Development and Optimization of H_2/CO-H_2 Reaction Model using PrIMe

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The current paper presents a continuation of the development of a modern methodology for the construction of uncertainty-quantified chemical reaction model on the base of the Bound-to-Bound Data Collaboration (B2B-DC) module of the automated data-centric infrastructure PrIMe. Some problems, postulated in the recent studies [1, 2], are in the focus of present investigation. The first point of interest is the quantity of targets (experimental data, Quantities of Interest (QoI)) selected for the analysis. To investigate this, the PrIMe dataset (QoI and reaction model, accomplished with uncertainty boundaries) will be extended, first, through addition of more QoIs from each experimental set already used in previous analysis [1]. The influence of such dataset extension on the dataset consistency, feasible parameter set, and model optimization will be studied and an algorithm for the selection of QoI in each experimental set will be postulated. Furthermore, this extended dataset will be updated by introducing new experimental data. The influence of this expansion will be analyzed. The second point of interest is the dataset consistency measure. Criteria for the increase of the input experimental data error and for the elimination of a QoI as a finally inconsistent target will be further investigated.

One of the most important properties of a reaction model in chemical engineering is to make predictions about the system when certain settings are changed. Appropriate handling and archiving of experimental data from different sources, and of the many uncertainties in the data embedded in the kinetic models, is a major challenge the chemical kinetics community has to tackle before becoming a predictive science. Methods for determining whether or not the model predictions are consistent with experimental data have been of great interest in combustion research over decades. Developing predictive models [3] has become the goal in many of the modeling studies on reaction systems. Numerical optimization of complex reaction networks, of the kind that guided the development of GRI-Mech [3-5], e.g., has now been accepted as one of the underlying methods in this pursuit [6-8]. In order to develop a predictive reaction model for complex chemical systems the integration of large amounts of theoretical, computational, and experimental data collected by numerous researchers is required. The integration entails assessment of the consistency of the data, validation of models, and quantification of uncertainties for model predictions and often requires calibrating unknown parameters based on experimental observations.

The interest for development of chemical models spurred the interest in the quality of experimental data, i.e. uncertainty quantification. There's been plenty of research on data collaboration over the years [3, 6, 9-11]; this also led to the development of cybersystems offering kinetic database platforms, calculation and data analysis tools. Based on a long research on such cybersystems, we chose an automated data-centric infrastructure, the Process Informatics Model (PrIMe) [9] and tested it for a syngas reaction model [1].

The Bound-to-Bound Data Collaboration (B2BDC) module of PrIMe was employed to discover the limits of parameter modifications based on the systematic uncertainty and con-

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sistency analysis of the model-data system and experimental data including shock-tube ignition delay times and laminar flame speeds. The B2BDC methodology has been developed [3, 5, 10-15] and applied to different systems [1, 2, 12, 16, 17]. This is an optimization-based framework for combining models and experimental data from multiple sources to explore their collective information content [3, 5, 8, 10-15, 18-20]. This approach can decisively indicate whether related experimental data are consistent with each other within a specified chemical kinetics model, explore sources of inconsistency, discriminate among differing models, make model interval predictions, and analyze sensitivity to uncertainty propagation.
In our recent research [1], the initial H2/CO reaction model, assembled from 73 reactions and 17 species, was subjected to a B2B-DC analysis. For this purpose, a dataset was constructed that included a total of 167 experimental targets and 55 active model parameters. Consistency analysis of the composed dataset revealed disagreement between models and data: the inconsistency of QoI means impossibility to be modeled within its experimental uncertainty bounds. Further analysis suggested that removing 45 experimental targets, 8 of which were self-inconsistent, would lead to a consistent dataset. The self-inconsistent targets are mostly experimental data, for which numerical tools could not determine ignition delay time, Figure 1. The so obtained dataset was a subject for to model optimization. PrIMe allows us to store experimental data with information about method of determination of ignition peak because not always the system is able to reproduce ignition gradient and identify the ignition delay time peak as it is shown on Figure 1; this leads to insensitivity of model.

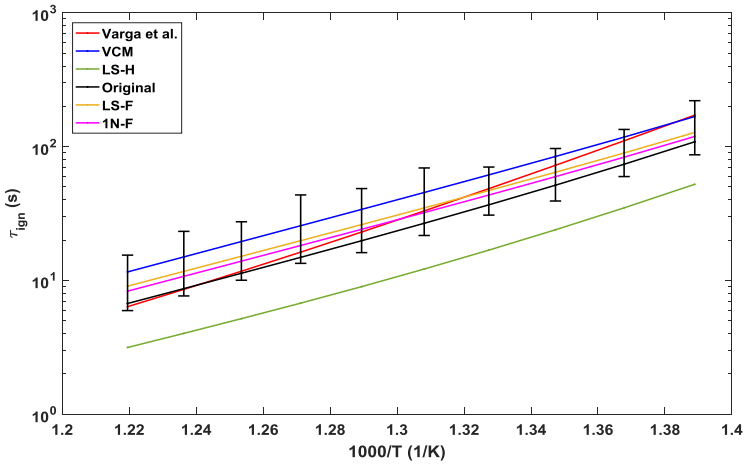


Fig. 1 Model predictions for ignition delay times (*Initial model, black solid line; Varga et al. [6] model, red; LS-H, green; VCM, blue; LS-F, yellow; 1N-F, purple; uncertainty intervals, black vertical bars).*

