# AN OPTIMIZED CORE MECHANISM FOR H2/CO COMBUSTION IN MILD-LIKE CONDITIONS

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**Abstract**

In this work, the $H_2$/CO core of the widely used Aramco 2.0 mechanism was optimized for improve performances in diluted conditions. The resulting model showed accurate agreement with a wide set of experimental data regarding hydrogen, carbon monoxide and syngas ignition delay time in RCM and ST. Comparison with the nominal mechanism and another optimized mechanism for the same fuels is given. The uncertain variables selection was performed using a two-step sensitivity analysis which links all the mechanism parameters of the most impactful reactions directly with the quantity of interest (QoI). This methodology coupled with an Evolutionary algorithm for global optima searching was found to be particularly effective. Finally, the impact of the core optimization on the ignition delay time of low alkanes and alkenes was tested, showing promising results and room for future work.

## Introduction

Reaching the low emission targets requires the use of alternative carbon-free fuels, like hydrogen, which is considered nowadays as a renewable energy source (RES). The latter fuel can be produced via water electrolysis exploiting the energy surplus of solar panels, converted into ammonia to facilitate its storage and transport, and then re-converted in-situ for power generation. Another promising RES is synthetic gas (syngas) which can be produced either via gasification of coal and burned directly in Integrated Gasification Combined Cycle (IGCC), or biomass. However, burning hydrogen and/or hydrogen-enriched fuels in air leads to very large NOx as their pronounced reactivity activates the thermal pathway. Moderate or Intense Low-oxygen Dilution (MILD) combustion [1] is well-known for the inhibition of pollutant formation, such as NOx and soot. Nonetheless, MILD combustion modelling is challenging as the presence of a relevant amount of diluent makes the mixing and the chemistry time scales overlap. Indeed, the low Damköhler numbers resulting from this overlapping suggest that chemistry has to be addressed with detailed kinetics when modelling this particular regime. Unfortunately, due to the central role of diluents in MILD regime, kinetic mechanisms validated using conventional combustion data, usually accomplish a non-accurate estimation for these, conditions [2]. The aim of this work is to improve the core mechanism of the widely-used

Aramco2.0 for MILD-like conditions using a new optimization procedure based on evolutionary algorithm (EA), and existing data from literature. A novel procedure for parameters selection supports the optimizer with a two-step approach, which digs into the impact of each individual parameter on the target variable directly.

**Database and kinetic simulations**

This work is based on experiments in Rapid Compression Machines (RCM) and shock tubes (ST), which were collected from literature. Table 1 summarizes the characteristics of the test cases, which are composed by several datasets in turn.

**Table 1:** Database details.

| Test Case | Fuel | Diluent, | Reference |
|---|---|---|---|
| 1 | $H_2$ | $H_2O$, $N_2$ | [3] |
| 2 | $H_2$ | $H_2O$, $N_2$, Ar | [4] |
| 3 | $H_2$ | $H_2O$, $N_2$ | [5] |
| 4 | CO | $H_2O$, $N_2$, Ar | [4] |
| 5 | Syngas | $H_2O$, $N_2$, Ar | [4] |
| 6 | Syngas | $CO_2$, $N_2$ | [6] |

Each experiment within the database has a virtual counterpart, which was reproduced with a 0-D simulation in OpenSMOKE++ [7]. Facilities effects were included into simulations. Regarding the RCM simulations, the experimental cold pressure traces were used to infer corresponding volume histories applying the adiabatic core assumption, following the procedure previously described in [8]. For shock tube simulations, constant volume conditions can be usually adopted, but often it is necessary to take into account the pressure rise before ignition. The ignition delay time was estimated accordingly with the experimental measurements.

