1	Experimental study on ammonia/hydrogen/air combustion in spark
2	ignition engine conditions
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8	Abstract

The mitigation of climate change requires the increasing use of variable renewable energy sources. Energy 9 storage and transport solutions will contribute to ensure the stability, reliability, and flexibility of the energy 10 systems in that context. Ammonia is a well-known chemical of formula NH<sub>3</sub> and, amongst other electrofuels, 11 12 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 13 premixed ammonia/hydrogen/air mixtures were assessed. Gaseous ammonia blends in a wide range of 14 hydrogen fuel fractions and equivalence ratios were tested at two different engine loads. Results show 15 performances comparable with conventional fuel operation when the appropriate promotion strategies are 16 used. Specifically, blending up to 20% hydrogen in the fuel by volume improves the cyclic stability and avoids 17 misfires, while granting the best work output and indicated efficiencies near stoichiometry. Higher hydrogen 18 fractions result in depleted efficiency, attributed to higher wall heat losses. The combustion duration is directly 19 correlated to the LBV of the mixtures, thus being accelerated by hydrogen blending. The accelerating effect 20 of hydrogen is particularly remarkable during the initial stage of the combustion. Hydrogen appears therefore 21 mainly as an ignition promoter. Increasing the engine load improves the furnished work and allows to extend 22 the operating boundaries in terms of mixture composition. 23

### 24 Keywords

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

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## 26 **1. Introduction**

Ammonia (NH<sub>3</sub>) is increasingly considered as a relevant enabler in the ongoing transition towards high shares 27 of Variable Renewable Energy Sources (VRES) in energy systems, as stated in *The Future of Hydrogen*, a 28 recent report by the International Energy Agency [1]. Indeed, VRES should account for more than 50% of the 29 total primary energy supply by 2050 to comply with the global warming mitigation objectives of the Paris 30 Agreement, according to the Intergovernmental Panel on Climate Change [2]. In this new energy paradigm, 31 energy storage and transport solutions will contribute to the efficiency and sustainability of the energy systems. 32 Ammonia appears as such a renewable and carbon-free energy carrier among other electrofuels, i.e. energy-33 dense chemicals producible from electricity, water and any other renewable feedstock. Its exhibits a high 34 hydrogen content of 17.8% by mass, a volumetric energy density of 11.3 GJ/m<sup>3</sup> when stored in liquid form at 35 1.1 MPa and 300 K, and is as such an efficient hydrogen carrier. 36

In order to avoid costly ammonia-to-hydrogen conversions and depending on the final energy use, direct 37 ammonia combustion can be considered. Related research efforts have been summarized recently by Valera-38 Medina et al. [3]. Those mainly focus on overcoming the nitrogen-based pollutant emissions and the 39 unfavorable combustion properties of NH<sub>3</sub>, illustrated in Table 1 by its low Laminar Burning Velocity (LBV), 40 high auto-ignition temperature and narrow flammability range. Recent efforts extended the experimental LBV 41 database [4–20], as well as the ignition delay time database [21–25] of ammonia-based mixtures. This data, 42 along with other fundamental combustion studies on species and temperature profiles allow the development 43 and improvement of detailed kinetic mechanisms of ammonia combustion [26–36]. 44

- 45
- **Table 1.** Ammonia properties and comparison with other fuels at 300 K and 0.1 MPa. Data from [3,37,38].

	Ammonia	Methanol	Hydrogen	Methane	Gasoline
Formula	NH3	CH <sub>3</sub> OH	H <sub>2</sub>	CH4	-
Storage	Liquid	Liquid	Compressed	Compressed	Liquid
Storage temperature (K)	300	300	300	300	300
Storage pressure (MPa)	1.1	0.1	70	25	0.1

Density under storage conditions (kg.m <sup>-3</sup> )	600	785	39	187	~740
Lower Heating Value (LHV) (MJ.kg <sup>-1</sup> )	18.8	19.9	120	50	44.5
Volumetric energy density (GJ.m <sup>-3</sup> )	11.3	15.6	4.7	9.35	33
Stoich. air-fuel ratio by mass	6.05	6.44	34.6	17.3	15
LBV @ $\phi = 1 \text{ (m.s^{-1})}$	0.07	0.36	3.51	0.38	0.58
Auto-ignition temp. (K)	930	712	773-850	859	503
Research Octane Number	130	119	>100	120	90-98
Flammability limits in air (vol.%)	15-28	6.7-36	4.7-75	5-15	0.6-8

