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Comparison of the performance of several recent syngas combustion mechanisms

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ABSTRACT

A large set of experimental data was accumulated for syngas combustion: ignition studies in shock tubes (732 data points in 62 datasets) and in rapid compression machines (492/47), flame velocity determinations (2116/217) and species concentration measurements from flow reactors (1104/58), shock tubes (436/21) and jet-stirred reactors (90/3). In total, 4970 data points in 408 datasets from 52 publications were collected covering wide ranges of temperature T, pressure p, equivalence ratio φ, CO/H_2 ratio and diluent concentration X_{dil}. 16 recent syngas combustion mechanisms were tested against these experimental data, and the dependence of their predictions on the types of experiment and the experimental conditions was investigated. Several clear trends were found. Ignition delay times measured in rapid compression machines (RCM) and in shock tubes (ST) at temperatures below 1000 K could not be well-predicted. Particularly for shock tubes, facility effects at temperatures below 1000 K could not be excluded. The accuracy of the reproduction of ignition delay times did not change significantly with pressure. The agreement of measured and simulated laminar flame velocities is better at low initial (i.e. cold side) temperatures, at fuel-lean conditions, for CO-rich and highly diluted mixtures. The reproduction of the experimental flame velocities is better when these were measured using the heat flux method or the counterflow twin-flame technique, compared to the flame cone method and the outwardly propagating spherical flame approach. With respect to all data used in this comparison, five mechanisms were identified that reproduce the experimental data similarly well. These are the NUIG-NGM-2010, Kéromnès-2013, Davis-2005, Li-2007 and USC-II-2007 mechanisms, in decreasing order of their overall performance. The influence of poorly reproduced experiments and weighting on the performance of the mechanisms was investigated. Furthermore, an analysis of local sensitivity coefficients was carried out to determine the influence of selected reactions at the given experimental conditions and to identify those reactions that require more attention in future development of syngas combustion models.

1. Introduction

In recent years, there has been an increased interest in studying the combustion of fuel mixtures consisting of carbon monoxide and hydrogen, referred to as syngas or "wet CO". These fuels can be produced from coal and biomass via gasification, and are considered to be a promising option toward cleaner combustion technologies for power generation [1]. The chemistry of syngas combustion forms the basis of the combustion of hydrocarbons and oxygenates, and has been the subject of many experimental and modeling studies for decades. Several new syngas combustion mechanisms have been published in the last ten years. In these publications, the agreement between the measurements and the simulations is typically characterized by plots, in which the experimental data and the simulation results are depicted together. However, quantitative agreement of a large number of simulation results with the corresponding experimental data has not been investigated. A quantitative evaluation enables the modeler to distinguish experiments that are well reproduced by simulations from those that are insufficiently described, which may have implications for model developers in the choice of development targets as well as for experimentalists in the design of new experiments. Furthermore, such a procedure allows for the detection of strengths and weaknesses of the mechanisms in certain ranges of operating conditions. Knowledge about the specific behavior of a

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mechanism is a necessary first step in attempts to reduce modeling uncertainties during mechanism development and optimization.

A similar comparison of reaction mechanisms for hydrogen combustion based on the quantitative characterization of the reproduction of experimental data was recently elaborated [2]. The present work has several novelties compared to this previous paper and other publications on the investigation of syngas combustion. The comparison performed here, on a very comprehensive set of experiments, is much wider ranging than those used in the previous investigations; various measurement types (ignition delay time, species concentration profile and flame velocity) and experimental techniques (e.g. shock tube and RCM experiments) are included in the analysis. The performance of 16 syngas combustion mechanisms is compared in detail, and the conclusions drawn are supported by reproducible numbers. Furthermore, the influence of data weighting to reduce the effect of multiple repeated measurements is described.

2. Methodology

In this work the agreement of experimental and simulation results is investigated using the following objective function:

$$E_i = \frac{1}{N_i}\sum_{j=1}^{N_i}\left(\frac{Y_{ij}^{sim} - Y_{ij}^{exp}}{\sigma\left(Y_{ij}^{exp}\right)}\right)^2$$

$$E = \frac{1}{N}\sum_{i=1}^{N} E_i$$

where

$$Y_{ij} = \begin{cases} y_{ij} & \text{if } \sigma\left(y_{ij}^{exp}\right) \approx \text{constant} \\ \ln y_{ij} & \text{if } \sigma(\ln y_{ij}^{exp}) \approx \text{constant} \end{cases}$$

