Applications of Sensitivity Analysis to Combustion Chemistry

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Sensitivity analysis has been widely used in chemical kinetics [1] and it has frequently been applied to combustion chemistry [2] for uncertainty analysis and for gaining insight into mechanisms. The main combustion simulation codes, including the programs of the CHEMKIN [3] package or the RUN1DL package [4], all calculate local concentration sensitivities.

Most rate parameters in combustion are known with rather large errors. The uncertainties of reaction parameters are listed in collections of evaluated reactions. Combustion mechanisms usually include several hundred reaction parameters, but only some of them have to be known with high precision. These parameters are usually identified on the basis of local concentration sensitivities. Note, that global methods have not been used in combustion chemistry, while such methods have been applied widely to the uncertainty analysis of atmospheric chemical models.

The sensitivity matrix itself accounts for the change of a single variable as a result of the change of individual parameters. The simultaneous effect of parameter changes on the concentration of several species can studied as the sensitivity of objective functions. If the objective function is the sum of squares of deviations, then the sensitivity of this objective function, called overall sensitivity [5], is equal to the sum of squares of sensitivity coefficients. In the summation only the species present in the objective function have to be considered.

Principal component analysis (PCA) of the sensitivity matrix [5] also investigates the sensitivity of an objective function. PCA is applicable to the study of the effect of simultaneous parameter changes on several outputs of a model. This method is based on the eigenvalue-eigenvector decomposition of the cross-product of local sensitivity matrices.

Overall sensitivities and principal components can be used for uncertainty analysis. As an example, if the measured concentrations are considered in the objective function, PCA shows which parameters can be determined from the measurement. It can also indicate if only e.g. the ratio of two parameters can be determined from the measurement. Changing the initial concentrations, measurement times etc. allows an optimization of experiments.

Sensitivity analysis methods are well suited to the investigation and reduction of combustion mechanisms. Inspection of concentration sensitivities has the advantage over the study of reaction rates in that sensitivities also account for non-direct effects.

The traditional approach for the identification of rate limiting steps was finding an appropriate analytical expression for production rates. This method is not applicable in the case of large reaction mechanisms. It has been assumed, without justification, that the high sensitivity reactions are identical to the rate limiting steps. Recently it was shown [1] that identification of rate limiting steps on the basis of the time derivative of the concentration sensitivity matrix is in agreement with the classical definition and yet can be applied to mechanisms of any size.

While, in uncertainty studies the initial time of sensitivity calculations is always identical to the initial time of simulations, in mechanism investigation sensitivity

analysis can be applied to a narrow interval during the simulation. The features of a mechanism depend on the concentrations and change continuously during a simulation. By moving this observation window, changing features of a mechanism can be monitored. For example, PCA can be used to detect which are the QSSA species and the redundant reactions during the interval inspected.

The logical extreme of this concept is the study of mechanisms at a single time, i.e. at a fixed concentration vector. Dynamical sensitivities are not applicable here, but the sensitivity of reaction rates becomes a useful measure. The partial derivative matrix of production rates with respect to kinetic parameters is equal to the matrix normed reaction rate contributions [6]. The principal component analysis of this matrix reveals kinetic details of the mechanism and allows the detection of ineffective parameters and hence leads to the reduction of the mechanism.

The Jacobian of the kinetic ODE shows the sensitivity of reaction rates to the concentrations. This matrix can be used for finding redundant species in the mechanism [7] and for the calculation of the instantaneous error of QSSA species [8].

A program has been written for the KInetic aNALysis of Combustion mechanisms. This program, called KINALC, is a postprocessor to the simulation programs of the CHEMKIN package. It has been interfaced to the programs of the CHEMKIN package (SENKIN, PREMIX, PSR, SHOCK, and EQLIB) and also to the RUN1DL package.

KINALC carries out three types of analysis: processing concentration sensitivity analysis results, extracting information from reaction rates and stoichiometry, and providing kinetic information about the species.

KINALC can extract the important pieces of information from the sensitivity results dumped by the simulation programs. It can also calculate the sensitivity of objective functions, formed from the concentrations of several species. Principal component analysis of the concentration sensitivity matrix can be used for uncertainty analysis, parameter estimation, experimental design, and mechanism reduction. The program can also suggest a list of rate limiting steps.

Principal component analysis of the algebraic rate sensitivity matrix provides an effective method for mechanism reduction. The program also offers traditional ways for mechanism investigation and reduction, such as rate-of-production analysis and calculation of the fluxes of elements from species to species and the contribution of each reaction to these fluxes. The analysis of the Jacobian allows a reduction in the number of species and the estimation of the instantaneous error of QSSA species.

KINALC has been designed to be very user friendly. It accepts simple keyword and may provide a detailed explanation of the results. The program has a modular structure and can be easily extended by other methods for the analysis of reaction mechanisms and can be interfaced easily to other simulation programs. KINALC is available from the World Wide Web at address:

http://chem.leeds.ac.uk/Combustion/Combustion.html

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