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A Relationship for Estimating the Ignition Delay of Hydrogen-Enriched Ammonia-Air Mixtures

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Abstract

Ammonia and hydrogen are two excellent solutions for decarbonization. Ammonia can be burnt as a neat fuel or in blends with hydrogen and can also be used as an energy carrier for hydrogen. In this paper, the authors used chemical kinetic mechanisms to evaluate the ignition delay of ammonia-hydrogen blends (from 10 to 50% of hydrogen by volume) using both tabulated data and a specific mathematical relationship. Using the Cantera environment, the method has been validated at first comparing the calculated data to the experimental ones. Then, the ignition delay has been calculated considering pressures from 10 to 130 bar and temperatures from 600 to 1200 K. The obtained correlation covers the whole range investigated with a mean deviation from the reference value within 5.7%.

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1. Introduction

Nowadays, ammonia[1] and hydrogen[2] are investigated as the most promising fuels allowing free CO_2 emission combustion processes (Table 1). Both these substances are carbon free, and both can be produced from renewable sources. Hydrogen shows very interesting technical properties, but its storage and distribution are difficult. Ammonia has poor combustion characteristics, but it is easily liquefiable and therefore can be easily stored and distributed. Besides, hydrogen can be obtained directly from ammonia using a cracking process[3,4] and hydrogen-ammonia blends, with a hydrogen content of about 10-20%, can effectively burn in light-duty piston engines.[5-7] Consequently, exploiting the pros and cons of these two fuels, the study of the combustion process of hydrogen-enriched ammonia-air mixtures become an interesting topic for the transportation sector.

Detailed chemical kinetic mechanisms are useful in predicting and analyzing the combustion behavior of air-fuel mixtures. However, mathematical relationships correlating overall parameters (such as laminar flame speed and ignition delay) to the main physical properties of the mixture (pressure, temperature, composition, *etc*.), could be very useful to define fast and efficient development tools for industrial purposes. In recent years, some authors investigated the combustion of ammonia-hydrogen-air mixtures proposing chemical kinetic mechanisms able to describe their oxidation pathways. Nakamura *et al*.[8] analyzed the ignition delay of ammonia-air mixtures in a microflow reactor. They considered weak flames at different equivalence ratio (0.8; 1; 1.2) and proposed a chemical kinetic mechanism able to reproduce the measured data. Otomo *et al*.,[9] starting from the work of Song *et al*.,[10] developed a chemical kinetic mechanism for ammonia-hydrogen-air mixtures. This model was able to reproduce both the laminar flame speed and ignition delay time of different kinds of mixtures at three different levels of pressure (1.4; 11; 30 bar). Stagni *et al*.[11] carried out experimental tests on a jet stirred reactor under lean conditions ($0.01 \leq \Phi \leq 0.375$) in a range of temperature from 500 to 2000 K. They also modified a mechanism previously developed for methane[12] to predict the ammonia pyrolysis and oxidation. Shrestha *et al*.[13] proposed a detailed mechanism for ammonia oxidation including NO_x formation. They considered both ammonia and ammonia-hydrogen blends. In Ref. [14] the authors focused their attention on the experimental determination of laminar flame speed for oxygen-enriched ammonia and ammonia

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hydrogen blends at high pressure and temperature to define a specific kinetic model considering also nitrogen oxides formation.

In the current literature, only a few studies presenting correlations for the calculation of both ignition delay and laminar flame speed of ammonia-air and ammonia-hydrogen-air mixture are available. Starting from a chemical kinetic approach, Goldmann and Dinkelacker[15] proposed two different correlations able to calculate the laminar flame speed of ammonia-air and ammonia-hydrogen-air mixtures respectively. Lhuillier *et al.*[16] subsequently updated these relationships to allow turbulent combustion simulations with satisfactory accuracy and low computational cost for hydrogen contents in the fuel smaller than 50%. Also, Pessina *et al.*[17] proposed a correlation for the calculation of the laminar flame speed of ammonia-hydrogen blends focusing on applications related to internal combustion engines. The effect of hydrogen addition, on the ignition delay of ammonia-air mixtures at high temperatures, was investigated in Ref. [18]. The authors considered a wide range of temperatures (from 1020 to 1945 K), two different pressure levels (1.2 and 10 bar), and a hydrogen mole fraction varying from 0 to 0.7. They compared the experimental measurements to different chemical kinetic mechanisms to test their reliability. Also, Chen *et al.*[19] proposed a correlation for the calculation of ignition delay of both neat ammonia and ammonia slightly enriched with hydrogen (95% NH_3, 5% H_2 in volume).

At present, therefore, there are no correlations capable of predicting the ignition delay of a hydrogen-enriched ammonia-air mixture when the hydrogen content becomes significant. The purpose of this work is to precisely define this correlation starting from the chemical kinetic mechanisms available in the literature. In particular, pressure, temperature and mixture compositions, typical of internal combustion engines, will be considered. This correlation could be useful for estimating the phenomena related to the mixture auto-ignition both in spark ignition and dual fuel engines.

