9th RGMT - Rostock Large Engine Symposium
October 13 - 14, 2026
www.rgmt.de

Interaction of engine control parameters and exhaust gas aftertreatment system in ammonia-fueled combustion engines for low-emission power generation

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https://doi.org/10.18453/rosdok_id00005726

Keywords: Ammonia, Dual-fuel, Mono-fuel, Combustion control, Exhaust gas aftertreatment

Abstract

Ammonia is a promising carbon-free fuel for maritime and non-road mobile applications, but its unfavorable combustion characteristics and the formation of NH_3, NO_x, and N_2O require suitable combustion and aftertreatment strategies. This study investigates two ammonia-fueled internal combustion engine concepts on dedicated single-cylinder test benches. A lean-burn NH_3–diesel compression-ignition (CI) engine equipped with selective catalytic reduction and ammonia slip catalysts (SCR+ASC), and a spark-ignited (SI) engine operated with 100% ammonia and a three-way catalyst (TWC).

For the NH_3–diesel CI concept, the effects of air–fuel equivalence ratio, ammonia energy share, and combustion phasing on engine-out emissions were analyzed. An air–fuel equivalence ratio of $1.2 < \lambda < 1.5$ provided favorable engine-out Ammonia-NO_x ratios (ANR), while ammonia energy shares of up to 95% were achievable at high engine load. The combination of SCR and ASC enabled substantial NO_x and NH_3 reduction over a wide load range. Additional ammonia dosing was required at selected operating points to achieve high $DeNO_x$ efficiency, while complete N_2O conversion was observed at sufficiently high exhaust temperatures.

The SI concept demonstrated stable 100% ammonia operation across the investigated engine map. TWC performance was strongly governed by the air-fuel equivalence ratio with a narrow optimum slightly on the rich side of stoichiometry. At $\lambda \approx 0.97$, a favorable compromise between NH_3, NO_x, and N_2O emissions was achieved. Overall, the results demonstrate the technical feasibility of both combustion concepts and highlight the importance of coordinated engine and aftertreatment control for low-emission ammonia operation.

1. Introduction

Shipping plays a crucial and largely irreplaceable role in global transportation, particularly with regard to the movement of goods. Due to its high transport efficiency, maritime shipping already represents one of the most climate-efficient modes of transport. Nevertheless, substantial further reductions in greenhouse gas (GHG) emissions are required to meet long-term sustainability targets. While battery-electric propulsion offers a viable pathway towards climate-neutral mobility in road transport, its applicability to maritime applications is severely limited by insufficient energy density. For most vessel types and operating profiles, alternative solutions for storing and supplying renewable energy on board are therefore required [1]. In this context, hydrogen produced from renewable sources represents a promising energy carrier. However, the low volumetric energy density of elemental hydrogen, whether stored in compressed or liquefied form, poses significant challenges for maritime use. One approach to overcoming these limitations is the conversion of hydrogen into liquid energy carriers [2]. Synthetic hydrocarbons produced via processes such as Fischer–Tropsch synthesis are attractive due to their compatibility with existing engine technologies. However, their large-scale production relies on the availability of concentrated carbon sources. Without extensive deployment of energy-intensive and costly direct air capture technologies, the limited availability of CO_2 represents a major constraint on production capacity, thereby restricting widespread application [3]. Ammonia offers an alternative pathway by enabling hydrogen storage without the need for carbon [4]. It can be synthesized from hydrogen and abundantly available nitrogen and has therefore gained increasing attention as an energy carrier for maritime applications. Owing to its established global infrastructure for production, storage, and transport, ammonia is particularly attractive for shipping.

Furthermore, ammonia is increasingly being considered as a fuel for non-road mobile machinery (NRMM), such as those used for GenSet-Application or in construction, mining, agriculture, and remote industrial operations. These applications often require high power output, long operational endurance, and operation in off-grid or remote environments, where refueling infrastructure is limited. In such contexts, ammonia-fueled gensets offer a viable alternative to diesel engines, enabling the decarbonization of heavy-duty mobile equipment without compromising performance or operational flexibility.

Ammonia can be used directly as a fuel in internal combustion engines. However, its unfavorable combustion characteristics, including high auto ignition temperature and low laminar flame speed, present challenges, especially for medium- and high-speed engines [5].

1.1. Ammonia combustion processes for internal combustion engines (ICE)

Due to ammonia's challenging ignition properties, measures are required to stabilize its combustion in engine applications. One option is the use of a combustion promoter, such as a reactive secondary fuel [6]. In dual-fuel concepts, diesel can be used as an ignition source in compression-ignition operation, while hydrogen can serve as a promoter in spark-ignition concepts. As an alternative to a promoter fuel, a high-energy ignition system can be employed in an otto-cycle combustion process, enabling spark-ignition engine operation with 100 % ammonia [7].

This paper compares two different engine concepts (**Fig. 1**). First, a diesel combustion process is examined that involves injecting gaseous ammonia into the intake manifold and a small amount of diesel fuel, which is injected directly into the combustion chamber. The injected diesel fuel ignites during the compression stroke, thereby igniting the premixed ammonia-air mixture. The second concept that was investigated is an otto-cycle engine combustion process with liquid ammonia injection into the engine's intake manifold. The stoichiometric air-fuel mixture in the combustion chamber is ignited using a spark plug and a high-energy ignition system.

Due to its carbon-free molecular structure, ammonia appears to be an ideal fuel for shipping and stationary power generation, reducing CO_2 as the most well-known greenhouse gas emission (GHG). Despite this, ammonia combustion can result in the formation of nitrous oxide (N_2O), which has a global warming potential (100y-GWP) 273-times higher than that of CO_2 [8]. Consequently, N_2O emissions can significantly reduce, or even offset, the GHG benefits of ammonia as a fuel. Considering the zero-impact requirement for future engine applications, pollutant emissions like nitrogen oxides (NO_x) and unburned ammonia, which inevitably occur during the combustion process, must also be reduced to a minimum. A promising approach is the coordinated optimization of the combustion process through engine parameter control like air-fuel equivalence ratio λ and injection or ignition timing, in combination with the downstream exhaust gas aftertreatment system.

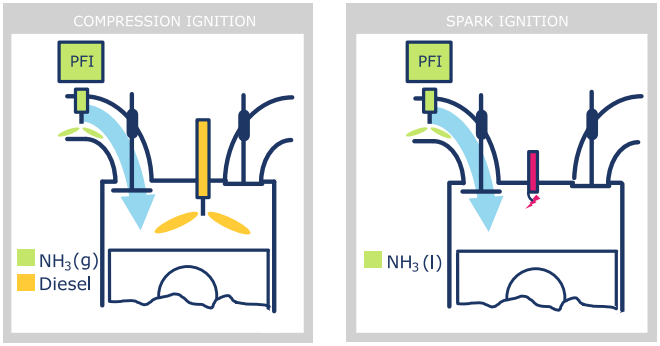


Fig. 1. *Schematic illustration of the NH_3-diesel CI and the 100% NH_3 SI combustion concepts investigated in this study*

1.2. Exhaust gas aftertreatment technologies for NH_3-fueled combustion engines

In addition to the two engine concepts, the corresponding exhaust aftertreatment technologies are also examined, which differ depending on the respective combustion process.

For dual-fuel engines operating under lean combustion conditions (λ > 1), selective catalytic reduction (SCR) represents a promising aftertreatment strategy. SCR catalysts are a well-established technology for diesel and natural gas engines and provide high NO_x conversion efficiency ($DeNO_x$) when combined with a suitable reducing agent. While aqueous urea solution (AdBlue) is commonly used in diesel engine applications, NH_3-fueled engines can utilize the ammonia already present in the engine-out exhaust gas for NO_x reduction. Depending on the $DeNO_x$ requirements, additional NH_3 can be injected into the exhaust gas stream.

Several SCR catalyst technologies are available, each offering specific advantages and limitations. Copper- (Cu) and vanadium- (V) based SCR catalysts exhibit high $DeNO_x$ activity under low-temperature conditions. However, both technologies provide none or only limited N_2O abatement (DeN_2O) capability, which is a key requirement for NH_3 combustion engines. In addition, vanadium-based SCR catalysts may promote formation of additional N_2O at elevated temperatures, while direct NH_3 oxidation becomes dominant, thus reducing $DeNO_x$ efficiency. Similarly, Cu-based SCR catalysts exhibit a pronounced tendency toward direct NH_3 oxidation under high-temperature conditions [9].

