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New Modeling Approaches Using Detailed Kinetics for Advanced Engines

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ABSTRACT

Ignition timing and control, as well as predictability of engine emissions, are critical factors in advanced-engine system design. The use of detailed chemical kinetics is key to simulating ignition performance and to predicting emissions. This paper describes a collaborative and systematic effort that is underway to enable computationally efficient use of accurate kinetics in engine simulation. The collaboration is focused on building a database of chemical information and on developing a complementary set of software tools that provide efficient engine-simulation capabilities. The goal is predictive simulations that capture the detailed behavior of complex fuels, such as gasoline and diesel, under homogeneous charge compression ignition (HCCI) and related operating conditions.

Since directly accounting for all of the hundreds of constituent molecules in a fuel during simulation of real-fuel combustion is intractable, we employ a "model-fuel" or surrogate-fuel approach instead. Mixtures of model-fuel molecules can be determined to adequately represent important real-fuel properties and engine-combustion characteristics. In this work, model fuel compositions are determined by matching a mixture behavior to that of the real fuel, focusing on distillation-curve characteristics, net-heating value, hydrogen-to-carbon ratio, and octane/cetane numbers. This surrogate-definition process requires detailed chemical-kinetics mechanisms for a variety of model-fuel compounds. To build such a database of model-fuel component mechanisms, we have used a combination of automatic mechanism-generation and manual mechanism-development approaches. These methods adhere to a systematic set of class-based rules in determining elementary reaction rates, as well as thermodynamic and transport properties of species. In addition, a comprehensive validation study of the mechanisms, using a wide variety of both fundamental and engine experiments, has allowed refinement of these rules and improvement of both the mechanisms' predictions and their consistency across components.

Even though model fuels have a small number of components, their detailed mechanisms contain large numbers of species (>1000) and reactions (>10000). Systematic mechanism reduction is therefore required for many engineering applications. To this end, we have also developed a package of automated mechanism-reduction techniques. In addition, we have advanced the solution algorithms used in the kinetics simulations and developed a multi-zone engine model that provides good predictions of ignition behavior and emissions.

We report on selected results of this systematic approach to using detailed kinetics in engineering simulation, as well as the challenges encountered.

INTRODUCTION

Simulation is an increasingly critical component of the design process. For simulation to support today's complex design criteria, however, accurate kinetics representation of fuel combustion is required. Kinetics is important to predicting ignition, emissions, and knocking phenomena. Since the conditions within an engine cylinder vary widely in terms of pressure, temperature, and fuel-air equivalence ratio, the combustion kinetics must be validated over a wide range of conditions to provide reliable predictions. In addition, model-fuel components used to represent real automotive fuels must be selected carefully to represent the essential properties of the fuels for the simulation application of interest. With a well matched and well validated detailed mechanism for fuel combustion, the next challenge is to reduce the overall model (either through geometry idealization or mechanism reduction) to allow practical simulations on an engineering

timescale.

A collaborative consortium has been formed between automotive engine and fuels manufacturers to address some of these challenges. The purpose of the collaboration is to advance the use of detailed kinetics information in design simulations for future engine and fuel technology [1]. The consortium addresses the following technological areas of development:

1. Generation of detailed reaction mechanisms for model-fuel components.
2. Validation of mechanisms for model-fuel components and mixtures, using systematic comparison to data from well controlled experiments.
3. Matching of model-fuel blends to real-fuel properties for use in simulating the fuel-combustion behavior.
4. Software tools to analyze, merge, and automatically reduce model-fuel mechanisms.
5. Efficient engine simulation using full or reduced mechanisms, through a multizone-engine model, advanced solvers, or table-lookup strategies.

The methods demonstrated and conclusions discussed in this paper represent preliminary results of this three-year effort.

