



**Keywords:** ammonia combustion, high-pressure dual fuel,

## **Fundamental investigation of an ammonia HPDF combustion process on high-speed engines**

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[https://doi.org/10.18453/rosdok\\_id00004642](https://doi.org/10.18453/rosdok_id00004642)

### **Abstract**

In this current scientific article, the core principles of HPDF (High-Pressure Direct Fuel) ammonia combustion are explored, and an extensive analysis of the various factors influencing combustion and emissions formation is conducted through experimental engine studies. This comprehensive investigation includes the scrutiny of parameters such as engine speed, load, air-fuel ratio, and various injection strategies, encompassing timing, quantity, and frequency of injection. Against the backdrop of global environmental concerns, ammonia's potential as an alternative fuel source is of great interest. However, realizing this potential necessitates addressing emissions challenges, including ammonia raw emissions and the greenhouse gas nitrous oxide. Furthermore, the research contributes to a deeper comprehension of combustion characteristics and emission dynamics, thereby facilitating effective emissions management. By advancing the understanding of ammonia combustion, this study not only aids in overcoming technical hurdles but also supports the broader effort to transition towards more sustainable energy sources, aligning with global initiatives to mitigate environmental impact and reduce emissions.

## 1. Introduction

In view of climate change and the need to reduce greenhouse gas emissions, ammonia is becoming increasingly important as a carbon-free fuel for combustion engines. Ammonia offers several advantages: It has a high volumetric energy density, is easy to store and transport and uses existing infrastructure for production and distribution. Ammonia can be used in various engine technologies, including combustion engines and gas turbines. Especially in marine and heavy-duty applications, ammonia is seen as a promising fuel due to its high energy density and the need to reduce CO<sub>2</sub> emissions. However, there are technical challenges in the combustion of ammonia, such as high ignition temperatures, slow flame speeds and the formation of nitrogen oxides (NO<sub>x</sub>) and nitrous oxide (N<sub>2</sub>O), which are also harmful to the climate. To overcome these challenges, various strategies are being explored, such as the use of ammonia in dual-fuel systems, where ammonia is mixed with diesel to aid ignition and optimize emissions. Overall, ammonia represents a promising opportunity to reduce CO<sub>2</sub> emissions in the transportation and energy sectors. Ongoing research is focused on further improving the efficiency and environmental compatibility of ammonia combustion.

## 2. Fuel Properties

Table I compares ammonia and the fuels hydrogen and methanol. Taking into account the typical pressure and temperature conditions for storage, it can be seen that ammonia has good volumetric calorific values due to its liquid storage capability.

Table I: Characteristics of selected alternative fuels [1] [2] [3] [4]

	Unit	Ammonia	Hydrogen	Methanol
Vol. heating value [T=300 K]	MJ/l	11,9 (10 bar)	4,8 (700 bar)	15,8 (1 bar)
Stoichiometric air requirement	kg/kg	6,05	34,3	6,45
Auto-ignition temperature	°C	651	600	465
Enthalpy of vaporization	kJ/kg	1371	446	1173
Lam. flame speed (p = 1 bar, T=300 K, λ=1)	cm/s	6,5	290	55

The low flame speed leads to a slower combustion process compared to other fuels, which can reduce combustion efficiency. The high auto-ignition temperature and extreme heat of vaporization make liquid injection and diesel-like compression ignition more difficult. The high minimum ignition energy means that it is more difficult to safely ignite an ammonia-air mixture. The resulting increased resistance to knock allows ammonia-fueled engines to operate at higher compression ratios, offering efficiency benefits. Although ammonia has a much lower energy content per mass compared to standard carbon-based fuels, its low stoichiometric air-to-fuel ratio partially compensates for this in terms of in-cylinder energy content. [3] [5]

Volumetric storage density is the challenging factor for vehicles, even ammonia requires about three times the volume of carbon-based fuels (at identical efficiencies) for the same range. However, hydrogen requires even more storage volume, especially if the tank itself (for 70 MPa pressure or -253 °C temperature) is included. Furthermore, a transportation infrastructure for ammonia already

exists and its handling is not significantly different from that of LPG or propane. In ammonia combustion, the ammonia can be introduced via the intake manifold or directly into the combustion chamber and burned by an ignition jet, like known methane dual-fuel concepts. In addition, ammonia can be made to ignite itself using suitable measures and can be diffusively converted instead of premixed combustion, which leads to higher conversion rates. [6] [7]

