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Explicit reduced reaction models for ignition, flame propagation, and extinction of $C_2H_4/CH_4/H_2$ and air systems

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Abstract

Large-scale simulations of multidimensional unsteady reacting flows with detailed chemistry and transport can be computationally extremely intensive even on distributed computing architectures. With the development of computationally efficient reduced chemical kinetic models, the smaller number of scalar variables to be integrated can lead to a significant reduction in the computational time required for the simulation with limited loss of accuracy in the results. A general MATLAB-based automated procedure for the development of reduced reaction models is presented. Based on the application of the quasi-steady-state (QSS) approximation for certain chemical species and on the elimination of selected fast elementary reactions, any complex starting reaction mechanism (detailed or skeletal) can be reduced with minimal human intervention. A key feature of the reduction procedure is the decoupling of the QSS species appearing in the QSS algebraic relations, enabling the explicit solution of the QSS species concentrations, which are needed for the evaluation of the elementary reaction rates. In contrast, previous approaches mainly relied on an implicit solution, requiring computationally intensive inner iterations. The automated procedure is first tested with the generation of an implicit 5-step reduced reaction model for CH_4/air flame propagation. Next, two explicit robust reduced reaction models based on ignition data (18-step) and on flame propagation data (15-step) are systematically developed and extensively validated for ignition delay time, flame propagation, and extinction predictions of C_2H_4/air, CH_4/air, and H_2/air systems over a wide range of equivalence ratios, initial temperatures, pressures, and strain rates. In order to assess the computational advantages of the explicit reduced reaction models, comparisons of the computational time required to evaluate the chemical source terms as well as for the integration of unsteady nonpremixed flames for each model are also presented.

Keywords: Reduced reaction mechanism; Chemical kinetics; Explicit solution; Steady-state approximation; Ethylene

1. Introduction

The concept of deriving simplified chemical kinetic models based on the quasi-steady-state (QSS) approximation for selected intermediate chemical species dates back to the early 1900s. Some examples are the homogeneous reaction models of Boden-

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stein [1] and the heterogeneous reaction models of Langmuir [2]. While these early investigations were motivated by the lack of chemical kinetic data, the recent efforts on mechanism reduction [3,4] were driven by the computational difficulty associated with the implementation of rather large detailed chemical kinetic models [5], especially in large-scale simulations of unsteady multidimensional combustion systems.

An early investigation aimed at reducing the computational effort using the rate-controlled partial equilibrium (or rate-controlled constrained equilibrium, RCCE) approach was first described by Keck and Gillespie [6]. A major weakness of the RCCE approach lies in the identification of the "kinetic constraints," which is still an active research topic [7]. The systematic application of the QSS approach of Peters [8] eliminated the arbitrariness of imposing "kinetic constraints" and established the field of reduced reaction modeling. A majority of early investigations using reduced reaction models based on the QSS approximation were analytical in nature [9–14]; hence the computational efficiency was not a primary factor in developing these reduced models. For example, highly stiff coupled algebraic relations arising from the QSS approximation were solved iteratively, i.e., with "inner" iterations [15], or the coupled QSS algebraic relations were truncated to yield "explicit" expressions for the species in QSS, albeit within a narrow range of validity or with diminished accuracy. The need for introducing "inner" iterations or "truncations" clearly increased with the complexity of the detailed reaction model, e.g., when dealing with models describing large hydrocarbon fuel oxidation. The formal computer-based reduction methods, e.g., the computational singular perturbation (CSP) method of Lam [16], the computer-aided reduction method (CARM) of Chen [17], and the intrinsic low-dimensional manifold (ILDM) method of Maas and Pope [18], facilitated the development of reduced reaction models for large detailed models, based on the quasi-steady-state/partial-equilibrium approximation in the homogeneous ignition system. Variants of the CSP approach have been used by others [19,20] to obtain reduced reaction models based either on ignition or on perfectly stirred reactor simulations. Application of CSP to transport-dominated flows has also been pursued by neglecting transport effects on QSS relationships [21]. Shortcomings associated with such decoupling of transport effects from chemistry have been investigated recently by Lam [22]. These mathematical/computational approaches still require the solution of highly stiff algebraic relations using computationally expensive "inner" iterations, which the RCCE approach intended to avoid via the potential element method. Once a reduced-order or low-dimensional model is identified, the only feasible way to minimize the dependence on computationally expensive "inner" iterations is to use either the in situ adaptive tabulation (ISAT) approach [23] or the artificial neural networks approach [24,25].

After careful consideration of the above literature, the present paper describes an automated mechanism reduction procedure developed in the MATLAB environment. A key distinction of the present approach from previous work is the ability to relax certain QSS relationships to obtain "explicit" expressions for the QSS species, i.e., to completely avoid costly "inner" iterations. The level of relaxation can be based on a predetermined tolerance satisfying the QSS approximation. A computational cost analysis is presented, highlighting the differences between the "explicit" reduced reaction model (ERRM) approach and the "inner" (or implicit) iteration approaches. Another important feature of the present ERRM approach is the ability to analyze solutions of the ignition process in a spatially uniform well-stirred reactor as well as solutions of premixed or nonpremixed flames with transport effects. As shown here, the reduced reaction models derived based on the ignition solution can be different from that derived using a steady-state flame structure solution, especially when considering the absence of transport effects in the homogeneous ignition problem. In this regard, the present MATLAB-based ERRM approach is more general than the CSP approach [16]. Other features include the ability to always obtain a unique reduced reaction model by elimination of the fast reactions in a logical manner and the ability to tailor the output from the MATLAB program to adapt to various computational codes.

The chemical reaction pathway analysis methods developed as part of this effort can be readily implemented to automatically extract "skeletal" reaction models for engineering applications from any selected "detailed" kinetic model. Ethylene (C_2H_4) was selected as a fuel of interest because of its importance in the reaction pathways of large hydrocarbon fuels [26–28]. Prior to the identification of a suitable skeletal model for C_2H_4, several detailed kinetic models available for CH_4 and C_2H_4 oxidation were considered, i.e., Wang and co-workers [29], Lawrence Livermore National Laboratory [30], UC San Diego [31], GRI-3.0 [32], and others [33]. Based on extensive comparisons of predicted ignition delay, laminar burning velocity, and nonpremixed flame extinction with experiments involving C_2H_4, CH_4, and H_2 as fuels (see Caltech Report [34]), Wang's mechanism consisting of 71 species in 469 reactions was selected as the baseline model for the present investigation. It must be emphasized that the MATLAB-based program developed here can be extended readily to any detailed kinetic model. The C_2H_4 skeletal model extracted based on Wang's model consists of 31 species