

Optimization of NH₃ chemical kinetics for low temperature combustion at high pressures

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Introduction

Nowadays, the global warming issue is demanding the energy scenario to change. In particular, recent agreements [1] prompted most countries to move toward a reduction in Greenhouse Gas (GHG) emissions. Indeed, the best way to achieve such objective is by replacing fossil fuels with Renewable Energy Sources (RES), which, on the other hand, do not guarantee continuous power production. Power to fuel is a possible solution to compensate for the fluctuations in energy production by means of RES. Hydrogen is a promising energy carrier as it can be produced via water electrolysis taking advantage of the surplus power generation from wind and solar power plants. The problem with hydrogen is more related to storage density and transportation, as it can be liquefied at temperatures below 20 K, or carried in gas phase using high pressures (~700 bar). Also, it has a very wide flammable range, which represents a safety issue as it may lead to catastrophic events, such as explosions. One way to bypass these complications is to convert H₂ to other molecules with different properties. Among all the hydrogen carriers, ammonia shows a very high potential, in both economic and technical aspects [2], as it has very high H₂ density and it can be liquefied at pressures higher than 9.9 bar at a temperature of 298 K. However, laminar flame speed measurements for ammonia in different conditions [3, 4] showed its limited reactivity. The average burning velocity for stoichiometric ammonia/air mixtures was found to be around 7 cm/s, which could cause early blow-off or difficulty in providing ignition. Recently, ammonia combustion doped with hydrogen was tested in an internal combustion engine [5, 6], and for swirling gas turbine combustors [7], where it was found to have significant NO_x emissions. Nevertheless, a combination of humidity and secondary airflow at elevated pressure was lately found to reduce the emissions in comparable systems [6, 8]. As hydrogen can be produced through ammonia dissociation [9, 10], additional H₂ storage is not required for ammonia combustion. The kinetics of ammonia oxidation has been of interest for its role in both fuel NO_x formation and abatement through selective non-catalytic reduction (SNCR)[11]. Almost all ammonia oxidation mechanisms available today are based on the pioneering work from Miller and Bowman [12], which validation was based on the several species measurements and laminar flame speeds [13, 14]. Lately, Glarborg et al. [15] reviewed the nitrogen chemistry in combustion, including the subset related to amines. The latter work highlights the importance of reactions $\text{NO} + \text{NH}_2 = \text{NNH} + \text{OH}$ and $\text{NO} + \text{NH}_2 = \text{N}_2 + \text{H}_2\text{O}$ for NH₃ consumption rate and NO/N₂ selectivity. Another major product channel was found to be related to the branch involving $\text{NO}_2 + \text{NH}_2 = \text{N}_2\text{O} + \text{H}_2\text{O}$ and $\text{NO}_2 + \text{NH}_2 = \text{H}_2\text{NO} + \text{NO}$. While for fuel lean conditions and high pressures the interaction between HO₂

and NH_2 could lead to nitroxide formation, which is then able to react with O_2 through $\text{H}_2\text{NO} + \text{O}_2 = \text{HNO} + \text{HO}_2$. Recently, Pochet et al. [16] measured the ignition delay time (IDT) for ammonia/hydrogen lean mixtures in a Rapid Compression Machine (RCM) at high pressures and low temperature conditions. Their comparison between experimental and zero-dimensional simulations with detailed kinetics led to a conclusion that several existing mechanisms give inaccurate predictions for the ignition delay time in such mixtures. The aim of this work is to propose new reaction rates parameters, derived from optimization techniques, to improve a mechanisms predictability with respect to ignition delay time of ammonia/hydrogen mixtures. Optimization and Uncertainty Quantification are powerful tools for mechanism development and improvements [17]. For instance, the widely used GRI-Mech 3.0 [18] mechanism was developed using the aforementioned techniques. Analogous methodologies have also been applied on hydrogen [19], syngas [20], methane and biomass pyrolysis gas [21] combustion kinetics.

