Optimization of chemical kinetics for Biogas combustion in MILD conditions

Magnus Fürst[1,2,4], Pino Sabia[3], Marco Lubrano Lavadera[3], Mariarosaria de Joannon[3], Alessio Frassoldati[4] and Alessandro Parente[1,2]

1. Aero-Thermo-Mechanical Department, Université Libre de Bruxelles, Brussels, Belgium
2. Université Libre de Bruxelles and Vrije Universiteit Brussel, Combustion and Robust Optimization Group (BURN), Bruxelles, Belgium
3. Istituto di Ricerche sulla Combustione-CNR, Naples, Italy
4. Department of Chemistry, Materials and Chemical Engineering, Politecnico di Milano, Milano, Italy

INTRODUCTION

The European energy market is moving towards a more carbon neutral energy production. The use of so called bio-fuels are therefore extremely important considering that combustion processes are the largest portion of our energy production, and according to all projections, this will not change drastically in the near future. Due to the fact that bio-fuels have a much lower calorific value compared to conventional fuels, an efficient combustion technology is needed to achieve these goals. One such technology is Moderate or Intense Low-oxygen Dilution (MILD) combustion. MILD conditions are reached when the fuel stream have a temperature above the self-ignition temperature of the fuel at the same as the maximum temperature increase compared to the inlet temperature is lower than the self-ignition temperature of the fuel [1]. This moderate temperature increase reduces the temperature peaks in the combustion process, which sequentially reduce the thermal NO_x created in the process. One methodology to reach MILD conditions is by recirculating the hot combustion products back to the fuel inlet, thus preheating and diluting the fuel stream. This creates very good mixing between the fuel and oxidizer, which in turn reduces the mixing time scale to the same order of magnitude as the chemical time scale, i.e. the Damköhler number is equal to 1. The use of detailed chemistry is therefore needed while simulating these conditions. But due to the increased concentration of combustion products and the lower temperature in the reaction zone, compared to conventional combustion, existing detailed chemical mechanism, which have been developed and validated against conventional combustion targets, are under-performing in MILD conditions. In order to improve the performance of existing chemical mechanisms with respect to MILD combustion, optimization through the use of Uncertainty Quantification (UQ) can be applied to this problem. There are several examples [2, 3, 4] in literature where UQ has been used for optimizing kinetic parameters in order to improve the performance of a mechanism with respect to specific experimental targets. This work is therefore dedicated to apply similar methodologies to improve the performance of existing detailed chemical mechanism with respect to MILD combustion.

METHODOLOGY

The experimental data use in this work is from Sabia et al. [5] and constitutes of auto-ignition delay times for biogas in a Plug Flow Reactor (PFR) at different inlet temperatures and mixture compositions. The oxidizer is diluted in order to ensure that MILD conditions are reached. The reactor consists of a 140 cm long tube with a diameter of 1 cm which was completely enclosed

corresponding author: magnus.furst@ulb.ac.be

inside a heater to minimize heat loses. The temperature along the axis of the reactor was measure by a series of N-type thermocouples located every 5 cm along the axis. The auto-ignition delay time was then evaluated as the time elapsed before the mixture had reached a temperature 10 K higher than the inlet temperature of the mixture. The simulations in this work were performed with the open-source software OpenSMOKE++ [6, 7].

Due to the fact that partially oxidized compounds are present in the fuel (biogas), an oxygen ratio (Ω) is used rather than the equivalence ratio as suggested in [8].

The UQ process in this work was performed within the framework of the so called Bound-To-Bound Data Collaboration (B2B) [2] method which is a deterministic approach of optimizing the chemical kinetics with respect to given experimental data and uncertainty bounds.

In order to determine which of the kinetic parameters to include in the UQ process, a so called impact factor ranking was performed. The impact factor constitutes of the absolute value of the sensitivity coefficient multiplied with the uncertainty factor of the reaction in question. This was initially introduced by Warnatz in [9] as a measure to know for which reactions more experimental work is necessary. In this work it is instead used as an indication of how impactful, changing the kinetic parameters of one reaction would be with respect to the Quantity of Interest (QoI).

The sensitivity coefficients were evaluated with respect to temperature at the moment of ignition and the uncertainty factors were extracted from the Baulch et al. database [10]. Once the reactions with the highest impact factor has been determined, the kinetic parameters are evaluated within their physical limits specified by their corresponding uncertainty factor, and new parameter values are found where consistency within the experimental uncertainty bounds is achieved.

