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2023 | 667

Decarbonization of high-power systems: ammonia-hydrogen and ammonia-diesel combustion in HS engines

New Engine Developments - Alternative Fuels & Other New Engine Concepts

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ABSTRACT

To achieve the internationally agreed climate targets, the energy and transport sectors must be converted to renewable energy sources. Solar and wind energy, however, are subject to fluctuations and are not available at all times. While hydrogen is well suited for short-term energy storage, liquid synthetic fuels with high energy density are needed for seasonal storage and for energy-intensive, mobile applications. Carbon-based fuels require additional carbon capture technologies, which lowers energy efficiency and increases system complexity. Ammonia is a carbon-free alternative, can be produced from renewable power and stored in liquid form at moderate pressure and temperature conditions and thus is a promising candidate for high-power systems. The physical and chemical properties of ammonia differ significantly from the fossil fuels typically used in large-bore engines and make it necessary to develop new combustion systems for already existing and new-built engines.

The Large Engines Competence Center (LEC GmbH) is developing combustion concepts for renewable fuels in high-power systems and recently commissioned the ammonia supply and test infrastructure for medium-speed and high-speed engines. A temperature controlled catalytic exhaust gas aftertreatment system ensures that no increased pollutant concentrations are emitted. Advanced sensorics for ammonia and nitrogen oxides are installed for pre- and post-catalyst monitoring and detailed exhaust gas specification is performed via FTIR measurements.

This paper presents results from an ammonia-diesel dual fuel investigation and an ammonia-hydrogen investigation using spark ignition on a high-speed single cylinder research engine as part of the COMET Center LEC EvoLET conducted by LEC and company and university partners. The focus of the investigation for the diesel-ammonia combustion concept was the assessment of feasible ammonia substitution rates, operating and performance parameters as well as engine-out emissions in dual-fuel operation. An additional focus of the spark ignition concept was the required hydrogen addition and its impact on pollutant formation. An assessment of the constraints and limitations for both combustion concepts will conclude the paper.

1 INTRODUCTION

With the growing interest in carbon-free power generation and propulsion, ammonia combustion is quickly becoming one of the most sought-after research topics for internal combustion engines. To this day no ammonia-fueled large-bore engines are commercially available. Ignition and combustion properties of ammonia are not beneficial compared to state-of-the-art fuels which is the reason why mixing of a more reactive fuel is useful [1]. Especially for marine applications where redundancy requirements are usually adhered to by providing diesel engine operation capability, diesel fuel is used in ongoing research as the reactive fuel component. Different fuel admission concepts are being investigated. Wärtsilä [2] investigated a single-injector concept with premixed fuels and has conducted successful laboratory tests on an engine with a 70 percent ammonia blend, but operation with 100 percent ammonia has not been achieved yet. Another single injector concept with separate nozzles for diesel and ammonia is currently under investigation in the AmmoniaMot project [3]. This concept with high-pressure ammonia direct injection was considered best suited to achieve low ammonia (NH_3) emissions. The spray layout of the injector was optimized based on experiments on a rapid compression machine. In the first experiments with this nozzle layout on the single cylinder research engine up to 90 % of the fuel energy was provided by ammonia. The concentration of NH_3 in the exhaust gas was nearly 10.000 ppm while the nitrogen oxide (NO_X) emission could be reduced compared to the diesel operating condition. In [4] the ammonia fraction was increased up to 84 % but already NH_3 emissions of 15.000 ppm were measured for this condition.

In [5] direct injection and combustion of ammonia in a small spark-ignition high-speed engine was investigated in a load range up to 12 bar mean effective pressure. Stable operating conditions could be achieved but the combustion efficiency with pure ammonia fueling was less than 96 % which was also reflected in the NH_3 concentrations in the exhaust gas of 7000 – 9000 ppm. The NO_X concentration in the exhaust gas was strongly influenced by the excess air ratio and varied from 1200 – 4000 ppm. In a different study [6] combustion performance and emissions were investigated for a small spark-ignition engine with homogenous ammonia-air mixtures. It could be shown that an increase of the compression ratio from 16:1 to 18:1 or 20:1 reduces the ignition delay time significantly and results in lower cyclic variability. At the same time the fraction of unburned fuel in the exhaust gas increased from approximately 1.5 % to 2.5 %. One hypothesis for the increased NH_3 emission was the higher fuel fraction in crevice volumes in the combustion chamber. There is some experience with exhaust gas aftertreatment of NH_3 in engine applications with conventional fuels where NH_3 is present in the exhaust gas as an unreacted reducing agent downstream of the SCR process. Basic catalyst concepts for unburned fuel in ammonia fueled engines are therefore available but need further refinement due to the higher concentrations of NH_3 emitted by the engine. There are, however, no exhaust gas aftertreatment catalyst available for the nitrous oxide (N_2O) emissions from ammonia fueled engines [7]. The N_2O catalyst that are used for other applications are not suitable for engine applications due to the differences in exhaust gas compositions and temperatures. In [8] the decomposition of N_2O over different Fe-exchange zeolite catalysts for various exhaust gas compositions was experimentally evaluated. The authors concluded that the decomposition of N_2O in a gas stream can be achieved via catalysis but that competing chemical reactions, especially in the presence of surplus oxygen, can dominate at the expense of N_2O reduction. For the development of future exhaust gas aftertreatment systems it will be crucial to have detailed knowledge of the exhaust gas compositions and temperatures for the engine over the whole operating range.

The LEC is currently investigating various fuel admission and ignition concepts for ammonia combustion on four-stroke high-speed single cylinder research engines (Figure 1). The two concepts in this study use external mixture formation of ammonia and air. The compression ignition concept uses diesel as the reactive component. The spark ignition concept employs hydrogen as an ignition promoter that is mixed with the ammonia and the charge air and is also supplied to the precombustion chamber to enhance the ignition conditions at the spark plug location.

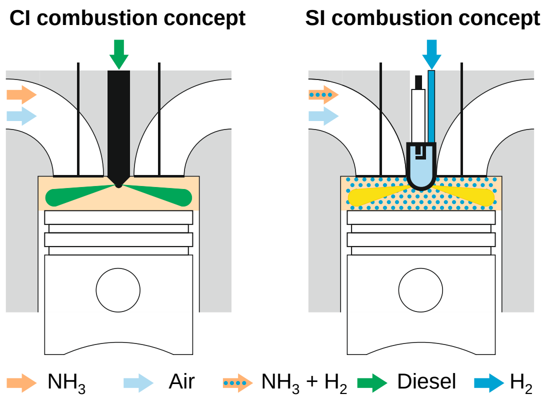

Figure 1: Investigated ammonia combustion concepts

The objective of this study is the identification of operational measures to reduce engine-out exhaust gas emissions and to demonstrate low and high load operation up to 25 bar brake mean effective pressure.

2 EXPERIMENTAL INVESTIGATION

2.1 NH_3 testing infrastructure

The test bed infrastructure at the LEC GmbH was expanded in order to provide the flexibility to investigate different ammonia combustion concepts and to fulfill all safety requirements. The ammonia supply for the engine test cells is provided by a mobile container in which up to 2000 kg of ammonia can be stored in liquid form. A temperature-controlled vaporizer unit provides a constant supply of gaseous ammonia to the engine test cell. A temperature-controlled catalytic exhaust gas aftertreatment system ensures that no increased pollutant concentrations are emitted. Advanced sensorics for ammonia and nitrogen oxides are installed for pre- and post-catalyst monitoring and detailed exhaust gas specification is performed via FTIR measurements. The fuel supply infrastructure provides the flexibility to use various fuels and fuel mixtures and enables the use of scavenged prechamber concepts as well as open chamber concepts for spark ignition operation and diesel pilot ignited operation. Hydrogen in adjustable quantities can be added to the ammonia upstream of the fuel-air mixing unit.

