1. Estimated emission characteristics of ammonia combustion engine exhaust gas

Engine emission characteristic	Case 1	Case 2	Case 3	Case 4
H₂O [vol.%]	10 – 25	10 – 25	10 – 25	10 – 25
ANR	0.8	1	1.2	2
NH ₃ [ppm]	2400	3000	3600	6000
NO _x [ppm]	3000	3000	3000	3000
N₂O [ppm]	100	100	100	100
CO ¹ [ppm]	100	100	100	100
HC ^{1, 2} [ppm]	80	80	80	80

¹ CO and HC emissions from diesel pilot fuel and lubrication oil strongly depend on the fuel share ² as C1

1.2 Current state-of-the-art catalyst technologies

Selective catalytic reduction (SCR) represents a NO_x reduction strategy in modern diesel or gas engines, using ammonia (typically from urea solution) as a reducing agent. The standard SCR reaction (Eq. 1) requires a stochiometric Ammonia-NO_x-Ratio (ANR) for high NO_x conversions.

$$4 NH_3 + 4 NO + O_2 \rightarrow 4 N_2 + 6 H_2O$$
 (Eq. 1)

The SCR technology is well-established for large engine exhaust gas aftertreatment systems as well as on- and off-road mobile applications using either vanadium or zeolite based catalysts. For NH₃-ICE, this technology is a necessity to lower both NO $_{\rm X}$ and NH $_{\rm 3}$ emissions.

Ammonia slip catalysts (ASC) are designed to address the issue of unreacted ammonia, or "ammonia slip," that can occur in SCR systems due to overdosed or inhomogeneously distributed NH₃. Target reaction is the formation of harmless nitrogen (N_2) in reaction with excess O_2 present in the exhaust gas (Eq. 2).

$$4 NH_3 + 3 O_2 \rightarrow 2 N_2 + 6 H_2 O$$
 (Eq. 2)

However, if the catalyst is not optimized for the specific exhaust gas conditions, undesired side reactions can occur on the catalysts forming N_2O (Eq. 3) or NO (Eq. 4).

$$4 NH_3 + 4 O_2 \rightarrow 2 N_2 O + 6 H_2 O$$
 (Eq. 3)

$$4 NH_3 + 5 O_2 \rightarrow 4 NO + 6 H_2O$$
 (Eq. 4)

ASC typically contain precious group metals (PGM) such as platinum or palladium and are not commonly used for large marine diesel engines exhaust gas aftertreatment systems due to their sulfur sensitivity and lack of NH $_3$ emission limits. However, its usage for engines using low-sulfur fuel (e.g. EN 590, natural gas) is well established. For NH $_3$ -ICE with NH $_3$ levels potentially exceeding NO $_{\rm X}$ concentration in the engine-out exhaust gas, this technology is a necessity to lower NH $_3$ emissions at ANR > 1. As NH $_3$ is a sulfur-free fuel, special care must only be taken in regards to the pilot fuel which is limited to low-sulfur fuel qualities such as ultra-low-sulfur diesel (ULSD) or EN 590 depending on the engine's fuel share.

Diesel oxidation catalysts (DOC) are commonly used to eliminate CO ((Eq. 5) and hydrocarbons ((Eq. 6) by oxidation to CO_2 from the exhaust gas.

$$CO + 4 O_2 \rightarrow 2 CO_2$$
 (Eq. 5)

$$HC + O_2 \rightarrow CO_2 + H_2O$$
 (Eq. 6)

Similarly to ASC, DOC contain PGM limiting the usage to low-sulfur fuel. As ammonia's lack of carbon atoms limits the source of CO and HC to the

pilot fuel and the lubrication oil thus making a dedicated oxidation catalyst only necessary for most stringent emission limits (e.g. EU Stage V).

Catalysts for the removal of N_2O from exhaust gas (de N_2O) containing high concentrations of H_2O and O_2 are not commercially available as N_2O emissions were mainly observed as secondary emissions from inadequate NH_3 oxidation (Eq. 3) on diesel or gas engines. Initial research identified the usage of highly-loaded rhodium-based catalysts [12] as possible de N_2O catalysts according to (Eq. 7).

$$2 N_2 O \rightarrow 2 N_2 + O_2$$
 (Eq. 7)

However, due to the price of rhodium being fivefold compared to platinum its usage for large engines remains doubtful. For this reason, the development of highly active, non-noble metal catalysts for N_2O removal for NH_3 -ICE is focus of current research.

