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Topics: Combustion Fundamentals

Introduction

Several countries, consortia and industries are increasingly publicizing in the press their willingness to consider ammonia as one of the zero carbon footprint fuels of the future. In the case of internal combustion engines, it was previously concluded that the ammonia as fuel can be used alone if boosted operating conditions or high compression ratio [1]. But most of the cases, the addition of small hydrogen amounts is needed [2] to match all operating conditions. Even if ammonia has a low laminar flame speed and high auto-ignition temperature, the addition of hydrogen can induce knock phenomena. To predict the occurrence of knock by models, kinetics mechanisms must be improved with auto-ignition delays in similar conditions to these engine conditions, i.e., at high pressure and middle temperature in order to well dimension engines.
Until now, only a few of studies have been focused on the ignition delay measurement for ammonia and ammonia with small amount of H_2, in these conditions, by means of a Rapid Compression Machine (RCM) or a Shock Tube (ST). He et al. [3] explored the pressure range from 20 to 60 bars with initial temperature varying from 950 K to 1150 K for NH_3/H_2 from until 20% of H_2 in volume. Dai et al. [4,5] explored the IDs at 70 bars for NH_3 only at an equivalence ratio of 3 and at 60 bars, for 0.5 to 2 of equivalence ratio, but without any temperature condition under 1050 K. Pochet et al. [6] explored the 1000 K to 1100 K temperature range at two pressures, 43.4 and 65.5 bars, but lean mixtures as 0.2, 0.35 and 0.5 of equivalence ratio. More recently Liao et al. [7] determined NH_3's IDT at 30 bars between 1200 K and 1450 K.
Faced with this lack of data, the objective of this study is to provide experimental IDT obtained in a Rapid Compression Machine for 40 bars to 70 bars of pressure range with 10 bars steps, for 950 K to 1150 K with 50 K steps, and an equivalence ratio variation from lean to rich mixtures from 0.5 to 2.5 with 0.2 steps, and to evaluate the different available kinetics mechanisms to predict NH_3 alone or blended with H_2 (until 20% in vol.) under knock engine conditions. Numerical simulations were done by using the ANSYS Chemkin PRO's Closed Homogeneous Batch Reactor. Numerous kinetic mechanisms were tested in order to find the most appropriates ones. From the first experimental dataset, the best predictive mechanisms are those proposed by Keylab 2019 [10] and Polimi 2021 [16].

Materials and Methods

The experiments are done in the Rapid Compression Machine, fully described in [8], but with a difference in the dead volume and its shape. This RCM is a pneumatic compression machine where the gases are compressed in less than 35 ms and a compression gradient which allows to reach Pmax from Pmax/2 with less than 4 ms. The stroke was switched to 300 mm while the bore is 50 mm diameter. Volumes can also be adapted thanks to some additional shims to obtain the desired compression ratio. The piston is braked, close to the top dead centre, in an oil chamber. The RCM is equipped with a QC34C AVL pressure sensor with a 0-250 bars range and a linearity of 0.2%. A thermocouple was used also to measure the initial temperature inside the combustion chamber through the head cylinder for non-reactive experiments.

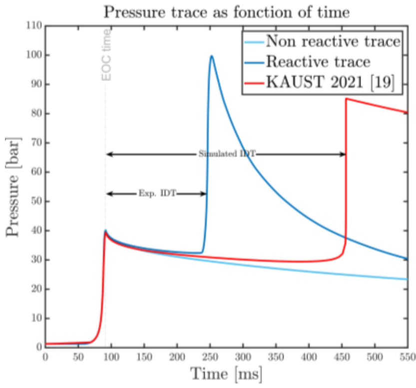

Figure 1: Experimental reactive and non-reactive pressure trace compared with a simulated pressure trace

To provide consistent experimental data to perform simulation, first experimental campaign is done with non-reactive blend, i.e., without oxygen to unable the oxidation reaction but to keep the same pressure evolution inside the combustion as they are strictly identical in term of temperature, pressure, proportion. As soon as the tank is filled with the various gases. They fill the combustion chamber by the means of

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pneumatically driven and heated valves to reach the right initial desired pressure and temperature conditions. The combustion chamber is previously vacuumed to less than a millibar. The piston is then released and compresses the gases in the combustion chamber. At least three experiments were realized at each condition to ensure repeatability and pressure were recorded in both cases to capture the thermal losses for simulations.

