



Reaction Path Analysis

PRO-APP-RPA (v2.0) August 30, 2010

Summary

In this application note, the Reaction Path Analyzer in CHEMKIN-PRO is used to provide both visual and quantitative data related to the reaction paths present at each point of a kinetic flame-speed simulation.

Using Reaction Path Analysis to Gain Better Understanding of Your Application

In any detailed chemistry model, understanding of the dominant reaction paths can be critical to filling out your understanding of the kinetic model results. Identifying the dominant reactions that dictate the formation or quenching of pollutant species, such as NO_x , CO and un-burned hydrocarbons, can be extremely valuable in identifying some means to reduce their formation, through manipulation of the reactor geometry and the process operating conditions.

Application Setup

In this application note, we seek to determine the laminar flame speed of an atmospheric-pressure, stoichiometric methane-air gas mixture and use the Reaction Path Analyzer to acquire a visual representation of the sequential reactions that form or deplete certain chemical species.

The Flame-speed Calculator simulates a freely propagating flame, in which the point of reference is a fixed position on the flame. In this coordinate system, the flame-speed is defined as the inlet velocity (velocity of unburned gas moving towards the flame) that allows the flame to stay in a fixed location.

CHEMKIN-PRO results for a Flame-speed Calculation are shown in Figure 1 and Figure 2, which show velocity and temperature profiles vs. distance, respectively. The laminar flame speed, by definition, is the relative speed between the unburned gas mixture and the flame front that allows the flame to freely propagate in an adiabatic environment. Since the coordinate system is fixed to the flame, all velocity solutions are actually relative velocities with respect to the flame front. Accordingly, the calculated flame speed is the velocity determined at the point where the temperature and composition are the same as the unburned gas mixture (i.e., the inlet to the computational domain, or the left-most point in Figure 1. The predicted flame speed for this case is 41.01 cm/sec.

Figure 1. Result of a Flame-speed Calculation —Axial Velocity vs. Distance

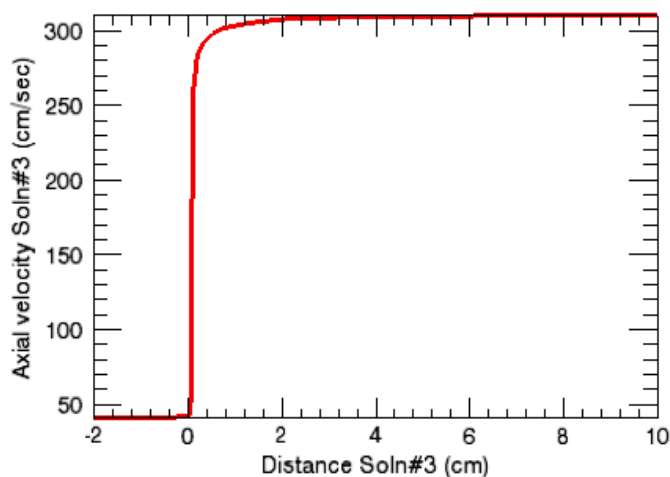
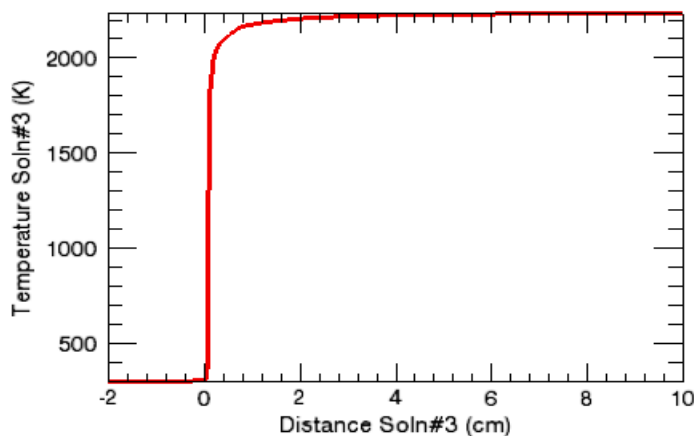


