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Skeletal reaction model generation, uncertainty quantification and minimization: Combustion of butane

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ABSTRACT

Skeletal reaction models for *n*-butane and *iso*-butane combustion are derived from a detailed chemistry model through directed relation graph (DRG) and DRG-aided sensitivity analysis (DRGASA) methods. It is shown that the accuracy of the reduced models can be improved by optimization through the method of uncertainty minimization by polynomial chaos expansion (MUM-PCE). The dependence of model uncertainty on the model size is also investigated by exploring skeletal models containing different number of species. It is shown that the dependence of model uncertainty is subject to the completeness of the model. In principle, for a specific simulation the uncertainty of a complete model, which includes all reactions important to its prediction, is convergent with respect to the model size, while the uncertainty calculated with an incomplete model may display unpredictable correlation with the model size.

1. Introduction

Detailed kinetic modeling is a useful tool to probe intricate fuel combustion and flame phenomena. The modeling approach usually involves the use of a detailed reaction model consisting of the relevant chemical species and elementary reactions that may participate in sequential and parallel kinetic processes of fuel oxidation. In such a model, the rate parameters are usually derived from experimental rate measurements, reaction rate theories, or, in many cases, estimations from analogous reactions. In all cases, the values of the rate parameters can be uncertain to various extents [1]. Consequently the uncertainty of the model parameters causes the prediction to be correspondingly uncertain—an issue that has received an increased attention and has been discussed in a variety of contexts in recent years (see, e.g., [2–25]).

Recent efforts directed at developing reaction models for practical liquid fuels and their surrogates have led to the emergence of large models, some of them may contain $O(10^{3-4})$ species and $O(10^{4-5})$ reactions (see, e.g., [26]). The use of these detailed models in computational fluid dynamics (CFD) introduces another problem. That is, the models are too large to be practical for CFD applications and must be reduced in size and complexity before they can be used [27,28]. Consequently, various model reduction strategies have been proposed (see, e.g., [28–30]). In general, the methods of model reduction may be categorized into skeletal reduction and time scale analysis. Skeletal reduction eliminates unimportant species and reactions, which can be achieved by sensitivity analysis [30–33], principal component analysis [34], Jacobian analysis [32], optimization [3], detailed reduction [35], directed relation graph (DRG) [36–38], DRG with error propagation [39], and DRG-aided sensitivity analysis (DRGASA) [40,41]. Time-scale analysis identifies fast species as well as reactions, and describes their time evolutions by algebraic equations. Methods of time-scale analysis are primarily based on quasi-steady-state (QSS) and partial equilibrium (PE) assumptions [42–46]. Several approaches to identifying the QSS species have been proposed [45–52]. Other, and perhaps more systematic approaches to time-scale analysis include intrinsic low-dimensional manifolds (ILDM) [53] and computational singular perturbation (CSP) [54–57].

In the present study, we propose an improved model reduction strategy by integrating the processes of skeletal reduction with model optimization and uncertainty quantification. In this strategy, a skeletal model is derived using DRGASA. The rate coefficients in skeletal models are then subject to a multi-parameter constraining against full-model predictions of a prescribed set of combustion properties, so that the model can be made predictive when DRGASA is used in an aggressive manner to generate ever-smaller models. We also explore the correlation between a model's size and the uncertainty in its predictions in order to identify when

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models are reduced beyond any capacity to be predictive. The paper is organized as follows. In Section 2, the research strategies of model skeletal reduction, optimization and uncertainty quantification are specified in detail. In Section 3, models of different sizes were generated from a detailed chemistry model, USC Mech II, [58], using *n*-butane and *i*-butane combustion as examples. The uncertainties of the skeletal models are quantified by the spectral expansion technique [20] and correlated to model size. Conclusions are summarized in Section 4.

2. Methodology

2.1. Skeletal reduction

A detailed reaction model is composed of three types of species: critical, nonessential, and marginal. For a given simulation, critical species participate in those reaction channels that largely determine the simulation results, while nonessential species only participate in reaction channels having little to no influence on the simulation results. The categorization of any particular species is conditional, subject to specific simulation circumstances. A successful skeletal reduction retains all critical species, eliminates all nonessential species, and properly deals with the marginal ones. The importance of species can be assessed by two types of method, examining the species conversion flux (e.g., [36–39]) or sensitivity analysis [30–32,41]. These two methods have their respective advantages and disadvantages. Flux analysis is affordable computationally and able to identify nonessential species efficiently. However, it can misestimate the importance of marginal and critical species. Sensitivity analysis quantifies the importance of species with better accuracy but it often requires prohibitive computational costs, hence preventing its application in reducing large models. Here, the skeletal model reduction adopts a two-stage procedure [41]: the detailed model is first reduced by flux analysis to an intermediate-size model from which a final skeletal model is generated by sensitivity analysis. In the present study, this two-stage strategy is conducted by combining DRG with DRGASA.

