



Determining the Uncertainty in Chemical Kinetic Modeling

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Overview

This application note reviews how the Uncertainty Analysis feature in CHEMKIN-PRO can be used to assess the relationship between the variability and probability of a kinetic model's input parameters and the variability and probability of the model's output results. The kinetic modeling result of a NO_x study is used to demonstrate uncertainty propagation through the model.

How Uncertainty Analysis Guides Better Technical and Business Decisions

Understanding the impact of uncertainty that is inherent in a model is critical to interpreting the results. Uncertainty analysis is different from sensitivity analysis. In sensitivity analysis, the sensitivity of the model's results to a small perturbation of a single input is understood. Uncertainty analysis focuses on how variability or inaccuracies in the model's inputs ultimately lead to a quantifiable degree of uncertainty in the result. Such analysis allows us to understand the accuracy, or error bars, that can be expected from the model, given what we know about the lack of certainty in the input parameter values. We can also gauge the amount of outcome-uncertainty associated with specific inputs, which guides better engineering decisions on where to invest for improved accuracy of input data. Better business decisions are also made through an understanding of how accurate the model results are. For example, if a specific model for NO_x emissions has uncertainty associated with it of ± 2 ppm, then a parametric variation of the model resulting in less than 2 ppm NO_x variation would be considered statistically insignificant.

Uncertainty Analysis Facility for NO_x Emission Study

The detailed study of emissions has become a vital part of the design and analysis of gas-phase combustion processes, because of increasingly stringent requirements imposed by government regulations. For many combustion systems, the emission limit for NO_x is approaching the ppm (parts per million) level. However, such combustion systems generally demonstrate variations in operating conditions due to certain design elements that are difficult to control. These variations can induce uncertainties in the level of NO_x emission. It is therefore helpful to account for these uncertainties during the design and analysis of the combustion process to make sure the emission level is still within the regulatory requirements. Uncertainty analysis can be performed to study the effect of variations in the operating conditions on the NO_x emission level.

In this application note, we apply an uncertainty analysis to investigate the effects of heat loss and equivalence ratio for the NO_x emission level of a perfectly stirred reactor. For the gas-phase kinetics, we employ the GRI-Mech 3.0 gas-phase mechanism and thermodynamic data for methane combustion. This mechanism contains NO_x chemistry relevant to methane or natural-gas combustion.

We choose to study the effect of the variations in heat loss from the wall of the reactor and the equivalence ratio (i.e., fuel/air ratio) for the NO_x emissions of a perfectly stirred reactor. These operating conditions are selected because (1) the exact heat loss from the wall of the reactor/combustor is often unknown for a particular combustor as it is difficult to measure and (2) non-perfect mixing in the combustor often leads to pockets of very fuel-rich or fuel-lean mixtures, thus making the fuel/air ratio that controls the overall combustion behavior uncertain.

To set up uncertainty analysis for heat loss and equivalence ratio in this NO_x study, we open the Reactor Physical Properties panel, as shown in Figure 1. Here, we click the Setup Uncertainty Analysis button next to the Heat Loss parameter of the reactor to view the uncertainty analysis setup panel, as shown in Figure 2. For this project, we select a normal (Gaussian) probability density function to represent the uncertainty in the heat loss, with a specified mean value and standard deviation. The mean value of the distribution is the nominal value of heat loss in the reactor and the standard deviation is assumed to be 1.0 cal/sec or 20% of the mean value for this analysis. Uncertainty input for the equivalence ratio parameter is setup in a similar manner, starting from the Species-specific Properties tab. For equivalence ratio, we assume a normal distribution also, but we assume a much smaller standard deviation in the analysis. We identify the final mole fraction of NO in the reactor as the uncertain output of interest to us in the NO emissions study.

Figure 1. Selecting the Heat-loss Parameter as “uncertain” and launching Uncertainty Setup Panel.

