ZURICH, MAY 19 – 23, 2025

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Exhaust gas treatment concept with coordinated combustion process management for NH3-diesel engines

Exhaust Gas Aftertreatment Solutions & CCS

Felix Wenig, University of Rostock, Chair of Piston Machines and Combustion Engines

Bert Buchholz, University of Rostock, Chair of Piston Machines and Combustion Engines
Uwe Etzien, University of Rostock, Chair of Piston Machines and Combustion Engines
Sascha Prehn, University of Rostock, Chair of Piston Machines and Combustion Engines
Robert Bank, FVTR GmbH
Thomas Sadlowski, FVTR GmbH

DOI: https://doi.org/10.5281/zenodo.15276108

ABSTRACT

The use of ammonia as fuel for internal combustion engines has been gaining increasing relevance recently. Especially for large engine applications like shipping or stationary power plants, ammonia is considered a promising carbon-free alternative to conventional fuels like diesel or natural gas. However, to fully utilize the advantages of ammonia, certain challenges regarding its combustion characteristics and emissions need to be addressed. The high minimum ignition energy as well as the low burning velocity can lead to unburned ammonia in the exhaust gas. Furthermore, the nitrogen contained in the NH3 molecule could result in N2O and increased NOx emissions. Recent studies have revealed that appropriate adjustments of the combustion process allow stable engine operation with low NH3-slip and N2O emissions. However, NOx emissions and NH3-slip exhibit a trade-off behavior, meaning that the development of adapted exhaust gas treatment concepts is essential. The application of SCR catalysts to lower nitrogen oxide emissions is a widely recognized method for conventional diesel engines. While urea is introduced into the exhaust in existing diesel engine SCR systems, using the ammonia already present in the exhaust due to NH3-slip is the logical choice for ammonia-powered engines. This method requires a coordinated combustion process management to maintain the NOx/NH3 concentration ratio at nearly a 1:1 level. A slight excess of NH3 might be needed to ensure an optimized SCR process, resulting in the necessity for an NH3-slip catalyst (ASC) located downstream the SCR catalyst. In this study, a potential exhaust gas treatment concept for an ammonia-diesel dual-fuel engine, which was developed using an experimental approach based on combustion process development and preliminary model-gas tests, is presented.

To evaluate the potential for controlling raw exhaust emissions, two engine parameter variations were conducted on a medium-duty single-cylinder engine operating in NH3-diesel dual-fuel mode with 90% ammonia energy share. The effects of center of combustion and the excess-air ratio (Lambda) on combustion and emission behavior were investigated. Based on the emission results obtained from the engine test bench, two different catalyst technologies were assessed under model-gas test bench conditions. A commercial SCR catalyst with DeN2O functionality was tested for NH3 and NO conversion as well as N2O reduction potential. Subsequently, two commercial ammonia slip catalysts were evaluated under emission conditions derived from measurements downstream of the SCR. In addition to their NH3 conversion potential, the focus was also placed on species formation over ammonia slip catalysts used for ammonia powered engines. Finally, a modular aftertreatment testing concept, including potential catalyst arrangements for ammonia engines, is presented using the information gathered during the combustion process development as well as the model gas tests.

1 INTRODUCTION

Currently, the use of alternative fuels as part of the climate transition is a highly discussed topic. In sectors requiring high amounts of energy for operation, chemical energy storage solutions with high energy densities represent a promising approach. Alongside methanol and methane, significant attention is being given to ammonia as a carbon-free alternative. Recent studies have primarily focused on the marine sector, investigating ammonia combustion concepts for internal combustion engines (ICEs). Mante et al. [1] carried out investigations for an ammonia-diesel dual fuel combustion process on a medium duty engine. In their study, a port fuel injection (PFI) concept with gaseous ammonia injected into the engine's intake air was used. Diesel fuel was directly injected into the combustion chamber, serving as a promoter fuel to provide ignition energy. Wermuth et al. [2] examined a NH_3-diesel dual fuel concept, in which both ammonia and diesel were directly injected into the combustion chamber of a large-bore medium speed marine engine. This setup utilized two separate high-pressure fuel systems with individual injectors, allowing independent injection timings. A further approach, investigated by Braun et al. [3], replaced diesel with hydrogen as the ignition promoter within a spark-ignited combustion process for ammonia-powered inland waterway vessels. For a detailed overview about feasible combustion concepts for ammonia engines, reference is made to Braun et al. [3].

Besides the transport sector, the stationary sector for power generation can also benefit from these new fuel concepts. While gensets are primarily used for partially mobile electricity production, stationary power plants often combine centralized heat and electricity generation at fixed locations. Modern stationary power plants are often designed as natural gas combustion engines, which can be quickly regulated in power output, allowing flexible interactions within the power grid and enhancing stability. Additionally, the low investment costs for combustion engines and their high fuel flexibility make this technology a reliable option for the future. To achieve GHG neutrality within this sector, ammonia could also play a key role. For stationary power plants, ammonia can serve as hydrogen supplier, especially in locations where H_2 grid infrastructure does not exist. For decentralized power generation applications with gensets, ammonia allows for simpler storage concepts compared to pure hydrogen.

However, the use of ammonia in combustion engines presents certain challenges, especially regarding emission behavior. Incomplete ammonia combustion can result in unburned NH_3 being released into the exhaust gas. Furthermore, nitrogen oxide emissions, such as NO_x or N_2O, may occur. While NO_x and NH_3 have severe toxicological effects, N_2O is a particularly harmful greenhouse gas, with a global warming potential 273 times greater than that of CO_2 (for 100-year time horizon) [4]. Therefore, minimizing these emissions is essential. Although, adjustments of the combustion process can help control these emissions, the stringent limits set by emission legislation for stationary engines (e.g., EU Stage V) make it difficult to rely only on combustion optimization. Rather, a combination of combustion process management and exhaust gas treatment will be necessary.

Exhaust gas treatment systems for ammonia engines are still in early stages of development. Currently, it remains unclear which catalyst technologies will be necessary and which combination will deliver the best performance. However, it is evident, that SCR technologies will play a critical role due to the presence of NO_x in the engine's raw exhaust gas [5]. Nitrogen based emissions are likely to be significantly higher than those of conventional engines due to nitrogen content in the NH_3 molecule. Additionally, NH_3 emissions from ammonia slip cannot be entirely avoided, especially in pre-mixed combustion concepts, where unburned ammonia may flow directly into the exhaust port during valve overlap. However, this behavior can be exploited for the SCR process, potentially making additional reducing agents like urea redundant [5]. This procedure requires an adequate combustion process management to maintain the ammonia-NO_x-ratio (ANR) as close as possible to stoichiometric conditions (ANR=1). ANR<1 might have to be compensated by additional NH_3 injection into the exhaust gas. Conversely, if the NH_3 concentration in the raw exhaust gas exceeds that of NO_x (ANR>1), or NH_3 leaves the SCR unreacted, an ammonia slip catalyst (ASC) must be provided.

To fully exploit the GHG advantages of using ammonia as a fuel, N_2O emissions must be minimized. Kröcher et al. [6] demonstrated, that N_2O conversion can be achieved using commercial catalyst technologies under model gas test bench conditions. However, the complete removal of N_2O with currently available materials requires high exhaust gas temperatures. Furthermore, the presence of H_2O and NH_3 can reduce catalyst reactivity. It should also be considered that N_2O formation might occur during NH_3 conversion over SCR catalysts and especially ammonia slip catalysts [7], [8], underlining the necessity of a well-designed aftertreatment system and its coordinated interaction with combustion process management.

To evaluate the performance of various catalyst technologies under realistic engine conditions, systematic investigations on an engine test bench are necessary. A modular system is required for these investigations, enabling multiple catalysts to be installed in sequence and allowing for easy exchange and reordering during testing. This study investigates an ammonia-diesel dual fuel combustion concept, including the consideration of exhaust gas treatment in the context of stationary combustion engines (gensets). For this purpose, combustion process investigations were conducted on a medium-duty single cylinder engine (SCE) with focus on achieving stoichiometric ANR for high ammonia energy share operation. Using the SCE emission data, preliminary evaluation of a commercial dual-function SCR catalyst and two commercial state-of-the-art ASCs on a model gas test bench was carried out. Based on these results, the modular exhaust gas treatment concept for the engine test bench will be presented.

2 EXPERIMENTAL SETUP

In this section the experimental setup of both the engine test bench, including the ICE and all relevant technical components, and the model gas test bench will be described. Furthermore, the methodology for both investigations will be presented.