2.2 Experimental test set-up

The experimental investigations were carried out on a high-speed 4-stroke single cylinder research engine (SCE).

Table 1: SCE technical data for spark ignition and diesel pilot combustion concepts

General information	
Rated speed	1800 min^{-1}
Displacement	≈ 5.2 dm^3
Valve timing	Miller valve timing
Number of intake and exhaust valves	2/2
Charge air	Provided by external compressors with up to 10 bar boost pressure
Diesel pilot combustion concept	
Diesel supply	Bosch fuel injector, max. PFINJ 2200 bar
Ammonia supply	Central mixture formation
Engine speed	1350 min^{-1}
Spark ignition combustion concept	
Hydrogen supply	Pre-mixed with NH3 mass flow
Ammonia supply	Central mixture formation
Engine speed	1500 min^{-1}

For the spark ignition combustion concept, the engine was configured with a scavenged precombustion chamber and a camshaft with early intake valve closing (IVC) before bottom dead center. The compression ratio (CR) was chosen in the range of typical gas engine applications with low flashpoint fuels. For the diesel-ammonia dual fuel combustion concept, the engine was configured with a centrally mounted wide-range diesel injector in an open combustion chamber and a camshaft with early intake valve closing (IVC) before bottom dead center. The compression ratio (CR) was chosen in the range of typical diesel engine applications. Table 1 shows further information about the engine.

2.3 Experimental results

The investigation of the diesel-ammonia dual fuel combustion concept consisted of two test sequences. The first part of the investigation was focused on the impact of the operating parameters on the engine performance and the exhaust gas emission at a brake mean effective pressure (BMEP) of 25 bar at a fixed engine speed of 1350 min^{-1}. Furthermore, a combustion phasing variation was carried out at 13 bar BMEP. The second part of the experimental investigation focused on engine load variations using operating conditions that were found to be beneficial in the first part of the measurement campaign. This investigation was performed for diesel-ammonia dual fuel operation and for ammonia-hydrogen spark-ignition operation.

2.3.1 Investigation of operating parameters for diesel-ammonia dual fuel operation

The variation of the diesel energetic fraction and the global excess air ratio (EAR) allowed the exploration of a wide operating window at a brake mean effective pressure of 25 bar and an engine speed of 1350 min^{-1}. Starting from a typical diesel operating condition with an EAR of 2.2, ammonia was added to the intake charge air by means of central mixture formation via a venturi mixer. For the present study, a distinction is made between two different EARs. The global excess air ratio is taking the mass of NH_3 and the mass of diesel (Equation 1) or the mass of H_2 (Equation 2) into account, depending on the investigated combustion concept. The EAR_{NH_3} uses only the NH_3 fuel mass and therefore describes the background mixture in the combustion chamber.

$$EAR = \frac{m_{Air}}{m_{NH_3} * AFR_{NH_3} + m_{Diesel} * AFR_{Diesel}} \qquad (1)$$

$$EAR = \frac{m_{Air}}{m_{NH_3} * AFR_{NH_3} + m_{H_2} * AFR_{H_2}} \qquad (2)$$

$$EAR_{NH_3} = \frac{m_{Air}}{m_{NH_3} * AFR_{NH_3}} \quad (3)$$

The intake mixture temperature was maintained at 50 °C and the total fuel mass was adjusted to maintain the target BMEP. The investigations were performed with five distinct fuel mixture compositions with diesel energetic fractions of 80 %, 60 %, 40 %, 20 %, and 14 %. The rail pressure for the diesel operation was set to 2200 bar. For the investigation of diesel energetic fractions of 80 % and 60 % the rail pressure was maintained at 2200 bar and the injection duration was reduced to achieve the target load. For 60 % diesel energetic fraction the energizing duration of the injector was already below 700 µs. In order to avoid increasing shot-to-shot variations with even lower diesel fractions the injection pressure was reduced such that the energizing duration of the diesel injector was maintained in a range of 600 to 700 µs. For this the rail pressure was first reduced to approximately 1700 bar for an energetic diesel fraction of 40 % and finally to approximately 1200 bar for the lowest two diesel fractions. For each of the five fuel mixture compositions the start of the injector current (SOC) was maintained at a fixed value. For the diesel energetic fractions of 80 % and 60 % the SOC was chosen such that the combustion phasing – the crank angle where 50% of the fuel energy was released (CA50) - of the pure diesel operation at 15 deg CA after top dead center (aTDC) was achieved with an EAR of 2.2. For other EAR the combustion phasing was allowed to deviate. For the lower diesel energetic fractions, the SOC was adjusted such that a combustion phasing of approximately 13 deg CA aTDC was achieved. The advancement of SOC that was required was the result of two effects. On one hand the ignition delay time and the combustion duration with higher ammonia content in the fuel is increasing. On the other hand, the lower diesel rail pressure that was used for the lower diesel fractions has an impact on the hydraulic delay of the injector and thus on the start of the injection. The boost pressure was adjusted to achieve the target EAR at each operating condition. For the higher diesel energetic fractions of 80 % and 60 % the EAR variation started at the diesel-typical EAR of 2.2 and was reduced in increments of 0.2. For lower diesel energetic fraction, the investigation was focused on lower EAR in the range of 1.4 to 1.7. The exhaust gas pressure was adjusted individually for each operating condition to achieve a fixed ratio of boost pressure to exhaust pressure of 1.6. The operating map depicted in Figure 2 shows that the feasible EAR range shifted with the diesel energetic fraction (φ_{Diesel}). In general the operating range was limited by excessive NH_3 emissions for high EAR and by exhaust gas temperatures exceeding 650 °C for low EAR. For high diesel energetic fractions, the high EAR of pure diesel operation is achievable but the operation with low EAR was limited to 1.8 and 1.6 for 80 % and 60 %, respectively. The opposite trend was observed for low diesel energetic fractions where the lowest EAR of 1.4 was achievable but high EAR operation was limited. The limitations of the operating window are explained in more detail in the following sections.

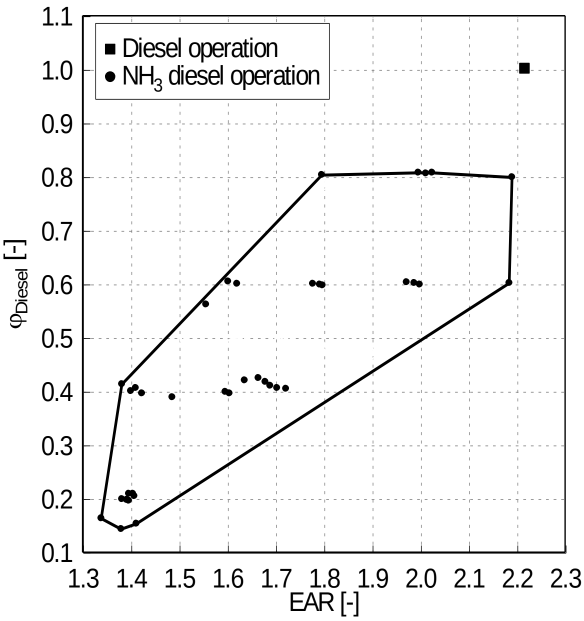

Figure 2: Operating window of the diesel-ammonia dual fuel combustion concept at 25 bar BMEP

The required boost pressures throughout the operating window are depicted in Figure 3.

