

# Applying Detailed Kinetics to Realistic Engine Simulation: The Surrogate Blend Optimizer and Mechanism Reduction Strategies

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## ABSTRACT

Designing advanced, clean and fuel-efficient engines requires detailed understanding of fuel chemistry. While knowledge of fuel combustion chemistry has grown rapidly in recent years, the representation of conventional fossil fuels in full detail is still intractable. A popular approach is to use a model-fuel or surrogate blend that can mimic various characteristics of a conventional fuel. Despite the use of surrogate blends, there remains a gap between detailed chemistry and its utilization in computational fluid dynamics (CFD), due to the prohibitive computational cost of using thousands of chemical species in large numbers of computational cells. This work presents a set of software tools that help to enable the use of detailed chemistry in representing conventional fuels in CFD simulation. The software tools include the Surrogate Blend Optimizer and a suite of automated mechanism reduction strategies.

We start with a detailed reaction mechanism that contains chemistry for over 26 fuel components (over 3800 species and 15000 reactions) including surrogate components suitable for modeling everything from natural gas to gasoline and diesel, including ethanol. The mechanism is capable of predicting NO<sub>x</sub> emissions and soot precursors, and has been validated using fundamental experimental data available in the literature. Using the components in the master mechanism, an optimum blend is generated automatically that can capture the specified physical, combustion, and emission characteristics of conventional fuels. Selected targets can be used to match the specific behavior of real fuels. These targets can include octane number, cetane number, and heating value for combustion characteristics; hydrocarbon

class of components and true boiling point curve for physical characteristics; and molar H/C ratio for soot emission characteristics. The master mechanism can then be reduced using the guided mechanism reduction tools based on any reactor model available in the CHEMKIN-PRO software suite, such as the multi-zone IC engine model and flame simulators. Several methods for mechanism reduction, including skeletalization and more severe reduction techniques, have been implemented in a software package that works in conjunction with the CHEMKIN-PRO software. The master mechanism can be reduced for the surrogate blend so that it can reproduce selected targets, such as ignition times, laminar flame speeds, fuel and emission concentration profiles, or any other property from the available reactor model, within a specified level of accuracy requested for the reduced mechanism. Strategies for combining different methods in automated reduction are suggested that result in reduced mechanisms for both gasoline and diesel surrogates, which are being used directly in engine CFD simulations employing fast chemistry solvers.

## INTRODUCTION

Fossil fuels contain hundreds of different chemical compounds. Developing a detailed reaction mechanism consisting of all the compounds in these fuels is an intractable problem. It is also expensive and time consuming to perform detailed fuel analysis to identify every component in these fuels. Surrogate blends, also called model fuels, are controlled blends of molecular components that may or may not actually be found in complex fuels, but that are designed to mimic various properties of actual fuels. With a limited number of components, they are useful for experimental or

modeling studies elucidating the combustion and emission behavior of fossil fuels.

The use of surrogates has been in practice for many decades, starting with primary reference fuels (PRF) that are used experimentally to represent gasoline and diesel. With the availability of detailed reaction mechanisms for n-heptane and iso-octane [1], along with faster computing power, PRF blends have been a popular choice for modeling gasoline. Over the years, many researchers have also proposed different model-fuel blends to represent gasoline [2, 3], diesel [4], and jet fuels [5]. Most of these blends have been targeted to mimic only the ignition behavior of the actual fuel with the model fuel. It is only recently that researchers are beginning to expand the complexity of the surrogate to match not only an ignition-quality target, but also the chemical and physical properties as well as emissions behavior. With the availability of complex reaction mechanisms for many different alkanes [6], alkenes [7], aromatics [8], and cyclic paraffin compounds [9], it is also possible to develop and model a more complex surrogate to closely represent real-fuel properties in multiple dimensions. Properties for average gasoline and diesel in the USA are listed in Table 1. One of the goals of this work is to develop an automated way to optimize the complex surrogate blend to closely match the properties of a real fuel, using a library of surrogate fuel components for which an accurate and validated reaction mechanism is available.

