THE OPTIMIZATION OF CHEMICAL KINETICS WITH RESPECT TO MILD COMBUSTION

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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 [1]. MILD conditions are reached when the fuel stream have a temperature above the self-ignition temperature of the fuel at the same time 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 NOx 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 close to unity. 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 [2–5] 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.

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Experimental data

The experimental data used in this work was extracted from [6] and consists of ignition delay time of biogas in a Plug Flow Reactor at atmospheric conditions. A mixture of biogas and air, diluted with nitrogen at an overall concentration of 90%, was injected at different inlet temperatures and oxygen ratios (Ω) [7]. The reference composition used for the fuel was 1% C_2H_4, 2% C_2H_6, 10% CH_4, 25% CO and 62% CO_2.

The ignition delay time was defined as the moment where the mixture has reached 10 K higher temperature with respect to the inlet temperature. These conditions were reproduced using the open-source software OpenSMOKE++ [8].

Optimization procedure

In order to determine which kinetic parameters to optimize, an initial screening of the reactions was performed based on a so-called impact factor [9].

The range of each parameter was then determined using the uncertainty parameter (f) for each reaction, which was used as a base for sampling and creating surrogate models with respect to each experimental data point. These surrogate models were then used to evaluate each possible combination of kinetic parameters, that still respected the uncertainty bounds of the rate coefficients, in order to find which combination that resulted in the optimal solution. This was evaluated by calculating the sum of least squared errors for each combination evaluated.

Results

An initial evaluation of different available detailed chemical mechanism was performed in order to determine which was closest in predicting the experimental values. A list of these mechanisms together with reference, number of species, number of reactions and average deviation from the experimental data are listed in Table 1. A brief discussion regarding the choice each mechanism is presented as follows:

- Both Aramco 1.3 and 2.0 were developed for combustion of C1-C4 species.
- The mechanism referred to as Galway was developed for natural gas and species up to C5.
- The GRI mechanisms were developed for natural gas combustion and are not necessarily suitable for biogas combustion. However, due to the fact that

these two mechanisms are widely used in the combustion community, the authors did not see any harm in evaluating their performance with respect to evaluated conditions. Same applies for the San Diego mechanism.

- The POLIMI mechanism was developed for combustion of C1-C3 species.
- The Zhukov mechanism is an extension of the GRI 1.2 mechanism together with the LLNL mechanism to include the oxidation of alkanes.

Considering the composition of the fuel, these mechanisms were therefore deemed reasonable for an initial evaluation.

Table 1 - List of chemical mechanisms used in this work with reference, number of species, number of reactions and average deviation from the experimental data.

Mech.	Ref.	# S	# R	Av. dev. [%]
Aramco 1.3	[10]	124	766	95.54
Aramco 2.0	[11]	502	2716	84.06
Galway	[12]	293	1593	88.30
GRI 2.11	[13]	49	279	100.2
GRI 3.0	[14]	53	325	115.3
POLIMI	[15]	107	2642	82.90
San Diego	[16]	57	268	117.0
Zhukov	[17]	549	2518	98.42

The results for these mechanisms are show only for one case, namely stoichiometric conditions in Figure 1. However, it should be noted that this work is based on more experimental data, but due to page limitations only one case is shown here.

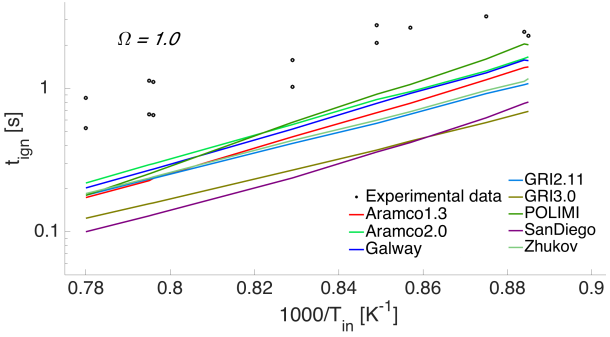

Figure 1 - Ignition delay time for stoichiometric conditions at different inlet temperatures, where the experimental data are represented by the black dots and the simulations by the colored lines.