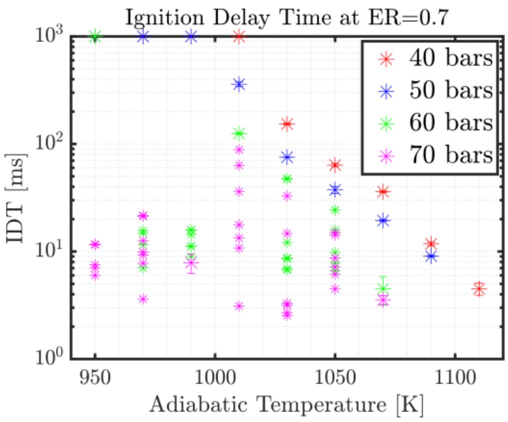
Study parameters	Values
Bore [mm] & Stroke [mm]	50 - 300
Time Pmax/2 to Pmax [ms]	3.5
Max. piston velocity [m/s]	11.5
Piston acceleration [m/s^2]	1500
Piston deceleration [m/s^2]	4500
Deceleration time [s]	5
Crevice volume [cm^3]	9.94
Compression Ratio []	11.75
Compression Temperature [K]	600 - 1150
Compression Pressure [bar]	0 – 70
Shim [mm]	12.7

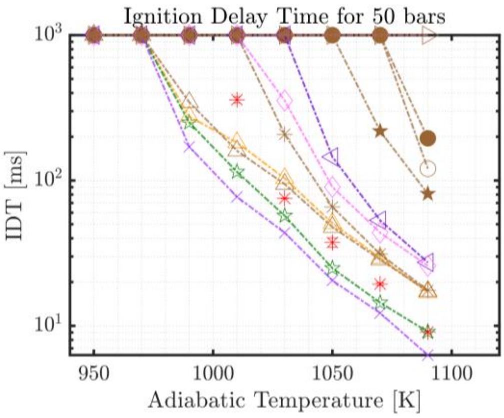
Table 1: Main characteristics of the RCM

Results and Discussions

In Figure 1, an example of IDT obtained for a 0.7 equivalence ratio mixture (NH_3=0.16388; AR=0.660535; O_2=0.175585 in molar fraction), without hydrogen for different pressures from 40 bars to 70 bars, by steps of 10 bars. The symbols at 1000 ms represent the conditions without ignition. When the combustion occurs before the compression conditions append, no indication is put on the graph (as 60 bars and 1090 K for example). For higher pressure, ammonia's IDTs look like very unstable, in this case, instead of having an error bar related to three to four points discrepancy, all experimental points are represented with a smaller size (see for 60 and 70 bars).

The experimental data (Figure 1.a) confirm that for this ER (0.7), the higher the temperature goes the shorter the IDT is as for the pressure. The comparison between some mechanisms and the experimental data in Figure 1.b, indicate different predictions than experimental data tendencies. Keylab 2019 [..] mechanism seems to be the one that matches the best for the lowest temperature and temperature above 1030 K, but it overpredicts at 990 and 1010 K. Polimi 2021 and 2023 mechanisms predict same tendency than Keylab 2019 but underpredict above 1030 K with an increase of the difference as the temperature increases. However, under this temperature, the overestimate is less than from Keylab 2019 mechanism.