2.1 Engine test bench

In this study a pre-mixed combustion concept with NH_3 mixed with air upstream of the engine cylinder and ignition via diesel-pilot is examined. For the experimental investigations a test bench equipped with a single-cylinder research engine (SCE) was used (see Figure 1). For load simulation the SCE is connected with a 220 kW dynamometer for medium-duty applications. To simulate turbocharged operation as in multi-cylinder engines, the test bench is equipped with a fully conditionable air system. The charge air can be supplied at pressures of up to 4 bar absolute and heated to 100°C. An exhaust gas flap is installed in the exhaust system to create backpressure. The diesel fuel system consists of a fuel meter and fuel conditioning system, enabling the measurement of fuel consumption and variation in fuel temperature. Additionally, the high-pressure diesel fuel system is equipped with a common rail high-pressure pump and a common rail injector for commercial vehicles.

The ammonia fuel system is installed in a vented safety cabinet to minimize the risk of leakage into the test cell. Liquid ammonia is stored in a pressurized gas bottle at approximately 9 bar absolute. After exiting the bottle, the ammonia passes through an evaporator to ensure it is in a fully gaseous state for PFI injection. A pressure regulator is installed to control the injection pressure, allowing it to be varied between 3 and 10 bar absolute. To monitor the ammonia fuel consumption, a Coriolis measurement system was installed. Finally, the gaseous ammonia is introduced into the engine's air system by a gas injector. For a detailed explanation of the ammonia fuel system, reference is made to previous publications by Mante et al. [1].

To ensure constant and reproducible engine conditions, all quasi-stationary values like pressure and temperature of every different medium are monitored by a measurement data acquisition and controlled by a LabView-based programmable logic controlling system. An open-access research engine control unit enables direct intervention in the combustion process, allowing for the adjustment of engine parameters such as diesel injection timing, injection pressure and number of injections per cycle.

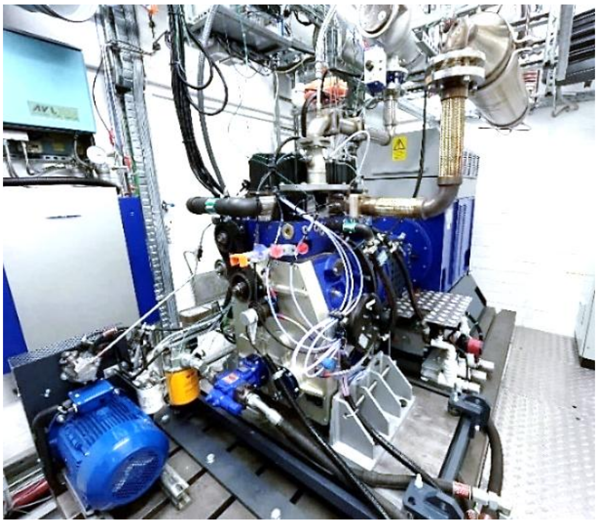

Figure 1. Single cylinder research engine

The SCE is based on the *DEUTZ TCD 5.2/7.8* diesel engine with 4/6 cylinders for mobile machinery applications. Relevant engine parameters of the SCE are shown in the table below:

Table 1: Engine parameters

1 cylinder, 4-stroke diesel	
Rated speed	2,300 rpm
Rated Power	45 kW
Bore	110 mm
Stroke	136 mm
Engine displacement	1.29 l
Compression ratio	16.4:1

In order to analyze and monitor the combustion process a flush-mounted piezoelectric pressure sensor and a combustion analysis system were used. The in-cylinder pressure is measured and referred to the piston position with a resolution of 0.1 bar/°CA. With different calculation tools, implemented in the indication system, parameters like indicated mean effective pressure (IMEP), peak pressure as well as start, center and end of combustion can be determined. The calculation of the mean values is based on 250 consecutive work cycles.

Besides the analysis of the combustion behavior, also the characterization of the emission matrix should have been taken into account. To continuously measure a wide range of exhaust gas components with high accuracy, a FTIR-spectrometer (Fourier-transform infrared spectroscopy) with a specific evaluation method for ammonia powered engines as well as an analyzer for hydrogen was installed. Therefore, it was possible to determine ammonia slip up to 10,000 ppm and H_2O-concentrations of up to 35 vol.-% in the exhaust gas. Unburned hydrocarbons were measured using a flame ionization detector (FID).

2.2 Model gas test bench

A model gas test rig (see Figure 2) was used to evaluate the performance of conventional catalytic converters with exhaust gas conditions typical for ammonia powered engines.

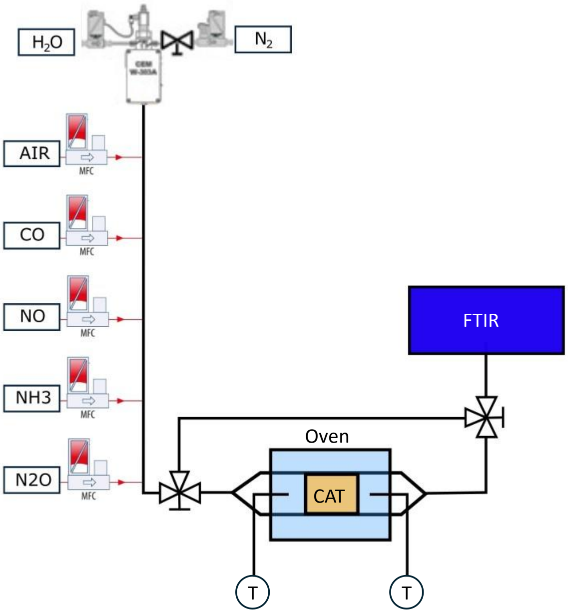

Figure 2. Schematic representation of the model-gas test bench setup

The set up consists of several mass flow controllers (MFC) for modelling the exhaust gas composition as well as an evaporation unit to ensure the added H_2O is fully vapored. Furthermore, the whole system is insulated and externally heated. The sample is installed in an oven with a defined heating zone including thermocouples and a differential pressure sensor. The gas temperature in the sample itself can be varied between 100-550 °C. Downstream the oven, a heated valve is integrated to adjust the system pressure up to 6 bar. Both, gas composition from the feed gas as well as behind the catalyst sample can be determined using a FTIR unit.

2.3 Methodology

Previous studies on the engine test bench focused on minimizing NH_3-slip at medium load points with 70-80% ammonia energy share (AES) [9]. With regard to future engine concepts including exhaust gas treatment, it should be investigated whether it is possible to achieve high AES operation (>80 %) with similar NH_3-to-NO_X values, resulting in an ANR close to 1. For this purpose, two engine parameters variations were carried out with the engine running in high load (18 bar IMEP) with 90 % AES. First, the effect of center of combustion (50 % mass fraction burned - MFB50) was investigated by varying it from 9 crank angle degree after top dead center (°CAaTDC) to 3 °CAaTDC through adjusting start of diesel injection (SODI). While later MFB50 resulted in unstable combustion with high amounts of unburned NH_3, earlier MFB50 was constrained by in-cylinder pressure gradients. Based on these results, a fixed MFB50 was chosen for the second test, which involved a variation of excess air ratio (Lambda) from λ=1.25 to λ=2.0. Leaner conditions were not feasible due to high NH_3-slip and N_2O emissions. Conversely, Lambda values lower than λ=1.25 were unreasonable because of increasing NH_3-slip and deteriorating ANR. Moreover, richer operation was also limited by in-cylinder pressure gradients. Table 2 shows the boundary conditions for both variations.

Table 2. Engine settings used for combustion process development

Engine parameter / Unit	Variation 1	Variation 2
Speed / rpm	1,500	1,500
IMEP / bar	18	18
AES / %	90	90
MFB50 / °CAaTDC	**3 - 9**	~5
Diesel injection pressure / bar	900	900
Lambda / -	1.7	**1.25 - 2.0**
Charge air temperature / °C	50	50

On the model gas test bench, the performance of two commercial state-of-the-art catalyst technologies should be evaluated for the use in scenarios involving ammonia-powered engines. For the first test, a commercial SCR catalyst with DeN_2O functionality was exposed to synthetic exhaust gas, based on engine-out emission data obtained from preceding combustion process development. Due to dosing limits of certain mass flow controllers, the final model gas composition had to be adjusted, while maintaining the same ANR as in the measured engine's raw exhaust gas. The mean temperature of the SCR was varied between 250-550 °C. For the second test, two commercial ammonia slip catalysts (ASCs) were tested using a gas composition derived from the concentrations downstream of the SCR in the first test. Here too, the exact concentrations had to be modified due to dosing limitations. For this test, the mean temperature of both catalysts was varied between 250-500 °C. The components and their respective concentrations for both tests are listed in Table 3.

