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Skeletal mechanisms of n-butanol, methyl butanoate, and syngas using Alternate Species Elimination (ASE)

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Skeletal mechanisms of methyl butanoate, n-butanol and syngas are derived from selected detailed chemical kinetic models for use in computational combustion applications. These reduced models are obtained using a species sensitivity mechanism reduction method termed the Alternate Species Elimination (ASE) approach. Ignition delay simulations are used as target combustion events to assess the relative change induced by the exclusion of a species under consideration. It is shown that a limited sample of ignition conditions is sufficient to provide a hierarchical ranking of chemical species from which skeletal models can be derived. The performance of the skeletal models presented in this study is assessed by comparing their predictions of ignition delay times, premixed flame propagation and diffusion flame structures with the predictions of the original detailed models. It is shown that ranking species on the basis of ignition simulations is capable of capturing a wide range of combustion phenomena, such as flame propagation and flame structure.

1   Introduction

Challenges in the design of high-efficient and less pollutant combustion devices increasingly necessitate the incorporation of chemical kinetic effects in computational analyses. Such analyses are also needed for maintenance of said devices as well as in the development of their control systems. In response to this need, combustion chemistry research in the last decade has led to a wide range of chemical kinetic models for transportation fuel surrogates, ranging from conventional fuels to biofuels [1–3].

However, direct implementation of the resulting models from the synergy of fundamental experiments and modeling is rendered difficult by the high computational costs and stiffness problems. Reduced chemical kinetic models are deemed a good compromise between the need for improved combustion chemistry descriptions in simulations and the high computational costs of detailed models. The development of these reduced chemical kinetic models presents a challenge on its own. Several mechanism reduction methods, such as in Refs. [4–9], have been proposed to derive skeletal mechanisms from the detailed models, retaining the ability to predict *essential* combustion properties. The designation of these *essential* properties may vary from one end-user to another but most often, the ability to predict ignition delay times, laminar burning velocity, flame extinction and the main features of premixed and non-premixed flame structures. In this work, skeletal chemical kinetic models are presented for some relevant fuels.

2 Reduction Approach

The species sensitivity approach to reduction is used, in a formulation referred to as Alternate Species Elimination [10]. It is further assumed that a homogeneous gas-phase chemically reacting system constitutes a rigorous test of the gas-phase chemistry of a given fuel/oxidizer system. Such a system evolves from an unburned state to a burned equilibrium state through a transient process of ignition. The chemical species constitute degrees of freedom of the homogeneous chemical system. The crucial degrees of freedom or chemical species can be identified by probing the effect of their alternate exclusion on ignition delay predictions.

This procedure is easily accomplished using a software package, such as CANTERA [11], whose "setMultiplier" feature enables the user to eliminate elementary reactions involving the species under consideration by simply setting the reaction rate multiplier to zero. It is then possible to perform a loop over the species of interest and generate for further analysis, a file which contains the ignition delay times and other combustion properties of interest resulting from ignition simulations with the respective species eliminated.

Based on a characteristic combustion property, a normalized change, NC, induced by the elimination of each species can be evaluated. For the ignition-based reduction, a convenient combustion property is the ignition delay time, τ, based on maximum temperature gradient. That is, the NC is defined as:

$$NC_i = \frac{\tau_i - \tau_0}{\tau_0} \tag{1}$$

All chemical species are then ranked by the absolute magnitude of their normalized changes, NC, and a skeletal model is obtained by direct elimination of chemical species whose NCs are below a user-defined threshold, NC_{thresh}. In the case of multiple ignition conditions, the ranking is based on the average of the absolute magnitudes of NCs. The NC_{thresh} is preferably determined from the iterative testing of the new mechanism against the detailed mechanism with respect to the prediction of a wide range of combustion properties. The simplest combustion chemistry model, the one-step global reaction, typically involves the fuel molecule, O_2, H_2O and CO_2, so that these can be automatically retained as indispensable in the mechanism. A skeletal mechanism is generated from the detailed model by excluding all elementary reactions in which the excluded species appear as reacting partners. An intermediate temperature, such as 1000 - 1100 K, is preferable as the initial temperature for ignition. The low-temperature chemistry is then captured by simply lowering the threshold of the Normalized Change, NC_{thresh}.

