ESTIMATION OF REACTION RATES BY NONLINEAR SYSTEM INVERSION

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Abstract: The estimation of reaction rates is an important problem in mechanistic modeling, monitoring and control of chemical reactors. In contrast to standard estimation techniques where a model must be chosen for the reaction rates, we consider them in this work as unknown time-varying functions, which also may be interpreted as inputs. The resulting estimation task is an ill-posed inverse problem. The paper addresses this estimation problem based on systematic methods for nonlinear system inversion and filtering resulting in efficient estimators. A theoretical analysis reveals the conditions for reaction rate reconstruction are those for system invertibility. Our estimation scheme is a regularization method which eliminates the difficulties arising with ill-posed problems. Guidelines for the design of the estimator structure and the selection of the regularization parameters are presented.

Keywords: Inverse problems, ill-posed problems, system inversion, filtering, regularization, reaction rates.

1. INTRODUCTION

Reaction rates are important quantities for mechanistic modeling, monitoring and control of chemical reactors. Since these quantities are not often directly measurable, they must be estimated from other measurable quantities, such as temperature, pressure and eventually concentrations. This necessitates however an accurate model of the process, which is rarely available. In reality, the reaction rates are complex functions of unknown structure of the temperature and the concentrations of the reacting species involving many kinetic parameters.

An approach to the estimation of reaction rates, which does not rely on kinetic expressions, has been investigated by Schuler and Schmidt (1992). It has been based on a calorimetric model comprising conservation equations for mass and energy. The estimator used is the Kalman filter. The authors report on estimation of reaction rates, conversion and rate of production and on the use of these quantities to control runaways and overfeeding. The problem has also been considered by Eliçabe *et al.* (1995). The authors use a stationary Kalman filter together with a simple linear model basically derived from the definition of the reaction rate and assuming knowledge of total mass of the reacting species derived from concentration measurements. In order to cast the problem in a form suitable to apply standard Kalman filtering techniques, a model must be chosen to represent the reaction rate (de Vallière and Bonvin, 1990; Eliçabe *et al.*, 1995; Schuler and Schmidt, 1992). In general, estimation results will depend on the model selected (de Vallière and Bonvin, 1990). Hence, the type of model chosen is a degree of freedom of the estimation scheme.

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In our earlier work (Mhamdi and Marquardt, 1999), we have developed an inversion-based regularization for the estimation of reaction rates without assuming any reaction rates model. Instead, the reaction rates have been considered as unknown input functions to be estimated from concentration measurements of the reacting species. Insight into this estimation problem has been gained by noticing that this task is actually an inverse problem, which is roughly defined by determining causes for desired or observed effects (Engl *et al.*, 1996). The solution of inverse problems is generally a difficult task since they are usually *ill-posed* (Engl *et al.*, 1996; Hansen, 1998), i.e. their solution is not unique and/or unstable with respect to data in the sense that small perturbations in the measurements cause large variations in the estimate. Ill-posedness is due to the smoothing character inherent to causal relations. Different causes, even well-separated, may result in almost an equal or the same effect.

In this paper, we consider the extension of our previous method (Mhamdi and Marquardt, 1999) to deal with MIMO linear and nonlinear systems. Our estimation scheme is based on regularization techniques (see e.g. Engl *et al.* (1996) for a review), which deal with the difficulties arising due to the ill-posedness of such problems. In general terms, regularization refers to the approximation of an ill-posed problem by a parameter dependent family of neighboring well-posed problems. Examples are Tikhonov regularization (Tikhonov and Arsenin, 1977) and regularization by projection (Kirsch, 1996). The inversion approach gives important insight into the inherent properties of the estimation problems and, in particular, the error trade-off to get the best solution.

The paper is organized as follows. The problem formulation and the solution framework are stated in Section 2 and 3 respectively. The design procedure based on system inversion for unknown input estimation is given for linear and nonlinear MIMO systems in Section 4. In Section 5, the case study of a bioreactor is presented. Conclusions are given in Section 6.

