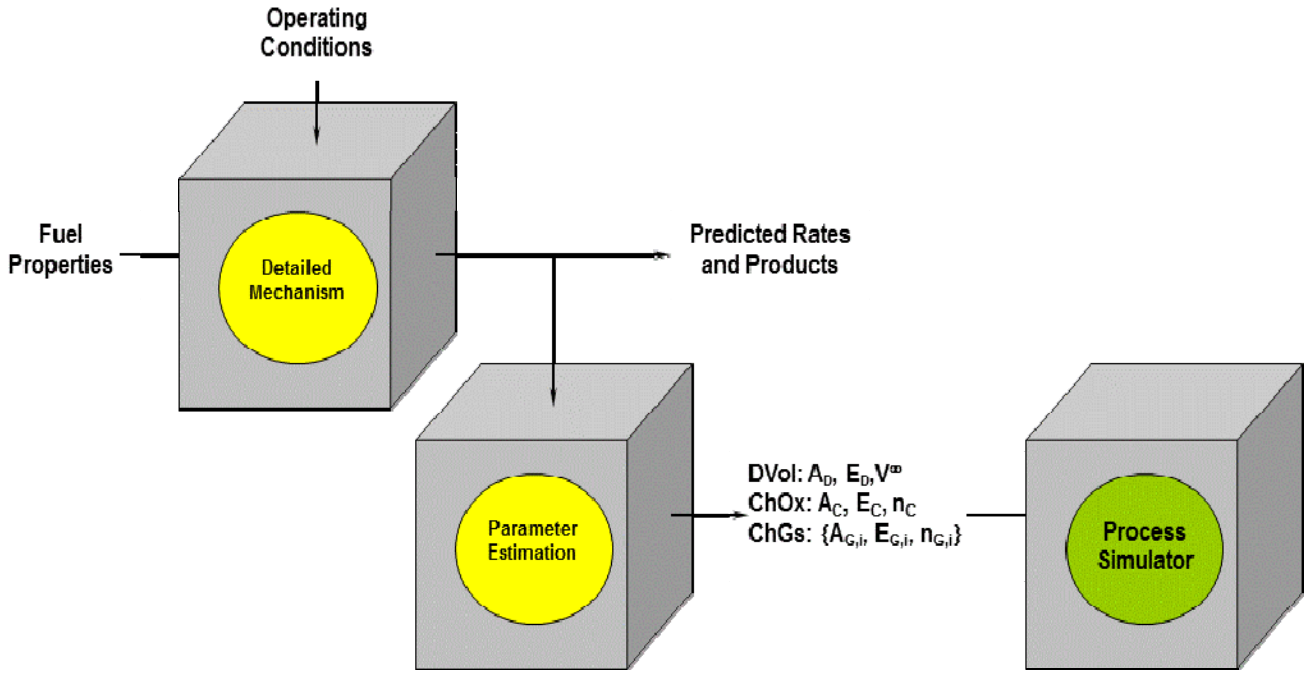
Assigning Rate Parameters in Simple Rate Laws From Comprehensive Reaction Mechanisms: Devolatilization Rates

Soon after the predicted volatiles yields from FLASHCHAIN® began to meet the demands of blind evaluations with test data for any coal sample, NEA released v.1.0 of PC Coal Lab® in the late 1990s. This release advanced the concept of a Virtual Fuels Laboratory (VFL) into the practical realm, and users soon recognized the value of accurately predicting devolatilization behavior in a few seconds on ordinary PCs instead of trying to measure it in complex and highly specialized laboratories. Then after demonstrating the basic imperative of any VFL to predict product yields as accurately as they can be measured, NEA expanded the VFL to specify the parameters in any rate law for devolatilization that is implemented in any process simulator.

This connection between the VFL and a process simulator carries a crucial implication: No simulation specialist want to run any laboratory test before he or she can simulate the utilization technology with any particular solid fuel sample. Since the only sample-specific fuel properties required by PC Coal Lab® are the proximate and ultimate analyses, and since these tests are readily available from in-house or contract analytical labs, PC Coal Lab® satisfies the demands of process simulation applications.