COMBUSTION MECHANISM DATABASE

The first challenge being addressed is the population of a combustion-chemistry reaction-mechanism database. The database is being populated for a wide range of fuel components that can be used in model-fuel blends to represent diesel and gasoline, as well as blends with biofuels. This involves first identifying the components needed and then building detailed reaction-kinetic descriptions of the fuel-component combustion. The fuel components currently included in the mechanism database include iso-paraffins, normal paraffins, olefins, cycloparaffins, single-ring aromatics and multi-ring aromatics, as well as ethanol and other oxygenates. Model fuel components chosen for inclusion in the database vary in size and complexity, to allow flexibility in building an appropriate model-fuel blend to match certain real-fuel properties.

Initial mechanisms for each fuel component of interest have been assembled from a variety of sources, including manual generation under this project, previously published data, and automatic generation using rule-based and group-additivity methods [2]. The main focus of improvement for these initial mechanisms has been to assure consistency in core reactions and species properties shared between mechanisms, identifying missing reaction paths, and improving rules used to determine reaction rates for similar pathways. Table 1 lists the model fuels that have been or are being studied as part of the consortium work. For each of these fuels, the goal is to achieve a "very good" rating for ignition, flame-propagation, pyrolysis and emissions behavior, where measured data are available for verification.

Table 1.   List of Fuels Mechanisms Assembled

Fuel Molecule	Class
n-heptane	Normal paraffin
iso-octane	Iso-paraffin
methylcyclohexane	Cycloparaffin
toluene	Aromatic
1-pentene	Olefin
1-hexene	Olefin
dimethylether	Oxygenate
ethyl tert-butyl ether	Oxygenate
ethanol	Alcohol
m-, o-, p-xylene	Aromatic
n-dodecane	Normal paraffin
n-decane	Normal paraffin
n-hexadecane	Normal paraffin
heptamethylnonane	Iso-paraffin
alphamethylnaphthalene	Multi-ring aromatic
methylstearate	Methyl ester
naphthalene	Multi-ring aromatic
n-propylbenzene	Multi-ring aromatic

The mechanisms for each fuel component are tested through rigorous comparison with data from well controlled experiments, which measure ignition delay, flame speed, product species fractions, and chemical conversion rates over a wide range of pressures, temperatures, and fuel-air equivalence ratios. Comparisons with experimental data require representation of the experimental conditions with a model of the experiment. Models have been set up using the CHEMKIN software [3] to represent shock-tube experiments, rapid compression machines (RCMs), jet-stirred reactors, flow reactors, burner-stabilized flames, flame-speed measurements, and opposed-flow flames. This allows rigorous testing of the mechanisms and has identified areas where improvements to the mechanism prediction are needed.

An example of how the mechanisms are being improved is shown in Figure 1. Here the initial mechanism tested by the consortium was a published mechanism for n-heptane [4]. This mechanism had been originally developed to address ignition-delay predictions and the mechanism performs very well for this purpose. However, it had not been tested extensively against flame-speed data. In the validation tests performed under the consortium, we found that the mechanism significantly over-predicts flame speed under most conditions. A thorough analysis revealed that this is a systematic issue with all the alkane mechanisms that share a common core set of reactions for hydrogen and for C_1-C_3 hydrocarbons, and that also share a common set of species transport-property data. By updating this mechanism core, based on recent work on high-temperature kinetics [5, 6], and by calculating a more self-consistent set of Lennard-Jones parameters used for transport-property calculations, we were able to improve predictions, as shown in Figure 1. Similar

improvements in flame-speed values were found for smaller alkanes after the same changes to the mechanisms were made. This shows the value of enforcing self-consistency across the mechanism database. Such consistency is especially important, because in some cases measured data are not available; in such cases we rely on the consistency between mechanisms and the validation of reaction-rate rules used to generate the mechanisms, as well as validation of sub-components, to build confidence in the mechanism reliability.
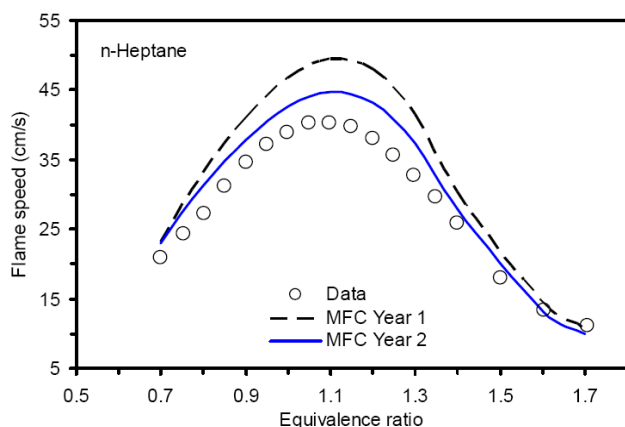
Figure 1.   Example of improved mechanism for n-heptane resulting in better flame-speed predictions. Data are from [7], for 298 K and 1 atm.

