

Incremental Model Identification for Reaction Systems using Concentration and Calorimetric Measurements

Sriniketh Srinivasan¹, Nirav Bhatt¹ and Dominique Bonvin¹

¹ Laboratoire d'Automatique,
Ecole Polytechnique Fédérale de Lausanne, Switzerland

Summary

Extent-based Incremental Model Identification (IMI) uses the concept of extent of reaction and the integral method of parameter estimation to identify reaction kinetics from transient concentration measurements. This study proposes to incorporate calorimetric measurements into the extent-based IMI approach. Calorimetric measurements are added to concentration measurements for two main purposes: (i) to be able to estimate the reaction enthalpies when all the concentrations are measured, and (ii) to be able to compute the extents of reaction in certain cases when only a subset of the concentrations are measured. The two approaches are demonstrated via the simulation of a semi-batch reactor.

Keywords

Reaction kinetics; Extents of reactions; Incremental identification; Calorimetry

Introduction

Models of chemical reaction systems are essential for model-based monitoring, control, and optimization. The identification of reaction kinetics, that is, rate expressions and rate parameters, represents the main challenge in building first-principles models for reaction systems.

An incremental identification approach for determining the kinetics of homogeneous reaction systems from transient concentration measurements has been developed in previous work [1]. This approach decomposes the identification task into a sequence of sub-tasks that include the identification of the rate expression and of the corresponding rate parameters for every reaction. The approach is of the “differential” type, because reaction rates are estimated through numerical differentiation of concentration measurements. Alternatively, an incremental identification approach based on the “integral method” using the concept of extents has been proposed recently [2]. Both approaches use concentration measurements for the identification of reaction kinetics.

In addition to concentration measurements, calorimetric measurements can help identify kinetic and thermodynamic parameters. In this work, we will incorporate calorimetric measurements in the incremental identification approach proposed in [2] to estimate reaction enthalpies and kinetic parameters.

Extent-Based Incremental Model Identification

The extent-based incremental model identification (IMI) approach uses the integral method of kinetic identification, i.e., it does not need to differentiate noisy measured concentrations, but instead it integrates candidate rate expressions. The approach consists of two steps:

1. Computation of extents of reaction from concentration measurements,
2. For each reaction individually, identification of the rate expression and the corresponding parameters from the computed extents.

In the first step, the extents of reaction can be computed from concentration measurements using the linear transformation proposed in [3]. In the second step, the rate expression candidates are integrated numerically to predict the extents; the unknown rate parameters are estimated by fitting these predictions to the extents computed in Step 1.

Use of Calorimetric Measurements

Calorimetry measures the heat flow during the course of a reaction. For a reaction system consisting of S species, and R reactions, the calorimetric signal at time t can be written as:

$$q_r(t) = -V(t)\Delta\mathbf{h}^T\mathbf{r}(t) \quad (1)$$

where q_r is heat flow (or power) of the reactions at time t , V is the volume of the reaction mixture,

$\mathbf{r}(t)$ and $\Delta\mathbf{h}$ are R -dimensional vectors containing the rate and heat of each reaction, respectively.

In the incremental approach, calorimetric measurements are used with concentration measurements for two purposes:

1. Estimation of reaction enthalpies. The reaction enthalpies can be estimated in two steps: (i) computation of extents of reaction from measured concentrations (as described in Step 1 of the IMI approach), and (ii) computation of the reaction enthalpies from calorimetric measurements using computed extents. In the second step, the calorimetric measurement $q_r(t)$ is integrated numerically to obtain the integral signal $Q_r(t)$. This signal can also be predicted using the computed extents vector $\mathbf{x}_r(t)$ as follows: $\hat{Q}_r(t) = -\Delta\mathbf{h}^T \mathbf{x}_r(t)$. Hence, the reaction enthalpies ($-\Delta\mathbf{h}$) can be estimated by minimizing the difference between $Q_r(t)$ and $\hat{Q}_r(t)$ over all observations.

2. Estimation of kinetic parameters in certain cases when only a subset of the concentrations are measured. Let $\mathbf{n}_a(t)$ be the numbers of moles of S_a available species at time t . Let the corresponding $(R \times S_a)$ -dimensional stoichiometric matrix \mathbf{N}_a be known. The flow-based method proposed by Bhatt [2] requires $\text{rank}(\mathbf{N}_a) = R$. If \mathbf{N}_a is rank deficient by one, i.e. $\text{rank}(\mathbf{N}_a) = R - 1$, the rank can be augmented using calorimetric measurements. For this, the stoichiometric matrix \mathbf{N}_a is augmented with the heat of reaction vector $-\Delta\mathbf{h}$ to get a rank- R matrix [4]. Similarly, the reaction heat term $Q_r(t)$ is added to the number of moles vector to give the augmented vector $\mathbf{n}_{aug}(t)$:

$$\mathbf{N}_{aug} = [\mathbf{N}_a \quad -\Delta\mathbf{h}^T] \quad (2)$$

$$\mathbf{n}_{aug}(t) = \begin{bmatrix} \mathbf{n}_a(t) \\ Q_r(t) \end{bmatrix}, \quad (3)$$

where \mathbf{N}_{aug} is a $[R \times (S_a + 1)]$ -dimensional augmented stoichiometric matrix and $\mathbf{n}_{aug}(t)$ is a $(S_a + 1)$ -dimensional vector. If $\text{rank}(\mathbf{N}_{aug}) = R$, then, the flow-based method in [2] can be applied to compute the extents of the reaction, from which the kinetic parameters can be estimated.

Simulation Study

The acetoacetylation of pyrrole described in [2] is considered. The reaction system consists of six species ($S = 6$) and four reactions ($R = 4$). The simulated noisy data are generated for a semi-batch reactor with one inlet. Two cases are considered in the simulation study:

- In the first case, measurements of all concentrations and of the reaction heat flow are used to estimate the reaction enthalpies.
- In the second case, it is assumed that the concentrations of three species and the heat signal $Q_r(t)$ are available. The calorimetric measurements are used to resolve the rank-deficiency problem. Then, the flow-based method described in [2] is applied to compute extents. Subsequently, the values of the rate parameters, the frequency factors and the activation energies are estimated from the computed extents as described in Step 2 of the IMI approach.

References

- [1] W. Marquardt, Model-based experimental analysis of kinetic phenomena in multi-phase reactive systems, *Chem. Eng. Res. Des.* 83 (2005) 561–573.
- [2] N. Bhatt, M. Amrhein and D. Bonvin, Incremental identification of reaction and mass-transfer kinetics using the concept of extents, *Ind. Eng. Chem. Res.* doi: 10.1021/ie2007196
- [3] M. Amrhein, N. Bhatt, B. Srinivasan and D. Bonvin, Extents of reaction and flow for homogeneous reaction systems with inlet and outlet streams, *AIChE J.* 56 (2010) 2873–2886.
- [4] M. Amrhein, Reaction and Flow Variants/Invariants for the Analysis of Chemical Reaction Data, Doctoral thesis No. 1861, EPF Lausanne, Switzerland, 1998.