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Experimental study on ammonia/hydrogen/air combustion in spark ignition engine conditions

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Abstract

The mitigation of climate change implies the increasing use of variable renewable energy sources. Energy storage and transport solutions will contribute to ensure the stability, reliability and flexibility of the energy systems in that context. Ammonia is a well-known chemical of formula \text{NH}_3 and, amongst other electrofuels, a promising energy carrier and carbon-free combustible fuel. In the present experimental study, engine performance, combustion characteristics and pollutant emissions of a recent spark ignition engine fueled with premixed ammonia/hydrogen/air mixtures were assessed. Gaseous ammonia blends in a wide range of hydrogen fuel fractions and equivalence ratios were tested at two different engine loads. Results show performances comparable with conventional fuel operation when the appropriate promotion strategies are used. Specifically, blending up to 20\% hydrogen in the fuel by volume improves the cyclic stability and avoids misfires, while granting the best work output and indicated efficiencies near stoichiometry. Higher hydrogen fractions result in depleted efficiency, attributed to higher wall heat losses. The combustion duration is directly correlated to the \text{LBV} of the mixtures, thus being accelerated by hydrogen blending. The accelerating effect of hydrogen is particularly remarkable during the initial stage of the combustion. Hydrogen appears therefore mainly as an ignition promoter. Increasing the engine load improves the furnished work and allows to extend the operating boundaries in terms of mixture composition.

Keywords

Ammonia ; Hydrogen ; Spark ignition engine ; Sustainable fuel ; Performance ; Emissions

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1. Introduction

Ammonia (NH₃) is increasingly considered as a prominent enabler of the ongoing transition towards high shares of Variable Renewable Energy Sources (VRES) in the energy systems, as stated in The Future of Hydrogen, a recent report by the International Energy Agency [1]. Indeed, VRES should account for more than 50% of the total primary energy supply by 2050 to comply with the global warming mitigation objectives of the Paris Agreement, according to the Intergovernmental Panel on Climate Change [2]. In this new energy paradigm, energy storage and transport solutions will contribute to the efficiency and sustainability of the energy systems.

Ammonia, along with other electrofuels, i.e. energy-dense chemicals producible from electricity, water and any other renewable feedstock, appears as such a renewable and carbon-free energy carrier. It exhibits a high hydrogen content of 17.8% by mass, a volumetric energy density of 11.3 GJ/m³ when stored in liquid form at 1.1 MPa and 300 K, and is as such an efficient hydrogen carrier.

In order to avoid costly ammonia-to-hydrogen conversions and depending on the final energy use, direct ammonia combustion can be considered. Related research efforts have been summarized recently by Valera-Medina et al. [3]. Those mainly focus on overcoming the unfavorable combustion properties of NH₃, illustrated in Table 1 by its low Laminar Burning Velocity (LBV), high auto-ignition temperature and narrow flammability range, as well as addressing the challenge of nitrogen-based pollutant emissions. To that aim, several practical combustion technologies were investigated, including gas turbines [4,5], compression-ignition engines, mostly in dual fuel configurations [6-16] and Spark Ignition (SI) engines [17-34].

Table 1. Ammonia properties and comparison with other fuels at 300 K and 0.1 MPa. Data from [3,23,35]

<table>
<thead>
<tr>
<th></th>
<th>Ammonia</th>
<th>Methanol</th>
<th>Hydrogen</th>
<th>Methane</th>
<th>Gasoline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formula</td>
<td>NH₃</td>
<td>CH₃OH</td>
<td>H₂</td>
<td>CH₄</td>
<td>-</td>
</tr>
<tr>
<td>Storage</td>
<td>Liquid</td>
<td>Liquid</td>
<td>Compressed</td>
<td>Compressed</td>
<td>Liquid</td>
</tr>
<tr>
<td>Storage temperature (K)</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
<td>300</td>
</tr>
<tr>
<td>Storage pressure (MPa)</td>
<td>1.1</td>
<td>0.1</td>
<td>70</td>
<td>25</td>
<td>0.1</td>
</tr>
</tbody>
</table>
The flexibility of the internal combustion engine makes it appealing for NH$_3$ fuel use, especially when assisting the ignition with a spark. SI engines can be run on ammonia blends at high compression ratio (CR) without risk of engine knock thanks to the high octane number of ammonia. This was demonstrated in early studies, where single-cylinder and multi-cylinder SI engine were successfully run on pure ammonia fuel [17–19]. However, gasoline-like performances were only achieved by using one or several promoting strategies, including an improved ignition system, increasing the engine load or CR and H$_2$ doping of the NH$_3$ fuel. A minimum H$_2$ amount depending on the engine speed and CR of some percent by mass was necessary to ensure satisfying performance and decrease NH$_3$ emissions but at the cost of increased NOx emissions.