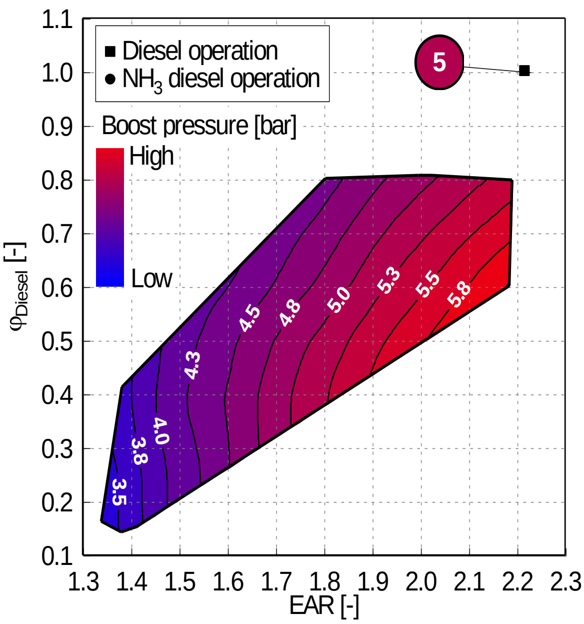

Figure 3: Boost pressure of the diesel-ammonia dual fuel combustion concept at 25 bar BMEP

Naturally the boost pressure decreases with reduced EAR. The impact of the ammonia fraction on the boost pressure is more interesting. There are several factors influencing the boost pressure demand. On the one hand the lower heating value of ammonia compared to diesel requires a higher fuel mass. On the other hand, the stoichiometric air-to-fuel ratio of ammonia (~ 6.05) is significantly lower than that of diesel (~ 14.3). Thus, the energy content of a stoichiometric ammonia-air mixture is approximately 5 % lower than a stoichiometric diesel-air mixture. An additional boost pressure difference between diesel and diesel-ammonia operation results from the location of fuel admission. While the diesel is injected directly into the cylinder after the intake valves have been closed, the ammonia is added to the charge air in the intake manifold and reduces the volumetric efficiency, thus making it necessary to increase the boost pressure. Furthermore, the boost pressure is impacted by the conversion efficiency of the fuel in the combustion chamber. Since the unburned fuel components with diesel-ammonia operation are higher than for the diesel operation (detailed further below) an additional boost pressure increase is required. The combination of these effects can be seen in Figure 3 where it is apparent that with increasing ammonia fractions in the fuel mixture the boost pressure is increasing for the same EAR.

The measured exhaust gas temperature approximately 40 cm downstream of the cylinder head is depicted in Figure 4 for the whole operating window.

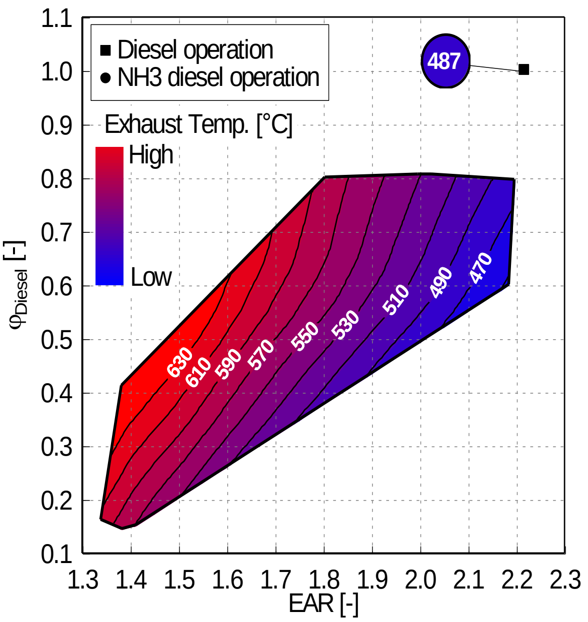

Figure 4: Exhaust gas temperature of the diesel-ammonia dual fuel combustion concept at 25 bar BMEP

Similar to the boost pressure the impact of the EAR on the exhaust gas temperature shows the same behavior that is to be expected for diesel operation as well. Again, the trend with increasing ammonia fractions is more complex. The physical and chemical fuel properties as well as the timing of the heat release in the cylinder play a significant role for the in-cylinder temperature and therefore for the exhaust gas temperature too. Reiter and Kong [9] performed thermodynamics calculations for the adiabatic flame temperature as a function of the fuel share between diesel and ammonia and the excess air ratio. They found that the adiabatic flame temperature for stoichiometric conditions was reduced from 2320 K for diesel to 2100 K for ammonia and indicated the impact on the overall in-cylinder temperature level when ammonia is used as a fuel. The effect described in [9] is superimposed by the effect of the combustion phasing on the exhaust gas temperature that was allowed to vary in this experiment and furthermore the impact of late in-cylinder combustion that is associated with long burn durations. The combined impact of these effects can be seen in the vertical development of the exhaust gas temperatures in Figure 4. For the same EAR lower diesel energetic fractions resulted in lower exhaust gas temperatures. This temperature difference also explains the different EAR range that was covered for high and low diesel energetic fractions. One of the limits that was imposed for the operating range, was an exhaust gas temperature limit of approximately 650 °C. On the single cylinder research engine this limit was set to protect cylinder head and exhaust gas system components. On a multicylinder engine the maximum acceptable exhaust gas temperature is typically determined by the inlet temperature for the turbine of the turbocharger. The lower temperature level with increased ammonia content in the fuel mixture allowed EAR reductions far beyond of what was feasible with diesel or low ammonia fraction operation.

The observed trends for the boost pressure and the exhaust gas temperature indicate that for the optimum operation of a diesel-ammonia dual fuel engine the turbocharging system should be optimized together with the combustion system. Without any changes to an existing turbocharger configuration the lower exhaust gas temperature (and potentially lower exhaust gas enthalpy) in combination with the higher boost pressure demand for a given EAR would likely result in an EAR reduction. For low target EAR for diesel-dual fuel combustion this might not pose a challenge for the turbocharging system.

The impact of a variation of the diesel energetic fraction and the EAR on cyclic variability is shown in Figure 5. Even small fractions of ammonia in the fuel mixture already increase the coefficient of variation of the indicated mean effective pressure

(COV_IMEP) that is used as a metric to assess combustion stability. But even with high fractions of ammonia the COV_IMEP was not exceeding 2 %. The EAR was found to have only a small impact on the cyclic variability for high diesel energetic fractions in this experiment.