Figure 2. Result of a Flame-speed Calculation —Temperature vs. Distance

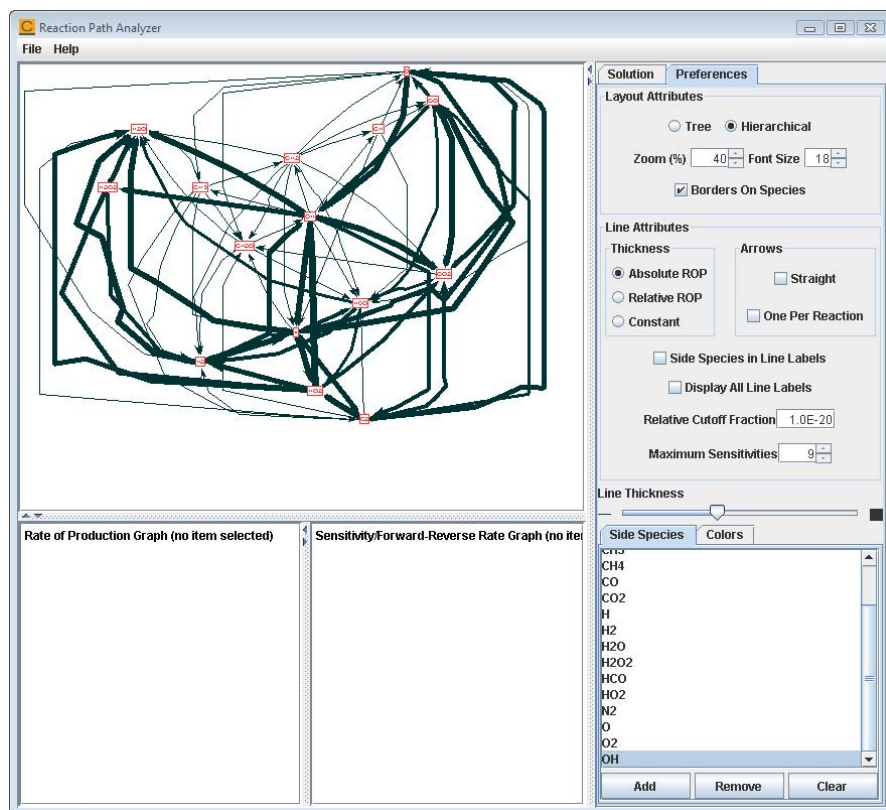


Reaction Path Analysis

Applying the CHEMKIN-PRO Reaction Path Analyzer (RPA) to the results provides a visual representation of the reaction paths that form or deplete chemical species. Employing the RPA, the decomposition pathways at different regions in the methane/air flame become evident. For the case presented here, sensitivity analysis for methane with respect to reaction-rate parameters was included in the flame-speed calculation. This information, along with species rates of production, can be viewed graphically within the RPA, in addition to the reaction-path network.