Methodology

This work was based on the experimental data from Pochet et al [16] which constitutes of auto-ignition delay times for lean ammonia and ammonia/hydrogen blends in a RCM with elevated pressure, low temperature and without dilution. The experimental pressure traces were used to infer corresponding volume histories applying the so called adiabatic core assumption. The latter volume histories were then used to simulate RCM deviations from ideal behaviours using a batch reactor in OpenSMOKE++ [22], following the procedure described by Sung and Curran [23]. The ignition delay time was then computed as the time elapsed between the maximum pressure time-derivative and the minimum volume, corresponding to the end of compression. The chemistry was modelled adopting a new kinetic mechanism from CRECK modelling group, involving low-hydrocarbons (C1-C3) and nitrogen chemistry. The selection of the parameter for optimization was carried out with a new technique, in two different steps. First, a local sensitivity analysis, with respect to temperature, was performed. From here, a sensitivity vector was extracted from the onset of ignition, and its absolute values were computed for each experimental data point. Subsequently an average sensitivity vector based on the overall data set was derived and used to compute a Cumulative Sensitivity Function (CSF). This allowed to select a number of reactions related to a certain percentage of the total sensitivity. Thereafter, their parameters were considered for further evaluations. The second step consisted in a local brute force sensitivity analysis capable of linking the ignition delay time variations to every single parameter directly. The latter process was performed by coupling OpenSMOKE++[22] and Dakota[24], using a python interface. The parameters related uncertainty were computed by following the methodology reported in [21]. Similarly as in the first step a CSF was derived for the considered parameters, although here the uncertainty range for each parameter was taken into account, resulting in a Cumulative Impact Function (CIF). Again a certain percentage of the global impact was considered, and a final subset of parameters was selected. Then the optimization was performed by coupling the two software OpenSMOKE++[22] and Dakota[24], using a C++ interface. The Dakota toolbox was developed by Sandia National Laboratories, and it is used to interface simulation codes with a number of different analysis tools, such as optimization, uncertainty quantification, sensitivity analysis, parameter studies, etc. The specific tool used for this study was the Evolutionary Algorithms optimization tool, which is suitable for strongly non-linear global optimization problems, such as the optimization of chemical kinetics. Evolutionary Algorithms uses the approach of "survival

of the fittest", which is initially determined by a set of random samples based on the parameter space. The samples which provides the best objective function value, is then chosen and further mutations/combinations of these samples are used in order to find the globally optimal point in the parameter space.

Results

Since the pure ammonia represents the biggest part of the average error on the overall data set, initially, only the experimental data with pure ammonia was considered in the optimization process. Thus, considering 36 out of 49 experimental conditions, a CSF was built using the methodology described above. By taking into account for 80% of the latter CSF, the reactions reported in Table 1 were considered for further evaluation. It's worth mentioning that this method automatically detected the same reactions that Glarborg et al. [15] found out to be relevant for these conditions. The nominal expressions for these reactions rates adopted for the Polimi mechanism are referenced in 1, together with the way they were determined. This 7 reactions rates are expressed using 19 parameters in total.

Table 1: List of reactions which showed high sensitivity to the ignition delay time.

Reaction Number	Reaction Formula	Reference	Source
R1865	$\text{HO}_2 + \text{NH}_2 = \text{OH} + \text{H}_2\text{NO}$	[25]	ab-initio
R1901	$\text{NO}_2 + \text{NH}_2 = \text{H}_2\text{O} + \text{N}_2\text{O}$	[15]	Experiments
R1902	$\text{NO}_2 + \text{NH}_2 = \text{NO} + \text{H}_2\text{NO}$	[15]	Experiments
R1903	$\text{NO} + \text{NH}_2 = \text{N}_2 + \text{H}_2\text{O}$	[26]	Experiments
R1904	$\text{NO} + \text{NH}_2 = \text{OH} + \text{NNH}$	[26]	Experiments
R2028	$\text{H}_2\text{NO} + \text{O}_2 = \text{HO}_2 + \text{HNO}$	[15]	ab-initio

