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Reduced Chemical Kinetic Mechanisms: Application to CFD Codes and Optimization

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Abstract

Reduced chemical kinetic mechanisms developed and tested using the CARM-PSE software have been implemented into a variety of CFD codes. When used in the commercial code Fluent, a CARM-PSE created reduced mechanism performs well for predicting the major species and temperature of the Sandia D flame. Predictions for radical and pollutant species are not as good. Much of this error may be due the the inadquacies of the EDC turbulence-chemistry model used in these simulations. Reduced mechanisms representing combution of Diesel fuel and gasoline perform well in simple reactors, but are presently hindered numerical innaccuracies within the engine combustion CFD simulation. Numerical optimization techniques have been implemented into CARM-PSE to automatically select the best species to include in reduced mechanisms for a given set of conditions. The genetic algorithm has been demonstrated to be robust and successful at creating reduced mechanisms that are improvements over previous species selection methods. A new algorithm, based on forming in-vs.-out pseudo-gradients has been developed and implemented. When procedures are implemented to deal with reduced mechanisms that crash the test codes, this algorithm is both efficient and robust.

1. INTRODUCTION

Computational Fluid Dynamics (CFD) codes aimed at solving practical engineering problems involving chemically reacting flow can presently incorporate only very simplified descriptions of the chemical processes involved. For example, detailed chemical kinetic descriptions of hydrocarbon oxidation may require the tracking of hundreds of chemical species and thousands of reaction steps. CPU and memory limitations prohibit implementation of full detailed chemistry into CFD simulations of practical combustors. Techniques are now available to create reduced chemical kinetic mechanisms that approximate the results of detailed chemical kinetic descriptions over a range of conditions using many fewer species, and thus less CPU time and memory.

If a reduced mechanism compares well to detailed chemistry over a given parameter range in zero-dimensional reactor codes that simulate perfectly stirred reactors (PSR's) and plug flow reactors (PFR's), it is reasonable to assume that it will perform similarly in a more complex calculation like a CFD code. Comparing reduced and detailed chemistry results over a multidimensional parameter space one case at a time is a tedious and time-consuming task. For reduced mechanisms to become reliable engineering tools, thorough characterization of the errors introduced during the reduction process is required.

A promising approach to creating reduced chemical kinetic mechanisms is to use steady-state assumptions for a number of chemical species [1,2]. Chen [3] has automated the mechanism reduction process into a computer code called CARM (Computer Assisted Reduction Method). CARM produces source code for calculation of chemical source terms defined by the reduced mechanism that can be linked easily to a combustion simulation code. The CARM code has been integrated into a problem solving environment (PSE) called CARM-PSE [4] that allows automated comparison of reduced and detailed chemical kinetic mechanisms in simple reactors over a parameter space of interest.

Reduced mechanisms created using CARM and CARM-PSE have been applied to combustion of hydrocarbons such as ethylene and *n*-heptane [5], NOx reduction in coalfired furnaces [6], incineration of hazardous chemicals [7], and combustion aviation fuel [8].

2. OVERVIEW

The CARM-PSE software was created using a combination of existing and emerging software technologies. Specifically, we combined:

- A problem solving environment called SCIRun [9],
- The CARM software [3] for automatic chemical kinetic mechanism reduction,
- Codes for modeling simple, zero-dimensional combustion reactors
- The Microsoft SQL Server database software and
- Advanced optimization techniques

This paper reports work on implementing reduced mechanisms created and tested with CARM-PSE into the general purpose commercial CFD code Fluent and into the research code KIVA for simulating engine combustion. The CARM-PSE software now has two different functioning optimization algorithms for choosing the best species to be kept in reduced mechanisms.

Reduced mechanisms produced with CARM-PSE have been implemented into the commercial CFD code Fluent using their user-defined function capability. Reduced mechanisms may be used in a post-processing mode, to model pollutant chemistry, which has little effect on the temperature or flowfield, or fully coupled to the flow and temperature solution using the Eddy Dissipation Concept turbulence-chemistry interaction model.

Reduced mechanisms produced with CARM-PSE have been implemented into the engine simulation CFD code KIVA. The reduced mechanisms result in a factor of 2-3 savings in CPU time for the simulations, but improved accuracy is needed in the CFD code's time integration routines.

3. REDUCED MECHANISM IMPLEMENTATION INTO FLUENT

Reduced mechanisms produced and tested by the CARM-PSE computational workbench have been implemented into the commercial CFD code Fluent. A 15-species reduced mechanism which has been tested in the workbench was integrated into Fluent using Fluent's user-defined functions capability. The implementation was tested by simulating Sandia National Laboratories Flame D, a piloted, turbulent, partially-premixed methane-air flame for which extensive measurements of temperature, velocity, and species concentration exist [10].