While working on the model optimization methodology, four sets of optimized model parameters were studied. The first method applied on the final consistent dataset DLR-SynG 2 is LS-H, a (weighted) Least-Squared fit constraining parameter values to their initially assessed uncertainty ranges, H. This is now quite common approach [3-8, 19]. The orther two refined methods of model optimization [20], LS-F and 1N-F. Method LS-F uses a weighted Least-Squared objective, while 1N-F is a 1-Norm minimization that aims at the smallest number of parameters to be changed. In these two methods, the objective is minimized with x's being constrained to the feasible set F.

The fourth set was obtained by using the vector consistency measure (VCM) [1, 2] approach, which was only partially applied in [1] since its development was not complete at that moment.

The optimized syngas models produced with B2B-DC framework demonstrated an improved agreement with the dataset constraints, as well as with experimental measurements not included in the analysis. The obtained optimized parameter values indicated parameter inadequacy, and the correlation analysis highlighted the direction of possible parameter modifications and model improvement. Inspection of the results depicted indicates that all models but one, LS-H, predict the new target within the B2BDC-predicted bounds. The LS-H predictions are definitely outside the bounds. Whether it is statistically established confidence region [23] (or credible region in the present Bayesian terminology) or deterministically defined feasible set [10, 15], analysis based on these regions of "optimality" should be more informative. Indeed, as we saw with the results [1], the LS-H minimization produces the lowest-value deviation, and yet there are a substantial number of individual predictions that exceed the prescribed experimental uncertainty. The practical implication of such an outcome can be paraphrased as follows: the LS-H optimization hides the truth by averaging good with bad.

Based on these conclusions, we chose LS-F optimization methodology for our further work and consequently for present paper.

To demonstrate the facilities of obtained with B2B-DC framework optimized models, we reproduce here the "blend" model predictions, i.e. the simulation of experiments not included in the analysis, Figure 2, along with those of Varga et al. [6]. Uncertainty intervals computed using B2BDC with the DLR-SynG 2 dataset is shown in the Figure 2 as black vertical lines. These intervals reflect all the uncertainty information of the DLR-SynG 2 dataset, those of the parameters and those of the dataset targets. Inspection of the results depicted in Figure 2 indicates that all models but one, LS-H, predict the new target within the B2BDC-predicted bounds. The LS-H predictions are definitely outside the bounds.