Contemporary studies also investigated ammonia/gasoline fueling of SI engine, either to reduce carbon-based emissions of gasoline engines, or to promote the combustion with ammonia as a main fuel. Granell et al. proposed a 70% NH$_3$ / 30% gasoline blend by energy as a good trade-off at full load in a Collaborative Fuel Research (CFR) engine [21,22]. The authors suggested supercharging the engine instead of increasing the CR, due to the detrimental thermodynamic consequences of the early spark advance required by the NH$_3$ fuel.

Engine-out NH$_3$ emissions proportional to the NH$_3$ input are reported, up to 22000 ppmvw for stoichiometric

<table>
<thead>
<tr>
<th>Density under storage conditions (kg.m$^{-3}$)</th>
<th>600</th>
<th>785</th>
<th>39</th>
<th>187</th>
<th>~740</th>
</tr>
</thead>
<tbody>
<tr>
<td>Lower Heating Value (LHV) (MJ.kg$^{-1}$)</td>
<td>18.8</td>
<td>19.9</td>
<td>120</td>
<td>50</td>
<td>44.5</td>
</tr>
<tr>
<td>Volumetric energy density (GJ.m$^{-3}$)</td>
<td>11.3</td>
<td>15.6</td>
<td>4.7</td>
<td>9.35</td>
<td>33</td>
</tr>
<tr>
<td>Stoich. air-fuel ratio by mass</td>
<td>6.05</td>
<td>6.44</td>
<td>34.6</td>
<td>17.3</td>
<td>15</td>
</tr>
<tr>
<td>LBV @ $\phi = 1$ (m.s$^{-1}$)</td>
<td>0.07</td>
<td>0.36</td>
<td>3.51</td>
<td>0.38</td>
<td>0.58</td>
</tr>
<tr>
<td>Auto-ignition temp. (K)</td>
<td>930</td>
<td>712</td>
<td>773-850</td>
<td>859</td>
<td>503</td>
</tr>
<tr>
<td>Research Octane Number</td>
<td>130</td>
<td>119</td>
<td>&gt;100</td>
<td>120</td>
<td>90-98</td>
</tr>
<tr>
<td>Flammability limits in air (vol.%)</td>
<td>15-28</td>
<td>6.7-36</td>
<td>4.7-75</td>
<td>5-15</td>
<td>0.6-8</td>
</tr>
</tbody>
</table>
NH₃/air at CR=10:1. Ryu et al. investigated direct gaseous NH₃ injection in a CFR engine (CR = 10:1) with gasoline as the base fuel, and reported acceptable performance but high nitrogen-based specific emissions [36]. The same authors suggested to partly dissociate NH₃ prior to direct injection, to use the beneficial effect of H₂ on the combustion efficiency, and reduce the pollutant emissions [32].

