



## CHEMKIN-PRO

# Fuel Flexibility Impacts on Ignition Delay in Burners and Boilers

Ignition delay is a critical kinetic parameter for burners that is affected by fuel composition. Burner designers need to assess how various fuel formulations, biofuels and additives affect boiler or furnace performance such as Lean Blow Off (LBO), flame attachment, flashback and flame shape. Ignition delay is also one of the primary methods in comparing the accuracy of a fuel model (or mechanism) with experimental data. CHEMKIN-PRO's fast and robust Closed Homogeneous Reactor can be used to test the impacts of various fuel compositions on ignition delay through automated parameter studies on operating conditions.

## Setting Up in CHEMKIN-PRO

This simulation is based on the shock-tube study of Ciezki and Adomeit<sup>1</sup>, which measured ignition-delay times of *n*-heptane/air mixtures behind reflected shock waves. The idealized CHEMKIN closed homogeneous batch reactor model is used to simulate the ignition-delay times over the following range of conditions, and compare with the experimental data: Temperatures of 675 to 1350 K, equivalence ratios of 0.5 to 3.0, and pressures of 1 to 100 atm. The detailed reaction mechanism for *n*-heptane tested here is made available by Lawrence-Livermore National Labs.<sup>1</sup> The gas-phase kinetics input file consists of 561 species and 2539 reactions, and includes both low- and high-temperature reaction pathways.

CHEMKIN-PRO provides the Parameter Study Facility, which allows setting up a project that can simulate a range of temperature and equivalence ratio conditions to cover the range reported in the experimental data source. Equivalence ratio values of 0.5, 1 and 3, and temperature increments of 25 K over a range of 675-1350 K have been used in this project. This results in a total of 84 parameter cases.

<sup>1</sup> H. K. Ciezki and G. Adomeit, "Shock-Tube investigation of self-ignition of *n*-heptane-air mixtures under engine relevant conditions," *Combustion and Flame*, vol. 93, pp. 421-433, 1993

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CHEMKIN-PRO also provides an ability to vary the ignition-time criteria to use in calculating the ignition-delay time. These criteria include: temperature inflection point, maximum species concentration of a selected species, specified ignition temperature, specified temperature increase beyond the initial temperature, and any user-defined criterion specified using a user routine. Data are often reported based on several of these criteria; while the different definitions typically result in similar ignition time values, there are instances, such as with very fuel-lean mixtures, where the definitions result in markedly different values<sup>2</sup>. For this case, we use the temperature inflection point and the peak of the OH species profile as the ignition-point criteria, and later compare the similarities in the calculated ignition times.

### Results

There are a total of 84 runs in this project, and all the projects converge quickly using the minimal inputs described earlier. Figure 1 shows a plot of ignition time versus  $1000/\text{temperature}$  for the various equivalence ratio cases and covering ignition times over about three orders of magnitude. The comparison with the experimental data of Ciezki et al. in Figure 1 shows the model generating consistent trends. The model shows the negative temperature coefficient regime (NTC), where ignition times increase with increasing initial temperatures. The low-temperature and NTC region autoignition behavior are of particular relevance to engine conditions, with that behavior being one of the main differences between low- and high-octane number fuels. Some of the interesting trends in Figure 1 include:

- The impact of equivalence ratio is most pronounced in the negative temperature coefficient regime.
- In the NTC regime, the fuel-rich mixtures exhibit the fastest ignition.

<sup>2</sup> [http://www-pls.llnl.gov/?url=science\\_and\\_technology-chemistry-combustion-nc7h16](http://www-pls.llnl.gov/?url=science_and_technology-chemistry-combustion-nc7h16)

<sup>3</sup> Davidson, D. F. and R. K. Hanson. "Interpreting shock tube ignition data." *International journal of chemical kinetics* (2004)36(9): 510-523.

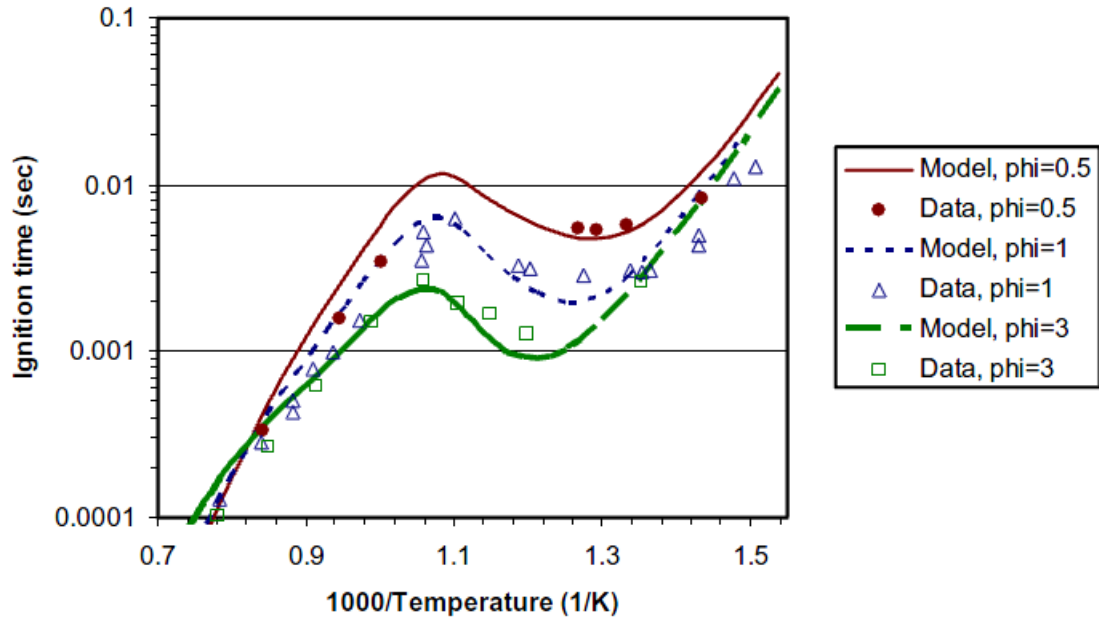


Figure 1. Comparison of CHEMKIN-PRO simulation results vs. experimental data of Ciezki et al. Figure studies effect on ignition-delay time of n-heptane/air mixtures, of temperature and equivalence ratio. Pressure for all cases is 13.5 bar.