Table 3. Model gas composition used for pre-testing catalyst technologies

Species / unit	Conc. for SCR	Conc. for ASCs
NO / ppm	2,400	0
NH_3 / ppm	2,650	400
N_2O / ppm	75	0
H_2O / vol.-%	8.0	8.0
O_2 / vol.-%	6.9	6.9
N_2 / vol.-%	balance	balance

Considering both, the investigations regarding the optimization of the dual fuel combustion process as well as the first results of the performance of two catalyst technologies on a model gas test bench, an exhaust gas treatment concept for NH_3-Diesel dual fuel engines is derived. Further investigations will focus on the performance of this concept, installed on the engine test bench running in NH_3-diesel dual fuel mode. Starting point for these upcoming tests will be the results from the combustion process development, presented in this paper. From there, the combustion process will be further refined, to optimize the interactions between combustion process and exhaust gas treatment system. Figure 3 illustrates the methodology for this project.

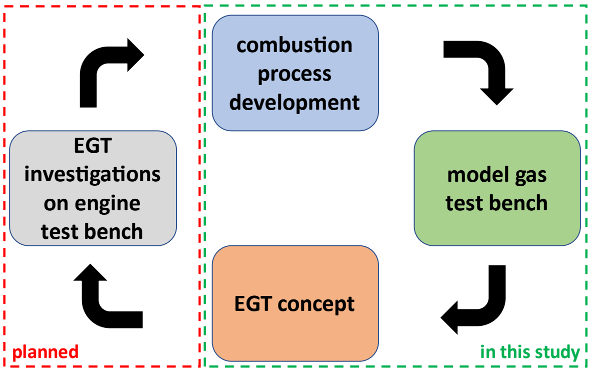

Figure 3. Methodology for NH_3-diesel combustion process and exhaust gas treatment concept investigations

3 RESULTS

This section describes the results from both the combustion development as well as from the model gas test bench. First, the effects of MFB50 and Lambda will be investigated in terms of combustion characteristics and emissions data. Next, the performance of the SCR and both ASCs will be evaluated based on variations in catalyst temperature. Finally, the exhaust gas treatment concept for the engine test bench will be presented.

3.1 Effect of center of combustion

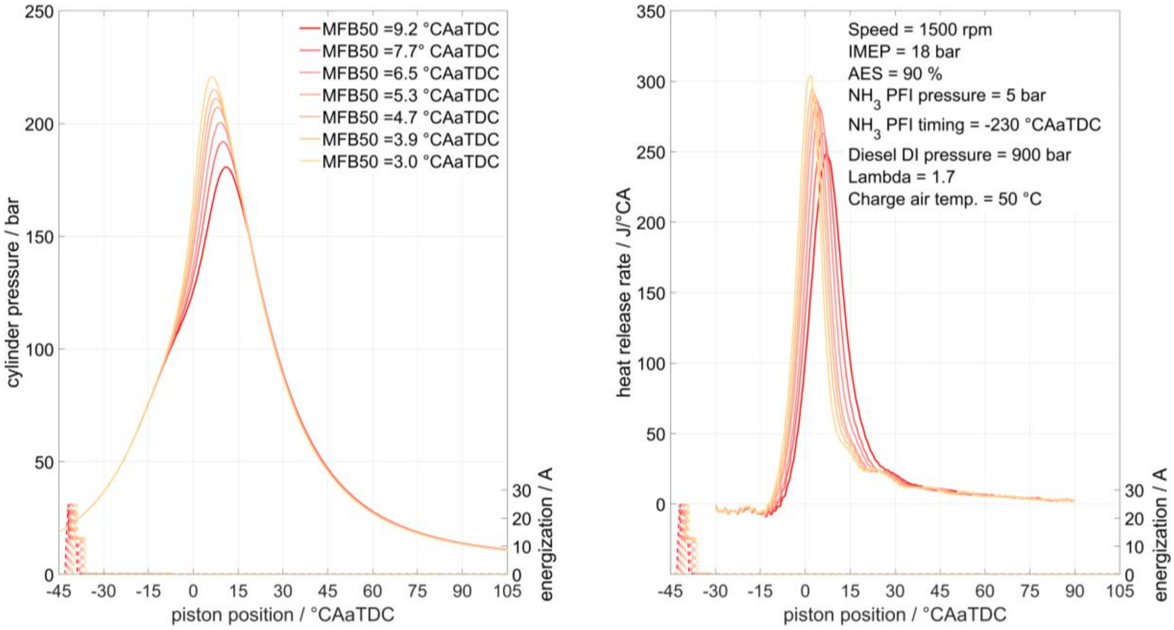

Figure 4. Impact of SODI/MFB50 on in-cylinder pressure curves and HRR

The effect of center of combustion on in-cylinder pressure and heat release rate (HRR) for a high load point with 90 % AES is depicted in Figure 4. In HRR, the influence of MFB50 is visible through the shift in the curve and the higher peaks for earlier MFB50. The dotted lines indicate the diesel injector energization. When MFB50 is advanced, more heat is released within a specific crank angle interval because the low piston velocity near top dead center provides more time for combustion. This effect leads to higher peaks in in-cylinder pressure as well as higher pressure gradients. The shift of combustion is also visible in Figure 5.

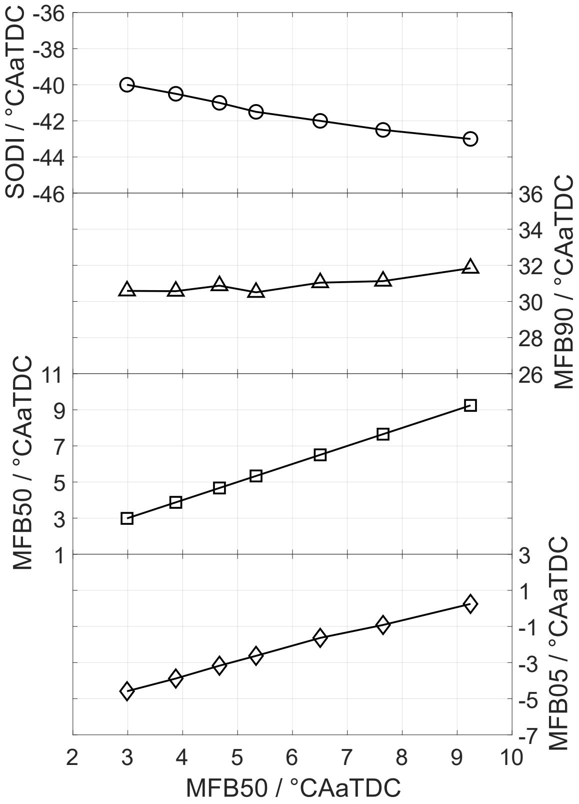

Figure 5. Effect of SODI/MFB50 on phases of combustion

As it can be seen in the upper graph, SODI was adjusted to change MFB50. Notably, to advance MFB50, SODI had to be delayed. This is due to the decreasing ignition delay at later injection timings as shown in Figure 6 or the graph for start of combustion (MFB05) in Figure 5. When diesel is injected later in compression phase, temperature and pressure of combustion chamber are increased, resulting in faster evaporation and therefore faster ignition of the diesel spray. While MFB05 and MFB50 are advanced, end of combustion (MFB90) seems to be only slightly affected, as it is only minimally advanced. This is because of an increased duration of the second half of combustion $CD_{50\text{-}90}$ (Figure 6). Due to the reduced ignition delay for early MFB50 with late SODI, it could be argued, that there is less time available for homogenization between the diesel spray and the NH_3-air mixture. Therefore, when diesel starts to ignite, less NH_3 is covered by diesel fuel, leading to fast burning areas with high diesel concentrations and slow-burning areas rich in NH_3.