That capability of molecular hydrogen of being producible in-situ through ammonia dissociation, possibly by recycling exhaust heat and requiring no additional tank, grants it a potential advantage over other combustion-promoting fuels. Therefore, further researchers investigated the use of hydrogen-enriched ammonia in SI engines. Koike et al. studied a single-cylinder SI engine (CR = 14:1) fueled with premixed stoichiometric NH₃/H₂/air and NH₃/gasoline/air mixtures [29]. Stable operation was achieved for 10 – 60 LHV% of H₂ (12.6 – 66.1 mol.%) or 40 – 100 LHV% gasoline (8 – 100 mol.%) fuel fractions for light load (Indicated Mean Effective Pressure, IMEP = 0.2 MPa), and up to 100 % NH₃ for high load (IMEP = 0.8 MPa). An auto-thermal cracker was successfully operated to provide H₂ from NH₃ dissociation. Similarly, Frigo and Gentili studied a twin-cylinder commercial SI engine fueled with premixed stoichiometric NH₃/H₂/air mixtures at half and full load and several engine speeds [27]. They found a minimum hydrogen-to-ammonia energy ratio of 7% at full load and 11% at half load to ensure stable engine operation, but with decremented performance with respect to gasoline operation. Maximum NOx emissions of 1700 ppm and surprisingly low NH₃ emissions are reported, although the latter have only been detected through a threshold sensor. Comotti and Frigo extended the previous study by demonstrating the successful use of a catalytic cracking reactor for in-situ H₂ production [24]. Mørch et al. fueled a CFR engine with NH₃/H₂ blends at various CR, with a metal ammine complex as NH₃ reservoir [23]. They showed increased engine performance and similar NOx emissions with respect to gasoline operation, thanks to the possibility of knock-free CR increase. Best performance is found at stoichiometry for 10 mol.% H₂ in the fuel. Selective Catalytic Reduction is suggested as a meaningful way to mitigate NOx emissions, thanks to appropriate exhaust temperatures and NH₃ availability, with the major challenge of avoiding NH₃ slip at the exhaust. Westlye et al. focused on nitrogen-based pollutant emissions of a CFR engine fueled with 80 mol.% NH₃ / 20 mol.% H₂ lean blends, and further demonstrated the feasibility of SCR for pollutants mitigation [30].
Therefore, the suitability of ammonia as an efficient carbon-free SI engine fuel has been demonstrated in the literature, and the relevance of H₂ as a combustion promoter has been underlined. However, most of the experimental data were obtained in outdated or basic engine geometries and covered only a partial range of mixture compositions. The objective of the present work is thus to actualize and extend the experimental database for NH₃/H₂/air combustion in a SI engine, so as to conduct further analysis that should provide useful understanding on ammonia combustion properties. To that end, one cylinder of a recent commercial SI engine was fueled with premixed gaseous NH₃/H₂/air mixtures for a wide range of mixture compositions at and beyond full load. Measurements for part-load operation close to stoichiometry were published elsewhere [33,34]. The experimental set-up and the operating conditions are first introduced. Extensive data derived from in-cylinder pressure and exhaust gas measurements are then presented, analyzed and discussed.

2. Experimental and numerical methods

2.1. Engine setup

The engine used for the experiments is a recent four-cylinder four-stroke SI engine, retrofitted to a single-cylinder by fueling only one cylinder. The engine specifications are shown in Table 2. This engine benefits from improved aerodynamics, thanks to its piston bowl optimized for gasoline direct injection, granting it a tumble ratio of about 2.4 [37].

<table>
<thead>
<tr>
<th>Table 2. Engine specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Model</td>
</tr>
<tr>
<td>Stroke</td>
</tr>
<tr>
<td>Bore</td>
</tr>
<tr>
<td>Connecting rod length</td>
</tr>
<tr>
<td>Displacement volume</td>
</tr>
<tr>
<td>Geometric compression ratio</td>
</tr>
<tr>
<td>Valves</td>
</tr>
<tr>
<td>Engine speed</td>
</tr>
</tbody>
</table>
A constant engine speed of 1500 rpm is imposed to the engine by an electric motor. A Kübler optical encoder monitors the angular position of the main shaft with a 0.1 Crank Angle Degree (CAD) resolution. Type K thermocouples and piezo-resistive pressure transducers are used to monitor the intake and exhaust temperature and pressure, respectively. The temperature of the cooling fluid is set and monitored at 353 K. The flows of the reactive gases, including dried ambient compressed air, bottled ammonia and bottled hydrogen are monitored by means of Brooks thermal mass flowmeters with 0.7% accuracy on their full scale, preheated to the intake temperature of 323 K and premixed in an intake plenum prior to injection. The original spark plug is used with a coil charging time of 2 ms. A water-cooled AVL piezoelectric pressure transducer measures the in-cylinder pressure with a 0.1 CAD resolution and a measuring range of 0 – 25 MPa. The absolute in-cylinder pressure is obtained by equalizing the previous signal with the mean absolute intake pressure, $P_{in}$, 20 CAD after inlet valve opening (pressure pegging). The exhaust gas composition is monitored by means of a Gasmet Fourier-Transform InfraRed (FTIR) gas analyser. The wet exhaust concentrations of $H_2O$, $NH_3$, NO, $NO_2$ and $N_2O$ were measured simultaneously for each test with a time step of 5 s. Figure 1 shows a scheme of the experimental setup.