An alternative approach is the use of iron- (Fe) based SCR catalysts. These catalysts offer high temperature resistance and show a low tendency for direct NH_3 oxidation and N_2O formation. Moreover, Fe-based SCR catalysts can provide simultaneous $DeNO_x$ and DeN_2O, with N_2O conversion occurring either via thermal decomposition or NH_3-and NO-assisted reduction. However, efficient N_2O abatement typically requires exhaust gas temperatures above 450 °C, while elevated H_2O concentrations can inhibit the DeN_2O activity [10].

Ammonia slip catalysts (ASC) are commonly placed downstream of the SCR catalyst to oxidize residual NH_3. In NH_3-diesel dual-fuel engine concepts, these catalysts can additionally convert carbon-containing species, including CO, HC and HCN, originating from the NH_3-diesel co-combustion. Although noble metal-based catalysts offer higher oxidation activity, they may also facilitate the formation of undesired by-products, particularly NO and N_2O, during NH_3 oxidation [11].

For a stoichiometric ($\lambda = 1$) combustion process using a spark plug, the use of a three-way catalytic converter (TWC) for exhaust gas aftertreatment is generally suitable. Therefore, the engine is not operating at a fixed air-fuel equivalence ratio of $\lambda = 1$ continuously, but rather switches between slightly rich and lean conditions. Due to this operation the TWC can simultaneously oxidize unburned ammonia and unburned hydrogen and reduce nitrogen oxides. In the past, for gasoline- or natural gas-powered engines, catalytic converters typically contain precious metals such as palladium, platinum, and rhodium. Beside noble metals ceria oxide is also a key component of the catalyst design, thus providing the availability of oxygen storage.

However, the use of TWC also presents challenges, as undesired by-products such as NH_3 and N_2O are produced during the phases in which sub-stoichiometric exhaust gas is passed through the catalyst [12]. Furthermore, during lean operation, the TWC will form additional NO_x and N_2O, which must also be minimized to be in compliance with emission legislation and the GHG reduction target.

2. Experimental setups

2.1. NH_3-diesel CI engine – Test bench setup

The experimental NH_3-diesel CI engine investigations were performed on a medium-duty single cylinder engine (SCE) test bench located at the University of Rostock. The SCE, based on the *DEUTZ TCD5.2* diesel engine (see **Tab. 1**), is coupled to a 220 kW dynamometer that absorbs the power generated during operation. For charged engine operation, the test bench is supplied with externally compressed air, allowing charge air pressures of up to 4 bar absolute. Furthermore, the intake air temperate can be regulated within a range of 20-100 °C. The low-pressure diesel fuel system comprises a fuel metering device and a fuel conditioning unit, enabling both fuel consumption measurement and fuel temperature control. The high-pressure fuel system includes a common-rail pump and a common-rail injector designed for injection pressures of up to 1,600 bar.

Tab. 1. *Data of NH_3-diesel CI single cylinder engine based on DEUTZ TCD5.2*

Single cylinder, 4 stroke NH_3-diesel CI engine	
Base engine	DEUTZ TCD5.2
Rated speed / rpm	2,200
Rated power / kW	45
Bore / mm	110
Stroke / mm	136
Engine displacement / l	1.29
Compression ratio / -	16.4

The ammonia supply system is housed within a continuously vented safety cabinet to ensure the safe removal of ammonia in the event of leakage. Liquid ammonia is stored in two pressurized cylinders. As the investigations focused on gaseous ammonia injection, the liquid NH_3 is routed into an evaporator after leaving the storage tanks. To control the injection pressure, a dome-loaded pressure regulator is installed downstream of the evaporator, allowing for injections pressures between 1 and 10 bar absolute. Fuel consumption is measured with a Coriolis flow meter. Finally, the gaseous ammonia is injected sequentially into the engine's intake manifold via PFI using a large engine gas valve (LEGV).

To have full engine control, an open-access research engine control unit (ECU) was installed, allowing direct intervention in the combustion process by adjusting fuel injection parameters such as number of injections per cycle, start and duration of injector energization (NH_3 and diesel) as well as diesel injection pressure. The combustion can be monitored via in-cylinder pressure measurement in combination with a modern indication tool.

To enable different catalyst configurations on the SCE, an extensive exhaust gas aftertreatment testing environment was integrated into the engine test bench. A schematic overview of the setup is presented in **Fig. 2**. The setup is designed for testing low-pressure aftertreatment concepts as the whole system is installed downstream of the exhaust flap, which simulates the backpressure of a turbo-charged full-cylinder engine. Downstream of the exhaust flap, the exhaust system is divided into two branches: a bypass line and the dedicated aftertreatment line. The aftertreatment line can be further subdivided into two identical sections. Section 1 consists of an initial dosing position, allowing the introduction of a reducing agent into the exhaust stream, when required for SCR operation. Instead of injecting an aqueous urea solution such as AdBlue, gaseous ammonia supplied directly from the fuel system is used. The ammonia dosing is controlled and monitored using a mass flow controller (MFC). A static mixer downstream of the NH_3 dosing location ensures thorough mixing of the ammonia with the exhaust gas before entering the first catalyst mounting unit (Reactor 1). Reactor 1 includes two identical catalyst mounting slots, each designed for catalyst substrates measuring 150x150 mm with a length of 300 mm. Section 2 mirrors the design of section 1 and allows for the investigation of more complex aftertreatment concepts, such as dual-dosing concepts with two individual reactors.

To enable investigations under full-cylinder engine conditions, the whole system can be externally heated, therefore offering the possibility to vary the temperature conditions prior to the EAT system.

For comprehensive emission characterization, five exhaust gas sampling locations are included into the system. The first sampling position is installed in the raw exhaust upstream of the aftertreatment line, while the remaining four are located downstream of each catalyst mounting slot. These measurement points are labeled I-V in **Fig. 2**. At all five sampling locations, exhaust gas composition can be analyzed using a Fourier-transform infrared (FTIR) spectrometer, a flame ionization detector (FID) for unburned hydrocarbons, a paramagnetic oxygen analyzer (PMA) and electron ionization mass spectrometer (EI-MS) for hydrogen concentration measurement.

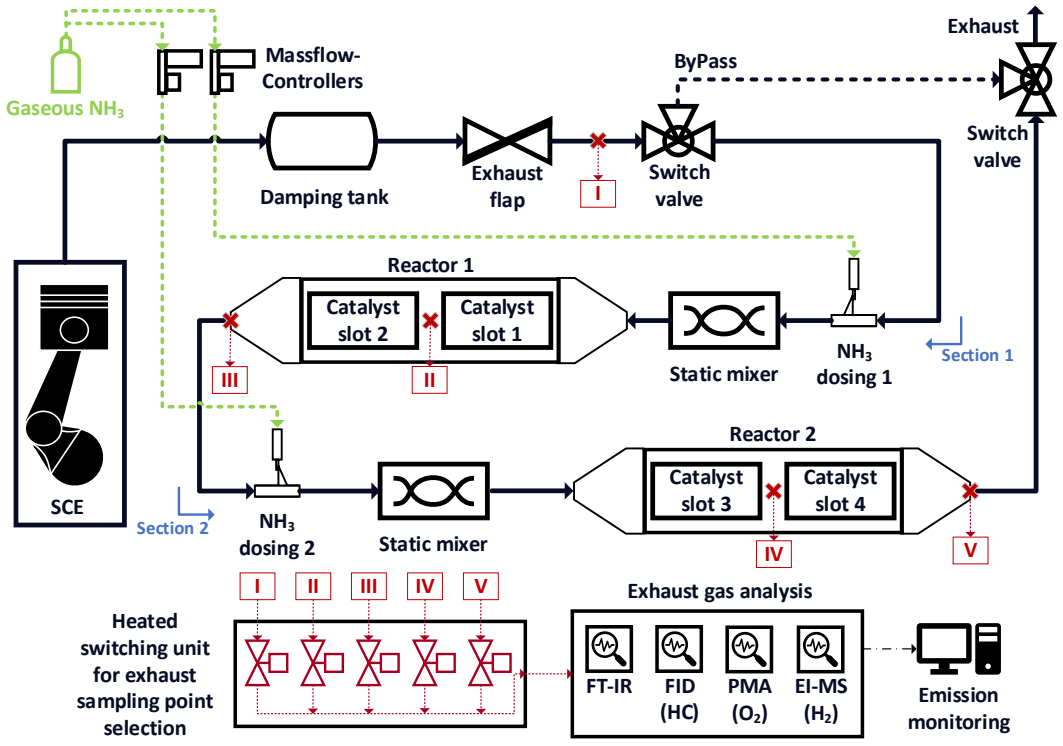


Fig. 2. *Exhaust gas aftertreatment testing environment installed on the NH_3-diesel CI SCE test bench*

2.2. 100% NH_3 SI Engine – Test bench setup

In comparison to the NH_3-diesel CI engine the second engine is operated with 100% ammonia in a spark ignited combustion process. The experiments were performed on a heavy-duty SCE test bench located at the Karlsruhe Institute of Technology. All experiments were carried out on a fully equipped single cylinder research engine derived from a *Liebherr* D966 diesel engine and converted to spark-ignited operation. The single cylinder engine is representative of a six-cylinder marine engine in terms of bore, stroke and compression ratio. The main engine data is summarized in **Tab. 2**.