2.1.1. Overview

Model reduction always requires that the conditions be defined against which the model will be reduced. In this work, we developed a reduced model for the oxidation of butane. As such, the model was reduced using a set of laminar flame and auto-ignitions of butane/air mixtures. The conditions considered are listed in Table 1 and cover pressure in the range of 1 atm $\leqslant p \leqslant$ 20 atm, equivalence ratio $0.6 \leqslant \phi \leqslant 1.5$, and initial temperature 800 K $\leqslant T_0 \leqslant$ 1500 K for auto-ignition, and inlet temperature T_{in} = 300 K for laminar flame speed. There are a total of 45 ignition delay times and 9 flame speeds. The auto-ignition and flame propagation of *n*-butane–air and *i*-butane–air mixtures were simulated using USC Mech II [58]. The model was developed for high-temperature oxidation of H_2, CO and C_1–C_4 hydrocarbons and consists of 111 species and 784 reactions.

Table 1
Combustion targets used to reduce and constrain the model.

Target[a]	Flame speeds	Ignition delay times
p (atm)	1, 10, 20	1, 10, 20
φ	0.6, 1, 1.5	0.6, 1, 1.5
T_0/T_{in} (K)	300	800, 1000, 1200, 1400, 1500

[a] The targets are constituted by taking the combination of pressures, equivalence ratios and initial/inlet temperatures.

2.1.2. Directed relation graph model reduction

Both DRG and DRGASA have been discussed in detail elsewhere [36–38,41], and as such are presented here only briefly. DRG represents a chemistry model by a directed relation graph, whose nodes are species and the width of the edge from node m to n, r_{mn}, is calculated as:

$$r_{mn} = \frac{\sum_{i=1,N_R} |\nu_{i,m}\omega_i \delta_n^i|}{\sum_{i=1,N_R} |\nu_{i,m}\omega_i|} \tag{1}$$

where

$$\delta_n^i = \begin{cases} 1, & \text{if the } i\text{th reaction involves species } n \\ 0, & \text{otherwise} \end{cases}$$

and the subscripts m and n identify the species. Additionally, N_R is the total number of reactions, $\nu_{i,m}$ the stoichiometric coefficient of species m in the ith reaction, and ω_i the net reaction rate of the ith reaction. The value of r_{mn} quantifies the importance of species n to the production of species m. For a given user-specified threshold ε, skeletal reduction is conducted by truncating edges narrower than ε. A species is eliminated when all edges linking to it are removed during this process. With increasing ε, an increased number of species is removed. The critical ε value, corresponding to the elimination of a certain species, is utilized as the DRG index of this species. An intermediate-size skeletal model is generated by removing species with a small DRG index, typically less than 0.1, and the remaining species are further examined in the subsequent sensitivity analysis through DRGASA. It should be noted that, since there are many conditions against which the model is reduced, the overall DRG index for a given species is defined to be the maximum DRG index across all conditions, so that if a species must be kept to reproduce one condition, it is kept for all conditions; in other words, the skeletal model reduced against all conditions is the union of skeletal models reduced for each condition.

2.1.3. Directed relation graph-aided sensitivity analysis

It is possible that DRG will result in the removal of relatively few species from the model, which would not be an especially useful model reduction technique. USC Mech II is an example of such a model, as will be shown in Section 3. As a result, the DRGASA method [40,41] was developed to enable a more aggressive reduction of the skeletal models. In DRGASA, species with a large DRG index, chosen to be greater than 0.5 in this work, are defined to be critical and kept in the final skeletal model without sensitivity test. What remains, then, is to sort the remaining species into the marginal and nonessential sets. To accomplish this, the importance of a particular species is defined as the maximum relative error, $err_{\max}$, in a model prediction caused by the removal of that species. In this case, each reduction condition has the reference value η_r^{ref} predicted by the skeletal model. When species k is removed from the skeletal model, there is a new predicted value $\eta_{r,k}^*$. There is then an error for each species, $err_{r,k} = (\eta_r^{\text{ref}} - \eta_{r,k}^*)/\eta_r^{\text{ref}}$, and $err_{\max}$ for a species is the maximum, over all conditions r, of the $err_{r,k}$. The examined species are ranked by their importance, and model reduction is carried out by successively eliminating species of the least importance, until the resulting model cannot satisfy a prescribed accuracy requirement.

2.2. Model optimization and uncertainty quantification

Removal of reaction pathways can lead to quantitative changes in the model prediction. Because the dimensionality of the reduced model generally remains large, it should be possible to constrain the reduced model against the detailed model by an error minimization procedure. Rate coefficients subject to the minimization procedure are selected using a one-at-a-time sensitivity analysis