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Reduced Chemical Kinetic Mechanisms for Hydrocarbon Fuels

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Several reduced chemical kinetic mechanisms for combustion of ethylene and *n*-heptane have been generated using CARM, a computer program that automates the mechanism-reduction process. The method uses a set of input test problems to rank species by the error introduced by assuming they are in quasi-steady state. The reduced mechanisms have been compared to detailed chemistry calculations in simple homogeneous reactors and experiments. Reduced mechanisms for combustion of ethylene having as few as 10 species were found to give reasonable agreement with detailed chemistry over a range of stoichiometries. Much better agreement with detailed chemistry was found for ethylene ignition delay when the reduced mechanism was tuned through selection of input test problems. The performance of reduced mechanisms derived from a large detailed mechanism for *n*-heptane was compared to results from reduced mechanisms derived from a smaller semi-empirical mechanism. The semi-empirical mechanism was clearly advantageous as a starting point for reduction for ignition delay, but the differences were not as notable for perfectly stirred reactor (PSR) calculations. Reduced mechanisms with as few as 12 species gave excellent results for *n*-heptane/air PSR calculations but 16–25 or more species are needed to simulate *n*-heptane ignition delay.

Introduction

DETAILED chemical kinetic descriptions of hydrocarbon combustion may require the tracking of hundreds of chemical species and thousands of reaction steps. For the foreseeable future, CPU time and computer memory limitations will prohibit implementation of fully detailed descriptions of combustion chemistry into three-dimensional computational fluid dynamics (CFD) simulations of combustion hardware. Issues such as ignition, flame stabilization, combustion efficiency, and pollutant formation are extremely important in the design of the next generation of aircraft engines. Accurate simulation of these phenomena requires that significant chemical kinetic detail be retained in computer models.

Within CFD simulations, the number of species tracked impacts the memory usage and CPU time. As a result, it is important to minimize this number while retaining essential features of the detailed chemistry. The number of species required for simulation of combustion processes depends on the nature of the phenomenon and the type of information desired from the simulation.

The recent development of comprehensive, validated, detailed mechanisms for combustion of large hydrocarbons[1,2] is a significant step forward. Reduced chemical kinetic mechanisms that can represent important aspects of the behavior of these detailed mechanisms using few enough scalars that they can be implemented into CFD simulations offer large potential improvement in the modeling of practical combustion devices.

The approach used here is to reduce mechanisms by employing quasi-steady-state (QSS) assumptions.[3–5] In this work we have used CARM,[6] a computer program that automates the reduction procedure, allowing large, detailed mechanisms to be reduced quickly.

Other approaches to automated chemistry reduction include intrinsic low-dimensional manifold methods[7] and computational singular perturbation.[8] The advantages of the method used in this work are its ease of use, robustness, and applicability to a wide variety of problems and detailed mechanisms.

Automated Mechanism Reduction

Mechanism reduction using QSS assumptions has been extensively applied to hydrogen and methane combustion; many examples can be found in the volumes edited by Smooke[4] and Peters and Rogg.[5] The QSS assumption consists of assuming that the net rate of production of a species is zero. This assumption is valid under combustion conditions for a large number of minor and intermediate species. Assuming the QSS approximation for a species is not equivalent to removing its effect from the chemical system, assuming its concentration does not change, or assuming it is unimportant to the combustion process.

Concentrations of the QSS species are calculated in the subroutine produced by CARM. These values are functions of the non-QSS species, temperature, and pressure and will change during a time-dependent integration or iterative solution as the inputs change. The QSS species help determine the reaction rates of the non-QSS species and, thus, play an important role in the chemical process. A species may be critical to the reaction dynamics yet still be well approximated by a QSS relation. In this work we use an automated technique to apply this method to larger mechanisms and larger hydrocarbons than in previous studies.

There are four basic steps in the formulation of a reduced chemical kinetic mechanism:

1) Identify a short or skeletal mechanism containing only the most essential species and reaction steps of the detailed mechanism.

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2) Identify appropriate QSS approximations.

3) Eliminate reactions using the algebraic relations obtained in step 2.

4) Solve the coupled and nonlinear set of algebraic equations obtained in the previous steps to find the QSS species concentrations reaction rates of the non-QSS species.

CARM automates this procedure, producing source code for the calculation of the chemical source terms defined by the reduced mechanism. As inputs, CARM uses a set of perfectly stirred reactor (PSR) solutions as test problem results representing conditions of interest. CARM ranks species by the error ε_i introduced by assuming they are in QSS using the expression

$$\varepsilon_i = X_i \frac{\left|\omega_i^p - \omega_i^c\right|}{\max\left(\left|\omega_i^p\right|, \left|\omega_i^c\right|\right)} \qquad (1)$$

where ω_i^p and ω_i^c are the rates of production and consumption for species i, respectively, and X_i is the mole fraction. The subroutine produced by CARM contains code that iteratively solves the coupled, nonlinear set of algebraic equations giving the concentrations of the QSS species. The CARM-produced subroutines typically consist of about 3000 or more lines of FORTRAN code.

