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A criterion based on computational singular perturbation for the identification of quasi steady state species: A reduced mechanism for methane oxidation with NO chemistry

Tianfeng Lu *, Chung K. Law

Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, NJ 08544, USA

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Abstract

A criterion based on computational singular perturbation (CSP) is proposed to effectively distinguish the quasi steady state (QSS) species from the fast species induced by reactions in partial equilibrium. Together with the method of directed relation graph (DRG), it was applied to the reduction of GRI-Mech 3.0 for methane oxidation, leading to the development of a 19-species reduced mechanism with 15 lumped steps, with the concentrations of the QSS species solved analytically for maximum computational efficiency. Compared to the 12-step and 16-species augmented reduced mechanism (ARM) previously developed by Sung, Law & Chen, three species, namely O, CH_3OH, and CH_2CO, are now excluded from the QSS species list. The reduced mechanism was validated with a variety of phenomena including perfectly stirred reactors, auto-ignition, and premixed and non-premixed flames, with the worst-case error being less than 10% over a wide range of parameters. This mechanism was then supplemented with the reactions involving NO formation, followed by validations in both homogeneous and diffusive systems.

Keywords: Mechanism reduction; Quasi steady state approximation; Computational singular perturbation; Methane

1. Introduction

The original objective of the present study was to develop an improved reduced mechanism for methane oxidation based on recent advances in the mathematical and computational algorithms in mechanism reduction. The activity, however, has led to the recognition of a major inadequacy in the suite of methodologies that have been developed for systematic reduction, namely the rigorous identification of quasi steady state (QSS) species. A criterion was subsequently developed and forms the fundamental core of the present work, and was then applied to the reduction for methane oxidation, yielding the desired reduced mechanism suitable for computational simulation.

In terms of our specific interest in developing a reduced mechanism for methane oxidation, it is first noted that several reaction mechanisms for methane

* Corresponding author.
E-mail address: tlu@princeton.edu (T. Lu).

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oxidation have been compiled [1–4], and reduced mechanisms of various complexities have also been developed for qualitative analysis as well as quantitative simulations [5–16]. Studies have further shown that while models with a few global steps could be used for qualitative analysis under limited ranges of parametric variations, reduced mechanisms with about 20 species can indeed mimic the detailed mechanisms with impressive accuracy over wide parametric ranges, even with NO chemistry [15].

Most of these reduced mechanisms are based on quasi steady state approximation (QSSA) [17], which solves the concentrations of the QSS species through algebraic equations. Skeletal reduction [18–28], which eliminates unimportant species and reactions from detailed mechanisms, has rarely been applied together with QSSA in the reduction of methane mechanisms, probably because many detailed methane mechanisms have already been trimmed to small sizes. Nonetheless, it was found in the present study that there are still a few species and reactions which can be eliminated in such detailed mechanisms as GRI 3.0 [4] using the method of directed relation graph (DRG) [24–26]. Therefore, skeletal reduction with DRG was first performed in the present study so as to eventually obtain a reduced mechanism of minimum size.

The resulting skeletal mechanism can then be further reduced by time-scale reduction. The reduction is based on the concept that fast chemical modes typically cannot self sustain and will result in algebraic relations of species when exhausted. Such exhausted fast modes can be identified with systematic approaches such as intrinsic low-dimensional manifold (ILDM) [29,30], which can be further facilitated by pre-image curves [31,32] and *in-situ* adaptive tabulation (ISAT) [33,34], and computational singular perturbation (CSP) [35–39]. These systematic approaches involve the evaluation and manipulation of Jacobian matrices, which can be very time consuming for large mechanisms.

QSSA and partial equilibrium (PE) approximations are more specific approaches in time-scale reduction. They are frequently more efficient to apply than the more systematic approaches of ILDM and CSP, and QSSA has been widely adopted for the reduction of small hydrocarbons. Indeed, there exist several intrinsic advantages in the application of QSSA. First, compared to the PE approximation, QSS species are typically present in low concentrations and can be removed from the conservation equations without significant error induced to the remaining species. Second, it has been shown that there is no violation of element conservation or entropy production for the remaining species if the QSS species are solved internally [40]. Third, a systematic procedure has been developed to derive the lumped global reactions given the list of QSS species [41], with the concentrations of the QSS species subsequently solved by internal algebraic iterations. Fourth, a systematic approach to obtain analytic solution for the QSS species has been recently developed based on QSS Graph (QSSG), through which the QSS algebraic equations can be solved with high efficiency [42].

Having emphasized the merits of the QSSA approach and the algorithms that have been developed to facilitate its application, it is then of interest to recognize that there is still no rigorously derived algorithm for the identification of the QSS species. In many previous studies, the QSS species are selected with such methods as normalized net production rate [16], life time analysis [43,44], concentration-weighted CSP pointer [12,13], normalized species time scale defined through CSP radical pointer [14], and genetic algorithm [45]. As will be discussed in due course, many of these methods involve semi-empirical criteria, which may result in misclassified QSS species. Consequently we propose in the present study a new criterion for the identification of QSS species based on CSP analysis. This criterion will then be applied to derive an accurate and efficient reduced mechanism for methane oxidation from GRI 3.0.

2. Methodologies

2.1. Skeletal reduction

The first step in the reduction of a detailed mechanism, for example the GRI 3.0, is to eliminate the unimportant species and reactions. For comparison with previously reduced mechanisms in [15], we shall develop reduced mechanisms without and with NO formation respectively. The NO chemistry was first removed from the detailed mechanism for the derivation of the mechanism for fuel oxidation, resulting in a 35 species mechanism (without Ar). Selected species for NO chemistry will then be appended to the reduced mechanism to obtain a reduced mechanism for the prediction of NO formation. The reduction in the present study is based on reaction states sampled from two homogeneous applications, namely auto-ignition and perfectly stirred reactor (PSR), which are typical applications for the study of ignition and extinction chemistries respectively. The parameter range covers pressure of 1–30 atm, equivalence ratio of 0.5–1.5, and initial temperature of 1000–1600 K for auto-ignition, and 300 K for PSR.

The method of DRG [24–26] was first applied to the 35-species mechanism. Briefly, DRG maps the species coupling to a directed graph. Weak species couplings, in a normalized form, are truncated based