1.3 Target emissions & concept

For the definition of target emissions and required conversion rates over the exhaust gas aftertreatment system, the respective legislation, health and safety standards as well as the GHG impact of the respective pollutants needs to be considered. However, the greatest uncertainty with regard to necessary pollutant conversion rates results from the low level of knowledge about engine raw emissions which can furthermore strongly change, depending on the latest engine developments.

However, the generally high levels of raw NO_x emissions are bound to require high conversions of more than 95% even if only considering IMO Tier III requirements. For ammonia emissions, the minimal conversion target is set by health and safety considerations such as the Immediately Dangerous Life or Health (IDLH) values currently determined by the National Institute Occupational Safety and Health (NIOSH) at 300 ppm [13]. As NH₃ raw emissions can be expected at levels higher than 3000 ppm, ammonia conversions of more than 90% are advised. Additionally, if stricter emission limits of 10 ppm (e.g. EU Stage V, EURO VI) must be considered, NO_x and NH₃ conversions of more than 99% become necessary.

While for non-poisonous N_2O no health and safety considerations are required, the tailpipe-end emissions are strongly limited by its high global warming potential (100y-GWP) of 273 [1]. If aspiring a GHG emission reduction of more than 90% compared to conventional fossil fuels by usage of CO_2 -neutrally produced ammonia, single

digit N_2O concentrations are required. Therefore, minimal required laughing gas conversions are expected to reach more than 90%.

Carbon monoxide (CO) and hydrocarbon (HC) emissions are expected to be significantly lower when using NH₃ as a carbon-free fuel in comparison with conventional diesel engine emissions. Besides the incomplete combustion of lubrication oil only a carbon-based pilot fuel can potentially produce CO and HC. However, if challenging emission limits such as EU Stage V must be complied with an oxidation catalyst is most likely necessary. As the raw emissions are even harder to estimate in comparison to N-based pollutant levels, no target conversion is estimated in this paper.

When comparing the expected characteristics of raw engine exhaust for the relevant cases (see Table 1) with the estimated necessary conversion rates for NO_x it becomes apparent that for raw emissions with ANR < 1 additional NH₃ will need to be added approaching ANR = 1. On the contrary, for ANR \geq 1 no additional NH₃ should be injected. A closed-loop control system measuring both NO_x and NH₃ is used to ensure compliance with emission limits such as EU Stage V or IMO Tier III.

This reduces the number of operating scenarios relevant for the catalytic benchmark tests to the following:

- 1 ANR = 1
- 2 ANR > 1
- 3 ANR >> 1

2 EXPERIMENTAL SECTION

The three scenarios described above with Ammonia-NO_x-Ratios (ANR) equal, slightly above and significantly above one are replicated using an catalytic benchmark test bench operating on diesel exhaust. To simulate NH₃-ICE exhaust with diesel pilot fuel, NO_x, NH₃ and N₂O are added at high levels.

2.1 Catalytic benchmark test bench



Figure 1. Test bench for catalytic benchmark experiments

The full system benchmark experiments were performed by employing a combined heat and power unit (Dachs HKA HR, SenerTec) running on EN 590 grade fuel oil with an engine displacement of 0.578 I and a maximal power output of 5.3 kW providing an exhaust mass flow of ca. 21 kg/h at approx. 240°C. An integrated diesel particulate filter removes all particles from the exhaust gas and gaseous water is dosed increasing the water content to NH₃-ICE levels. The exhaust mass flow is then measured by a vortex flowmeter (Vortex-Strömungssensor VA Di, Höntzsch) and controlled by exhaust gas flaps to replicate the desired mass flow to catalyst volume ratio. The exhaust gas is consecutively heated to the relevant temperature by an exhaust gas heater and the crucial, gaseous pollutants (NOx, NH3, N2O) are added by mass flow controllers (Bronkhorst) at levels considered typical for NH₃-ICE. The modified exhaust gas is then homogenized by dedicated gas-gas mixers and directed into the exhaust gas system. This consists of multiple reactors (max. dimensions 50x50x450 mm) with measuring and NH₃ injection ports between each reactor. The exhaust gas is measured by an FTIR (SESAM i60 FT, AVL) using a dedicated NH₃-ICE method.

To simulate all relevant cases for the catalysts in the exhaust gas aftertreatment systems, the testing conditions as defined in Table 2 mimicking stochiometric conditions (ANR = 1, Testing conditions 1), slightly above stochiometric conditions (ANR = 1.2, Testing conditions 2) and highly above stochiometric conditions (ANR = 2, Testing conditions 3) are set.