Detailed Mechanisms

In this work, we have chosen to use n-heptane (n-C_7H_{16}) and ethylene for application of the CARM reduction technology. N-C_7H_{16} is a fairly large hydrocarbon of a weight approaching that found in aviation fuels and is also widely used as a simulant for diesel fuel. The recent publication of a very detailed mechanism[1] and a much shorter semi-empirical mechanism[2] make this fuel ideal for the study of reduced mechanisms for larger hydrocarbons. Earlier detailed mechanisms for n-C_7H_{16} include those created by Chakir et al.[9] and Lindstedt and Maurice.[10] Ethylene (C_2H_4) is a considerably simpler fuel than n-C_7H_{16}, but we are unaware of any previous work on reduced mechanisms of the type we consider here for C_2H_2. C_2H_2 is also a fuel of interest in scramjet combustion research.[11]

Reduced mechanisms can perform no better than the detailed mechanisms on which they are based. Thus, it is important to select up-to-date detailed mechanisms that have compared well to experiments over a variety of conditions as a starting point for reduction. An updated version of the propane mechanism of Westbrook and Pitz[12] is used as the detailed mechanism for C_2H_4 combustion. Two different mechanisms were used to create reduced mechanisms for n-C_7H_{16} combustion.

The detailed n-C_7H_{16} mechanism of Curran et al.[1] is intended to cover the entire range of conditions from low-temperature (600–900 K) pyrolysis and oxidation to high-temperature combustion. For our investigation, we have focused on a subset of this mechanism derived using sensitivity analysis to remove those reaction steps and species that are only important at lower temperatures (<900 K). With 105 species and 808 elementary steps, this subset mechanism, called Curran–Gaffuri–Pitz–Westbrook (CGPW), is still a large and complex mechanism. This mechanism is much larger, and models combustion of a significantly more complex fuel, than has previously been attempted using automated reduced-mechanism techniques. Previous studies have focused mainly on combustion of hydrogen methane.[4–6,13–15]

In contrast, the n-C_7H_{16} mechanism of Held et al.[2] was selected because of its relative simplicity. This mechanism compares well to experiments with comparatively very few species by empirically modeling the initial fuel breakdown. A very detailed mechanism, such as the CGPW mechanism, contains reaction steps for abstraction of H atoms from the fuel by a number of radical species to form several heptyl radical isomers. These heptyl radicals then decompose through a number of routes to form various species with 2–5 carbon atoms. Held et al.[2] achieve considerable simplification by bypassing the formation of assorted heptyl radicals and their breakdown by allowing the n-C_7H_{16} fuel to decompose directly into smaller reaction products, often with three or four products on the right-hand side of an elementary reaction step. For brevity we will hereafter refer to this mechanism and reduced mechanisms as Held–Marchese–Dryer (HMD).

Results

We have compared results of reduced mechanisms using various numbers of species and elementary reactions with those of the full mechanism, and in some cases, experiments in PSR and thermal ignition delay calculations. Examination of how reduced mechanisms perform in simplified calculations is necessary to ensure adequate performance in a more complex calculation like an engine simulation. Adiabatic PSR results, especially the temperature, are a good test of a reduced mechanism's ability to reproduce the heat release rate of the original mechanism for a given set of conditions.

The data shown in this paper were computed on a 300-MHz Pentium personal computer. Most run times were a few seconds. The run times when using reduced mechanisms vary from somewhat faster (2–3 times) to significantly (10 times) slower depending on the conditions and the mechanism. The iterative solution of the QSS relations can be time consuming and can add stiffness to the kinetic system. For CFD applications, advanced tabulation techniques[16] may help to reduce source term evaluation times. Very significant savings compared to detailed chemistry do occur in CFD simulations because many fewer scalar transport equations need to be solved. Reduced mechanisms of this type have been recently applied successfully to reduction of nitrogen oxide pollutant in coal-fired boilers.[17]

We have created reduced mechanisms for C_2H_4/air combustion designed to work over a range of equivalence ratios. We have also attempted, by choosing appropriate input test problems, to create reduced mechanisms for C_2H_4 tailored to the modeling of ignition delay.

For n-C_7H_{16}, we have examined how the choice of the type of starting mechanism, either very large and detailed (CGPW) or shorter and semi-empirical (HMD), impacts the results of mechanism reduction. Table 1 summarizes the reduced mechanisms used in this work.

Reduced Mechanisms for C_2H_4

In our study of reduced kinetic mechanisms for C_2H_4, we have examined the effects of the number of species treated kinetically (as