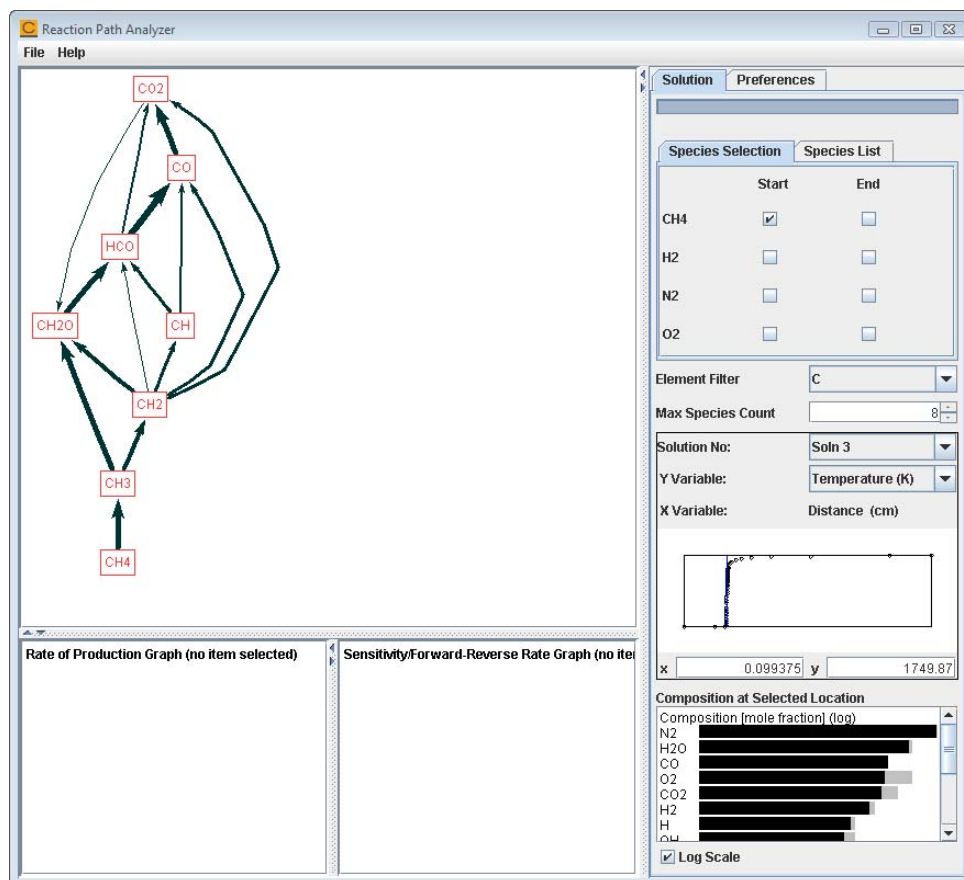
Once the RPA is selected in the CHEMKIN-PRO Analyze Results panel in the User Interface, the RPA will generate a diagram for the initial point in the flame solution. The Y variable is chosen by default to be temperature, so we have a quick visual map of where the flame front begins. The focal point for the RPA can be altered by moving the thin blue line along the solution into the hot region of the flame (see Figure 4). In Figure 3 we have also increased the number of species visible in the RPA path diagram to 15. The complexity of the diagram increases due to the high temperature activation of various reaction channels, as well as the increased number of species allowed in the diagram. To see the entire diagram in the RPA window, we have also changed the zoom setting, with the result shown in Figure 3.