Tab. 2. *Data of the NH_3 SI single cylinder engine based on Liebherr D966*

Single cylinder, 4 stroke 100% ammonia SI engine	
Base engine	Liebherr D966
Rated speed / rpm	2,100
Bore / mm	135
Stroke / mm	157
Engine displacement / l	2.24
Compression ratio / -	18.5
Compression ratio / -	16.4

The engine is operated with 100% ammonia under stoichiometric conditions. The ammonia injector is located in the intake manifold, directly before the intake valve. Ammonia is injected in liquid phase at a pressure of 20 bar. Ignition is provided by a spark plug mounted in the center of the combustion chamber, see **Fig. 1** (right). The ignition system has been replaced by a high-energy ignition system [13]. This allows the duration and current of the ignition spark to be adjusted as required, enabling 100% ammonia combustion across the entire load range [7].

To ensure precise monitoring and control, the engine was installed on a fully instrumented test bench, enabling comprehensive data acquisition and real-time combustion analysis with *DEWE*-800, see **Fig. 3**. The test bench also features conditioning for cooling water, oil, and charge air. Charge air heating is applied upstream of the intake manifold using an inline electric air heater to increase the intake air temperature up to 60 °C which is crucial due to the high enthalpy of NH_3 vaporization. Emissions of CO_2, O_2 and NO_x were measured via an NDIR and a CLD by a standard exhaust gas analyzer, while NH_3, NO_x and N_2O were quantified using a FTIR spectrometer. For each operating point, at least 200 consecutive cycles were recorded and averaged to evaluate combustion stability via the Coefficient of Variation (COV) of the Indicated Mean Effective Pressure (IMEP) COV_{IMEP}.

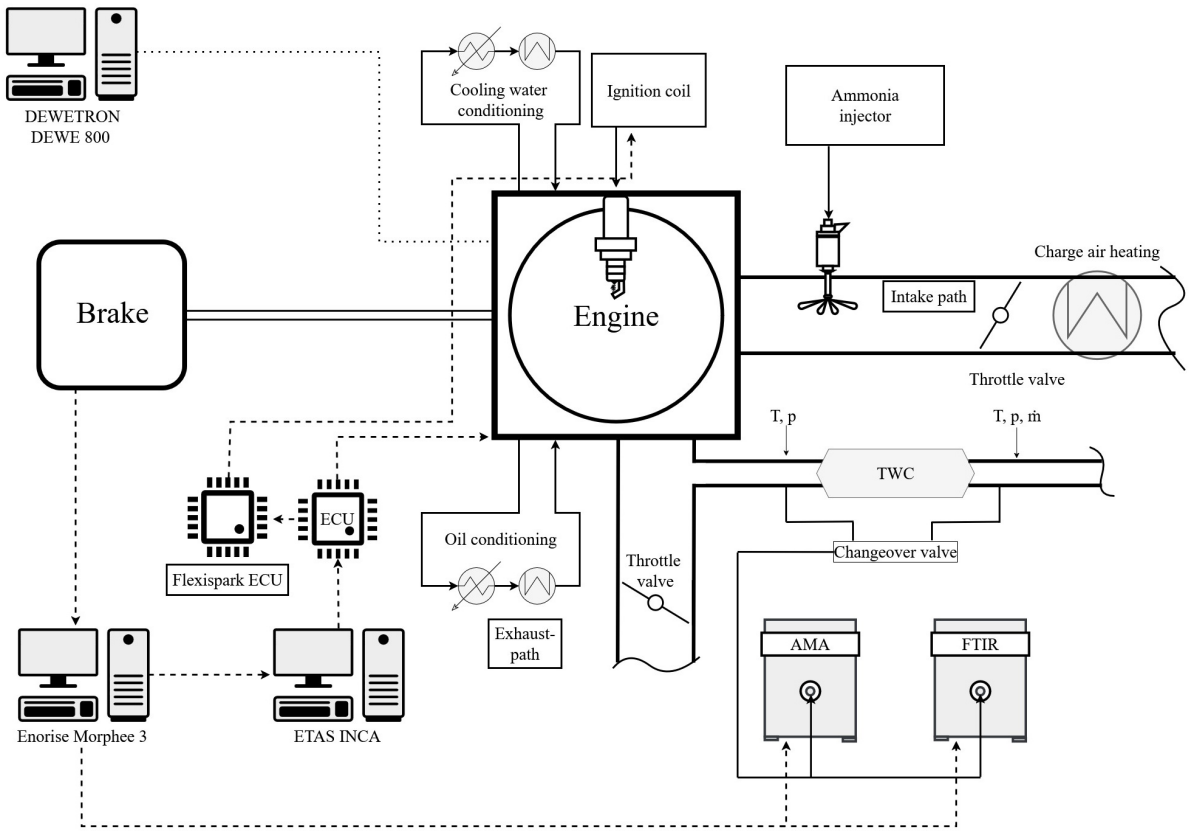


Fig. 3. *Testbench setup of the NH_3 SI single cylinder engine operated with 100% ammonia*

3. Methodology

3.1. NH_3-diesel CI engine - Combustion strategy

Before the aftertreatment setups were tested on the SCE test bench, a comprehensive combustion strategy for the diesel-pilot ignited concept was developed considering highest possible ammonia energy shares (AES) with optimized engine-out emission levels. The ammonia energy share is defined as:

$$AES = \frac{\dot{m}_{NH_3} \cdot H_{u,NH_3}}{\dot{m}_{NH_3} \cdot H_{u,NH_3} + \dot{m}_{Diesel} \cdot H_{u,Diesel}} \quad (1)$$

With $\dot{m}_{NH_3}$ and $\dot{m}_{Diesel}$ as fuel mass flow rates and H_{u,NH_3} and $H_{u,Diesel}$ as the respective lower heating values of ammonia (18.6 MJ/kg) and diesel (42.79 MJ/kg).

To assess the engine-out emission conditions with respect to their suitability for combined engine and aftertreatment operation, the engine-out concentration ratio of NH_3 and NO_x was defined as a key parameter:

$$ANR_{engine-out} = \frac{c_{NH_3,engine-out}}{c_{NO_x,engine-out}} \quad (2)$$

By managing the combustion such that engine-out emission conditions result in an $ANR_{engine-out}$ close to 1, it can be expected that high NO_x conversion rates can be achieved without risking too much of untreated NH_3 leaving the SCR.

In order to define optimized combustion settings, multiple engine parameter variations were conducted on the SCE. For this study, the effects of varying the air-fuel equivalence ratio λ at two different AES and with two different MFB_{50} (50% mass fraction burned) settings under 15 bar IMEP engine load conditions will be discussed. The corresponding engine settings for the experiments are listed in **Tab. 3**.

3.2. NH_3-diesel CI engine - Aftertreatment strategy

For the diesel-pilot ignited NH_3 engine operating under lean combustion conditions, a basic aftertreatment concept, consisting of state-of the art SCR and ASC technologies, was investigated under different engine load conditions (see **Fig. 4**). This concept is based on a single reactor approach with a single SCR and a single ASC catalyst substrate, provided by *Umicore AG & Co. KG, Hanau, Germany*. Technical information of the used catalysts is listed in **Tab. 4**.

Based on the results from the combustion development, 4 optimized engine operating points, ranging from 5 bar to 20 bar IMEP, have been selected for the aftertreatment testing. The setup was tested under $ANR_{engine-out}$ > 1 conditions in all 4 operating points.