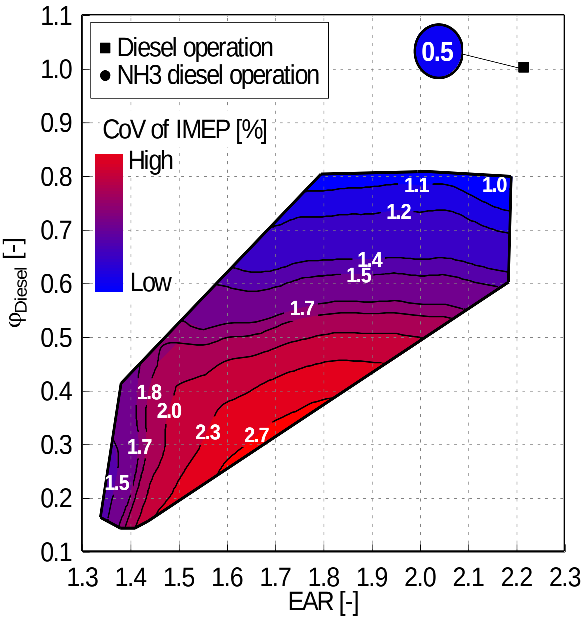

Figure 5: COV of IMEP of the diesel-ammonia dual fuel combustion concept at 25 bar BMEP

The impact of the diesel energetic fraction and the excess air ratio on the combustion process is illustrated in Figure *6* and Figure *8*. Figure *6* shows a comparison of the heat release rate, the cumulative heat release and the injector current signal for a 100 % diesel operation and a diesel fraction of 60 % for EAR of 1.6. In the lower part of the figure the injector current signals for both cases are depicted. The start of injector current was maintained at a fixed value while the duration of the energizing signal varies due to the different diesel fuel masses that are injected. The rail pressure was maintained at a fixed value for this comparison and thus the injector dynamics is expected to be the same as well. The heat release rate for the diesel operation shows the typical shape with a premixed peak at the beginning followed by the mixing-controlled combustion in the main part of the energy release. While the general shape of the heat release for the diesel-ammonia dual fuel operation looks similar to the diesel case, there are also some differences. Most obviously the premixed peak for the diesel-ammonia operation is higher than the one for the pure diesel operation. One hypothesis for the larger premixed peak for the diesel-ammonia dual fuel combustion is that the diesel spray entrained sufficient ammonia-air mixture that at the end of the ignition delay time more fuel energy is contained in the well mixed zone that releases its energy nearly instantaneously once the combustion starts. This hypothesis is supported by Yousefi et al. [10] who performed 3D CFD simulations for diesel and diesel-ammonia operation and found that at the time the combustion started the local EAR inside the ignition kernels was lower for the diesel-ammonia combustion mode than for the diesel mode. They also observed that the second peak in the heat release rate that is associated with the mixing-controlled combustion of the diesel spray and the premixed combustion of the ammonia-air mixture further away from the diesel spray is lower for the diesel-ammonia dual fuel combustion. Their simulation showed that the flame propagation towards the center of the combustion chamber was slower for the diesel-ammonia combustion and attributed this to the lower diesel fuel mass in that region and the low flame speed of ammonia.

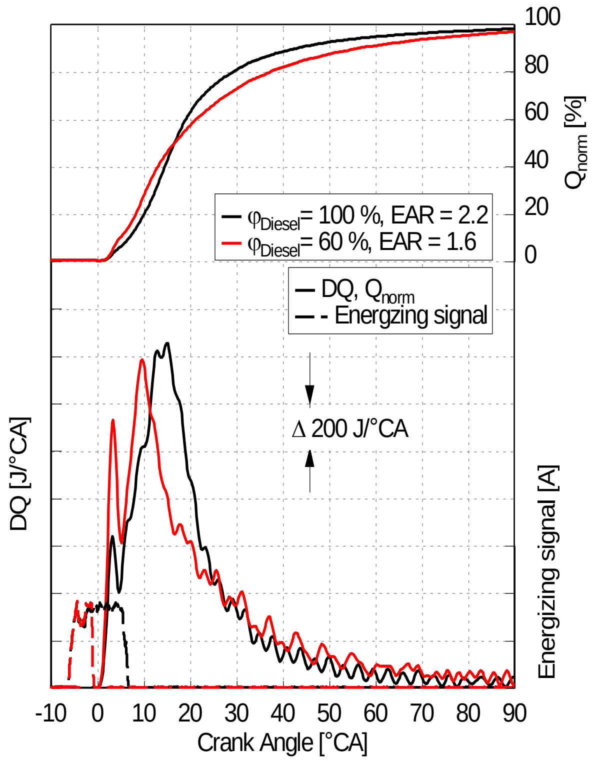

Figure 6: Comparison of diesel and diesel-ammonia dual fuel combustion at 25 bar BMEP

The second peak for the diesel-ammonia dual fuel operation is only slightly lower in Figure *6* but it occurs earlier in the expansion stroke, i.e., closer to TDC. This is likely caused by the fact that for diesel operation the injection is still taking place while the combustion is already in progress and the peak heat release is reached roughly at the end of the injection. For the diesel-ammonia dual fuel operation the injection duration is shorter and takes place mostly before the combustion starts. This effect was not observed in [10] which might be explained by the low engine speed of 910 min^{-1} and the low load operation with 8 bar BMEP where the diesel injection was finished before TDC – even for pure diesel operation. In the cumulated heat release in Figure *6* it becomes apparent that the diesel-ammonia dual fuel operation lags the diesel combustion in the second halve of the combustion process. With a further decrease of the diesel energetic fraction the proportions of premixed combustion on the one hand and mixing-controlled or flame propagation combustion on the other hand start to shift. To understand the observed behavior the EAR_{NH_3} in the ammonia-air mixture is shown in Figure 7. For diesel energetic fractions of 80 % the EAR in the ammonia-air mixture is approximately 10.0. No matter if the global EAR is 2.2 or 1.8 the ammonia-air mixture is too lean to sustain a flame. For these operating conditions the ammonia has to be consumed with the diesel combustion. For lower diesel energetic fractions of 60 % the diesel spray might not penetrate the whole combustion chamber anymore while the EAR in the ammonia-air mixture is still very high with approximately 5.0, making it more difficult to achieve full energetic conversion. With the lowest diesel energetic fractions EAR lower than 2.0 are finally achieved, allowing for a more rapid flame propagation in the mixture not penetrated by the diesel spray.

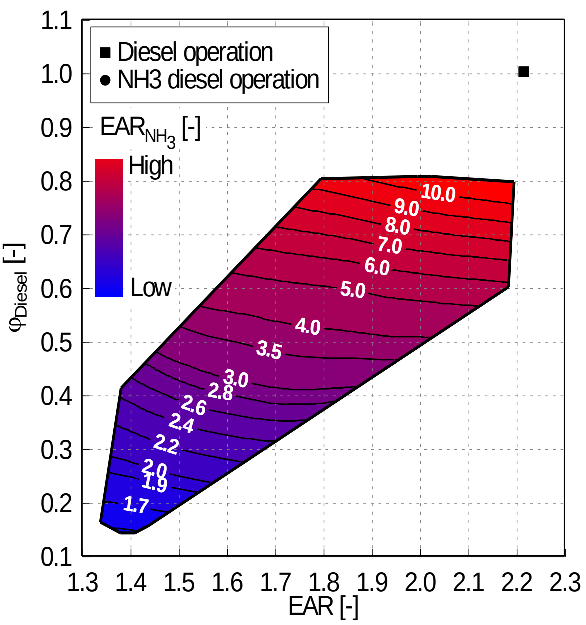

Figure 7: EAR_{NH3} for the diesel-ammonia dual fuel combustion concept at 25 bar BMEP

The impact of the changing ammonia-air mixture strength can be seen in Figure *8* that shows the heat release rates for two diesel-ammonia dual fuel cases with the same global EAR = 1.4 and different diesel energetic fractions of 40 % and 20 %, respectively. For both cases the premixed peak is higher than for the diesel operation or the operation with a high diesel energetic fraction of 80 %. Not only is the premixed peak higher, the fraction of the energy that is released during this premixed combustion is also higher. While with pure diesel operation approximately 5 % of the energy is released in the pre-mixed peak, this portion increases with the low diesel energetic fractions. The case with the lowest diesel fraction of 20 % shows a longer ignition delay than the case with 40 % diesel fraction, which is in alignment with the expectations based on the ignition delay assessment in [11] where the minimum was observed at an EAR of approximately 2.5. The second peak in the heat release rate is higher for the lowest diesel energetic fraction which can be attributed to the lowest EAR in the ammonia-air mixture and the higher flame speed that it supports.