A solution in which the chemical species, energy, and momentum equations (which determine the fluid flow) are all fully coupled, was computed for the Sandia D flame. Contour plots showing results of this calculation are shown in Figure 1.

Figure 2 shows comparisons of this calculation to experimental measurements, along the flame axis. Some curves are shown from an earlier chemical equilibrium calculation in Figure 3 for comparison.

The agreement between the calculation and experiment is excellent for the temperature, velocity, and major species (CH_4, O_2, H_2O, CO_2), so-so for intermediates OH and CO, and poor for pollutant NO. We plan to retry the calculation using a 25-species reduced mechanism, which should give a better representation of the chemistry (although we believe that the 15-species mechanism should do well). This will answer the question of whether the discrepancies for OH, CO, and NO are due to the chemical model or to other factors, the most likely of which is the turbulence-chemistry interaction model used in the calculations. This model, known as the eddy dissipation concept (EDC), has been found before to be unable to correctly predict pollutant concentrations in similar flames. Further work using the more accurate but computationally expensive PDF transport model will also help clarify this issue.

4. ENGINE SIMULATIONS USING REDUCED MECHANISMS

Reduced mechanisms produced using CARM-PSE have been used to simulate the engine combustion. The reduced mechanisms for both *n*-heptane and iso-octane have been developed to simulate the fuel chemistry of diesel fuel and gasoline, respectively. It was found that the reduced mechanisms performed well in predicting the fuel ignition delay time in simple reactor simulations under engine conditions. However, in diesel engine combustion simulations that coupled the detailed chemistry with the engine CFD code KIVA-3V, the use of the reduced mechanism resulted in a shorter ignition delay prediction than the data obtained with the original mechanism. Hence the predicted cylinder pressure and heat release rate data are not in good agreement with the experimental measurements. On other hand, it was also found that the required computer time was reduced by a factor of 2 to 3 by using the reduced mechanism. Additional effort is in progress to investigate the causes of the ignition delay discrepancies.

The CARM reduced mechanism for *n*-heptane fuel was validated by predicting constant pressure ignition delay times as a function of equivalence ratio and temperature. The original mechanism consisted of 40 species and 165 reactions, while the reduced mechanism contains 25 species with 21 reaction steps. The results of ignition delay predictions are shown in Figure 3. The ignition delay data predicted by a large detailed mechanism (with 570 species and 2520 reactions) [11] are also shown in the figure for comparison. The initial mixture conditions are at 40 bars, equivalence ratio ranging from 0.15 to 0.6, EGR (exhaust gas recirculation) ranging from 0 to 60%. The above conditions are typical averaged in-cylinder conditions in a diesel engine during the ignition stage. Figure 3 shows that the reduced mechanism performed well in predicting the ignition delay data over the above range of conditions.

The model was further applied to simulate the combustion process with the modeling of the diesel fuel spray process. The computation used a 60-degree 3-D sector mesh considering the symmetry of the 6-hole injector. Figure 4 shows the in-cylinder fuel drop and temperature contours on the center plane of the fuel spray. It appears that, in the case of using the reduced mechanism, ignition occurs immediately once there is favorable combustible mixture. Therefore, as can be seen in the temperature contours, the ignition location is at the center of the bowl and is very different from that predicted by the original mechanism.

On other hand, using the reduced mechanism indeed reduces the computer time. The CPU time on an SGI Origin 2000 machine was reduced from approximately 60 hours to 20 hours by using the reduced mechanism.

The model was also applied to simulate experiments using a gasoline hollow-cone spray to produce HCCI combustion. The intake charge was heated to help the vaporization of gasoline. The start of injection was 130 degrees BTDC with a lean overall equivalence ratio of 0.24.

A reduced mechanism (45 species, 41 steps) for iso-octane was generated from its original mechanism (79 species, 398 reactions). The results for this mechanism were similar to those for *n*-heptane.

5. OPTIMIZATION OF REDUCED MECHANISMS

Optimization Techniques

Integration of the CARM automatic mechanism reduction software into CARM-PSE allows the entire mechanism reduction, optimization, and testing process to occur seamlessly within a single computational environment. CARM-PSE can automatically compare detailed and reduced chemistry over a specified set of simple reactor test cases. The differences between reduced and detailed chemistry become the objective function that an optimization algorithm can seek to minimize by selection of which species to approximate as being in QSS.