2. Methodology

The ignition delay of stoichiometric ammonia-hydrogen-air mixtures has been investigated using the chemical mechanisms reported in Table 2. They have been mainly developed to reproduce the ammonia oxidation. However, they can also be used for hydrogen-enriched ammonia-air mixtures.[15,17]

Table 2 shows the charge conditions under which the mechanisms were validated. Simulations have been carried out using the Cantera environment[20] and imposing an ideal gas constant pressure reactor. The ignition delay has been evaluated by considering the inflection point of the temperature curve. The ignition delay is calculated as a function of the maximum derivative of the temperature curve.[21] Fig. 1 shows an example of the estimated ignition delay for one of the cases investigated.

Table 1. Ammonia properties vs. Hydrogen properties.[1,2,19]

	Ammonia	Hydrogen
Chemical formula	NH_3	H_2
Storage	Liquid [300K – 11 bar]	Compressed [300K, 700 bar]
LHV [MJ/kg]	18.8	120
Stoichiometric air to fuel ratio [-]	6.05	34.3
Heat released by a volume unit of stoichiometric air-fuel mixture [MJ/m^3]	2.81	2.88
Laminar burn velocity [m/s] at ambient condition	0.015	3.51
Octane number	130	>130
Auto-ignition temperature [K]	930	503
Explosion limit [% volume ratio]	16-28	4.5-75
Density [kg/m^3]	0.703	0.082

Table 2. Chemical kinetic mechanism details and validation ranges.

Mechanism	Nakamura [8]	Otomo [9]	Stagni [11]	Shrestha [13]
Number of species	38	33	31	135
Number of reactions	232	213	203	> 1000
Validated for:				
Pressure [bar]	1	1	1	1.4-30
Temperature [K]	300-1400	1538-2000	650-1200 (500-2000)	1428-2857
Overall Air-fuel equivalence ratio [-]	0.8/1/1.2	0.5 - 2	0.5-2 (0.01-0.375)	0.5-2
Fuel blend H_2 content	0	0.2-0.3	0	-

3. Results and discussion

In the following, the ignition delay is calculated using the chemical kinetics mechanisms presented in Table 2, are compared with experimental data available in the present literature. Then, a database for the ignition delay has been built,

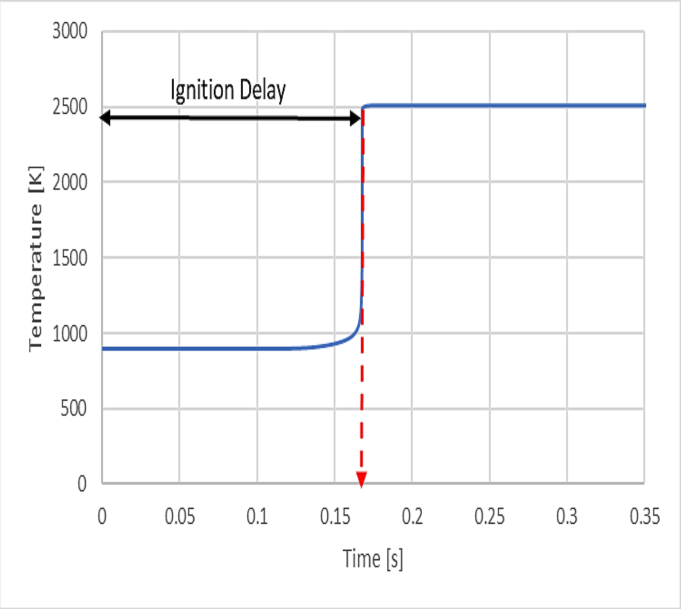

Fig. 1 Temperature profile and calculated ignition delay. 10 % hydrogen content by volume, 900 K and 10 bar.

and a mathematical relationship has been derived to correlate the calculated data to the physical conditions of the mixtures considered.

3.1 Comparison with available experimental data

At first, some calculated data have been compared to the experimental data presented in Ref. [19] to assess their reliability. Two ammonia-hydrogen blends have been evaluated: 5% of hydrogen by volume and 30% of hydrogen by volume. All the mixtures are stoichiometric, at 1.2 and 10 bar and different at temperatures. Figs. 2 and 3 report the comparisons for both 5% and 30% of hydrogen by volume.

All the mechanisms well reproduce the measured ignition delays. Increasing the pressure, the calculated data tend to underestimate the measured ones. The calculated data scatter shows a coefficient of variation ranging from about 13.9% (30% H_2 content, 1.2 bar, 1657 K) to about 27% (30% H_2 content, 1.2 bar, 1270 K). The average coefficient of variation is 17.1%. At 1.2 bar, the difference between the average ignition delay calculated with the four mechanisms and the measured one varies approximately from a minimum of less than 1% (30% of H_2 content at 1440 k) to a maximum of 22% (30% H_2, 1270 K). At 10 bar, the same difference varies approximately from a minimum of 14% (5% H_2, 1440 K) to a maximum of 30% (30% H_2, 1870 K).

Keeping in mind the comparison with the available experimental data, calculations have been carried out to obtain tabulated ignition delays as a function of pressure, temperature and hydrogen content. Pressure levels from 10 to 130 bar, temperatures from 600 to 1200 K and a Hydrogen content in the fuel blend varying from 10% to 50% have been considered. It is worth noting that all the mechanisms will be used at pressure levels higher than those for which they have been validated (Table 2). This is moreover quite usual[17-19] as the tests used for the validation of the mechanisms cannot reach excessively high pressure levels.