Table 1 Characteristics of reduced mechanisms

Mechanism	No. of steps	No. of species	Non-QSS species
C_2H_4 10	6	10	H_2, O_2, OH, H_2O, CO, CO_2, C_2H_2, C_3H_3, C_2H_4, N_2
C_2H_4 10 (ignition)	6	10	H, H_2, O, O_2, OH, H_2O, CO, CO_2, C_2H_4, N_2
C_2H_4 15	11	15	H, H_2, O, O_2, OH, H_2O, CO, CO_2, CH_3, CH_4, C_2H_2, C_2H_3, C_3H_3, C_2H_4, N_2
C_2H_4 15 (ignition)	11	15	H, H_2, O, O_2, OH, H_2O, CO, CO_2, CH_4, HO_2, CH_2O, C_2H_2, C_2H_3, C_2H_4, N_2
C_2H_4 20	16	20	H, H_2, O, O_2, OH, H_2O, CO, CO_2, CH_3, CH_4, CH_2O, C_2H, C_2H_2, C_2H_3, CH_2CO, a-C_3H_4, p-C_3H_4, C_3H_3, C_2H_4, N_2
C_2H_4 20 (ignition)	16	20	H, H_2, O, O_2, OH, H_2O, CO, CO_2, HCO, CH_3, CH_4, HO_2, CH_2O, CH, C_2H, C_2H_2, C_2H_3, CH_2CO, C_2H_4, N_2
HMD 9	5	9	n-C_7H_{16}, O_2, CO, CO_2, C_2H_2, H, H_2, H_2O, N_2
HMD 12	8	12	n-C_7H_{16}, O_2, CO, CO_2, CH_4, C_2H_2, H, O, H_2, H_2O, OH, N_2
HMD 16	12	16	n-C_7H_{16}, O_2, C_2H_4, CO, CO_2, CH_4, C_6H_6, C_2H_2, CH_3, CH_2CO, H, O, H_2, H_2O, OH, N_2
CGPW 16	12	16	n-C_7H_{16}, H, H_2, O, O_2, OH, H_2O, CO, CO_2, CH_3, CH_4, C_2H_6, C_2H_4, C_2H_2, C_3H_3, N_2
CGPW 20	16	20	n-C_7H_{16}, H, H_2, O, O_2, OH, H_2O, CO, CO_2, CH_3, CH_4, HO_2, CH_2O, C_2H_6, C_2H_4, C_2H_5, C_2H_2, C_3H_6, C_3H_3, N_2
CGPW 25	21	25	n-C_7H_{16}, H, H_2, O, O_2, OH, H_2O, CO, CO_2, CH_3, CH_4, HO_2, H_2O_2, CH_2O, C_2H_6, C_2H_4, C_2H_5, C_2H_2, CH_3OH, CH_2CO, a-C_3H_4, p-C_3H_4, C_3H_6, C_3H_3, N_2

opposed to assuming they are in QSS), as well as the influence of the type of problems input to CARM during the mechanism-reduction process. As described earlier, these input problems, which are PSR solutions, are used by CARM to rank the errors for assuming each species is in QSS and to choose the elementary reaction step to be eliminated for each QSS relation. Thus, the reduced mechanisms produced by CARM are tuned or optimized to the conditions of the input problems. Nevertheless, note that mechanism reduction using CARM is not simply a curve-fitting process in which the results of the input problems are trivially reproduced. If the detailed mechanism is reduced too far, that is, too many species are assumed to be in QSS, the input problem results will not be well reproduced. Reproducing the input problems is a minimum test of a reduced mechanism, especially if the input problems cover only a narrow range of conditions. A more difficult test is how well a reduced mechanism performs under off-design conditions.

For C_2H_4, we have examined reduced mechanisms with 10, 15, and 20 species. In describing the number of species in a mechanism, inert diluents such as nitrogen or argon are included. In this paper we show results for two sets of mechanisms that have been tuned through selection of the set of input PSR solutions. The input problems for the first set of mechanisms were PSR solutions for C_2H_4/air mixtures at 1.0 atm, initial temperature 300 K, and equivalence ratio $\phi = 1.0$, with adiabatic conditions and residence times varying from 10^{-2} to 5×10^{-5} s and for $\phi = 2.0$, with residence times from 10^{-2} to 5×10^{-4} s. This range of residence times gives conditions from near equilibrium to near blowout. A lean ($\phi < 1.0$) case was not included in the set of input cases to test the hypothesis that a reduced mechanism that is generated for stoichiometric and fuel-rich conditions will also work for a lean mixture.

We have attempted to tailor a second set of mechanisms to reproduce results of the detailed chemistry for thermal ignition of stoichiometric C_2H_4/air mixtures for initial temperatures of 1400–2000 K. The input problems selected were constant-temperature PSR solutions over the temperature range of interest for residence times of 10^{-2}–10^{-5} s. This set of mechanisms is designated ig for ignition. We have also attempted to use selected time steps from ignition calculations as input problems to CARM. The resulting reduced mechanisms differed very little from those created using constant temperature PSR results as inputs.

In comparing reduced mechanisms for C_2H_4 over a range of conditions and problems, considerable sensitivity to the choice of problems input to CARM was found. Reduced mechanisms created using only stoichiometric PSR inputs gave excellent results for the design conditions and for fuel-lean combustion, but produced significant errors for fuel-rich mixtures. Reduced mechanisms created with PSR solutions covering a range of equivalence ratios were able to give reasonable agreement for rich situations, at the cost of worse performance for stoichiometric and lean conditions. As the number of species retained in the reduced mechanisms was increased, the range of problems for which satisfactory agreement with detailed chemistry could be obtained increased.