As it was observed that even under $ANR_{engine-out}$ > 1 conditions additional NH_3 supply can be required, the NH_3 dosing into the exhaust gas stream was carefully adjusted for each operating point individually, depending on the $DeNO_x$ and DeN_2O requirements. As this aftertreatment concept

Tab. 3. *Settings used for engine parameter variations on the NH_3-diesel CI engine*

Speed / rpm	IMEP / bar	AES / %	MFB_{50} / °CAaTDC	p_{Diesel} / bar	p_{NH3} / bar	λ / -	$T_{Charge-air}$ / °C
1,500	15	85	6.0	900	5	varied	50
1,500	15	85	9.0	900	5	varied	50
1,500	15	90	6.0	900	5	varied	50
1,500	15	90	9.0	900	5	varied	50

Tab. 4. *Properties of the catalysts installed on the NH_3-diesel CI engine*

Catalyst / -	Technology / -	Cross section / mm*mm	Length / mm	Cell density / cpsi
SCR	Fe-Zeolite	150*150	300	230
ASC	Pt-based with SCR Layer	150*150	75	230

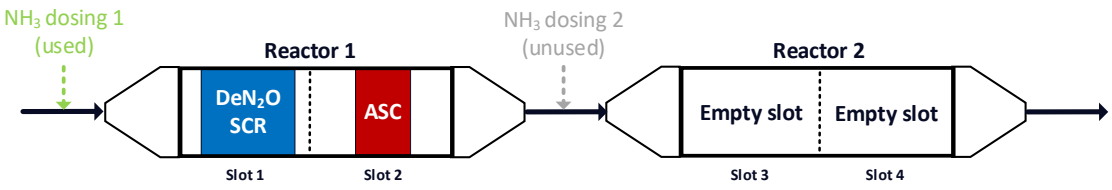


Fig. 4. *Schematic illustration of the investigated aftertreatment concept on the NH_3-diesel CI engine*

features only a single reactor, only the first NH_3 dosing position, upstream of Reactor 1, was applied for these experiments. Further details will be discussed in the Results section.

To account for the additional NH_3 introduced at the dosing position, the ANR calculation method must be adapted. Upstream of reactor 1, the engine-out NH_3 concentration and the dosed NH_3 concentration are summed and then divided by the engine-out NO_x concentration, resulting in ANR_{EAT}:

$$ANR_{EAT} = \frac{c_{NH_3,engine-out} + c_{NH_3,dosing}}{c_{NO_x,engine-out}} \quad (3)$$

3.3. 100% NH_3 SI engine - Combustion strategy

The spark-ignited combustion concept was originally developed as a dual-fuel ammonia/hydrogen combustion process. Experimental investigations showed that the required hydrogen fraction strongly depends on the ignition system. By replacing the conventional inductive ignition system with a high-energy capacitive ignition system (SEM FlexiSpark), stable operation without hydrogen became possible. The high-energy ignition system allows independent adjustment of both the spark current and the spark duration over a wide operating range. While increasing the spark current improves the instantaneous ignition energy, the investigations revealed that the spark duration has a significantly larger influence on combustion stability. This observation is consistent with the fundamental combustion characteristics of ammonia, which exhibits a comparatively high minimum ignition energy, low laminar flame speed and narrow flammability limits compared to conventional hydrocarbon fuels [14, 15, 16]. Extended spark durations maintain the ignition plasma over several milliseconds, thereby increasing the probability of igniting a locally combustible mixture in the vicinity of the spark plug. Moreover, the prolonged energy input supports the early flame kernel development, allowing the flame to overcome the critical quenching phase and establish self-sustained combustion [17]. In addition, the flame kernel continues to receive energy during its initial growth, which improves flame stabilization under the unfavorable ignition conditions of ammonia-air mixtures.

A comparison of the engine-out emissions revealed only minor differences between the pure ammonia combustion process and the previously investigated ammonia/hydrogen dual-fuel concept. The remaining emissions are therefore primarily governed by the nitrogen chemistry of ammonia combustion rather than by the presence or absence of hydrogen. In both cases, considerable concentrations of unburned NH_3, NO_x N_2O were measured, making exhaust gas aftertreatment indispensable. Since residual ammonia is already present in the exhaust gas, it can be directly utilized as the reducing agent for NO_x conversion. Furthermore, the engine is operated under stoichiometric conditions, making the application of a three-way catalyst particularly suitable. Previous investigations demonstrated that the air-fuel equivalence ratio is the dominant parameter governing catalyst conversion efficiency and the balance between NH_3 slip, NO_x and N_2O emissions. Therefore, the influence of the air-fuel equivalence ratio on catalyst performance is the primary focus of the present study [18].

The measurements presented in this work were carried out at an engine operating point of 11 bar IMEP and an engine speed of 1,500 rpm. A comprehensive description of the combustion system, ignition strategy and combustion process development has been presented by the authors in previous publications and is therefore not repeated here [7, 19].

3.4. 100% NH_3 SI engine - Aftertreatment strategy

To investigate the exhaust gas aftertreatment during stoichiometric ammonia combustion, a palladium-based three-way catalyst manufactured by the Institute for Technical Chemistry and Polymer Chemistry (ITCP) at the Karlsruhe Institute of Technology (KIT) was employed. The catalyst consisted of a cordierite honeycomb substrate with a diameter of 16 mm, a length of 30 mm, a cell density of 400 cpsi, a wall thickness of 4 mil and 97 flow channels, see **Fig. 5**. The monolith was coated with a ceria–zirconia (CeO_2–ZrO_2) mixed oxide washcoat serving as catalyst support and oxygen storage material. Palladium was used as the active catalytic component with a noble metal loading of 2 gPd L^{-1}. The catalyst coating was prepared by incipient wetness impregnation followed by dip coating of the cordierite substrate. An AlO(OH) binder was added to improve the adhesion and mechanical stability of the washcoat. Further details regarding the catalyst preparation procedure are available in the work of Hodonj et al. [18].

The catalyst was designed for operation under stoichiometric conditions ($\lambda \approx 1$), where three-way catalyst functionality can be fully utilized. In contrast to conventional gasoline operation, the exhaust gas of an ammonia-fueled engine contains no carbon-containing species, while significant concentrations of NH_3, H_2, NO_x and H_2O are present. Under these conditions, the residual reducing species, primarily ammonia and hydrogen, react with the available oxygen on the catalyst surface, whereas nitrogen oxides are simultaneously reduced to molecular nitrogen. The ceria–zirconia mixed oxide provides a high oxygen storage capacity, allowing the catalyst to rapidly alternate between oxidizing and reducing surface states and thereby maintaining high conversion efficiencies even during transient changes in exhaust gas composition.

During the experiments, only a partial flow of the engine exhaust gas was directed over the catalyst surface. The exhaust mass flow was adjusted to achieve a gas hourly space velocity (GHSV) of 75,000 h^{-1}, corresponding to representative operating conditions of full-scale automotive exhaust aftertreatment systems. The exhaust mass flow through the catalyst was continuously monitored. In addition, the exhaust gas temperature and pressure were measured upstream and downstream of the catalyst to determine the operating conditions during each test point. A schematic representation of the catalyst installation and the corresponding measurement positions is shown in **Fig. 6**.



Fig. 5. *Three way catalytic converter prior to installation in the exhaust system of the NH_3 SI engine*

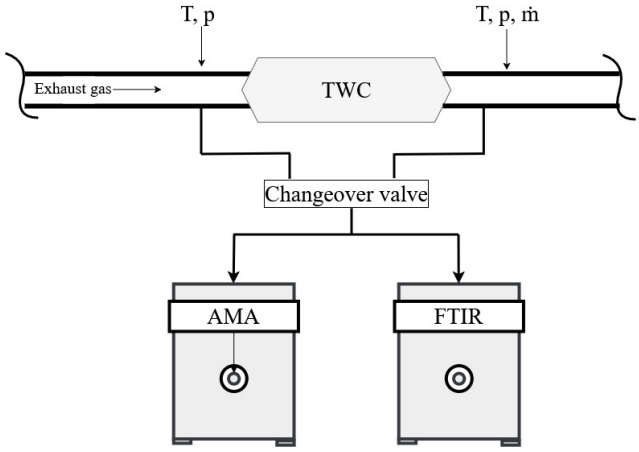


Fig. 6. *Schematic setup of TWC exhaust gas aftertreatment system installed on the 100% NH_3 SI SCE test bench*

4. Results

4.1. NH_3-diesel CI engine – Combustion testing

In order to evaluate the influence of different engine settings on engine-out exhaust gas composition, several engine parameters were varied systematically while maintaining a constant engine load. As described in the methodology section, the objective was to develop a combustion strategy that can be effectively combined with the exhaust gas aftertreatment system. The EU Stage V emission regulation for stationary engine with power outputs ≥ 560 kW was defined as the end-of-pipe emission target.

Fig. 7 illustrates the influence of the air-fuel equivalence ratio λ on engine-out emission at 85% and 90% AES for combustion phasing settings of MFB_{50} = 6.0 °CAaTDC and 9.0 °CAaTDC, respectively. All measurements were conducted at a constant operating point of 15 bar IMEP and 1,500 rpm.

NO_x emissions exhibit a clear λ-dependent behavior, reaching a maximum at approximately λ = 1.4. At lower λ values, NO_x emissions decrease due to the limited oxygen availability for nitrogen oxide formation. Under very lean conditions, NO_x emissions also decrease as a result of reduced combustion temperatures, which suppress thermal NO formation. Within the investigated AES range, influence of AES on NO_x is negligible. In contrast, combustion phasing has a pronounced effect, with earlier MFB_{50} resulting in higher NO_x because of the increased heat released and consequently higher peak combustion temperatures.

