reaction DESIGN

CHEMKIN-PRO: Reaction Workbench
Reducing Fuel Mechanisms for Burners and Boilers

Researchers at Reaction Design and around the world have focused efforts to develop and validate highly accurate master mechanisms that define the combustion of fuels for burners, boilers, furnaces and incinerators. These master mechanisms contain all the required detail of species and reactions that occur during the combustion process. However, while these master mechanisms cover a large number of surrogate fuels and blends and include very comprehensive chemistry in terms of ranges of combustion conditions, the direct use of the mechanisms in engine simulations is impractical, due to the mechanism size.

The mechanisms, then, must be reduced as needed for the application of interest. Here we demonstrate the reduction of a 980-species master mechanism to a 134-species reduced mechanism, focusing on accurately capturing *n*-heptane chemistry; the single component *n*-heptane surrogate is used to represent diesel combustion chemistry.

Setting Up in CHEMKIN-PRO: Reaction Workbench

In this example, we focus on *n*-heptane as the fuel, which is frequently used as a 1- component diesel surrogate. The goal is to generate a reduced mechanism for *n*-heptane that is as small as possible while maintaining our specified level of accuracy over the desired range of operating conditions. We use a 14-component gasoline surrogate mechanism as the master mechanism for this project: this mechanism has the requisite *n*-heptane chemistry pathways of interest, while also not being too large for simulation in a CFD code such as FORTÉ.

The following steps are taken to set up a mechanism reduction in Reaction Workbench (Figure 1):

1. **Definition of operating range**: Specify the operating conditions of interest, such as temperature, pressure, equivalence ratio and dilution. The operating range settings for this example are:
    - Initial equivalence ratios of 1-3.
    - Initial temperatures of 700-1200 K.
    - Initial pressure of 50 atm. This pressure was chosen as indicative of pressure close to TDC, where ignition occurs.

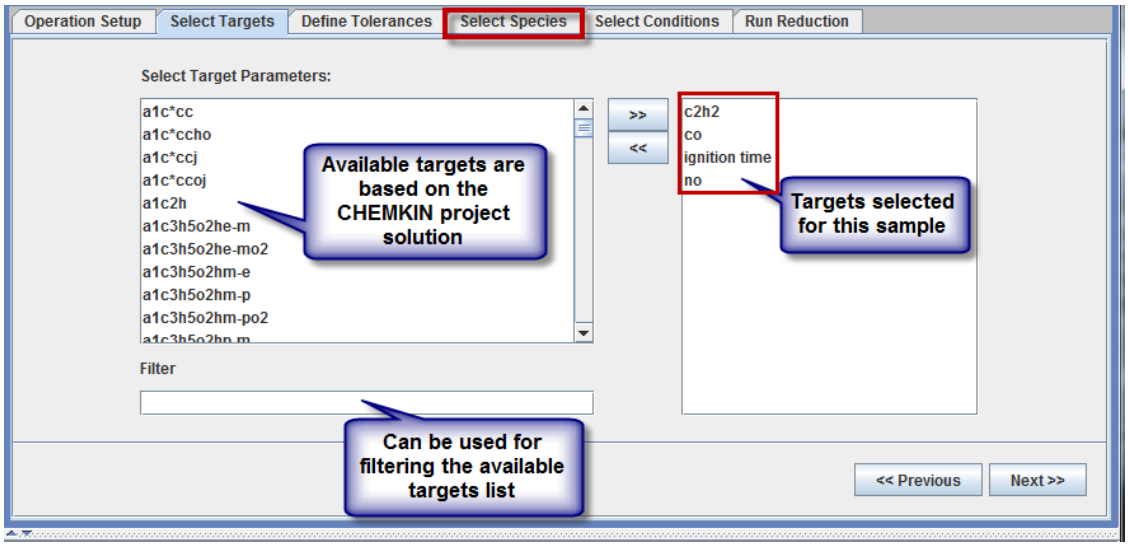

Figure 1. Mechanism reduction in Reaction Workbench (specifying reduction targets shown).

2. **Definition of success criteria**: Define the success criteria for the mechanism reduction. This involves defining targets of interest, such as ignition times and emitted species concentrations, and the degree to which predictions for these targets with the reduced mechanism should match with the predictions made with the master mechanism. The user sets the error tolerances for how well the predictions for the targets using the reduced mechanism should match those using the master mechanism. This is specified using absolute and relative tolerances for each target. The relative tolerances are set to 10% for all targets, except for acetylene, which is set to 20%. The specific targets for this example are:
   - Ignition delay time
   - Emissions-related species:
     - NO
     - CO
     - Acetylene (soot-precursor)
3. **Selection of reduction technique**: Decide which reduction technique to use. The Reaction Workbench offers seven reduction techniques, as listed below. This example will highlight how the Workbench facilitates the use of any combination of these techniques.
   - DRG (Directed Relation Graph)
   - DRGEP (Directed Relation Graph with Error Propagation)
   - Sensitivity Analysis Option in DRG/DRGEP
   - PCA (Principal Component Analysis)

- CSP (Computational Singular Perturbation)
- QSSA (CSP-based Quasi-Steady-State Approximation)
- Linear lumping of isomer species

Reaction Workbench automatically creates and tests reduced mechanisms in CHEMKIN-PRO as they are created, until the optimal reduced mechanism is generated. At the end of each step you can decide the next step to take and/or archive the current optimal mechanism. The predictions from CHEMKIN-PRO are used to evaluate the accuracy of the reduced mechanism, by comparison with the master mechanism predictions, for targets of interest (such as ignition time and emission species).

Results

A series of reduction runs are performed automatically, gradually getting more aggressive. Reductions that exceed user-specified tolerances are rejected. If the sequential reduced mechanism fails to meet the error tolerance, it is rejected. In this example, DRGEP is used initially to generate a reduced mechanism having 307 species. This is followed by Isomer Lumping which reduces the mechanism further to 272 species. This is followed by more DRGEP reduction which generates a 208-species optimal reduced mechanism. All of the trial runs are performed in an automatic fashion, so as to generate the smallest mechanism possible while obeying user-specified tolerances for the targets specified.

Additional mechanism reductions are run eventually yielding a 134-species reduced mechanism. The sequence is shown below in Table 1. It can be seen that beyond a certain point, further reductions do not yield substantial returns on the mechanism reduction. In this sample, DRG, DRGEP, isomer lumping, and species sensitivity analysis techniques were used.

Table 1. Summary of Reaction Workbench mechanism reduction results.

Reduction Technique Used	Size of Reduced Mechanism
DRGEP + Lumping	208
DRG + Lumping	167
DRGEP + Lumping + Sensitivity	161
DRG + Lumping + Sensitivity	145
DRGEP + Lumping + Sensitivity	134