2. INPUT ESTIMATION PROBLEM

We consider in this work systems Σ_{NL} given by the following nonlinear equations

$$\dot{x}(t) = A(x) \ + \ B(x)\ w(t), \tag{1}$$

$$y(t) = C(x) \ + D(x)\ w(t) \tag{2}$$

where the quantities w and y are vector-valued functions, i.e. $w(t) \in \mathbb{R}^m$ and $y(t) \in \mathbb{R}^p$ for $t \in [t_0, t]$ and $x(t) \in \mathbb{R}^n$ are the system states. The quatities $w(t)$ represent the unknown inputs to be estimated from measurements of the outputs y. In the application context considered these inputs are the reaction rates of interest.

Since the observations are always corrupted with errors, the measurements, denoted by $\tilde{y}$, are different from the true values y. We assume that the two quantities are related through the following equation

$$\tilde{y}(t) = y(t) + n(t), \tag{3}$$

in which n represents an additive measurement error.

We formulate the problem as follows. Let $T_{w\to y}$ be the operator mapping the unknown input vector $w \in \mathbb{W}$ to the measured output $y \in \mathbb{Y}$, i.e.

$$T_{w\to y}\ w = y \tag{4}$$

The sets $\mathbb{W}$ and $\mathbb{Y}$ are function spaces. The input-output operator $T_{w\to y}$ is implicitly given by the system Σ_{NL}.

The unknown input estimation (UIE) problem is to find an approximation $\hat{w}$ of the unknown input functions $\{w(\tau), \tau \in [t_0, t]\}$ from the noisy observations $\{\tilde{y}(\tau), \tau \in [t_0, t]\}$. In other words, the estimation problem is to solve the integral equation (4) for w using the available noisy measurements $\tilde{y}$, i.e.

$$T_{w\to y}\ w = \tilde{y}, \tag{5}$$

3. SOLUTION FRAMEWORK

In this work, we approach the UIE problem from the perspective of inverse problems and regularization theory. In general the UIE problem is ill-posed, which means that one or more of the following well-posedness properties, due to Hadamard (Engl *et al.*, 1996), does not hold: (i) for all admissible data a solution exists, (ii) for all admissible data the solution is unique and (iii) the solution is stable. Of major concern is the stability condition, which means, that the solution must depend continuously on the data such that small perturbations in the data cause small variations in the solution.

The standard method to guarantee the solution existence and uniqueness for problem (5) is to consider generalized solutions denoted by $w^\dagger$ (Engl *et al.*, 1996). In the L_2-norm, $w^\dagger$ is the *minimum norm least-squares solution* of the integral equation (5). The generalized inverse operator $T^\dagger$ maps y to $w^\dagger$. The generalized solution $w^\dagger$ may be hence determined through

$$w^\dagger = T^\dagger \tilde{y}. \tag{6}$$

However, the usefulness of this solution depends strongly on the properties of the inverse operator $T^{\dagger}$, i.e. its continuity. Therefore, within the UIE problem, we are interested in the inverse operator and its properties.

The generalized inverse is generally unbounded such that stability cannot be guaranteed. Regularization methods are used to recover this property of the solution. A regularization method is a family of well-posed transformations T_α, such that

$$\lim_{\alpha\to 0} T_\alpha y = T^{\dagger} y, \quad \forall\ y, \tag{7}$$

where α is called the *regularization parameter* (Engl *et al.*, 1996; Tikhonov and Arsenin, 1977). In other terms, the introduction of regularization is connected to the approximation of the inverse operator in the family of continuous operators.

Regularization, however, introduces an extra error term to the estimate. To see this, consider measurements satisfying

$$\|\tilde{y} - y\| \le \epsilon, \tag{8}$$

where ϵ is an error level. For any bounded linear operator T_α, the error in the regularized solution $w_\alpha^\epsilon = T_\alpha \tilde{y}$ can be calculated according to

$$\hat{w}_\alpha^\epsilon - w^{\dagger} = T_\alpha \tilde{y} - T^{\dagger} y \tag{9}$$

$$= T_\alpha(\tilde{y} - y) + (T_\alpha - T^{\dagger})y. \tag{10}$$

The term $T_\alpha(\tilde{y} - y)$ is called *data error* and $(T_\alpha - T^{\dagger})y$ *regularization* or *approximation error*. As a function of α these two error types have different behavior, such that the minimization of the total error results in a trade-off between them. No regularization method is therefore complete without a procedure for choosing the regularization parameter α.