**Sensitivity-based parameters selection**

A local sensitivity analysis, with respect to temperature, was performed for each experimental point using sensitivity analysis capabilities in OpenSMOKE++ [7]. Since, the QoI for the optimization is the IDT for each simulation the sensitivity coefficients are extracted on the onset of ignition. Subsequently, the testcase D related impact factor ($I_{r,D}$) for each reaction r is evaluated following equation **1**.

$$I_{r,D} = s_{r,D} \cdot f_r = \frac{1}{D}\sum_{d=1}^{D} \left|s_{r,d}\right|_{ign} \cdot f_r \quad (1)$$

Where $s_{r,D}$ is the testcase-related sensitivity coefficients vector for reaction r, which is obtained as the average of the absolute value of the sensitivity coefficients $s_{r,d}$ related to each experiment d belonging to the testcase of dimensionality D. The uncertainty factor $f_r$ of the $r^{th}$ reaction is then multiplied with the sensitivity

coefficient. The $I_{r,D}$ vector is then used to rank reactions in term of importance and enable the user to choose which ones to optimize. Thereafter, the P parameters, which correspond to the selected reactions were considered for further evaluations. First, the uncertainty of the reaction rate is propagated to the parameters to obtain their uncertainty ranges, following the methodology reported in [9]. Subsequently, a local brute force sensitivity analysis, which is capable of linking the ignition delay time variations to every single parameter directly, was performed for each unit of the dataset. The local brute force impact coefficients $I_{P,D}$ are computed according to equation **2** for each unit of the experimental dataset:

$$I_{P,D} = \sum_{d=1}^{D} \left[ \left( \frac{p_n}{\tau_{n,d}} \frac{\Delta \tau_d}{\Delta p} \right) \right] \cdot UI_P \tag{2}$$

Where $\Delta\tau_{\mathbf{d}}$ is the ignition delay time (IDT) variation due to the variation $\Delta\mathbf{p}$ of the p-th parameter of nominal value $\mathbf{p_n}$ on a specific data unit **d**, and $\tau_{\mathbf{n,d}}$ is the ignition delay time obtained with the nominal combination of selected kinetic parameters on that specific data-unit **d**. The uncertainty index ($UI_P$) is an equivalent of $f_r$ for each parameter p. Again, parameters are sorted according to their $I_{P,D}$ to facilitate the choice of the optimization active variables.

**Sensitivity-based parameters selection**

The optimization was performed by coupling OpenSMOKE++ [7] and Dakota [10]. The optimisation of pre-selected parameters of nominal values x is constrained between previously mentioned uncertainty range, within this range they are assumed to be uniformly distributed. The parameters hyperspace is then explored using a mono-objective evolutionary algorithm (EA) which performs a searching over the error function space to find global optima following the principle of the survival of the fittest combination of uncertain variables. Equation 3 reports the adopted objective function.

$$F_{norm,k} = \sum_{i=1}^{SDS} \frac{1}{E_i} \sum_{j=0}^{E_i} \frac{\left| Y_{i,j}^{exp} - Y_{i,j}^{sim} \right|}{Y_{i,j}^{exp}} \tag{3}$$

Where $F_{norm,k}$ is a normalized objective function for the $k^{th}$ dataset. SDS is the number of considered datasets within the complete database. $E_i$ is the number of discrete experiments belonging to the lastly mentioned dataset. $Y_{i,j}^{exp}$ and $Y_{ij}^{sim}$ are the values of the $j^{th}$ measurement and simulation belonging to the $i^{th}$ dataset. The third body efficiencies for $H_2O$ and $CO_2$, were directly included in the optimization together with the other Arrhenius parameters, to account for their interdependency.

**Results**

Figure 1 displays the results of this work showing only one dataset for each test cases. More than 300 targets compose the overall database. A comparison between the nominal mechanism, the optimized one and another available mechanism from ELTE group was performed. The latter was optimized for conventional conditions using an impressive number of targets. The agreement with experimental data is significantly improved.