As originally developed, CARM used a set of input test problems (perfectly stirred reactor (PSR) solutions) to rank species by the errors, e_i, introduced by assuming they are in steady state. This error is evaluated by the expression

$$e_i = X_i \frac{|w_i^p - w_i^c|}{\max(|w_i^p|,|w_i^c|)} \qquad \textbf{Eqn. 1}$$

where w_i^p and w_i^c are respectively the rates of production and consumption for species i, and X_i is the mole fraction. The N_{in} species with the lowest values of e_i were selected for inclusion in the mechanism, where N_{in} is the desired number of species in the reduced mechanism. This method often works reasonably well, but sometimes considerable trial and error is needed to find a mechanism that works well. The flaw in using Eqn. 1 to choose QSS species is that it does not take into account the sensitivity of the desired calculation outputs (i.e. NO mole fraction or temperature) to the mole fractions of the species. For example, the radical species, O, H, and OH may be more important to retain out of QSS than Eqn. 1 would suggest, because the combustion and pollution formation processes are sensitive to errors in their mole fraction, despite these mole fractions being relatively low.

For purposes of optimization, species in the detailed mechanism are separated into three groups. The "Definitely In" group consists of species known to be necessary for the functioning of the reduced mechanism. Among the "Definitely In" species are the fuel species, and oxygen and nitrogen. Combustion products and important intermediates are also included in this set; CO, H_2, CO_2, and H_2O are always in the "Definitely In" set, as are important outputs such as NO. Species known to exist only in very small concentrations and/or to be unimportant to the processes of interest can be consigned to the "Definitely Out" set. Placing unimportant species in this set simplifies the optimization problem and reduces runtimes. Care must be exercised in selecting the "Definitely Out" set, however; placing too much restriction on the optimization algorithm's freedom to explore can produce suboptimal results.

Genetic Optimization

A genetic optimization algorithm [12] has proven to be successful at finding combinations of non-steady-state species that perform better than those chosen by the original CARM software. A genetic optimization algorithm mimics biological evolution by selecting the most "fit" members of a "population" to produce "offspring".

Reduced mechanisms are represented by binary "chromosomes" which determine whether a species is in QSS or calculated kinetically. The algorithm is started with a randomly created population (20-30 reduced mechanisms). Reduced mechanisms believed to be promising can be inserted into the starting population. Pairs of "parents" are selected through a "tournament". This is done by selecting three members of the population at random. The reduced mechanism with the lowest error (highest "fitness") is chosen to be a parent. This process is repeated to find a partner for the first parent. Each set of parents has two "children".

Parent chromosomes are mixed using randomly selected breakpoint and interchanging the chromosome pieces to create children. This process is repeated for many generations until no further improvement is found.

Use of any optimization algorithm will result in some reduced mechanisms that so poorly approximate the chemical process that they result in numerical difficulties from which the codes use to compare detailed and reduced chemistry cannot recover.

Handling of these “crash” cases is an important aspect of optimizing reduced mechanisms. The genetic algorithm is able to handle these cases quite naturally. Any reduced mechanism that crashes the test codes is assigned a very low fitness value. The selection process built into the algorithm insures that the characteristics these reduced mechanisms are not passed on to succeeding generations.

In our first optimization attempts, CARM-PSE could optimize a reduced mechanism to minimize the error for a single quantity (i.e. temperature, or a single species concentration). This was found to lead to selection of a reduced mechanism that performed well for the quantity selected but had significant errors for other important quantities. This has been improved by adding the capability to create an objective function for optimization that is the weighted sum or maximum of several quantities. We have found that using an objective function consisting of the weighted sum of important model outputs works reasonably well. Using the reciprocal of the error found using the best known reduced mechanism as the weighting function is a reasonable approach. As the optimization algorithm finds better mechanisms, the weights can be adjusted and the algorithm restarted.

Another feature of our genetic algorithm is the use of 'elitism', in which the genetic algorithm assures that the best design is always carried forward into the next generation.

Figure 5 shows genetic algorithm results for the CO mole fraction error (difference between detailed and reduced chemistry results) for 15-species reduced mechanisms. This error is a statistical norm calculated in a PSR over a range of conditions. In this case the conditions are those studied earlier [4]: adiabatic PSR solutions for methane-air combustion, an equivalence ratio, f, of 0.5, 1.0 and 2.0, and inlet temperatures of 300, 500, and 700 K. The residence time was 0.01 sec. and the pressure was 1.0 atm. The detailed mechanism was GRI 3.0 [13]. The starting population for the run shown in Figure 5 was generated randomly. The line labeled “CARM default” shows the results of using a reduced mechanism containing species selected using the criterion given by Eqn. 1. Within a few generations, the genetic algorithm has created a better reduced mechanism than the CARM default method. The best reduced mechanism created by the algorithm gives errors about a factor of 20 smaller than by using Eqn. 1 as the criterion for choosing QSS species.