Table 2. Test conditions

Test conditions	1	2	3
H ₂ O [vol.%]	11	11	11
CO ₂ [vol.%]	5.4	5.4	5.4
O ₂ [vol.%]	10	10	10
ANR [-]	1	1.2	2
NH ₃ [ppm]	2000	2400	4000
NO _x [ppm]	2000	2000	2000
N₂O [ppm]	110	110	110
CO [ppm]	120	120	120
HC ¹ [ppm]	80	80	80
Balance		N_2	

¹as C1 calculated based on measured diesel-specific HC compounds by FTIR

3 RESULTS & DISCUSSION

Two different combined catalyst systems are tested under the conditions specified above (see Table 2). EAT system #1 has a space requirement similar to a Diesel engine EU Stage V aftertreatment system and consists of PGM-free stages of SCR-, ASC and deN₂O. EAT system #2 requires slightly more total catalyst volume but offers significantly lower light-off temperatures for CO, HC and NH₃ in comparison to EAT system #1 by adding a PGM component. Note that in all the diagrams presented, the lines connecting the measured stationary points are interpolated.

3.1 Performance for ANR = 1

For engine operating points emitting NH_3 at levels equal to NO_x , high conversion rates can be achieved over a wide temperature range starting as low as 300°C using EAT system #1 (see Figure 2). Hereby, the stochiometric SCR reaction eliminates both pollutants equally with high efficiency as known for engines running on fossil fuels. In contrast, no deN_2O performance is detectable at temperatures of 350°C or lower. Only if the exhaust gas temperature reaches 400°C, significant N_2O conversion of around 70% is observed. At exhaust gas temperatures of 450°C or higher, N_2O removal equals to more than 97% thus achieving the N_2O abatement required for significant GHG emission reduction compared to fossil fuels.

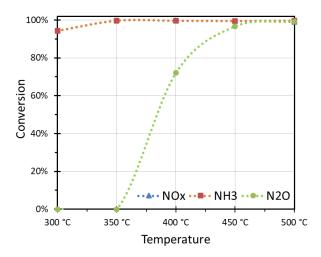


Figure 2. NO_x, NH₃ and N₂O conversion (NO_x curve hidden under NH₃ curve) of catalyst system #1 under conditions specified as testing conditions 1 in Table 2.

However, using EAT system #1 no significant CO conversion is achievable. If it becomes necessary, EAT system #2 is possible to enable CO conversions of more than 80% at temperatures ranging from $400-500^{\circ}\text{C}$ and HC conversion of over 95% at all relevant temperatures (see Figure 3). At the same time, NO_x, NH₃ and N₂O conversions are on the same level as shown for EAT system #1 in Figure 2.

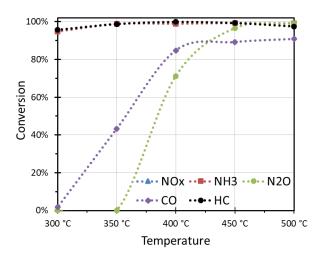


Figure 3. NO_x, NH₃, N₂O, CO and HC conversion of catalyst system #2 under conditions specified as testing conditions 1 in Table 2.

Overall, for exhaust gas from NH₃-ICE containing either stochiometric or below stochiometric concentrations of NH₃ and NO_x, ammonia (ANR = 1) even strict emissions limits for NH₃ and NO_x (e.g. EU Stage V) are achievable with significant N₂O reduction at exhaust gas temperatures of 400°C or above. Note that for ANR < 1 additional NH₃

injection will become necessary to reach an optimal NH $_3$ to NO $_x$ ratio. However, for GHG emission reduction of more than 90%, temperatures above 450°C are strictly required. If CO and HC conversion is required, EAT system #2 with slightly higher space requirements is an option. With the latter setup, in case of pilot fuel ignited NH $_3$ dual fuel engines also fuel share modes with higher amounts of Diesel fuel can be treated regarding HC and CO. These emissions are covered as well during backup fuel mode operation. However, the abatement of NO $_x$ will remain on the discretion of sufficient amounts of NH $_3$, unless a reducing agent dosing system as required for ANR < 1 can be utilized.

The presented catalyst systems #1 and #2 can both be continued to be operated in Diesel fuel backup mode, but the catalyst formulations require the use of ultra-low sulfur Diesel fuel.