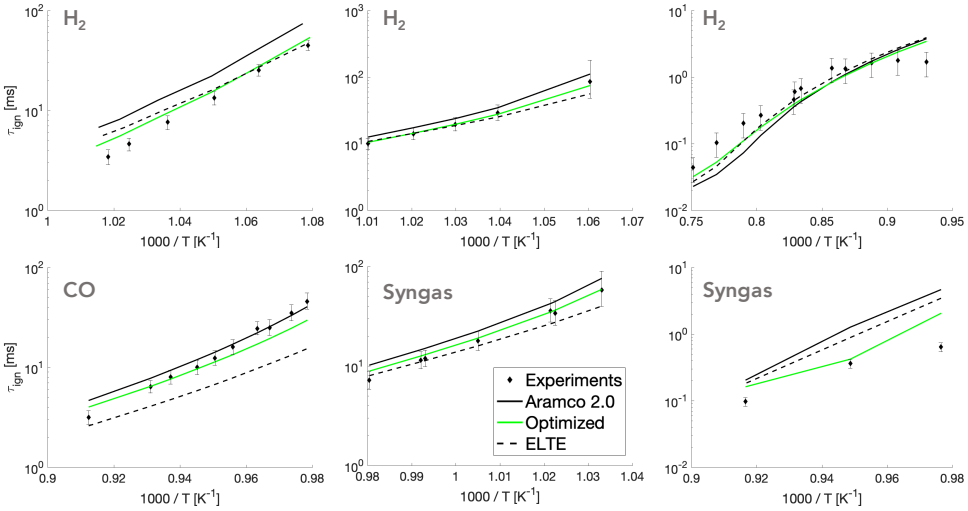


**Figure 1:** Optimization mechanism validation against experimental data. Comparison between Aramco 2.0, ELTE and this work.

The optimization procedure involved 38 out of 50 kinetic parameters from 15 elementary reactions. It is important to say that the third body efficiencies of both $H_2O$ and $CO_2$ were found to be strongly impactful as well as in previous studies [2], especially because of their participation as colliders in the reactive process. Though, they were considered as active variable during the optimization. The search of the global optima was not performed directly on the complete set of experimental conditions but proceeded systematically and hierarchically. First, the algorithm was run using a single test case and related selected parameters. Subsequently, the obtained mechanism was used as a starting point for a new search, considering not only the targets from a second test case, but also a new set of parameters, union between old and new ones. This operation was repeated iteratively until all data for hydrogen were handled. At this point, in order to respect the hierarchical structure of the mechanism, sensitive reactions for hydrogen ignition were frozen, even though the process always accounted for related targets, when considering carbon monoxide and syngas experiments. Indeed, the reactions uncertainty bounds were always calculated from the original mechanism along the process, so to avoid the final rates to exceed the nominal boundaries. This was crucial to not lose mechanism

comprehensiveness. Eventually, the mechanism was validated against other data in diluted conditions involving the same fuel, in particular perfectly stirred reactors (PSR) and laminar flame speed (LFS) calculation were performed and showed good agreement. Finally, since Sabia et al. [2] stated the importance of fall-off reactions involving hydrogen for their experiments on more complex fuels, the optimized core was introduced within the original Aramco 2.0 to verify the impact of the performed optimization. The ignition delay time of biomass pyrolysis gas, composed by CO, $CO_2$, $CH_4$, $C_2H_6$, $C_2H_4$, was simulated in a plug flow reactor (PFR). Figure 2 shows the remarkable improvements due to the optimization of lower layers of the mechanisms. While significant error reduction was obtained in $N_2$ and $CO_2$, the optimization potential for $H_2O$ dilution remains much larger. This is due to the direct participation of water in reactions involving the methyl, ethyl and vinyl radical, which were found to be particularly sensitive in this study.