Gradient-Like Set Optimization

The genetic algorithm has proven to be robust and able to find reduced mechanisms that perform better than those created previously. However, the algorithm can be very time-consuming, requiring many thousands of evaluations of the objective function.

Optimization methods that work on continuous functions often rely on gradients of the objective function with respect to the independent variables to move the design in a direction that decreases the objective function. Non-gradient methods such as the genetic algorithm and simulated annealing have been developed for discreet problems for which gradient information is not readily available.

However, for the problem of choosing the best species to be in a reduced mechanism, a gradient-like quantity can be calculated and used for reduced mechanism optimization. The algorithm starts with a base mechanism, with the species ranked arbitrarily or based on some prior knowledge. Using Eqn. 1 is a good way to initially rank the species. The idea is to form in vs. out "gradients" for each species in the most reasonable manner possible.

For the gradient-like algorithm we consider four groups of species: Definitely In, Currently In, Currently Out, and Definitely Out. The Definitely In and Definitely Out species are not really considered. We are interested in what to do with those in the middle groups. The base reduced mechanism consists of the N_d Definitely In species plus the $N_{in} - N_d$ highest ranked candidate species that are not in the Definitely In or Definitely Out set. These species form the Currently In set. The other candidate species form the Currently Out set. As in the genetic algorithm, the number species to be retained in the reduced mechanism is specified at the outset of the optimization. The algorithm proceeds as follows:

Step 1. Get Error norm (fitness) of current base design.

Step 2. Create reduced mechanisms with $N_{in} - 1$ species by deleting each member of the Currently In set one at a time. Get fitness, F_i for each variation. Calculate a pseudo-gradient, $D_i = F_{i,in} - F_{i,out}$.

Step 3. Swap each member of the Currently Out set with lowest ranking member of Currently In set. Get fitness for each variation. Compare these variations to a reduced mechanism with the top N_{in} -1 species. Again calculate $D_i = F_{i,in} - F_{i,out}$ for the Currently out species. We now have D_i's for all species in the Currently In and Currently Out sets.

Step 4. Rank all D_i's. Species with the highest D_i's go into the new Currently In set. The new Currently In set plus the Definitely In set form the new base set.

Go to Step 1 unless convergence has been achieved.

The difficulty with the pseudo-gradient method is handling "crash" cases. The following procedures have been developed. If the crash case is one of the variations, it is assigned a fitness that is 20% worse than worst converged case:

$F_{crash} = 0.8F_{worst}$, $F_{worst} = 0.0$
$F_{crash} = 1.2F_{worst}$, $F_{worst} < 0.0$

If a crash occurs for a new base case, a revised base case is taken to be the best variation from the previous iteration. This generally gives some improvement to the former base case and provides a new starting point for the algorithm. If a crash occurs for the reduced mechanism with $N_{in} - 1$ species that is used for comparison in step 3, the algorithm steps up the species ranks until it finds a mechanism for which a converged solution can be found. These crash protocols make the gradient-like algorithm reasonably robust.

When the gradient-like algorithm was run for the PSR problem described above for the genetic algorithm it converged to the same optimum found by the genetic algorithm in ten generations.

The gradient-like algorithm has been tested for the problem of creating a reduced mechanism with 15 species that can reproduce the calculated ignition delay of a detailed mechanism [ref]. To speed the solution, the test problem was limited to a single ignition delay calculation for a stoichiometric *n*-heptane-air mixture at a fixed pressure of 1 atm and an initial temperature of 1200 K. The starting base reduced mechanism was formed using Eqn. 1 for a PSR solution for stoichiometric *n*-heptane-air. The ignition delay was taken as the time needed for the temperature to rise 400 K. Figure 6 shows the ignition delay error for the base reduced mechanism as a function of iteration. For the first five iterations the new base reduced mechanism crashed, resulting in slow improvement or worsening of the results. Once stable new designs are consistently created the solution improves rapidly. The error in the calculated ignition delay for the final reduced mechanism is a factor of nearly 100 less that that of the starting mechanism.