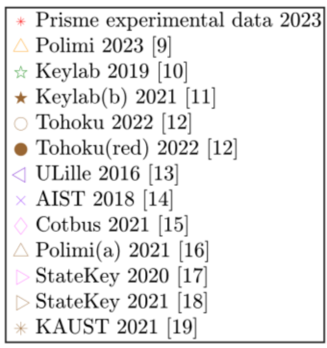


Figure 2: (a-left) Ignition Delay Time at ER=0.7 as function of Temperature for 40 to 70 bars with 10 bars steps. (b-right) Comparison between experimental IDT and simulated IDT from 12 kinetics mechanisms at 50 bars.

A CFD study has been done with Converge software to understand the 40 and 70 bars discrepancy but as no difference for turbulence and temperature field between 40 and 70 bars configurations was found, the main hypothesis is related to chemical kinetics phenomena, which require other complementary studies.

Conclusions

Experimental IDTs of ammonia/air/argon mixture at an equivalence ratio of 0.5 and 0.7 have been acquired by the means of the PRISME's RCM for high pressure conditions (from 40 to 70 bars). For the highest pressures, i.e., 60 and 70 b, the IDTs for shot to shot show a very high discrepancy for all tested temperature conditions, contrary to the 40 and 50 bars conditions. Moreover, numerous kinetics oxidation mechanisms have been tested, some of them are close to the experimental data of this study for some conditions but none of the mechanisms fit data well, even if the tendency is globally well predicted by mechanisms.

References

[1] Mounaïm-Rousselle C, Mercier A, Brequigny P, Dumand C, Bouriot J, Houillé S. Performance of ammonia fuel in a spark assisted compression Ignition engine. *International Journal of Engine Research. 2022;23(5):781-792. doi:10.1177/14680874211038726*

[2] Mounaïm-Rousselle, C., Bréquigny, P., Dumand, C., Houillé, S., Operating limits for ammonia fuel spark-ignition engine. Energies 14 (2021), *14, 4141. https://doi.org/10.3390/en14144141*

[3] He, X., Shu, B., Nascimento, D., Moshammer, K., Costa, M., & Fernandes, R. X. (2019). Auto-ignition kinetics of ammonia and ammonia/hydrogen mixtures at intermediate temperatures and high pressures. *Combustion and Flame*, *206*, 189–200. https://doi.org/10.1016/j.combustflame.2019.04.050

[4] Dai, L., Gersen, S., Glarborg, P., Levinsky, H., & Mokhov, A. (2020). Experimental and numerical analysis of the autoignition behavior of NH3 and NH3/H2 mixtures at high pressure. *Combustion and Flame*, *215*, 134–144. https://doi.org/10.1016/j.combustflame.2020.01.023

[5] Dai, L., Gersen, S., Glarborg, P., Mokhov, A., & Levinsky, H. (2020). Autoignition studies of NH3/CH4 mixtures at high pressure. *Combustion and Flame 218*, 19–26. https://doi.org/10.1016/j.combustflame.2020.04.020

[6] Pochet, M., Dias, V., Moreau, B., Foucher, F., Jeanmart, H., & Contino, F. (2019). Experimental and numerical study, under LTC conditions, of ammonia ignition delay with and without hydrogen addition. *Proc. Combust. Inst.*, *37*(1), 621–629. https://doi.org/10.1016/j.proci.2018.05.138

[7] Liao, W., Chu, Z., Wang, Y., Li, S., & Yang, B. (2022). An experimental and modeling study on auto-ignition of ammonia in an RCM with N2O and H2 addition. *Proc. Combust. Inst.* 000, 1-9. https://doi.org/10.1016/j.proci.2022.07.264

[8] Pochet, M., Dias, V., Moreau, B., Foucher, F., Jeanmart, H., Contino, F., Experimental and numerical study, under LTC conditions, of ammonia ignition delay with and without hydrogen addition, Proc. Combust. Inst. 37 (2019). https://doi.org/10.1016/j.proci.2018.05.138