Figures 4 and 5 show a comparison of the ignition delay prediction for some cases. All the mechanisms provide similar results at high and medium temperatures where the ignition

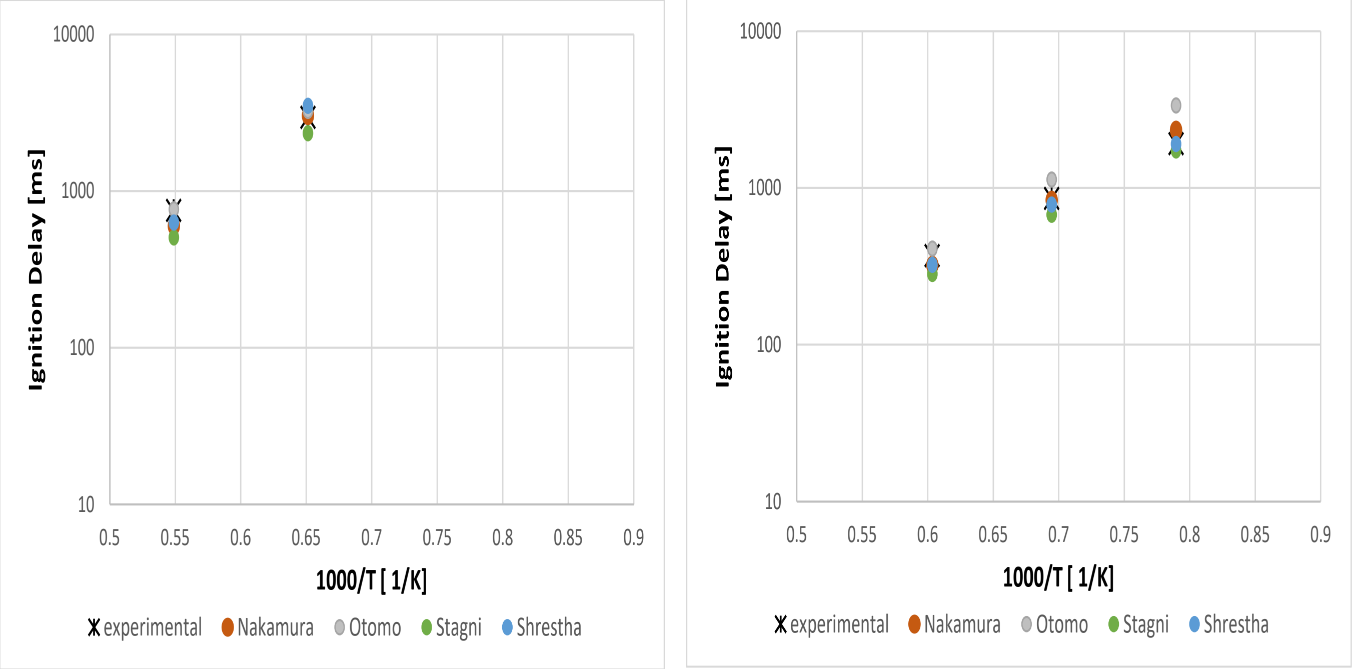

Fig. 2 Comparison with experimental data at 1.2 bar. Fuel blend 5% hydrogen content (left) and 30% hydrogen content (right).