A broad range of data is considered in the validation process. For example, Figure 2 shows the breadth of data used to test ignition-delay for n-heptane. Here each point in the Figure represents an experiment that we have modeled to predict a specific ignition-delay time and to compare with the experimental result. The spread of the data is due to inclusion of points representing different fuel-air equivalence ratios, different initial temperatures, and different pressures. These data are from a variety of sources [8-24].
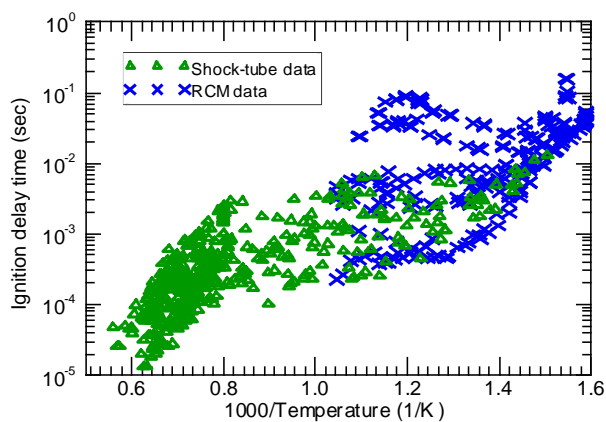

Figure 2.   Range of ignition-delay data considered for n-heptane [8-24].

An example of a specific comparison for ignition-delay time is shown in Figure 3 for n-heptane at 40 atm. Here, the initial mechanism performed quite well and the updates to improve flame-speed did not adversely affect the low-temperature kinetics predictions.
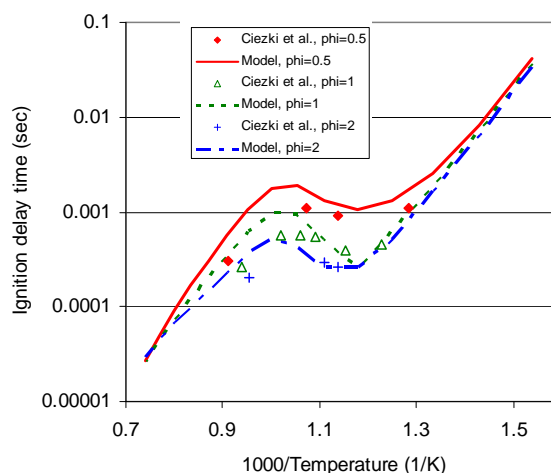

Figure 3.   Example of model comparison to ignition-delay data from high-pressure (40 atm) shock-tube experiments of Ciezki et al. [11].

Similar validation comparisons and mechanism improvements have been or are in the process of being performed for the other model-fuel components listed in Table 1. Tests of model-fuel mixtures are also being made where data is available.

MODEL-FUEL SELECTION

Once the combustion-mechanism database has been established and validated, the next challenge is to establish an automated method to match real-fuel properties to a specific model-fuel blend or composition. Here the choice of fuel properties to be matched will depend on the type of simulations that will be performed using the model-fuel mechanism. Some of the characteristic properties of the fuel may be more important than others for certain applications. In addition, model-fuel blend selection may require trade-offs between matching certain properties and reducing the size of the model-fuel mechanism for efficient simulations. For these reasons, we are developing a methodology that automates the matching of fuel properties subject to specified requirements and criteria for the final mechanism.