## 2.1. Oxidation pathways of ammonia

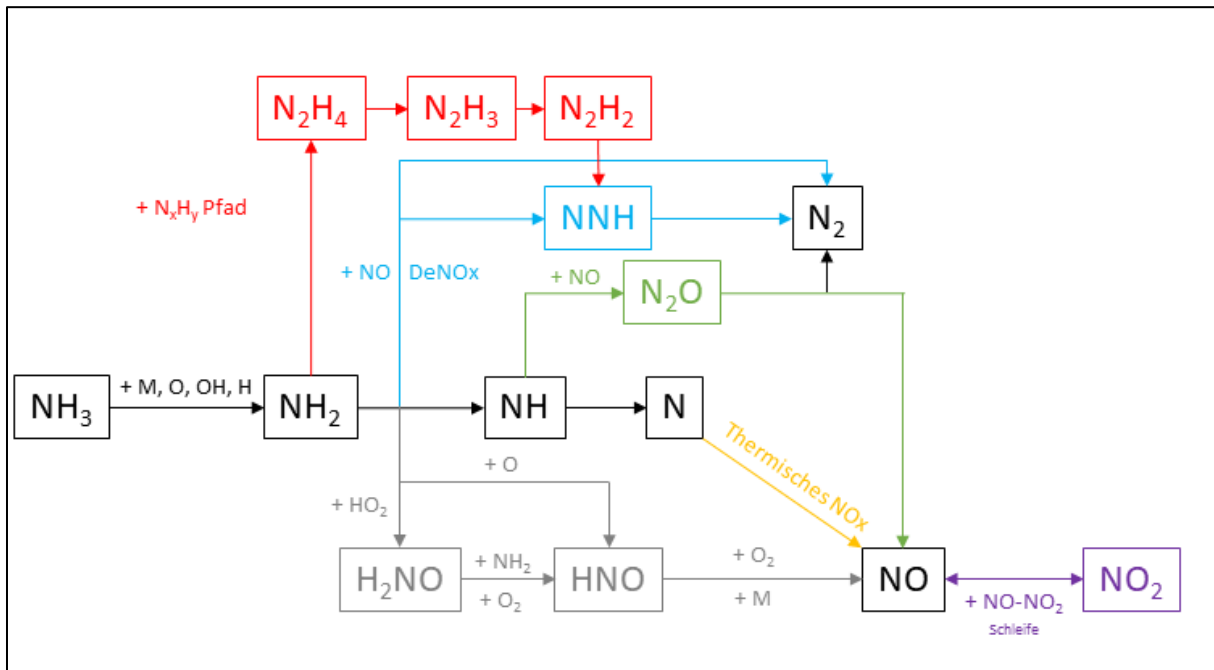


Figure 1: Schematic oxidation pathways of ammonia according to Tornatore et al. [8]

Ammonia is stable because the covalent bonds between the nitrogen atom and the three hydrogen atoms require a lot of energy to dissociate. The first step in ammonia oxidation is dehydrogenation to  $\text{NH}_2$ , which consumes highly reactive  $\text{OH}$ ,  $\text{O}$  and  $\text{H}$  radicals. After dehydration to  $\text{NH}_2$ , there are several chemical reaction pathways that can now take place. Firstly, the  $\text{NH}_2$  radicals can combine to form longer-chain  $\text{N}_x\text{H}_y$  compounds. This reaction is favoured by excess fuel and high pressure. [8]

Under fuel-rich conditions, the importance of  $\text{O}$  and  $\text{OH}$  as reaction partners in the radical pool decreases. The reactions of  $\text{NH}_2$  with  $\text{H}$  and other  $\text{NH}_2$  radicals increase, which leads to the considerable formation of  $\text{H}_2$ . A lack of oxygen suppresses the oxidation of  $\text{NH}_i$ , which means that less  $\text{NO}$  is produced, and more  $\text{N}$  atoms can be combined to form  $\text{N}_2$  instead. [9] [10]

At high pressure and low temperature, the  $\text{NH}_2$  radicals react with  $\text{HO}_2$  to form  $\text{H}_2\text{NO}$ . The  $\text{H}_2\text{NO}$  molecule then oxidizes to  $\text{HNO}$ , which reacts further to form  $\text{NO}$ . This is the main route for the formation of fuel  $\text{NO}$  in ammonia flames, as  $\text{HNO}$  is subsequently oxidised to  $\text{NO}$ . This differs from hydrocarbon flames, where  $\text{NO}$  formation mainly occurs via the Zeldovich mechanism. [11] [12]

Another reaction pathway is through the oxidation of  $\text{NH}_2$  with  $\text{NO}$  to molecular nitrogen and water or just  $\text{NNH}$  and hydroxide radicals. The  $\text{NNH}$  radical then reacts further to form molecular nitrogen and hydrogen radicals, which are now available for further reaction. The thermal  $\text{DeNO}_x$  mechanism just described predominates between 1100 K and 1400 K and was first described by Miller and Glarborg and Bowmann. [13] [14]

If the  $\text{NH}_2$  dehydrogenates further to  $\text{NH}$  at temperatures above 1400 K, it is possible that  $\text{N}_2\text{O}$  is formed by adding  $\text{NO}$  at low  $\text{O}_2$  concentrations or by the reaction of  $\text{NH}_2$  with  $\text{NO}_2$  at high  $\text{O}_2$  concentrations. On the one hand,  $\text{N}_2\text{O}$  can subsequently decompose by reaction with  $\text{H}$  radicals to form molecular nitrogen  $\text{OH}$  radicals at temperatures above 1600 K. Another reaction pathway is that the  $\text{N}_2\text{O}$  decomposes and then the reaction of molecular hydrogen with oxygen radicals leads to hydrogen or hydroxide radicals. However, under high pressure conditions or extremely lean fuel conditions, this reaction is reversed and forms a significant formation route for  $\text{N}_2\text{O}$ . [15] [16]