Several practical combustion technologies were investigated in the literature, including gas turbines [39,40] 48 49 and compression-ignition engines, however mostly in dual fuel configurations [6-16] and Spark Ignition (SI) engines [17-34]. The flexibility of the internal combustion engine makes it appealing for NH<sub>3</sub> fuel use, 50 especially when assisting the ignition with a spark. SI engines can be run on ammonia blends at high 51 compression ratios (CR) without risk of engine knock owing to the high octane number of ammonia. This was 52 demonstrated in early studies, where single-cylinder and multi-cylinder SI engines were successfully run on 53 pure ammonia fuel [52,61,62]. However, gasoline-like performances were only achieved by using one or 54 several promoting strategies, including an improved ignition system, increasing the engine load or CR and  $H_2$ 55 doping of the NH<sub>3</sub> fuel. A minimum amount of H<sub>2</sub>, depending on the engine speed and CR, was necessary to 56 ensure satisfying performance and decrease NH<sub>3</sub> emissions but at the cost of increased NOx emissions. 57

58 Contemporary studies also investigated ammonia/gasoline fueling of SI engines, either to reduce carbon-based 59 emissions of gasoline engines, or to promote the combustion when ammonia is the main fuel. Granell et al. 60 proposed a 70% NH<sub>3</sub> / 30% gasoline blend by energy as a good trade-off at full load in a Collaborative Fuel 61 Research (CFR) engine [64,65]. 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<sub>3</sub> fuel. Engine-out NH<sub>3</sub> emissions proportional to the NH<sub>3</sub> input are reported, up to 22000 ppmvw for stoichiometric NH<sub>3</sub>/air at CR=10:1. Ryu et al. investigated direct gaseous NH<sub>3</sub> injection in a CFR engine (CR = 10:1) with gasoline as the base fuel, and reported acceptable performance but high nitrogen-based specific emissions [69]. The same authors suggested to partly dissociate NH<sub>3</sub> prior to direct injection, to use the beneficial effect of H<sub>2</sub> on the combustion efficiency, and reduce the pollutant emissions [58].

The in-situ producibility of molecular hydrogen through ammonia dissociation, possibly by recycling exhaust 68 69 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. 70 studied a single-cylinder SI engine (CR = 14:1) fueled with premixed stoichiometric  $NH_3/H_2/air$  and 71 NH<sub>3</sub>/gasoline/air mixtures [55]. Stable operation was achieved for 10 - 60 LHV% of H<sub>2</sub>(12.6 - 66.1 mol.%) 72 or 40 – 100 LHV% gasoline (8 – 100 mol.%) fuel fractions for low load (Indicated Mean Effective Pressure, 73 IMEP = 0.2 MPa), and up to 100 % NH<sub>3</sub> for high load (IMEP = 0.8 MPa). An auto-thermal cracker was 74 75 successfully operated to provide H<sub>2</sub> from NH<sub>3</sub> dissociation. Similarly, Frigo and Gentili studied a twincylinder commercial SI engine fueled with premixed stoichiometric NH<sub>3</sub>/H<sub>2</sub>/air mixtures at half and full load 76 and several engine speeds [53]. They found a minimum hydrogen-to-ammonia energy ratio of 7% at full load 77 and 11% at half load to ensure stable engine operation, but with decremented performance with respect to 78 gasoline operation. Maximum NOx emissions of 1700 ppm and surprisingly low NH<sub>3</sub> emissions are reported, 79 80 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 H<sub>2</sub> production 81 [66]. Mørch et al. fueled a CFR engine with NH<sub>3</sub>/H<sub>2</sub> blends at various CR, with a metal ammine complex as 82 NH<sub>3</sub> reservoir [38]. They showed increased engine performance and similar NOx emissions with respect to 83 gasoline operation, thanks to the possibility of knock-free CR increase. Best performance is found at 84 stoichiometry for 10 mol.% H<sub>2</sub> in the fuel. Selective Catalytic Reduction is suggested as a meaningful way to 85 mitigate NOx emissions, thanks to appropriate exhaust temperatures and NH<sub>3</sub> availability, with the major 86 challenge of avoiding NH<sub>3</sub> slip at the exhaust. Westlye et al. focused on nitrogen-based pollutant emissions 87 of a CFR engine fueled with 80 mol.% NH<sub>3</sub>/20 mol.% H<sub>2</sub> lean blends, and further demonstrated the feasibility 88 of SCR for pollutants mitigation [56]. 89

