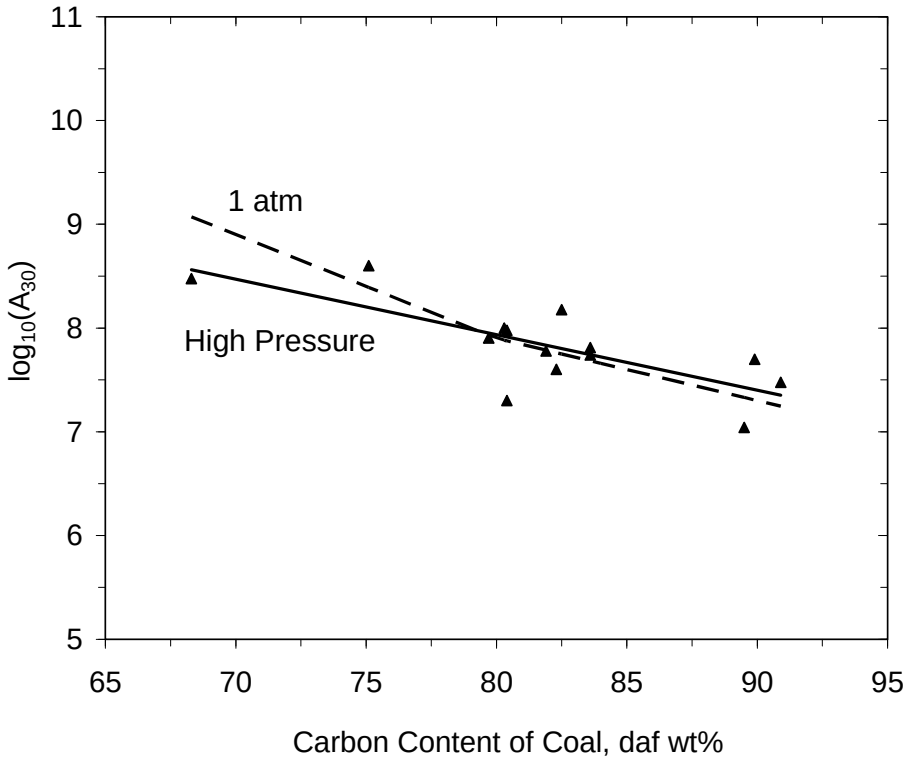
Assigning Rate Parameters in Simple Rate Laws From Comprehensive Reaction Mechanisms: Char Oxidation Rates

The char oxidation mechanism in PC Coal Lab® is called CBK/E, an extended version of Prof. Robert Hurt's Carbon Burnout Kinetics (CBK) model for elevated pressures. This mechanism was one of the first to interpret the extremely long times to burnout the final few percent of combustibles in char, based on an annealing step and, for low-rank fuels, ash encapsulation during the latest stages of burnout. The mechanism also automatically adjusts the rate limiting step to accommodate different ambient conditions, and will smoothly transition from control by reaction kinetics to pore diffusion to film diffusion across a broad temperature range. Consequently, CBK/E is one of the few char oxidation mechanisms that can accurately depict how particle size, ambient temperatures, and O_2 partial pressures affect char burnout histories in virtually any coal combustion technology, including those operating at very high pressures.

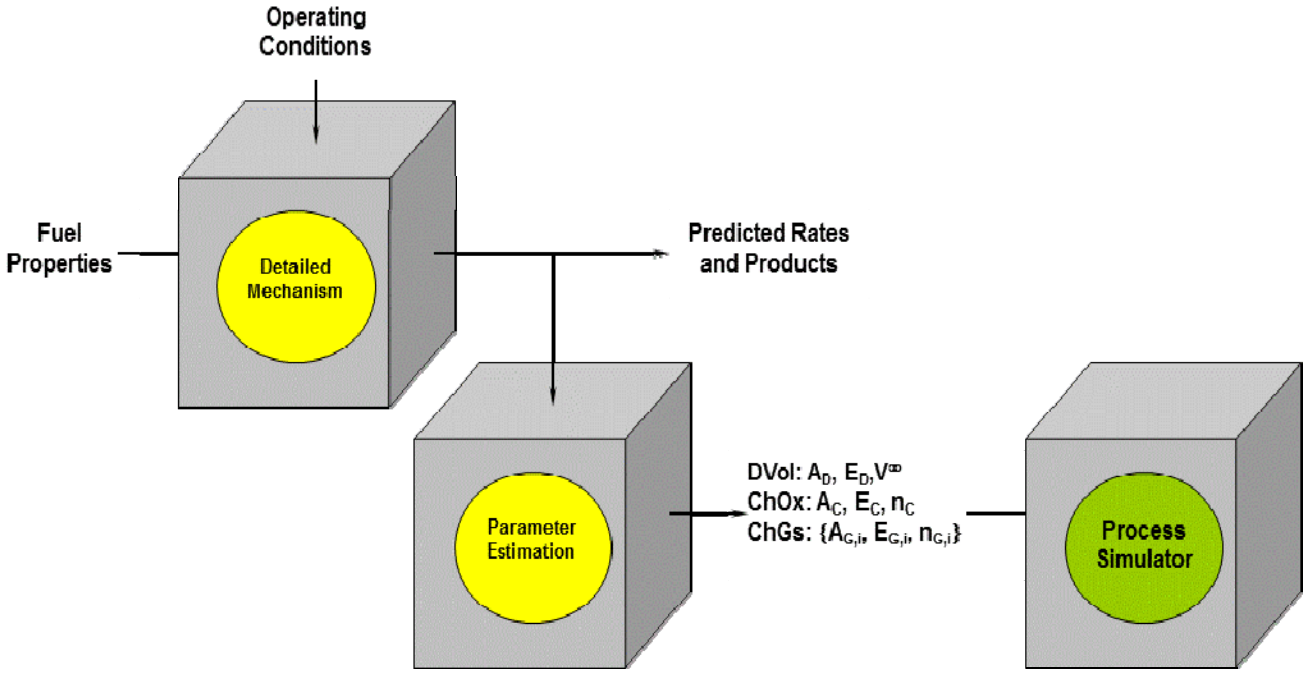
Notwithstanding these distinctive and very important advantages for practical applications, CBK/E does not contain a submodel that can assign the initial char oxidation reactivity for any char from any parent solid fuel. Indeed, combustion experts have compiled a few dozen physical, chemical, morphological, and structural factors that affect char conversion kinetics, including the levels of alkali and alkaline earth cations, major mineral species such as iron, various segments of the pore size distribution, as well as a host of pretreatment conditions. But the literature does not describe a single testing program in which these factors were reported for different solid fuels along with time-resolved extents of conversion and detailed operating conditions. So it is simply impossible for NEA or anyone else to accurately predict intrinsic char conversion reactivities from even an extensive series of analytical tests on the fuel.