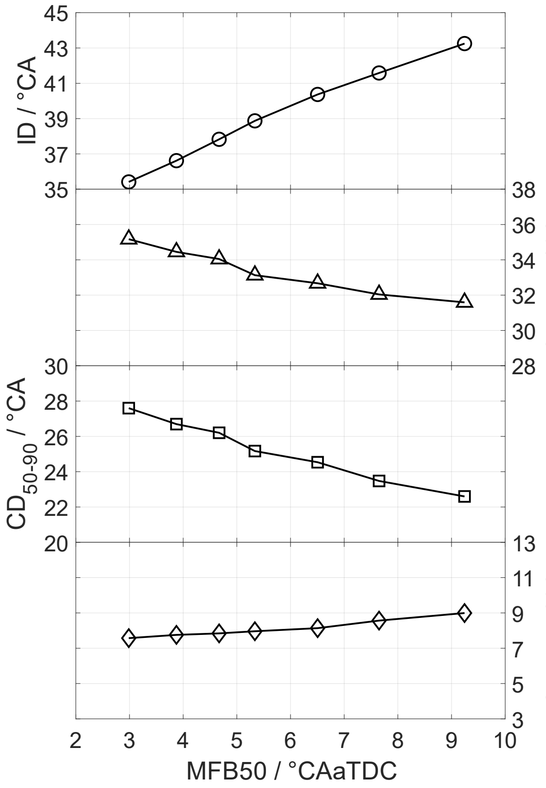

Figure 6. Effect of SODI/MFB50 on ignition delay and combustion duration

Figure 7 illustrates the effect of SODI/MFB50 on NH_3-slip and NO_x emissions. Additionally, the resulting ANR is depicted in the lower graph. Due to faster heat release (high HRR) at earlier MFB50, combustion temperatures rise and NO_x emissions increase, as it is commonly known from conventional diesel engines. Unburned NH_3 emissions appear to decrease with advancing MFB50, possibly due to improved dissociation of the molecule at higher combustion temperatures. Although, the effect is very limited a correlation appears to exist between NH_3-slip and MFB90. When the end of combustion is delayed, flame quenching effects are more likely to occur, leaving more ammonia unburned.

In any case, the ANR decreases, mainly due to the increasing NO_x emissions. However, an ANR of 1 cannot be achieved only by varying MFB50 for this specific operational point.

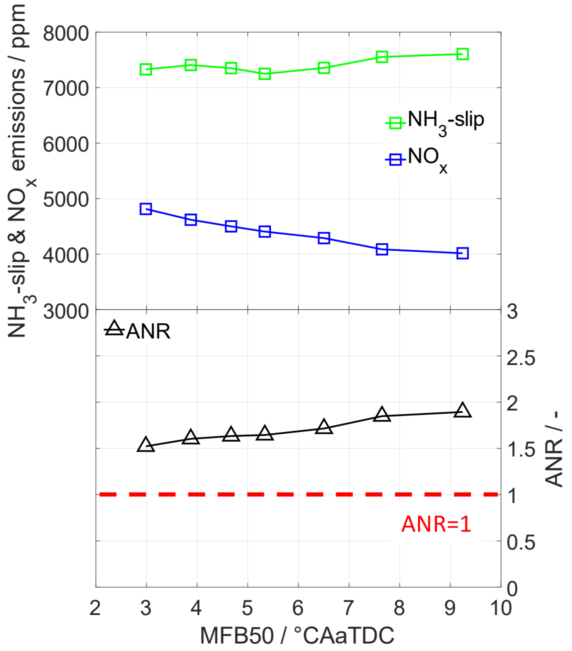

Figure 7. NH_3-slip, NO_x emissions and ANR depending on SODI/MFB50

Figure 8 shows the influence of MFB50 on N_2O and the resulting specific indicated GHG emissions (CO_2 + N_2O) using a GHG-factor of 273 [4] for N_2O.

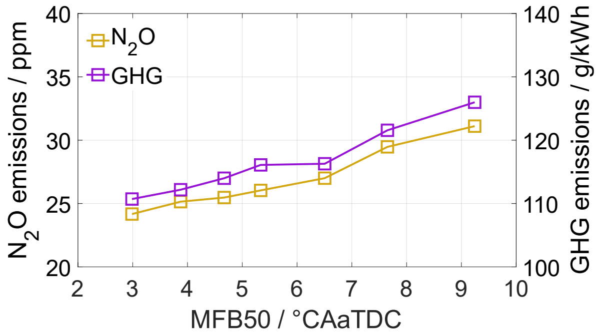

Figure 8. N_2O and specific indicated GHG emissions as CO_2-equivalent (CO_2+N_2O) depending on SODI/MFB50

Similar to NO_x, N_2O-formation depends on the presence of oxygen. While for low oxygen concentrations N_2O is mostly generated by the reaction of NH radicals with NO, for high oxygen levels the reaction of NH_2 with NO_2 is dominant [10, 11]. While thermal nitrogen oxide emissions occur at higher temperatures, most of the NO and NO_2 responsible for N_2O formation originate from the nitrogen contained in the NH_3 molecule. The typical temperature range for N_2O formation lies below 1500 K, indicating that most of the N_2O formed during NH_3 oxidation is fuel-derived [11]. At higher temperatures thermal decomposition of N_2O occurs, resulting in formation of N_2 or NO [10, 12]. As it can be seen, early MFB50 with higher process temperatures lead to a significant decrease in N_2O and therefore GHG emissions.

In Figure 9, CO and HC emissions are depicted as a function of MFB50. Both emissions result from incomplete diesel combustion, though both levels are already quite low due to the minimal amount of diesel burned during the test. Basically, carbon monoxide is generated during the absence of oxygen and the resulting incomplete oxidation to CO_2 [13]. In this case, oxygen concentration should be sufficient with Lambda at λ=1.7. However, also for lean conditions with surplus oxygen, CO emissions can occur, which is due to low combustion temperature. Extinguishing effects, especially near the cylinder wall, can be promoted at high Lambda values [13]. When MFB50 is advanced, CO emissions decrease due to increasing combustion temperature.

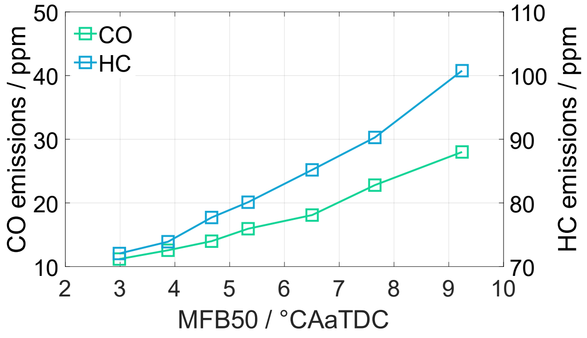

Figure 9. CO and HC emissions depending on SODI/MFB50

The conditions required to form unburned HC emissions are quite similar to those for CO. Excess air ratios below λ=1 can lead to incomplete combustion due to the lack of oxygen. For lean conditions, temperature is the crucial factor. Unburned HC emissions are often formed near the cylinder wall due to wall quenching, where low temperatures can inhibit flame propagation [13]. When MFB50 is advanced, combustion temperature increases, resulting in lower HC emissions. Furthermore, combustion duration decreases at later MFB50 (see Figure 6), shortening the flame's residence time and resulting in less complete fuel oxidation [13].

The effects of MFB50 are also evident in the exhaust gas temperature (see Figure 10). As expected, the exhaust temperature increases with later MFB50. However, the difference is minimal due to the slight shift in MFB90 (see Figure 5). The indicated thermal efficiency (ITE) is affected by MFB50 due to variations in wall heat loss intensity, which tends to be higher for early MFB50. For very late MFB50, ITE is reduced due to higher exhaust gas temperature and therefore increased heat loss.

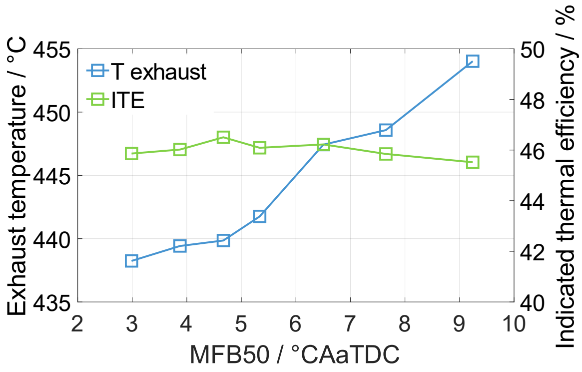

Figure 10. Effect of SODI/MFB50 on exhaust gas temperature and indicated thermal efficiency

It was revealed, that this specific engine operational point with high AES can be optimized by adjusting SODI and, therefore, MFB50. Especially N_2O, CO and HC emissions are adequately controllable. However, NH_3-slip was only slightly affected by MFB50, resulting in an ANR of 1.5 for the best case. This ratio, with a large excess of NH_3, could lead to significant amounts of NH_3, not participating in the SCR process. Consequently, an ASC downstream of the SCR would be mandatory, but it is unclear whether the ASC can handle these large amounts of NH_3 [5].

Although N_2O emissions are already quite low, a DeN2O-catalyst must be included in future aftertreatment concepts for ammonia engines. As it is already known, catalytic decomposition of N_2O requires high temperatures [6]. For this test, even at high load, the exhaust gas temperature did not exceed 455 °C. Additionally, the potential formation of N_2O over ammonia slip catalysts with these large amounts of excess NH_3 poses a significant challenge. As a consequence of these findings, it is important to investigate the impact of air-fuel ratio (Lambda), which will be discussed in the next section.

