COMBUSTION PROPERTIES OF H2/CO MIXTURES: CONSISTENT CHEMICAL MECHANISM FROM COLLABORATIVE DATA PROCESSING

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1 Introduction

The kinetic characterization of the H_2/CO system is of interest due its role in sustainable combustion processes and promising application of syngas as a direct fuel is the electricity generation in an Integrated Gasification Combined Cycle (IGCC). However the interest in syngas chemistry at present is provoked not simply because of its role in IGCC and renewable energy, but also due to primary role of the CO/H_2/O_2 kinetic model in the fundamental hierarchal structure of the hydrocarbon combustion chemistry. The main objective of the present study is to provide a revision of the state of the H_2/CO kinetic sub-mechanism underlying in the DLR hierarchal hydrocarbon reaction data base for practical fuel application, i.e. oriented mostly for heavy hydrocarbon oxidation processes [1,2].

To reliably develop predictive reaction models for complex chemical systems requires integration of large amounts of theoretical, computational, and experimental data collected by numerous researchers. The integration entails assessment of the consistency of the data, validation of models, and quantification of uncertainties for model predictions. Approach to the development of mechanistic reaction models consists of conjecturing the reaction mechanism and comparing the predictions of the constructed model to available experimental observations. Typically, such comparisons result in mixed outcomes: some show a reasonably close agreement and some do not. In the latter case, the apparent inconsistency obtained between the model and the experiment is argued to imply either that the model is inadequate or that the experiment (or, rather, its interpretation) is incorrect. DataCollaboration module of the automated data-centric infrastructure, Process Informatics Model (PrIMe) [3-6], can establish consistency or inconsistency of a data-and-model system, when the kinetic parameters of a reaction mechanism and experimental observations used for model validation are known within its uncertainties.

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DataCollaboration [3-5] was applied to the H_2/CO system of the kinetic model [1,2] to perform a systematic uncertainty and consistency analyses of the model parameters and related experimental data (ignition delay times and laminar flame speeds), to revise and to optimise the model parameters and finally to obtain the predictive model with evaluated uncertainty level, addressing questions of practical significance.

2 DataCollaboration

DataCollaboration is a set-based data analysis method that puts models, theory, and experimental data on the same footing [3-6], applicable to any data-and model system. DataCollaboration can decisively indicate whether related experimental data are consistent with each other within a specified chemical kinetics model. The model parameter uncertainties are included in the analysis as well. A framework is designed to make inferences from experimental observations in the context of an underlying model, discriminate among alternative hypotheses, quantify uncertainties of model predictions, analyze sensitivities to uncertainty levels, and optimize a model considering all uncertainties. In other words, instead of the two-stage approach—i.e., estimation of model parameters from fitting experimental data followed by model predictions using the obtained estimates, — DataCollaboration transfers the uncertainties of the "raw" data into model prediction directly. This approach casts a given problem as a constrained optimization over the feasible region of the parameter space, drawn on the entire knowledge content of a dataset. Numerical efficiency is attained through the use of surrogate models in numerical algorithms of DataCollaboration. The surrogate models (mechanisms with parameters modified through current step of optimization) are developed by Solution Mapping— approximation of model responses via computer experiments and regression. The approach combines solution mapping, which generates each surrogate models, and robust control techniques, which are used to solve the constrained optimizations. The mathematical details can be found in [3-5].

A key requirement for such analysis is the formulation of a dataset, which entails creation of dataset units from experimental observations and a common kinetic model. A dataset unit should consist of the measured observation, uncertainty bounds on the measurement and thermokinetic data, and a model that transforms active parameter values into a prediction for the measurement. Identification of active parameters via sensitivity analysis and development of a quadratic response surface via computer experiments arranged according to a factorial design.

Organized in this manner, the dataset can be subjected to rigorous numerical analysis. The results of the analysis suggest a sequential procedure with step-by-step identification of outliers and inspection of the causes. The analysis identifies a specific direction to follow for improving dataset consistency and provides an estimate of the extent of possible improvement. Altogether, this numerical approach offers a tool for assessing experimental observations and model building and improvement.

3 Experimental observations and a common kinetic model

The presented kinetic CO/H_2/O_2 sub model follows from recently developed C_0-C_2 reaction kinetic model [1,2]. The active parameters, i.e. reaction rates of the most important reactions, Table1, identified via sensitivity analysis and will be optimized applying DataCollaboration procedure [3-5]. The selected for the Consistency Analysis [3-5] experimental observations are collected in Tables 2 for ignition delays [7-13], and in Table 3 for premixed laminar speed data [14-19]. 400 experimental targets were analysed.

Table 1: Reactions identified for the reaction rates optimization.