$\text{NO}_2$  is mainly formed by the oxidation of  $\text{NO}$  via the reaction  $\text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH}$ . The  $\text{NO}_2$  formed is returned to ammonia either directly or via intermediate products such as  $\text{H}_2\text{NO}$  ( $\text{NO}$ - $\text{NO}_2$  loop). The oxidation processes of ammonia, which favour the black and grey paths, lead to low  $\text{NO}_x$  and  $\text{N}_2\text{O}$  emissions and are particularly active under fuel-rich conditions. [8]

## 2.2. Classification of the HPDF Combustion

As early as the 1960s, ammonia was considered as a fuel in a compression-ignition engine by Gray et al. Running a CI engine on pure ammonia is technically feasible but requires significant modifications to both the engine and the operating conditions. The main requirements are high compression ratios, increased temperatures in the intake manifold to improve ignitability. With high-speed four-stroke engines and today's performance requirements, the implementation of these measures is only possible at great expense, so that alternative methods must be used to utilise ammonia in combustion engines. The basics of the high-pressure dual-fuel combustion process with ammonia utilisation are described below. By using diesel as the ignition fuel to burn the ammonia, it is possible to reduce the compression ratio from 35:1 to 15.2:1. This is due to the increased ignition energy resulting from the addition of diesel. [17] [18]

The HPDF process (High-Pressure Dual-Fuel) combines the injection of two different fuels, a main fuel (e.g. methane or ammonia) and a pilot fuel (e.g. diesel). The main fuel is burnt in a diffusive flame, which is initiated by the ignition of the pilot fuel. Direct injection ensures that no unburnt fuel enters the exhaust gas during the charge change. Furthermore, no ammonia enters the intake duct, which could cause the corrosive properties of ammonia coupled with the humidity in the air to take effect. By injecting both fuels directly, compression ratios typical of diesel engines can be achieved, resulting in similar efficiencies to those of conventional diesel engines. HPDF combustion takes place in several phases: Firstly, the pilot fuel is injected and ignites. This is followed by the main injection, whereby the main fuel is injected and ignites when it meets the hot products of the pilot combustion. Part of the main fuel mixes with the combustion chamber air before ignition and burns suddenly, which leads to a local maximum in the heat release rate (premixed peak). The remaining main fuel burns diffusively until the end of injection and beyond in a pronounced burn-out phase. Ammonia dual-fuel combustion offers several advantages. Ammonia is carbon-free and therefore produces no direct  $\text{CO}_2$  emissions during combustion. When stored in liquid form, ammonia has good volumetric calorific values and can be safely stored and transported at relatively low pressures and temperatures. [19] [20]

## 2.3. Experimental setup

The engine tests were carried out on the FM18 single-cylinder research engine at the WTZ Roßlau. The boundary conditions are shown in the following Table 2.

Table 2: FM18 Engine data

Parameter	Value	Unit
<b>Bore x Stroke</b>	175 x 215	mm
<b>Displacement</b>	5,17	l
<b>Conrod length</b>	457	mm
<b>rated power</b>	180	kW
<b>Rated speed</b>	1800	min <sup>-1</sup>
<b>Injection pressure NH<sub>3</sub></b>	500	bar
<b>Injection pressure Diesel</b>	1000	bar

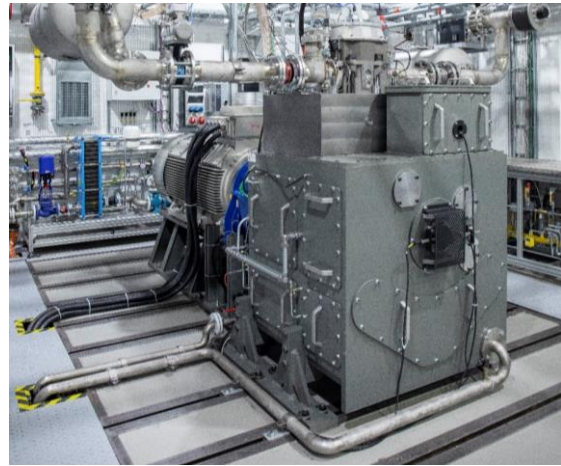


Figure 2: Single Cylinder Test Engine FM18

The ammonia supply system for the tests was designed and planned by project partner Neptun Ship Design (NSD). Due to the simplicity of the system, pressure-based storage of the ammonia was favoured. However, for future applications on ammonia carriers, liquefaction of the ammonia by lowering the temperature is being considered. The downstream high-pressure ammonia system enables injection pressures of up to 500 bar. In this context, reference is made to the work of Stenzel and Arndt et al [21], in which the ammonia system is described in detail. A Fourier transform infrared spectrometer (FTIR), which can measure nitrous oxide, ammonia and all other emissions produced in conventional combustion engines, was used to record the exhaust emissions. This measuring device ensures a comprehensive characterization of exhaust emissions and thus enables a detailed analysis of ammonia combustion.

The injector used for the study was provided by Woodward L'Orange, another project partner. This injector has two separately controllable nozzles, allowing diesel and ammonia to be injected directly into the combustion chamber via two different channels.

