289e Improved Exploitation of Fixed-Bed Reactor Experiments for Estimating Kinetic Parameters

Milind Joshi and Andreas Seidel-Morgenstern

Reaction rate data are important for the design and optimisation of chemical reactors. Classical approaches used for performing kinetic experiments are either based on applying gradient free or fixed-bed laboratory scale reactors. In general in the analysis of experimental data the assumed reactor models (perfect CSTR, perfect PFTR) are presumed to be error free. This is a strong assumption because of unavoidable errors in both data and models (Hafley et al. 1963). Statistics offer tools to perform a detailed analysis of uncertainties in experiments and models (Mezaki et al. 1967). Box et al. (1959) pointed out that sometimes, specific functional forms of the models lead to highly correlated and poorly estimable parameters. In a recent article by Verenich et al. (2003) the importance of sensitivity analysis and the study of cross-correlation coefficients between the parameters have been discussed convincingly again in detail. The main objective of this study is to apply statistical principles during the analysis of kinetic measurements, which have been performed using a laboratory scale fixed-bed reactor (FBR).

The model reaction studied in a laboratory scale FBR was the oxidative dehydrogenation of ethane on a VOx/Al2O3 catalyst. A network was derived from experimental data consisting of several parallel and consecutive reactions (Klose et al. 2004). There are several errors that could not be completely eliminated during the experiments (in particular uncertainties in the measured flow rates and compositions at the reactor outlet). The simplified reactor model applied to analyse the primary data suffers from incorrect representation of back mixing and temperature gradients. Various rivalling kinetic models such as simple Power-Law equations (Hamel 2002) and more complicated Langmuir-Hinshelwood & Hougen-Watson equations (Klose et al. 2004) were alternatively analysed in a comparative manner. Conventional non-linear least square technique was used for parameter estimation. Due to the errors in experimental data it was difficult to estimate a high number of parameters in the kinetic models considered. For this reason, statistical techniques such as sensitivity and cross-correlation coefficient analysis as well as the determination of confidence intervals were applied to verify the reliability of the parameters. This approach also allows determining the number of parameters that could be identified in a reliable manner.

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