Isomerization of 1-decene in a liquid multiphase thermomorphic multicomponent solvent system: Model formulation, kinetic experiments and parameter estimation

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Introduction

In this contribution the double bond isomerization of 1-decene was analyzed experimentally and theoretically in terms of kinetic modeling and parameter estimation. This reaction is a very important side reaction in hydroformylation reaction networks, since it is generally believed to be responsible for the production of undesired branched aldehydes [1]. The aim of this work was to reduce and to parameterize a detailed mechanistic kinetic model, which was developed for quantifying the isomerization rate of long chain olefins in complex reaction systems based on selected experiments. The catalyst pre-equilibrium was also included. The used method explained below avoids overparameterization and allows estimating the kinetic parameters of the reduced model with low uncertainties. With the presented method it is possible to design a set of experiments to increase its informational content and the number of sensitive kinetic parameters, respectively.

Experimental

The kinetic experiments were performed with 1-decene as model substance in a thermomorphic multicomponent solvent system (consisting of DMF, dodecane and 1-decene) and a Rh-BIPHEPHOS complex as catalyst. The reactions were realized in a 90 ml high pressure multiple batch reactor system (Parr Instrument Co.) under careful consideration of the catalyst pretreatment at 15-18 bar syngas and a molar Rh-to-ligand ratio of 1:3 to guarantee reproducible initial conditions and a defined catalyst state at the beginning of the reaction. The set of experiments was planned with the method mentioned below so that a maximum number of sensitive parameters can be reached (figure 1). The reactions were carried out at different temperatures, CO partial pressures and initial 1-decene concentrations (figure 2), while the molar Rh-to-olefin ratio was kept constant at 1:10000 as well as the Rh-to-ligand ratio at 1:3.

Methodological

Detailed kinetic models often contain more parameters that can be identified and estimated with low uncertainties because of their linear dependencies. To identify the set of linearly independent parameters and therefore to improve the nonlinear parameter estimation, the method of parameter subset selection (PSS) was developed [2]. The PSS is based on the transient analysis of the Fischer Information Matrix (*FIM)*. This matrix is generated with the local parameter sensitivity matrix *S*.

$$S(t) = \begin{bmatrix} \frac{\partial y_1(t)}{\partial \theta_1} & \cdots & \frac{\partial y_1(t)}{\partial \theta_{N\theta}} \\ \vdots & \ddots & \vdots \\ \frac{\partial y_{Ny}(t)}{\partial \theta_1} & \cdots & \frac{\partial y_{Ny}(t)}{\partial \theta_{N\theta}} \end{bmatrix} \qquad FIM(t) = S(t)^T S(t) \qquad (1)$$

The matrix *S(t)* can be easily calculated from the known derivative matrices of the right hand sides *f(y,θ)* of the model equations with respect to states *Fy* and parameters F_θ.

$$\dot{S} = F_y\, S + F_\theta \qquad S_{i,j}(t=0) = 0 \qquad (2)$$

General mechanistic kinetic model equations for a similar reaction system in their fully unreduced form derived by [3] are adopted and used in this work. Once the *FIM(t)* is known, it can be treated with a rank revealing QR-decomposition which includes a singular value decomposition (SVD) as well. This SVD yields a sparse matrix with the singular values σ_i of the decomposed matrix as diagonal elements. Introducing the condition numbers $\kappa_i = \sigma_{max}/\sigma_i$ allows to calculate the transient rank *z* of the *FIM* with respect to numerical accuracy. This rank corresponds to the number of identifiable parameters. The QR-decomposition reveals a permutation matrix *P* which rearranges the columns of the *FIM* in descending parameter linear independency order. Consequently the first *z* columns correspond to the most identifiable parameters which can be estimated. The procedure is illustrated in figure 1 (example reaction: isomerization of 1-decene). It can be seen that two not identifiable model parameters in the example reaction of the isomerization of 1-decene exist (K^{III}_{iso}, K_2). The values of this non identifiable parameters can be fixed to an arbitrary physical meaningful value. If possible, this value can be zero and therefore the model can be reduced. Experimental design is also possible with the PSS method via finding experimental conditions that increase the number of identifiable parameters and decrease their uncertainty. Optimization of initial conditions for a different number of experiments was performed in this contribution but optimal control to design dynamic experiments is also possible.