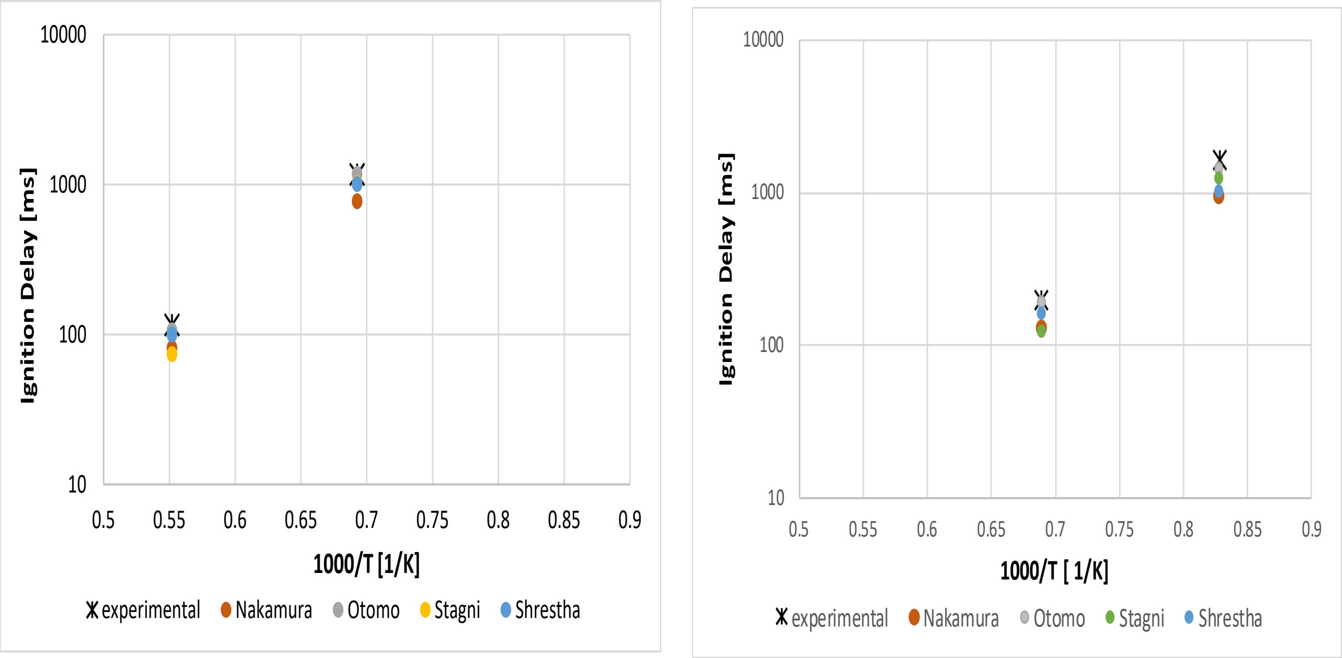

Fig. 3 Comparison with experimental data at 10 bar for 5% hydrogen content (left) and 30% hydrogen content (right).

delay varies with the temperature according to a classical Arrhenius law. Differences arise at low temperatures, approximately when the charge temperature is less than 700 K. This temperature is generally considered the auto-ignition limit for ammonia-air mixtures. For every mechanism, there is a threshold temperature below which the ignition time tends to become constant. This threshold temperature decreases as the pressure increases.

3.2 Ignition delay correlation

A fitting procedure has been performed using the Curve Fitter tool available in the Matlab environment. A temperature limit (T_{LIM}) has been found referring to the transition between an essentially constant value of the ignition delay (equal to 2000 ms, Eq. 1) and a trend well described using Eq. 2:

$$600\ K \leq T < T_{LIM}: \tau = 2000\ ms \quad (1)$$

$$T_{LIM} \leq T \leq 1200\ K: \tau = a \cdot p^m \cdot exp\left(b \cdot p^n \cdot \frac{1}{T}\right) \quad (2)$$

Where τ is expressed in ms, p is the pressure expressed in bar and T is the temperature expressed in K. The coefficients a, b, m and n are calculated as a function of the volumetric hydrogen content in the fuel blend (x_{H2}, expressed in %), as reported in Table 3. T_{LIM} varies according to Eq. 3:

$$\begin{cases} T_{LIM} = 1023.15 \quad if\ P > 70 \\ T_{LIM} = 1083.15 - 0.83 * (P - 10) \quad if\ P < 70 \end{cases} \quad (3)$$

Where pressure is expressed in bar, while temperature in K.

The correlation results have been compared with the mean

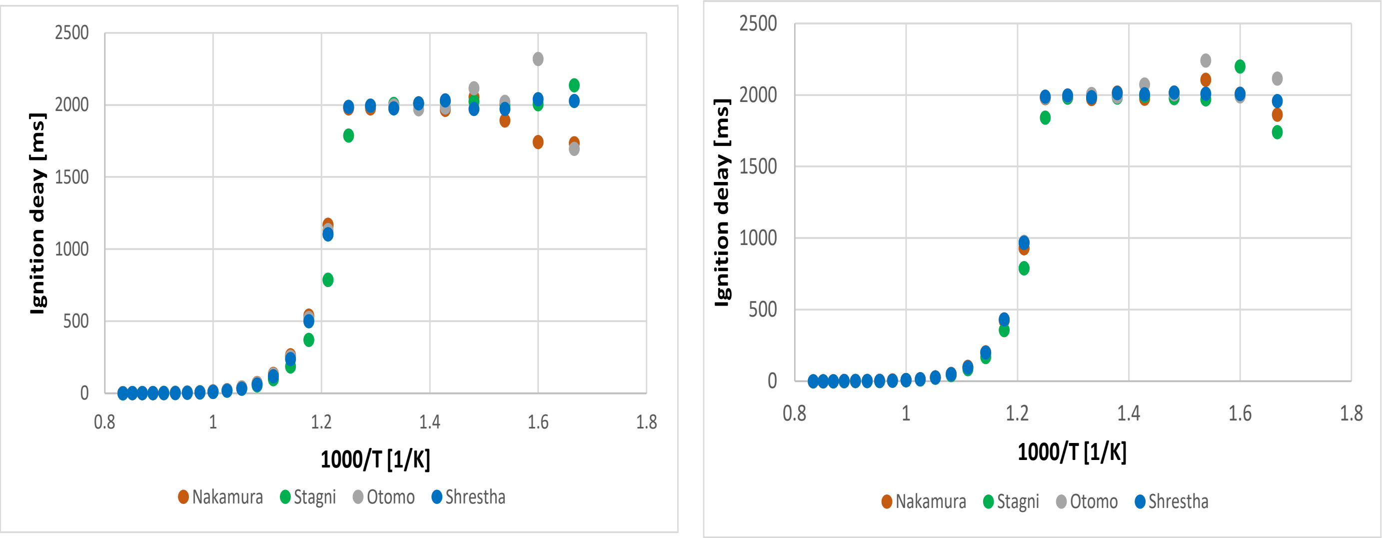

Fig. 4 Calculated Ignition delays. 10 bar, 20% H_2 content (left), 50% H_2 content (right).