The suitability of ammonia as an efficient carbon-free SI engine fuel has thus been demonstrated in the 90 literature, and the relevance of H<sub>2</sub> as a combustion promoter has been underlined. However, most of the 91 experimental data were obtained in "legacy" or basic engine geometries and covered only a partial range of 92 mixture compositions. Therefore, new experimental data covering typical thermodynamic and aerodynamic 93 conditions of modern engines are required for concept and numerical models validation. The results of SI 94 engine tests focusing on near-stoichiometric ammonia/air mixtures with modest H<sub>2</sub> content at various engine 95 loads were published elsewhere [59,60]. The objective of the present work is to provide new understanding 96 of the practical combustion characteristics of ammonia/hydrogen blends in modern engine geometries, with a 97 specific focus on the influence of the LBV of the mixtures, including non-stoichiometric and highly hydrogen-98 enriched ones. To that end, one cylinder of a recent commercial SI engine was fueled with premixed gaseous 99 NH<sub>3</sub>/H<sub>2</sub>/air mixtures for a wide range of mixture compositions at and beyond full load. The experimental set-100 up and the operating conditions are first introduced. Extensive data derived from in-cylinder pressure and 101 exhaust gas measurements are then presented, analyzed and discussed. 102

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### 104 2. Experimental and numerical methods

# 105 **2.1.** Engine setup

The engine used for the experiments is a recent four-cylinder four-stroke SI engine, retrofitted to a singlecylinder by fueling only one cylinder. The engine specifications are shown in Table 2. This engine benefits from improved aerodynamics, due to its piston bowl optimized for gasoline direct injection, granting it a tumble ratio of about 2.4 [70].

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### Table 2. Engine specifications

Model	PSA EP6DT
Stroke	85.8 mm
Bore	77 mm
Connecting rod length	138.5 mm
Displacement volume	399.5 cm <sup>3</sup>
Geometric compression ratio	10.5:1

Valves	4
Engine speed	1500 rpm

A constant engine speed of 1500 rpm is imposed to the engine by an electric motor. A Kübler optical encoder 112 monitors the angular position of the main shaft with a 0.1 Crank Angle Degree (CAD) resolution. Type K 113 114 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 115 the reactive gases, including dried ambient compressed air, bottled ammonia and bottled hydrogen are 116 monitored by means of Brooks thermal mass flowmeters with 0.2% zero uncertainty on their full scale and 117 0.7% accuracy on the process value, preheated to the intake temperature of 323 K and premixed in an intake 118 plenum prior to injection. The original spark plug is used with a coil charging time of 2 ms. A water-cooled 119 AVL piezoelectric pressure transducer measures the in-cylinder pressure with a 0.1 CAD resolution and a 120 measuring range of 0-25 MPa. The absolute in-cylinder pressure is obtained by equalizing the previous 121 signal with the mean absolute intake pressure,  $P_{in}$ , 20 CAD after inlet valve opening (pressure pegging). The 122 exhaust gas composition is monitored by means of a Gasmet Fourier-Transform InfraRed (FTIR) gas analyzer. 123 The wet exhaust concentrations of H<sub>2</sub>O, NH<sub>3</sub>, NO, NO<sub>2</sub> and N<sub>2</sub>O were measured simultaneously for each test 124 with a time step of 5 s. Figure 1 shows a scheme of the experimental setup. 125



126

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Figure 1. Scheme of the experimental setup

129 The global stoichiometric reaction of NH<sub>3</sub>/H<sub>2</sub>/air combustion is as:

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$$(1 - x_{H_2})NH_3 + x_{H_2}H_2 + \frac{3 - x_{H_2}}{4}(0_2 + 3.76N_2) \rightarrow \left(\frac{3 - x_{H_2}}{2}\right)H_2O + \left(\frac{1 - x_{H_2}}{2} + 3.76 * \frac{3 - x_{H_2}}{4}\right)N_2$$
(1)

132

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

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136 
$$\phi = \frac{\frac{X_{H_2} + X_{NH_3}}{X_{air}}}{\left(\frac{X_{H_2} + X_{NH_3}}{X_{air}}\right)_{st}}$$
(2).