3 Application of the ASE method to mechanism reduction

The ASE approach is employed in this work to develop skeletal models from selected detailed chemical kinetic models. Although reduction is based on ignition delay time predictions, the skeletal mechanisms obtained are also tested with respect to their ability to predict flame propagation phenomena.

3.1 Skeletal model of methyl butanoate (MB)

The detailed model for methyl butanoate (MB) by Dooley et al. [12] is used to obtain an appropriate skeletal model for high-temperature combustion. As mentioned above, the combustion event used for the reduction is homogeneous gas-phase ignition of fuel/air mixtures at an initial pressure of 15 atm, temperature of 1050 K and for three MB/air mixtures with equivalence ratios, ϕ of 0.5, 1.0 and 2.0. For consistency, during species elimination, the ignition delay time is defined as the time to maximum temperature gradient. The normalized change in ignition delay time is calculated as shown in eqn. 1. The average absolute NC value for the three equivalence ratios is used to rank the species. It is observed that under these conditions, only approximately 100 species of the 275 species in this model significantly influence the reactivity of the system. Further details of the MB reduction are provided in Ref. [10].

In Fig. 1, the 25 most important species, exclusive of MB, O_2, H_2O and CO_2, are plotted. Negative NC values indicate shorter delay times or increased reactivity when reactions involving the indicated species are eliminated, while the positive values indicate reduced reactivity upon exclusion of the species subchemistry. This sensitivity representation, in contrast to the traditional elementary reaction-based sensitivity, can provide further insight on reactivity and model performance. The NC signs indicate the overall effect of the sub chemistry of each species on reactivity and the magnitudes provide information on the relative importance of a species in any group of species of interest. It is observed that most of these species are from the hydrogen and methane systems. Elimination of any of the first three species, OH, H_2O_2 and CH_2O, leads to failure of the system to ignite, even after a duration which is 3 times as long as the normal ignition delay. Closely linked to the fuel are the primary radicals, MB2J, MBMJ and MB3J, in order of importance. These radicals result from hydrogen abstraction reactions. The other important species closely linked to the fuel is MP2DMJ, which results from a beta-scission reaction of the most important primary radical, MB2J, and subsequent hydrogen abstraction by various radicals. MP2DMJ mainly decomposes to C_2H_3CO and CH_2O, which also feature among the first 15 species in Fig. 1. Thus, important reaction channels can be reconstructed from the ranked species. It also demonstrates
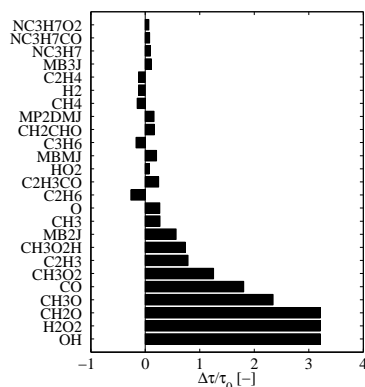