Figure 4 provides a flowchart of the fuel-composition matching process. Key to matching fuel properties is being able to estimate the targeted properties for the model fuel. For example, to match the cetane number of a diesel fuel, we need to be able to calculate the cetane number (CN) of different model-fuel mixtures on the fly. For gasoline, calculation of research and motored octane numbers (RON/MON) are required. We have developed virtual tools to perform such calculations, based on simulating the essential behavior of the experimental measurements for these fuel characteristics, using detailed kinetics mechanisms for

the model-fuel components in ignition calculations. Other calculations provide estimations of the heating value and distillation-curve points, as well as elemental ratios and molecular-class composition.
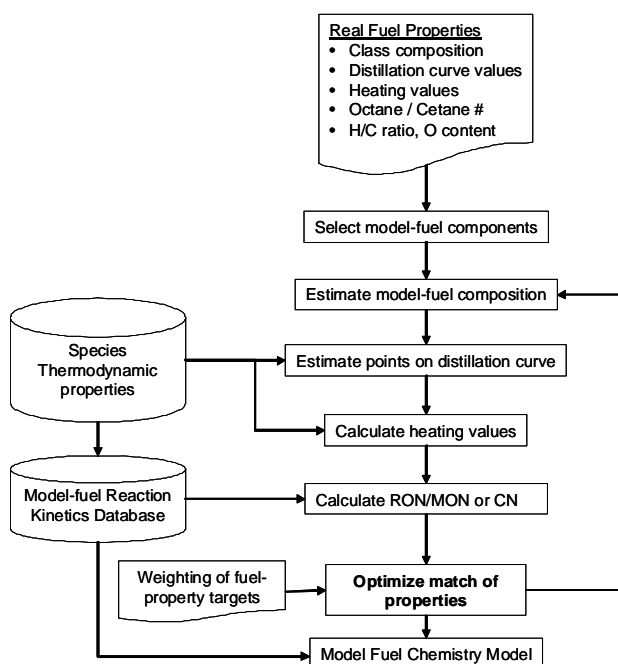

Figure 4. Flowchart showing the procedure for matching model-fuel to real-fuel properties.

A key aspect of this procedure is the ability to take component mechanisms and merge them together to form an appropriate model-fuel blend. This requires consistency between mechanisms, where there is overlap of species and reactions within sub-mechanisms for smaller hydrocarbon species. It also requires that we can automatically identify when reactions or species are duplicated between component mechanisms. The latter issue is addressed by storing canonical species identifiers, in the form of SMILES [25] strings for each species included in each mechanism stored in the model-fuel reaction-kinetics database. This allows automated comparison of reaction strings, removal of duplications, and easy flagging of any inconsistencies that may exist. The resulting merged mechanisms that match class composition and other important fuel properties can then be used with confidence in detailed kinetics simulations to represent the real fuel.

MECHANISM REDUCTION

With the desired model-fuel mechanism defined for a specific real-fuel and engine-simulation application, the next challenge is to reduce the detailed kinetics model as much as possible to allow efficient simulation of the desired fuel behavior under a specified set of conditions. To this end, we have developed a suite of automated mechanism-reduction tools that can operate on the detailed kinetics model. Conditions for the reduction are specified through a CHEMKIN-based project, which may provide ignition-delay calculations, flame-speed calculations, or some other idealized representation of

the engine conditions. The mechanism-reduction project may use many different discrete simulations to represent a range of conditions that vary, for example, the equivalence ratio, pressure, or temperature. In the mechanism-reduction process, fully detailed kinetics simulations are first used to establish a baseline and then different reduction techniques are applied to reduce the chemistry model, based on kinetic information extracted from the baseline results. Resulting reduced mechanisms can then be easily compared with the baseline to measure the error introduced through reduction to any simulation target.