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 $X_{\rm s}$  represents the molar fraction of the species s in the reactive mixture, and subscript "st" stands for 138 stoichiometric. The stoichiometric air/fuel ratio by mass is about 6 for pure NH<sub>3</sub> fuel and thus less than half 139 the one of gasoline, as shown in Table 1, but increases slightly with hydrogen enrichment. The investigated 140 operating conditions are summarized in Table 3, and are intended to cover a broad range of mixture 141 compositions representative of possible ammonia/hydrogen operating modes of SI engines at and beyond full 142 load. In order to make optimal performance considerations, the spark ignition timing (SIT) is set to maximize 143 the net Indicated Mean Effective Pressure (IMEP<sub>n</sub>), a quantification of the net work furnished by the 144 expanding gas on the piston. This is equivalent to the Maximum Brake Torque (MBT) timing, but the absence 145 of direct torque measurement due to the friction losses caused by the three unproductive pistons led to the 146 previous approach. 147

- 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.
- 150

 Table 3. Overview of the operating conditions.

Intake temperature (K)	Intake pressure (MPa)	H <sub>2</sub> fraction in the fuel		$\phi$
323	0.1, 0.12	By volume	[0-0.6]	

By energy (LHV)	[0 - 0.54]	[0.6 – 1.2]
By mass	[0 - 0.15]	

#### 152 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 153 accurate analysis based on the in-cylinder pressure signal and calculated in-cylinder volume. Therefore, the 154 methodology proposed by Tazerout et al. [25-26] for CR determination and pressure-volume lag elimination 155 is implemented within the classical analysis of the cylinder pressure-volume data proposed by Heywood [73]. 156 Crevices effects are neglected and no in-cylinder mass variation are considered between Inlet Valve Closing 157 (IVC) and Exhaust Valve Opening (EVO). Performance indicators such as the IMEP<sub>n</sub> and its coefficient of 158 variation over 100 cycles COVIMEP can be deduced accurately, as well as the bulk in-cylinder temperature 159 between IVC and EVO. The latter is determined by means of the ideal gas law, assuming the gas temperature 160 to be equal to the inlet temperature  $T_{in} = 323$  K at IVC. The combustion analysis is also performed by 161 calculating the net heat release rate (HRR) by means of the first law of thermodynamics in a one-zone model. 162 The in-cylinder heat capacity at constant pressure is calculated using the bulk in-cylinder temperature and an 163 in-cylinder charge composition modeled by a representative mixture of burned and unburned gases weighted 164 by the burned mass fraction (that can be determined iteratively), assuming complete combustion. The gross 165 HRR from the combustion is estimated by considering the wall heat losses by means of the model of 166 Hohenberg [74]. Combustion phasing in the cycle is established by assessing the crank angles at which 10%, 167 50% and 90% of the cumulated gross heat release is reached, yielding CA10, CA50 and CA90, respectively. 168 The laminar burning velocity of the reactive mixtures under the thermodynamic conditions at SI timing is 169 calculated by means of a newly developed LBV correlation for NH<sub>3</sub>/H<sub>2</sub>/air flames proposed by Goldmann and 170 Dinkelacker [75] on the basis of the detailed reaction mechanism of Mathieu and Petersen [23]. This 171 correlation takes the presence of hydrogen in the fuel into account and was validated against measurements at 172 173 normal temperature and up to 500 kPa of pressure for various mixture compositions. However, the coefficients presently used in the correlations where the ones given in [75] corresponding to the actual mixture 174 composition, in-cylinder temperature and pressure estimated at SIT for each test condition. Therefore, the 175 calculation of the LBV incorporates an experimental validation in a few cases only (early SIT), but the 176

- 177 observed trends are expected to be meaningful as the mechanism of Mathieu and Petersen [23] on which the
- 178 <mark>correla</mark>

correlations were based showed a good accuracy and no abrupt extrapolation behavior.