4. REGULARIZATION BY SYSTEM INVERSION AND FILTERING

In our earlier work, a filter-based regularization, originally investigated in (Tikhonov and Arsenin, 1977) for SISO problems, has been developped for the solution of inverse heat conduction problems (Blum and Marquardt, 1997) and the estimation of reaction rates in chemical reactors (Mhamdi and Marquardt, 1999). In the following section, we consider the extension of the method for MIMO linear and nonlinear systems.

4.1 Linear systems

We consider the operator $T_{w\to y}$ given by the MIMO LTI system Σ_L

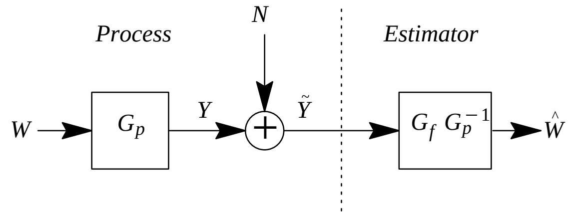

Fig. 1. Filter-based regularization

$$\dot{x}(t) = A\ x(t)\ +\ B\ w(t), \tag{11}$$

$$y(t) = C\ x(t)\ +\ D\ w(t). \tag{12}$$

The considered regularization method is more easily presented in the frequency domain. In this context, the estimation problem is to solve the equation

$$\tilde{Y}(s) = \ G_p(s)W(s) + N(s). \tag{13}$$

using the observations $\tilde{y}$ of the outputs y.

Assume we are able to compute the inverse transfer function $G_p^{-1}(s)$, a regularization method is constructed as follows. To suppress the high frequencies due to the measurement errors, the considered regularization (Tikhonov and Arsenin, 1977; Blum and Marquardt, 1997; Mhamdi and Marquardt, 1999) suggests the design of a parameter dependent family of functions $G_f(s,\alpha)$ operating on $\tilde{Y}$ according to

$$\hat{W}(s) = G_f(s,\alpha)\ G_p^{-1}(s)\tilde{Y}(s). \tag{14}$$

α is the regularization parameter (see Figure 1). $G_f(s,\alpha)$ is chosen such that $\hat{W}(s)$ approximates the true input $W(s)$ as good as possible despite non-vanishing noise $N(s)$. In particular, $G_f(s,\alpha)$ should be chosen such that

- $0 \le G_f(s,\alpha) \le 1,\ \forall\ \alpha, s;$
- $G_f(s,\alpha) \to 1$ non-decreasingly as $\alpha \to 0$ and $G_f(s,0) = 1;$
- $\lim_{s\to\infty} G_f(s,\alpha) = 0$, $\forall \alpha > 0$, and $\lim_{\alpha\to\infty} G_f(s,\alpha) = 0$.

These conditions are sufficient for the time-domain operator T_α corresponding to $G_e(s) = G_f(s,\alpha)G_p^{-1}(s)$ to qualify as a regularization operator in the sense of equation (7) (Tikhonov and Arsenin, 1977).

These design specifications are in general conflicting, as seen from the expression of the estimation error $E_w(s) = \hat{W}(s) - W(s)$:

$$E_w(s) = (G_f(s,\alpha) - 1)\ W(s) + \ G_f(s,\alpha)\ G_p^{-1}(s)\ N(s). \tag{15}$$

The choice of an appropriate regularization parameter α is in general difficult. However, many methods have been proposed in the literature for its computation (Engl *et al.*, 1996). Most of them are based on residual norms. They can be divided into two classes: (i) methods based on knowledge of the error level ϵ, e.g. Morozov's discrepancy principle; and (ii) methods that do not require the knowledge of ϵ, e.g. Generalized Cross Validation or the L-Curve Criterion (Hansen, 1998). The last method is used in this work.

