Computer Aided Design of Complex Chemical Mechanism for Combustion Applications

F. Mauss

Division of Combustion Physics, Lund University, P.O. Box 118
SE-22100 LUND, Sweden

Introduction

Combustion, in technical applications, occurs under turbulent flow conditions. In modeling combustion devices with numerical tools it is necessary to consider the interaction of chemistry and flow. Chemistry-flow interaction models are demanding in both, computational time and memory. Thus, they limit the number of chemical species that can be explicitly taken into account. Technical fuels are mixtures of aliphatic and aromatic hydrocarbons that introduce chemical mechanism with hundreds of species and thousands of reactions. These numbers make it difficult to compile, analyze or optimize such a mechanism; they make it impossible to use these mechanisms together with computational fluid dynamical (CFD) programs. In addition to computational tools for mechanism generation, analysis and optimization, a variety of reduction methods are needed to lump parallel reaction paths, to detect unnecessary reactions and species, and to simplify the model equations for species reacting on time scales that are much shorter than the relevant physical time scales. In this paper an overview over available methods and their interaction is given.

Mechanism development for combustion applications

The compilation of detailed kinetic reaction mechanisms is a difficult and time consuming task. A set of elementary reactions is stated for each fuel. The data for the kinetic rate constants are taken from experiments or, if experiments are not available, from quantum mechanical calculations. Together with the rate constants the uncertainty of the kinetic data has to be stated. If the set of chemical reactions is complete, the mechanism has to be validated against experiments for global parameter such as ignition delay times, flame velocities of freely propagating premixed flames, and extinction limits of counterflow diffusion flames.

The first estimation of the mechanism will, caused by the uncertainties in the elementary reactions, result in a poor agreement between simulation and experiments, and improvements are necessary. The next step in compiling the reaction mechanism is to perform a detailed sensitivity analysis of the global parameter against all chemical rate coefficients. As a result of the analysis one gets a set of reactions that is most important for the current experiment. Hence the kinetic rate constants of these reactions need to be as accurate as possible. An iterative process of adjusting these rate coefficients and recalculating the experiments for the mechanism validation is utilized until the first set of optimized rate coefficients is reached.

In a second step the mechanism will be refined by controlling local parameter instead of the global ones. These are usually the time- or space resolved profiles for temperature, fuel, oxidizer, and for some intermediate and final products. Again an iteration procedure, as explained above, is employed that finally leads to a more improved reaction mechanism. Further improvement can be reached by controlling more sensitive local parameter like pollutants such as NOx and soot. For each step, in refining the reaction mechanism special emphasis must be taken to guarantee that the prediction of the targets defined for the prior optimization step is not worsened.

In the past such mechanisms have been constructed manually for hydrocarbon fuels up to butane. These mechanisms contain about 600 reactions and 80 species (see for example reference [1]). But for most of the mechanisms, found in the literature, the more complicated low-temperature kinetics for butane is missing. This is partly caused by, that in most technical application the low temperature oxidation of butane is not sensitive.

For higher hydrocarbon fuels this neglect is not possible, since for some technical relevant processes—for example the occurrence of the engine knock phenomenon in spark ignition engines—low temperature reaction pathways are essential. However the detailed inclusion of low temperature reaction for fuels like n-heptane involves more than 500 species and 4000 reactions [2]. It is almost impossible to compile such a mechanism by hand, and early reaction mechanisms were based on simplified models for the low-temperature oxidation of aliphatic fuels. These mechanisms have been validated for global parameter such as ignition delay times and flame velocities, only.

A more detailed description of the low-temperature oxidation is weakly motivated, since the high number of reactions and species involve many practical problems—the demanded effort in computational time and memory, the high number of reactions with unknown rate coefficients. It became visible that an automation of the steps, performed to develop a chemical reaction mechanism is needed to accelerate the progress in the field.

Automation of the mechanism development

The first automation in the process was the development of tools to analyze the chemical processes during combustion processes, i.e. the reaction flow analysis and the sensitivity analysis (see for example the overview article [3]). For the former the reaction fluxes from species to species are calculated in a post process to the combustion calculation, and a map can be drawn that visualizes the flow of atoms. For the latter the frequency factor in the Arrhenius approximation for the reaction velocity is used as a parameter in the system of differential equations. The sensitivity of unknowns on the reaction rate coefficient can be calculated from the sensitivity of the residual of the respective differential equation and the jacobian matrix of the underlying system of equations.