Table 1. Overall chemical composition of typical gasoline and diesel. [3, 4, 10]

| Hydrocarbon Class (liq. vol %) | Gasoline                           | Diesel       |
|--------------------------------|------------------------------------|--------------|
| n-, iso-paraffins              | 33-79                              | 25-50        |
| Olefins                        | 1-18                               | 0-2          |
| Aromatics                      | 10-45                              | 15-40        |
| Naphthenes                     | 2-10                               | 15-60        |
| Molar H/C ratio                | 1.72-2.03                          | 1.8          |
| Octane or Cetane number        | 90-100 (81-88)                     | 40-56        |
| LHV (MJ/kg)                    | 42.5-44.8                          | 43           |
| Molecular weight (g/mol)       | 98.9-105                           | 222          |
| Density (g/cc)                 | 0.738                              | 0.82-0.86    |
| T50 (K)                        | 368                                | 548          |
| Carbon number range            | 5-8 (4-12)                         | 10-17 (9-24) |
| Avg. formula                   | C <sub>7.3</sub> H <sub>14.8</sub> | Varies       |

Since a good surrogate is typically a multi-component blend, the detailed reaction mechanism for such surrogates grows to be very large. The large size of the mechanisms can be computationally very expensive, even using the latest computing resources, and often prohibitive for use in multi-dimensional CFD modeling. Though such large mechanisms can be handled easily with 0-D modeling using CHEMKIN-PRO software [11], the need is to reduce the detailed master reaction mechanisms for surrogates to a more manageable

size so that they can be applied efficiently in 1-D flame simulations as well as in CFD simulations. There have been several methods reported in literature for generating a skeletal mechanism that keeps the elementary form of the original master mechanism. These methods are helpful for reducing the mechanisms under specified conditions and still keeping the integrity of the reactions and rate constants of the master mechanism. However, these methods still produce large mechanisms that may not be suitable for use in CFD modeling. Other techniques perform more severe reduction. These methods generally result in loss of the elementary form of the master mechanism and in the use of global reaction steps. In this work, we have implemented several different methods for mechanism reduction and from testing these, we propose strategies to reduce mechanisms that can be confidently used in CFD modeling with a minimal loss of accuracy.

## ASSEMBLY OF THE MASTER MECHANISM

Since the ultimate goal is to derive a reaction mechanism for surrogate blends to use for modeling, it is important to start from the components for which there are accurate detailed reaction mechanisms available. We have assembled and developed detailed reaction mechanisms for many hydrocarbon components that can be used in surrogate blends for gasoline, diesel, and jet fuels. These components are listed in Table 2. Their importance for use in surrogates for gasoline and diesel are also marked in the table.

<table 2 here>

We have assembled a master mechanism containing all of the components listed in Table 2. This master mechanism enforces self-consistency between each component mechanism, which is necessary for using the mechanism as a predictive tool. This self-consistent mechanism has been extensively validated for most of the individual components, as described in the following section. In addition to combustion mechanisms for fuel components, we have also assembled a comprehensive NO<sub>x</sub> mechanism, based on recent work by Glarborg et al. [17, 18]. Polycyclic aromatic hydrocarbons (PAH) growth reactions have also been included, based on a combination of previous studies. Based on comprehensive comparisons to experimental data, our improvements to the master mechanism resulted in significantly improved predictions for many components relative to the initial source mechanisms.

<table 3 here>

## COMPONENT MECHANISM VALIDATION

We have assembled an extensive library of experimental data that were reported in the literature for the fuel components listed in [Table 2](#) [14]. These data range from shock-tube, jet stirred reactor, plug-flow reactor, premixed flames, diffusion flames, laminar flame speed, as well as internal combustion engine experiments. The experimental conditions cover a wide range of temperatures, pressures, and equivalence ratios. A detailed report on validation is outside the scope of this article, but can be found in our companion publications (SAE World Congress papers 2010-01-0545 [23] and 2010-01-1084 [24]) and elsewhere [25].

## SURROGATE BLEND OPTIMIZATION

Having the accurate detailed reaction mechanism containing a sufficient number of possible surrogate components of choice, we have taken further steps towards establishing a methodology to develop model-fuel blends for gasoline, diesel, or jet fuels. In this work, we will focus only on gasoline and diesel for internal combustion engine applications.

## TARGETED FUEL PROPERTIES

There are several quality standards a mixture needs to satisfy before it can be considered as a model fuel. These targets will be used in the methodology for model-fuel blends described in the next Section. Targeted fuel properties and their roles in designing model fuels are shown in [Table 4](#). It should be noted that each target may be more or less important depending on the model-fuel application. Ultimately these can be weighted according to the desired application for the model, but for the purposes of building a methodology, we have assumed that the goal would be to match all targets.

