

Incremental Model Identification of Fluid-Fluid Reaction Systems – Dynamic Accumulation and Reactions in the Diffusion Layer

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The identification of kinetic models is an important step for the monitoring, control and optimization of industrial processes. This is particularly the case for highly competitive business sectors such as chemical and pharmaceutical industries, where the current trend of changing markets and strong competition leads to a reduction in the process development costs [1]. Moreover, the PAT initiative of the FDA advocates a better understanding and control of manufacturing processes by the use of modern instrumental technologies and innovative software solutions [2].

Reaction systems can be represented by first-principles kinetic models that describe the time evolution of states – numbers of moles, temperature, volume, pressure – by means of conservation and constitutive equations of differential and algebraic nature. These models are designed to include all kinetic phenomena, whether physical or chemical, involved in the reaction systems. Generally, such kinetic phenomena include the dynamic effects of reactions (stoichiometry and reaction kinetics), transfer of species between phases (mass-transfer rates), and operating conditions (initial conditions as well as inlet and outlet flows).

The identification of reaction and mass-transfer rates as well as the estimation of their corresponding rate parameters represents the main challenge in building first-principles models. The task of identification is commonly performed in one step via ‘simultaneous identification’, in which a dynamic model comprising all rate effects is postulated, and the corresponding model parameters are estimated by comparing the measured and modeled concentrations [3]. This procedure is repeated for all combinations of model candidates, and the combination with the best fit is usually selected. The main advantage of this identification method lies in its capability to model complex dynamic effects in a concomitant way and thus to generate enough constraints in the optimization problem so that indirect measurements such as spectroscopic and calorimetric data can be modeled without the use of a calibration step [4, 5]. However, the simultaneous approach can be computationally costly when several candidates are available for each dynamic effect. Furthermore, this method often leads to high parameter correlation with the consequence that any structural mismatch in the modeling of one part of the model can result in errors in all estimated parameters and, in addition, convergence problems can arise from a poor choice of initial guesses [6, 7].

As an alternative, the incremental approach decomposes the identification task into a set of sub-problems of lower complexity [8]. The approach consists in transforming the measured concentrations into decoupled rates or extents, which can then be modeled individually. When needed, prior to the modeling step, the missing or unmeasured states can be reconstructed using the computed rates or extents. In the ‘rate-based incremental identification’ [9], rates are first obtained by differentiation of concentration measurements. Then, postulated rate expressions

and rate parameters are estimated one at a time by comparing the measured and modeled rates. However, because of the bias introduced in the differentiation step, the rate parameters estimated by this method are not statistically optimal. That is why, another approach, termed 'extent-based incremental identification' [10], that is based on the integral method of parameters estimation has been introduced. In this approach, extents are first computed from measured concentrations, and then postulated rate expressions are integrated individually for each extent and the corresponding rate parameters estimated by comparing the measured and modeled extents. The extent-based identification can also be adapted to analyze calorimetric and spectroscopic data using a calibration step [11, 12]. The transformation to rates or extents reduces the dimensionality of the dynamic model since all redundant states (invariants) can be discarded. More importantly, the remaining states (variants) isolate the effects of the reactions, mass transfers and operating conditions, which can then be analyzed individually [13]. This allows substantially reducing the computational effort, the convergence problems and the correlation between the estimated rate parameters.

Recently, the extent-based incremental identification has been extended to fluid-fluid reaction systems undergoing unsteady-state mass transfer and reactions at the interface of the two immiscible phases. This situation is commonly encountered in reaction systems that are limited by diffusion, such as CO₂ post-combustion capture and nitration reactions. Such reaction systems can be modeled using the film theory, where the two bulks are separated by a spatially distributed film, located in either of the two phases, in which diffusing species can accumulate and react. In both bulks, the mass balance equations describing the dynamics of chemical species are expressed as ordinary differential equations (ODE) and serve as boundary conditions for the film. The dynamic accumulation in the film is described by Fick's second law combined with a reaction term, thus leading to partial differential equations (PDE), which can be solved by appropriate spatial discretization and rearrangement in ODEs.

The extent-based model identification of fluid-fluid reaction systems with unsteady-state mass transfer and reactions requires a large number of measurements for reconstructing all the states and modeling the dynamics of the film [14]. The difficulty lies in the fact that, with the current state of sensor technology, such measurements can only come from the two homogeneous bulks, which provide information from a well-mixed reactor region and consequently are resolved only in time and not in space. Nevertheless, extents of reaction and extents of mass transfer can be extracted from these bulk measurements. These extents of reaction represent the effect of slow reactions that take place in the bulks of the two phases and can be modeled as before. On the other hand, the extents of mass transfer represent now the combined effect of mass transfer by diffusion through the film and of fast reactions taking place at the interface or in the film. Hence, both the diffusion coefficients and the rate constants of the fast reactions can be estimated by comparing the measured extents of mass transfer and the extents obtained by solving the corresponding PDEs. In the absence of coupling terms in the PDEs due to interactive diffusion and/or reactions, the diffusion coefficients of each species transferring through the film can be estimated incrementally. However, in the case of interactive diffusion and/or reactions, the interdependence of species via the coupling terms of the PDEs calls for a simultaneous identification of the diffusion coefficients and rate constants within the film.

This contribution extends the extent-based incremental identification to the analysis of reaction systems with dynamic accumulation and reactions in the film. In particular, the question of whether to use incremental or simultaneous estimation of the diffusion coefficients and rate constants within a diffusion layer will be addressed.

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