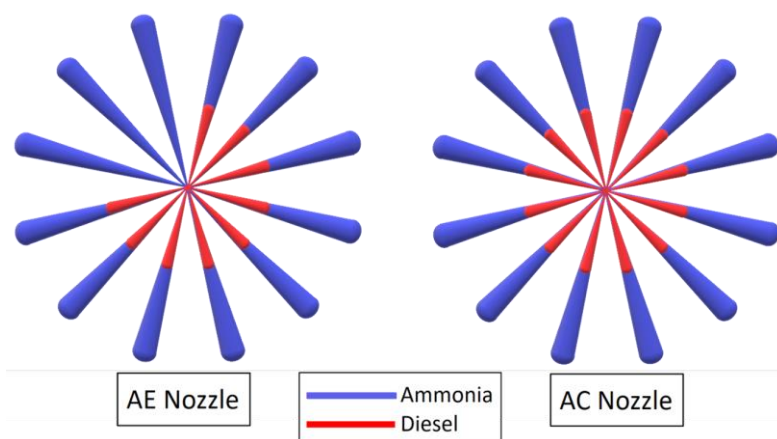


Figure 3: Schematic spray configurations of the investigated nozzles

Both injector sides are based on a servo-hydraulic principle. On the ammonia side it is necessary to use a separate control fluid circuit, which is also operated with diesel. Figure 3 shows the spray configurations of the investigated nozzle variants schematically.

Table 3: Investigated nozzle designs

	AC-Nozzle	AE-Nozzle
Number of nozzle holes for ammonia	12 (3x4)	12 (3x4)
Hydraulic flow rate of the ammonia side [l/min] @100 bar	22.8	22.8
Number of nozzle holes for diesel	12	9
Hydraulic flow rate of the diesel side [l/min]	3.0	2.25

### 3. Analysis of the combustion process investigations

This study analyzes the influence of the time offset between the injection of ammonia and diesel on combustion. Due to the servo-hydraulic principle of the HPDF injector, there is a time offset between the start of current (SOE) and the start of injection (SOI), which can be measured by a drop in pressure of the respective medium. In addition, the time delay of the pressure drop up to the measuring point was considered, considering the speed of sound.

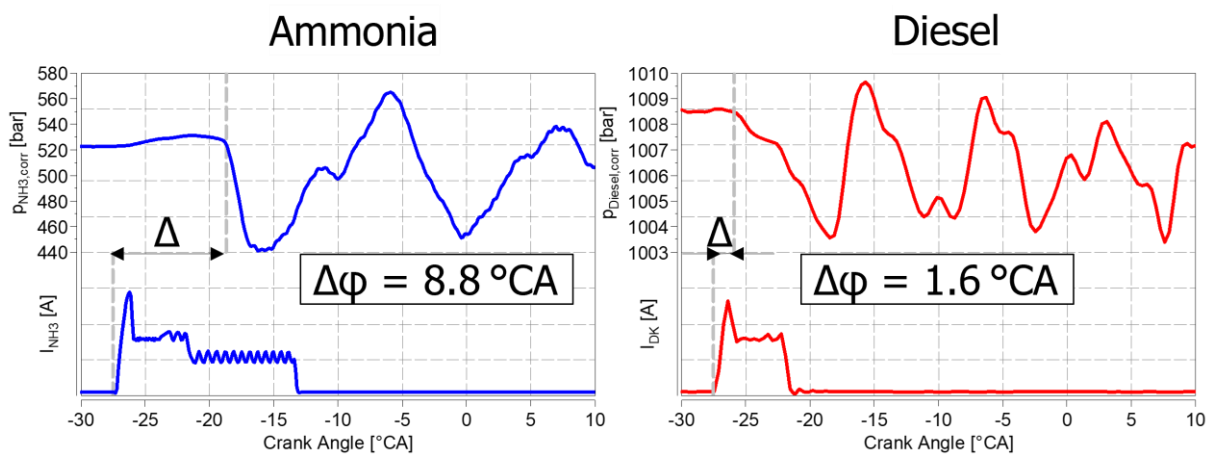


Figure 4: Description of the injection delay of the two fuel paths with corrected indicated pressure curve of both fuel lines

The difference in hydraulic injection time between the two fuels with simultaneous actuation is approximately  $7.2^\circ$  CA and can be considered constant throughout the measurement campaign since the engine speed and rail pressure were kept constant throughout the experiment. The setting values of the tests are shown in Table 4.

Table 4: Setpoints of the operation point

Parameter	Definition	Value	
$p_{mi}$	Indicated mean effective pressure	17,2	bar
$n_{MOT}$	Engine speed	1800	$\text{min}^{-1}$
$SOE_{DK}$	Start of current diesel	-28	$^{\circ}$ CA ATDC
$SOE_{NH_3}$	Start of current ammonia	-28	$^{\circ}$ CA ATDC
$x_{Q_{NH_3}}$	Energetic ammonia share	> 90	%
$p_{NH_3}$	Ammonia injection pressure	500	bar

Figure 5 illustrates the pressure, heat release, and cumulative heat release curves of the two nozzles at the operating point. The left diagram illustrates the pressure curve  $p_{CYL}$  as a function of the crank angle. It can be observed that the AC nozzle exhibits a higher pressure peak than the AE nozzle. The two graphs below present the indicated injection pressure of ammonia and diesel. Both nozzles demonstrate comparable injection curves, with injection commencing at approximately  $-20^{\circ}$  CA. The graphs on the right depict the heat release rate and the cumulative heat release, with the AC nozzle displaying an earlier heat release.