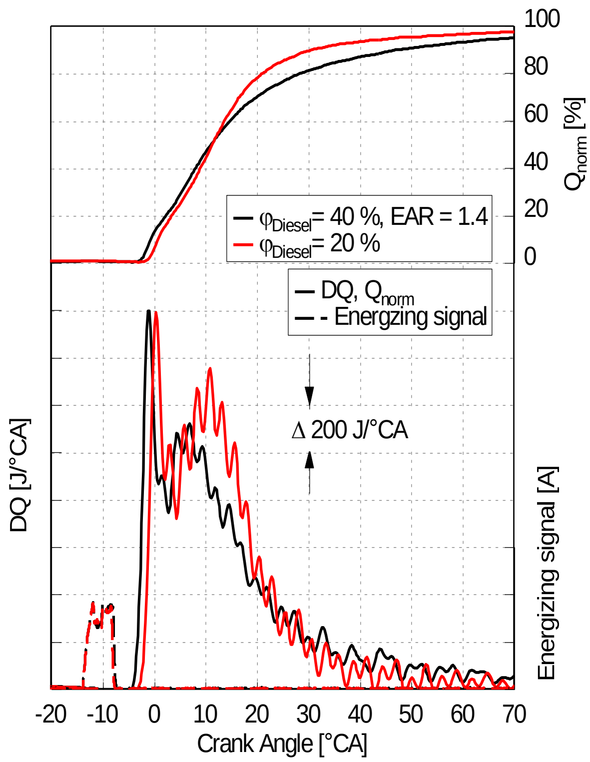

Figure 8: Comparison of diesel-ammonia dual fuel combustion at 40 % and 20 % diesel energetic fraction at 25 bar BMEP

The impact of the ammonia content and the EAR on the emissions of nitric oxide (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O) and unburned ammonia (NH_3) are shown in Figures 9 – 12, respectively. In hydrocarbon-fueled internal combustion engines nitric oxide is formed by oxidation of dissociated atmospheric nitrogen at high temperatures in the presence of oxygen, a process well predicted by the Zeldovich chemical kinetic mechanism [12]. For ammonia combustion the formation of nitric oxide from the oxidation of fuel-bound nitrogen also plays a role. Westley et al. [13] found that this reaction path is even dominant in fuel-lean conditions, leading the NO emissions to peak at EAR = 1.35 in a spark-ignition engine. Yousefi et al. [10] found that NO emissions were reduced for diesel-ammonia dual fuel combustion compared to pure diesel combustion. Their simulation results showed that NO formation from fuel-bound nitrogen takes place when nitrogenous radicals react with an oxygenated species at temperatures above 1400 K. They also found that in the later part of the combustion, in a temperature range of 1100 – 1400 K, NO is consumed by the thermal DeNOx process reported in [14] with NH_3 acting as a thermal DeNOx agent. Apart from these reaction pathways the in-cylinder temperature differences between diesel and diesel-ammonia combustion further influence the NO exhaust gas emissions. In Figure *9* the combined impact of these influencing factors can be seen. The increase of the ammonia share at high EAR leads to a reduction of the NO emissions, presumably due to the reduced in-cylinder temperature. A reduction of the EAR has only a small impact on the NO emissions. The oxygen availability and the temperature trends seem to offset each other. Only at the lowest EAR where the in-cylinder temperature is high and the mixture approaches the conditions for peak NO according to Westley [13] the measured NO emissions rise significantly again.

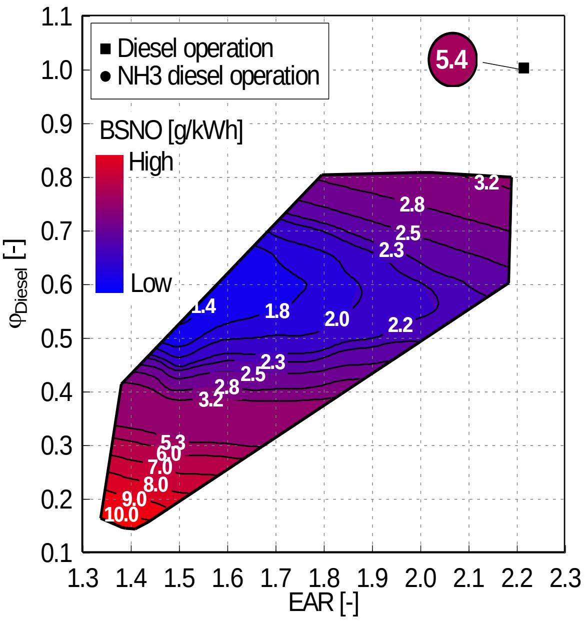

Figure 9: Measured NO emissions for variations of EAR and diesel energetic fraction at 25 bar BMEP

The emissions of NO_2 play a minor role in the diesel-ammonia dual fuel combustion. NO_2 is formed in the flame zone from NO and subsequently converted back to NO in the post-flame reaction [10]. The consumption of NO_2 is stopped when the reaction freezes, for example due to mixing of hot products with cooler gases in the combustion chamber that are present with inhomogeneous mixtures. This might explain the trend observed in Figure *10*, where only the diesel operation and the diesel-ammonia dual fuel operation with a diesel energetic fraction of 80 % show a significant amount of NO_2 in the exhaust gas.

The emission of N_2O which in hydrocarbon-fueled engines usually stems from the exhaust gas after-treatment [15], gets more important in ammonia-fueled engines. Westlye et al. [13] reported that N_2O is formed when NH_3 is in the presence of NO and NO_2 at low temperatures during the expansion and exhaust stroke in a reaction known as selective non-catalytic reduction [16].

