



Verifying Ignition Delay Predictions of a Detailed Kinetics Mechanism for Automotive Fuels

APP-nH (v2.0) August 30, 2010

Overview

This application note describes a method for validating a detailed chemical mechanism against shock-tube data to verify ignition delay predictions relevant for practical gasoline and diesel surrogate fuel components. We focus on autoignition modeling under shock-tube reactor conditions using the CHEMKIN closed homogeneous batch reactor model. This type of modeling can be used for mechanism validation purposes, and for analysis of the chemical kinetic effects. We will compare the simulations with some experimental ignition delay data from the literature. The operating conditions considered, including temperature, pressure and equivalence ratio, are pertinent to engine combustion. We will explore some of the features available in the model, and the analysis tools.

Introduction

With increasing regulation of NO_x and particulate emissions and goals for improved fuel efficiency, there is an increasing need to employ reliable complex chemical kinetic mechanisms in engine combustion modeling, particularly in the prediction of ignition timing. The complexity of the mechanisms range from tens of species typically used in CFD calculations, to hundreds of species used in more accurate representations of fuel combustion. Testing and validation of these kinetic mechanisms over a wide range of engine operating conditions is necessary for predictive engine modeling. This application note focuses on how CHEMKIN can be used to calculate ignition delay using detailed chemistry and how to set up a library of validation cases.

Engine measurements are typically not optimal for testing and validating chemical kinetic mechanisms since there are several factors that impact the data in addition to chemical kinetics, such as turbulence, spray effects and heat loss, which have large degrees of uncertainty. Consequently, it is common to use more well controlled, fundamental laboratory experiments, such as ignition-delay measurements in shock tubes, for kinetic mechanism validation. Shock-tube data for several fuels are available in the

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literature over a wide range of temperatures, pressures, equivalence ratios and diluent concentrations. Shock tubes typically involve short compression and heating times¹, which are more conducive to zero-dimensional modeling. However, the lower end of the temperature range for shock tubes is somewhat limited, due to boundary layer effects that introduce more experimental uncertainties at large ignition times. Diluents used in shock tubes include nitrogen and argon.

In this application note, we focus on the shock tube study of Ciezki and Adomeit¹, which analyzes ignition-delay times of n-heptane/air mixtures behind reflected shock waves. We use the idealized CHEMKIN closed homogeneous batch reactor model to simulate the ignition delay times over the following range of conditions, and compare with the experimental data of Ciezki and Adomeit¹:

1. Temperatures of 675 - 1350 K
2. Equivalence ratios of 0.5 – 3, with air as the oxidizer
3. Pressure of 13.5 bar

Normal-Heptane (n-Heptane) is a commonly used surrogate component for modeling both gasoline and diesel fuels. The procedure outlined here can also be used for analyzing and validating mechanisms for more complex surrogate mixtures. While we focus in this application note on the idealized batch reactor model as a validation tool, CHEMKIN also supports methods for more accurate simulation of engine combustion, such as the multi-zone engine simulator (See the CHEMKIN application note entitled: [Using Multi-Zone Engine Modeling with Detailed Chemistry for Accurate Ignition and Emissions Predictions in HCCI Engines](#) for more information.

It may be noted that while CHEMKIN also has models that can simulate normal and reflected shocks, these models are not necessary here since Ciezki and Adomeit¹ provided the temperature and pressure conditions behind their reflected shock wave. With this information, the batch reactor model is sufficient to model their conditions.

¹ 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.

Project Setup

Kinetic Mechanism

The n-heptane reaction mechanism tested here is made available by Lawrence-Livermore National Labs.² The gas-phase kinetics input file consists of 561 species and 2539 reactions, and includes both low- and high-temperature reaction pathways.

Inputs in the Graphical User Interface

The model allows the use of constrained-volume or constrained-pressure conditions, in the Reactor Physical Properties panel. We use the constrained volume condition for this example.

To demonstrate the ease of project setup, we will provide only a minimum set of inputs, and use the default values wherever applicable. Several optional advanced user inputs are additionally available to the user. Inputs we will provide include:

1. Initial Temperature
2. Fuel/Air equivalence ratio, and the associated necessary definitions such as molecular composition of the fuel and air

For setting up a project that can simulate the whole range of temperature and equivalence ratio conditions of the experimental data source, we use the Parameter Study Facility in CHEMKIN-PRO. 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.

3. Pressure
4. End time for calculations. Even though we are modeling a wide range of conditions, it is sufficient to provide a single (relatively large) value of end time for all cases. The solver adaptively determines when large time steps can be taken (i.e., when there is little activity) and when it needs to resolve small time steps during ignition. Solution data are output according to the adaptive solution process to provide very accurate ignition-timing data. An end time of 0.1 sec should be sufficient for all conditions.
5. Volume, for which we use an arbitrary value of 1 cm³. Since we do not employ any surface reactions, and therefore do not have to account for surface-to-volume ratio, the value for volume input can be arbitrary for this particular example.