**Figure 1.** Scheme of the experimental setup

### 2.2. Operating conditions

The global stoichiometric reaction of $NH_3/H_2/air$ combustion is as:
\[(1 - x_{H_2})NH_3 + x_{H_2}H_2 + \frac{3 - x_{H_2}}{4} (O_2 + 3.76N_2) \rightarrow \left(\frac{3 - x_{H_2}}{2}\right)H_2O + \left(\frac{1 - x_{H_2}}{2} + 3.76 \cdot \frac{3 - x_{H_2}}{4}\right)N_2\] (1)

with \(x_{H_2}\), the hydrogen molar fraction in the fuel mixture. Non-stoichiometric mixtures are defined by the equivalence ratio, \(\phi\):

\[
\phi = \frac{\frac{X_{H_2} + X_{NH_3}}{X_{air}}}{\left(\frac{X_{H_2} + X_{NH_3}}{X_{air}}\right)_{st}}
\] (2)

\(X_s\) represents the molar fraction of the species \(s\) in the reactive mixture, and subscript “st” stands for stoichiometric. The stoichiometric air/fuel ratio by mass is about 6 for pure NH\(_3\) fuel and thus more than twice smaller than for gasoline, as shown in Table 1, but increases slightly with hydrogen enrichment. The investigated operating conditions are summarized in Table 3, and are intended to cover a broad range of mixture compositions representative of possible ammonia/hydrogen operating modes of SI engines at and beyond full load. In order to make optimal performance considerations, the spark ignition timing (SIT) is set to maximize the net Indicated Mean Effective Pressure (IMEP\(_n\)), a quantification of the net work furnished by the expanding gas on the piston. This is equivalent to the Maximum Brake Torque (MBT) timing, but the absence of direct torque measurement due to the friction losses caused by the three unproductive pistons led to the previous approach. Cycle-to-cycle variability is considered by recording 100 consecutive pressure cycles for each test. Averaged values over 100 cycles are presented in this paper.

**Table 3. Overview of the operating conditions.**

<table>
<thead>
<tr>
<th>Intake temperature (K)</th>
<th>Intake pressure (MPa)</th>
<th>H(_2) fraction in the fuel</th>
<th>(\phi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>323</td>
<td>0.1, 0.12</td>
<td>By volume [0 – 0.6]</td>
<td>[0.6 – 1.2]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>By energy (LHV) [0 – 0.54]</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>By mass [0 – 0.15]</td>
<td></td>
</tr>
</tbody>
</table>

2.3. Combustion analysis and laminar burning velocity calculation
A precise determination of the CR and detection of the Top Dead Center (TDC) position is required for an accurate analysis based on the in-cylinder pressure signal and calculated in-cylinder volume. Therefore, the methodology proposed by Tazerout et al. [25-26] for CR determination and pressure-volume lag elimination is implemented within the classical analysis of the cylinder pressure-volume data proposed by Heywood [40]. Crevices effects are neglected and no in-cylinder mass variation are considered between Inlet Valve Closing (IVC) and Exhaust Valve Opening (EVO). Performance indicators such as the $\text{IMEP}_n$ and its coefficient of variation over 100 cycles $\text{COV}_{\text{IMEP}}$ can be deduced accurately, as well as the bulk in-cylinder temperature between IVC and EVO. The latter is determined by means of the ideal gas law, assuming the gas temperature to be equal to the inlet temperature $T_{\text{in}} = 323$ K at IVC. The combustion analysis is also performed by calculating the net heat release rate (HRR) by means of the first law of thermodynamics in a one-zone model. The in-cylinder heat capacity at constant pressure is calculated using the bulk in-cylinder temperature and an in-cylinder charge composition modeled by a representative mixture of burned and unburned gases weighted by the burned mass fraction (that can be determined iteratively), assuming complete combustion. The gross HRR from the combustion is estimated by considering the wall heat losses by means of the model of Hohenberg [41]. Combustion phasing in the cycle is established by assessing the crank angles at which 10%, 50% and 90% of the cumulated gross heat release is reached, yielding CA10, CA50 and CA90, respectively.