Looking at the current profiles, for the same indicated load on the motor at the AC nozzle, a significantly shorter start-up time is required on the ammonia side. Although the same hydraulic flow rate was defined through the nozzle, slight differences in the needle stroke setting led to changes in the flow rate. Additionally, it can be postulated that a reduction in the availability of diesel jets will precipitate a decline in the efficiency of ammonia conversion, necessitating a compensatory increase in fuel injection to maintain the indicated power output.

Moreover, an elevated pressure rise gradient and the heat release resulting from the higher ammonia mass flow can be discerned at the AC nozzle. A premix peak is observable at approximately  $-20^{\circ}$  CA ATDC, which analogous for both nozzle variants. Based on the pressure curves of the two fuel paths ( $p_{NH_3}$  &  $p_{Diesel}$ ), it can be determined that this premix peak originates mainly from the diesel injection, but that a partially premixed portion of ammonia is already combusted at this point.

The main part of the ammonia then combusts at different rates depending on the nozzle variant. When comparing the cumulated heat release, the 10% conversion point is earlier with the AC Nozzle. This indicates a better oxidation of the ammonia due to higher penetration from the diesel spray.

The maximum heat release of the AC Nozzle already takes place in the TDC, where the AE Nozzle is delayed. This leads to an earlier center of combustion on the part of the AC nozzle and results in lower energy consumption and increased efficiency, as measured by the global maximum of the cumulated heat release curve at same indicated power. The reason for the earlier center of combustion of the AC-Nozzle is the improved penetration area of the spray lobes, which improves the mixture preparation and the resulting fuel conversion.

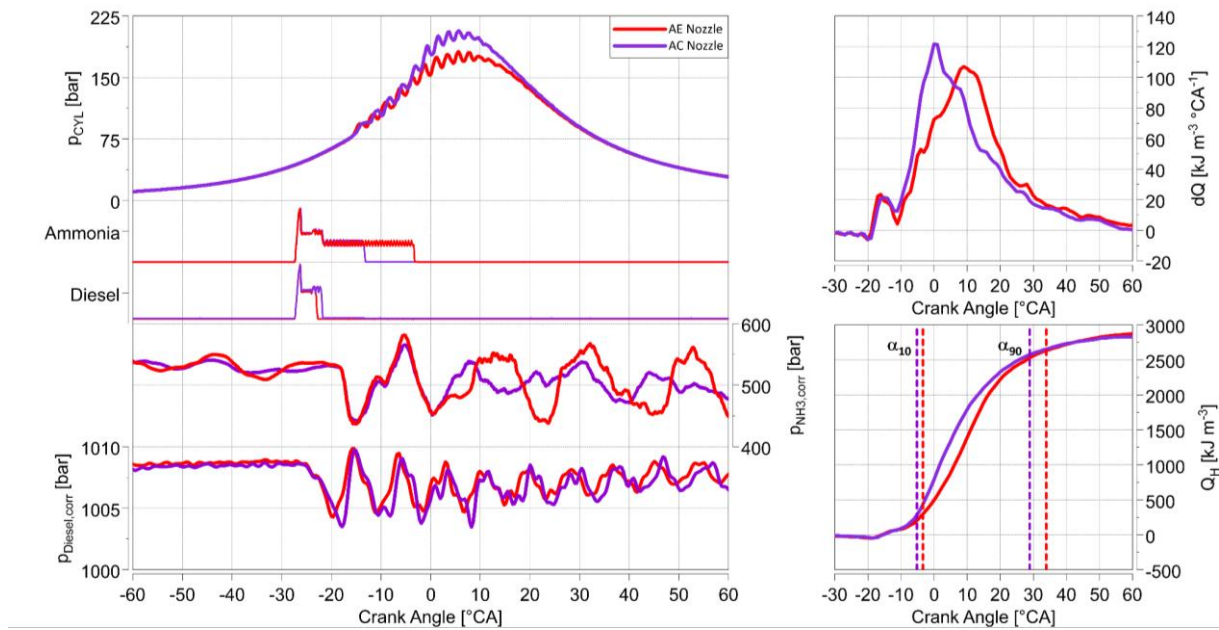


Figure 5: cylinder pressure, heat release and cumulated heat release of both nozzle variants at IMEP = 17 bar and simultaneous current

Based on the results of the simultaneous current injection of both fuel paths, the time difference of the current injections was then varied to evaluate the combustion process with earlier diesel or ammonia injection.

Figure 7 shows that a positive start of current difference corresponds to an earlier ammonia start of current. As already explained in Figure 6, a shortened duration of current on the ammonia side with the AC nozzle continues over the entire variation range. Furthermore, the shortest injection duration was set on the diesel side, which still ensures a clean opening of the injector without cycle fluctuations due to operation in the ballistic range. The injector of the AE-Nozzle requires a 100  $\mu$ s longer energization time, whereupon the diesel mass flow in the diagram inevitably increases and leads to an increased diesel and a reduced ammonia content. The AC nozzle offers efficiency advantages over the entire variation range. This can be explained by the shorter burn duration. In addition, due to the higher mass flow on the ammonia side, the AC nozzle results in higher maximum pressures and higher maximum cylinder pressure gradients.