It is possible to further explore these trends using CHEMKIN-PRO tools such as the Reaction Path Analyzer.

To further understand the autoignition behavior at such conditions, for example, we can use an analysis as shown in Figure 2. The first graph in the figure is similar to Figure 1, but for the stoichiometric mixture case only. The next graph shows a temperature vs. time profile for one value of the initial temperature in the ignition-time graph, namely the initial temperature of 800 K. This figure shows the 2-stage ignition characteristic of low-temperature ignition. To further understand the chemistry behind the 2-stage ignition, we use the CHEMKIN-PRO graphical Reaction Path Analyzer. A snapshot from the Reaction Path Analyzer at a particular temperature from the temperature vs. time profile shows the influence of alkyl peroxy type species at low temperatures. As engines operate over a wide range of conditions of pressures, temperatures, equivalence ratios and exhaust-gas recirculation, the relative importance of the several competing reaction pathways change and it is useful to perform an analysis similar to that in Figure 2.

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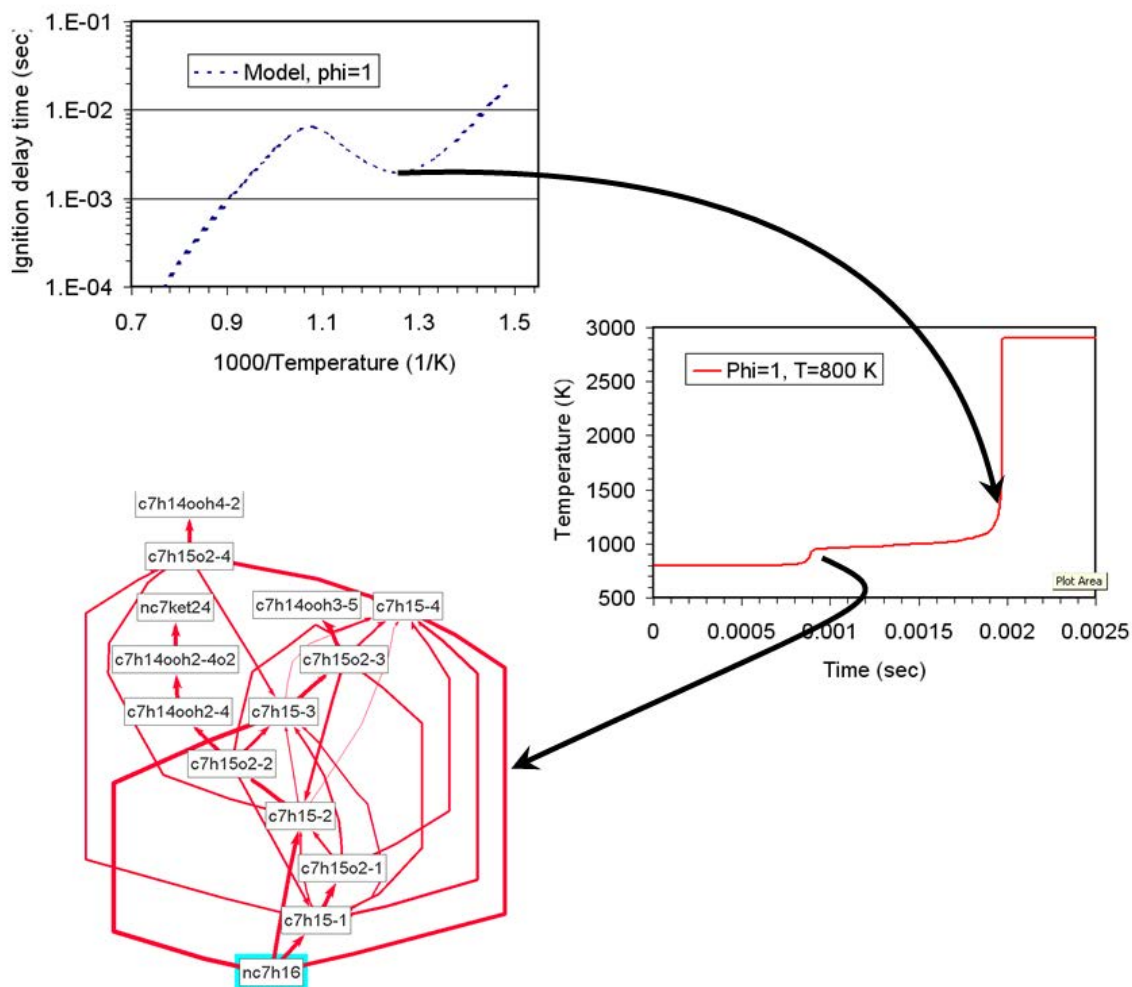


Figure 2. Analysis of the autoignition phenomena for the 800-K initial temperature and stoichiometric mixture case. The reaction path analysis is at a temperature of 820 K.