From Figure 1 it can clearly be seen that none of the mechanisms are able to predict the experimental data well. However, in Table 1 it can be seen that the POLIMI mechanism has the smallest average deviation from the experimental data. This mechanism was therefore used for the continued evaluation.

After an initial screening of the impact factors, three reactions were chosen for the optimization, namely R1 ($O_2 + H = O + OH$), R271 ($HO_2 + CH_3 = OH + CH_3O$) and R405 ($CH_4 + H = H_2 + CH_3$). By allowing the kinetic parameters for these three reactions to vary within the uncertainty bounds of the reaction rate, a more optimal combination of parameters could be found, which gave better predictions with respect to the experimental data. These new parameters are presented in Table 2 together with the nominal parameter values for comparison.

Table 2 - Nominal and Optimal kinetic parameter values for reactions R1 ($O_2 + H = O + OH$), R271 ($HO_2 + CH_3 = OH + CH_3O$) and R405 ($CH_4 + H = H_2 + CH_3$) form the POLIMI mechanism [15]. The units of the different kinetic parameters are as follows: A [s-cm3-mol], β [-], E [cal/mol].

Kinetic param.	Nominal value	Optimal value
A_{R1}	9.6×10^{11}	6.1×10^{11}
β_{R1}	-0.2	-0.2
E_{R1}	16 625	16 556
A_{R271}	6.0×10^{9}	2.56×10^{10}
A_{R405}	3.0×10^{4}	7.54×10^{4}
β_{R405}	2.0	2.0
E_{R405}	10 000	10 139

A comparison between the original POLIMI prediction, vs the optimized mechanism can be seen in Figure 2. It can clearly be seen that the new mechanism gives large improvements, especially at high inlet temperatures.

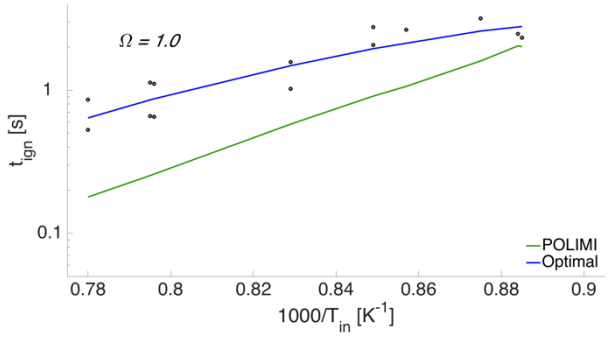

Figure 2 – Comparison of ignition delay time prediction between nominal and optimal mechanism for stoichiometric conditions. The experimental data is represented by the black dots.

Conclusions

From this work, it can be seen that existing mechanisms are not able to predict MILD combustion well, and there exists large discrepancies between the different mechanisms. The use of optimization techniques such as presented in this work, can therefore be used to improve the performance of existing mechanism with respect to the experimental targets. The choice of parameters to be included in this study was based on a so-called impact factor ranking and each possible combination of these parameters was evaluated using surrogate models. Finally, a modified mechanism was proposed based on a least squared fit with respect to the experimental targets, which showed drastic improvements with respect to the nominal mechanism.

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References

[1] A. Cavaliere and M. de Joannon, "Mild Combustion," Prog. Energy Combust. Sci, vol. 30, no. 4, pp. 329–366, 2004.

[2] M. Frenklach, A. Packard, G. Garcia-Donato, R. Paulo, and J. Sacks, "Comparison of Statistical and Deterministic Frameworks of Uncertainty Quantification," SIAM/ASA J. Uncertain. Quantif., vol. 4, no. 1, pp. 875–901, 2016.

[3] T. Varga, C. Olm, T. Nagy, I. G. Zsély, É. Valkó, R. Pálvölgyi, H. J. Curran, and T. Turányi, "Development of a Joint Hydrogen and Syngas Combustion Mechanism Based on an Optimization Approach," Int. J. Chem. Kinet. , vol. 48, no. 8, pp. 407–422, 2016.

[4] J. Prager, H. N. Najm, K. Sargsyan, C. Safta, and W. J. Pitz, "Uncertainty quantification of reaction mechanisms accounting for correlations introduced by rate rules and fitted Arrhenius parameters," Combust. Flame, vol. 160, no. 9, pp. 1583–1593, 2013.