3.2 Effect of excess-air ratio (Lambda)

The impact of excess-air ratio (Lambda) on in-cylinder pressure and HRR can be seen in Figure 11. The dotted lines represent the diesel injector energization. While injection duration was kept constant, the start of energization was adjusted to maintain MFB50 at approximately 5 °CAaTDC. As it can be clearly seen, Lambda has a major influence on combustion behavior. Low Lambda leads to larger peak in HRR with high combustion temperatures. However, the maximum in-cylinder pressure decreases for lower Lambda due to decreased charge air pressure.

Figure 12 and Figure 13 show more detailed aspects of combustion behavior. As it can be seen in the top graph (Figure 12), SODI had to be adjusted to maintain MFB50 constant. At low Lambda values, SODI had to be delayed to achieve the same MFB50, indicating that the ignition conditions worsened.

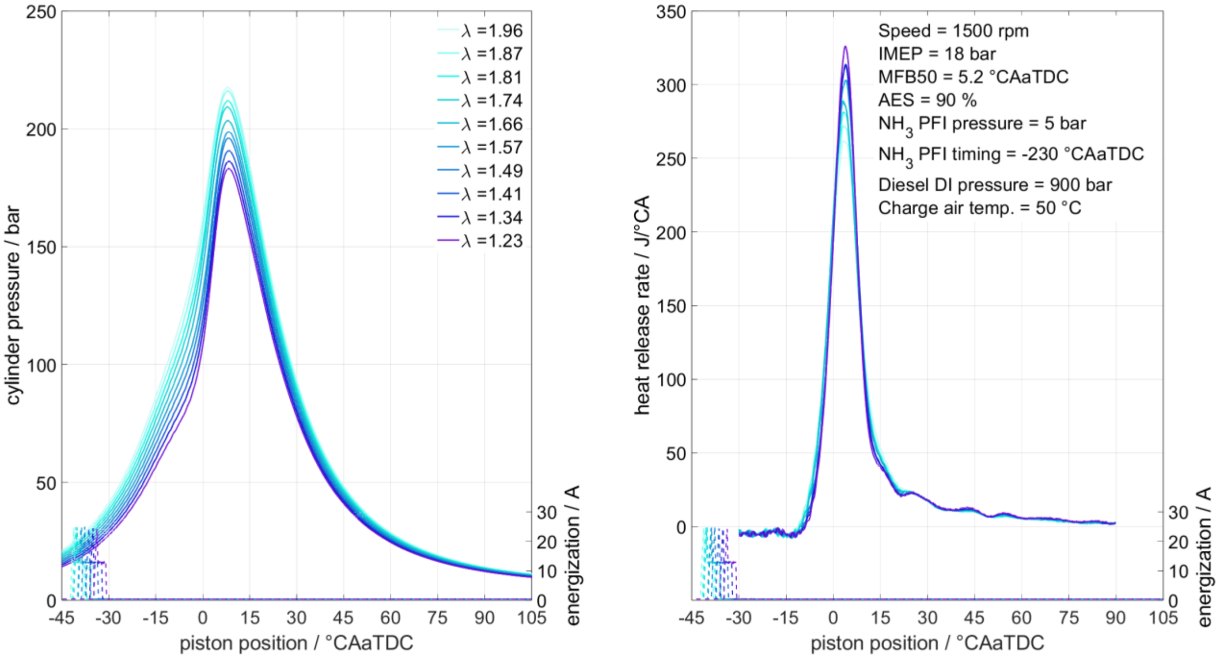

Figure 11. Impact of Lambda on in-cylinder pressure curves and HRR

Ignition conditions are influenced by both physical and chemical effects. Generally, low Lambda values are expected to improve fuel ignition due to reduced air dilution (chemical). However, at high Lambda values, charge air pressure and therefore chamber pressure during compression stroke are increased, allowing for enhanced spray atomization (physical). In this case, the reduced pressure at low Lambda values appears to have a more dominant effect. However, due to the required delay of SODI to maintain a constant MFB50, ignition delay decreases (Figure 13). This can be attributed to better ignition conditions for later SODI, where higher chamber temperatures enable faster diesel spray evaporation and ignition of the diesel spray.

As MFB50 does not change and MFB05 is slightly postponed, probably due to later SODI, the duration of the first half of combustion slightly decreases for low Lambda. In contrast, MFB90 is delayed the second half of combustion is extended.

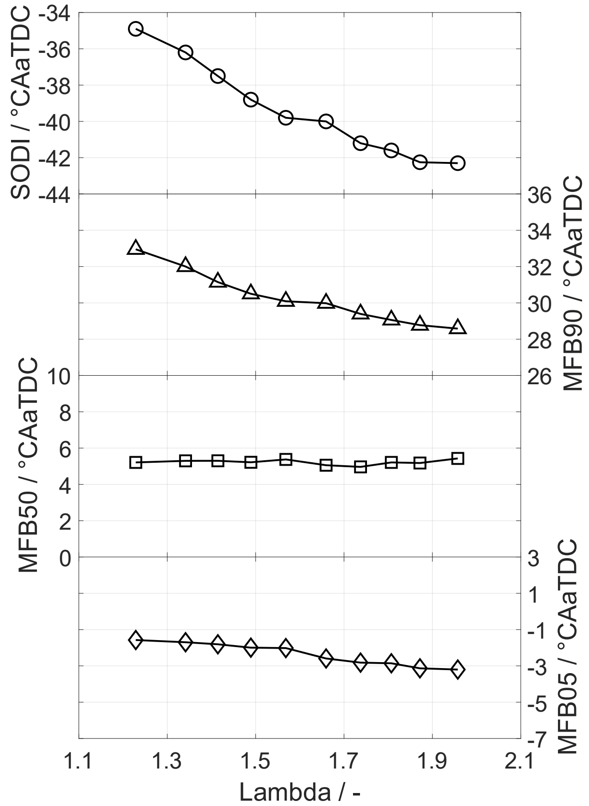

Figure 12. Effect of Lambda on phases of combustion

Overall, the combustion duration increases under richer conditions, which is unexpected because of the increased laminar burning velocity of NH_3-air mixtures for low Lambda. The longer combustion duration might be explained by the rate of homogenization between the NH_3-air mixture and the diesel spray. Because of later SODI and decreased ignition delay there is less time for homogenization which could imply that the diesel is burned almost immediately before covering sufficient amounts of NH_3. As a result, during later stages of combustion, large volumes of rich NH_3 mixtures remain, burning much more slowly.

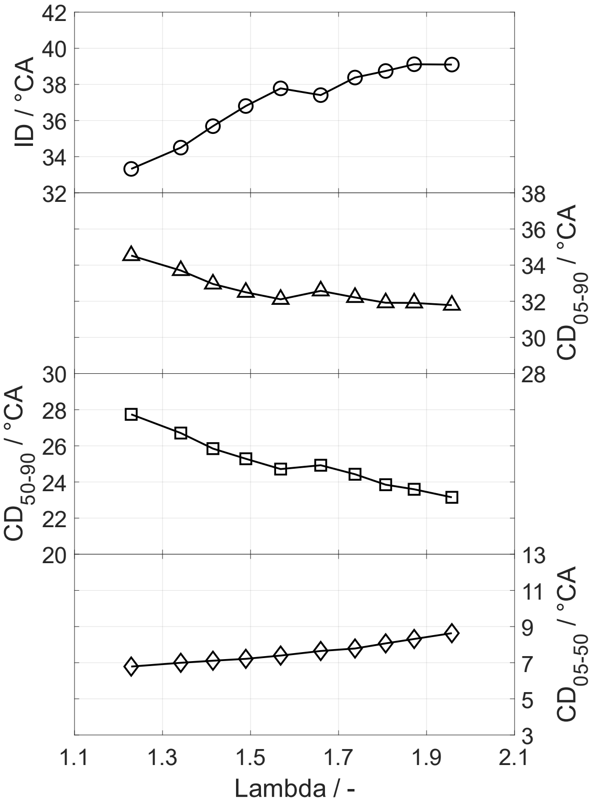

Figure 13. Effect of Lambda on ignition delay and combustion duration

Variation of Lambda also impacts exhaust gas composition. Figure 14 shows the influence of Lambda on NH_3-slip and NO_x emissions as well as the resulting ANR. It is known that unburned NH_3 emissions and NO_x exhibit a trade-off-behavior, as confirmed during this test. NO_x is primarily formed during combustion phases with high temperatures, whereas NH_3-molecules dissociates more easily because hydrogen splits more rapidly from nitrogen, leaving less NH_3 unburned. By reducing Lambda, the process temperatures rise due to less air dilution, leading to higher NO_x emissions and lower NH_3-slip. At a Lambda of approximately $\lambda=1.4$, ANR reaches its optimum, nearest to 1. For very low Lambda, the trend is inverted: NO_x emissions decrease and NH_3-slip increase.