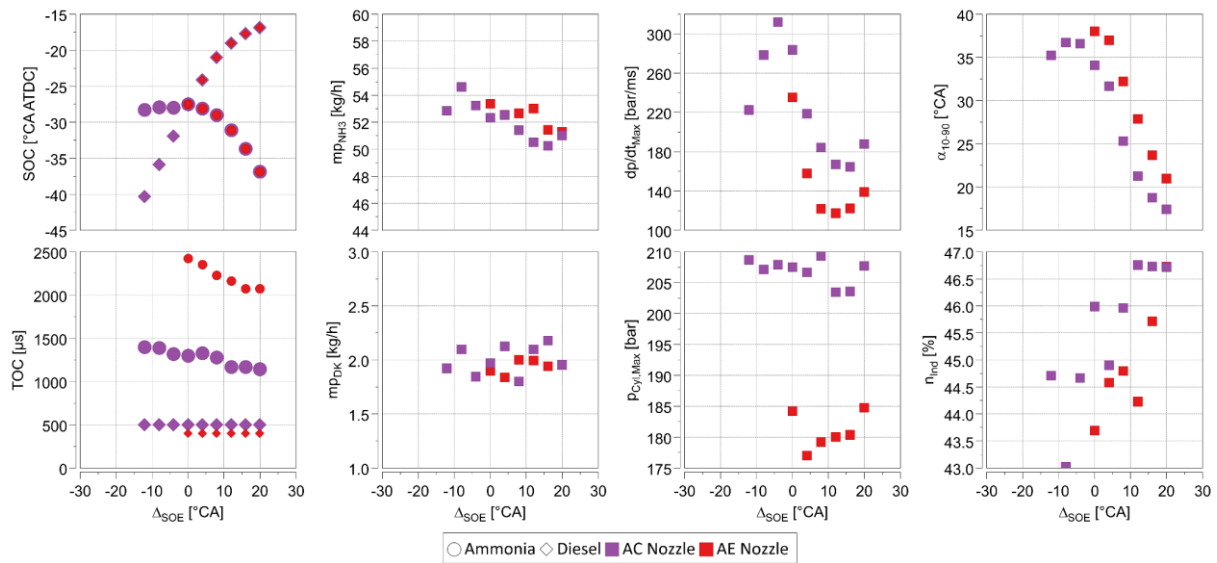


Figure 7: Setpoints values for the variation of the injection difference at IMEP = 17,2 bar

The diagrams in Figure 8 show the emission values of  $\text{NH}_3$ ,  $\text{NO}_x$ ,  $\text{N}_2\text{O}$  and  $\text{CO}_2$  as a function of the time offset of the injection and illustrate the complex relationship between the injection timing and the resulting emissions. The variation range is limited on both sides by misfiring. The reason for this is that if diesel injection is too far upstream, diesel combustion starts too early and therefore ammonia combustion cannot be started. If the ammonia injection is also moved too far forward at the other limit of the variation range, this results in increased ammonia emissions due to wall deposits and misfiring due to a lack of jet interaction.

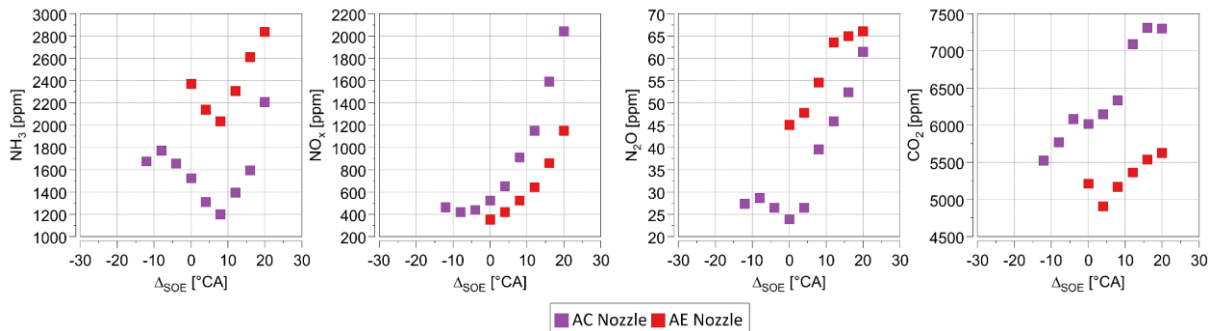


Figure 8: Reasonable emissions for the variation of the injection difference at IMEP = 17,2 bar

The  $\text{NH}_3$  emissions reach their minimum at a  $\Delta_{\text{SOE}}$  of  $8^\circ \text{CA}$ . This indicates that this injection point is particularly favorable for the reduction of  $\text{NH}_3$  emissions. Considering the hydraulic delay of the separate fuel paths, it can be determined that according to Figure 4, a difference of the start of energization of  $\Delta_{\text{SOE}} = 7.2^\circ \text{CA}$  corresponds to simultaneous injection. Looking at a  $\Delta_{\text{SOE}} = 8^\circ \text{CA}$  the resulting ammonia emissions are lowest at this flow difference, regardless of the nozzle geometry.