Figure 3. Example Reaction-Path Diagram at the Flame Front



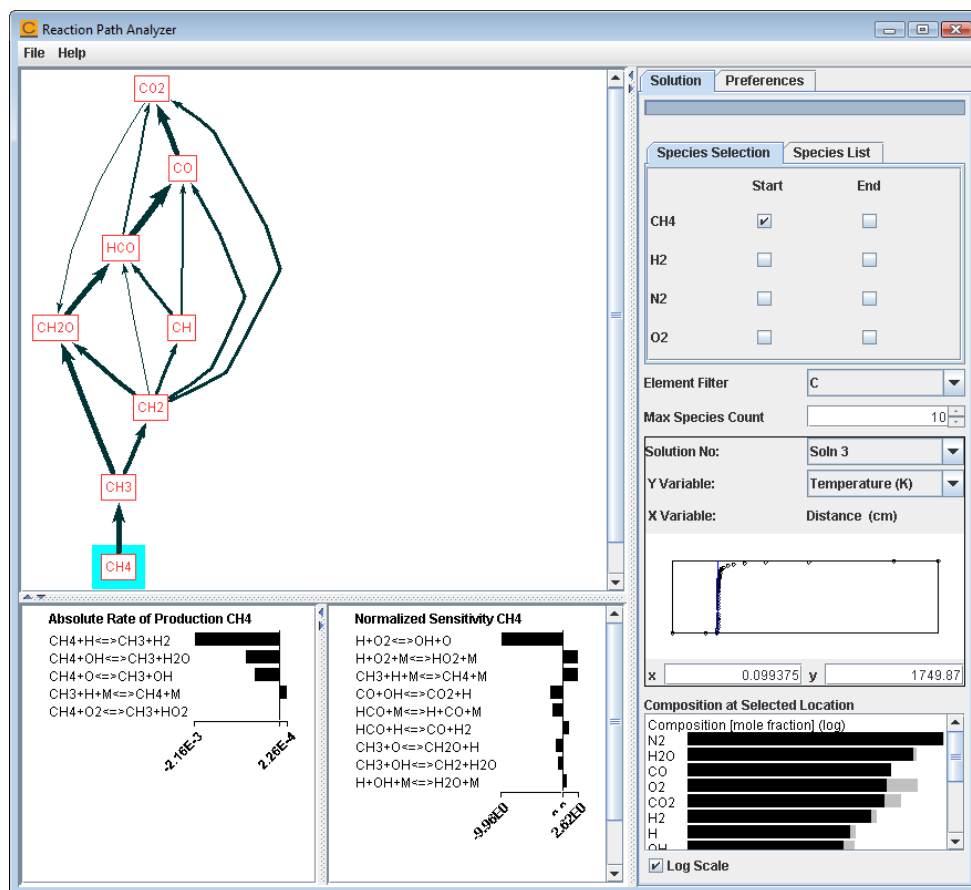
Changing the focus back to the colder side of the flame, the diagram changes to highlight the initial decomposition pathways for methane. This results in a simpler diagram that follows the major pathways flowing out from methane, as shown in Figure 4 (here we've reduced the number of species back to ten). With a C element filter applied, the RPA displays only paths between species containing Carbon.

Figure 4. Decomposition pathways starting with methane



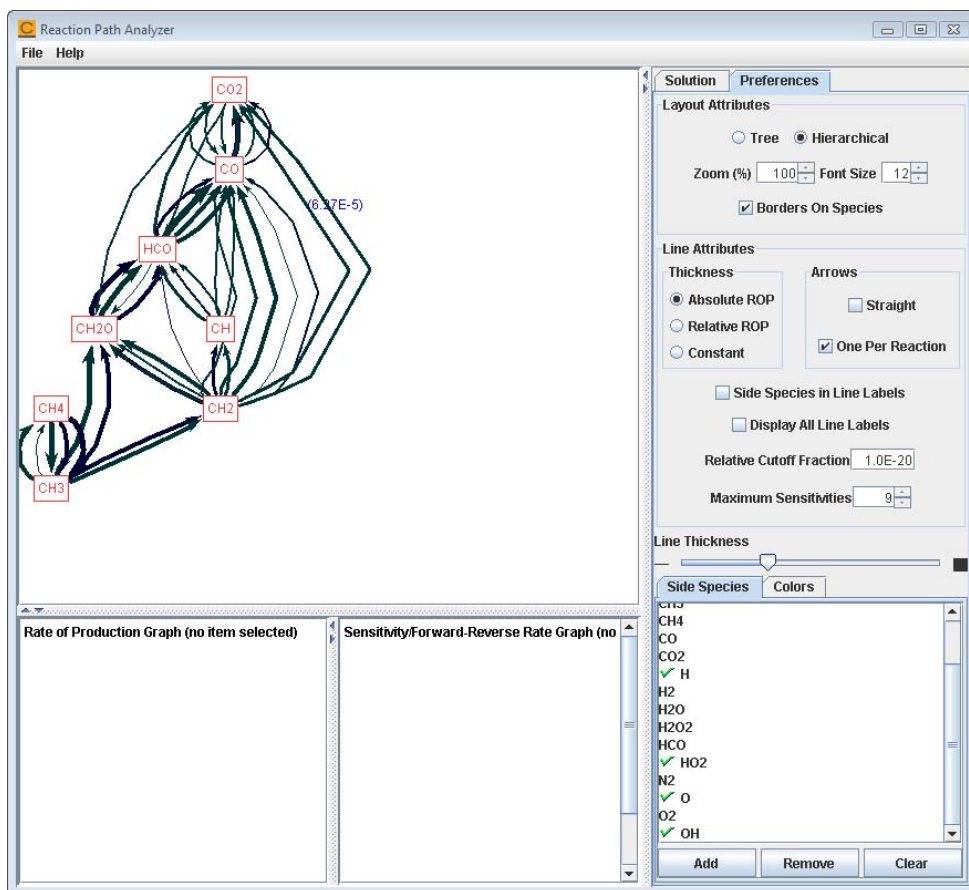
Selecting the methane species in this diagram results in two new bar-charts below the reaction-path diagram, as shown in Figure 5. The left-hand chart shows the Rates of Production of all reactions that contribute to the formation or destruction of methane at the selected solution point. The right-hand chart shows the calculated sensitivity coefficients for methane, with respect to each of the reactions in the mechanism. The sensitivity data provide a measure of the effect of perturbing the rate of any reaction in the system on the predicted species composition. These data are complementary to the rate-of-production data, as they identify reactions that indirectly (as well as directly) affect the predicted results.