The behavior of NH_3 slip differs considerably from that of NO_x. Under richer conditions, the limited oxygen excess restricts NH_3 oxidation, particularly within locally fuel-rich regions around the diesel spray. At 90 % AES and under very lean conditions, the reduced reactivity of the NH_3-air mixture, combined with lower combustion temperatures, leads to incomplete combustion and thus increased NH_3 slip. The optimal λ range depends on the used fuel share. When less diesel is used (higher AES), operation with λ between 1.1 and 1.2 exhibits the lowest NH_3 emissions, while higher diesel shares shift the optimal λ range into a leaner regime (1.3 < λ < 1.6). The above-mentioned local fuel-rich regions around the diesel spray become more relevant under lower AES conditions, resulting in an increased global oxygen excess requirement for efficient NH_3 combustion.

A higher AES has a significant impact on NH_3 emissions. Increasing AES up to 90% results in substantially higher NH_3 slip, which can be attributed to the reduced amount of diesel fuel available for ignition. The lower ignition energy weakens the interaction between the diesel spray and the premixed NH_3-air charge, thereby reducing overall combustion efficiency.

Notably, combustion phasing shows a non-typical effect on unburned fuel emissions. For λ < 1.5, retarding MFB_{50} from 6.0 °CAaTDC to 9.0 °CAaTDC reduces NH_3 emissions by up to 1,000 ppm. However, this trend reverses under very lean conditions (λ > 1.5), where earlier combustion phasing becomes beneficial. Two mechanisms may explain this behavior. In general, retarded combustion phasing increases unburned emissions because the combustion duration is

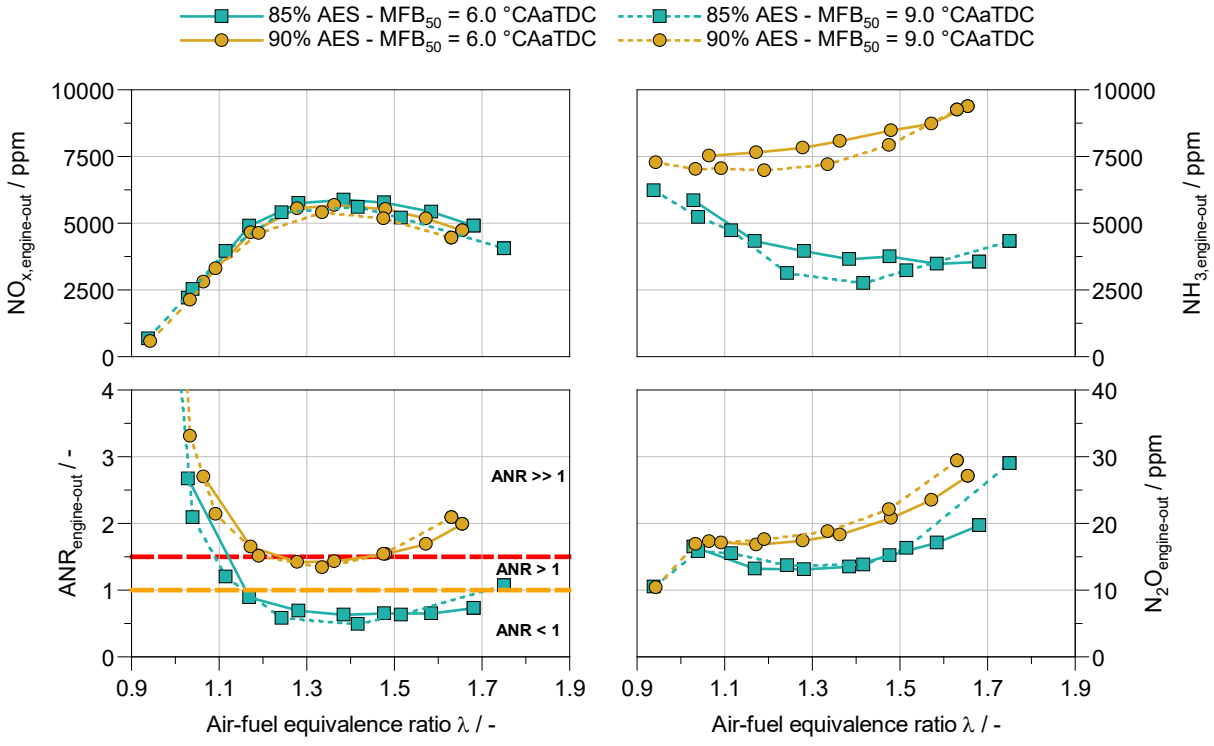


Fig. 7. *Effects of varying λ on engine-out emissions for different AES and MFB_{50} settings at 15 bar IMEP & 1,500 rpm on the NH_3-diesel CI engine*

prolonged and flame quenching effects near the cylinder wall are promoted. Similar effects have been reported for lean-burn LNG-diesel dual-fuel engines [20] and appear to be also present in NH_3-diesel dual-fuel combustion under accordingly lean conditions. Under richer operating conditions, however, a second mechanism may partially compensate for these quenching losses. A portion of the NH_3-air mixture is trapped within the piston crevice volume during compression. With retarded combustion phasing, the combination of prolonged combustion and relatively high in-cylinder temperatures at low λ may promote the oxidation of NH_3 releases from the crevice during later stages of the expansion stroke, when the cylinder pressure has decreased sufficiently for the trapped NH_3 to escape. Under lean conditions, this post-oxidation mechanism is likely less effective because the lower combustion temperatures allow flame quenching effects to dominate resulting in increased NH_3 slip.

Considering these results, it becomes evident that $ANR_{engine\text{-}out}$ can also be effectively controlled through optimization of engine operating parameters. The λ range between 1.2 and 1.5 exhibits higher NO_x emissions and low NH_3 slip, resulting in a near-stoichiometric $ANR_{engine\text{-}out}$. Within this λ range, adjusting AES enables transition between sub-stoichiometric and over-stoichiometric $ANR_{engine\text{-}out}$, providing an effective control parameter for selecting the desired operating mode. Since variations in MFB_{50} reduce both NH_3 and NO_x emissions simultaneously within the preferred λ range, its influence on $ANR_{engine\text{-}out}$ remains limited.

In addition to ANR control, engine-out N_2O emissions should be minimized, to reduce the DeN_2O demand of the aftertreatment system. Controlling λ for the preferred $ANR_{engine\text{-}out}$ operating window also results in comparatively low N_2O emissions. In general, lower λ facilitates N_2O decomposition due to higher combustion temperatures. Higher AES were observed to increase N_2O, presumably because the reduced diesel pilot quantity lowers the heat release intensity [21]. A similiar trend can be observed at later MFB_{50}. However, compared with λ, the effect of AES and MFB_{50} on N_2O are less pronounced.

Evaluation of carbon-based emissions (THC and CO), originating from the small amounts of diesel fuel burned, was not considered in this study. A detailed analysis was carried out during previous investigations [21].

4.2. NH_3-diesel CI engine – Aftertreatment testing

To evaluate the performance of the aftertreatment system over a wide engine operating range, the combustion strategy investigated in the previous section was applied at different engine load levels. The corresponding AES and λ settings over IMEP are shown in **Fig. 8**. Since the previous results demonstrated that MFB_{50} has only a minor influence on $ANR_{engine\text{-}out}$, no load-specific adjustment of MFB_{50} was performed. Instead, its was kept within a range of 6.0 - 9.0 °CAaTDC for all investigated engine loads.

The results presented in this study focus on operating conditions with $ANR_{engine\text{-}out} > 1$. A detailed comparison between $ANR_{engine\text{-}out} < 1$ and $ANR_{engine\text{-}out} > 1$ operation was shown in a previous publication [21].

To maintain the target $ANR_{engine\text{-}out}$ within a range of $1 < ANR_{engine\text{-}out} < 1.5$, AES had to be limited to 60 % at 5 bar IMEP. Higher AES at this load resulted in excessive NH_3 slip and thus $ANR_{engine\text{-}out} > 1.5$, which is expected to be unsuited for combined engine and aftertreatment operation. At the highest investigated load of 20 bar IMEP, AES could be increased up to 95 %.

λ was also adjusted individually for each engine load. At lower loads, a higher oxygen excess was required because the larger diesel pilot share creates local fuel-rich zones with increased oxygen consumption around the diesel spray.