The laminar burning velocity of the reactive mixtures under the thermodynamic conditions at SI timing is calculated by means of a newly developed LBV correlation for $\text{NH}_3/\text{H}_2/\text{air}$ flames proposed by Goldmann and Dinkelacker [42] on the basis of the detailed reaction mechanism of Mathieu and Petersen [43]. This correlation takes the presence of hydrogen in the fuel into account and was validated against measurements at normal temperature and up to 500 kPa of pressure for various mixture compositions.

3. Results and discussion

3.1. Engine performance

The engine was operated successfully with an excellent cycle-to-cycle stability for a wide range of $\text{H}_2$ fractions and equivalence ratios, when the spark ignition was sufficiently advanced, as shown in Figure 2a and 2b. An acceptable cyclic variability boundary was set at $\text{COV}_{\text{IMEP}} \leq 5\%$ (coefficient of variation of the $\text{IMEP}_n$), but most of the conditions verified $\text{COV}_{\text{IMEP}} \leq 3\%$, as shown in Figure 2c and 2d. It should be emphasized here
that stable operation could be achieved for a stoichiometric NH$_3$/air mixture for both intake pressures. Only mixtures with high hydrogen fraction were found suitable for very lean operation. When increasing the NH$_3$ content in the fuel, advancing the SI timing is unsurprisingly required to maintain the cyclic stability and reach the maximum power output, as shown in Fig. 2a and 2b. This is primarily attributed to the low LBV of NH$_3$ that slows down the early stages of the flame propagation, and explains the bell-shaped dependence of the SI timing to the equivalence ratio. For a given fuel blend, the SI timing closest to TDC is obtained near stoichiometry, corresponding to the region of maximum LBV.

Figure 2. Optimized Spark Ignition Timing and Coefficient of Variation of the IMEP$_n$.

Figure 3 shows the IMEP$_n$ as a quantification of the piston work, along with a “Fuel Mean Effective Pressure” (Fuel MEP) for the ratio between the cyclic energy input on a LHV basis and the displaced volume. The Fuel MEP is an increasing function of the intake pressure and the equivalence ratio, but volumetric hydrogen enrichment of the fuel at given $\phi$ does not modify the energy content of the fuel/air mixture, as the lower volumetric energy density of H$_2$ happens to be compensated by its lower stoichiometric air-fuel ratio, as shown in Fig. 3c and 3d. As a result, the IMEP$_n$ increases as the equivalence ratio is increased up to 1.1, as shown in Fig. 3a and b. In spite of excess fuel presence when $\phi = 1.1$, the extra work obtained at this equivalence ratio may be explained by the maximum LBV reached close to that value as compared to stoichiometry [42], allowing to operate closer to an ideal thermodynamic cycle. Further increase of the equivalence ratio only results
in more excess fuel with no LBV benefit, thus explaining the stagnation or decrease of the $\text{IMEP}_n$ when $\phi = 1.2$. In spite of nearly identical Fuel MEP, mixtures with low to moderate hydrogen fractions exhibit higher maximum $\text{IMEP}_n$ than highly enriched mixtures, consistently with the observations in [23]. Unsurprisingly, increasing the intake pressure allows to increase the power output up to values typical of full-load conventional fuel operation of the engine.

Figure 3. Net Indicated Mean Effective Pressure and Fuel Mean Effective Pressure.

The ratio of the $\text{IMEP}_n$ and the Fuel MEP yields the indicated efficiency and is shown in Figure 4. It is optimal for slightly hydrogen-enriched near-stoichiometric lean mixtures with highest values close to 39%. The dependence on the intake pressure is not fully consistent but tends to indicate a slight improvement of the indicated efficiency as the load is increased. Highly hydrogen-enriched near-stoichiometric mixtures experience a depleted indicated efficiency, assumedly due to higher wall heat losses linked to high flame temperatures, but the efficiency improves when operating towards leaner equivalence ratios while the flame temperatures decrease accordingly.
3.2. Combustion analysis

Figure 5 shows the in-cylinder pressure data, along with the bulk in-cylinder temperature for stoichiometric mixtures. Pentagram symbols identify the spark ignition. While the thermodynamic conditions at ignition may differ with respect to the fuel hydrogen fraction due to the optimization of the SIT, the magnitude of the in-cylinder pressure rise remains comparable especially for atmospheric intake pressure. However, the estimated bulk in-cylinder temperatures shown in Figs. 5c and 5d exhibits higher peaks for highly hydrogen-containing mixtures, thus supporting the assumption of higher wall heat losses for such mixtures near stoichiometry.
Figure 5. Measured in-cylinder pressure and estimated bulk in-cylinder temperature for $\phi = 1.1$. Symbols: spark ignition.