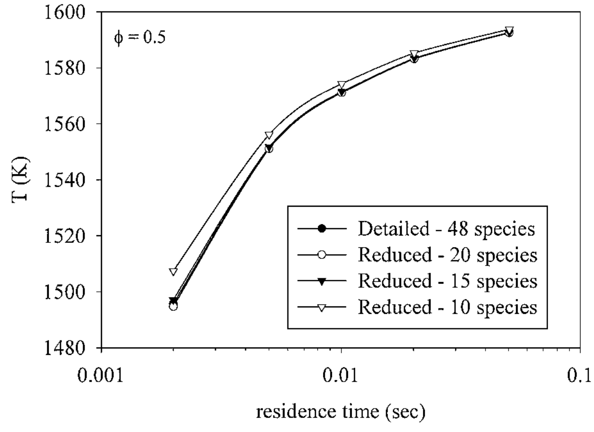

Fig. 1 **Comparison of adiabatic PSR solutions for C_2H_4/air at 1.0 atm, inlet temperature = 300 K, and equivalence ratio = 0.5.**

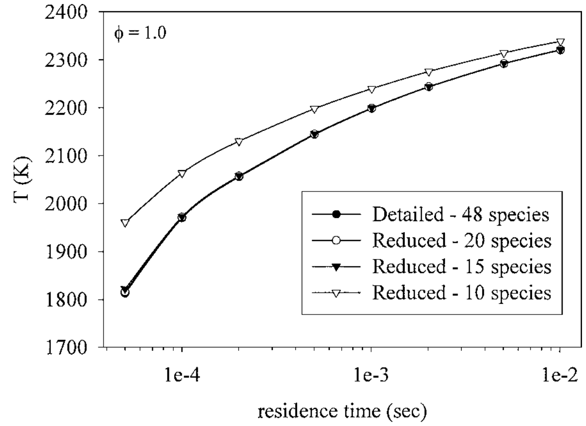

Fig. 2 **Comparison of adiabatic PSR solutions for C_2H_4/air at 1.0 atm, inlet temperature = 300 K, and equivalence ratio = 1.0.**

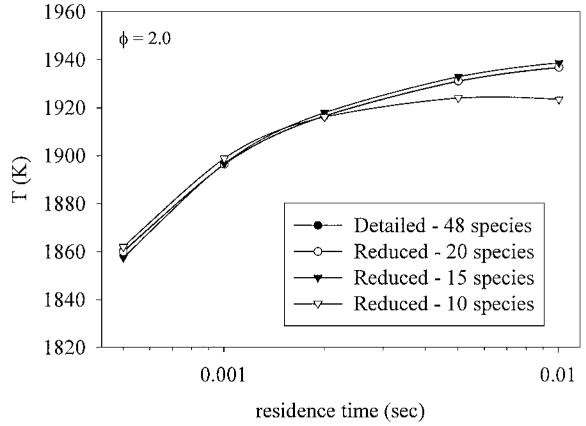

Fig. 3 **Comparison of adiabatic PSR solutions for C_2H_4/air at 1.0 atm, inlet temperature = 300 K, and equivalence ratio = 2.0.**

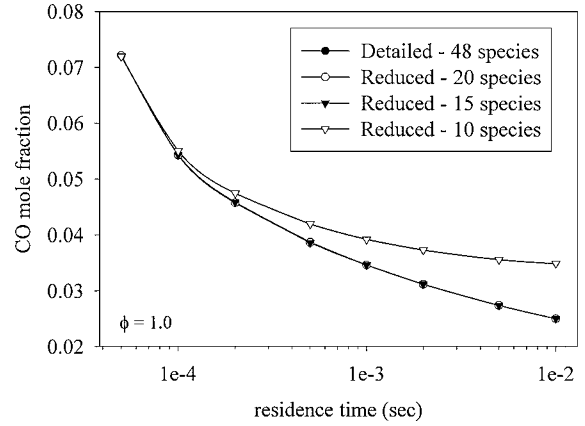

Fig. 4 **Comparison of adiabatic PSR solutions for C_2H_4/air at 1.0 atm, inlet temperature = 300 K, and equivalence ratio = 1.0.**

Figures 1–4 compare results of PSR calculations using detailed chemistry and the reduced mechanisms for C_2H_4 with 10, 15, and 20 non-QSS species as described in Table 1. All PSR calculations were performed using the code of Glarborg et al.[18] Figures 1–3 show temperature for $\phi = 0.5$, 1.0, and 2.0. Figure 4 shows CO mole fraction for $\phi = 1.0$. Results for other species and equivalence ratios (not shown) are similar. The results for the reduced mechanisms with 15 and 20 species are nearly indistinguishable from those for detailed chemistry for all quantities. Errors are larger for the 10-species mechanism. The results of the fuel-lean calculations, of which Fig. 1 is an example, demonstrate that a reduced mechanism tailored for stoichiometric and rich conditions is likely to work for lean conditions as well.

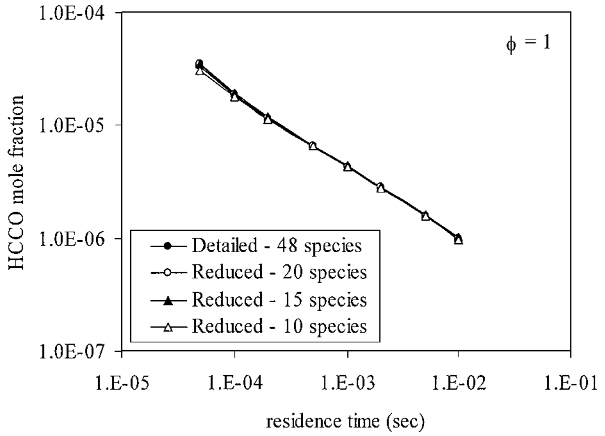

Fig. 5 Comparison calculated steady-state mole fractions of HCCO with detailed chemistry in an adiabatic PSR for C_2H_4/air at 1.0 atm, inlet temperature = 300 K, and equivalence ratio = 1.0.