Figure 1: Illustration of the relative change in ignition delay times for each of the 25 most important species in the mechanism, in addition to the automatically retained fuel, O$_2$, CO$_2$ and H$_2$O (Adapted from Ref. [10]).
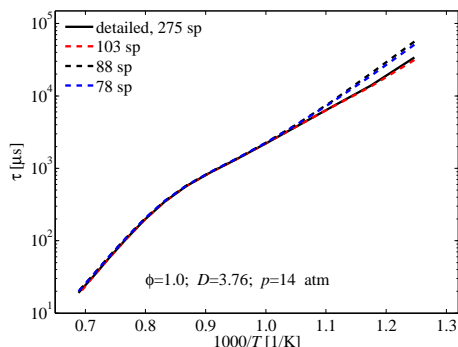
Figure 2: Comparison of ignition delay time predictions for stoichiometric MB/air mixtures at an initial pressure of 14 atm. The parameter, D, denotes the molar ratio of nitrogen to oxygen, which is 3.76 for air (Adapted from Ref. [10]).
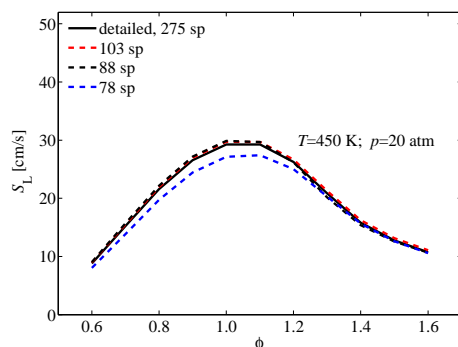
Figure 3: Comparison of laminar burning velocity predictions for MB/air flames at unburned temperature of 450 K and pressure of 20 atm (Adapted from Ref. [10]).
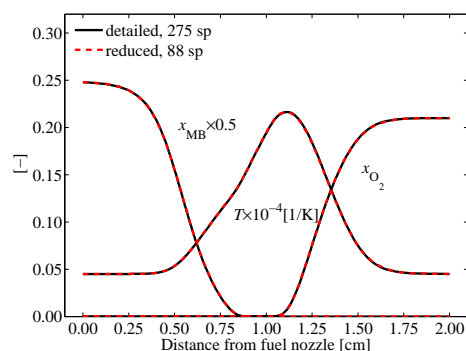
Figure 4: Comparison of detailed and skeletal model performance with respect to predictions of the structure of an MB opposed flow flame. Here a stream of MB/N$_2$ (50% MB and 50% N$_2$) with an inlet velocity of 5 cm/s flows against a stream of air, with an inlet velocity of 10 cm/s. The initial temperature for both streams is 450 K.

that direct application of the method preserves the connectivity of the important species to ensure a hierarchical breakdown of the fuel to simpler molecules and radicals of the hydrogen and small hydrocarbon systems. From Fig. 1, one may state that in most cases, molecular intermediates tend to act as chain-breaking agents, through their action as sinks for radicals, while radicals act as chain initiators and or propagators.

A satisfactory skeletal model can be obtained by evaluating reduced models at various values of NC_{thresh}. Three skeletal mechanisms are derived from the detailed mechanism [12] using NC_{thresh} values of 3.0×10^{-4}, 2.0×10^{-3} and 1.0×10^{-2}, correspondingly leading to mechanisms with 103, 88 and 78 species, respectively. An example of the performance of these models with regards to ignition prediction is shown in Fig. 2. Despite the significant reduction from 275 species based on ignition at 1050 K, the skeletal model with 103 species (over 60 % reduction), accurately predicts ignition delay times even for temperatures as low as 800 K. Further reduction to 88 species is possible, especially for combustion at temperatures above 900 K. The skeletal model with 88 species has 843 reactions (ratio of reactions-to-species of about 9.6) compared to the detailed model with 275 species and 2891 reactions (ratio of reactions-to-species of about 10.5). In Figs. 3- 4, the 88-species skeletal mechanism is found to accurately predict laminar burning velocities of premixed flames as well as the structure of a diffusion flame.

3.2 Skeletal model of *n*-butanol

A skeletal model for *n*-butanol is derived from a high-temperature model for C1-C6 alkanes and alcohols [13]. Species are ranked based on simulations of homogeneous gas-phase ignition of fuel/air mixtures at an initial pressure of 20 atm, temperature of 1050 K and for three *n*-butanol/air mixtures with equivalence ratios, ϕ, of 0.5, 1.0 and 2.0. A suitable skeletal mechanism is derived using an NC_{thresh} of 3.0×10^{-4}. This skeletal mechanism is found to accurately predict ignition delay times over a wide range of conditions. Figures 5-6 show comparisons of the skeletal mod-
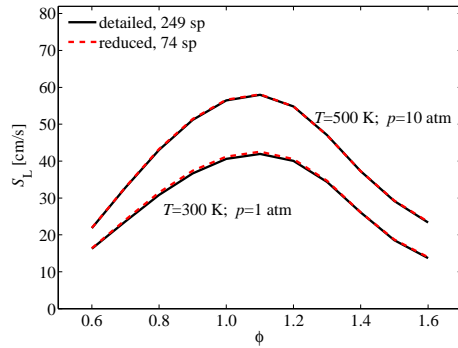
Figure 5: Comparison of laminar burning velocity predictions for *n*-butanol/air flames at unburned temperature of 300 K and pressure of 1.0 atm.
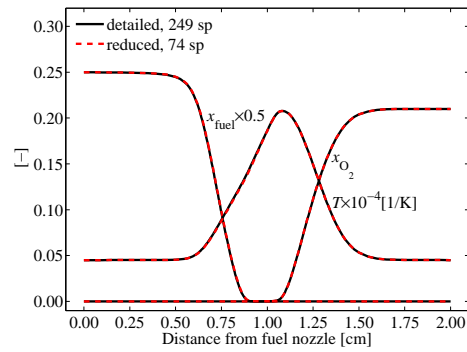