[5] V. Samu, T. Varga, I. Rahinov, S. Cheskis, and T. Turányi, "Determination of rate parameters based on NH_2 concentration profiles measured in ammonia-doped methane-air flames," Fuel, vol. 212, no. February 2017, pp. 679–683, 2017.

[6] P. Sabia, M. Lubrano Lavadera, G. Sorrentino, P. Giudicianni, R. Ragucci, and M. De Joannon, "H2O and CO2 Dilution in MILD Combustion of Simple Hydrocarbons," Flow, Turbul. Combust., vol. 96, no. 2, pp. 433–448, 2016.

[7] Mueller, C. J.; Musculus, M. P. B.; Lyle, M.; Pitz, W. J.; Westbrook, C. K. The Oxygen Ratio: A Fuel-Independent Measure of Mixture Stoichiometry; 2003.

[8] A. Cuoci, A. Frassoldati, T. Faravelli, and E. Ranzi, "OpenSMOKE++: An object-oriented framework for the numerical modeling of reactive systems with detailed kinetic mechanisms," Comput. Phys. Commun., vol. 192, no. July, pp. 237–264, 2015.

[9] M. Frenklach, "Transforming data into knowledge-Process Informatics for combustion chemistry," Proc. Combust. Inst., vol. 31 I, pp. 125–140, 2007.

[10] W. K. Metcalfe, S. M. Burke, S. S. Ahmed, and H. J. Curran, "A hierarchical and comparative kinetic modeling study of C1 - C2 hydrocarbon and oxygenated fuels," Int. J. Chem. Kinet., vol. 45, no. 10, pp. 638–675, 2013.

[11] C. Zhou, Y. Li, E. O. Connor, K. P. Somers, S. Thion, C. Keesee, O. Mathieu, E. L. Petersen, T. A. Deverter, M. A. Oehlschlaeger, G. Kukkadapu, C. Sung, M. Alrefae, F. Khaled, A. Farooq, P. Dirrenberger, P. Glaude, F. Battin-leclerc, J. Santner, Y. Ju, T. Held, F. M. Haas, F. L. Dryer, and H. J. Curran, "A comprehensive experimental and modeling study of isobutene oxidation," Combust. Flame, vol. 167, pp. 353–379, 2016.

[12] D. Healy, D. M. Kalitan, C. J. Aul, E. L. Petersen, G. Bourque, and H. J. Curran, "Oxidation of C1 - C5 Alkane Quinternary Natural Gas Mixtures at High Pressures," Energy & Fuels, no. 18, pp. 1521–1528, 2010.

[13] C. T. Bowman, R. K. Hanson, D. F. Davidson, W. C. J. Gardiner, V. Lissianski, G. P. Smith, D. M. Golden, M. Frenklach, and M. Goldenberg, "GRI-Mech 2.11." [Online]. Available: http://www.me.berkeley.edu/gri_mech/.

[14] G. P. Smith, D. M. Golden, M. Frenklach, N. W. Moriarty, B. Eiteneer, M. Goldenberg, C. T. Bowman, R. K. Hanson, S. Song, W. C. J. Gardiner, V. V Lissianski, and Z. Qin, "GRIMech 3.0." [Online]. Available: http://combustion.berkeley.edu/gri-mech/version30/text30.html/

[15] E. Ranzi, A. Frassoldati, R. Grana, A. Cuoci, T. Faravelli, A. P. Kelley, and C. K. Law, "Hierarchical and comparative kinetic modeling of laminar flame speeds of hydrocarbon and oxygenated fuels," Prog. Energy Combust. Sci., vol. 38, no. 4, pp. 468–501, Aug. 2012.

[16] "Chemical-Kinetic Mechanisms for Combustion Applications."San Diego" [Online]. Available: http://web.eng.ucsd.edu/mae/groups/combustion/mechanism.html

[17] V. P. Zhukov, "Verification, Validation and Testing of Kinetic Models of Hydrogen Combustion in Fluid Dynamic Computations," 4th Eur. Conf. Aerosp. Sci., vol. 2012, 2011