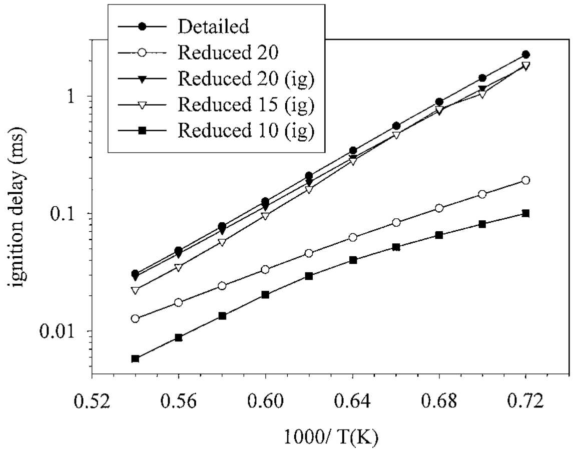

Fig. 6 Comparison of calculated ignition delay times for C_2H_4/air at 1.0 atm and equivalence ratio = 1.0.

Figure 5 shows calculated mole fractions of representative intermediate compound HCCO, from detailed chemistry and from the algebraic QSS relations within the reduced mechanism subroutines produced by CARM. The agreement for HCCO, as well as for other species that have been examined, is generally quite good. Note that the mole fractions of HCCO are large enough that it plays a significant part in the combustion process.

Ignition delay times were calculated for a stoichiometric mixture of C_2H_4 and air at 1 atm using the SENKIN code,[19] assuming the system to be a constant pressure, adiabatic plug flow reactor. Results are shown in Fig. 6. The 15- and 20-species reduced mechanisms tailored to ignition delay give excellent agreement with detailed chemistry. None of the other mechanisms tested performed satisfactorily.

The success of tailoring reduced mechanisms to the ignition delay problem is shown by the difference in the results for the two 20-species reduced mechanisms for C_2H_4, one of which was optimized for ignition delay whereas the other was not. Table 1 shows that the species included in these mechanisms differ only in one instance; HO_2 is substituted for CH_3 in the ignition mechanism. However, the difference in the performance of the mechanisms for modeling thermal ignition is quite pronounced. The reduced mechanisms tailored for ignition give results (not shown) of similar quality to those for nonignition reduced mechanisms when used at the stoichiometry to which they are tuned. The results for other stoichiometries are rather poor.

These results show that thermal ignition is a considerably more difficult problem than the PSR. Whereas the PSR problem requires a steady-state solution at a range of burning conditions, thermal ignition requires accurate modeling of all steps of fuel breakdown and initial fuel fragment oxidation through near equilibrium conditions. The QSS assumption is valid for many fewer species during low-temperature ignition. Furthermore, the controlling kinetic mechanism of thermal ignition is often a strong function of equivalence ratio. It is, therefore, not surprising that a large number of species or a mechanism tuned to a very specific set of conditions is required.

Reduced Mechanisms for n-C_7H_{16}

N-C_7H_{16} was chosen as a fuel for study because it is among the largest hydrocarbon fuels for which comprehensively validated detailed kinetic mechanisms exist. N-C_7H_{16} is also advantageous in that two recently published mechanisms of very different characters exist for modeling n-C_7H_{16} combustion. These are the large, very detailed mechanism of Curran et al.[1] (CGPW) and the shorter, semi-empirical mechanism of Held et al.[2] (HMD).

In creating reduced mechanisms for n-C_7H_{16}, we wish to test the hypothesis that the considerable human effort and insight that went into the formulation of the HMD mechanism would pay off in greater accuracy for the same number of species or in fewer non-QSS species being required to get the same degree of accuracy. To this end, we have created reduced mechanisms from the CGPW mechanism with 25, 20, and 16 species and from the HMD mechanism with 16, 12, and 9 species. The n-C_7H_{16} reduced mechanisms are designated by their parent mechanism (CGPW or HMD) and a number giving the number of species included kinetically, including a diluent.

The six n-C_7H_{16} reduced mechanisms examined here were generated with input PSR test cases for equivalence ratios $\phi = 1.0$ and 2.0, with residence times chosen to give conditions ranging from near blowout to near equilibrium. The reduced mechanisms are compared to detailed chemistry for PSRs for $\phi = 1.0$. The results for rich and lean conditions (not shown) are similar. Ignition delay results are compared to detailed chemistry and to the experiments of Vermeer et al.[20] No n-C_7H_{16} reduced mechanisms designed specifically to model thermal ignition were created.

Figures 7–10 show PSR results for detailed and reduced chemistry for the CGPW and HMD mechanisms for $\phi = 1.0$. Temperature, OH, CO, and fuel mole fractions are shown. The reduced mechanism HMD 9 does not include OH as a kinetically calculated species, and so no OH results are shown for it.