3.2 Performance for ANR = 1.2

For engine operating points emitting NH_3 at levels slightly above NO_x , full NO_x conversion is possible from $300-500^{\circ}C$ using EAT system #1 (see Figure 4). In contrast, only 80-90% ammonia conversion is achievable for temperatures of $400^{\circ}C$ or below. However, if exhaust gas temperatures reach $450^{\circ}C$ or higher, 99% NH_3 conversion is possible. N_2O removal is, similar to ANR = 1, limited at temperatures below $400^{\circ}C$ reaching conversion rates above 90% only at temperatures of $450^{\circ}C$ or higher thus achieving the N_2O abatement required for significant GHG emission reduction compared to fossil fuels.

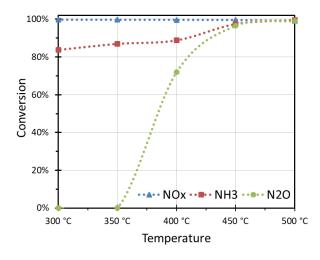


Figure 4. NO_x, NH₃ and N₂O conversion of catalyst system #1 under conditions specified as testing conditions 2 in Table 2.

For increased NH₃ conversion at temperatures below 450°C, EAT system #2 is an appealing option delivering more than 99% NH₃ conversion at

temperatures as low as 400°C (see Figure 5), lowering the required temperature by 50°C in comparison to EAT system #1. Simultaneously, high HC and NO_x conversion of more than 99% are possible at temperatures ranging from 300 – 500°C with CO conversions above 80% observed at or higher. However, while performance is around 70% at 400°C and above 90% at 450 - 500°C, at temperatures around 350°C a negative N2O conversion (indicating N2O formation by the exhaust gas system) is observed which cannot be counteracted by the deN2O catalyst in the EAT system #2. Hence, some additional N2O is produced by the undesired side reaction from NH₃ oxidation (Eq. 3). It needs to be pointed out that only around 350°C additional N2O formed while at all other exhaust gas temperature, N2O levels are either at raw gas emission concentrations or significantly lower.

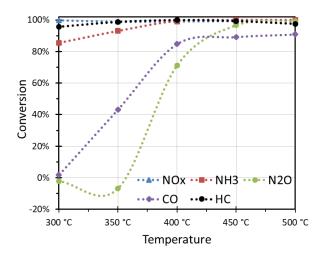


Figure 5. NO_x , NH_3 , N_2O , CO and HC conversion of catalyst system #2 under conditions specified as testing conditions 2 in Table 2.

In short, while EAT system #1 shows high NOx conversions over the entire temperature range at slightly above stochiometric conditions (ANR = 1.2), 450°C or more are required for high N₂O and performance. When removal temperatures for NH₃ removal are required, using EAT system #2 enables the removal of more than 99% of emitted ammonia at temperatures as low as 400°C alongside high NO_x or N₂O conversions. Additionally, high CO and HC conversions become possible. However, when operating the EAT system #2 at 350°C, additional N2O formation from inadequate NH₃ oxidation is observed, limiting the aftertreatment operation to higher temperatures. However, as 400°C or more are required for significant N₂O conversion which in turn is necessary to achieve significant GHG emission reduction, lower temperatures should be avoided in any case. In Diesel fuel backup operation this minimum temperature requirement would be lifted, as the concerned N_2O reaction will not be necessary.

3.3 Performance for ANR = 2

For engine operating points emitting NH₃ concentrations strongly exceeding NOx levels, full NO_x conversion can be achieved over the entire temperature range using EAT system #1 (see Figure 6). However, at ANR = 2 NH₃ conversions are limited to 50% at temperatures below 400°C reaching approx. 90% at 450°C with near full conversion is only possible Simultaneously, DeN₂O is strongly inhibited at temperatures below 400°C reaching a maximum N₂O conversion of 87% at approx. 450°C. However, contrary to the EAT system #1's behavior at NH3 to NOx ratios only slightly above one as shown above (see Figure 4), N₂O performance decreases at 500°C to 63%. Here, oxidation of excess NH3 strongly exceeding NOx levels forms small amounts of N2O which in turn cannot be compensated by the deN2O catalyst.

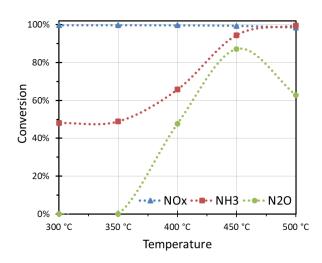


Figure 6. NO_x, NH₃ and N₂O conversion of catalyst system #1 under conditions specified as testing conditions 3 in Table 2.