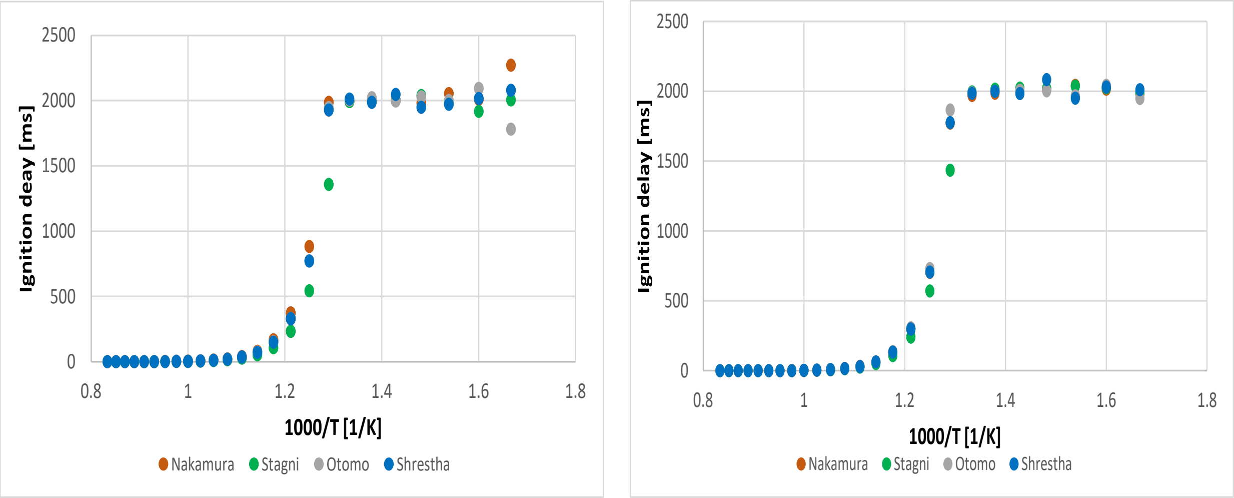

Fig. 5 Calculated Ignition delays. 55 bar, 20% H_2 content (left), 50% H_2 content (right).

Table 3. Coefficients for Eq. 2.

	$T_{LIM} \leq T \leq 825\ K$	$825\ K < T < 1000\ K$	$1000 \leq T \leq 1200\ K$
a	2.947528E-11x_{H2}^4 - 4.126567E-09x_{H2}^3 + 2.094349E-07x_{H2}^2 - 4.548702E-06x_{H2} + 3.551934E-05	1.56415E-11x_{H2}^4 - 2.25675E-09x_{H2}^3 + 1.19344E-07x_{H2}^2 - 2.74862E-06x_{H2} + 2.34252E-05	-4.65000E-13 x_{H2}^3 + 9.18857E-11 x_{H2}^2 - 5.13864E-09 x_{H2} + 1.17376E-07
b	2.966667E-01x_{H2}^3 - 3.541429E+01x_{H2}^2 + 1.296190E+03x_{H2} + 7.112000E+03	0.0408x_{H2}^3 - 6.1964x_{H2}^2 + 360.95x_{H2} + 13812	8.54167E-03x_{H2}^4 - 1.07750E+00x_{H2}^3 + 4.74958E+01 x_{H2}^2 - 8.66750E+02x_{H2} + 2.65200E+04
m	1.436667E-06x_{H2}^4 - 1.247333E-04x_{H2}^3 + 1.141333E-03x_{H2}^2 + 1.008233E-01x_{H2} - 2.782000E+00	-1.77250E-05x_{H2}^3 + 1.77354E-03x_{H2}^2 - 3.29321E-02x_{H2} - 1.45684E+00	6.08704E-06x_{H2}^4 - 7.87202E-04x_{H2}^3 + 3.57175E-02 x_{H2}^2 - 6.68488E-01x_{H2} + 3.92785E+00
n	-2.820833E-08x_{H2}^4 + 1.235833E-06x_{H2}^3 + 1.217208E-04x_{H2}^2 - 7.171583E-03x_{H2} + 1.075400E-01	-0.0009x_{H2} + 0.0521	-3.61612E-07 x_{H2}^4 + 4.70157E-05 x_{H2}^3 - 2.15676E-03 x_{H2}^2 + 4.13011E-02x_{H2}- 2.91454E-01

tabulated data coming from the chemical-kinetic mechanisms, in the pressure range of 25-130 bar and for temperatures in the range 600-1200 K. Table 4 shows an overview of the errors of the proposed correlation.

Table 4. Errors of the proposed correlation.

Mean absolute error [%]	Points with absolute error greater than 15% [%]
5.7	9.5

Figure 6 shows the percentage error maps obtained comparing the ignition delay provided by the proposed correlation and the mean tabulated data coming from the chemical-kinetic mechanisms, as a function of pressure and temperature for the different fuel mixtures considered. The contour plots have been obtained using the “thin-plate spline” interpolation method available in Matlab.

Referring to a spark ignition engine, the correlation found can be useful to estimate the knock-onset, which depends on the evolution of the ignition delay in the “so called” end gas, *i.e.* the part of the charge not yet reached by the flame during the combustion phase.

As an example, Fig. 7 shows both pressure and temperature behaviors of the end gas region for a typical light duty, four cylinders, turbocharged spark ignition engine. Data have been calculated by means of the numerical approach described by the authors in Ref. [7]. In particular, the engine burns an ammonia-hydrogen blend (15% hydrogen by volume) running at 2000 rpm and delivering 260 Nm.