<[table 4](#) here>

Various fuel components can be blended to match one or more targets, such as combustion, emissions, sooting behavior, and physical properties. Matching the combustion targets does not require complex mixtures as proven by the successful use of conventional PRFs such as *iso*-octane plus *n*-heptane for gasoline, and *n*-hexadecane plus heptamethylnonane for diesel. Such simple reference fuels can match the ignition behavior of a real fuel very well. To match the emission behavior of a real fuel, however, requires more complex mixtures that include more complex molecules. As mentioned by other researchers, adding components from various fuel classes such as aromatics, cyclic alkanes, olefins, etc., is necessary to match the emissions targets. Mimicking sooting and the physical

properties of a real fuel are probably the most difficult goals and will require blending of more complex fuel components.

## METHODOLOGY FOR DEFINING MODEL FUELS

Based on prior work [2,3,4,5, 27], we have developed and applied a general methodology for defining model-fuel blends for any practical fuel. We note that the model-fuel blends determined by this method are not necessarily unique, because there are several optional compounds that can be used in the model fuel and there are fewer targets to match than there are available compounds and composition parameters. Following are the steps required to generate and optimize a surrogate blend for a specific fuel:

1. Select the components available in the master mechanism.
  - a. Consider the carbon number distribution in the real fuel.
  - b. Consider using at least one component from each fuel class.
2. Select the target properties for the surrogate to match.
  - a. Use measured properties values from the real-fuel analysis.

<[figure 1](#) here>

We have developed a software program, the Surrogate Blend Optimizer, which automates this process. An overall flow chart for the program is shown in [Figure 1](#). The Surrogate Blend Optimizer is flexible in that it takes one or more of the fuel properties as target inputs. Based on the surrogate-fuel components selected by the user and any composition restrictions, it first performs global optimization based on a genetic algorithm. After a global optimum is reached, a local optimum solution is obtained using the Powell's Direction Set method. Both optimization methods require calculation of properties, including the ignition quality indicators Research Octane Number (RON) and Motor Octane Number (MON) for gasoline or Cetane number for diesel, boiling point curve, H/C ratio, and lower heating value (LHV) of the blend. The molar H/C ratio is calculated simply based on the candidate composition. LHV is calculated using linear blending of pure component properties. Boiling curve points are calculated based on the ASTM D-2892 method for the True Boiling Point distillation. This implementation also requires the input of actual fuel properties, based on the TBP distillation curve.

We have implemented and tested two different options to calculate the octane and cetane numbers for the surrogate blend. The simplest way is to estimate the blend property based on linear blending of the pure component properties. Calculating blend RON-MON and Cetane numbers based on linear blending of pure component properties provide a quick estimation with reasonable accuracy. However, this method

may not be sufficiently accurate for estimating the octane sensitivity. An alternate way is to use CHEMKIN-based Octane Number and Cetane Number Calculator models [28]. The Octane Number Calculator is based on the Currant et al. [29] method that uses the detailed reaction mechanism to calculate Critical Compression Ratio (CCR) and then employs correlations of CCR to estimate RON and MON. The estimation of CCR iteratively calls the CHEMKIN-PRO IC Engine model with different compression ratios until ignition is detected. Using the full master surrogate mechanism, it becomes CPU intense to run such calculations. The Cetane Number Calculator is based on the modified ASTM D-6890 method. It uses a CHEMKIN-PRO closed homogeneous reactor model to compute the ignition-delay time, again using the detailed reaction mechanism, and then estimates the cetane number using correlations to the ignition-delay time. Several assumptions and adjustments related to spray effects were made during the implementation of the Cetane Number Calculator, which may limit the accuracy of it for broader range of components; however, we have found it to be reasonably accurate for the surrogate-fuel components of interest. As seen in [Figure 2](#), predicted cetane numbers are within 5 cetane numbers of those measured over the applicability range of the ASTM method for many neat components [30] and binary diesel surrogate blends [31]. The accuracy of estimated cetane numbers using the Cetane Number Calculator may not be better than that estimated using the linear blending of pure component properties, it may be useful in case accurate cetane numbers are not available for pure components, or when the measured value have significant scatter. A snapshot of Surrogate Blend Optimizer software interface is shown in [Figure 3](#).