- 179 **3. Results and discussion**
- 180 *3.1. Engine performance*

The engine was operated successfully with an excellent cycle-to-cycle stability for a wide range of H<sub>2</sub> fractions 181 and equivalence ratios, when the spark ignition was sufficiently advanced, as shown in Figure 2a and 2b. An 182 acceptable cyclic variability boundary was set at  $COV_{IMEP} \le 5\%$  (coefficient of variation of the *IMEP*<sub>n</sub>), but 183 most of the conditions verified  $COV_{IMEP} \leq 3\%$ , as shown in Figure 2c and 2d. It should be emphasized here 184 that stable operation could be achieved for a stoichiometric NH<sub>3</sub>/air mixture for both intake pressures. 185 However, a small amount of hydrogen is necessary to ensure the ignitability and stability in most cases, and 186 187 only mixtures with high hydrogen fraction were found suitable for very lean operation due to improved ignitability. When increasing the NH<sub>3</sub> content in the fuel, advancing the SI timing is unsurprisingly required 188 to maintain the cyclic stability and reach the maximum work output, as shown in Fig. 2a and 2b. This is 189 primarily attributed to the low LBV of NH<sub>3</sub> that slows down the early stages of the flame propagation, and 190 191 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. 192



193



195	Figure 3 shows the "Fuel Mean Effective Pressure" (FMEP), the ratio between the cyclic energy input on a
196	LHV basis and the displaced volume. The FMEP is an increasing function of the intake pressure and the
197	equivalence ratio, but volumetric hydrogen enrichment of the fuel at a given $\phi$ does not modify substantially
198	the energy content of the fuel/air mixture, as the lower volumetric energy density of H <sub>2</sub> happens to be
199	compensated by its lower stoichiometric air-fuel ratio, as shown in Fig. 3a and 3b. However, in practical
200	applications where H <sub>2</sub> would be produced from NH <sub>3</sub> decomposition prior to injection, the presence of large
201	amounts of $N_2$ should mitigate the previous statement. Error bars in Fig. 3 reflect the experimental
202	uncertainties on the mixture composition due to the mass flowmeters accuracy, assuming a negligible
203	uncertainty from the displacement volume, and show the good reliability of the intake parameters.



204

**Figure 3.** Fuel Mean Effective Pressure, a quantification of the cyclic energy input for each mixtures.

As a result of increasing *FMEP* with increased  $\phi$ , the *IMEP*<sub>n</sub> increases as the equivalence ratio is increased up to 1.1, as shown in Fig. 4. Error bars in Fig. 4 depict a conservative assumed uncertainty of 2%, as in [76]. 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 [75], allowing to operate closer to an ideal thermodynamic cycle. Further increasing the equivalence ratio only results in more excess fuel with no LBV benefit, thus explaining the stagnation or decrease of the *IMEP*<sub>n</sub> when  $\phi = 1.2$ . In spite of nearly identical *FMEP*, mixtures with low to moderate hydrogen fractions exhibit higher maximum









Figure 4. Net Indicated Mean Effective Pressure.

The ratio of the *IMEP*<sup>n</sup> and the *FMEP* yields the indicated efficiency and is shown in Figure 5. 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, presumably due to higher wall heat losses linked to high flame temperatures, but the efficiency improves when operating towards leaner equivalence ratios while the flame

- 231 temperatures decrease accordingly. Other phenomena than a temperature difference, such as turbulence-
- flame interactions may also contribute to the efficiency difference between lean and rich mixtures.
- 233 Therefore, lean operation of engines may be considered with ammonia blends with significant hydrogen
- contents, if efficiency should be the main operational driver.



236

Figure 5. Indicated efficiency.

# 237 *3.2. Combustion analysis*

Figure 6 shows the in-cylinder pressure data, along with the bulk in-cylinder temperature for stoichiometric 238 mixtures. Pentagram symbols identify the spark ignition. The error bars depict the experimental uncertainty, 239 that is assumed to be close to 1 bar for pressure and 5% for the temperature throughout the engine cycle as 240 estimated in [76]. While the thermodynamic conditions at ignition may differ with respect to the fuel hydrogen 241 fraction due to the optimization of the SIT, the magnitude of the in-cylinder pressure rise remains comparable 242 especially for atmospheric intake pressure. However, the estimated bulk in-cylinder temperatures shown in 243 Figs. 6c and 6d exhibit higher peaks for high hydrogen-containing mixtures, thus supporting the assumption 244 of higher wall heat losses for such mixtures near stoichiometry. 245





Figure 6. Measured in-cylinder pressure and estimated bulk in-cylinder temperature for  $\phi = 1.1$ . Symbols: spark ignition.