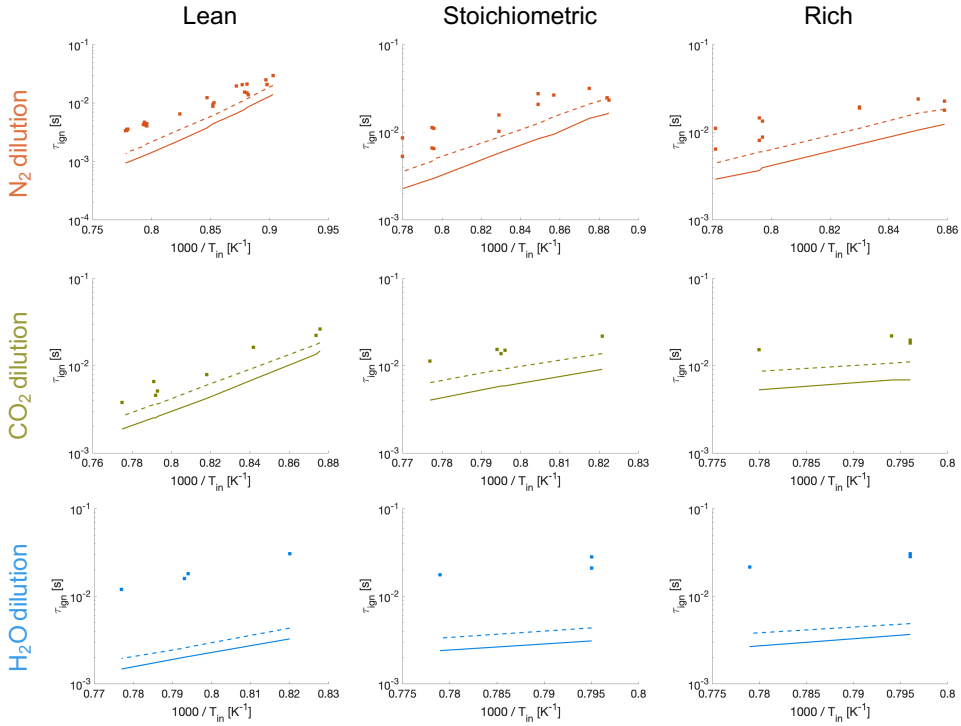


**Figure 2:** Biomass pyrolysis gas ignition delay time in a PFR at atmospheric pressure. Comparison between optimized (--) and nominal (-) mechanism for dilution from different colliders. Experimental data from Sabia et al [2].

## Conclusion

This study aimed at improving our knowledge about detailed kinetics in diluted conditions through heuristic methods. A new optimization procedure was proposed and tested on al relatively large amount of experimental evidences. Evolutionary algorithms were found to be particularly effective when coupled with a rigorous pre-

process for parameters selection based on a two-step sensitivity analysis reaching the parameters level. The well-characterized core of the Aramco 2.0 mechanism was improved using a pool of 300 experiments in RCM and ST collected from literature for $H_2$/CO/Syngas in diluted conditions and validated on as many data on PSR, and LFS. The impact on the ignition of biomass pyrolysis gas was also assessed. In fact, this study demonstrates further that the core fall-off reactions are responsible for a great part of the non-accurate prediction of diluted conditions using existing mechanisms, especially the third body efficiency of colliders such as $H_2O$ and $CO_2$. Future work has to focus on water dilution for low alkanes and alkenes.

## References


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

[2] 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.

[3] A. K. Das, C.-J. Sung, Y. Zhang, and G. Mittal, "Ignition delay study of moist hydrogen/oxidizer mixtures using a rapid compression machine," *Int. J. Hydrogen Energy*, vol. 37, no. 8, pp. 6901–6911, 2012.

[4] N. Donohoe *et al.*, "Influence of steam dilution on the ignition of hydrogen, syngas and natural gas blends at elevated pressures," *Combust. Flame*, vol. 162, no. 4, pp. 1126–1135, 2015.

[5] B. L. Wang, H. Olivier, and H. Grönig, "Ignition of shock-heated H2-air-steam mixtures," *Combust. Flame*, vol. 133, no. 1, pp. 93–106, 2003.

[6] S. S. Vasu, D. F. Davidson, and R. K. Hanson, "Shock Tube Study of Syngas Ignition in Rich CO2 Mixtures and Determination of the Rate of H + O2 + CO2 → HO2 + CO2," *Energy & Fuels*, vol. 25, no. 3, pp. 990–997, Mar. 2011.

[7] 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, pp. 237–264, 2015.

[8] C.-J. Sung and H. J. Curran, "Using rapid compression machines for chemical kinetics studies," *Prog. Energy Combust. Sci.*, vol. 44, pp. 1–18, 2014.

[9] M. B. Fürst *et al.*, "Optimization of chemical kinetics for methane and biomass pyrolysis products in MILD combustion," *Energy and Fuels*, 2018.

[10] B. M. Adams *et al.*, "DAKOTA, a multilevel parallel object-oriented framework for design optimization, parameter estimation, uncertainty quantification, and sensitivity analysis: version 5.0 user's manual." Sandia National Laboratories, Tech. Rep. SAND2010-2183, 2009.