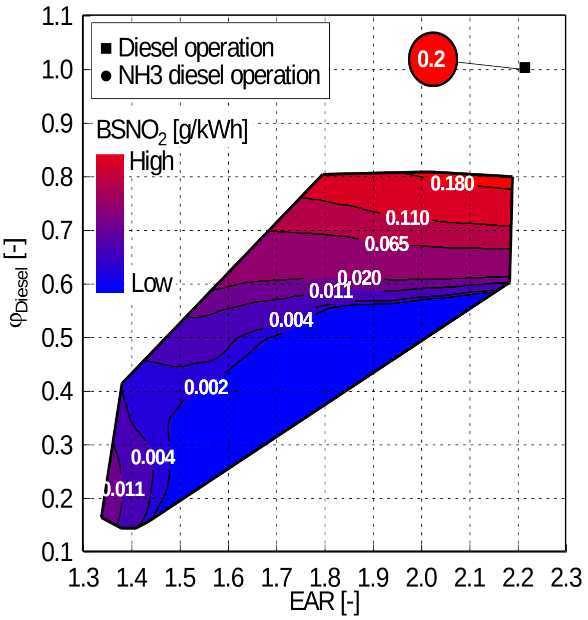

Figure 10: Measured NO_2 emissions for variations of EAR and diesel energetic fraction at 25 bar BMEP

At higher oxygen levels NH_2 radicals are formed by ammonia pyrolysis [13] in the temperature range of 800 to 1200 K and react with NO_2 to form N_2O. Ammonia that is released from crevices during the expansion can thus promote the formation of N_2O. Late combustion phasing that leads to higher exhaust gas temperature is exacerbating this effect. In Figure 11 the dominating influence of the EAR on the N_2O emission can clearly be seen. The lowest N_2O emissions are achieved with EAR=1.4 which was the lowest EAR that was explored in this measurement campaign. The diesel energetic fraction also seems to have an impact at high EAR. Here the N_2O emission is higher for the lower diesel fraction. This might be explained by the higher ammonia-air ratio in the combustion chamber and therefore also in the crevices, thus increasing the amount of NH_3 available for N_2O production in the expansion stroke.

Emission of unburned NH_3 stem from various sources. Apart from incomplete combustion, NH_3 emissions from crevices have to be taken into account. Due to the ammonia admission in the intake manifold also the NH_3 emission from scavenging losses during the valve overlap need to be considered. Experimentally these different sources cannot be differentiated easily. In Figure *12* two trends can be observed. For a given diesel energetic fraction the NH_3 emissions are drastically reduced with lower EAR. This can be explained by the higher flame speed and therefore the faster flame propagation in the ammonia-air mixture, the increased gas temperature and the lower in-cylinder pressure that reduces the amount of unburned fuel in the crevices at the end of the combustion.

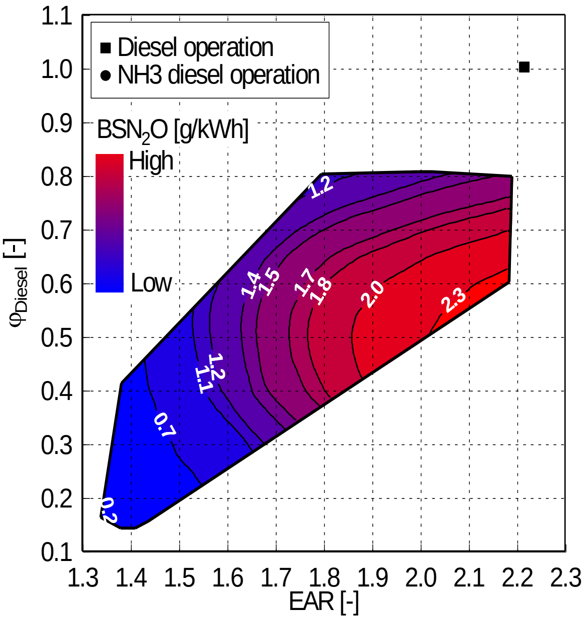

Figure 11: Measured N_2O emissions for variations of EAR and diesel energetic fraction at 25 bar BMEP

The impact of the diesel energetic fraction is most clearly seen at high EAR where the NH_3 emission strongly increase with lower diesel fraction. In this range the EAR in the ammonia-air mixture is very high such that a propagating flame cannot be sustained. With the lower diesel fraction there is more gas in the combustion chamber that is not completely consumed by the diesel jets and also cannot be burned via flame propagation. Additionally, the higher ammonia fraction leads to more ammonia mass in the crevices that might escape combustion. The observed trend for the NH_3 emission also helps to explain the observed trend of the N_2O emissions that are largely produced late in the cycle from unburned NH_3.

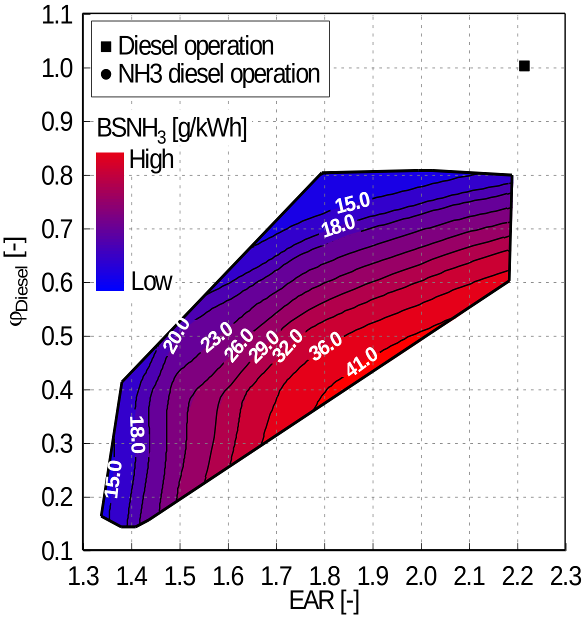

Figure 12: Measured NH_3 emissions for variations of EAR and diesel energetic fraction at 25 bar BMEP

The ratio of the NH_3 and NO_X emissions are depicted in Figure *13*. The favorable range for efficient exhaust gas aftertreatment with selective catalytic reduction is approached at the edges of the explored operating window. Although the ratio of 0.9 – 1.0 that is often targeted in engine applications is not achieved.

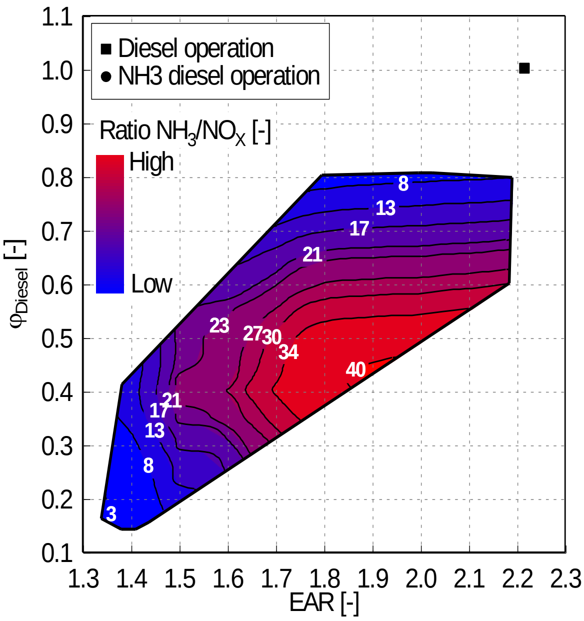

Figure 13: NH_3 to NO_X ratio for variations of EAR and diesel energetic fraction at 25 bar BMEP

In order to assess the global warming potential (GWP) of the exhaust gas components the CO_2

equivalent emissions are calculated based on CO_2 and N_2O emissions according to Equation (3):

$$BSCO_{2\ equivalent} = BSCO_2 + BSN_2O * 300 \qquad (3)$$

The CO_2 equivalent throughout the operating window is shown in Figure *14*. The lowest GWP can be achieved with low diesel energetic fractions and low EAR. At least 50 % NH_3 substitution was required in this investigation to actually achieve a reduction in GWP compared to diesel operation. Therefore, a diesel fraction of 20 % and an EAR of 1.4 was selected for the following load variations.

