

Collaborative development of reaction mechanisms using PrIME data files

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Abstract

Detailed reaction mechanisms have to be validated before application. Agreement of the simulation results with experimental data should be demonstrated at several reaction conditions. The PrIME database (<http://www.primekinetics.org/>) contains data for several hundred combustion experiments. These XML data files define the experiment and cite the measured values. We have created a computational tool that is able to use the information content of the PrIME database and thus may speed up collaborative mechanism development work.

Introduction

Improvement of combustion technologies can be based on the simulation of combustion devices (furnaces, engines, gas turbines), provided that the chemical processes are well defined by reaction mechanisms. Before industrial application of chemical modelling, the accuracy of a reaction mechanism has to be proven.

The development of accurate combustion mechanisms can be promoted by the application of advanced information technology. We have elaborated computational tools for the simulation of combustion experiments defined in PrIME format data files, which contain the experimental conditions and results. Using these tools, enhancement and validation of combustion mechanisms can be carried out in an effective way.

Mechanism development

The creation of a detailed reaction mechanism involves many steps. First, the chemical species to be included in the mechanism and the corresponding reaction steps have to be selected. The temperature and maybe pressure dependence of each rate coefficient has to be parameterized. These parameters can be obtained by direct measurements, theoretical calculations or on the basis of analogue reactions.

The detailed reaction mechanisms compiled from literature values of rate coefficients usually do not reproduce adequately the results of indirect measurements, such as laminar flame speed, or time-to-ignition experiments. To achieve good agreement between simulations and experiments over a wide range of physical conditions, frequently some parameter values have to be modified. Sensitivity analysis methods [1,2] can provide information on which reactions should be investigated further.

The simulations include the solution of large ordinary or partial differential equations. This can be very computer time consuming, since the number of variables can be as high as several thousand. When the mechanisms are tested with many different parameter sets, the calculations can be carried out faster using the response surface methodology [3].

According to this method, large number of parameter sets is generated within their domain of uncertainty, the simulation results are calculated at these parameter sets and the results are approximated by a multivariate polynomial of the parameters. Using this methodology, the testing of new parameter sets can be accelerated by several hundred times. This concept has been successfully used in mechanism development (see *e.g.* [4,5]).

During the improvement of detailed reaction mechanisms, most of the efforts are devoted to the collection of experimental data, setting up simulation data files and creating plots that compare the measured and the simulated data. Each research laboratory uses their own format for the collection and plotting of the data, which hinders data exchange and collaboration. The PrIME initiative [6] intends to solve this problem by providing a general and expandable data format, leading to an open database for combustion chemistry.

The PrIME initiative

The PrIME database contains data of several hundred experiments. It is even more important, that the PrIME data format is well defined and can be expanded. These XML data files contain the type of the experiment (*e.g.* shock tube, laminar flame), the circumstances of the experiment (*e.g.* initial temperature, pressure and composition) and the measured values. Currently the PrIME database contains more than 370 experimental data files, each describing a set of shock tube, flow reactor, laminar flame or burner stabilized flame experiments.

There is a utility code in the PrIME database that allows uploading new experimental data.

Specific objectives

The aim of this work was to create a computational tool that utilizes the PrIME database and format, to help mechanism development. Our program can interpret PrIME experimental data files, perform simulations, compute local sensitivity coefficients and calculate response surfaces.

Results and discussion

A MATLAB code was written that reads and interprets the PrIME experimental data files. Given

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the experiment type, physical conditions and chemical composition, the simulation environment is set up using the open-source chemical simulation package Cantera [7]. This code is capable of performing the simulation of systems that can be well modelled by assuming homogeneous conditions (*e.g.* shock tube, flow reactor) or freely propagating flames. Cantera uses an own format for chemical mechanisms, but conversion from CHEMKIN format mechanism files is well supported.

Simulation of shock tube experiments are performed at constant pressure, assuming an adiabatic reactor. In most cases the measured value is the ignition delay time. The definition of the ignition delay can vary, but the actual definition is recorded in the PrIME data files and it is calculated by our code accordingly.

If the results of the experiments are concentration – time profiles (*e.g.* in flow reactor experiments), then our program simulates the corresponding species concentration profiles.

Freely propagating flame simulations are done with the Python version of Cantera as this function is not implemented yet in the MATLAB code of the package. These simulations are used for the calculation of laminar flame speed.

In all cases, the normalized local sensitivity coefficients are also calculated for the measured data. The investigated parameter is the A factor of each reaction (including the low pressure limit A -factors). The calculations are done with a finite difference method, using the following equation:

$$s_{ij} = \frac{\partial \ln Y_i}{\partial \ln p_j} \approx \frac{p_j}{Y_i} \frac{(Y_i - Y_i)}{(p_j - p_j)} \quad (1)$$

where Y_i is the simulation result with the original parameter set, p_j is a parameter used in the mechanism. Y_i and p_j are the simulation result obtained with the modified parameter set and the modified parameter value, respectively.

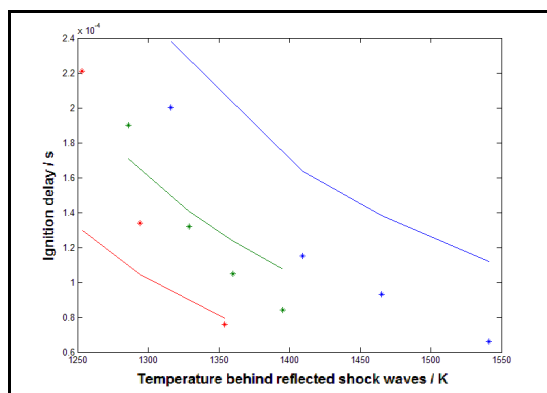


Figure 1. Ignition delay measurement results from Horning [8]. Plot of the measured (asterisks) and simulated (lines) results, at 1 atm (blue), 2 atm (green), 4 atm (red).