It can be seen from Figs. 7–10 that the detailed CGPW and HMD mechanisms disagree substantially for these conditions with temperature differences up to about 100 K, as well as large disagreement in species mole fractions. Both of these mechanisms have been extensively validated against experiments, although not at the generic conditions used here. However, both detailed mechanisms agree well with measurements for ignition delay. The disagreements give a consistent picture, with HMD always predicting lower temperatures,

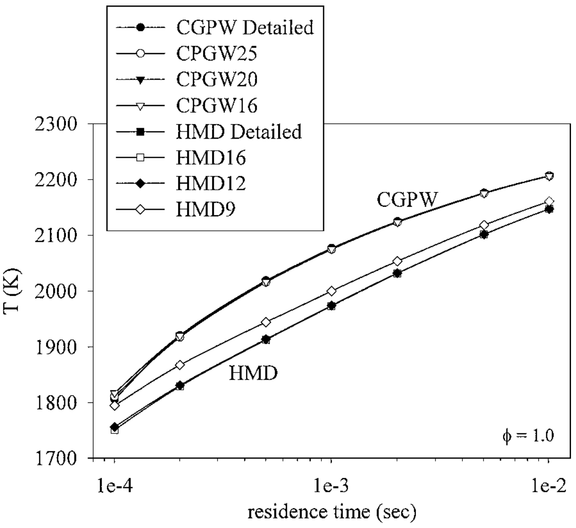

Fig. 7 Comparison of adiabatic PSR solutions for n-C_7H_{16}/air at 1.0 atm, inlet temperature = 300 K, and equivalence ratio = 1.0.

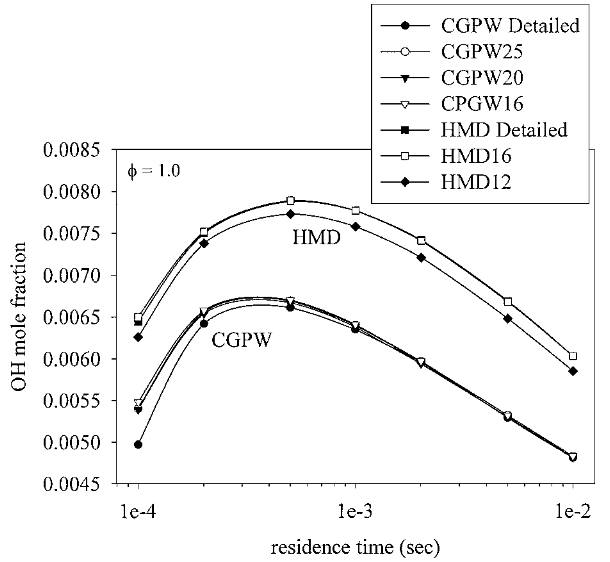

Fig. 8 **Comparison of adiabatic PSR solutions for n-C_7H_{16}/air at 1.0 atm, inlet temperature = 300 K, and equivalence ratio = 1.0.**

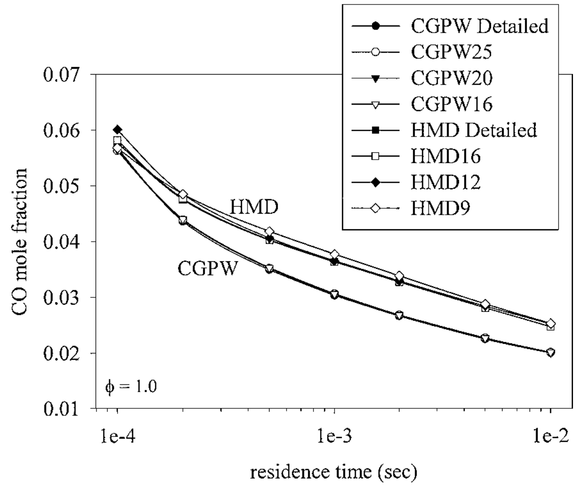

Fig. 9 **Comparison of adiabatic PSR solutions for n-C_7H_{16}/air at 1.0 atm, inlet temperature = 300 K, and equivalence ratio = 1.0.**

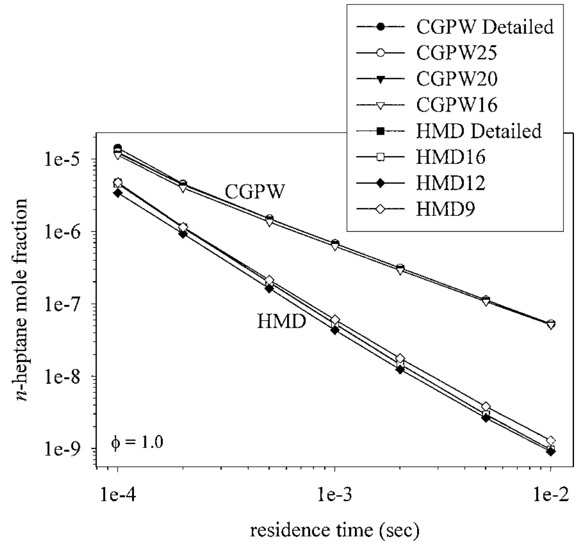

Fig. 10 **Comparison of adiabatic PSR solutions for n-C_7H_{16}/air at 1.0 atm, inlet temperature = 300 K, and equivalence ratio = 1.0.**

less fuel consumption, and higher concentrations of radical species. Because the purpose of this work was to apply and examine a mechanism reduction technique (CARM) and not to compare detailed mechanisms, we shall hereafter concern ourselves only with the level of agreement between detailed and reduced chemistry.

Overall, the agreement between detailed and reduced chemistry in Figs. 7–10 is quite good. With a few exceptions, the expected trend of improving agreement with detailed chemistry as the number of kinetically treated species in the reduced mechanism increases is seen.