In contrast, the emissions of  $\text{NO}_x$  and  $\text{N}_2\text{O}$  increase continuously with increasing  $\Delta_{\text{SOE}}$  and reach their highest values at around  $20^\circ \text{CA}$ . The AE-Nozzle tends to have higher  $\text{NH}_3$  emissions compared to the AC-Nozzle.

If ammonia injection is shifted increasingly earlier, the proportion of premixed ammonia increases and leads to an increase in Fuel-NO emissions due to higher cylinder pressure. It should also be noted that due to the increasing premixed combustion, the low flame speed of the ammonia leads to increased  $\text{NH}_3$  emissions instead of combusting diffusive.

$\text{N}_2\text{O}$  emissions follow a similar trend, with the AC nozzle reducing emissions by almost 50%, especially with upstream diesel injection. At negative  $\Delta_{\text{SOE}}$  values,  $\text{N}_2\text{O}$  emissions are low, while at positive values they increase continuously and peak at around  $20^\circ \text{CA}$ . As already mentioned in Chapter 2.1, it arises as a product of incomplete combustion in locations with low temperature and is thus reduced as soon as combustion becomes hotter. If the AE nozzle has no diesel holes, ammonia can reach lean edge areas before it is ignited by neighbouring diesel jets, leading to increased  $\text{N}_2\text{O}$  emissions. A similar trend of increasing nitrous oxide emissions can also be observed with upstream ammonia injection.

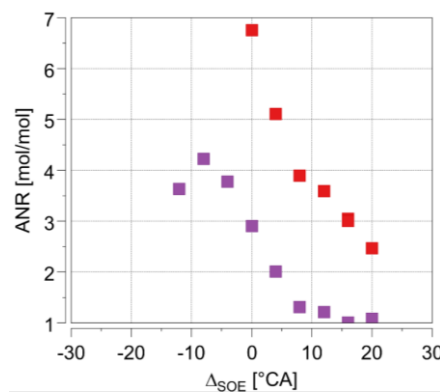


Figure 9: Ratio between ammonia and nitrous oxide emissions (ANR) at IMEP = 17.2 bar for various injection differences between both fuel paths

The ratio of  $\text{NO}_x$  to  $\text{NH}_3$ , shown in Figure 9, which provides a measure of the applicability of an SCR catalytic converter, shows that a ratio of one can already be achieved with an  $8^\circ \text{CA}$  upstream flow of the ammonia path from the AC nozzle. However, it must be considered that particularly high nitrous oxide emissions occur at precisely these operating points where the  $\text{N}_2\text{O}$  emissions are at the highest

point. As a result, a trade-off between the  $\text{NH}_3\text{-NO}_x$  ratio and laughing gas emissions must be found in the future.