Fig 8 depicts the unburned gases pressure vs temperature conditions of the overmentioned operating point within the percentage error maps of the correlations found. It is important to underline that in these conditions the proposed correlations are within the 10% error with respect to the mean calculated data predicted by the mechanisms.

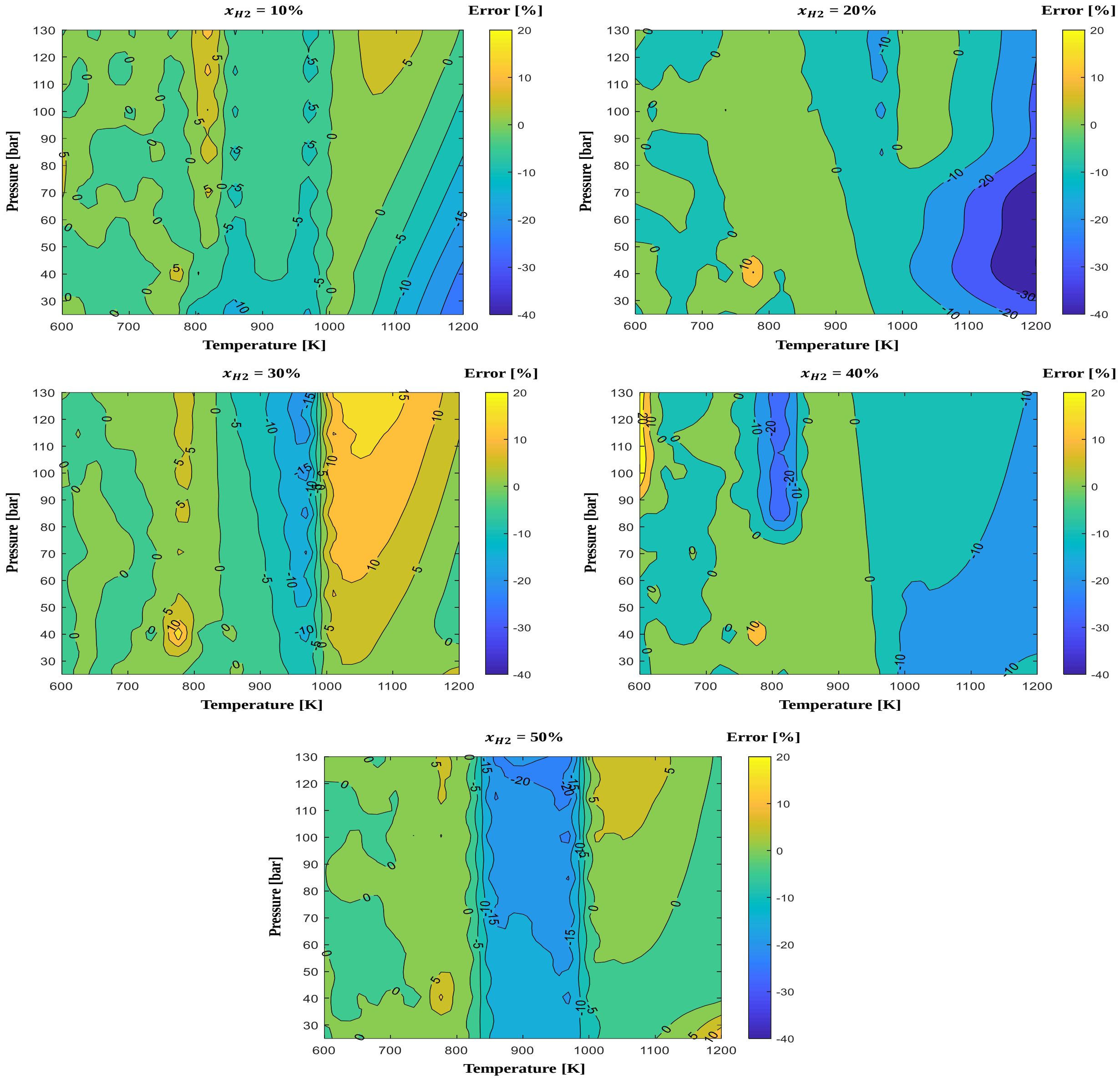

Fig. 6 percentage error maps of the proposed correlation as a function of pressure and temperature for the different fuel blends considered.

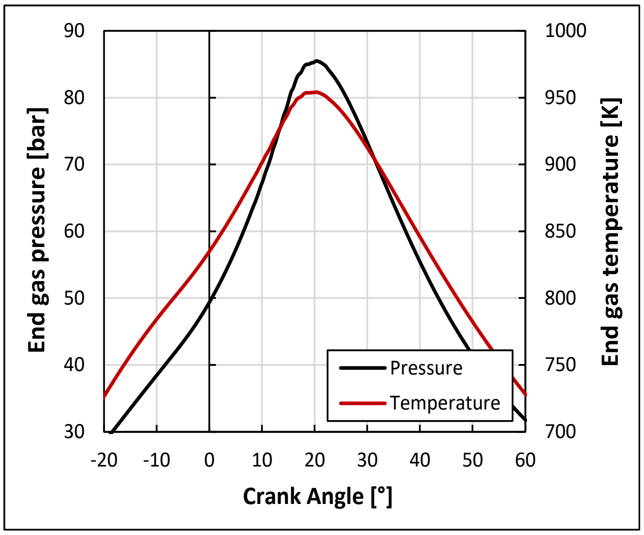

Fig. 7 in-cylinder pressure and temperature of the unburned gases during the combustion evolution as a function of crank angle for a spark-ignition engine fueled with an ammonia-hydrogen blend. Reproduced with the permission.[7]