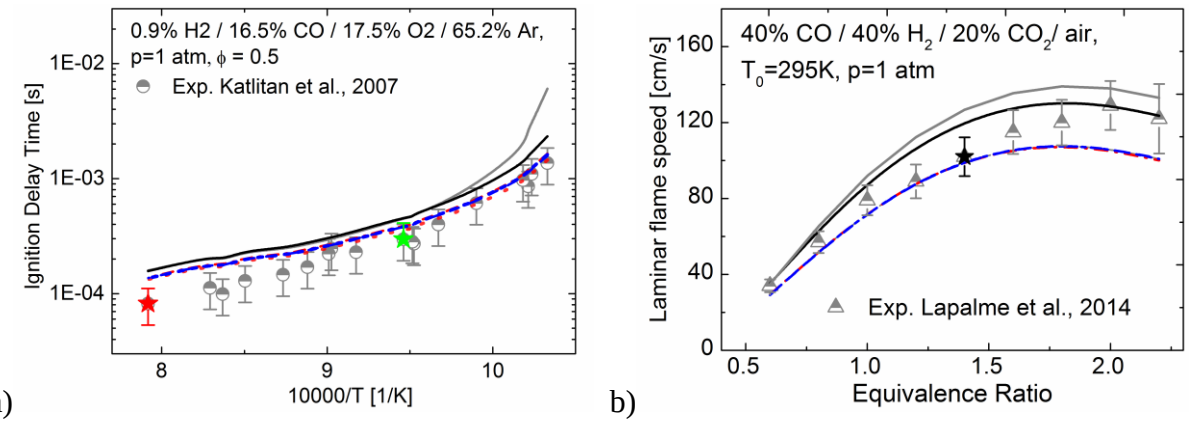


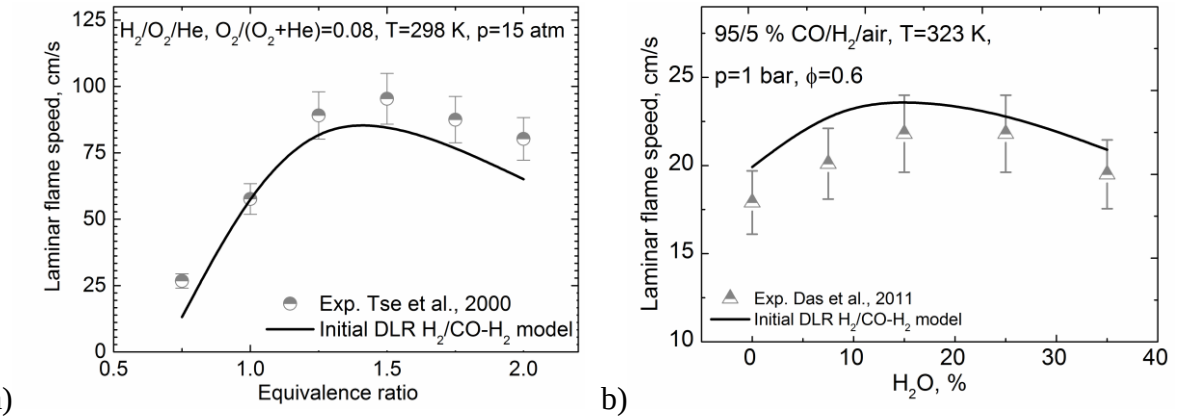
Fig. 2 Targets selected for dataset construction: a) for ignition delay times [24]; b) for laminar flame speeds [25]. (*Symbols, experimental data; initial DLR model, black line; Varga et al. [6] model, gray line; LS-H, red dotted line; VCM, red dash-dotted line; LS-F, blue dash line; 1N-F, blue short dash line. Black stars are targets of DLR-SynG 2 dataset; red stars are self-inconsistent targets; green stars are targets deleted from the DLR-SynG 1 dataset.*

While working on dataset construction and consistency analysis, the following questions occurred: what is the optimal number of targets that we need to take to reach a consistent dataset and obtain the best predictive model? At present, it is unfortunately not guaranteed that a huge amount of data leads to a perfect well-predictive model, see Figure 1, partly because the uncertainty prediction cannot be measured. What action should be taken regarding incon-

sistent constraints - either to eliminate such inconsistent constraints or increase their experimental uncertainty bounds? If a constraint needs to be expanded by some large amount, is there a limit of expansion?

To investigate that we expanded the dataset through addition of more targets from already known experimental observations and created a new dataset DLR-SynG 3. This dataset is based on the DLR-SynG 2 dataset which has only minor number of targets. Examples are shown in Figure 2. As we can see, only 1-2 targets from each experimental observation have been selected for DLR-SynG 2. To create DLR-SynG 3, more data units were selected. The selection criteria were the minimum amount of constraints but enough for description of experimental trend was established. For selection simplification, those observations with same experimental conditions and similar results as those already taken for analysis were not considered. The influence of this expansion on the consistency analysis result, feasible set, and model optimization was analyzed.

The new dataset DLR-SynG 3 will not only include experimental data for syngas. In order to create a model which can be used for wider range of applications, experiments of H2 ignition delay time and laminar flame speeds were included in the dataset. Thus, the investigated DLR model will cover both syngas and hydrogen experiments. The final dataset DLR-SynG 3 consists of 366 QoIs for ignition delay time and 158 QoIs for laminar flame speed experiments. The dataset also includes initial DLR H_2/CO-H_2 mechanism which was applied to model the experimental results (Fig. 3).



a) b)

Fig. 3 Initial DLR H_2/CO-H_2 mechanism within the DLR-SynG 3 dataset a) for ignition delay times [26]; b) for ignition delay times [27]. (*Symbols, experimental data; initial DLR model, black line)*

The consistency of DLR-SynG 3 dataset will be performed with a newly-developed method of the vector consistency measure (VCM). It is now finally developed and suggested as an alternative method to scalar consistency measure (SCM) for resolving massively inconsistent datasets; fundamental research is presented in [2]. This methodology will be implemented in PrIMe and is used in the present work for the data consistency analysis. Results obtained with the new developed vector consistency measure module will be analyzed. In this method, independent relaxations to each model-data constraint are considered instead of a single relaxation to all constraint. The aim of such approach is to find the fewest number of relaxations. VCM optimization method is based on the classical technique of replacing the 0-norm with 1-norm and determines the minimal bound changes, each bound by its own extent, that result in dataset consistency.

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