NO_x-formation in general requires high combustion temperatures and sufficient oxygen concentration. For conventional diesel engines, highest NO_x emissions occur at Lambda of $\lambda=1.1$. However, for pre-mixed NH_3-diesel dual fuel engines this peak is shifted to leaner mixtures, possibly due to the NH_3

already present in the mixture reducing the local oxygen concentration while diesel is injected. For Lambda below λ=1.4, NH_3-slip increases, also indicating a significant lack of oxygen that leads to incomplete ammonia oxidation.

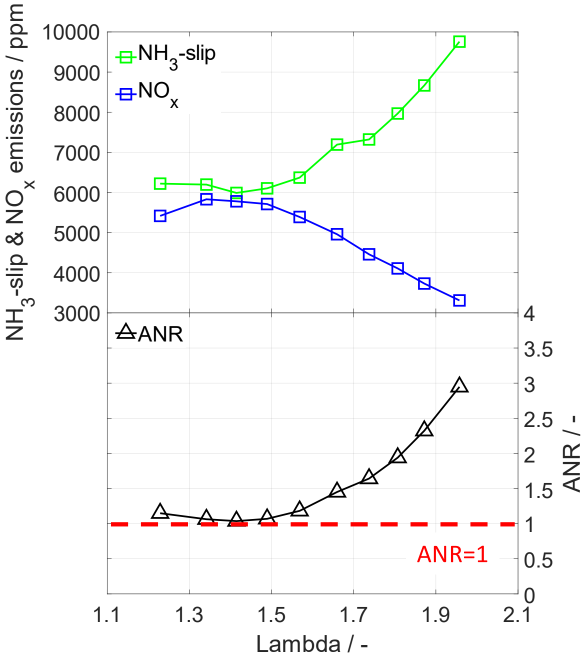

Figure 14. NH_3-slip, NO_x emissions and ANR depending on Lambda

Figure 15 shows the influence of Lambda on N_2O and the resulting specific indicated GHG emissions (273 as GHG-factor for N_2O). Similar to the effects described for the MFB50 variation, N_2O is mainly affected by temperature.

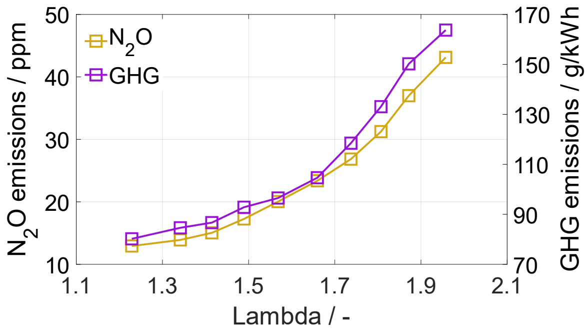

Figure 15. N_2O and specific indicated GHG emissions as CO_2-equivalent (CO_2+N_2O) depending on Lambda

High combustion temperatures under richer conditions allow more thermal decomposition of N_2O, resulting in a significant decrease at low Lambda. Furthermore, N_2O formation is reliant on the presence of oxygen, which is reduced for richer conditions.

Figure 16 presents CO and HC emissions as a function of Lambda. As discussed earlier, carbon monoxide is generated in the absence of sufficient oxygen. For Lambda below λ=1.3 this effect is visible through the small increase of CO. However, the increase for lean conditions is more intense, indicating that combustion temperature has a greater influence within this specific Lambda range. At high Lambda values, flames extinguish easier due to lower combustion temperature, which leads to higher CO emissions [13].

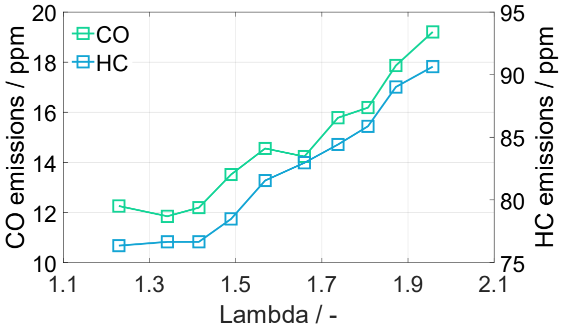

Figure 16. CO and HC emissions depending on Lambda

Similar to the effects described for the MFB50 variation, unburned HC emissions are also affected by temperature and oxygen availability. By decreasing Lambda, HC emissions decrease, which means that the effect of oxygen deficiency can be neglected for this Lambda range. Rather, combustion temperature becomes decisive for unburned HC emissions. For high Lambda values, combustion temperature decreases, promoting wall quenching effects and, therefore, increasing HC emissions. Similar to the effects observed during the MFB50 variation, the increased combustion duration for richer conditions (see Figure 13) might influence the formation of HC, allowing more time for complete oxidation [13].

Finally, the exhaust gas temperature and ITE depending on Lambda shall be evaluated (see Figure 17). Decreasing Lambda, thereby lowering air dilution, leads to an increase in combustion temperature. Additionally, AI90 is postponed, resulting in reduced cooling during expansion stroke. Both effects contribute to a nearly continuous increase in exhaust gas temperature, which is likely beneficial for N_2O aftertreatment. However, attention must be paid regarding the thermal stability of SCR catalysts, as exhaust gas temperatures exceed 500 °C may lead to a loss of reaction selectivity or catalyst degradation [5]. ITE is particularly affected under very lean conditions, likely due to incomplete combustion, indicated by high NH_3-slip (see Figure 14). A slight decrease in ITE for Lambda values below 1.3 may be explained by increased heat loss through wall heat transfer and elevated exhaust gas temperatures.

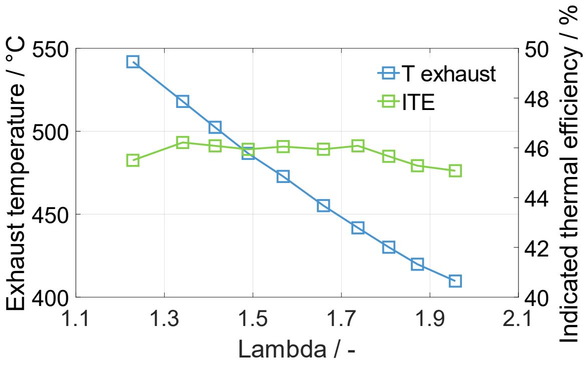

Figure 17. Effect of Lambda on exhaust gas temperature and indicated thermal efficiency

By varying both MFB50 and Lambda, it was demonstrated, that adjustments in combustion and emission behavior of an ammonia-diesel combustion concept are feasible and raw exhaust gas emissions are already manageable. An ANR of 1.1 was achieved, suggesting that the SCR process will be capable of eliminating both NO_x and NH_3 emissions. Slight excess NH_3 should be manageable by using an ASC downstream of the SCR. With approximately 15 ppm of N_2O emissions, GHG benefits are evident. To provide a preliminary assessment of end-of-pipe emissions for this operational point, a DeN_2O-SCR and two commercial ASCs should be evaluated on a model gas test bench. Catalytic reduction of carbon-based emissions (CO, HC) will be excluded, due to the already very low levels, measured in the raw exhaust gas.

3.3 SCR performance on model gas test bench

For the investigations conducted on the model gas test bench, the dual-function SCR catalyst with DeN_2O functionality was tested first, using a space velocity of 25,000 h^{-1}. In Figure 18 the conversion rates of NO, NH_3 and N_2O are depicted as a function of mean temperature of the catalyst. As expected, an ANR of nearly 1 enables sufficient NO and NH_3 conversion. Notably, these effects are already evident at 250 °C, where conversion rates of 90 % for NO and 97 % for NH_3 were achieved. Although excess NH_3 is present, its conversion at lower temperatures is slightly higher compared to NO conversion, indicating that ANR>1 can be beneficial for the SCR process. At higher temperatures above 400 °C, this trend reverses, with NO conversion slightly surpassing NH_3 conversion, though both are at high levels near 100 %.

The light-off temperature for N_2O conversion was determined to be at approximately 400 °C, indicating that for sufficient N_2O conversion the catalyst must be as close as possible to the engines exhaust manifold. At temperatures above 500 °C a N_2O conversion between 96 - 100 % is feasible.