As described in the methodology section, additional NH_3 dosing was manually adjusted, according to the $DeNO_x$ and DeN_2O requirements observed during test bench operation. Although the engine was operated under $ANR_{engine\text{-}out} > 1$ conditions, additional NH_3 dosing was still required at 5 and 10 bar IMEP to achieve the desired EAT performance. In contrast, operation at 15 and 20 bar IMEP was feasible without additional NH_3 dosing. The additional NH_3 demand can be attributed to oxidation reactions occurring across the SCR catalyst, which consume NH_3 and thereby decrease the amount available for $DeNO_x$. **Fig. 9** compares $ANR_{engine\text{-}out}$ with the resulting ANR upstream of the EAT system (ANR_{EAT}), which accounts for the additional NH_3 supplied by the dosing system.

The exhaust gas temperature upstream of the EAT system is determined by both the temperature directly downstream of the engine's exhaust valve and the temperature drop occurring between engine and EAT system. The engine-out temperature depends on the applied engine settings and engine load. The temperature drop can be estimated from the enthalpy decrease across the turbocharger turbine, referenced to the equivalent full-cylinder engine. On the SCE test bench, the calculated temperature drop was reproduced using the external heating system of the EAT testing environment, thereby providing representative temperature conditions at the EAT inlet.

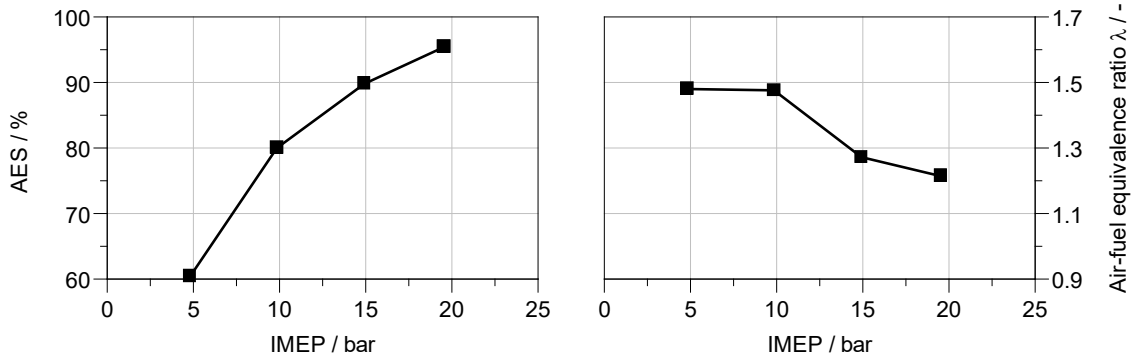


Fig. 8. *AES and λ settings over IMEP used for testing the aftertreatment concept on the NH_3-diesel CI engine*

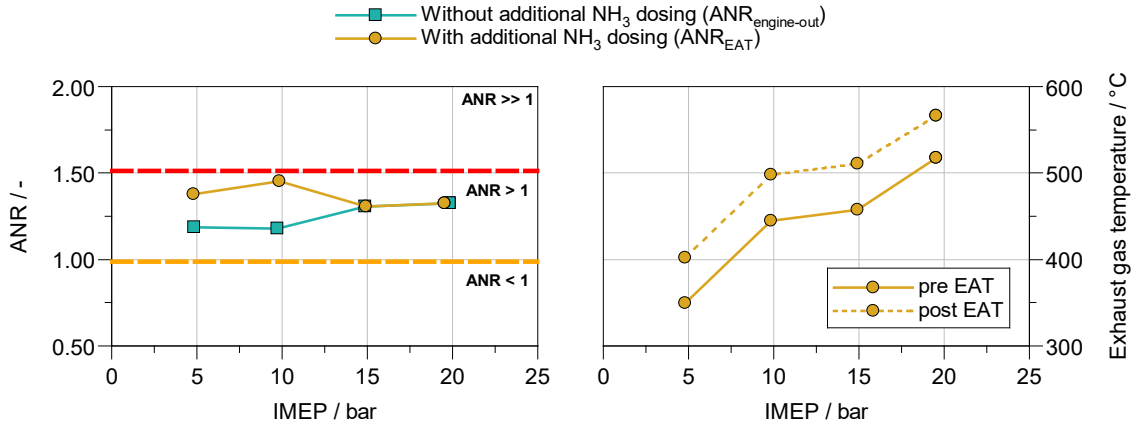


Fig. 9. *ANR settings (with and without additional NH_3 dosing) and exhaust gas temperature conditions used for testing the aftertreatment concept on the NH_3-diesel CI engine*

The exhaust gas temperature downstream of the EAT system is primarily governed by exothermic reactions, which can result in a significant increase across the catalyst samples.

Fig. 10 summarizes the engine-out and end-of-pipe emissions obtained using the defined combustion strategy in combination with the proposed EAT concept under $ANR_{engine\text{-}out} > 1$ conditions and the corresponding additional NH_3 dosing strategy presented in **Fig. 9**.

Engine-out NO_x emissions exhibit an increasing trend towards higher engine-load which can be attributed to intensified fuel-NO_x formation resulting from higher AES, as well as increased thermal-NO_x formation caused by higher combustion temperatures. However, 20 bar IMEP represents an exception. Operation with $\lambda = 1.2$ shifts combustion into an operating regime below the NO_x peak, as already shown in **Fig. 7**.

Using the proposed aftertreatment concept together with the defined ANR_{EAT}, high $DeNO_x$ efficiency was achieved across a wide range of engine load. However, at 20 bar IMEP, NO_x concentrations exceeded the EU Stage V limit (0.67 g/kWh). This behavior is presumed to result from the increased GHSV across the SCR (>13,000 h^{-1}), which limits $DeNO_x$ efficiency. In addition, the high engine-out NH_3 slip may not be fully oxidized across the downstream ASC because of the GHSV already exceeding 50,000 h^{-1}. Under these conditions, the inherent selectivity of the ASC towards NO formation during NH_3 oxidation further contributes to the observed end-of-pipe NO_x emissions.

Engine-out NH_3 slip generally increases with higher engine load, due to less diesel pilot fuel share used. Again, 20 bar IMEP deviates from the trend, most likely because the higher combustion temperatures at high load promote efficient ammonia combustion, despite the diesel pilot accounting for only 5% of the total fuel energy. Overall, the SCR+ASC configuration proved highly effective in reducing engine-out NH_3 with NH_3 concentrations below the EU Stage V limit (10 ppm) achieved at 5 - 15 bar IMEP. However, elevated end-of-pipe NH_3 concentrations were still observed at 20 bar IMEP, presumably due to the high GHSV across the ASC, which limits complete NH_3 conversion.

Engine-out N_2O emissions show an increasing trend towards lower IMEP, which is due to low-temperature combustion regimes under low-engine load. However, using the proposed EAT concept, N_2O can be effectively mitigated between 10 and 20 bar IMEP, where DeN_2O efficiencies of 100% were observed. Considering the moderate pre EAT