[9] Stagni, A., Suphaporn Arunthanayothin, Dehue, M., Herbinet, O., Battin-Leclerc, F., Bréquigny, P., Mounaïm-Rousselle, C., Tiziano Faravelli (2023). Low- and intermediate-temperature ammonia/hydrogen oxidation in a flow reactor: experiments and a wide-range kinetic modeling. *Chemical Engineering Journal, submitted*

[10] B. Mei, X. Zhang, S. Ma, M. Cui, H. Guo, Z. Cao, Y. Li, (2019) Experimental and kinetic modeling investigation on the laminar flame propagation of ammonia under oxygen enrichment and elevated pressure conditions *Combustion and Flame 210 236–246*. https://doi.org/10.1016/j.combustflame.2019.08.033

[11] Mei, B., Ma, S., Zhang, X., & Li, Y. (2021). Characterizing ammonia and nitric oxide interaction with outwardly propagating spherical flame method. *Proceedings of the Combustion Institute*, *38*(2). https://doi.org/10.1016/j.proci.2020.07.133

[12] Gotama, G. J., Hayakawa, A., Okafor, E. C., Kanoshima, R., Hayashi, M., Kudo, T., & Kobayashi, H. (2022). Measurement of the laminar burning velocity and kinetics study of the importance of the hydrogen recovery mechanism of ammonia/hydrogen/air premixed flames. *Combustion and Flame*, *236*. https://doi.org/10.1016/j.combustflame.2021.111753

[13] Lamoureux, N., Merhubi, H. El, Pillier, L., de Persis, S., & Desgroux, P. (2016). Modeling of NO formation in low pressure premixed flames. *Combustion and Flame*, *163*. https://doi.org/10.1016/j.combustflame.2015.11.007

[14] Otomo, J., Koshi, M., Mitsumori, T., Iwasaki, H., & Yamada, K. (2018). Chemical kinetic modeling of ammonia oxidation with improved reaction mechanism for ammonia/air and ammonia/hydrogen/air combustion. *International Journal of Hydrogen Energy*, *43*(5), 3004–3014. https://doi.org/10.1016/j.ijhydene.2017.12.066

[15] Shrestha, K. P., Lhuillier, C., Barbosa, A. A., Brequigny, P., Contino, F., Mounaïm-Rousselle, C., Mauss, F. (2021). An experimental and modeling study of ammonia with enriched oxygen content and ammonia/hydrogen laminar flame speed at elevated pressure and temperature. *Proc. Combust. Inst.*, *38*(2), 2163–2174. https://doi.org/10.1016/j.proci.2020.06.197

[16] Arunthanayothin, S., Stagni, A., Song, Y., Herbinet, O., Faravelli, T., & Battin-Leclerc, F. (2021). Ammonia-methane interaction in jet-stirred and flow reactors: An experimental and kinetic modeling study. In *Proceedings of the Combustion Institute* (Vol. 38). https://doi.org/10.1016/j.proci.2020.07.061

[17] Han, X., Wang, Z., He, Y., Zhu, Y., & Cen, K. (2020). Experimental and kinetic modeling study of laminar burning velocities of NH3/syngas/air premixed flames. *Combustion and Flame*, *213*. https://doi.org/10.1016/j.combustflame.2019.11.032

[18] Wang, Z., Han, X., He, Y., Zhu, R., Zhu, Y., Zhou, Z., & Cen, K. (2021). Experimental and kinetic study on the laminar burning velocities of NH_3 mixing with CH_3OH and C_2H_5OH in premixed flames. *Combustion and Flame*, *229*. https://doi.org/10.1016/j.combustflame.2021.02.038

[19] Zhang, X., Moosakutty, S. P., Rajan, R. P., Younes, M., & Sarathy, S. M. (2021). Combustion chemistry of ammonia/hydrogen mixtures: Jet-stirred reactor measurements and comprehensive kinetic modeling. *Combustion and Flame*, *234*. https://doi.org/10.1016/j.combustflame.2021.111653