For achieving high NH_3 conversions at lower temperatures with NH_3 levels significantly higher than NO_x concentrations, employing EAT system #2 presents a viable alternative. This system delivers 97% NH_3 conversion at temperatures as low as 400°C. Simultaneously, NO_x and HC conversion of more than 95% over the entire temperature range can be achieved. DeN_2O performance reaches up to 87% at 450°C but drops significantly to 63% at 500°C. Also, at exhaust gas temperatures of around 350°C, a negative N_2O conversion is detectable which in both cases indicates additional N_2O formation from inadequate NH_3 oxidation (Eq. 3) that cannot be compensated by the deN_2O catalyst. Additionally, some CO

oxidation activity is detectable reaching more than 50% starting at temperatures around 400°C.

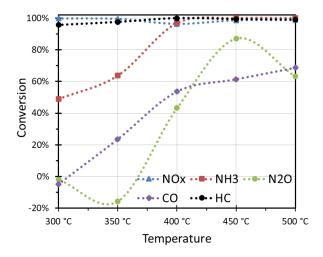


Figure 7. NO_x, NH₃, N₂O, CO and HC conversion of catalyst system #2 under conditions specified as testing conditions 3 in Table 2.

To summarize, EAT system #1 demonstrates excellent NO_x conversion across all temperatures tested under highly above stochiometric conditions (ANR = 2), but requires 450°C for optimal N₂O and NH₃ removal, with diminishing deN₂O performance at higher temperatures. EAT system #2 instead, can eliminate approximately 97% of emitted ammonia at temperatures as low as 400°C, while maintaining high NO_x or N₂O conversions. This system also allows for some CO and substantial HC conversions. However, operating EAT system #2 at 350°C or 500°C results in reduced N2O conversion due to inadequate NH₃ oxidation, restricting optimal aftertreatment operation with high removal for all pollutants to a narrow temperature range around 450°C. This highlights the catalytic limitations of even advanced exhaust gas aftertreatment systems, as even optimized catalyst selectivities of NH3 oxidation towards N2 exceeding 99% cannot completely prevent N2O formation as a byproduct. Given that NH₃ engine raw gas concentrations are anticipated to be in the thousands, avoiding significant N2O formation is extremely difficult, making a 90% GHG emission reduction a formidable challenge for highly above stochiometric NO_x NH_3 to Increasing the Diesel fuel share may alleviate the issue if restricted to specific engine load points, but the GHG reduction requirement will remain and can also be challenging when the Diesel fuel share is increased.

4 CONCLUSION

Overall, achieving lower greenhouse impact by switching to alternative fuels such as ammonia is possible even if engine out emissions of NH₃, NO_x and N₂O are drastically higher compared to engines powered by traditional carbon based fuels. Due to the good fuel quality of NH₃, no temperature requirements are imposed for adequate NOx conversion, but a reducing agent injection in the aftertreatment system at ANR < 1 becomes necessary to comply with strict emission limits such as EU Stage V. Even optimized exhaust gas aftertreatment systems as presented in this paper strictly require temperatures around 400°C for significant N2O conversions while temperatures above 450°C are necessary for more than 90% N₂O abatement. Such a removal rate is mandatory if aspiring GHG emission reductions in comparison to fossil Diesel fueled engines. Additionally, while NH₃ levels in the raw exhaust gas slightly exceeding NO_x concentrations compensated by the exhaust gas aftertreatment system without penalizing NO_x or N₂O conversion, excessive NH3 to NOx ratios pose the risk of additional N2O being formed by side reactions from NH₃ oxidation. This in turn can potentially nullify the GWP reduction potential by switching from fossil fuel to NH₃ as an alternative fuel.

For pilot fuel ignited NH₃ dual fuel engines, the additional pollutant emissions from the carbonbased pilot fuel, namely HC and CO can be eliminated only by the catalyst system #2 in parallel to the removal of NH₃ combustion pollutants. When the engine is running in fuel share modes containing high amounts of Diesel fuel or even in the Diesel fuel backup mode, the NH3 engine pollutant removal catalyst systems #1 and #2 will continue to operate, but as the NH₃ to NO_x ratio in the raw exhaust is falling below 1, there must be additional dosing of a reducing agent, preferably NH₃. Low pollutant emissions could also be achieved during such operation, aside from particle emissions. In order to cope with strict particle mass and particle number emission regulations also under such circumstances, a DPF could be added to the system, without impacting the NH₃ emission treatment.