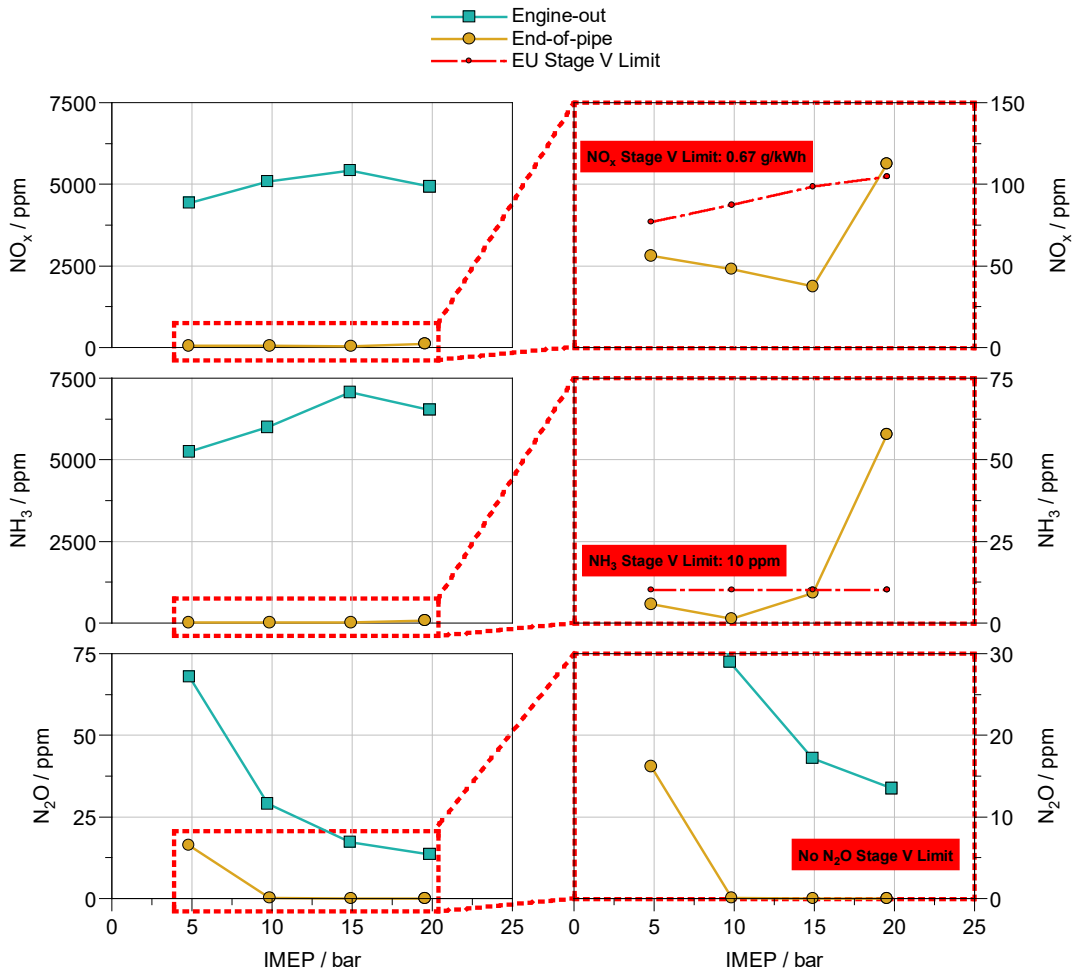


Fig. 10. *Comparison of engine-out and end-of-pipe emissions achieved using the optimized AES, λ and ANR settings together with the aftertreatment concept on the NH_3-diesel CI engine*

exhaust temperatures, which are lower than those typically required for full N_2O conversion [10], these high conversion rates are noticeable. This behavior can be explained by additional heat released by the exothermic SCR reactions (compare temperature levels in **Fig. 9**), which is further amplified by the elevated NH_3 and NO_x engine-out concentrations. However, at 5 bar IMEP, only 76 % DeN_2O was possible, which can be attributed to two factors. First, engine-out N_2O concentrations are elevated at 5 bar IMEP. Second, the lower engine-out exhaust gas temperature, which is also reflected in the decreased pre EAT exhaust gas temperature of approximately 340 °C (**Fig. 9**), limits the catalyst activity. It should be noted that higher pre EAT temperatures could not be realized due to limitations in the external heating system. Consequently, higher conversion potential may still be available under optimized thermal conditions.

The measured end-of-pipe CO and HC concentrations remained below the EU Stage V limits. For a detailed discussion on CO and HC emissions, see [21].

4.3. 100% NH_3 SI engine – Combustion + Aftertreatment testing

This section presents the exhaust gas emission results of the single cylinder engine operated with 100 % ammonia in a spark-ignited combustion process. The following section analyzes the thermal and chemical behavior of the TWC and its impact on exhaust gas temperature, oxygen storage dynamics, and the ANR as a function of the air–fuel equivalence ratio λ. At an investigated IMEP of 11 bar and an engine speed of 1,500 rpm, the exhaust gas temperature upstream of the catalyst is approximately 275 °C, placing the catalyst close to the lower limit of its effective operating window. In a more conventional TWC layout positioned closer to the engine, the exhaust gas temperature would typically be higher, providing more favorable conditions for ammonia conversion. Downstream of the catalyst, the temperature increases by approximately 50 °C to about 325 °C, see **Fig. 11**. This temperature rise is attributed to the strongly exothermic oxidation of NH_3 and H_2 within the catalyst. In addition, the ceria–zirconia oxygen storage component stabilizes catalyst performance by temporarily storing oxygen under lean conditions and releasing it locally during richer operation. This oxygen buffering capability extends the effective operating range of the catalyst and enables oxidation reactions to proceed even when the overall exhaust gas composition is close to or slightly below stoichiometric. The resulting heat release further promotes catalyst activity and contributes to the high ammonia conversion observed near λ = 1.

Fig. 11 (right) illustrates the ANR as a function of the air–fuel equivalence ratio λ. Upstream of the three-way catalyst, the ANR remains below unity under lean operating conditions (λ ≥ 1), indicating that the exhaust contains more NO_x than NH_3. As the mixture becomes richer, the ANR increases markedly, reaching values of approximately 4 at λ = 0.95. In contrast to conventional NH_3 SCR systems, in which an ANR of about 1 is typically considered optimal, this constraint cannot be directly transferred to the TWC used in pure ammonia operation. The TWC is supplied with an exhaust gas that, in addition to NO_x and NH_3, already contains H_2 and N_2O formed in the engine. As a result, several reaction pathways proceed in parallel inside the catalyst: NH_3 acts as a reductant for NO_x but is simultaneously (partly) oxidized to N_2 and H_2O; the H_2 formed in the engine is further oxidized to water; and N_2O can be additionally formed in the TWC within certain regions of the operating window. An "optimal" operating condition therefore cannot be defined solely by a specific ANR (e.g. ANR ≈ 1), but rather emerges from a compromise between NO_x conversion, minimization of NH_3 slip, and limitation of H_2 and N_2O emissions. Accordingly, ANR is used in this work primarily as a parameter to describe the NO_x/NH_3 ratio upstream of the TWC, while the downstream behavior of the system is evaluated based on the individual species emissions (NO_x, NH_3, N_2O, H_2).

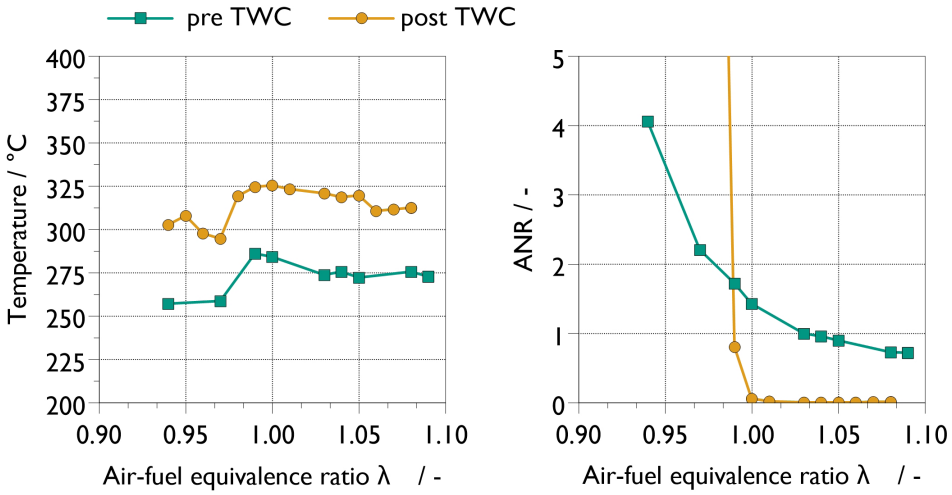


Fig. 11. *Temperature and ANR over air-fuel equivalence ratio λ at 1,500 rpm, 11 bar IMEP and 100% NH_3 on the NH_3 SI engine*

Fig. 12 compares the engine-out (pre TWC) and end-of-pipe (post TWC) emissions of NO_x, N_2O and NH_3 as a function of the air-fuel equivalence ratio.

Before discussing the catalyst performance, the engine-out emissions are considered. As the air-fuel equivalence ratio increases from rich to lean conditions, the raw NO_x emissions increase continuously from approximately 500 ppm to more than 3,500 ppm. This behavior is expected, as increasing oxygen availability promotes the oxidation of fuel-bound nitrogen to NO. In contrast, the engine-out NH_3 emissions remain over the entire investigated operating range, between approximately 2,000 and 2,900 ppm. A slight minimum is observed at $\lambda \approx 0.94$, followed by an increase towards stoichiometric and lean operation. In addition to the nitrogen-based species, Figure 12 also shows the engine-out hydrogen concentrations as a function of λ. Under slightly rich conditions, a pronounced increase in H_2 is observed, which is consistent with enhanced fuel-bound nitrogen and hydrogen conversion in the absence of excess oxygen. The simultaneous decrease in NH_3 and increase in H_2 suggest that part of the unburned ammonia is further converted via dehydrogenation and cracking reactions, thereby reducing the NH_3 slip despite globally fuel-rich operation. The engine-out N_2O emissions remain comparatively low throughout the investigated λ range and increase only slightly from approximately 20 to 40 ppm, indicating that only minor amounts of N_2O are formed during the combustion process.