Figure 5 shows some sample results from applying the reduction method of directed relation graph (DRG) [26], as implemented in CHEMKIN-MFC [3]. Here the method has been applied to producing a skeletal version of the n-heptane fuel-component mechanism for the purpose of ignition-delay predictions over a range of equivalence ratios. The DRG method reduced the original mechanism by more than 50% in terms of the number of species (from 561 to 256). The agreement between reduced and master mechanism is quite good over the entire range of interest (within 10%) for this level of reduction.
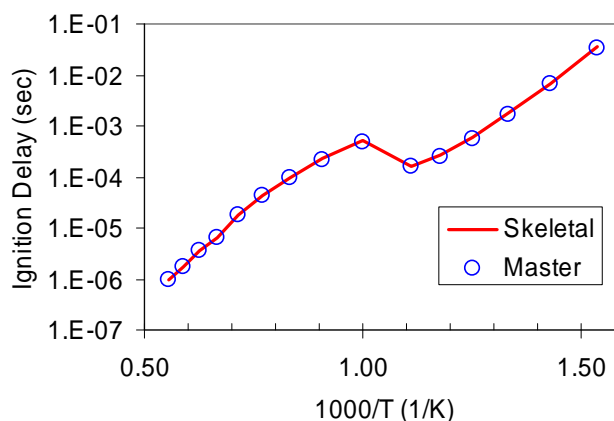

Figure 5   Comparison of ignition-delay predictions for a skeletal mechanism vs. the original, master mechanism for n-heptane.

Other reduction methods have been implemented, including principal component analysis (PCA) [27] and computational singular perturbation (CSP) [28-33] methods. However, significant issues were found with both these methods when applied to realistic fuel surrogates and large ranges of operating conditions. PCA-reduced mechanisms did not provide sufficient fidelity to the original mechanism when applied to a broad range of conditions. The CSP method, on the other hand, was successful at further reducing the number of species compared to DRG; however, the computational time required to solve the quasi-steady species equations actually took longer than solving for all active species in the master mechanism, due to inherent stiffness in the system. Focus has therefore shifted to two other ways of reducing computational time from chemistry: (1) implementation of manifold-based

table-lookup methods and (2) re-design of the underlying solution algorithms used in solving for active species in the kinetics simulation.

REDUCED ENGINE MODEL

In addition to automating the reduction of detailed-chemistry models for use in engine simulation, a complementary effort has been undertaken to reduce the geometric model as another means to reduce computational time but maintain kinetics accuracy. This approach attempts to reduce the geometric description of the engine to that which is essential for accurate kinetics predictions. For this purpose, we have developed a new multi-zone model [34, 35] that builds on CHEMKIN's single-zone HCCI engine model. The multi-zone model allows definition of an arbitrary number of zones within the engine cylinder, which are each treated as constant-mass regions. The zones may perform work on each other as the volumes undergo compression and expansion. The model follows the methods reported by Aceves, et al. [36] The CHEMKIN implementation includes the flexibility to perform the simulation from intake-valve closure (IVC) with fully detailed kinetics, or to use a prescribed temperature profile derived from a computational fluid dynamics (CFD) simulation. In the latter approach, the CFD simulation is run up to a designated crank angle, prior to ignition and prior to top-dead-center (TDC), allowing better accounting for mixing and heat-transfer effects prior to ignition. With the temperature-profile information taken from the resulting CFD solution, the multizone model overlays a kinetics simulation prior to ignition and then "takes over" the simulation (including solution of the energy equation) at the designated crank angle to predict detailed kinetics effects through ignition and volume expansion.

The multi-zone model has initially been validated through comparison with the results and experimental data reported by Aceves, et al. [36]. For this initial test of the model, a 10-zone simulation was created for the 2-bar boost case described by Aceves et al. [36]. The simulated conditions are for a natural-gas HCCI engine, running at a very low fuel-air equivalence ratio ($\varphi = 0.26$). The natural-gas fuel was represented by a mixture of CH_4, C_2H_6, C_3H_8, and n-C_4H_{10}, as described by Aceves et al. [36].