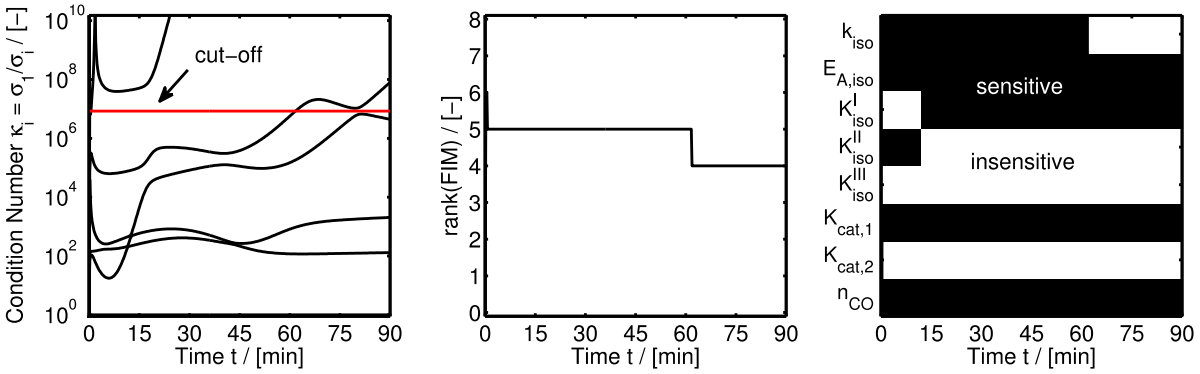


Figure 1: Transient parameter sensitivity analysis over experimental time (t_{exp} = 90 min); left to right: condition number κ_i of the *FIM*, transient rank of the *FIM*, model parameter identifiability chart

Results

The PSS method was applied successfully to the Rh-catalyzed isomerization of 1-decene as important side reaction of the hydroformylation. A detailed kinetic model was reduced and parameterized. In total 6 kinetic parameters were estimated. They show low “95% confidence intervals” between 4 - 25%. A good agreement between the model and experiments was achieved (figure 2). Hence, the method is suited to enhance parameter estimation in chemical reaction engineering and will be applied to all occuring reactions in the hydroformylation scheme, mainly isomerization, hydrogenation and the intrinsic hydroformylation reaction.

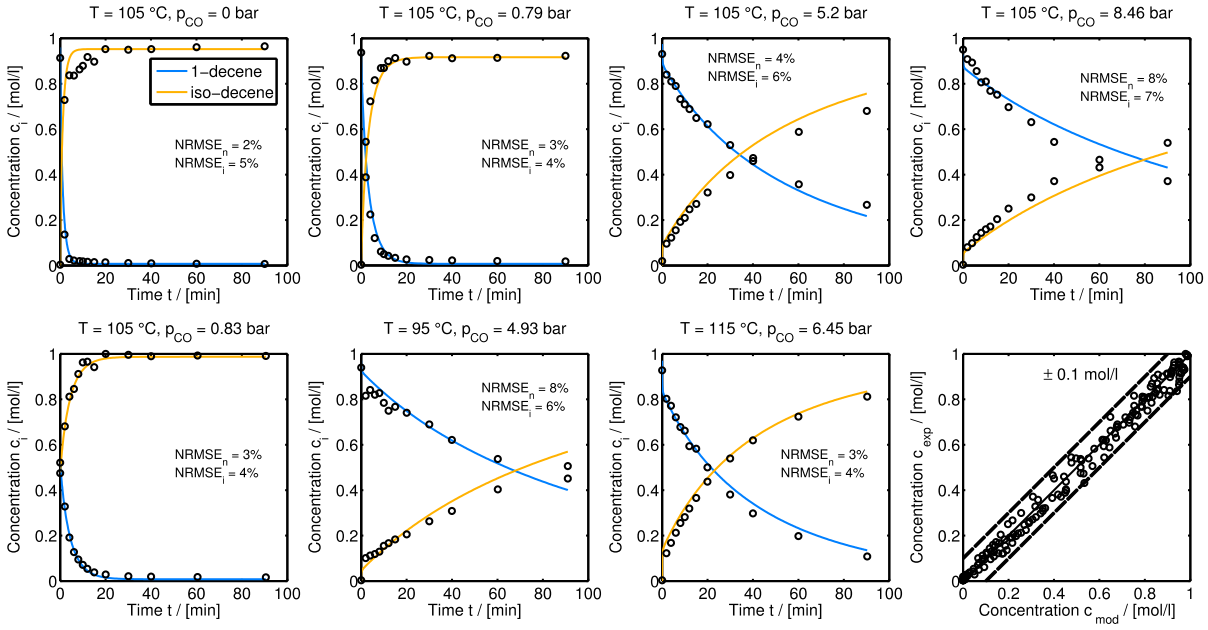


Figure 2: Experimentally observed concentrations of 1-decene and iso-decene at different reaction conditions, fit of the model derived for isomerization in [3] to experimental data, normalized root mean squared error (NRMSE) and parity plot; molar Rh-to-ligand ratio = 1:3; molar Rh-to-olefin ratio = 1:10000; thermomorphic multicomponent solvent system: 49%-mol DMF, 38 %-mol dodecane, 13 %-mol decene

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