N	**Reaction**
1	H + O2 = OH + O
2	OH + H2 = H2O + H
3	H2 + O =OH + H
4	H+HO2 = H2 + O2
5	H2O2 + H = HO2 + H2
6	OH + OH (+M) =H2O2(+M)
7	H + O2 (+M) = HO2 (+M)
8	O2 + CO = CO2 + O
9	CO + O (+M) =CO2 (+M)
10	CO + OH =CO2 + H
11	CO + HO2 =CO2 + OH
12	HCO (+M) = H + CO (+M)

Table 2: Experimental data for ignition delays simulation.

***P*, atm**	**Composition**	φ	T_5, **K**	**Ref.**
0.6 - 18	20%CO/ 80%H_2 40%CO/ 60%H_2 80%CO/ 20%H_2 90%CO/ 10%H_2	0.5	890 -1285	[7]
11 - 32	CO/ H_2/CO_2/O_2/N_2	0.5	630 - 1150	[8,9]
5.5 - 26	H_2:CO=0.25 - 4.0	0.1 - 1.0	855 - 1055	[10]
1.15 – 1.4	80%CO/ 20%H_2 90%CO/ 10%H_2	0.5 and 1.0	909 - 965	[11]
15, 30, 50	CO:H_2=0.0 - 0.8	0.36 to 1.6	1029,1011, 1044	[12]
14 - 17	50%CO/ 50%H_2 95%CO/ 5%H_2 Dilution 1: 2, 5, 10	0.5 – 1.0	1048 - 1259	[13]

Table 4. Experimental data for laminar flame speed simulation.

***P*, atm**	**Composition**	φ	T_0, **K**	**Ref.**
1	50%CO/ 50%H_2 95%CO/ 5%H_2	0.5 – 6	300	[14,15,16]
2,5,10, 20,40	50%CO/ 50%H_2 95%CO/ 5%H_2	0.5 – 5	300	[14]
1	50%CO/ 50%H_2	0.6– 1	500, 700	[17]
1	50%CO/50%H_2+20%CO_2	0.5 – 1	300	[17]
15	50%CO/ 50%H_2	0.6	600	[18]
15	CO/H_2+40%CO_2	0.75	600	[18]
1	50%CO/50%H_2 95%CO/5%H_2+ H_2O	0.6, 0.9	323	[19]

4 Results and discussion

Obtained reaction model described satisfactory the experimental data ignition delay times, laminar flame speed and concentration profiles measured for different operating conditions, Figure 1-3.