Figure 5. The Rate of Production and Sensitivity Charts of Methane



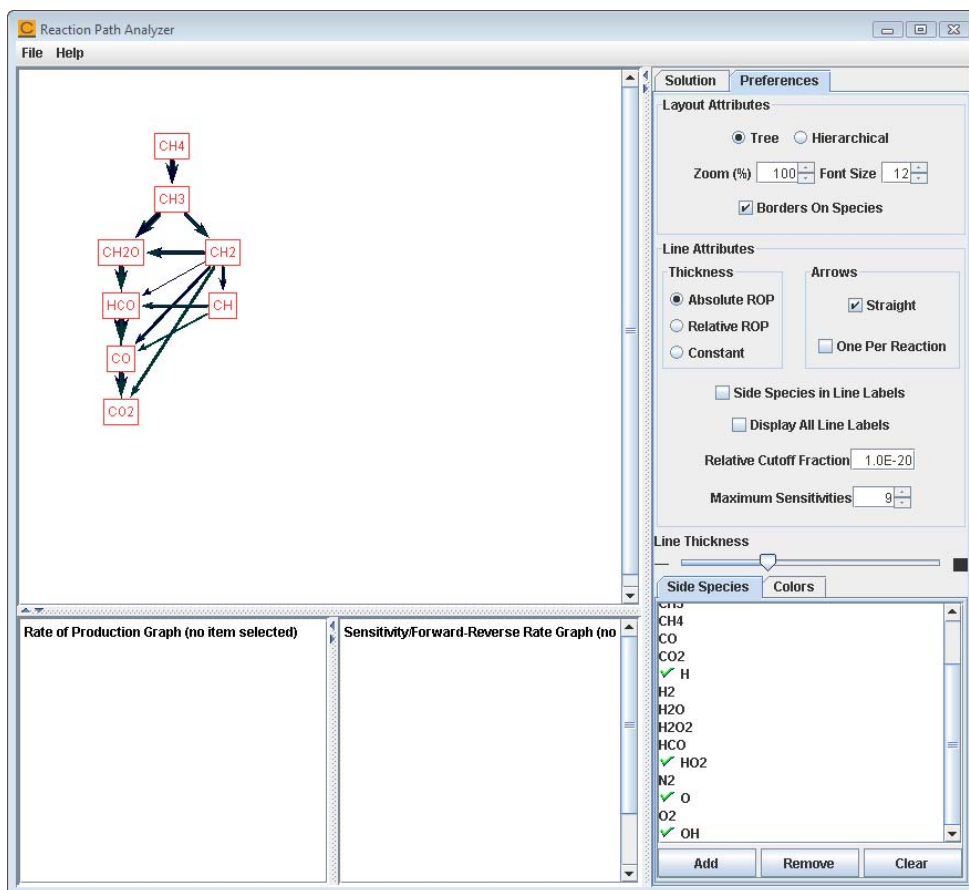
There are many interactive visualization options within the RPA that allow us to drill down into the information provided. For example, each connection can be split into separate lines that represent constituent reactions for that “path”, as shown in Figure 6. A relative rate analysis can be accomplished while the reaction paths are split in this manner. The relative-rate analysis will scale the width of exiting lines relative to the total of all reactions depleting a species. This scaling helps to visually determine which reaction has the largest influence on the removal of a species under the local conditions. The absolute-rate analysis scales every reaction pathway relative to a single global value, providing a different perspective on the data.