The parameter values were increased by 1% in the current work to avoid both numerical errors that might be originated from very small changes of parameters and non-linear effects originated from large deviations compared to the original parameters values. The results of the sensitivity analysis were transferred to an Excel table. An Excel macro was written that colours the cells that contain sensitivities which are at least 10% of the highest value at the given condition. This way the highly sensitive reactions can be selected quickly.

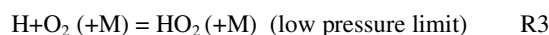
The program is also capable of generating polynomial response surfaces. At a given experimental condition the highly sensitive reactions are selected. Large numbers of parameter sets are generated by sampling all three Arrhenius parameters (A , n , E) of the selected reactions. Parameters are generated within their uncertainty bounds, taking into account the correlation between them.

The parameters of the non-sensitive reactions are used at their original value. Simulations are performed using each parameter set and a high order polynomial (up to 8th order) is fitted to the simulation results. This methodology is very advantageous in cases where a single result was obtained from an experiment (ignition delay, laminar flame speed). For experiments where species profiles were measured, a series of several hundred concentration values can be calculated faster by solving differential equations than by evaluating a response surface.

The program was tested using experimental data files of the PrIME database and PrIME format files created from literature measurements currently not included in the PrIME database. The investigated cases were the ignition measurements of H_2 , CH_4 and C_2H_4 in shock tubes; turbulent flow reactor experiments on H_2/O_2 mixtures; and laminar flame speed measurements of H_2/O_2 , H_2/air and wet CO flames.

The simulations were performed with the appropriate subsets of the NUIG natural gas combustion mechanism (version C5_44) [9]. Example plots of measured and simulated data are shown in Figs. 1 and 2.

In each case, a small number of highly sensitive reactions could be identified. As an example, in case of ignition delay measurements of H_2/O_2 mixtures in shock tube, the rate parameters of the following three reactions showed significant sensitivity:



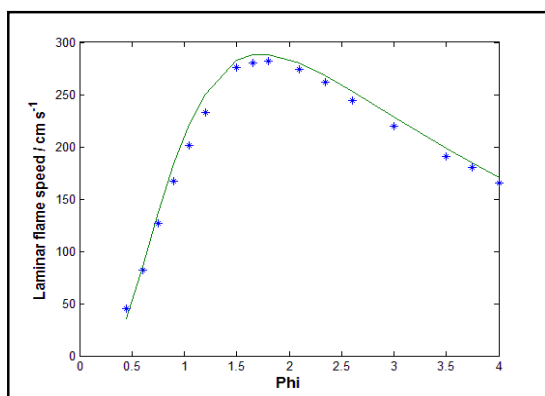
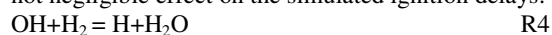


Figure 2. Laminar flame speed measurements of hydrogen-air mixtures performed by Tse *et al.* [10]. Plot of the measured (asterisks) and simulated (line) results.

In each case, reaction R1 was found to have the largest effect on the ignition delay. At temperatures higher than 1600 K, usually reaction R2 was the second most important one, while below 1600 K it was reaction R3.

Typically four further reactions had a smaller, but not negligible effect on the simulated ignition delays:



In the calculation of response surfaces, the two reactions with the largest sensitivities were taken into consideration in each case.

Polynomials were fitted to simulation results in 10000 points of the parameter space. On the edge of the uncertainty interval, the fitted polynomial did not describe the simulation results well. A maximum relative error of $\pm 5\%$ was obtained by calculating the difference between 1000 new parameter sets sampled from a smaller interval.

Evaluation of the polynomial response surface was approximately 300 times faster than the Cantera simulations for the ignition delay experiments.

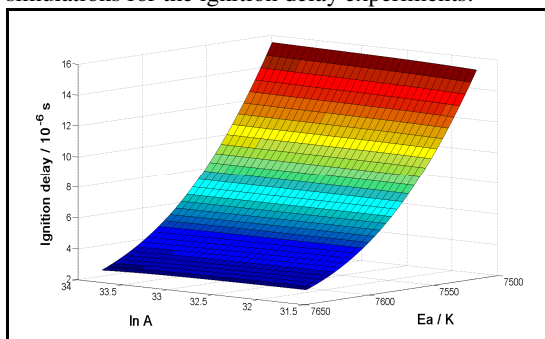


Figure 3. Response surface for ignition delay measurement of stoichiometric H_2/O_2 mixtures diluted in Ar, performed by Petersen *et al.* [11]. Independent variables: $\ln A$ and E_a of reaction $\text{H} + \text{O}_2 = \text{OH} + \text{O}$. Experimental conditions: $T = 1704 \text{ K}$, $p = 87 \text{ atm}$.

Conclusions

The presented computational tool makes the use of the PrIME database and in general the PrIME format data files easier, thus promoting collaborative work between institutions.

Measurement data together with the description of the related combustion experiments (own results and/or data collected from the literature) can be all encoded in PrIME format, using the utility code of the PrIME collection. The several hundred measurements currently present in the PrIME database can also be utilized.

Using the MATLAB code presented here, the agreement between the experimental and the simulation data can be checked for any Cantera or CHEMKIN format combustion mechanism. The coloured Excel table of local sensitivities provides hints for further mechanism development.

The code is also capable of creating response surfaces based on the experimental data files. This way the computational cost can be drastically decreased when large number of simulations is needed with different parameter sets.

Acknowledgements

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