RESULTS

An initial study of different available detailed chemical mechanisms was performed. The mechanisms with corresponding reference, number of species and number of reactions are available in Table 1 below.

Table 1: List of chemical mechanism used in this work with, reference, number of species and number of reactions.

Chemical Mechanism	Reference	Number of species	Number of reactions
AramcoMech 1.3	[11]	124	766
AramcoMech 2.0	[12]	502	2716
Galway	[13]	293	1593
GRI 2.11	[14]	49	279
GRI 3.0	[15]	53	325
POLIMI C1-C3 V. 1412	[16]	107	2642
San Diego V. 2016-12-14	[17]	57	268
Zhukov	[18]	549	2518

The results for Ω = 1.67 in 90 % dilution of nitrogen are shown in an Arrhenius plot in Figure 1, where the auto-ignition delay time is plotted in logarithmic scale versus one thousand divided by the inlet temperature. The experimental data are represented by the scatter with corresponding experimental uncertainty for each point and the different mechanism results are represented by the colored solid lines. Only one case is presented here due to page restriction.

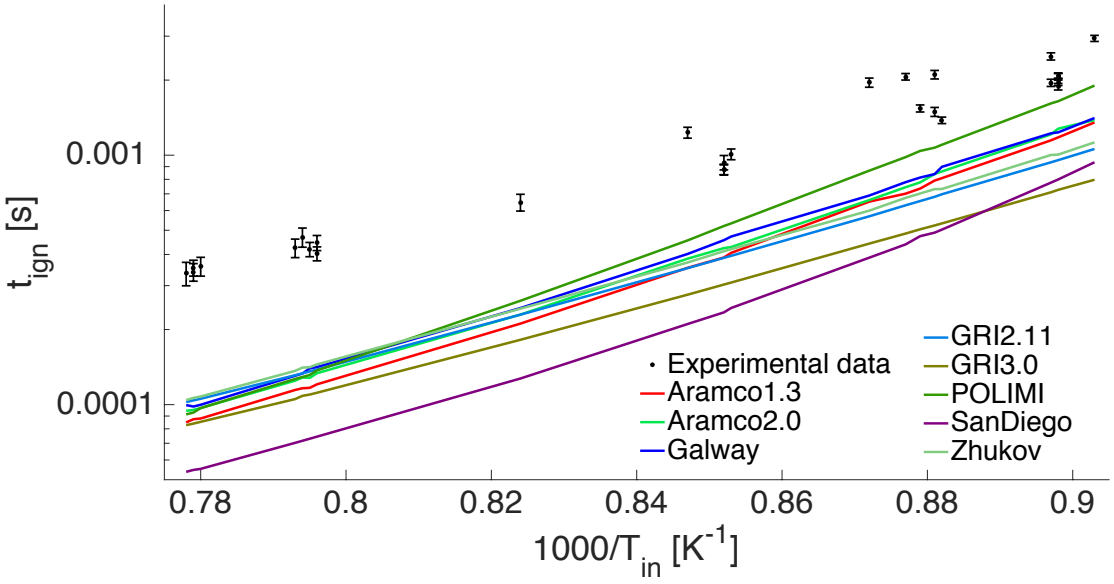

Figure 1: Auto-ignition delay times at different inlet temperatures at $\Omega = 1.67$ and 90 % dilution of nitrogen. The experimental data from [5] are represented by the black dots with corresponding uncertainty bars and the simulation results from the different chemical mechanisms presented in Table 1 are represented by the solid colored lines.

Based on this primary analysis, the POLIMI mechanism seems to be performing the best with respect to the experimental data, especially at low inlet temperatures. This mechanism was therefore used for the impact factor analysis. The reaction which overall showed to have the highest impact was: $O_2 + H = O + OH$. Although the uncertainty factor for this reaction is quite low ($10^{0.2}$), it is very sensitive with respect to temperature at the moment of ignition for these conditions.

CONCLUSION

The initial evaluation of different chemical mechanisms show that none of the mechanism are able to predict the experimental results accurately. This indicates that there are room for improvements. The analysis also show that the POLIMI mechanism is performing better with respect to the experimental data. The use of this mechanism for further work will therefore be initiated based on the framework of UQ and these preliminary results endorses that.

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