Remarkably, the crank angle at occurrence of the maximum in-cylinder pressure is weakly affected by the variations of the mixture composition, as shown in Figure 7. 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*<sup>n</sup> is reached. This should facilitate future optimal engine control strategies, even during variations of the reactive mixture composition. However, a certain data scatter remains, probably partly due to the manual tuning of the optimized spark ignition timing.



**Figure 7.** Maximum in-cylinder pressure as a function of its crank angle of occurrence,  $\alpha_{P_{max}}$ . 256 Even though no other major differences are observed for the in-cylinder pressure and temperature curves of 257 different mixtures, the composition of the mixtures does impact the heat release rate and hence the duration 258 of the combustion phases. This is highlighted in Figure 8, where the flame initiation phase between SIT and 259 CA10, the first flame propagation phase between CA10 and CA50, and the combustion duration between 260 CA10 and CA90, are shown as a function of the equivalence ratio in the case  $P_{in} = 0.12$  MPa. Uncertainties 261 were approximated conservatively with 1.5 CAD for CA50 and 4 CAD for CA90, while those on CA10 were 262 neglected following results in [76]. Similar results are obtained at  $P_{in} = 0.1$  MPa and are thus not presented 263 here. For hydrogen fuel fractions lower than 20%, the duration of the combustion phases decreases at a faster 264 rate than the hydrogen fraction is increased. It then becomes nearly proportional to the hydrogen fuel fraction 265 for 40% and 60% H<sub>2</sub>. The effect of hydrogen on the initiation phase is always greater than proportional, with 266 34% and 62% acceleration relative to the pure  $NH_3$  case for stoichiometric mixtures with 10% and 40% H<sub>2</sub>, 267 respectively. This may be partly due to the more favorable thermodynamic conditions due to an ignition closer 268 to TDC in the latter cases, but also to the increase of the turbulent flame speed due to hydrogen addition. The 269 influence of the equivalence ratio appears mainly correlated to the LBV of the mixture, since the different 270

271 phases are accelerated when increasing  $\phi$  from lean to stoichiometric and decelerated when further increasing 272 it from stoichiometric to rich. A stagnation or further acceleration of the phases as a function of  $\phi$  is observed 273 for mixtures with high H<sub>2</sub> content, due to the shift of the peak LBV towards richer mixtures in those cases. 274 This is highlighted in Figure 9, where the different combustion phases are plotted as a function of the LBV, 275 estimated at the thermodynamic conditions at SIT (cf. Section 2.3).



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Figure 8. Combustion phases at  $P_{in} = 0.12$  MPa. a) Initiation phase. b) Propagation phase. c) Combustion duration.

279 A clear non-linear correlation between the duration of the different combustion phases and the LBV of the

280 mixture at SIT is observed, that seem to be independent of the hydrogen fraction in the case of the

propagation phase and the bulk combustion duration. The data are more scattered for the initiation phase,

- likely 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. 9a. Once a quasi-steady combustion regime has been reached, around CA10, the
- 286 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  $s_{\rm L}^0$  at  $P_{\rm in} = 0.12$
- 289 MPa was determined by means of a least-square algorithm:

290 
$$CA90 - CA10 = 20.0037 \cdot \exp(-11.7506 \cdot s_{\rm L}^0) + 27.9146 \cdot \exp(-0.5374 \cdot s_{\rm L}^0)$$
 (3)

- It is also found to be mostly valid at  $P_{in} = 0.10$  MPa with some limitations due to the presence of some
- 292 outliers, as illustrated in Fig. 10. It appears important to notice that H<sub>2</sub>-containing mixtures with lower LBVs

than stoichiometric pure NH<sub>3</sub> were successfully operated in the engine, thus indicating that the LBV is not

the only governing parameter of NH<sub>3</sub> combustion in the engine.



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Figure 9. Combustion phasing at  $P_{in} = 0.12$  MPa as a function of the calculated mixture LBV under SIT

thermodynamic conditions.



Figure 10. Combustion phasing at  $P_{in} = 0.1$  MPa as a function of the calculated mixture LBV under SIT thermodynamic conditions.