<[figure 2](#) here>

<[figure 3](#) here>

## GENERATION OF OPTIMUM SURROGATE BLENDS

Using the Surrogate Blend Optimizer and the detailed reaction mechanism, we have developed surrogates for a typical U.S. street gasoline and diesel. Though both gasoline and diesel surrogates follow the same methodology, there are subtle differences, such as the choice of fuel components used, as well as the indicator of combustion characteristics in the engine (octane vs. cetane ratings). The properties of typical U.S. diesel are shown in [Table 1](#). [Figure 4](#) shows the boiling point curves for a typical gasoline in the U.S.A. [3, 32] In addition to distillation curves, information on the carbon-number distribution is also shown for typical gasoline in [Figure 5](#) [10, 32]. Ranges of other properties for gasoline are shown in [Table 1](#).

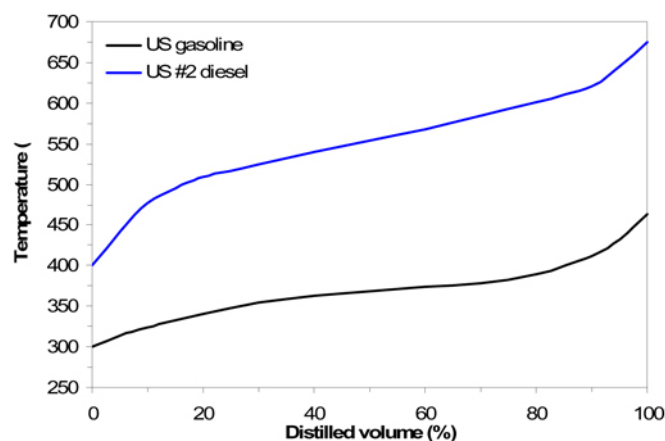


**Figure 4. Distillation curve for typical US gasoline and diesel.**

<[figure 5](#) here>

There can be numerous ways to represent gasoline structure using a fuel mixture. All components mentioned in [Table 2](#) that are applicable for gasoline can potentially be used to generate gasoline surrogates. However, for this example, we have limited the number of surrogate components to eight, which is sufficient to match most target properties of gasoline. As discussed by Naik et al. [2], at least one fuel component from each class of components is chosen to begin with. These core components are *iso*-octane, *n*-heptane, toluene, methylcyclohexane, and 1-pentene. Based on the data on carbon number distribution and distillation curve, we added *iso*-hexane, *n*-pentane, and *n*-propyl benzene to the blend. Composition of the surrogate gasoline and estimated properties of the blend are shown in [Table 5](#). The surrogate closely matched various properties of a typical gasoline including the boiling point curve.

**Table 5. Model fuels for typical US gasoline based on the proposed methodology and data collected. Some of the blend properties are also shown. Composition is in mole %.**

| Components                  | Surrogate           |
|-----------------------------|---------------------|
| 1-Pentane                   | 8.7                 |
| <i>n</i> -Propylbenzene     | 19.3                |
| Toluene                     | 11.6                |
| Methyl cyclohexane          | 7.6                 |
| <i>iso</i> -Hexane          | 19.9                |
| <i>iso</i> -Octane          | 21.3                |
| <i>n</i> -Pentane           | 7.4                 |
| <i>n</i> -Heptane           | 4.1                 |
| Research Octane Number      | 90.6                |
| Motored Octane Number       | 85.8                |
| Molar H/C Ratio             | 1.89                |
| Lower heating value (MJ/kg) | 43.8                |
| T50 (K)                     | 372.1               |
| Chemical formula            | $C_{7.08}H_{13.36}$ |

Unlike gasoline, variation in diesel fuels worldwide is much larger. This makes it difficult to generate a typical diesel surrogate for all purposes. However, we have tried to generate a surrogate which is closest to a typical #2 diesel in the USA. Surrogate 1 shown in Table 6 is a seven-component diesel surrogate that contains all hydrocarbon classes in diesel. However, additional higher boiling point components may be required to closely match the distillation curve for heavier cut fractions. Due to the need for larger-carbon-number components along with components from all different hydrocarbon classes for diesel surrogates, it can be difficult to reduce the size of the master reaction mechanism. Therefore, we have proposed a simpler four-component Surrogate 2 (Table 6) that matches most characteristics of a typical diesel. It also matches the T50 point on the boiling point curve. For the rest of the validation and mechanism-reduction work reported here, Surrogate 2 is used.

<table 6 here>

## VALIDATION OF SURROGATES

Before reducing the surrogates, we first validated that the surrogate blends, with the full master mechanism, provide good prediction of gasoline or diesel behavior, where the data were available. These comparisons generally involve fundamental experiments that can be modeled using 0-D or 1-D reacting-flow simulations, which allows use of the fully detailed kinetics for the surrogate blend.

