## **Coupling Reaction Chemistry With Fluid Dynamics: Methods And Applications**

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# Introduction

Reactive flow simulations of combustion processes require as an input reliable chemical reaction models. In addition to the energy release rate, the chemical input is required for prediction of combustion-generated pollutants. The advance in computational fluid dynamics (CFD) and in computer technology makes it feasible to examine more realistic combustion systems by incorporating larger, more realistic reaction models. This presentation outlines the state of the art in the development and use of chemical reaction models for CFD applications. The focus is on the origin of reliable chemical mechanisms and approaches to development of reaction models in the form amenable to CFD simulations. (Within the scope and format of the present manuscript, only representative references are cites, mostly as pointers to further literature.)

## **General Strategy**

The experience gained by the combustion community for the past several decades seems to support the adopted strategy of first developing what became known as *detailed chemical kinetic mechanisms* and then reducing them in size for applications with CFD codes. Founded on fundamental chemistry and physics, detailed mechanisms allow extrapolation beyond conditions under which they are developed, the primary benefit when dealing with combustion phenomena. The difficulty, as far as CDF modeling is concerned, lies in the large size of detailed

mechanisms, typically comprised of hundreds and possibly thousands of reaction steps and hence dozens and hundreds of chemical species. It is possible, however, to reduce the size of the problem, and a number of different approaches have been pursued over the past two decades. "Reduction" does not merely imply "simplification" of the chemistry involved, but rather reduction in the complexity of the mathematical form and increase in numerical efficiency in evaluation of the chemical transformations.

### **Source of Reaction Models**

Historically, one composes a reaction mechanism from individual steps, combining information available from earlier reaction mechanisms, data compilations such as those of NIST [1] and Baulch et al. [2], and newer reaction rate measurements as they appear. The next step in the "quality control" consists in comparing the predictions of the newly composed mechanisms against experimental observations, usually limited to one or a small number of such sets. Comparison among different mechanisms serves grounds for moving to larger and "fuller" descriptions.

At the early days, when the size of detailed mechanisms was small and the number of mechanisms available for comparison was small, one could compare the performance of several such mechanisms against essentially all the data available. As the mechanisms, their number, and the experimental datasets available are all increase in size, such comparisons become more tedious and sometimes impossible due to practical limitations, and incorporation and propagation of errors and inconsistencies start to plague the progress. One frequent example is adjustment of the mechanism by fitting one's own data without testing what such adjustment does to comparison with other data. Automation of reaction set generation alleviates only some of the problems.

The GRI-Mech project [3] introduced a different approach. The GRI-Mech project was launched by four research teams with the objective of replacing development of "competing" reaction mechanisms with a single, unified reaction model. Funded by the Gas Research Institute, the project focus was on the combustion of natural gas.

The novelty of the GRI-Mech approach was rooted in its organization of data collection and evaluation, supported by rigorous numerical optimization. The assembled dataset included both thermochemical parameters and experimental observations, all with assessed uncertainties. The experimental data were classified into two groups: optimization targets (i.e., the training set), those observations that the final model is required to match closely, and validation targets, those the model is tested against after optimization for general agreement. The assignment of a given experimental data set into one of these groups was based on the ability to correctly model the physical environment of the experiment, the level of its documentation, the uniqueness, and the error bounds of the observation. A constrained optimization against the training set produced a candidate model. The latter was subjected to tests against validation targets, ultimately producing the best current model. The best current model was released publicly, with documentation of all the details (reasoning behind selection of data, the nature of constraints, etc). As a typical outcome, the optimization revealed inconsistencies in the initially assembled dataset along with failures for some validation tests. Focusing on the identified problems, new experimental and theoretical studies were initiated, the available literature data re-assessed, and the process repeated itself from the beginning toward generation of the next best current model, and so on.

Experience gained with the GRI-Mech project demonstrated an immediate benefit to the CFD community—a single reaction model with a documented source and pedigree. Released as

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a "public domain", GRI-Mech models have served as a starting and often as a reference point for comparison among different applications.

The experience gained with the GRI-Mech project is currently being expanded to a wider and broader group of collaborators, open to the entire combustion community. It is named PrIMe, for <u>Process Informatics Model</u>. The Web and software technology will be applied to automate numerous tasks and further enable operation of such a broad-based reaction-model collaboratory. Bringing together all accumulated data and all available human talent into a single enterprise will change the way chemical kinetics models are built, with even further and deeper benefits to the CFD community.

#### Adaptation of Models to CFD Needs

The PrIMe initiative reinforces further the strategy of starting with detailed kinetic models followed by their reduction in size. The *PrIMe Library*, one of the key elements of PrIMe, will provide an "infinite" collection of peer-reviewed reaction rate data. The objective is to assemble this information into a predictive reaction model and then to reduce it in size.

The first step in this direction is an automated assembly of individual pieces of information on reactions, species thermodynamics, and reaction rates into a single numerical model. Several approaches have been pursued to address this challenge [4,5]. Given a large, and presumably complete (in the context of a given application) detailed reaction model, the next objective is to reduce the numerical burden of its use with CFD codes. From the point of view of mathematical representation of the reduced model, numerous approaches applied to the latter problem can be classified into three basic groups: pruning, lumping, and parameterization.

*Pruning*. The initial detailed kinetic model is presumably constructed by inclusion of all potentially significant reactions and species. Not all of them contribute significantly to specific

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responses of a given application, and those can be safely removed. The result of such pruning is still a detailed kinetic model, but with a smaller number of reactions and species than in the initial model. Several approaches have been pursued in this category [1,4-6], all essentially based on comparing individual reaction terms, and removing those below a certain threshold value.

*Lumping*. In this class of methods, the objective is to transform (or reduce or lump) a given set of species into a few dynamically equivalent lumped variables. The resulting model seldom takes the form of mass-action-law kinetics. The underlying idea rests on the fact, known since the beginning of the 20<sup>th</sup> century, that the actual dimensionality of the dynamic evolution of a given reaction system is much lower than the number of chemical species. Steady-state and partial-equilibrium approximations [7], principal-component transformations [8], Computational Singular Perturbation (CSP) [9], Intrinsic Low-Dimensional Manifold (ILDM) [10], and the method of moments [11,12] are all building on this principle.

*Parameterization*. A system of differential equations describing evolution of a chemical kinetic system establishes a relationship between model responses and model variables. Capturing needed relationships by simple algebraic models can replace the calls to an ODE solver with a computationally more economical evaluation of such algebraic models. The latter took the form of flamelet libraries [13], Solution Mapping using quadratic polynomials [14] and their piecewise implementation (PRISM) [15], high-order polynomials [16], and In Situ Adaptive Tabulation (ISAT) [17].

It has been argued [18,19] that it is unlikely for a single, all-purpose reduction method to satisfy all the needs, and many situations may require several reduction techniques to be used concurrently. Recent developments [4,20,21] provide examples of such combined applications.

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