568b A New Adaptive Representation of Complex Kinetic Models

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Hydrocarbon oxidation, one of the leading chemical transformations in transportation applications, is a process easily stated, yet very complicated to understand in detail and even more intricate to properly model. Macroscopic models of combustion, such as the so-called Shell Model, have been used for the longest time in order to predict the rate of heat release or the rate of consumption/production of the main fuel/product molecules (Halstead, Kirch et al. 1977; Crua, Kennaird et al. 2004). However, due to environmental concerns combustion models are revisited to address critical issues such as predictive response over extended ranges of operation, and increased accuracy requirements at the ppm level. It has been realized that macroscopic characteristics are inadequate and therefore a detailed description of combustion chemistry is needed (Gardiner 1996). A distinguishing feature of the combustion of many hydrocarbons is the "negative temperature coefficient", NTC (Pilling and Hancock 1997) At very low temperatures, as the temperature is raised the ignition delay of a fuel is decreased. However, for many fuels, at a certain temperature the ignition delay reverses its coarse and becomes longer as the temperature is raised. At some higher temperature the ignition delay decreases again. In order to capture all the intricate details of fuel-like molecules (Griffiths 1995) mechanisms of significant size are required, potentially involving thousands of species and tens of thousands of reactions (Curran, Pitz et al. 1998). One of the key complications is that different temperature regimes are known to activate different reaction pathways. Multi-point ignition in homogeneous charge compression ignition engines is a great manifestation of the impact of chemistry induced due to spatial inhomogeneities in composition, temperature and pressure. The effects of non-homogeneous fuel-air mixtures are key to understanding the nature of multi-point ignition and further conceptualize potential embodiments that enhance or control the simultaneous ignition of the mixture (Echekki and Chen 2003).

Although, extensive research in the modeling of combustion kinetics has led to the development of detailed kinetic networks, consisting of hundreds of species and thousands of reactions the solution of the detailed combustion flow along with such large kinetic mechanism is a computationally infeasible task. Hence the need for representing the complex chemical reactions by simple reduced models, which can retain considerable accuracy while rendering computational feasibility.

In practice, to alleviate the computational complexity, the reacting flow models use a skeletal kinetic model instead of the detailed mechanism. There has been considerable effort towards reduced representation of detailed kinetic mechanism to alleviate the computational workload, a detailed review of which can be obtained in Tomlin et al. (1997). Most of the techniques are based on the concept of timescale separation. These include Quasi Steady State Approximation (QSSA) (Peters, 1988), Intrinsic Low Dimensional Manifold (ILDM) (Mass and Pope, 1992) method, Computational Singular Perturbation (CSP) (Lam and Goussis 1994), and more recently In situ Adaptive Tabulation (ISAT) technique proposed by Pope 1997. Another suggested approach towards automation of the mechanism reduction is the mathematical programming based approach (Androulakis 2000), (Petzold and Zu 1997), (Banerjee and Ierapetritou 2003), (Bhattacharjee, Schwer et al. 2003) the basic idea of which is followed in the present work.

For most of the existing reduction schemes mentioned before, the simplified kinetic model represents the chemical activity tolerably well in a limited region of the flow field and is not accurate over the entire temperature/ composition space of interest. Moreover, in many burner simulations there are large areas of relatively little or no chemical activity, and a small region of intense chemical reaction. (Schwer, Lu et al. 2003a; Schwer, Lu et al. 2003b), presented a burner simulation by using three reduced models and one non-reactive chemistry model. Accurate prediction of the flow simulation was obtained by using the non-reactive models for considerable regions of the simulation. Hence, when a single chemistry model is used for such simulation, the reaction equations are unnecessarily integrated even in the nonreactive zones.

In this paper we present a comprehensive framework extended our previous work in representation of complex kinetic transformations (Androulakis, Grenda et al. 2004) and adaptive chemistry development ((Banerjee and Ierapetritou 2003). The proposed approach is capable of capturing the important combustion characteristics over time and efficiently integrate detailed flow simulations with complex reaction schemes. We will demonstrate the methodology by analyzing both high temperature oxidation (flame speeds) and low temperature (autoignition delay) characteristics. The intriguing complication of the latter is that it requires the development of reduced mechanism that captures fundamentally different reaction chemistries.

The proposed methodology is developed in this work to automatically construct reduced mechanisms by utilizing mathematical programming techniques, where the objective is to minimize the dimension of the system while retaining sufficient accuracy in the prediction of specific species profiles. The reduced mechanism thus obtained has the property of accurately predicting the system behavior over a range of conditions in and around the nominal point at which reduction is performed. This scheme indeed gives rise to accurate and flexible reduced models, but is itself an expensive operation, since it requires multiple integration of the stiff, nonlinear ODEs describing the kinetic source term. Also, the number of binary variables handled by the MINLP formulation can be restrictive. Thus direct application of this procedure in very large mechanisms may prove to be inefficient. For such cases it is found to be efficient to use a two-stage reduction procedure, where a first level reduction can be performed using less expensive methodologies based on flux-analysis (Androulakis, Grenda et al. 2004), followed by more detailed reduction using the integer programming approach.

The developed scheme has great flexibility in capturing the behavior of the system, along with specific combustion characteristics like laminar flame speed and ignition delays. The approach is illustrated with highly complex kinetic mechanisms describing high temperature oxidation (flame speed) of light hydrocarbons (C1-C4) (Marinov, Castaldi et al. 1997) and low temperature auotoignition delay of primary reference fuels (nC7-iC8 mixtures) (Curran, Pitz et al. 1998).

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