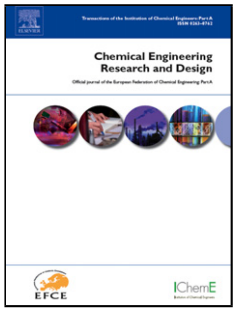

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Dynamic parameter estimation and identifiability analysis for heterogeneously-catalyzed reactions: Catalytic synthesis of nopol

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Abstract

In this work, a methodology for the parameter estimation of heterogeneously-catalyzed reactions is presented. A simulation-optimization framework based on a dynamic model was coupled with an *identifiability analysis*, in order to detect for which parameters the dynamic model is most sensitive. The implemented identifiability analysis was based on rank-revealing matrix factorizations, with singular values as criteria for parameter selection. As the dynamic equation systems describing catalytic reactions are expected to be ill-posed, a *subset selection* step based on identifiability analysis was included. In order to illustrate the methodology, the ODE system describing the heterogeneously-catalyzed reaction system for the production of nopol from β-pinene and formaldehyde was used as a case study. After applying the methodology, two out of five kinetic parameters were found to be identifiable, consistent with a Langmuir Hinshelwood Hougen Watson (LHHW) mechanism that considers adsorption on catalytic sites of different nature. Confidence intervals of the estimated parameters belonging to the identifiable subset were not higher than 3 % of the parameter value. The results of this work show that the proposed mechanism is capable of reproducing the dynamics of the reaction system, and are an important input for the design of a three-phase reactor for nopol production.

Keywords: dynamic parameter estimation, identifiability analysis, nonlinear kinetics, nopol

1. Introduction

Embedding kinetic mechanistic descriptions of chemical reactions within mathematical models of chemical processing plants, is important for model-based studies of process scale-up, design and optimization. Mathematical models of heterogeneously-catalyzed systems often consist of highly non-linear rate equations, which arise from describing the catalytic phenomenon as a series of fundamental steps, e.g. the well-known Langmuir-Hinshelwood-Hougen-Watson kinetic models, resulting in dynamic models that contain those mechanisms, which are hard to obtain in an integrated form but rather have to be posed as complex sets of ordinary differential equations (ODE), differential-algebraic equations (DAE) or partial differential equations (PDE). Value for the parameters of such mathematical models are determined by fitting the predictions of the proposed models to a given set of measured concentration data, using optimization procedures. However, this procedure may become complex because the systems often exhibit multiple local minima, there is usually lack of good or sufficient experimental data or the system is over-parameterized. Additionally, computational time can be a limiting issue with models with large number of parameters or with numerical difficulties such as stiffness in ODE and DAE systems.

Parameter estimation of dynamic models usually requires analysis of the process sensitivity matrix in order to: i) provide the optimization algorithm with accurate gradient information, ii) determine the confidence intervals to test significance of the obtained solutions, and iii) assess identifiability of the obtained solution, i.e. whether it is likely or not that a different set of numerical estimates lead to a near optimal objective function [1]. This con-

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