6. CONCLUSIONS

Reduced chemical kinetic mechanisms developed and tested using the CARM-PSE software developed during this project show promise when implemented into a variety of CFD codes. When used in the commercial code Fluent, a CARM-PSE created reduced mechanism performs well for predicting the major species and temperature of the Sandia D flame. Predictions for radical and pollutant species are not as good. Much of this error may be due the the inadquacies of the EDC turbulence-chemistry model used in these simulations. Further work using larger reduced mechanisms and the more accurate but computationally expensive PDF transport model will clarify this issue. Reduced mechanisms representing combution of Diesel fuel and gasoline perform well in simple reactors, but lead to numerical innaccuracies when implemented into CFD simulations of engine combustion. Work is progressing to resolve these difficulties.

Numerical optimization techniques have been implemented into CARM-PSE to automatically select the best species to include in reduced mechanisms for a given set of conditions. The genetic algorithm has been demonstrated to be robust and successful at creating reduced mechanisms that are improvements over previous species selection methods. A new algorithm, based on forming in-vs.-out pseudo-gradients has been developed and implemented. When procedures are implemented to deal with reduced mechanisms that crash the test codes, this algorithm is both efficient and robust. Detailed, quantitative comparisons of the algorithms are underway.

7. ACKNOWLEDGEMENTS

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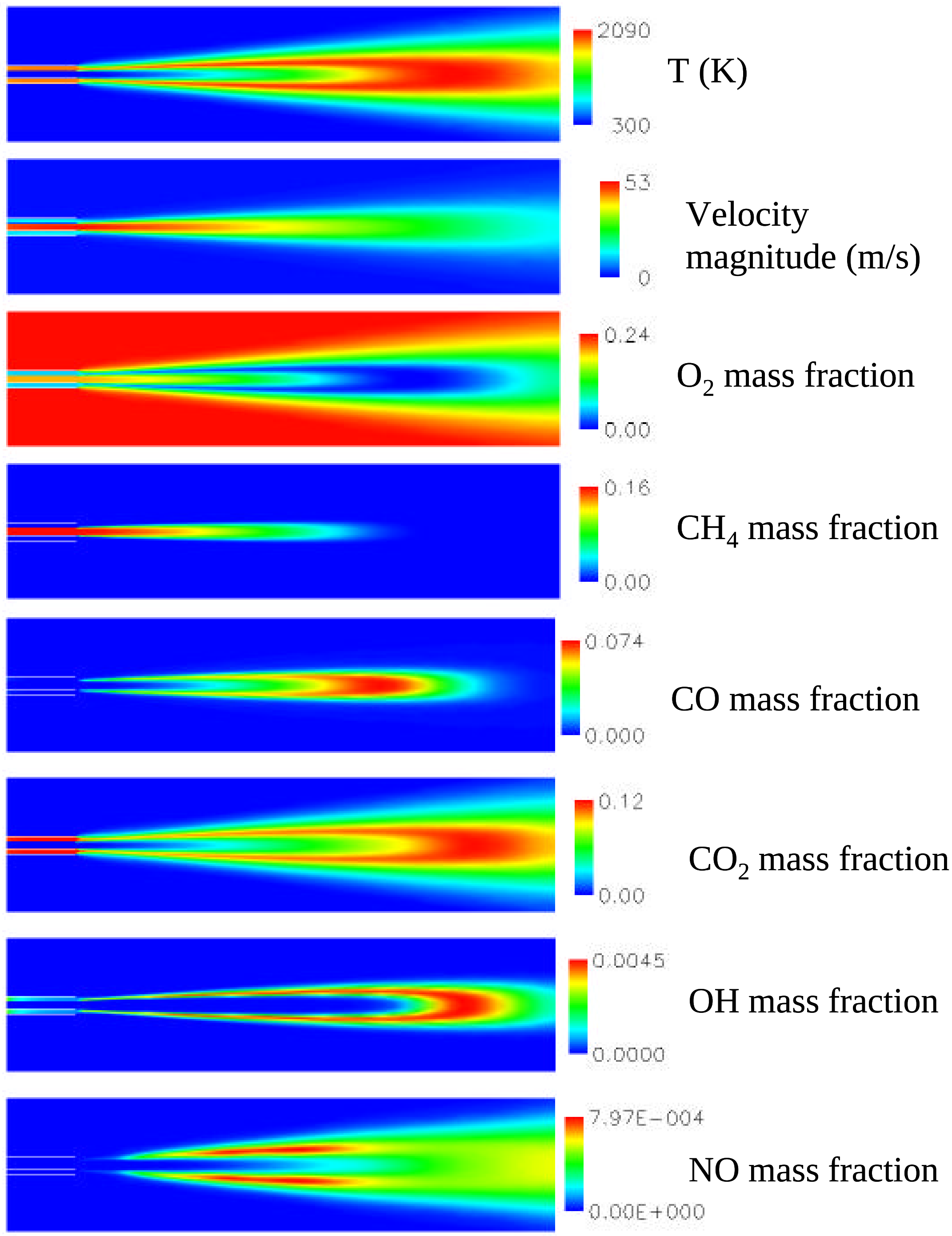

Figure 1. Results of Fluent simulation of piloted, partially-premixed methane-air flame using a 15-species reduced mechanism.