Figures 11 and 12 show, respectively, calculated mole fractions of representative minor species CH_2 for the HMD mechanism and HCO for the CGPW mechanism. All of the reduced mechanisms obtain these mole fractions from algebraic QSS relations. It can be seen that the QSS relations give very good approximations for these species. Other QSS species (not shown) showed similar levels of agreement.

A direct comparison of reduced mechanisms based on the CGPW and HMD detailed mechanisms can be made by comparing the CGPW 16 and HMD 16 reduced mechanisms in Figs. 7–10. Both of these reduced mechanisms give results almost indistinguishable from those of the detailed mechanisms for temperature, and for CO and n-C_7H_{16} mole fraction (Figs. 7, 9, and 10). However, CGPW 16 overpredicts the OH mole fraction (Fig. 8) by 5–10% for residence times below about 7×10^{-4} s, whereas HMD 16 almost exactly mimics the parent mechanism for OH mole fraction. Furthermore, the 9- and 12-species reduced mechanisms based on the

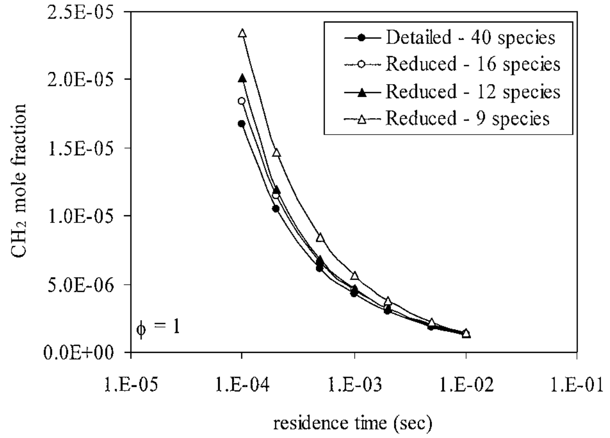

Fig. 11 **Comparison calculated steady-state mole fractions of CH_2 with detailed chemistry in an adiabatic PSR for n-C_7H_{16}/air at 1.0 atm, inlet temperature = 300 K, and equivalence ratio = 1.0 for the HMD[2] mechanism and reduced mechanisms based on it.**

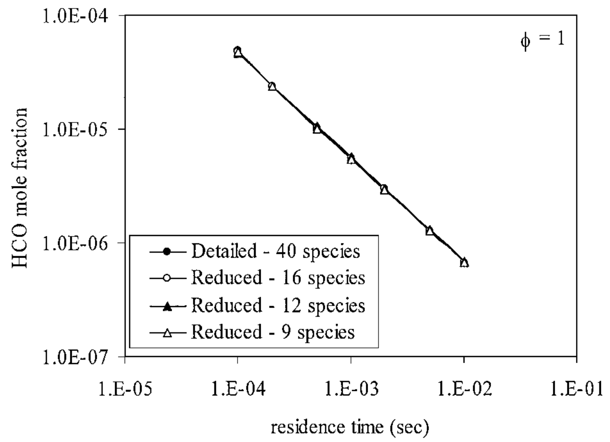

Fig. 12 **Comparison calculated steady-state mole fractions of HCO with detailed chemistry in an adiabatic PSR for n-C_7H_{16}/air at 1.0 atm, inlet temperature = 300 K, and equivalence ratio = 1.0 for the CGPW[1] mechanism and reduced mechanisms based on it.**

semi-empirical HMD mechanism give generally reasonable results. Thus, basing reduced mechanisms on a semi-empirical detailed mechanism does have some advantage. Later it will be shown that this effect is more pronounced for ignition delay.

Reduced mechanisms based on the HMD detailed mechanism may perform better in an important area that has not been studied quantitatively in this work. Even with the same number of species being treated kinetically, reduced mechanisms based on HMD will require less CPU time for computation of the chemical source terms than those based on larger mechanisms. A smaller starting mechanism means fewer QSS species to be solved for iteratively and fewer elementary rates to be computed.

Figures 13 and 14 show ignition delay results for one of the conditions studied by Vermeer et al.[20] The mixture is stoichiometric n-C_7H_{16}/oxygen diluted with 70% argon. In these experiments, ignition was initiated by a reflected shock, and so the system is modeled as a constant-volume PFR. Results are shown separately in Fig. 13 for the CGWP and Fig. 14 for HMD for clarity. We wish to point out that none of the n-C_7H_{16} mechanisms were tailored for ignition delay, and the experimental conditions we are attempting to simulate are quite different from the conditions (stoichiometric and rich PSRs at 1.0 atm) for which these reduced mechanisms were generated.

Figures 13 and 14 show that the detailed CGPW and HMD mechanisms agree very well with the experimental data. The agreement of the reduced mechanisms with detailed chemistry and experiment is not as good as for the PSRs or for the C_2H_4 ignition delay calculations. This is probably because experimental conditions (composition and pressure) are significantly different from those for which the reduced mechanisms were generated. As with the C_2H_4 results, the quality of the ignition delay predictions drops markedly with the number of non-QSS species in the approximation.