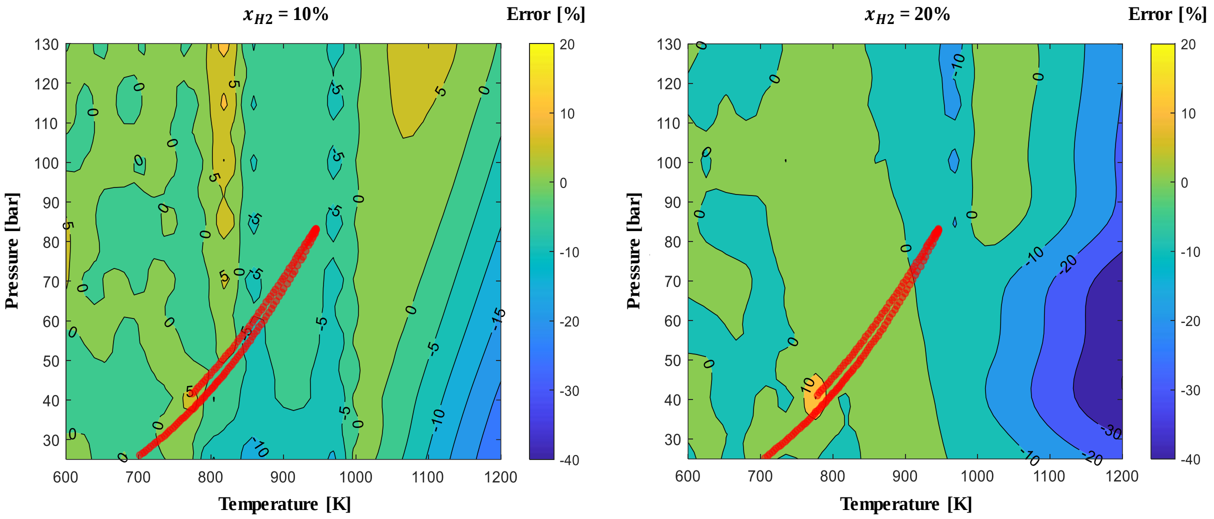

Fig. 8 Percentage error maps of the proposed correlation as a function of pressure and temperature for 10 and 20% of hydrogen by volume. Red circles show typical pressure vs temperature trends of unburned gas in a light duty SI engine fueled with an ammonia-hydrogen blend. Reproduced with the permission.[7]

4. Conclusions

In this paper a correlation for the prediction of the ignition delay of ammonia-hydrogen-air mixtures is proposed; the analysis has been carried out referring to typical engine applications. A database for the ignition delay has been obtained using the Cantera environment in which four mechanisms have been tested.

Considering the available literature data, the mechanisms reproduce quite well the measured values. Then also results obtained for a wider range of physical conditions have been considered reliable for the aim of this work. The predicted ignition delays are close enough to each other and the average coefficient of variation is equal to 17.1%. The mathematical relationship, obtained by fitting the tabulated data, allows estimating the mean predicted ignition delay with a mean deviation equal to 5.6% and only a few points (9.5%) present a deviation bigger than 15%.

In the end, the correlations presented in this work can predict the ignition delay for ammonia hydrogen mixtures considering the operating range of typical spark-ignition engines. Furthermore, it is also worth noting that these correlations can also be useful and easy to apply to a CFD code.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

References

[1] A. Valera-Medina, H. Xiao, M. Owen-Jones, W. I. F. David, P. J. Bowen, Ammonia for power, *Progress in Energy and Combustion Science*, 2018, **69**, 63-102, doi: 10.1016/j.pecs.2018.07.001.

[2] A. Onorati, R. Payri, B. M. Vaglieco, A. K. Agarwal, C. Bae, G. Bruneaux, M. Canakci, M. Gavaises, M. Günthner, C. Hasse, S. Kokjohn, S.-C. Kong, Y. Moriyoshi, R. Novella, A. Pesyridis, R. Reitz, T. Ryan, R. Wagner, H. Zhao, The role of hydrogen for future internal combustion engines, *International Journal of Engine Research*, 2022, **23**, 529-540, doi: 10.1177/14680874221081947.

[3] M. Comotti, S. Frigo, Hydrogen generation system for ammonia–hydrogen fuelled internal combustion engines, *International Journal of Hydrogen Energy*, 2015, **40**, 10673-10686, doi: 10.1016/j.ijhydene.2015.06.080.

[4] H. Yousefi Rizi, D. Shin, Green hydrogen production technologies from ammonia cracking, *Energies*, 2022, **15**, 8246, doi: 10.3390/en15218246.

[5] C. Lhuillier, P. Brequigny, F. Contino, C. Rousselle, Performance and Emissions of an Ammonia-Fueled SI Engine with Hydrogen EnrichmentSAE Technical Paper Series. 400 Commonwealth Drive, Warrendale, PA, United States: SAE International, 2019, doi: 10.4271/2019-24-0137.