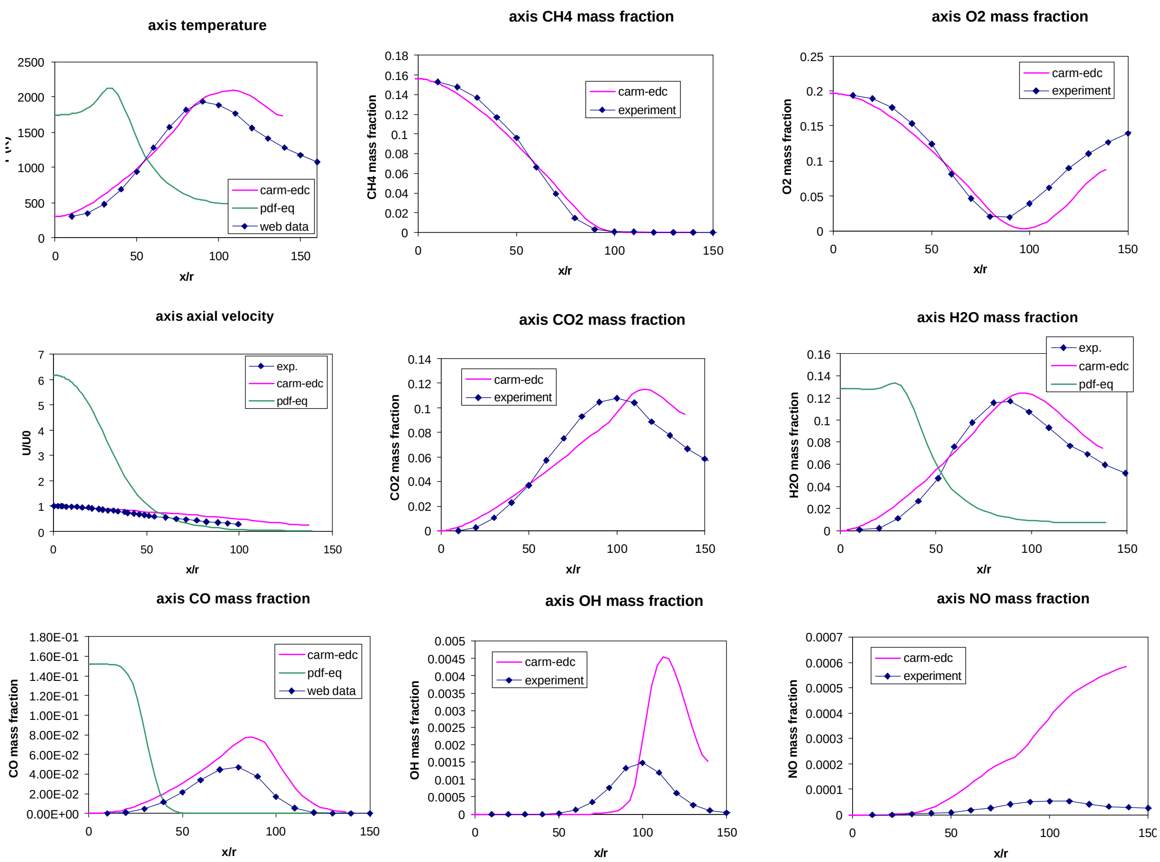

Figure 2. Comparison of Fluent simulation of piloted, partially-premixed methane-air flame using a 15-species reduced mechanism to experiments.