The next automation was the automatic generation of reaction mechanisms. The definition of chemical reactions for certain molecules was replaced by the definition of reactions of certain groups appearing in the molecules [4, 5]. Programs were written that scan through the fuel molecules and the intermediate species to find the specific molecule groups and to apply the corresponding reactions. At the first glance, this approach appears to be simple but the approach is leading to explosions in the number of species and the number of reactions, if no limitation is set. The first generated reaction mechanisms appeared a decade ago, and the number of applications, where a generated reaction mechanism is used is still low.

Finally the optimization of the reaction rate coefficients was automated. In a first step sensitive reactions for the targets—for example, unknowns at certain data points—to be optimized are selected from the matrix of sensitivity coefficients and from the uncertainties in the rate coefficients. Response surfaces for the difference between the experimental values for the targets and the numerically calculated values are produced, and the optimum set of rate coefficients is found by searching the set of rate coefficients with the minimum difference for all targets [6, 7].

Mechanism Reduction

The gap between the number of species allowable for CFD-applications and the number of species introduced by detailed reaction mechanisms shows that the knowledge transfer from fundamental research in combustion kinetics to engineering applications relies on the availability of mechanism reduction.
methods. The major reduction methods in use today can be divided into four groups. 1) removal of unnecessary reaction, 2) lumping methods, 3) simplification of the system of differential equation, through time scale analysis, and 4) tabulation methods.

The removal of unnecessary species and reactions is the oldest strategy in reducing chemical mechanism. It is intuitive to demand that an unnecessary species or an unnecessary reaction has a low chemical flux [8] and a low sensitivity on unknowns that the modeler wants to predict with high accuracy [9, 10]. However, the calculated sensitivity coefficients are only of first order accuracy and they may fail to predict, what happens if a species or a reaction is removed from a reaction mechanism. In addition the calculation of sensitivity coefficients is demanding in CPU-time. It is therefore often proposed to detect candidates for removal by reaction flow analysis, only. All strategies demand that the detailed reaction mechanism is first analyzed by a simple reactor model, for the chemistry flow interaction. Further it is demanded that the reduced reaction mechanism is validated against the detailed mechanism. The range of validity of the reduced mechanism is limited by the parameter range for the validation calculations, and by the physical importance of the employed reactor model.

A shortcoming of the necessity analysis is that it is not able to reduce the number of species or reactions in reaction systems, where the chemical flux occurs in many parallel and equally strong paths. This is the situation found for automatic generated reaction mechanisms for low temperature kinetics of aliphatic hydrocarbon fuels. In this situation the chemical lumping can lead to simplified reaction mechanisms [4, 5].

Instead of solving differential equations for the individual species one differential equation for the sum of the lumped species is solved. From this equation, the rate coefficients for the new (or general) species can be calculated. However, it is often necessary to estimate the ratio of concentrations of the lumped species [11]. This is possible if they have similar thermodynamic properties—they have almost equal concentrations.

The quasi steady state assumption (QSSA) is often applied in chemical systems. In combustion system it demands that the chemical processes are much faster than the relevant physical processes. [12] With computational singular perturbation (CSP) the set of equations governing the chemistry is described by a set of base vectors. The resulting eigenvalue problem allows the separation of fast and slow modes. Species found in the fast modes only are in steady state [13—15].

Another way to detect steady state species is to compare the chemical time of species consumption with the physical times of change in species concentration, convection and diffusion [16]. This species lifetime does not take coupled lifetimes into account. It assumes that the Jacobian matrix is diagonal [17].

Species concentrations can be solved from a set of algebraic equations if the QSSA is applied. This decreases the number of species that need to be transported in a CFD application, and thereby the demand on CPU-time and memory. In estimating how much a numerical error in species profile influences the accuracy of a target of a model calculation the sensitivity analysis, as described above can be applied [16]. In this application, sensitivity analysis gains a higher accuracy, since the error in the steady state species profile should be low; the influence of non-linearity in the sensitivity coefficients can be neglected. More steady state species can be detected, by combining the lifetime analysis with sensitivity analysis.

By using CSP fast and slow modes can be separated. A chemical system will move on the fast modes to a lower dimensional manifold, if it is started at any point in the number of species-dimensional chemical hyperspace. The development on the fast modes can be often described as a projection of the starting point on the low-dimensional manifold. A strong reduction in computational time is gained, if the intrinsic low-dimensional manifold (ILDM) is tabulated. This tabulation is done in a pre-process [18].

Conclusion

A variety of algorithms have been developed during the recent years that help the developer to generate, optimize and reduce reaction mechanisms for combustion applications. These developments build on each other and allow a fast knowledge transfer from chemical kinetic development to engineering applications. It got visible that a combination of these tools will allow computer aided design of chemical mechanism for technical applications in the near future.

References