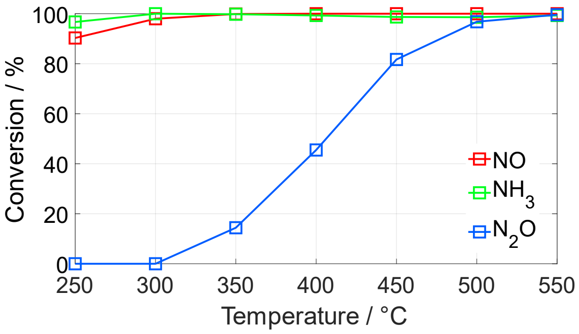

Figure 18. Conversion of NO, NH_3 & N_2O over commercial DeN_2O dual-function SCR catalyst

3.4 ASC performance on model gas test bench

During the SCR test, it was observed that NO and NH_3 could be almost completely converted over a wide temperature range. However, under engine operating conditions with higher excess of NH_3, an ASC downstream of the SCR becomes essential. To address this, two commercial diesel engine ASCs with different coating compositions were tested under exhaust gas conditions downstream of the SCR. The coating of ASC1 is based on transition metals without noble metals, whereas ASC2 features a noble-metal-based coating. Both catalysts were tested using a space velocity of 75,000 h^{-1}.

Figure 19 illustrates the NH_3 conversion for both ASCs as a function of mean temperature of the catalyst. ASC1 shows an almost continuous increase in NH_3 conversion with temperature, achieving approximately 84 % conversion at 500 °C. Due to the missing noble metals in the coating of ASC1 the reactivity is limited, resulting in a high light-off temperature for NH_3 conversion. For ASC2, the noble-metal coating allows earlier NH_3 conversion with a light-off temperature at 270 °C due to increased reactivity. With already 80 % NH_3 conversion at 300 °C, ASC2 reaches its maximum conversion of over 95 % at temperatures above 350 °C.

Due to the high space velocity of 75,000 h^{-1} ASC1 was run over by exhaust gas, preventing sufficient NH_3 conversion. It is expected that lower space velocities between 15,000 – 25,000 h^{-1} can compensate the lower reactivity, allowing high NH_3 conversion at moderate temperatures. Currently, these investigations are still ongoing.

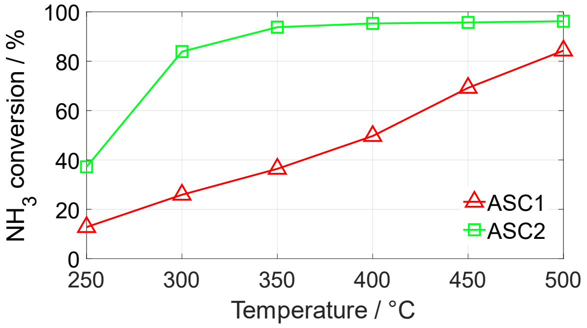

Figure 19. NH_3 conversion over two commercial ammonia slip catalysts with exhaust gas composition downstream of the SCR

During NH_3 conversion over both ASCs, formation effects for specific species were observed. In Figure 20 the formation of NO and N_2O for both catalysts are visible. The formation of NO_2 is neglected in this illustration because its concentration remained at a very low level throughout the tests. For ASC1 without noble metal coating almost no formation of any of these species occurred. In contrast, ASC2 showed significant formation of both NO and N_2O. These effects are attributed to following reactions:

$$2NH_3 + 2.5O_2 \rightarrow 2NO + 3H_2O \qquad (1)$$

$$2NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \qquad (2)$$

Both reactions are dominant at temperatures between 300 - 350 °C with high selectivity for the case involving ASC2, leading to significant concentrations within this temperature range. At higher temperatures the formed NO reacts with NH_3 and O_2 as part of the standard SCR reaction, which is dominant for these conditions:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (3)$$

Due to minimal amounts of NO_2 present also fast SCR reaction can take place:

$$NO + 2NH_3 + NO_2 \rightarrow 2N_2 + 3H_2O \qquad (4)$$

ASC2 also exhibits a significant activity in converting N_2O. Typically, higher temperatures are required for this process, as indicated by the low N_2O concentration observed at temperatures above 400 °C. The conversion proceeds according to the following reaction:

$$2N_2O \rightarrow 2N_2 + O_2 \qquad (5)$$

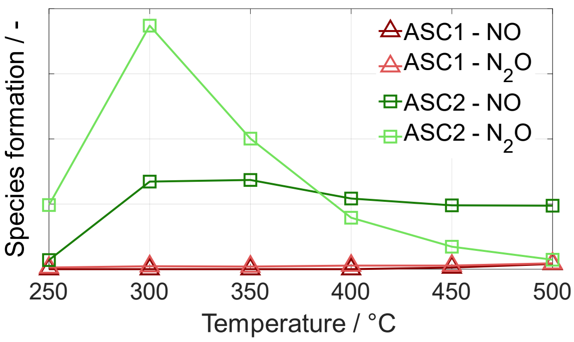

Figure 20. Formation of NO & N_2O over both commercial ammonia slip catalysts with exhaust gas composition downstream of the SCR

Both ASCs represent commercial state-of-the-art catalyst technologies used in diesel engine applications. It was demonstrated that both catalysts have the potential to convert NH_3 effectively. While the use of noble metals allows for a lower light-off temperature, it can result in NO and N_2O formation. By employing a non-noble-metal-based coating for the ASC, these formation effects can be avoided, making this approach potentially more relevant for ammonia-powered engines. In such cases, low space velocities should be used to guarantee sufficient NH_3 conversion.

3.5 EGT concept presentation

This section presents the exhaust gas treatment system to be installed on the SCE test bench. Figure 21 shows a schematic representation of this aftertreatment concept. The concept provides for the installation of four individual catalysts, arranged in series. The catalyst path is located downstream of a volume designed for pressure fluctuation damping, and an exhaust gas flap, which simulates back pressure similar to turbo-charged engines.

The whole catalyst section can be bypassed, allowing further combustion process investigations without exposing the samples to unconventional engine operational conditions. Additionally, the bypass can be used during engine start up and engine parameter switches. When the engine operates in stationary mode, the bypass can be closed using a switch valve, directing the exhaust gas flow through the catalysts for defined exposure.

To gather comprehensive emission data, exhaust gas sampling is conducted at five positions: in the engine's raw exhaust gas and behind each catalyst. These sampling points, labeled I-V, are indicated in the schematic representation (see Figure 21).

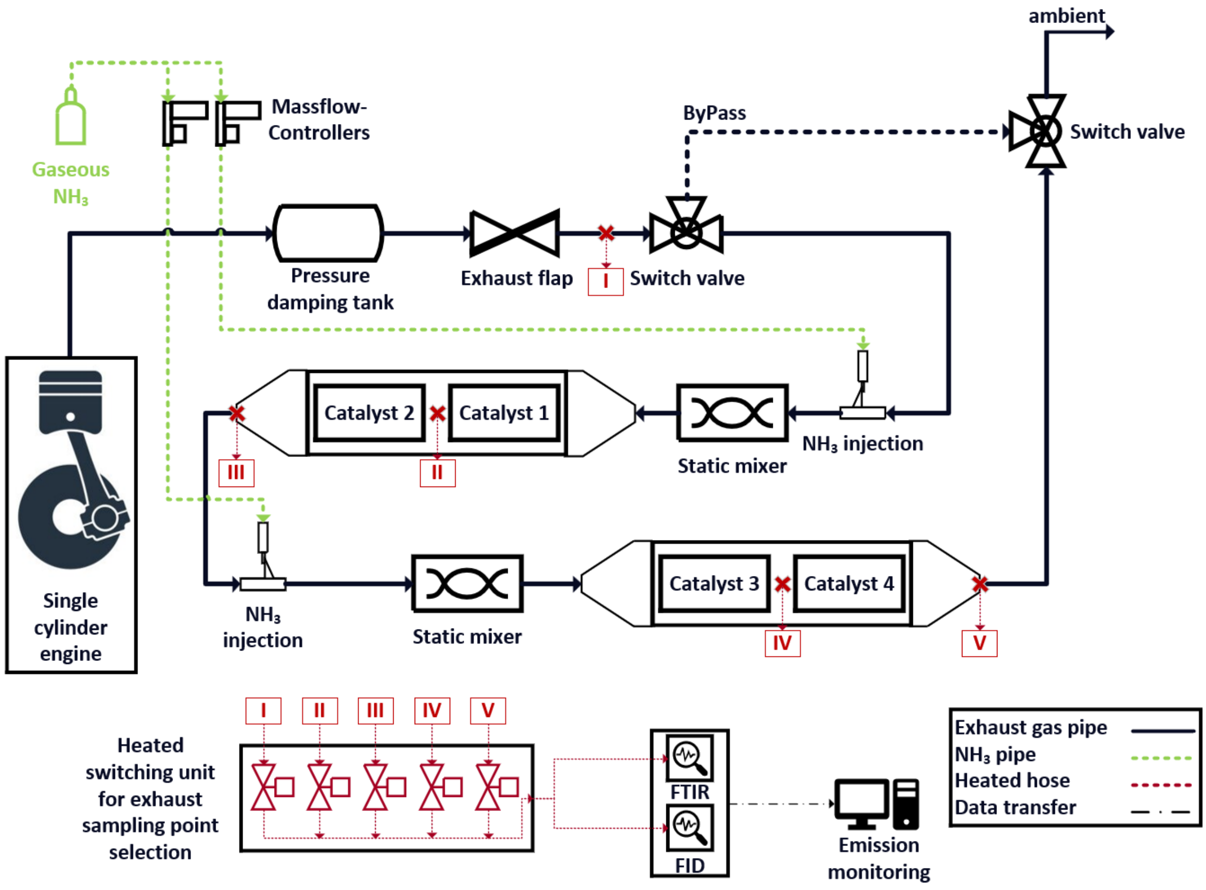

Figure 21. Schematic representation of the exhaust gas treatment concept for the engine test bench