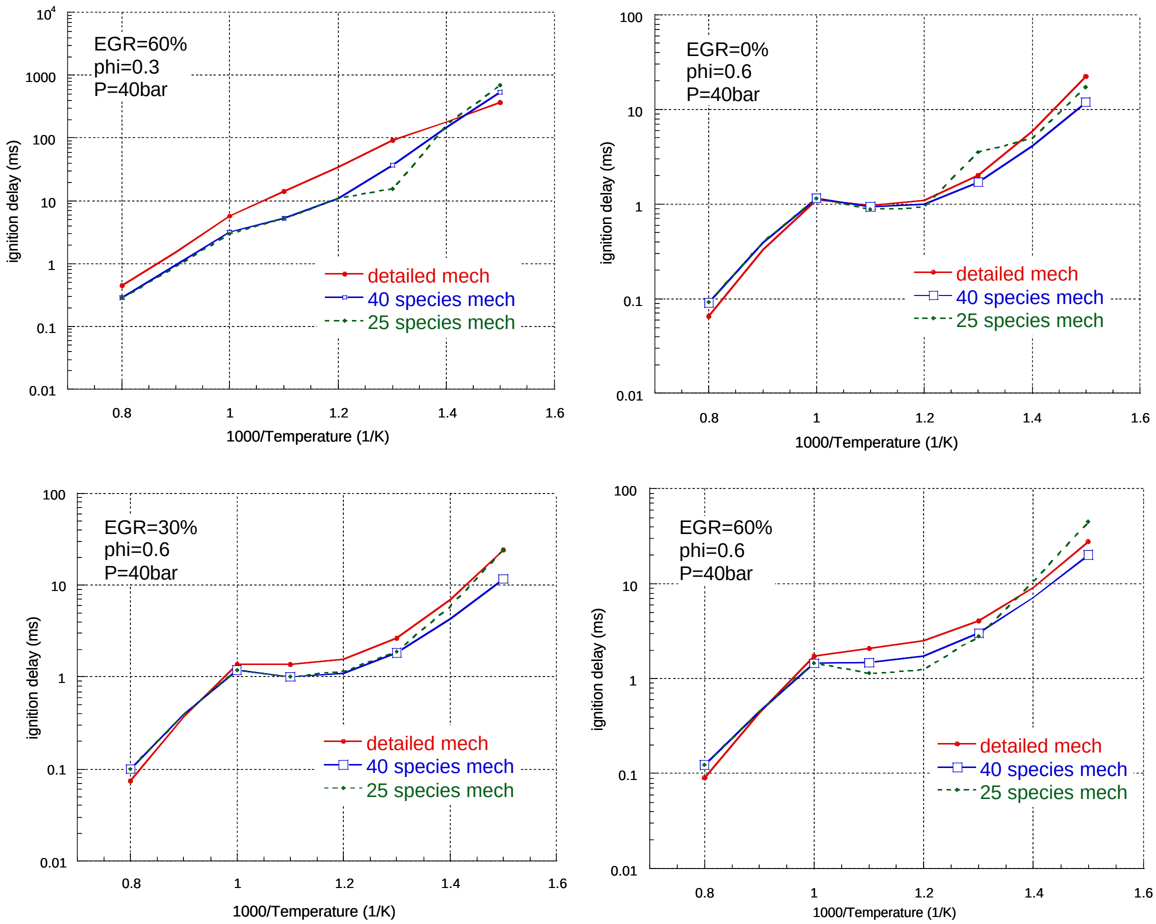

Figure 3. Comparisons of constant pressure ignition delay predictions of *n*-heptane by (1) detailed mechanism [11], (2) original 40-species mechanism (Chalmers University), and (3) 25-species reduced mechanism (generated by CARM-PSE).

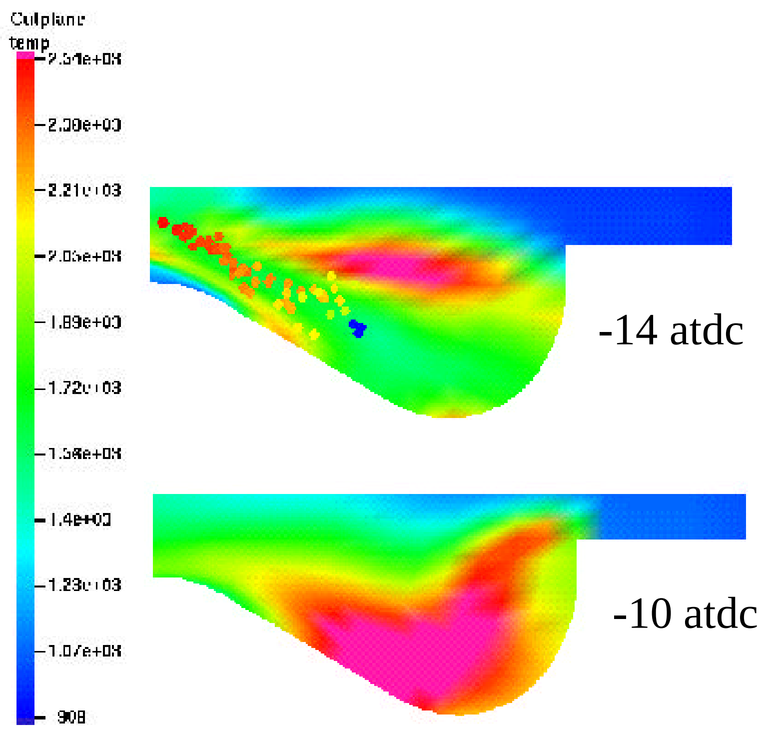

Figure 4. Computed in-cylinder fuel drop and temperature distributions using the reduced mechanism.