² http://www-cmls.llnl.gov/?url=science_and_technology-chemistry-combustion-nc7h16

6. The ignition-time criteria to use in calculating the ignition-delay time. This is an advanced feature where CHEMKIN allows specification of alternative or multiple criteria for determination of ignition times in its output panel. 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 values³. 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.

No further inputs are explicitly provided for this example. For other parameters, we use default values, such as solver tolerances, that are provided by CHEMKIN. For saving solution data, CHEMKIN has incorporated adaptive time stepping so that more information is saved to the solution file in regions of large gradients. As a consequence, the solution file is a reasonable size, even though we are using a large mechanism.

Since the project has all the necessary information to cover the range of conditions of the experiment, the same project (.ckprj) can later be used to test other mechanisms, or to test any update to the existing mechanism, with minimal changes to the project. In this way, CHEMKIN allows a user to create a library and history of validation data. The project inputs, output and solution files can also be compressed and archived into a single file for easy future reference, or for sharing the project, using the **Project >Archive** option.

Summary

There are a total of 84 runs in this project, and all the projects converge quickly using the minimal inputs described earlier. The CPU time taken is much reduced from previous versions of CHEMKIN. Although we employ a fairly large kinetic mechanism of 561 species and 2539 reactions, the typical CPU time for each of the parameter study run is 1-2 minutes on a 3-GHz PC. Once the runs are complete, the Analyze Results panel allows us to either plot the results using the Graphical Post-Processor or analyze the reaction pathways at various points in the solution using the visual Reaction Path Analyzer.

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

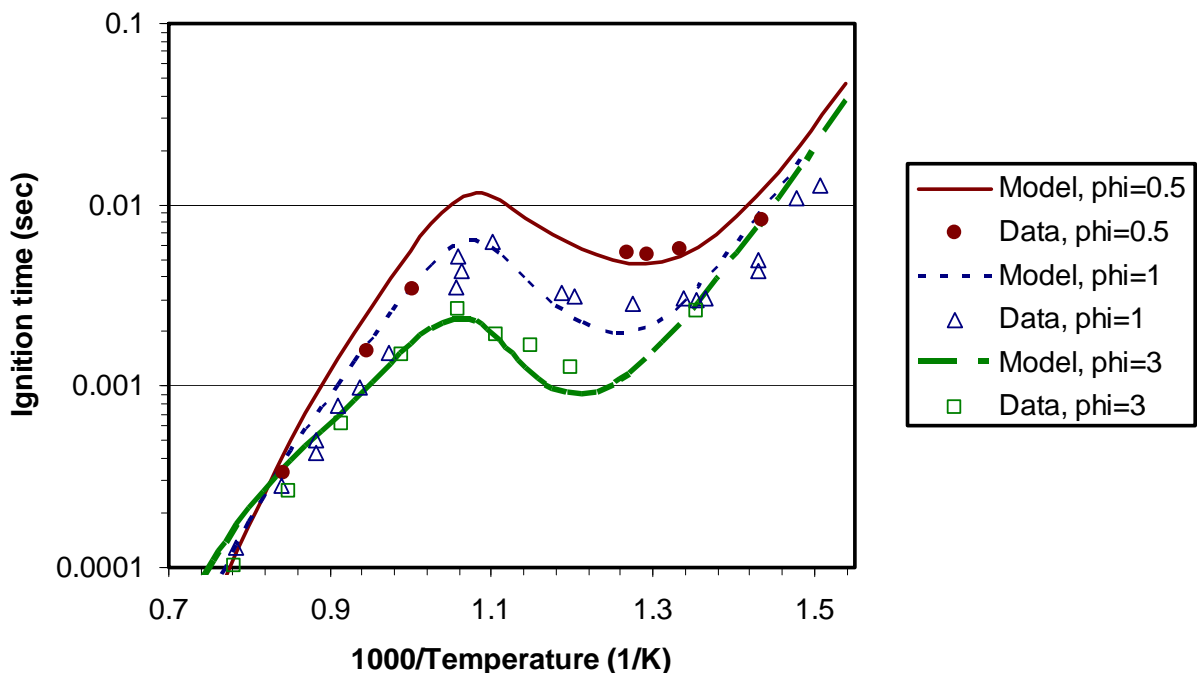
³ Davidson, D. F. and R. K. Hanson (2004). "Interpreting shock tube ignition data." *International journal of chemical kinetics* **36**(9): 510-523.

experimental data of Ciezki et al.¹ 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:

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

In the simulations reported here, we used different ignition criteria for determining the ignition times. The values plotted above use temperature inflection. However, ignition-time values calculated using OH-peak profiles were within 0.5% for 76 of the 84 cases, and within 4% for all cases. Note that for some conditions such as dilute conditions, however, the different criteria might result in a greater difference in calculated values.