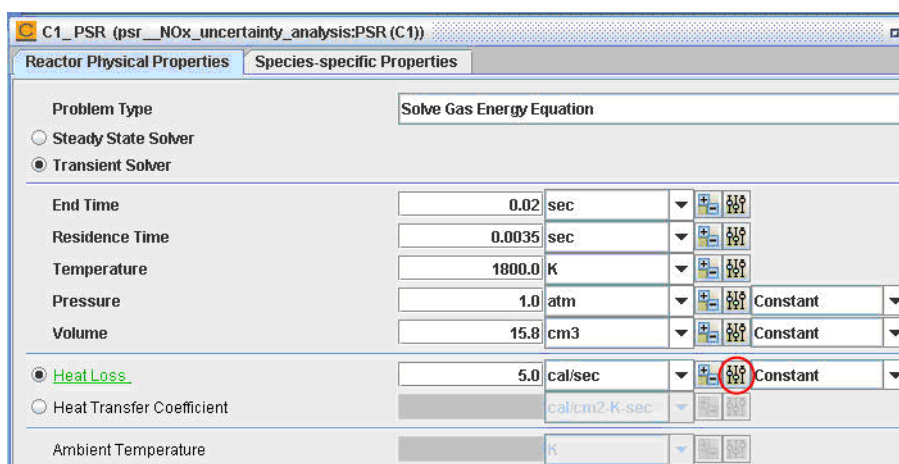
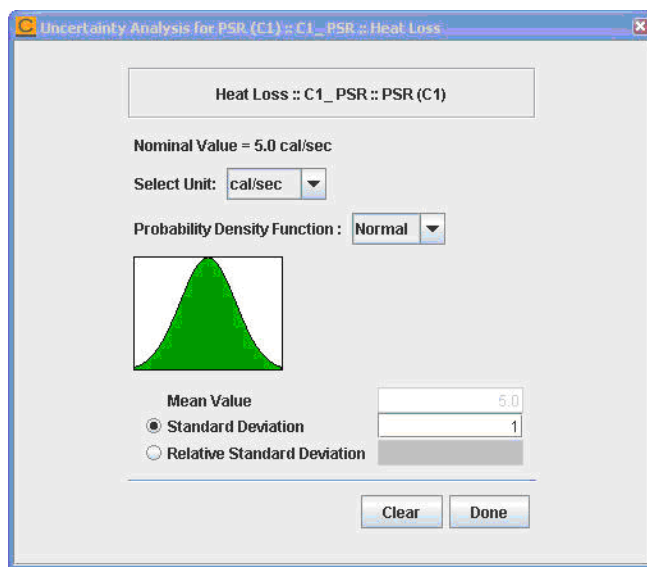


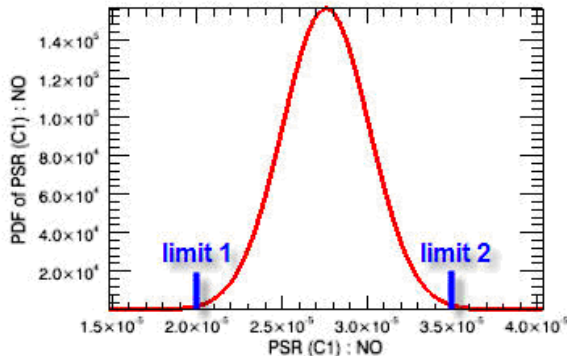
Figure 2. Setting Up the Probability Distribution Function of an Input Parameter for the Uncertainty Analysis



Once the input-parameter probability functions have been defined and the outputs of interest in the uncertainty analysis have been identified, we can run the uncertainty analysis from the Run Calculations panel. By Viewing Detail in the Run panel, you can see the different model cases that are set up to provide the uncertainty-propagation results. Once all of these cases are run to success, we take the next step to analyze the data to determine the uncertainty in the NO_x emission level and to perform a variance analysis, which provides the relative contribution to that uncertainty from the variability in two input parameters: heat loss and equivalence ratio. From Section 2, Error Analysis, of the displayed analysis file, you can see that the accuracy of the uncertainty model is high in the predictions of NO emission level. From Section 3, Variance Analysis, you can see that the uncertainty in the NO emission level is quite moderate, since the standard deviation of the NO emission level is about 10% of the mean value. The more interesting results from the variance analysis is that variability in the equivalence ratio has much more impact on the uncertainty of the NO emission level than does the variability associated with the heat loss value. This suggests that good mixing to accurately determine the equivalence ratio is more important to predictably maintain a required level of NO_x emissions in this perfectly stirred reactor than is accurate control of heat-loss from the reactor.

Further analysis of the NO_x emissions can be achieved by examining the probability density function (pdf) of fraction of NO that is predicted by the model, which is shown in Figure 3. The pdf of the NO_x fraction shows the distribution given the variations in the heat loss and equivalence ratio of the reactor. From the pdf, we can conclude that the most likely emission level of NO is between 23 ppm and 32 ppm. If the emission requirement were 20 ppm (i.e., limit 1), then it is very likely that the system will exceed this limit, since most of the pdf curve lies above the level of limit 1. On the other hand, if the emissions requirement was 35 ppm (i.e., limit 2), it is almost certain that the NO_x emissions would satisfy the requirement, regardless of the variations in the heat loss and equivalence ratio of the reactor.

Figure 3. The Probability Distribution Function for NO Emissions Based on the Heat Loss and Equivalence Ratio Input Accuracy



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 that provides 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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