Remarkably, the crank angle of occurrence of the maximum in-cylinder pressure is weakly affected by the variations of the mixture composition, as shown in Figure 6. This indicates that, in spite of a wide variation range of the spark ignition timing, the peak in-cylinder pressure is almost constantly phased in the cycle when the optimum $IMEP_n$ is reached. However, a certain data scatter remains, probably partly due to the manual tuning of the optimized spark ignition timing.
Figure 6. Maximum in-cylinder pressure as a function of its crank angle of occurrence, $\alpha_{P_{\text{max}}}$.

Even though no other major differences are observed on the in-cylinder pressure and temperature curves for different mixtures, the composition of the mixtures does impact the heat release rate and hence the duration of the combustion phases. This is highlighted in Figure 7, where the flame initiation phase between SIT and CA10, the first flame propagation phase between CA10 and CA50 and the combustion duration between CA10 and CA90 are shown as a function of the equivalence ratio in the case $P_{\text{in}} = 0.12 \text{ MPa}$. Similar results are obtained at $P_{\text{in}} = 0.1 \text{ MPa}$ and are thus not presented here. For hydrogen fuel fractions lower than 20%, the duration of the combustion phases decreases at a faster rate than the hydrogen fraction is increased. It then becomes nearly proportional to the hydrogen fuel fraction for 40% and 60% H$_2$. The effect of hydrogen on the initiation phase is always greater than proportional, with 34% and 62% acceleration relative to the pure NH$_3$ case for stoichiometric mixtures with 10% and 40% H$_2$, respectively. This may be partly due to the more favorable thermodynamic conditions due to an ignition closer to TDC in the latter cases, but also to the increase of the turbulent flame speed due to hydrogen addition. The influence of the equivalence ratio appears mainly correlated to the LBV of the mixture, since the different phases are accelerated when increasing $\phi$ from lean to stoichiometric and decelerated when further increasing it from stoichiometric to rich. A stagnation
or further acceleration of the phases as a function of $\phi$ is observed for mixtures with high H$_2$ content, due to
the shift of the peak LBV towards richer mixtures in those cases. This is highlighted in Figure 8, where the
different combustion phases are plotted as a function of the LBV, estimated at the thermodynamic conditions
at SIT (cf. Section 2.3).

**Figure 7.** Combustion phases at $P_{in} = 0.12$ MPa. a) Initiation phase. b) Propagation phase. c) Combustion
duration.

A clear non-linear correlation between the duration of the different combustion phases and the LBV of the
mixture at SIT is observed, that seem to be independent of the hydrogen fraction in the case of the propaga-
tion phase and the bulk combustion duration. The data are more scattered for the initiation phase, probably
due to different ignition behavior, as well as to the manual tuning of the SI timing. The effects of hydrogen
are believed to be critical during that phase, since it has a strong influence on the flame response to stretch
and thermal-diffusive instabilities, and thus on the turbulent flame speed that could explain the different
slopes in Fig. 8a. Once a quasi-steady combustion regime has been reached, around CA10, the maximal flame stretch may be reached, thus explaining the dependence of the combustion duration on the LBV only. The following empirical expression of the correlation between the combustion duration and $s_L^0$ at $P_{in} = 0.12$ MPa was determined by means of a least-square algorithm:

$$CA90 - CA10 = 20.0037 \cdot \exp(-11.7506 \cdot s_L^0) + 27.9146 \cdot \exp(-0.5374 \cdot s_L^0)$$

(3)

It appears important to notice that H$_2$-containing mixtures with lower LBVs than stoichiometric pure NH$_3$ were successfully operated in the engine, thus indicating that the LBV is not the only governing parameter of NH$_3$ combustion in the engine.

Figure 8. Combustion phasing at $P_{in} = 0.12$ MPa as a function of the calculated mixture LBV under SIT thermodynamic conditions.