For this comparison, a natural-gas chemical kinetics mechanism was derived by reducing a detailed chemistry mechanism for primary reference fuel (PRF) mechanism [37] for the application to lean methane combustion. The reduction involved removing large hydrocarbon species and related reactions from the PRF mechanism using the DRG method. The resulting mechanism has 144 species and 819 reactions.

Temperature profiles of individual zones predicted by the multi-zone model are shown in Figure 6. The multi-zone model automatically switches from the "temperature profile" mode to the "energy equation" mode at the transition angle, which is set to -3° ATDC for this case in accordance with the original

implementation by Aceves, et al [36]. Here the temperature profile up to the transition crank angle is also taken from the Aceves work. Figure 7 compares the predicted cylinder pressure profiles from Aceves, et al [36] and from this work. This shows very good agreement between the two models.
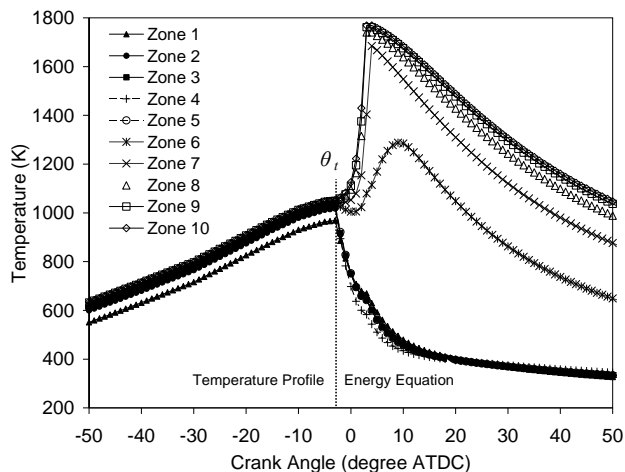

Figure 6. Temperatures predicted by the multi-zone model. The energy-equation is engaged at -3° ATDC.
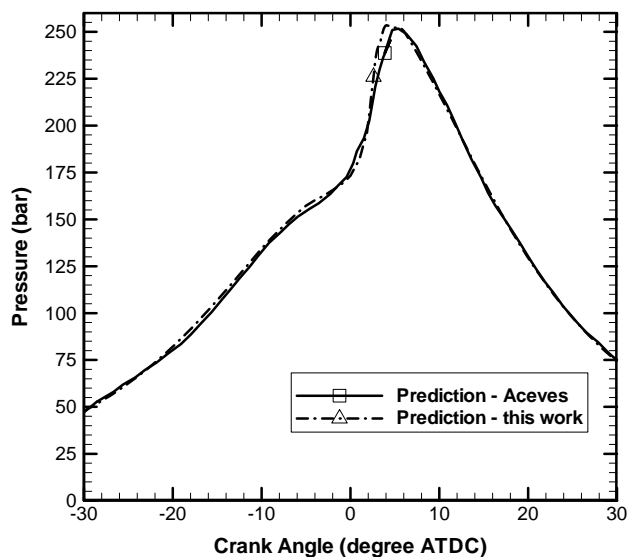

Figure 7. Comparison between predicted cylinder pressure profiles from Aceves et al [36] and this work.

The multi-zone is currently being further tested with more complex fuel models. Particular focus has been placed on improving solution algorithms to minimize the computational time for large reaction mechanisms. Preliminary results suggest that inclusion of the fully detailed mechanisms for multi-component fuel models that contain hundreds to thousands of chemical species will be feasible for 1-2 day computational time on single-CPU PCs, using this multi-zone modeling approach. The further use of overlay with CFD may allow a good compromise between cylinder-geometry or spray-model fidelity and kinetics accuracy.

CONCLUSIONS

Results are reported from a collaborative effort to systematically build tools and a database that enable more accurate simulation of chemical kinetics effects in automotive engine combustion. The use of a Multi-zone engine model as the vehicle for testing mechanism-reduction strategies has been demonstrated to be an efficient means towards accurate mechanisms that maintain fidelity under engine conditions, though more severe reduction strategies will likely be required.

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