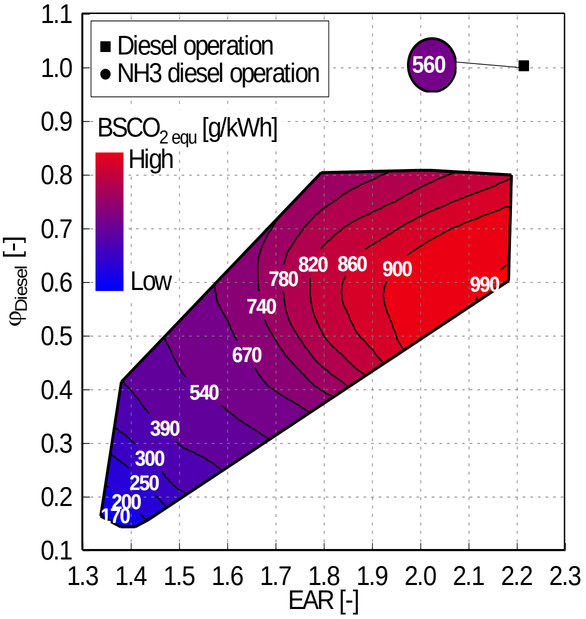

Figure 14: CO_2 equivalent emissions for variations of EAR and diesel energetic fraction at 25 bar BMEP

The heat release rate for the diesel-ammonia dual fuel operation for the selected operating parameters in comparison to a diesel operating point is shown in Figure *15* for 25 bar BMEP. It can be clearly seen that due to the significantly longer ignition delay the start of the diesel injection needs to be advanced for the diesel-ammonia dual fuel operation compared to diesel operation for the same combustion phasing. The cumulated heat release shows that very similar combustion processes and durations can be achieved with this set-up. The impact of the combustion phasing on exhaust gas emissions is shown for one selected operating condition in Figure *16*. A combustion phasing advance of 4 deg CA resulted in a reduction of NH_3 emission of nearly 10 g/kWh and N_2O emissions of approximately 0.2 g/kWh while the NO_X emissions increased by nearly 6 g/kWh.

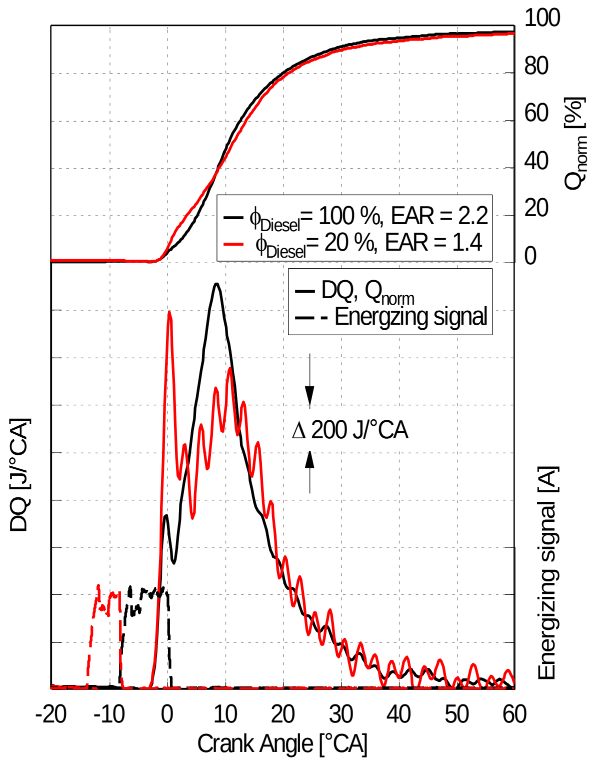

Figure 15: Comparison of diesel and diesel-ammonia dual fuel combustion at 25 bar BMEP

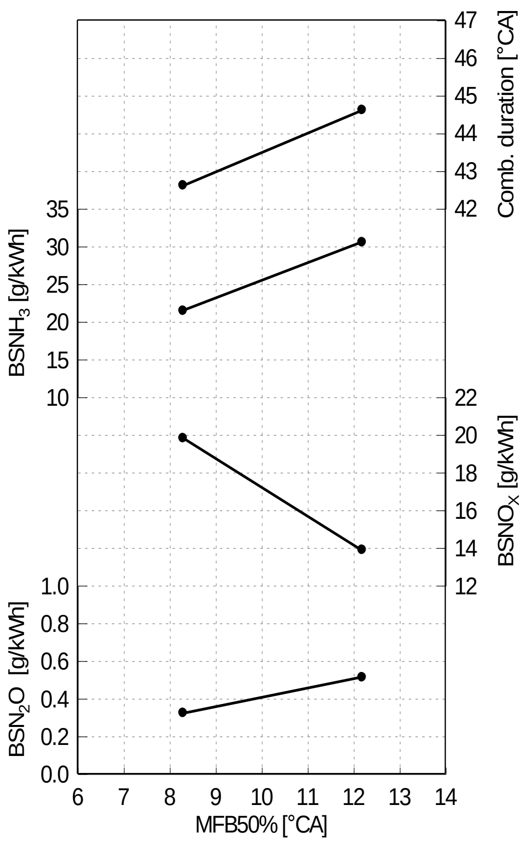

Figure 16: Impact of combustion phasing on exhaust gas emissions for diesel-ammonia dual fuel combustion

2.3.2 Load variations for diesel-ammonia and ammonia-hydrogen operation

The second part of the experimental investigation targeted the exploration of the feasible operating range and the impact of the brake mean effective pressure on key performance parameters and exhaust gas emissions. For the diesel-ammonia dual fuel operation the diesel energetic fraction was maintained at 20 % and the EAR was fixed at 1.4. The diesel rail pressure was not fixed at a given set-point but instead was adjusted to maintain the duration of the injector current at approximately 750 µs. This resulted in a rail pressure of 1200 bar at the high load operation with 25 bar BMEP and a reduction to approximately 700 bar for the lowest load conditions of 4 and 8 bar BMEP, respectively.

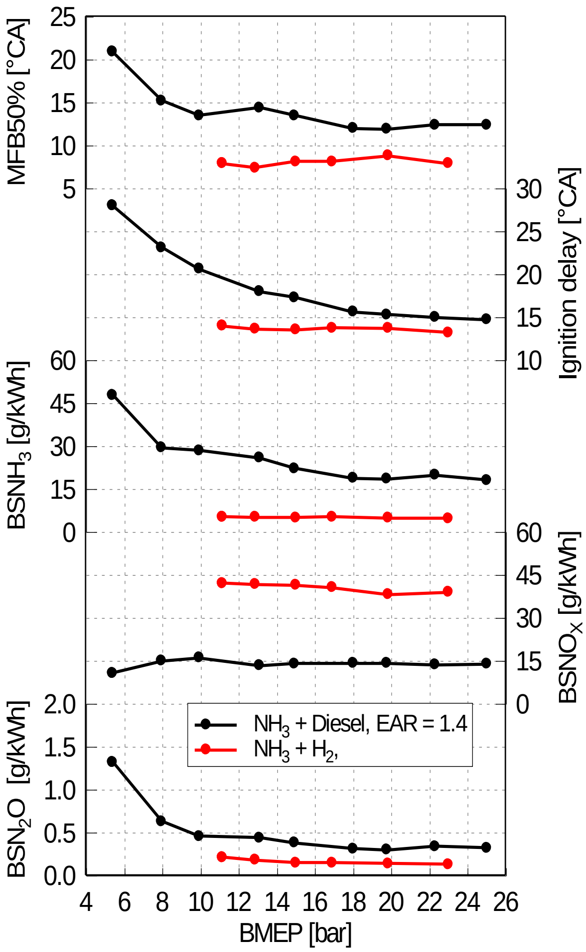

Figure 17: Exhaust gas emissions, combustion phasing and ignition delay for a load variation with diesel-ammonia and ammonia-hydrogen dual fuel operation