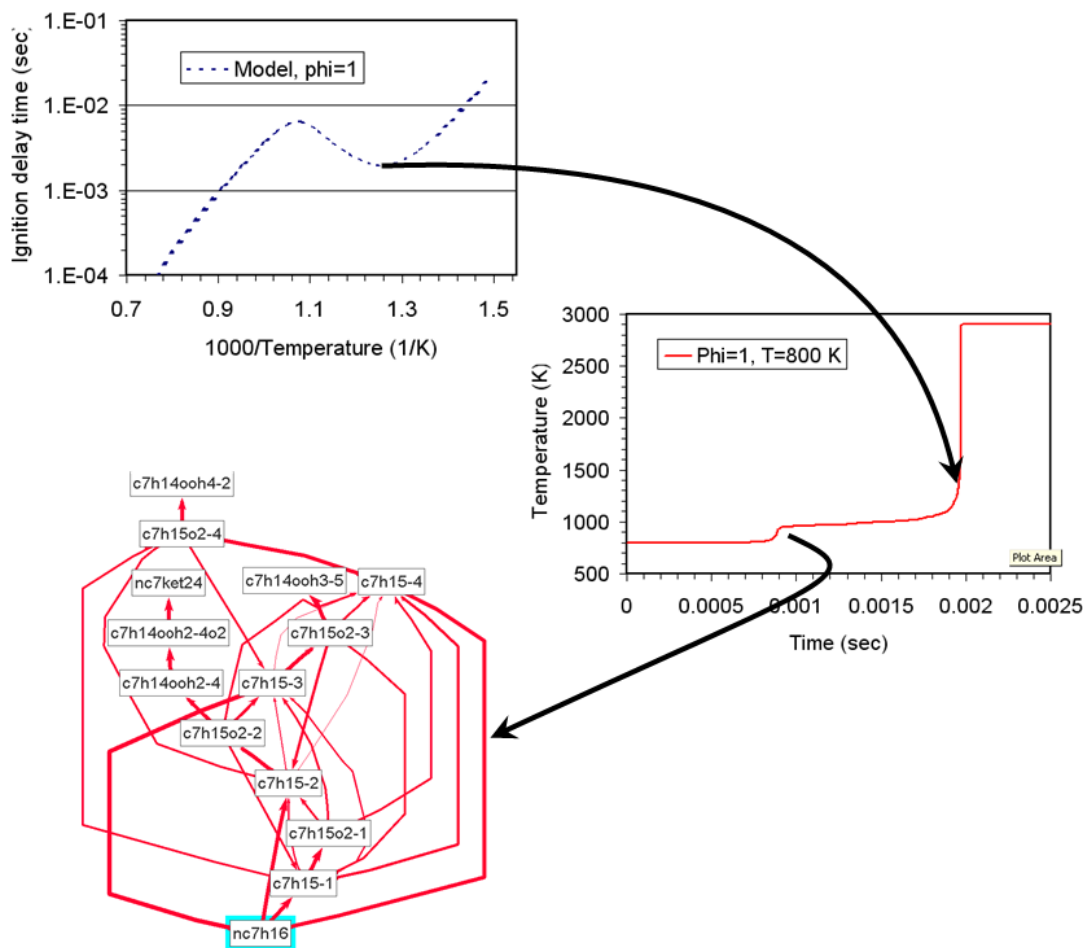
Figure 1. Comparison of CHEMKIN Simulation vs. Experimental Data of Ciezki et al.¹
 Figure studies effect on ignition delay time of n-heptane/air mixtures, of temperature and equivalence ratio. Pressure for all cases is 13.5 bar.



It is possible to further explore these trends using CHEMKIN 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 graphical Reaction Path Analyzer (see the Application Note for [Reaction Path Analysis](#)). A snapshot from the Reaction Path Analyzer, at a particular temperature from the temperature vs. time profile, is also shown in Figure 2. This 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 to understand which affects are dominant under different conditions.

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.



About Reaction Design

Reaction Design helps transportation manufacturers and energy companies rapidly achieve their Clean Technology goals by automating the analysis of chemical processes via simulation and modeling solutions. Reaction Design is the exclusive developer and distributor of CHEMKIN and CHEMKIN-PRO, the *de facto* standards for modeling gas-phase and surface chemistry, providing engineers ultra-fast access to reliable answers that save time and money in the development process. Reaction Design also offers the CHEMKIN-CFD software module, which brings detailed kinetics modeling to other engineering applications, such as Computational Fluid Dynamics (CFD) programs. Reaction Design's world-class engineers, chemists and programmers have expertise that spans multi-scale engineering from the molecule to the production plant. Reaction Design serves more than 350 customers in the commercial, government and academic markets.

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