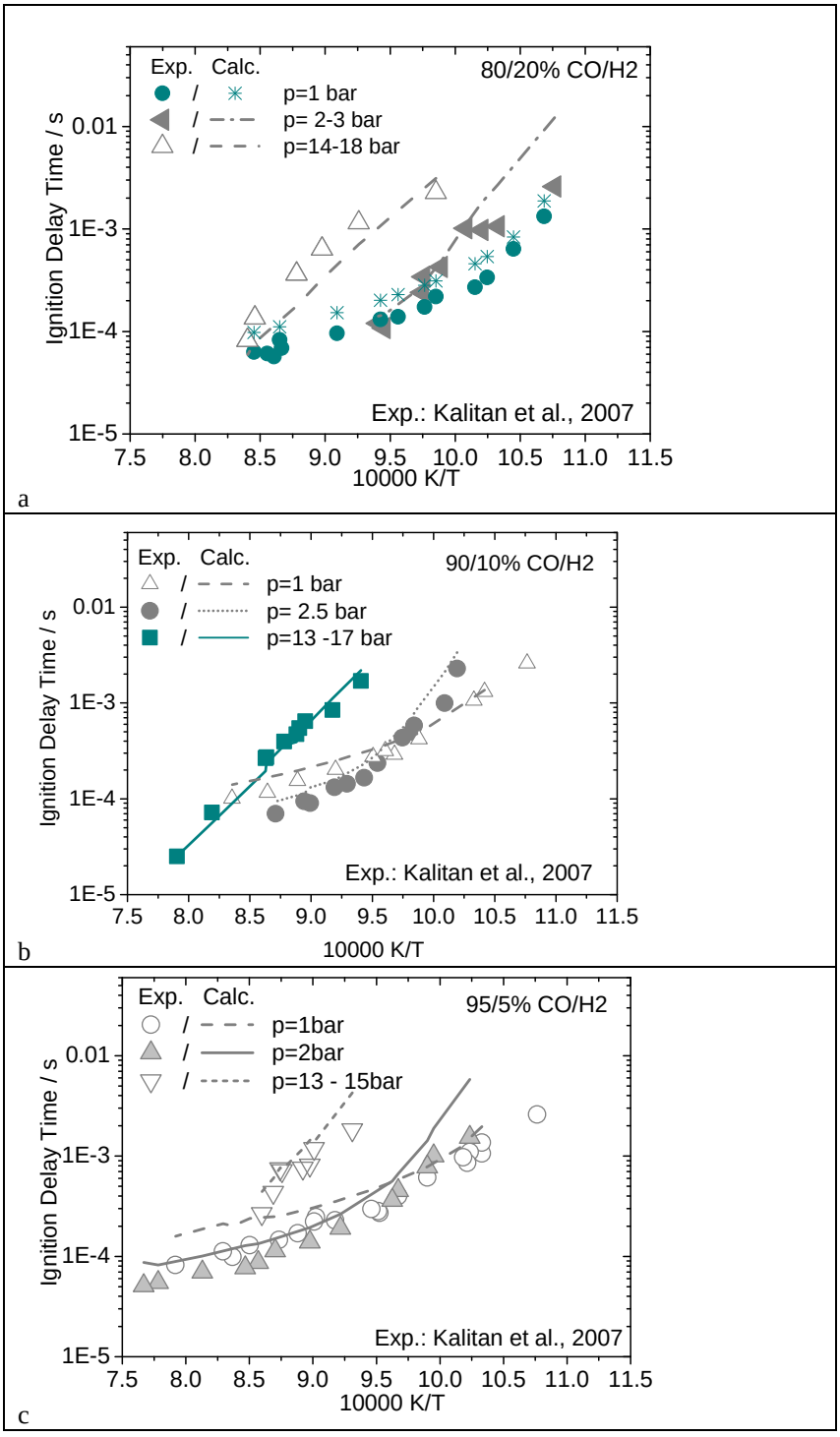

Figure 1. Comparison of modeled ignition delays for H_2/CO/air mixtures with experimental data [7] at different pressure, ϕ = 0.5

b

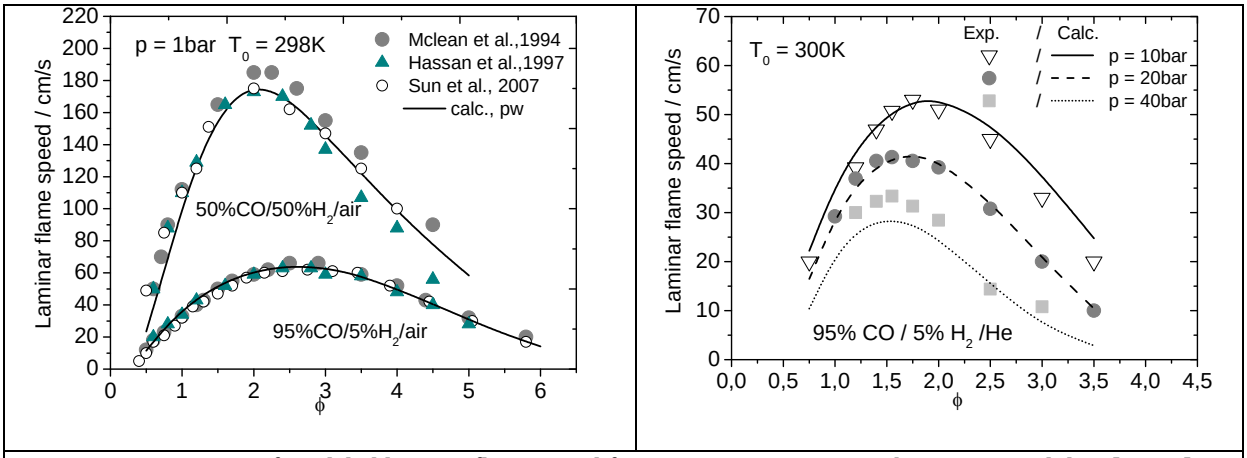

Figure 2. Comparison of modeled laminar flame speed for H_2/CO/air mixtures with experimental data [14-16]

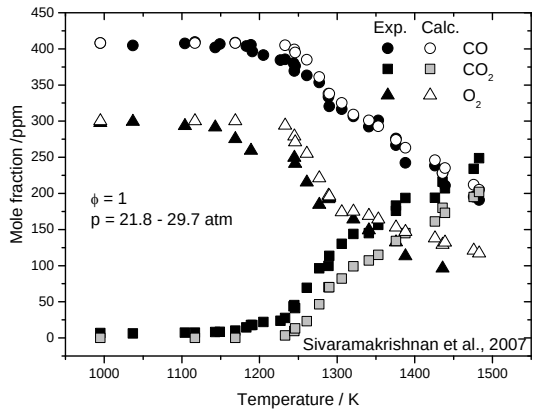

Figure 11. 70%CO/30%H_2 mixtures oxidation behind reflected shock waves [20], at p = 21 – 30 atm, experimental and modelled concentration profiles for CO, CO_2, O_2.

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