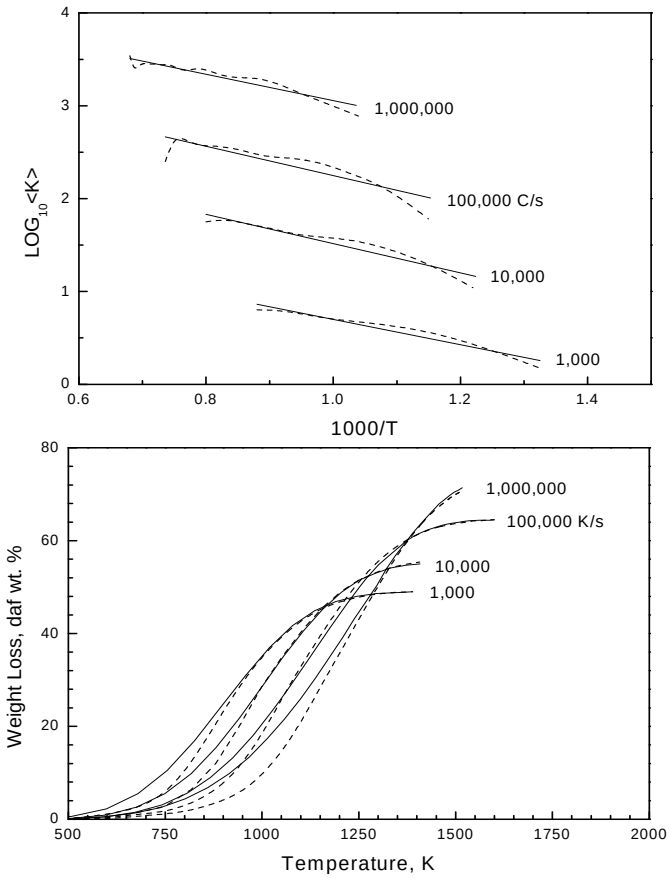
Given these prerequisites, expanding the VFL to assign the parameters in any rate law for devolatilization is a straightforward mathematical exercise. According to the scheme in the above figure, the detailed reaction mechanism for devolatilization accepts only

standard fuel properties and nominal operating conditions for the utilization technology to predict a complete devolatilization history; that is, the transient yields of all major products from the start of the process until devolatilization has run its course. The predicted transient product distributions are then post-processed in a parameter estimation routine to evaluate the pseudo-frequency factors, activation energies, and hypothetical ultimate yield parameters in the target rate expressions for devolatilization. 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 achieve. Finally, the rate parameters are entered into the CFD simulations or process design application to incorporate essentially the same devolatilization history as the one from the detailed reaction mechanism.

There is no need to actually install the detailed reaction mechanism into the simulation application, which circumvents an extremely laborious and expensive programming task. Simply specify the rate parameters in the simple rate laws from the devolatilization history from the detailed reaction mechanism, and the predicted devolatilization behavior will be essentially the same – but only for the test conditions used in the analysis. Of course, rudimentary rate laws for devolatilization cannot possibly depict devolatilization behavior over broad domains of operating conditions as accurate 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 three devolatilization rate laws, although any rate expression could be programmed into the analysis upon request. The single first-order reaction (SFOR) is usually the best choice, particularly for applications in which the operating conditions are fairly uniform, as in the rapid heating rates and atmospheric pressure in most large-scale coal flames. In the figure below, a familiar Arrhenius diagram was prepared by assigning a pseudo-frequency factor and apparent activation energy from the devolatilization histories for a bituminous coal heated at 10^3, 10^4, 10^5, and 10^6°C/s to temperatures hot enough to attain an ultimate devolatilization yield in every test. Whereas the assigned activation energies are insensitive to heating rate variations, the frequency factors increase in near-proportion to changes in the heating rate.

The lower panel in the figure compares the devolatilization histories from the detailed reaction mechanism (dashed curves) to the SFOR assignments (solid curves). At every heating rate there are minor discrepancies during the first third of the history, but excellent agreement thereafter. Certainly the ultimate volatiles yields from the SFOR assignments will be indistinguishable from the FLASHCHAIN® predictions. The performance is very similar for the thermal histories and pressures imposed in both fluidized bed and entrained flow combustors and gasifiers.



A competing two-step reaction (C2SM) model is often preferred by CFD practitioners. PC Coal Lab® supports this rate law, although only because of its popularity. It is actually a poor choice for most applications, especially flames, because it introduces an inadvertent dependence on heating rate into the predicted ultimate volatiles yield. Of course, ultimate volatiles yields increase for progressively faster heating rates at atmospheric pressure. But the magnitude of this effect predicted by a C2SM is much greater than the impact on measured ultimate yields. This is a particularly serious flaw in coal-fired furnace simulations, where the broad particle size distribution is associated with a very broad range of particle heating rates. With a C2SM for devolatilization, the predicted ultimate volatiles are bound to be much too large for the smaller particles in the size distribution.

PC Coal Lab® also supports a distributed activation energy model (DAEM), which is the best choice for processes that impose slow heating rates but would probably not be needed for entrained flow coal utilization technologies.