### 3.3. Pollutant emissions
In order to wrap-up this analysis, pollutant exhaust emissions are shown in Figure 9. Only the measurements for an intake pressure of $P_{in} = 0.12$ MPa are depicted, since no qualitative difference with the other case was observed. NH$_3$ emissions increase monotonically with the NH$_3$ fraction in the fuel, as shown in Fig. 9a. Minimal emissions are observed for near-stoichiometric lean conditions, tending towards leaner mixtures as H$_2$ is added. That observation is not unexpected since it is the usual region for maximum combustion efficiency, combining the absence of excess fuel with the best reactivity properties. Increasing the hydrogen content allows to extend the range of acceptable reactivity towards leaner mixtures. When the equivalence ratio is increased above stoichiometry, the emissions increase significantly due to the presence of excess fuel and incomplete combustion, reaching very high values of more than 15,000 ppmv. Heading towards very lean mixtures, the NH$_3$ emissions increase as well, because of poor combustion efficiency.

NOx emissions are shown in Fig. 9b. Minimal values are obtained for rich mixtures with high ammonia content. Mixtures with high H$_2$ fuel fractions exhibit the highest emissions, probably due to higher flame temperatures that promote thermal NOx formation. Maximal values are found for equivalence ratio 0.8-0.9, as could be expected due to the presence of excess oxygen. Very high values up to 9000 ppm are observed at lean conditions, while low values well below 500 ppm are seen at rich conditions, possibly after partial recombination with unburned NH$_3$ in the exhaust pipe.
Figure 9. Pollutant emissions in exhaust at $P_{in} = 120$ kPa. a) Unburned NH$_3$. b) Total NOx.

Either way, mitigation strategies for both NH$_3$ and NOx are required in order to make ammonia acceptable as a fuel for commercial applications. These could be achieved by means of a SCR catalyst, since both heat and NH$_3$ reducing agent are available in the exhaust, as demonstrated by Westlye et al. [30]. The feasibility of that approach is verified in Figure 10 that shows the exhaust temperatures measured in the present study. The best operating temperature for usual catalysts are in the range 550-750 K. This could be achieved by operating the present engine in lean conditions. For instance, a mixture with 20% H$_2$ in the fuel and $\phi = 0.7$ exhibits exhaust temperatures in the appropriate range and also balanced NH$_3$ and NOx emissions, i.e. NH$_3$/NOx $\approx 1$. Alternatively, exhaust gas recirculation could be used to reduce the exhaust temperatures, while taking advantage of the exhaust H$_2$ concentrations that were evidenced in [33,34] for rich mixtures to promote the combustion. If intake H$_2$ is to be produced in-situ from ammonia dissociation, the nitrogen co-product will also act as a diluent and thus help reducing the temperatures.
4. Summary and conclusions

Experiments were conducted in a modern SI engine in order to assess the feasibility and the characteristics of ammonia combustion at various blended hydrogen fractions, equivalence ratios and intake pressures. In future applications, hydrogen could be provided by in-situ NH$_3$ dissociation in a catalytic reformer. The main conclusions are as follow:

- A new measurement database of performance, combustion characteristics and emissions data is provided for numerical validation purposes.
- NH$_3$ is confirmed as a very suitable SI engine fuel for modern engines since neat ammonia operation could be achieved under supercharged conditions, even slight ones.
- Highest indicated pressure and efficiency were achieved at low and moderate hydrogen addition, at slightly fuel-rich and slightly fuel-lean conditions respectively. However, lean mixtures with high hydrogen content also showed promising performance.
- Supercharged operation is expected to be beneficial in all cases, while increasing the compression ratio remains an open question. In that matter, the interest of engine design modification for optimal NH$_3$ fuel operation still needs to be assessed.
Hydrogen is an ignition promoter, allowing significant performance and stability improvement when added in small quantities, mainly beneficial for the early stages of the combustion. Wall heat losses are thought to play a significant role at high hydrogen fractions.

The phasing of the combustion is correlated with the Laminar Burning Velocity of the mixture under spark ignition timing conditions, in a non-linear fashion and mainly independently of the hydrogen fraction. However, the LBV does not fully explain the ignition and stability behavior of hydrogen-enriched mixtures with very low LBVs.

High NOx and NH\textsubscript{3} emissions need to be appropriately mitigated in future applications, possibly by means of already existing technologies. A fuel blend with 20% H\textsubscript{2} and \(\phi = 0.7\) exhibited both exhaust temperatures in the range 550-750 K and a NH\textsubscript{3}/NOx ratio close to unity, compatible with the use of a dedicated SCR after-treatment system.

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**Declarations of interest**

None.

**References**


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