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#### 302 3.3. Pollutant emissions

To complete this analysis, pollutant exhaust emissions are shown in Figure 11. Only the measurements for an 303 intake pressure of  $P_{in} = 0.12$  MPa are depicted, since no qualitative difference with the other case was 304 observed. The uncertainty on the exhaust emissions measurement was roughly estimated to be 10% of the 305 process value. NH<sub>3</sub> emissions increase monotonically with the NH<sub>3</sub> fraction in the fuel, as shown in Fig. 11a. 306 Minimal emissions are observed for near-stoichiometric lean conditions, tending towards leaner mixtures as 307  $H_2$  is added. That observation is not unexpected since it is the usual region for maximum combustion 308 efficiency, combining the absence of excess fuel with the best reactivity properties. Increasing the hydrogen 309 content allows to extend the range of acceptable reactivity towards leaner mixtures. When the equivalence 310 ratio is increased above stoichiometry, the emissions increase significantly due to the presence of excess fuel 311

and incomplete combustion, reaching very high values of more than 15,000 ppmv. Heading towards very lean
mixtures, the NH<sub>3</sub> emissions increase as well, due to a poor combustion efficiency.

NOx emissions are shown in Fig. 11b. Minimal values are obtained for rich mixtures with high ammonia 314 content. Mixtures with high  $H_2$  fuel fractions exhibit the highest emissions, probably due to higher flame 315 temperatures that promote thermal NOx formation. However, chemical kinetic effects may additionally be at 316 stake, since H<sub>2</sub> has a strong effect on the radical pool that influences the NOx formation mechanism, as 317 discussed in [77,78]. Maximal values are found for equivalence ratio 0.8-0.9, as could be expected due to the 318 presence of excess oxygen. Very high values up to 9000 ppm are observed at lean conditions, while low values 319 well below 500 ppm are seen at rich conditions, possibly after partial recombination with unburned NH<sub>3</sub> in 320 the exhaust pipe. 321

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323

324

**Figure 11.** Pollutant emissions in exhaust at  $P_{in} = 120$  kPa. a) Unburned NH<sub>3</sub>. b) Total NOx.

Either way, mitigation strategies for both NH<sub>3</sub> and NOx are required in order to make ammonia acceptable as a fuel for commercial applications. This could be achieved by means of a SCR catalyst, since both heat and a NH<sub>3</sub> reducing agent are available in the exhaust, as demonstrated by Westlye et al. [56]. The feasibility of that approach is verified in Figure 12 that shows the exhaust temperatures measured in the present study. The

329	highest exhaust temperatures are obtained around $\phi = 1.1$ , where the maximum LBV is reached, thus bringing
330	the operating conditions closer to an ideal cycle. The temperatures are maximum and the heat losses minimum.
331	The best operating temperature for usual catalysts are in the range 550-750 K. This could be achieved by
332	operating the present engine in lean conditions. For instance, a mixture with 20% H <sub>2</sub> in the fuel and $\phi = 0.7$
333	exhibits exhaust temperatures in the appropriate range and also balanced NH3 and NOx emissions, i.e.
334	$NH_3/NOx \approx 1$ . Alternatively, exhaust gas recirculation could be used to reduce the exhaust temperatures, while
335	taking advantage of the exhaust H <sub>2</sub> concentrations that were evidenced in [59,60] for rich mixtures to promote
336	the combustion. If intake H <sub>2</sub> is to be produced in-situ from ammonia dissociation, the nitrogen co-product will
337	also act as a diluent and thus help reducing the temperatures.





Figure 12. Measured exhaust gas temperature.

- 340 **4. Summary and conclusions**
- A new experimental database obtained in a modern SI engine is provided in order to assess the feasibility and the characteristics of ammonia combustion at various blended hydrogen fractions, equivalence ratios and intake pressures. Results regarding engine performance, combustion characteristics and pollutant emissions are presented. The main conclusions are as follow:
- NH<sub>3</sub> is confirmed as a very suitable SI engine fuel for modern engines with no or little design modification.

- Highest indicated pressure and efficiency were achieved at low and moderate hydrogen addition, with
   slightly fuel-rich and slightly fuel-lean conditions respectively. However, lean mixtures with high
   hydrogen content also showed promising performance.
- Hydrogen allows performance and stability improvement when added in small quantities as an ignition
   promoter, 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 hydrogenenriched mixtures with very low LBVs. New studies have to be conducted in order to provide
- 357 understanding on the turbulent combustion process specific to ammonia combustion.

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#### 361 **Declarations of interest**

362 None.

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