## Fundamental experimental studies: Simulations using CHEMKIN ideal reactor models

Limited fundamental data are available for gasoline and diesel that can be used for model validation. Gauthier et al. [33] measured homogeneous ignition delay time for gasoline/air mixture in high-pressure shock tube at pressure from 15 to 65 atm. They grouped their data in two pressure ranges: 15-25 atm with nominal pressure of 20 atm, and 46-65 atm with nominal pressure of 60 atm. Comparison of measured gasoline ignition time to those predicted using gasoline surrogate is shown in Figure 6. For both pressure ranges, predictions agree well with the data.

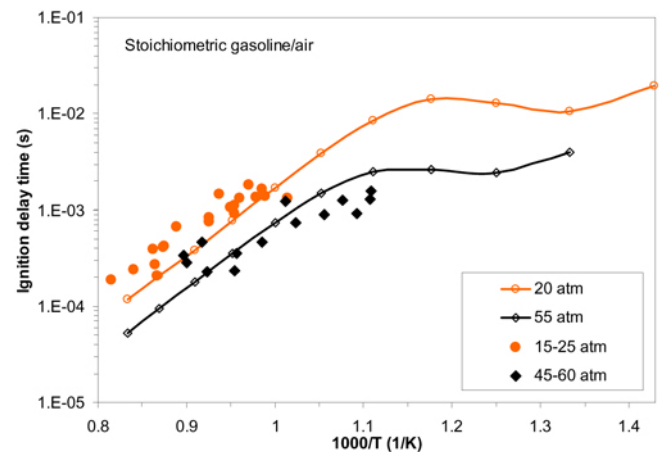


**Figure 6. Comparison of predicted and measured ignition-delay time for gasoline/air mixture in a high pressure shock-tube by Gauthier et al. [33] Solid lines represent predictions and symbols represent measurements.**

Mati et al. [34] measured the oxidation characteristic of diesel in a jet stirred reactor (JSR) at fuel-lean to fuel-rich conditions and measured concentration of various species over a range of temperatures. They used synthetic diesel with chemical composition of  $C_{15.5}H_{30}$  in the experiments. Since our diesel surrogate has lower molecular weight than the fuel used in the experiments, we increased the fuel mass proportionally to match the mass of synthetic diesel in the simulations. Comparisons of predicted and measured species profiles at 10 atm at fuel-lean conditions are shown in Figure 7 and Figure 8. Major intermediate products of oxidation are CO,  $H_2$ ,  $CH_4$ , and  $CH_2O$  with peak levels appearing between 850 K to 1000 K. The model captures all major products well, as shown in Figure 7. Minor products ethylene ( $C_2H_4$ ) and propylene ( $C_3H_6$ ) are also captured well (Figure 8). However, the model could only capture the trends in acetylene ( $C_2H_2$ ); it overpredicts the concentration. Under fuel-rich conditions, the model predictions show similar agreement with the measurements as seen in Figure 9 and Figure 10.

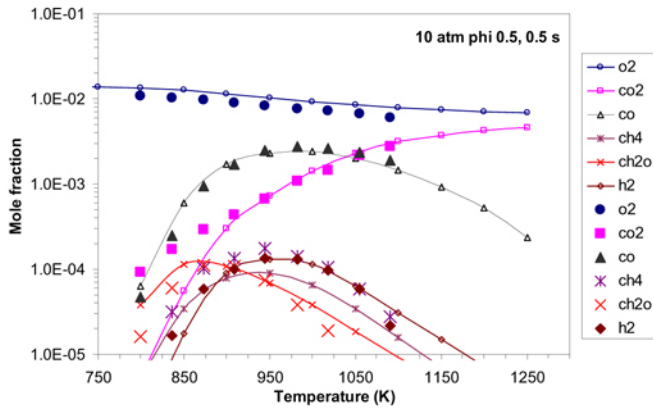


**Figure 7. Comparison of predicted and measured profiles of major species during oxidation of synthetic diesel ( $C_{15.5}H_{30}$ ) in a jet-stirred reactor by Mati et al. [34]. Initial composition is diesel: $O_2$  0.03:1.38 mol% with balance of  $N_2$ . Lines represent predictions and symbols represent measurements.**