The three-way catalyst substantially alters the emission characteristics. Under rich operating conditions ($\lambda < 1$), NO_x and N_2O emissions remain very low, while NH_3 remains the dominant nitrogen-containing species downstream of the catalyst. Nevertheless, the comparatively low NH_3 concentration observed at $\lambda \approx 0.94$ indicates that ammonia oxidation is already taking place despite the globally fuel-rich exhaust composition. This behavior can likely be attributed to the oxygen storage capacity of the ceria-zirconia (Ce–Zr) component of the catalyst washcoat. Oxygen previously stored within the catalyst can be released locally, providing sufficient oxygen to oxidize part of the ammonia even when the overall exhaust gas composition is slightly rich. As the catalyst oxygen storage becomes depleted under richer conditions, the oxidation of NH_3 is increasingly limited, resulting in the higher ammonia slip typically observed under rich operation.

A distinct transition occurs as the air-fuel equivalence ratio approaches stoichiometric conditions. Between $\lambda \approx 0.98$ and $\lambda \approx 1.00$, the NH_3 concentration decreases rapidly to almost zero, while both NO_x and N_2O emissions increase sharply. The simultaneous decrease in NH_3 and increase in NO_x and N_2O clearly indicate that ammonia is not selectively converted to N_2. Instead, a considerable fraction of the fuel-bound nitrogen is oxidized to NO_x and N_2O. In particular, N_2O concentrations increase to approximately 500 ppm, which is more than one order of magnitude higher than the corresponding engine-out values. Thus, although the catalyst effectively removes ammonia slip, it simultaneously promotes the formation of undesired nitrogen oxides under oxygen-rich conditions.

This behavior illustrates the fundamental trade-off associated with ammonia conversion over a three-way catalyst.

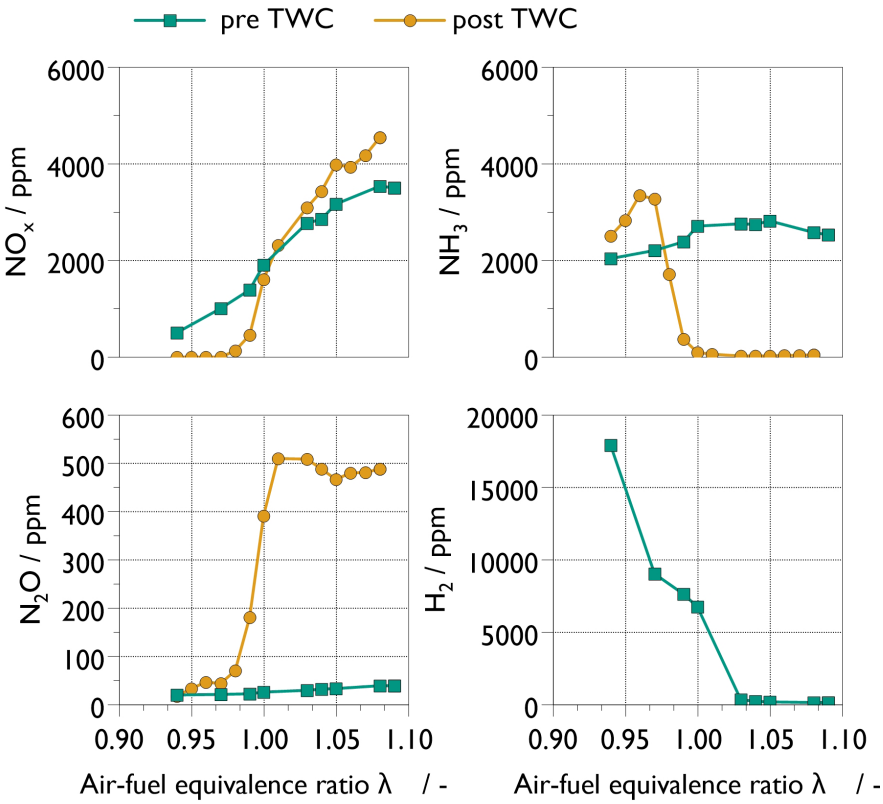


Fig. 12. *Exhaust gas emissions over the air-fuel equivalence ratio λ at 11 bar IMEP, 1,500 rpm and 100% NH_3 on the NH_3 SI engine*

Rich operation results in high NH_3 slip but low NO_x and N_2O emissions, whereas lean operation almost completely eliminates NH_3 emissions at the expense of significantly increased NO_x and N_2O formation. Consequently, the optimum operating window is located slightly on the rich side of stoichiometry ($\lambda \approx 0.97–0.99$), where the concentrations of all three nitrogen-containing species remain comparatively low and a reasonable compromise between NH_3 conversion and by-product formation is achieved.

Overall, the results demonstrate that the performance of the three-way-catalyst in an ammonia SI engine is predominantly controlled by the air–fuel equivalence ratio. While lean operation effectively suppresses NH_3 slip, it promotes the formation of NO_x and, in particular, N_2O. Conversely, rich operation minimizes NO_x and N_2O emissions but results in increased NH_3 slip due to oxygen deficiency. The optimum operating point is therefore located in a narrow region close to stoichiometric conditions ($\lambda \approx 0.97$), where the competing formation pathways can be balanced and all three nitrogen containing emissions remain at comparatively low levels. The Ammonia–NO_x ratio thus primarily serves as a descriptor of the inlet exhaust gas conditions and illustrates the transition from efficient NH_3 oxidation under lean conditions to oxygen limited catalyst operation under rich conditions.

5. Conclusion

This paper examined two different combustion concepts for NH_3-fueled internal combustion engines intended for maritime and non-road mobile machinery applications, each evaluated on a dedicated single cylinder test bench. While the first concept features a lean-burn ($\lambda > 1$) NH_3-diesel CI engine coupled with an SCR+ASC aftertreatment system, the second engine is operated with 100% ammonia in spark-ignited (SI) mode in combination with a three-way catalyst under near-stoichiometric conditions ($\lambda = 1$). The primary objective was to evaluate the effect of various engine control parameters on the engine-out exhaust gas composition and to develop a strategy for effective coupling of engine and aftertreatment.

The main findings for each engine concept are summarized below:

NH_3-diesel CI engine with SCR and ASC:

- A λ range of $1.2 < \lambda < 1.5$ provided optimal conditions for maintaining a near-stoichiometric engine-out Ammonia-NO_x-ratio ($ANR_{engine\text{-}out}$)
- Combustion phasing (MFB_{50}) control can reduce engine-out NH_3 slip
- Within the preferred λ range, MFB_{50} similarly affected both NO_x and NH_3 emissions, resulting in only a minor effect on $ANR_{engine\text{-}out}$
- Considering the target $ANR_{engine\text{-}out}$, the ammonia energy share (AES) had to be limited to 60% at low engine load while high load allowed AES up to 95%
- Despite high NO_x and NH_3 concentrations present in the engine-out exhaust gas, high $DeNO_x$ and NH_3 conversion efficiencies are possible using conventional SCR and ASC technologies
- As NH_3 can be used directly as a reducing agent (via engine-out NH_3 slip or additional NH_3 dosing) no AdBlue system is required
- Even under $ANR_{engine\text{-}out} > 1$ conditions, additional NH_3 dosing into the exhaust gas may be required for high $DeNO_x$ efficiency
- When the effective ANR_{EAT} (including NH_3 dosing) is controlled within a range between 1.3 and 1.5, NO_x and NH_3 can be reduced below the EU Stage V limits over a wide range of engine load
- 100% N_2O conversion is achievable, but care must be taken at low engine load due to lower exhaust gas temperature

100% NH_3 SI engine with TWC:

- 100 % ammonia operation in a spark-ignition combustion process is feasible across the entire engine map.
- The exhaust temperature upstream of the TWC is relatively low (≈275 °C at 11 bar IMEP and 1,500 rpm) due to the 2 m distance between the engine and the catalyst; an engine-near layout would result in higher temperatures.
- Once light-off is reached, the TWC exhibits stable activity at this temperature level; higher temperatures are not essential but could widen the usable λ-window.
- Conversion is strongly governed by λ, with a narrow operating window around stoichiometry. Slightly rich operation ($\lambda \approx 0.97$) provides the best compromise between NH_3, NO_x and N_2O emissions.
- The results demonstrate the technical feasibility of TWC-based aftertreatment for NH_3-fueled SI engines; optimized λ-control and catalyst formulations with lower low-temperature N_2O selectivity could enable competitive emission levels.

Acknowledgments

The authors of the Karlsruhe Institute of Technology would like to express our gratitude to *Liebherr Machines Bulle SA* for providing the engine and for their support throughout this study.

The authors of the University of Rostock would like to thank the German Federal Ministry for Economic Affairs and Energy for funding the project "NH3-Stat" (project number: 03EE5146D) as well as *Umicore AG & Co. KG* for providing the SCR and ASC catalyst samples.

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