Here N is the number of datasets and N_i is the number of data points in the ith dataset. Values y_{ij}^{exp} and $\sigma(y_{ij}^{exp})$ are the j-th data point and its standard deviation, respectively, in the ith dataset. The corresponding simulated (modeled) value is Y_{ij}^{sim} obtained from a simulation using an appropriate detailed mechanism and simulation method. If a measured value is characterized by absolute errors (the scatter is independent of the magnitude of y_{ij}), then $Y_{ij} = y_{ij}$. We used this option for laminar flame velocities and measured concentrations. If the experimental results are described by relative errors (the scatter is proportional to the value of y_{ij}), then we used the option $Y_{ij} = \ln(y_{ij})$, which is characteristic for ignition time measurements. Error function values E_i and E are expected to be near unity if the chemical kinetic model is accurate, and deviations of the measured and simulated results are caused by the scatter of the experimental data only. Note that due to the squaring in the definition of E, a twice as high deviation of the simulated and experimental values of one mechanism in comparison to another leads to a four times higher value of E. This objective function has been used in our previous studies on the comparison of reaction mechanisms [2] and the estimation of rate parameters from experimental data [3–6].

In addition to the average error function E, the average absolute deviation D was used to characterize the behavior of the mechanisms:

$$D = \frac{1}{N}\sum_{i=1}^{N}\frac{1}{N_i}\sum_{j=1}^{N_i}\frac{D_{ij}}{\sigma\left(Y_{ij}^{exp}\right)} = \frac{1}{N}\sum_{i=1}^{N}\frac{1}{N_i}\sum_{j=1}^{N_i}\frac{\left(Y_{ij}^{sim} - Y_{ij}^{exp}\right)}{\sigma\left(Y_{ij}^{exp}\right)}$$

with the absolute deviation belonging to an individual data point D_{ij} and using the same transformation $y_{ij} \rightarrow Y_{ij}$ as given above. In contrast to E, the sign of the difference $Y_{ij}^{sim} - Y_{ij}^{exp}$ is maintained in the definition of D. In contrast to our previous work [2], we modified the above equation by dividing D_{ij} by the estimated standard deviation. This allows for a better comparison of data obtained from different types of experiments with respect to their D values. The drawback of the D value is that positive and negative deviations in different data points can cancel each other out and the resulting averaged value would suggest an unrealistically good overall agreement. However, trends such as systematic under- or over-prediction are thereby captured in the D_{ij} values. The D values are displayed in Fig. 11 and in Figs. S2–S5 and S7–S12 of the Supplementary Material. These D value plots may deliver a better understanding of the trends associated with changes of certain operating conditions and should be interpreted alongside their corresponding E value plots.

It is possible to characterize the similarity of simulation results using different mechanisms by calculating Pearson correlation coefficients based on the values of D_{ij}. Similar to the definitions of E and D, correlation coefficients C are calculated for each dataset and then averaged over all N datasets. Details of the calculation of C values as well as a brief discussion in the context of comparisons of the performance of mechanisms can be found in [2].

3. The investigated mechanisms

Our aim was to test all major syngas combustion mechanisms that were published in the last decade. Furthermore, GRI-Mech 3.0 [7] was added to the comparison, which was published in 1999 and primarily developed for methane combustion, but is nevertheless widely used in the syngas-related literature. In the forthcoming discussions, an identifier of each mechanism is used, which combines the name of the publishing author(s) or research group and the year of publication.

Earlier mechanisms from the same research group were tested only if they were conceptually different from the latest one. For instance, two mechanisms published by the Galway group, NUIG-NGM-2010 and Kéromnès-2013, were used because the latter features a sub-model for the reactions of the excited OH radical (OH^*) largely based on the work of Tamura et al. [8] and updated by Kathrotia et al. [9]. It can be shown that these reactions are of high importance for a more accurate reproduction of shock tube ignition studies at high temperatures. In a similar way, both the SaxenaWilliams-2006 and the SanDiego-2014 mechanisms were included in the comparison. In our previous paper [2] we used the 2011 version of the San Diego mechanism. A recently published update of several reaction rates, fall-off parameters and third body collision coefficients in the hydrogen chemistry [10], which forms the basis of the new 2014 version, led to a substantially better description of hydrogen ignition delay times, at the cost of less accuracy at the conditions in flames. The same trends apply to syngas combustion, for which hydrogen chemistry is known to be very important.

Several of these mechanisms were originally developed for syngas combustion [11–19], while other mechanisms were elaborated for the combustion of hydrocarbons or oxygenates [7,20–25], but also used to interpret syngas data. MECHMOD [26] was used to remove unnecessary species and reactions from the mechanisms (e.g. nitrogen chemistry, C_2 and above). Table 1 contains the list of these mechanisms and provides further information about size and included diluents. The numbering of the mechanisms in Table 1 is according to their overall performance from the best (1) to the worst (15). The mechanism of Dagaut-2003, which could not be tested for the complete set of experimental data, was given the number 16.

All mechanisms can handle N_2 bath gas, while only some mechanisms include He as a species. Unlike all other mechanisms, that of Dagaut-2003 [20] does not contain Ar either. This affects the