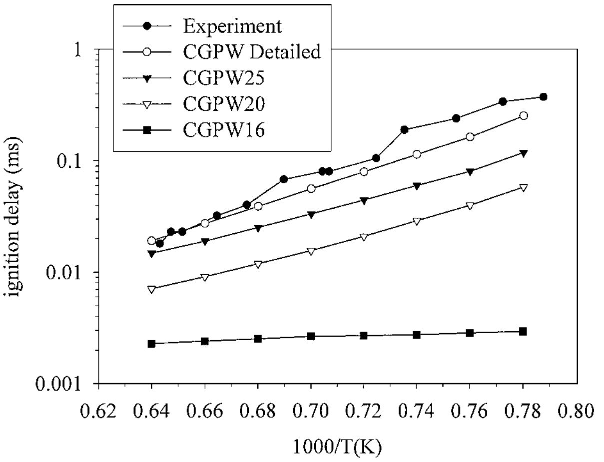

Fig. 13 Comparison of measured[20] and calculated ignition delay times for 70% Ar, 27.5% O_2, 2.5% n-C_7H_{16} initially at 2.5 atm, for the CGPW[1] mechanism and reduced mechanisms based on it.

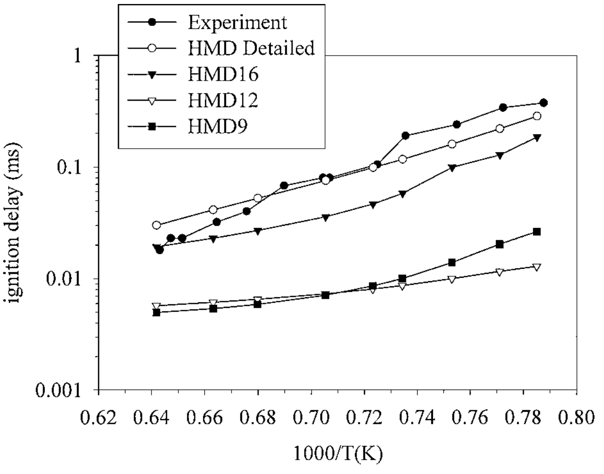

Fig. 14 Comparison of measured[20] and calculated ignition delay times for 70% Ar, 27.5% O_2, 2.5% n-C_7H_{16} initially at 2.5 atm, for the HMD[2] mechanism and reduced mechanisms based on it.

For both C_2H_4 and n-C_7H_{16} the predicted ignition delay time decreases steadily with decreasing numbers of species retained kinetically in the reduced mechanism. This may be because reduced mechanisms with fewer kinetically treated species do a poorer job modeling the initial breakdown of the fuel, which is critical in predicting ignition times. It may be speculated that, as the mechanism is simplified further, this aspect of the process is given increasingly approximate treatment, especially for reduced mechanisms not designed for ignition delay. The more globally oriented fuel breakdown rates given calculated by small reduced mechanisms may work reasonably well in fully burning situations, but these fully burning rates will be too fast for lower temperature thermal ignition.

Figures 13 and 14 show the improved performance of mechanisms based on the smaller HMD mechanism that we looked for but failed to find unambiguously in the PSR cases. Notice that reduced mechanism HMD 16 agrees with its parent mechanism and with experiment at least as well as CGWP 25 and much better than CGWP 16.

Conclusions

The results presented here demonstrate that the automated chemical kinetic mechanism-reduction strategy employed by CARM can be applied to detailed mechanisms for larger hydrocarbon fuels. These reduced mechanisms can be applied over a range of conditions and for a variety of problems.

For any engineering approximation, the level of detail required depends on the exact problem to be analyzed and the information desired. This has proven to be entirely true for reduced mechanisms. It was shown that for C_2H_4 and n-C_7H_{16} that as few as 12–15 species could give excellent agreement for PSR calculations near the design conditions of the reduced mechanism. At the other extreme, it was found that 25 species may not give satisfactory results for n-C_7H_{16} ignition delay when the reduced mechanism is used at off-design conditions. Overall, thermal ignition is a more difficult problem for reduced mechanisms, requiring either more non-QSS species or a more narrowly focused mechanism. We believe that this is largely because thermal ignition is a more complex phenomenon than PSR combustion, requiring accurate modeling of comparatively low-temperature initial fuel pyrolysis and oxidation through rapid high-temperature burning. The chemical reasons for the loss of accuracy for ignition delay are similar to those for rich conditions: A number of species, mainly hydrocarbon fragments including oxygenated compounds, are present in significant quantities and with nonnegligible rates of change, rendering the QSS approximations less valid.

It was found that by using constant-temperature PSR input test problems to CARM that improved reduced mechanisms for modeling thermal ignition could be generated.

We have compared reduced mechanisms based on a large, detailed, n-C_7H_{16} mechanism and a much smaller, semi-empirical n-C_7H_{16} mechanism. The two detailed mechanisms differ significantly when used in PSR calculations, but agree well with experimental data and each other for ignition delay. In the PSR calculations, all but the reduced mechanisms retaining the fewest (nine) species gave excellent results. The PSR comparisons showed that beginning with a semi-empirical mechanism is somewhat advantageous. The difference between starting with a large, detailed mechanism or a smaller semi-empirical mechanism was more pronounced, however, for ignition delay calculations. The 16-species reduced mechanism based on the HMD mechanism was far superior to the reduced 16-species reduced mechanism based on the CGWP mechanism and gave results similar to the 25-species reduced mechanism based on the CGWP mechanism.

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