Figure 6. Splitting a Composite Reaction Pathway into One Per Reaction



A second layout method, the tree format, is available, which represents the downward flow of reactions from a starting species. The selected start species is placed at the top of the diagram and the other species are laid out in successive generations from this root, as shown in Figure 7. This view is useful in following the fate of a particular species through the reaction system.

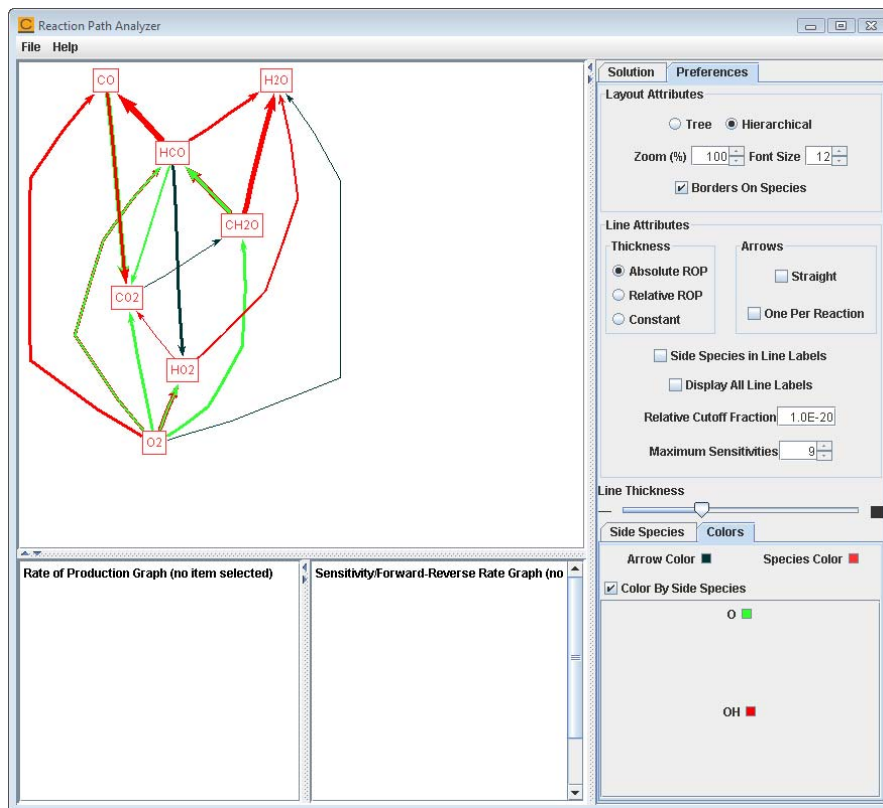
Figure 7, Tree Layout Method of the Decomposition of Methane



Another very useful option for reducing the complexity of the diagram is to demote certain radicals that participate in many reactions from explicit species in the diagram to “side species”. For example, in Figure 8, the hydroxide radical (OH) and oxygen radical (O) are specified as side species. Consequently, these radicals will not be drawn in the diagram. However, the lines can be labeled and/or colored according to the side species, to quickly see where these radicals participate in the reactions. In Figure 8, after setting the color preferences, reactions involving OH are displayed in red, and any reaction involving O is shown in green.

These diagrams graphically show the decomposition pathways of the fuel, and the primary formation pathways of the flame products.

Figure 8. Result of Setting the Hydroxide Radical and Oxygen Radical as Side Species. The source species was switched from methane to oxygen, and the element filter was changed to O element.



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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