Accordingly, NEA strongly recommends a one-point calibration of the initial reactivity in CBK/E with char conversion data whenever accurate predictions are needed for specific fuel samples. The calibration data can be obtained with an entrained-flow reactor or thermogravimetric analyzer (TGA), or lab- or pilot scale furnace or gasifier. Whatever the system, calibration conditions closer to the conditions in the application of interest will always improve the accuracy of the model predictions. Once the initial reactivity has been calibrated, CBK delivers accurate predictions for broad ranges of particle size, gas composition, and pressure. Note the contrast with the self-contained parameter definitions for devolatilization simulations with FLASHCHAIN®. Whereas PC Coal Lab® accurately simulates devolatilization given only the proximate and ultimate analyses but no laboratory support whatsoever, the accuracy of char conversion simulations is usually determined by calibrations for the initial char reactivity.



When accuracy is not the highest imperative, PC Coal Lab® will automatically specify default values for the intrinsic reactivity based on the carbon-content of the parent fuel. The above figure shows the frequency factor for the key surface reaction in CBK/E on a log scale vs. the carbon content of the parent fuel. The reactivity values are based on fits to reported char conversion histories of more than a dozen fuels at normal and elevated pressures. The curves are used to evaluate the default reactivities in PC Coal Lab®. But the scatter in the assigned reactivities about the curves is actually more significant. If all the data points fell on a single curve, then the one-point calibration described above would be unnecessary. But since the reactivities are scattered by almost an order of magnitude for even the chars from similar hv bituminous coals, users who need high accuracy should not rely on default parameter assignments.

The complexity of CBK/E's mathematical implementation raises another obstacle to its incorporation into furnace simulations. Fortunately, it is unnecessary to actually install CBK/E into a CFD simulation or any other process design application. According to the scheme in the figure below, where CBK/E is the detailed mechanism, CBK/E accepts only standard fuel properties and nominal operating conditions for the utilization technology – plus the calibrated initial reactivity if high accuracy is an imperative - to predict a complete char burnout history; that is, the transient extents of burnout plus the partial pressure of O_2 on the surface and the particle temperature, size, and density from ignition until the char has reached the furnace outlet. The predicted transient



extents of char burnout, temperatures, and surface O_2 pressures are then post-processed in a parameter estimation routine to evaluate the activation energy, and apparent reaction order in a global rate expression for char oxidation. This routine imposes the same mathematical analysis normally applied to laboratory data, except that the time resolution in the simulation results is much finer than any lab tests could impose. Finally, the rate parameters are entered into the CFD simulations or process design application to incorporate essentially the same char burnout history as the one from the detailed reaction mechanism.

There is no need to actually install CBK/E into the simulation application, which circumvents an extremely laborious and expensive programming task. Simply specify the rate parameters in the global rate law from the char burnout history from CBK/E, and the char oxidation history from the global rate will be essentially the same – but only for the test conditions used in the analysis. Of course, global rate laws for char burnout cannot possibly depict char oxidation behavior over broad domains of operating conditions as accurately as needed in a process simulation. So rate parameters must be re-assigned for every new set of operating conditions and, certainly, for every fuel sample. But since PC Coal Lab® fully automates the parameter assignments, this is a very small task.

PC Coal Lab® supports only a single global rate law for char oxidation, and it is not one of the forms that is implemented in most CFD furnace simulations. The reason that the familiar rate expressions were avoided is that they simply cannot track the char burnout

histories from CBK/E, because they cannot depict the extended times for consumption of the final few percent of the combustibles in char. Since this feature is absolutely essential for accurate predictions of unburned carbon emissions and flyash loss-on-ignition (LOI), NEA developed a global rate law that retained it. We use the conventional nth-order expression for burnout multiplied by a fifth-order polynomial in the extent of char burnout that diminishes the char burning rate continuously throughout a char burnout history. This additional factor accurately describes times to reach even complete burnout, so that the burnout histories from the global rate expression are essentially the same as those from CBK/E. Coefficients for all terms in the polynomial are specified automatically during the rate parameter assignments. To facilitate installation of this rate expression in CFD simulations, NEA provides a user-defined function for v.5.4 of Fluent that covers all the necessary equations and supporting transport coefficients.