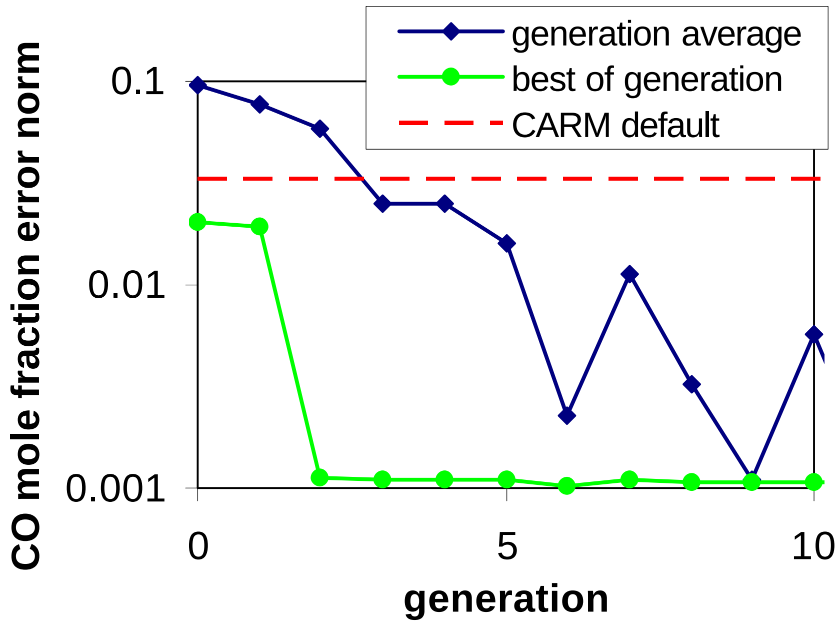

Figure 5. Genetic algorithm results for methane/air combustion. This figure shows decrease in the CO mole fraction error compared to detailed chemistry for adiabatic PSR calculations, equivalence ratio = 0.5, 1.0, 2.0, and inlet temperature = 300, 500, 700 K.

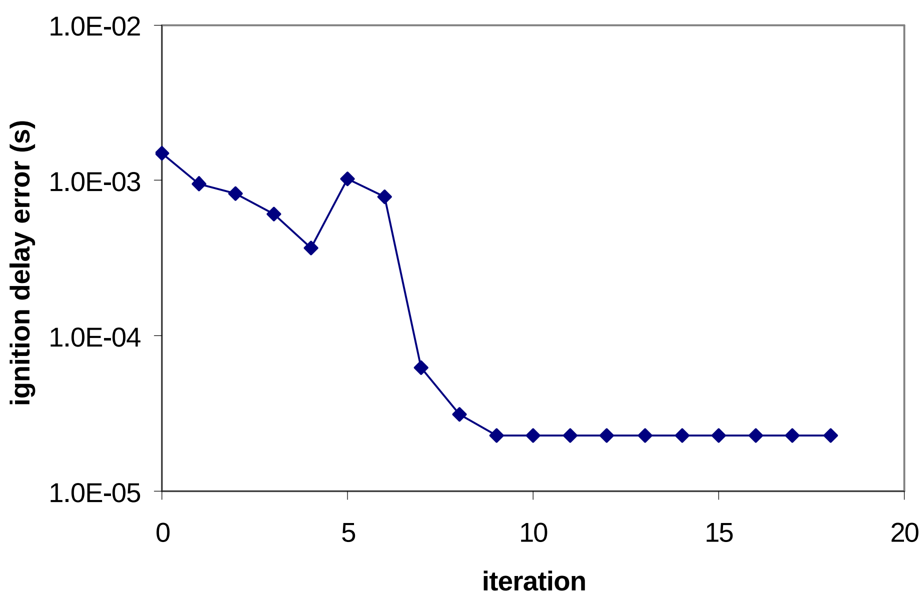

Figure 6. Gradient-like optimization results for reduced mechanisms for *n*-heptane ignition delay.