[6] S. Frigo, R. Gentili, Analysis of the behaviour of a 4-stroke Si engine fuelled with ammonia and hydrogen, *International Journal of Hydrogen Energy*, 2013, **38**, 1607-1615, doi: 10.1016/j.ijhydene.2012.10.114.

[7] G. D'Antuono, D. Lanni, E. Galloni, G. Fontana, Numerical modeling and simulation of a spark-ignition engine fueled with

ammonia-hydrogen blends, *Energies*, 2023, **16**, 2543, doi: 10.3390/en16062543.

[8] H. Nakamura, S. Hasegawa, T. Tezuka, Kinetic modeling of ammonia/air weak flames in a micro flow reactor with a controlled temperature profile, *Combustion and Flame*, 2017, **185**, 16-27, doi: 10.1016/j.combustflame.2017.06.021.

[9] J. Otomo, M. Koshi, T. Mitsumori, H. Iwasaki, K. Yamada, Chemical kinetic modeling of ammonia oxidation with improved reaction mechanism for ammonia/air and ammonia/hydrogen/air combustion, *International Journal of Hydrogen Energy*, 2018, **43**, 3004-3014, doi: 10.1016/j.ijhydene.2017.12.066.

[10] Y. Song, H. Hashemi, J. M. Christensen, C. Zou, P. Marshall, P. Glarborg, Ammonia oxidation at high pressure and intermediate temperatures, *Fuel*, 2016, **181**, 358-365, doi: 10.1016/j.fuel.2016.04.100.

[11] A. Stagni, C. Cavallotti, S. Arunthanayothin, Y. Song, O. Herbinet, F. Battin-Leclerc, T. Faravelli, An experimental, theoretical and kinetic-modeling study of the gas-phase oxidation of ammonia, *Reaction Chemistry & Engineering*, 2020, **5**, 696-711, doi: 10.1039/C9RE00429G.

[12] Y. Song, L. Marrodán, N. Vin, O. Herbinet, E. Assaf, C. Fittschen, A. Stagni, T. Faravelli, M. U. Alzueta, F. Battin-Leclerc, The sensitizing effects of NO_2 and NO on methane low temperature oxidation in a jet stirred reactor, *Proceedings of the Combustion Institute*, 2019, **37**, 667-675, doi: 10.1016/j.proci.2018.06.115.

[13] K. P. Shrestha, L. Seidel, T. Zeuch, F. Mauss, Detailed kinetic mechanism for the oxidation of ammonia including the formation and reduction of nitrogen oxides, *Energy & Fuels*, 2018, **32**, 10202-10217, doi: 10.1021/acs.energyfuels.8b01056.

[14] K. P. Shrestha, C. Lhuillier, A. A. Barbosa, P. Brequigny, F. Contino, C. Mounaïm-Rousselle, L. Seidel, F. Mauss, An experimental and modeling study of ammonia with enriched oxygen content and ammonia/hydrogen laminar flame speed at elevated pressure and temperature, *Proceedings of the Combustion Institute*, 2021, **38**, 2163-2174, doi: 10.1016/j.proci.2020.06.197.

[15] A. Goldmann, F. Dinkelacker, Approximation of laminar flame characteristics on premixed ammonia/hydrogen/nitrogen/air mixtures at elevated temperatures and pressures, *Fuel*, 2018, **224**, 366-378, doi: 10.1016/j.fuel.2018.03.030.

[16] C. Lhuillier, P. Brequigny, N. Lamoureux, F. Contino, C. Mounaïm-Rousselle, Experimental investigation on laminar burning velocities of ammonia/hydrogen/air mixtures at elevated temperatures, *Fuel*, 2020, **263**, 116653, doi: 10.1016/j.fuel.2019.116653.

[17] V. Pessina, F. Berni, S. Fontanesi, A. Stagni, M. Mehl, Laminar flame speed correlations of ammonia/hydrogen mixtures at high pressure and temperature for combustion modeling applications, *International Journal of Hydrogen Energy*, 2022, **47**, 25780-25794, doi: 10.1016/j.ijhydene.2022.06.007.

[18] C. S. Mørch, A. Bjerre, M. P. Gøttrup, S. C. Sorenson, J. Schramm, Ammonia/hydrogen mixtures in an SI-engine: engine performance and analysis of a proposed fuel system, *Fuel*, 2011, **90**, 854-864, doi: 10.1016/j.fuel.2010.09.042.

[19] J. Chen, X. Jiang, X. Qin, Z. Huang, Effect of hydrogen blending on the high temperature auto-ignition of ammonia at elevated pressure, *Fuel*, 2021, **287**, 119563, doi: 10.1016/j.fuel.2020.119563.

[20] D. Goodwin, H. Moffat, R. Speth, Cantera: An Object-Oriented Software Toolkit for Chemical Kinetics, Thermodynamics, and Transport Processes, Version 2.2, 1; Cantera Developers: Warrenville, IL, USA, 2017, doi :10.5281/zenodo.6387882.

[21] M. Schiffner, M. Jud, T. Sattelmayer, Reaction kinetics analysis of dual fuel internal combustion engines based on ignition delay times using n-heptane/methane fuel blends, Proceedings of the 8th European Combustion Meeting, *Dubrovnik, Croatia*， 2017, 18-21.