104c Analysis of Fluctuations of Lumped Kinetics in Reactors

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Since 1950's, complex feedstocks in a reaction network have often been lumped into simplified kinetics for subsequent design of reactors and chemical processes. Due to the reduction of a large number of variables, lumped kinetics inevitably exhibit uncertainties or fluctuations in their practices. The fact that Wei and Kuo (1969) adopted the theories of Markov chain in its early development suggests the inherent random nature of the lumped kinetics. The time-dependent statistics of continuous mixtures have been analyzed by population dynamics. Nevertheless, formal stochastic algorithms have not been systematically adopted in analyzing the statistics, such as the uncertainties or fluctuations, of the populations of lumped species in reacting systems. The objectives of this paper are to summarize the major stochastic algorithms and present their examples in modeling fluctuations of lumped kinetics in batch and flow reactors.

Stochastic algorithms have been developed for analyzing two distinct types of noise, internal and external noise (Nicolis and Prigogine, 1977; Hill, 1977; Oppenheim et al., 1977; van Kampen, 2001; Gardiner, 2004). Internal noise is caused by the fact that the system itself consists of discrete particles and is governed by an unmanageably large number of variables. The internal noise is inherent in the very mechanism by which the process evolves. For this reason, it is often called minimal, signifying the noises are free from external influences. Discrete systems of small (mesoscopic) populations often exhibit notable internal fluctuations whose analysis requires stochastic algorithms including master equation, Chapman-Kolmogorov equation, or Markov chain. Since the internal fluctuation is approximately inversely proportional to the square root of the size of population, which is generally large for a lumped species, their internal fluctuations are usually negligibly small and a deterministic model suffice to the prediction of the reaction pathways. Consequently, the stochastic approaches for the analysis of internal noises are unnecessary for modeling the fluctuations of populations due to uncertainty in feed concentration or reduced mechanism.

External noises are the fluctuations created in an otherwise deterministic system by the application of an external random force, whose stochastic properties are supposed to be known. The evolution of external noise is analyzed by stochastic equations (SDE). A SDE is a differential eqiation whose coefficients are random numbers of the independent variables (Karlin and Taylor, 1981; van Kampen, 1992; Risken, 1996; Oksendal, 2002; Gardiner, 2004). The Langevin equation is one type of the SDE's that has been widely adopted for finding the effect of noise in the forcing function, or the nonhomogeneous term, in macroscopically known systems governed by differential equations. The noise is introduced by adding a random terms, to the deterministic equation. White noise, i.e., a Dirac-delta function on time scale, is often adopted in modeling the external noises. Alternatively, when a SDE involves random coefficients, method of cumulant expansion has been adopted in its analysis.

The SDE algorithms for external noises are theoretically vigorous for the analysis of the fluctuations due to the uncertainties in the feed concentration or that of reduced kinetics of a lumped species in both batch and flow reactors. In the first part of our presentation, we will present the analyses of two types of lumped reactions in CSTR, one is a first-order reaction, and the other, a second-order recombination reaction. To illustrate the algorithm under simplified conditions, only the statistics under steady states are analyzed. In the first case, the first and second moments of the reactant and product populations in the effluent stream are obtained by taking averaging of the linear Langevin equation. These moments are related to system parameters and statistics of feed concentration. In the second case, the quasi-linear Langevin equation is first converted to a nonlinear Fokker-Planck (F-K) equation. The statistics of the effluent stream are obtained by integrating the resultant F-P equations.

In the second part of the presentation, we will present the analysis due to the uncertainties in reduced kinetics and flow rate. Cumulant expansion is adopted in the analysis of evolution of product populations.

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