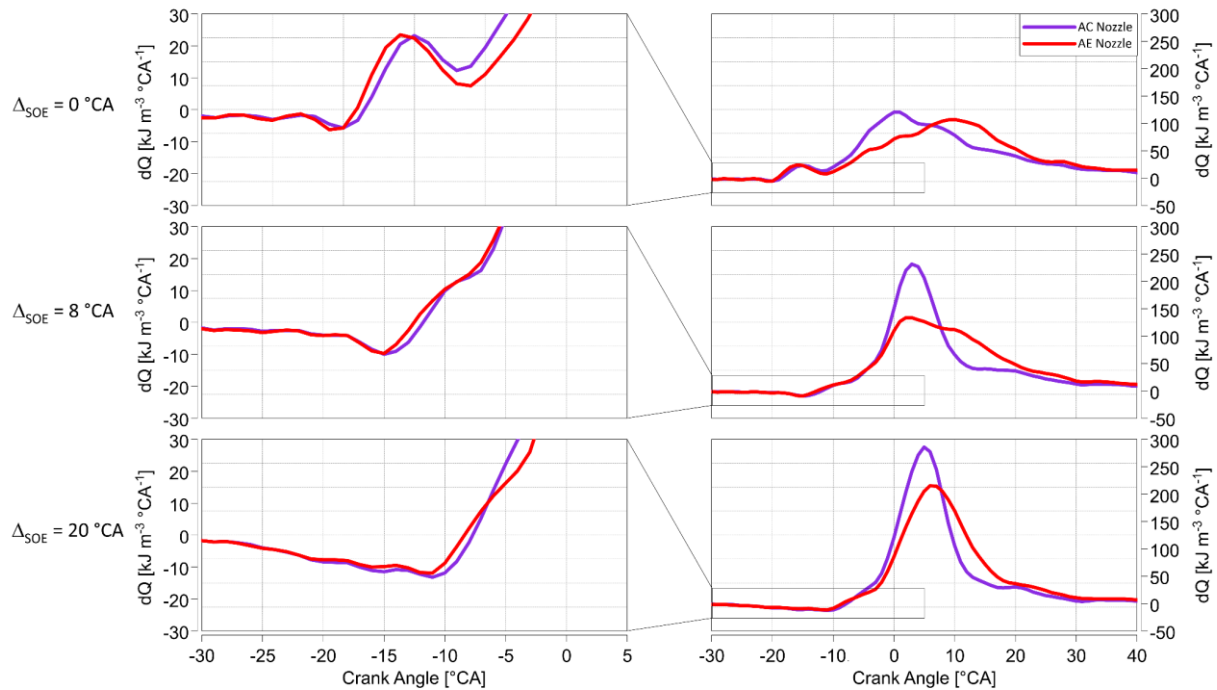


Figure 10: Heat release rates of different injection timings at IMEP=17.2 bar

The diagrams above show the heat release rate as a function of the crank angle. Each row contains diagrams for different current differences of  $0^\circ$  CA,  $8^\circ$  CA and  $20^\circ$  CA. The red line represents the heat release with the AE nozzle and the purple line the AC nozzle. Basically, it can be stated that the heat release of the diesel injection is almost identical under all the injection differences investigated and may be superimposed by the heat release of the ammonia.

When looking at the simultaneous flow, it can be seen in the left-hand column for  $\Delta_{\text{SOE}} = 0^\circ$  CA that the heat release rate for the AC nozzle shows an increase shortly before top dead center, followed by a peak shortly after TDC. The AE nozzle shows a similar curve, but with a slightly later heat release rate shortly after TDC. Simultaneous energizing shows that diesel (hydraulic delay + ignition delay) has a predominantly premixed combustion, followed by ammonia, which enters the combustion chamber about  $9^\circ$  CA after energization. It can also be assumed that the AC nozzle enables a more homogeneous mixture and temperature distribution in the combustion chamber, presumably due to the better distribution of the ammonia jets. This leads to a shorter ignition delay for ammonia, which is why the heat release with the AC nozzle always remains positive

At  $\Delta_{\text{SOE}} = 8^\circ$  CA, in the middle row of the graphs, the AC nozzle again shows an increase in heat release rate just before TDC, followed by a higher and shorter peak after TDC compared to  $0^\circ$  CA. The AE nozzle also shows an increase compared to simultaneous start of current, but with a higher peak and a slightly different shape. In the right column with the expanded scale, the differences between the two nozzles can be seen more clearly, with the AC nozzle achieving a higher and narrower peak than the AE nozzle.

At a flow rate difference  $\Delta_{SOE} = 20^\circ \text{ CA}$ , the AE nozzle shows an even more pronounced increase in the heat release rate before TDC, followed by a very high peak after TDC. The AC nozzle also shows a very high peak in this case, but it is slightly before the peak of the AE nozzle and has a slightly different shape. The AC nozzle reaches a higher peak than the AE nozzle, but with a narrower curve. If the ammonia injection is brought earlier into the combustion, the high enthalpy of vaporization of the ammonia leads to a delay in the diesel combustion. The AC nozzle enables better mixing, which means that the premixed phase of combustion begins immediately after the evaporation, while the AE nozzle leads to a longer ammonia ignition delay due to poorer mixture preparation.

## 4. Conclusion

The investigation into the combustion process involving high pressure dual-fuel injection of ammonia and diesel reveals significant insights into the interaction between these two fuels and the impact of injection timing on combustion efficiency and emissions. The study highlights the critical role of the time offset between the ammonia and diesel injections, demonstrating that even small differences in timing can lead to notable changes in the combustion characteristics.

Key findings include the observation that the AC nozzle, with its better mixture preparation and shorter ignition delay for ammonia, consistently produced a more efficient combustion process compared to the AE nozzle. This is evident in the earlier heat release, higher peak pressures, and a more favorable center of combustion with the AC nozzle, leading to lower energy consumption and higher efficiency at the same indicated power output.

The emission analysis further underscores the complexity of optimizing the dual-fuel combustion process. While a timing offset of around  $8^\circ \text{ CA}$  was found to minimize ammonia emissions and a ratio of  $\text{NH}_3$  and  $\text{NO}_x$  (ANR), it simultaneously led to increased  $\text{N}_2\text{O}$  emissions, highlighting the trade-offs inherent in tuning the injection timing. The AC nozzle demonstrated better overall performance, particularly in reducing  $\text{N}_2\text{O}$  emissions, but the study suggests that further optimization is needed to balance emissions of  $\text{NH}_3$ ,  $\text{NO}_x$ , and  $\text{N}_2\text{O}$  while maintaining efficient combustion.

In summary, the study provides a detailed understanding of how injection timing and nozzle configuration affect the combustion process and emissions in dual-fuel systems. These insights are crucial for developing more efficient and cleaner combustion strategies, particularly in applications where ammonia is used as a renewable fuel. Future research should focus on refining these findings to optimize the balance between combustion efficiency and emission control.

## Abbreviations

- SOC – start of current
- TOC – time of current
- $dp/dt_{\text{Max}}$  – maximum gradient of cylinder pressure
- $p_{\text{CYL}_{\text{Max}}}$  – maximum cylinder pressure
- $\eta_i$  – indicated efficiency
- $\alpha_{10-90}$  – burn duration between the 10% and 90% cumulated heat release point

ANR – ratio between unburned ammonia and nitrogen oxides

$\Delta_{SOE}$  – difference between both start of currents of both fuel paths

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