Only close collaboration on this topic between engine development and exhaust gas aftertreatment ensures to meet legal pollutant requirements while maintaining low emissions of undesired, currently non-regulated substances.

5 DEFINITIONS, ACRONYMS, ABBREVIATIONS

ANR: Ammonia-NOx-Ratio

ASC: Ammonia slip catalyst

CI: Compression ignition

CO: Carbon monoxide

CO2: Carbon dioxide

DOC: Diesel oxidation catalyst

EAT: Exhaust gas aftertreatment

GHG: Greenhouse gas

GWP: Global warming potential

HC: Hydrocarbon

ICE: Internal combustion engine

NH₃: Ammonia

N₂O: Nitrous oxide

NO: Nitrogen monoxide

NO₂: Nitrogen dioxide

SCR: Selective catalytic reaction

SI: Spark ignition

ULSD: ultra-low-sulfur diesel

6 REFERENCES AND BIBLIOGRAPHY

- [1] P. Forster, T. Storelvmo, K. Armour, W. Collins, J. Dufresne, D. Frame, D. Lunt, T. Mauritsen, M. Palmer, M. Watanabe and M. Wild, "The Earth's Energy Budget, Climate Feedbacks, and Climate Sensitivity," in Climate Change 2021: The Physical Science Basis. Contribution of Working Group I to the Sixth Assessment Report of the Intergovernmental Panel on Climate Change, Cambridge, Cambridge University Press, 2021, pp. 9923-1054.
- [2] A. Wong, N. Selin, S. Eastham, C. Mounaïm-Rousselle, Y. Zhang and F. Allroggen, "Climate and air quality impact of using ammonia as an alternative shipping fuel,"

- Environmental Research Letters, vol. 19, no. 8, p. 084002, 2024.
- [3] P. Dimitriou and R. Javaid, "A review of ammonia as a compression ignition engine fuel," *International Journal of Hydrogen Energy*, vol. 45, no. 11, pp. 7098-7118, 2020.
- [4] C. Lhuillier, P. Brequigny, F. Contino and C. Rousselle, "Combustion characteristics of ammonia in a modern spark-ignition engine," SAE Technical Paper 2019-24-0237, 2019.
- [5] V. Sharma, A. Panesar, G. de Sercey and S. Begg, "A Review of Ammonia Combustion and Emissions Characteristics in Spark-Ignition Engines and Future Road Map," *Energies*, vol. 18, no. 1, p. 41, 2025.
- [6] S. C. Kong, "Combustion efficiency and exhaust emissions of ammonia combustion in diesel engines," in 2008 Annual NH3 Fuel Conference, Minneapolis, 2008.
- [7] C. Lhuillier, P. Brequigny, F. Contino and C. Mounaïm-Rousselle, "Experimental study on ammonia/hydrogen/air combustion in spark ignition engine conditions," *Fuel*, vol. 269, p. 117448, 2020.
- [8] S. Geng, A. Ambalakatte and A. Cairns, "Ammonia and Hydrogen Co-Fuelling in a Modern Spark Ignition Engine," in 2024 MariNH3 Conference, Nottingham, 2024.
- [9] T. Imhoff, S. Gkantonas and E. Mastorakos, "Analysing the Performance of Ammonia Powertrains in the Marine Environment," *Energies*, vol. 14, no. 21, p. 7447, 2021.
- [10] S. Mashruk, H. Shi, L. Mazzotta, C. Ustun, B. Aravind, R. Meloni, A. Alnasif, E. Boulet, R. Jankowski, C. Yu and Alnajideen, "Perspectives on NOx Emissions and Impacts from Ammonia Combustion Processes," *Energy & Fuels*, vol. 38, no. 20, pp. 19253-19292, 2024.
- [11] C. Tornatore, L. Marchitto, P. Sabia and M. De Joannon, "Ammonia as green fuel in internal combustion engines: State-of-the-art and future perspectives," Frontiers in

- Mechanical Engineering, vol. 8, p. 944201, 2022.
- [12] M. Jabłońska and R. Palkovits, "It is no laughing matter: nitrous oxide formation in diesel engines and advances in its abatement over rhodium-based catalysts," *Catalysis Science & Technology*, vol. 6, no. 21, pp. 7671-7687, 2016.
- [13] The National Institute for Occupational Safety and Health (NIOSH), [Online]. Available: www.cdc.gov/niosh/npg/npgd0028.html. [Accessed January 2025].

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