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Optimization of a hydrogen combustion mechanism using both direct and indirect measurements

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Abstract

The Kéromnès et al. (2013) mechanism for hydrogen combustion has been optimized using a large set of indirect experimental data, consisting of ignition measurements in shock tubes (566 datapoints in 43 datasets) and rapid compression machines (219/19), and flame velocity measurements (364/59), covering wide ranges of temperature (800 K–2300 K), pressure (0.1 bar–65 bar) and equivalence ratio ($\varphi = 0.2$–5.0). According to the sensitivity analysis carried out at each experimental datapoint, 30 Arrhenius parameters and 3 third body collision efficiency parameters of 11 elementary reactions could be optimized using these experimental data. 1749 directly measured rate coefficient values in 56 datasets belonging to the 11 reaction steps were also utilized. Prior uncertainty ranges of the rate coefficients were determined from literature data. Mechanism optimization has led to a new hydrogen combustion mechanism, a set of newly recommended rate parameters with their covariance matrix, and temperature-dependent posterior uncertainty ranges of the rate coefficients. The optimized mechanism generated here was tested together with 13 recent hydrogen combustion mechanisms and proved to be the best one.

Keywords: Hydrogen combustion; Detailed mechanisms; Mechanism optimization; Parameter uncertainty

1. Introduction

The reaction mechanism of hydrogen combustion plays a central role in combustion chemistry. Several new hydrogen combustion mechanisms were published in the last years; see e.g., the reviews of Ó Conaire et al. [1], Konnov [2], Hong et al. [3], Burke et al. [4], and Kéromnès et al. [5]. In all of these mechanisms, most of the parameters were based on directly measured or theoretically calculated rate coefficients, but also some of the rate parameters were tuned to improve the agreement with measured ignition delay times or flame velocities. These types of experimental

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data are usually referred to as indirect measurements, since such experimental results can be compared with simulation results based on a detailed mechanism. Although these mechanisms contain almost identical reaction steps and were developed by utilizing a similar set of experiments, several of the rate parameters and also the performance of the mechanisms at various experimental conditions are different [6].

Mechanism optimization is the process during which the rate parameters of several reaction steps are systematically changed within their uncertainty limits to achieve a better reproduction of experimental results. The first articles in this topic were written by Frenklach and Miller [7–9] and an algorithm was described in the article of Frenklach, Wang, and Rabinowitz [10]. The most widely used optimized mechanism is the GRI-Mech 3.0 [11]. Frenklach et al. extended the mechanism optimization approach towards data collaboration [12–16], recommending the services of the PrIMe website [17] and the application of the PrIMe data format [15]. Another series of mechanism optimization papers was published by Wang et al., who applied this approach to the combustion mechanisms of syngas [18], ethylene [19], propane [20], and *n*-heptane [21].

In the mechanism optimization works of Frenklach et al. and Wang et al. "optimization targets", based on indirect measurement data, were selected and the most influential rate parameters (called "active parameters") were identified by local sensitivity analysis. They optimized *A*-factors of the rate expressions, third body collision efficiency parameters, and enthalpies of formation. During the parameter optimization, the simulation results were calculated indirectly, using polynomial surrogate models ("response surfaces"). Both Frenklach et al. and Wang et al. reported that a large number of the obtained optimized *A*-factors were at the edges of their uncertainty interval, which usually meant a factor of 2 or 3 difference from the previously recommended values. To overcome this problem, in their recent works [16,21–23] the objective function was extended in such a way that deviation from the evaluated *A*-factor (determined on the basis of direct measurements) was penalized, and therefore the *A*-factors optimized in this way were closer to the evaluated ones.

Cai and Pitsch [24] suggested optimization of rate rules for larger hydrocarbon models, which reduce the dimensionality of the task and also guarantee the consistency of rate coefficients of kinetically similar reactions. This approach is not applicable for the combustion mechanisms of small fuel molecules.

Davis et al. [18] produced an optimized syngas combustion mechanism, including a hydrogen combustion mechanism subset. They considered 36 (22) optimization targets, including 12 (6) measured laminar flame velocities, 2 (2) concentration maxima in flat flames, 10 (6) flow reactor measurements and 12 (8) ignition delay measurements in shock tubes. The original mechanism consisted of 14 (11) species and 30 (20) reactions. Optimization of 28 (21) rate parameters (including 22 (16) *A*-factors and 6 (5) 3rd body efficiencies) was then carried out. The numbers in parentheses refer to the values belonging to the hydrogen subsystem. The optimized mechanism of Davis et al. [18] became highly successful and was used in many modeling studies.

You et al. [23] recently published an article about the PrIMe Workflow Application. The applicability of this software was demonstrated by the optimization of a hydrogen combustion mechanism, considering 8 ignition delay times measured in shock tubes and 4 flow reactor measurements. The authors optimized the *A*-factors of all of the 21 reaction steps. The obtained mechanism is applicable within the PrIMe modeling framework and the authors did not publish it in CHEMKIN format.

The methodology used here has several similarities and differences compared to the methods used by the authors above. We also apply local sensitivity analysis for the identification of active parameters, the PrIMe data format [17], and response surfaces for improving the numerical efficiency. The differences are that (i) we use a large number of indirect experimental data (instead of selected optimization targets), (ii) all Arrhenius parameters are optimized (instead of only the *A*-factors) and (iii) new approaches are used for the generation of response surfaces and global parameter estimation. Agreement of the optimized parameters with the previous rate parameter evaluations is achieved by taking into account direct measurements of rate coefficients on which the evaluations had been based, instead of guiding the optimized parameters towards the evaluated values. The methodology applied here has been described in detail in a previous article [25].

The hydrogen combustion mechanism of Kéromnès et al. [5] was selected as the initial mechanism on the basis of our previous investigations [6], since this mechanism provided the best overall description of the experimental data. The optimization is based on 1149 indirect measurements (ignition delay times measured in shock tubes and rapid compression machines (RCMs), and flame velocities), and also on 1749 direct measurements of the rate coefficients of important reaction steps. 33 rate parameters were optimized here, including 30 Arrhenius parameters and 3 third body collision efficiency parameters of 11 elementary reactions. The optimized mechanism obtained was tested together with 13 recently published hydrogen combustion mechanisms.

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