The start of injector current was set to achieve a combustion phasing of CA50 = 12 deg CA aTDC for 25 bar BMEP and subsequently maintained during the load variation. This resulted in a phasing retard for the low load operation. For the ammonia-hydrogen operation the EAR was also maintained at 1.4 and the spark timing was set to achieve a combustion phasing of 8 deg aTDC. The hydrogen energetic fraction was maintained at 15 %. Figure *17* depicts the exhaust gas components NO_X, N_2O and NH_3 as well as the combustion phasing and the ignition delay time for the diesel-ammonia and the ammonia-hydrogen operation. A wide load range of 6 bar – 25 bar BMEP was covered with the diesel-ammonia dual fuel variation. Due to the increasing ignition delay time for low load operation the combustion phasing was retarded which also explains the observed increase in the cyclic variability. The NO_X emissions did not change very much with engine load while the NH_3 and the N_2O emissions stayed nearly constant down to approximately 15 bar BMEP and increased with further reduced BMEP. At least the stronger increase in the low load range is likely caused by the retarded combustion phasing as was explained in the previous chapter.

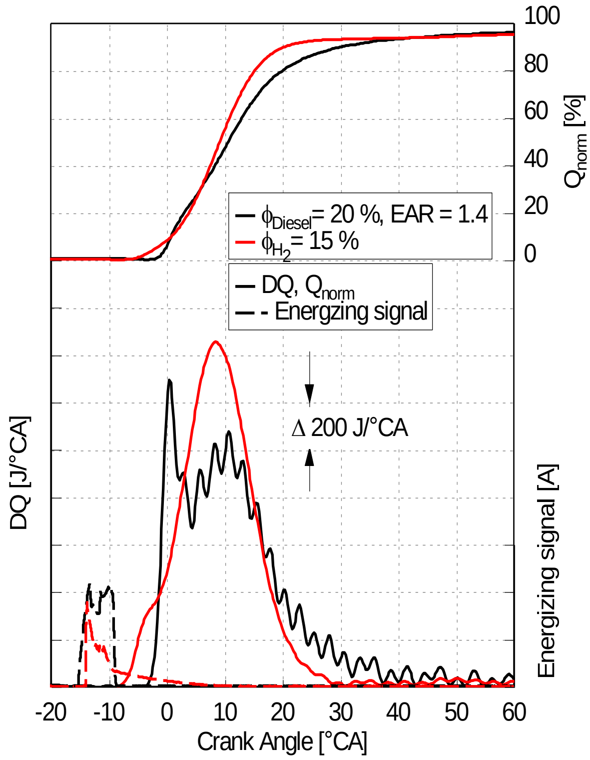

Figure 18 : Comparison of diesel-ammonia and ammonia-hydrogen combustion at 25 bar BMEP

A different picture is presented by the spark-ignition operation. The ignition delay time did not increase with lower load and the combustion phasing was nearly constant, although at an earlier crank angle than for the diesel-ammonia operation which is reflected in the significantly higher NO_X emissions. The N_2O and NH_3 emissions stayed nearly constant over the whole load variation and at a significantly lower level than for the diesel-ammonia operation. This effect is likely caused by three factors. The hydrogen content in the gas mixture is assumed to be homogeneously mixed with the ammonia and promotes faster and more complete combustion of the ammonia whereas the diesel jets might not reach the whole in-cylinder charge.

With lower compression ratio the amount of unburned mixture in the crevice volumes is lower and the higher temperature due to the early combustion also contributes to higher NH_3 consumption. The lower fraction of unburned NH_3 later in the combustion / expansion stroke will in turn prevent large amounts of N_2O to be formed. And here again the earlier combustion phasing and the resulting lower exhaust gas temperature have a mitigating effect on the N_2O formation. A comparison of the heat release rates for the diesel-ammonia and ammonia-hydrogen operation in shown in Figure *18*. The heat release rate for the ammonia-hydrogen operation shows the typical first peak that is caused by the pre-chamber combustion, subsequently a rapid increase and compared to the diesel-ammonia operation a much faster second part of the combustion process.

3 CONCLUSIONS

Ammonia is a promising candidate to replace carbon-based fuels in internal combustion engines, for example in power generation and marine applications, and thus play a vital role in the decarbonization of these sectors. The physical properties of ammonia, especially the low flame speed and the high ignition energy, can pose challenges to achieving robust engine operation and higher performance under all operating condition while the risk of N_2O emission formation also challenges the presumption to reduce the global warming potential of engine exhaust gas emissions. In this study two different combustion concepts were experimentally investigated on a single cylinder research engine with regard to their potential to cover high load as well as low load operation and to identify the key operating parameters that enable low emission operation.

The diesel-ammonia dual fuel combustion concept with central mixture formation of air and ammonia was shown to cover a wide operating range from 4 bar to 25 bar brake mean effective pressure. The study of key operating parameters at high load operation revealed that in order to achieve overall low emission levels but most of all a low global warming potential the engine should be operated with low diesel energetic fractions of 20 % or less and with low EAR of 1.4 or lower. Due to the high GWP of N_2O at least 50 % of diesel had to be replaced by ammonia to achieve a lower CO_2 equivalent emission than pure diesel combustion.

The ammonia-hydrogen operation with 15 % hydrogen energetic fraction was demonstrated over a load range of 11 bar to 23 bar brake mean effective pressure without reaching any operating limits. With this combustion concept lower emission levels of NH_3 and N_2O could be achieved.

In order to further optimize the combustion concept and lower the emission levels several measures can be taken. While port fuel injection of ammonia can help reduce scavenging losses during the valve overlap, the reduction of crevice volumes in the combustion chamber has the potential to lower NH_3 emissions and also the N_2O formation. At higher load operation a further reduction of the diesel fraction and EAR has the potential for reduction of the GWP.

4 DEFINITIONS, ACRONYMS, ABBREVIATIONS

AFR_{Diesel}: Stoichiometric air/fuel ratio of diesel fuel

AFR_{H2}: Stoichiometric air/fuel ratio of H_2 fuel

AFR_{NH3}: Stoichiometric air/fuel ratio of NH_3 fuel

aTDC: After top dead center

BMEP: Brake mean effective pressure

CA: Crank angle

CA50: Crank angle where 50 % energy is released

CO_2: Carbon dioxide

COV: Coefficient of variation

CR: Compression ratio

DQ: Heat release rate

EAR: Global excess air ratio

EAR_{NH3}: Excess air ratio of background mixture

GWP: Global warming potential

IMEP: Indicated mean effective pressure

IVC: Intake valve closing

m_{Diesel}: Diesel mass

m_{H2}: Hydrogen mass

m_{NH3}: Ammonia mass

NH_3: Ammonia

NO: Nitric oxide

NO_2: Nitrogen dioxide

N_2O: Nitrous oxide

NO_X: Nitrogen oxide

Q_{norm}: Normalized cumulative heat release

SCE: Single cylinder engine

SOC: Start of injector current

TDC: Top dead center

φ_{Diesel}: Diesel energetic fraction

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