The catalyst section consists of two identical segments, each including an injection unit for additional NH_3 as a reducing agent, a static mixer to enhance the mixing of NH_3 with exhaust gas, and the mounting unit itself. The mounting unit is sufficiently large to facilitate the investigation of different space velocities. Additionally, the entire exhaust system will be insulated and externally heated to be able reproduce any level of wall heat loss. The second NH_3 injection is provided for scenarios involving two SCR catalysts or an oxidational catalyst (e.g., diesel oxidational catalyst - DOC) in one of the first two slots. The choice of injection position depends on the catalyst concept and the arrangement order. Following arrangements are conceivable:

a) DOC – *empty* – SCR – ASC

b) SCR – *empty* – DeN$_2$O – ASC

c) SCR – DeN$_2$O – SCR - ASC

d) SCR – ASC – DeN$_2$O - *empty*

Arrangement a) is a well-known approach commonly used for conventional diesel engines (excluding DPF). In this configuration unburned hydrocarbons, CO and NO emissions can be oxidized using the DOC. The SCR would be installed in Slot 3, combined with the second NH_3 injection to compensate for potentially insufficient NH_3 concentrations in the raw exhaust gas. The ASC would be installed last for reducing any remaining NH_3. Although, this arrangement is a well-known concept, it might be less suitable for ammonia engines because the DOC already converts NH_3 contained in the raw exhaust gas, leaving less for the SCR catalyst. However, if this concept is used, care should be taken to select a DOC with suitable selectivity, as it is possible for NO or N_2O to form during NH_3 oxidation.

In arrangement b) the DOC is omitted, foregoing the potential to oxidize NO to NO_2 for the fast SCR, but preventing early NH_3 conversion. Instead, a DeN$_2$O catalyst is included, enabling N_2O conversion at appropriate temperatures. The ASC would also be installed last for converting remaining NH_3.

Arrangement c) represents an approach using two SCR catalysts. In this concept the first SCR might act as a passive SCR, utilizing the NH_3 already present in the raw exhaust gas, while the second can be designed as an actively controlled SCR, using the second NH_3 injection position for reducing remaining NO_x emissions. The ASC at the end could be designed similarly to those in conventional diesel engine systems, as it is expected that most of NH_3 will be converted by the two SCRs, leaving only small amounts of NH_3-slip.

As observed during the model gas tests, especially noble metal-coated ASCs could increase N_2O formation. To address this, the DeN_2O catalyst could be placed last (arrangement d)), which helps prevent N_2O formed over the ASC from leaving the exhaust path. However, it should be noted, that exhaust gas temperatures can decrease significantly before reaching the DeN_2O catalyst, making it unclear if this concept is suitable, as for N_2O conversion high temperatures are mandatory.

Currently, it remains unclear which combination of catalyst technologies will deliver the best performance under real ammonia engine conditions. Several potential arrangements have been proposed, focusing on their use in stationary ammonia engines. Cold-start procedures and transient operation present additional challenges and may require different technologies and configurations; however, these will not be part of the upcoming investigations.

The concept presented allows for flexibility in investigating various configurations with different numbers of catalysts and different space velocities. Providing two separate injection positions for additional NH_3 enables the investigation of multiple SCR catalysts or the compensation for reduced NH_3 concentration if oxidational catalysts are included.

4 CONCLUSIONS

To establish ammonia combustion processes for future engine applications and ensure compliance with emission legislation, it is essential to optimize both the combustion process and the associated aftertreatment concepts.

In this study, combustion process development and preliminary model gas test bench investigations were carried out. For combustion process investigations a medium-duty single-cylinder engine was operated in NH_3-diesel dual fuel mode with 90 % ammonia energy share. It was shown, that emissions of N_2O, CO and unburned hydrocarbons can be reduced to low levels by optimizing MFB50 and the excess-air ratio. Although NO_x emissions and NH_3-slip are not entirely avoidable, the NH_3-NO_x-ratio (ANR) can be effectively controlled, enabling an optimal SCR process. As demonstrated on the model gas test bench, a slight NH_3 excess in the exhaust gas (ANR>1) results in high conversion rates of both species using an SCR catalyst even at low temperatures. Catalytic N_2O conversion was also shown to be feasible, but required high temperatures exceeding 400 °C. For the engine operation condition studied, exhaust gas temperatures above 500 °C were achievable at low Lambda values, indicating that N_2O conversion could be manageable.

In the presence of excess NH_3, an ammonia slip catalyst should be implemented. This study evaluated the performance of two ASCs using exhaust gas compositions representative of conditions downstream of an SCR. The results demonstrated that NH_3 conversion depends significantly on the catalyst coating. Noble-metal coatings can enhance reactivity and therefore reduce the light-off temperature. However, they also can increase selectivity for NO and N_2O, as confirmed by the observed formation of both species during the tests. In contrast, for the ASC without noble-metal coating no significant formation was visible, making this technology more suitable for ammonia engines. To also guarantee for high levels of NH_3 conversion with such catalysts, the space velocity should be reduced to approximately 15,000 h^{-1}.

Key findings:

- NH_3-diesel engine operation with 90 % ammonia energy share (AES) and low N_2O emissions is feasible, offering significant GHG-reducing potential compared to conventional diesel engines
- nearly stoichiometric NH_3-NO_x-ratios (ANR=1) can be achieved by optimizing MFB50 and reducing excess-air ratio, enabling an optimized SCR process
- catalytic N_2O conversion can be achieved at sufficiently high exhaust gas temperatures, which are attainable through Lambda adjustments
- ASCs without noble-metal coating are considered to be better suited for ammonia engines, as nearly no formation of NO and N_2O occurred

Building on these findings a flexible testing concept was developed to evaluate aftertreatment systems under real engine conditions. This concept will be applied in upcoming investigations to assess catalyst performance and refine the combustion process.

5 DEFINITIONS, ACRONYMS, ABBREVIATIONS

°CA	Degree crank angle
°CAaTDC	Degree crank angle after top dead center
CDxx-xx	Combustion duration
AES	Ammonia energy share
ANR	Ammonia-NO_x-ratio
ASC	Ammonia slip catalyst
CO	Carbon monoxide
CO_2	Carbon dioxide
DOC	Diesel oxidational catalyst
EGT	Exhaust gas treatment
FID	Flame ionization detector
FTIR	Fourier-transform infrared spectroscopy
GHG	Greenhouse gas
H_2	Hydrogen
H_2O	Water
HC	Hydrocarbons
HRR	Heat release rate
ICE	Internal combustion engine
ID	Ignition delay
IMEP	Indicated mean effective pressure
ITE	Indicated thermal efficiency
MFBxx	xx % mass fraction burned
MFC	Mass flow controller
N_2	Nitrogen
N_2O	Nitrous oxide
NH_3	Ammonia
NO	Nitrogen monoxide
NO_2	Nitrogen dioxide
NO_x	Sum of NO and NO_2
NRMM	Non-road mobile machinery
O_2	Oxygen
PFI	Port fuel injection
SCE	Single cylinder engine
SCR	Selective catalytic reaction
SODI	Start of diesel injection

6 ACKNOWLEDGEMENTS

The authors would like to thank the German Federal Ministry for Economic Affairs and Climate Actions for funding the project “NH3-Stat” (project number: 03EE5146D).

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8 CONTACT

M.Sc. Felix Wenig

University of Rostock – Chair of Piston Machines and Internal Combustion Engines

E-Mail: felix.wenig@uni-rostock.de

Phone: +49 3814989155

www.lkv.uni-rostock.de