Figure 6: Comparison of detailed and skeletal model performance with respect to predictions of the structure of an *n*-butanol opposed flow flame. Here a stream of *n*-butanol/N$_2$ (50% *n*-butanol and 50% N$_2$) with an inlet velocity of 15 cm/s flows against a stream of air, with an inlet velocity of 15 cm/s. The initial temperature for both streams is 450 K.

els with the original high-temperature model with respect to predictions of the laminar burning velocity and the structure of a diffusion flame. It is observed that the skeletal model predictions are in excellent agreement with those of the original model. Thus, a skeletal model for a chosen component is conveniently extracted from a multi-fuel mechanism.

3.3 Skeletal model of syngas

Analogously, the reduction method is applied to a detailed chemical kinetic mechanism for C1-C5 alkanes [14] in order to extract a skeletal mechanism for the analysis of syngas combustion.
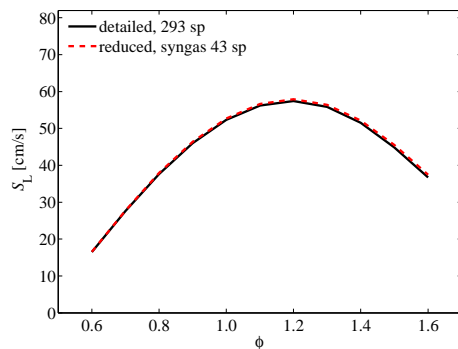

Figure 7: Comparison of laminar burning velocity predictions for fuel/air flames at pressures of 10 atm. The initial temperature for the syngas (25% CO, 35% H$_2$, 5% CH$_4$ and 35% CO$_2$) flame is 500 K.
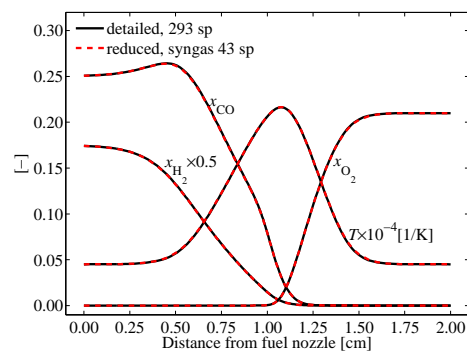

Figure 8: Comparison of detailed and skeletal model performance with respect to predictions of the structure of a syngas opposed flow flame. Here a stream of syngas (35% H$_2$, 5% CH$_4$, 25% CO and 35% CO$_2$) flows against a stream of air, both with an inlet velocity of 15 cm/s and initial temperature of 450 K.

The detailed model has 293 species and 1593 elementary reactions. A syngas composition is adopted such that the fuel comprises 35% hydrogen, 25% carbon monoxide, 5% methane and the rest is carbon dioxide. The resulting skeletal model with 43 species and 393 reactions is found to accurately predict ignition delay times relative to the detailed model. In Figs. 7 - 8, the performance of the skeleltal model relative to the detailed C1-C5 model is assessed with respect to the prediction of laminar burning velocities of premixed flames and the structure of diffusion flames. It is observed that the predictions of the skeletal model are in excellent agreement with those of the detailed model. In the case of the diffusion flame, further agreement has been observed for key intermediates and radicals, such as H_2O_2 and OH.

4   Conclusion

Skeletal models for methyl butanoate, *n*-butanol and syngas are derived from their respective detailed chemical kinetic models, using a species sensitivity method, in a formulation known as Alternate Species Elimination (ASE). Mechanism reduction is realized on the basis of ignition simulations and the resulting models are found to adequately predict other combustion events, such as laminar premixed flame propagation and the structure of diffusion flames.

Acknowledgments

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