The impact related to each of the kinetic parameter on the IDT was then evaluated through a local brute force sensitivity study. Again, 80% of the aforementioned CIF was considered, resulting in a subset of 12 parameters, which are displayed in Table 2, together with their nominal, maximum and minimum value. The optimum values presented in Table 2 were found by the optimizer, based on minimizing the sum of squared residuals. A comparison between the performance of the nominal and the optimized kinetic mechanism can be appreciated in Figure 1. As expected, the performance for the pure ammonia case shows large improvements. However, for the two cases with includes 10% and 25%vol. percent of hydrogen in the fuel mixture, there were no drastic changes. This is to be expected as these experimental data points were not included as targets in the optimization, as well as for the selection of parameters. There is therefore room for improvements in this aspect, especially for the 10%vol hydrogen case where the mechanism shows much faster ignition with respect to the experimental measurements. However, the sum of squared residuals for the complete set of data was reduced from 5.44×10^{-4} to 3.71×10^{-5} , which is more than one order of magnitude lower.

Table 2: List of kinetic parameters taken in account for optimization in this work, with related nominal, maximum, minimum and optimum values.

Reaction	Parameters	Nominal	Minimum	Maximum	Optimum
R1865	A	2.50E+10	1.25E+10	4.99E+10	2.29E+10
R1901	A	2.20E+08	8.76E+07	5.53E+08	2.85E+08
	β	0.11	-0.759	0.979	-0.0184
	E	-1186	-2.43E+03	61.79	-1540
R1902	A	8.60E+08	3.42E+08	2.16E+09	8.05E+08
	β	0.11	-0.759	0.979	0.232
	E	-1186	-2430	61.79	-1220
R1903	E	870	558	1180	878
R1904	β	0.29	0.0728	0.507	0.284
	E	-866	-1180	-554	-772
R2028	A	0.23	0.0835	0.63	0.21
	β	2.99	2.04	3.95	2.98

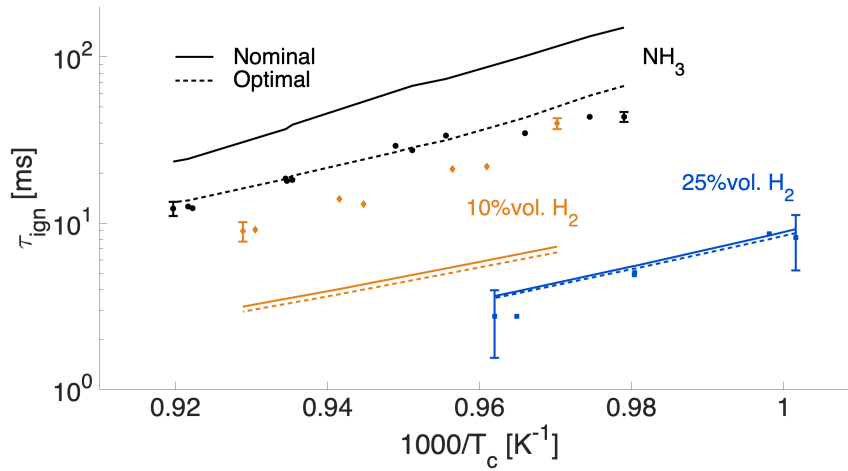


Figure 1: Ignition delay time for pure ammonia, mixture of 10%vol. and 25%vol. hydrogen vs temperature after the compression stroke. The experimental data are from [16].

Conclusion

The evaluation of the ignition delay time for ammonia combustion, in an RCM at intermediate temperatures, is still not accurately predicted by even the most updated kinetic mechanism. In this work, the optimization of said kinetic mechanism was therefore performed in order to better predict this key quantity for ammonia combustion. By applying a new approach for selecting which kinetic parameters to optimize, 12 parameters were optimized, and the performance with respect to the experimental data was drastically improved for pure ammonia combustion. For future prospects, the optimization of the mixtures including both ammonia and hydrogen will be considered, as well as other experimental data available in the literature.

Acknowledgments

The first Author acknowledges the support of Funds pour la Recherche Scientifique (FNRS) through a FRIA fellowship of the project “HOPTIMAL: Hierarchical development of OPTimised kinetic Mechanisms for Advanced combustion technoLogies”. This work has also received funding from the European Union's Horizon 2020 research and innovation program under the Marie Skłodowska-Curie grant agreement No 643134, and the research of A. Parente was sponsored by the European Research Council, starting grant 714605.

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