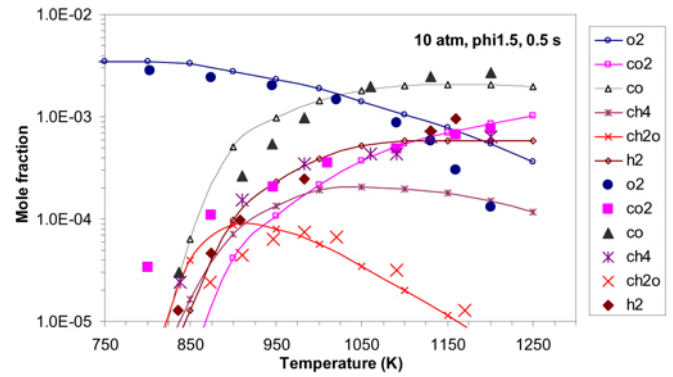


**Figure 9. Comparison of predicted and measured profiles of major species during oxidation of synthetic diesel ( $C_{15.5}H_{30}$ ) in a jet-stirred reactor by Mati et al. [34]. Initial composition is diesel: $O_2$  0.0225:1.38 mol% with balance of  $N_2$ . Lines represent predictions and symbols represent measurements.**

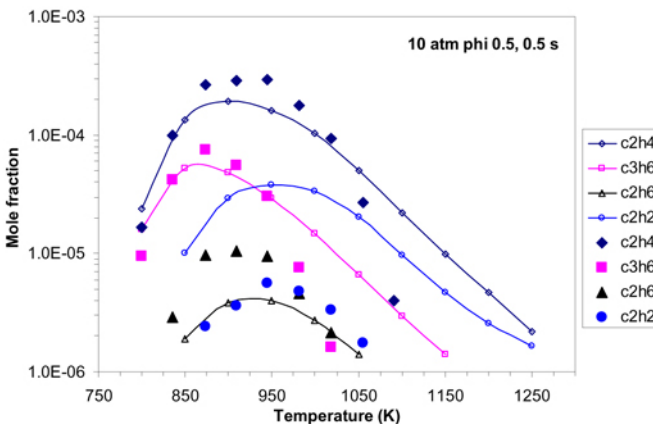


**Figure 8. Comparison of predicted and measured profiles of minor species during oxidation of synthetic diesel ( $C_{15.5}H_{30}$ ) in a jet-stirred reactor by Mati et al. [34]. Initial composition is diesel: $O_2$  0.03:1.38 mol% with balance of  $N_2$ . Lines represent predictions and symbols represent measurements.**

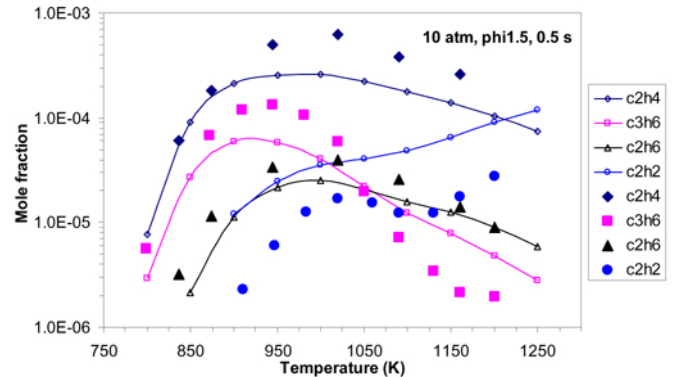


**Figure 10. Comparison of predicted and measured profiles of minor species during oxidation of synthetic diesel ( $C_{15.5}H_{30}$ ) in a jet-stirred reactor by Mati et al. [34]. Initial composition is diesel: $O_2$  0.0225:1.38 mol% with balance of  $N_2$ . Lines represent predictions and symbols represent measurements.**

As demonstrated in comparisons above, predictions by the detailed mechanism, using the proposed surrogates for gasoline and diesel, agree well with fundamental experimental data for the street fuels. These data covered a range of conditions that are likely to be applicable in an engine combustion environment.

### HCCI engine studies: Modeling use of the CHEMKIN Multi-zone HCCI Engine Model

Recently Bunting et al. [35] studied ignition and emission characteristics of unleaded regular (ULR) gasoline in an HCCI engine. Details about the engine and experimental conditions can be found in previous publications [35, 36]. In short, they varied the inlet temperature from 429 K to 449 K and measured its effect on combustion characteristics and