Inversion of LTI systems has been considered in many publications. The approach developed by Silverman (Silverman, 1969) is most fruitful. The basic idea is to construct a sequence of systems system Σ_k

$$\dot{z}_k(t) = A_k\ z_k(t)\ +\ B_k\ w(t), \tag{16}$$
$$y_k(t) = C_k\ z_k(t)\ +\ D_k\ w(t), \tag{17}$$

by iteratively differentiating the output equation (12) until we reach an iteration $k = r$ where the corresponding matrix D_r is invertible.

Therefore D_r^{-1} exists, and we have after some algebraic manipulations the inverse system $\Sigma_L^\sharp$

$$\dot{z}(t) = (A - BD_r^{-1}C_r)\ z(t) + BD_r^{-1}y_r(t) \tag{18}$$
$$w(t) = -D_r^{-1}C_r z(t) + D_r^{-1}y_r(t) \tag{19}$$

with input vector y_r comprising time derivatives up to the order r of the system output y Hence, the obtained inverse system $\Sigma_L^\sharp$ is given by a cascade of the bank of differentiators to get y_r and the dynamical system given by (18)-(19).

A construction for the case $m \neq p$ has been given by Silverman and Payne (Silverman and Payne, 1971). The question of invertibility without knowledge of the initial states has been addressed by Moylan (1977).

4.2 Nonlinear systems

Consider now the nonlinear system (1)-(2) Σ_{NL}

$$\dot{x}(t) = A(x)\ +\ B(x)\ w(t),$$
$$y(t) = C(x)\ + D(x)\ w(t)$$

Since the the iterative procedure of Silverman for the construction of the inverse system is done in the time domain using differentiation and elementary algebraic operations, it has been already extended to time-varying and nonlinear systems (Hirschorn, 1979). A closed representation of the inverse system is (Daoutidis and Kravaris, 1991):

$$\dot{z} = A(z) - B(z)M^{-1}(z)\begin{bmatrix} L_f^{\beta_1}C_1(z) \\ \vdots \\ L_f^{\beta_p}C_p(z) \end{bmatrix}$$

$$+ B(z)M^{-1}(z)\begin{bmatrix} \frac{d^{\beta_1}y_1}{dt^{\beta_1}} \\ \vdots \\ \frac{d^{\beta_p}y_p}{dt^{\beta_p}} \end{bmatrix}, \tag{20}$$

$$w = B(z)M^{-1}(z)\left(\begin{bmatrix} L_f^{\beta_1}C_1(z) \\ \vdots \\ L_f^{\beta_p}C_p(z) \end{bmatrix} - \begin{bmatrix} \frac{d^{\beta_1}y_1}{dt^{\beta_1}} \\ \vdots \\ \frac{d^{\beta_p}y_p}{dt^{\beta_p}} \end{bmatrix}\right).$$

with

$$M(z) = \begin{bmatrix} L_{b_1}L_A^{\beta_1}c_1(z) & \cdots & L_{b_p}L_A^{\beta_1}c_1(z) \\ \vdots & & \vdots \\ L_{b_1}L_A^{\beta_p}c_p(z) & \cdots & L_{b_p}L_A^{\beta_p}c_p(z) \end{bmatrix}$$

As in the linear case, not only the system outputs, but also their derivatives are used as system inputs. This inverse is not suitable for input estimation without additional regularization, since unavoidable measurement errors lead to an error amplification in the solution.

The determination of the derivatives of the involved measured variable requires the solution of linear inverse problems. The method presented in the previous section is used here to solve them.

5. ILLUSTRATING EXAMPLE

The regularization procedure is illustrated by an example taken from (Farza *et al.*, 1998) using the same set of constant model parameters.

In a bioprocess, product P is made from biomass X and substrate S. The process modelling leads to the nonlinear system

$$\dot{X} = \mu X - DX, \tag{21}$$
$$\dot{P} = \nu X - DP, \tag{22}$$
$$\dot{S} = -\eta_1\mu X - \eta_2\nu X + D(S_{in} - S), \tag{23}$$

with initial conditions X_0, P_0 and S_0. where D is the dilution rate and η_1 and η_2 are yield coefficients. The quantities μ and ν define the specific reaction rates for the growth of the biomass and for the biosynthesis respectively, which are to be estimated from measurements of X and P. For the generation of the measured data in simulation the following models for μ and ν are used:

$$\mu = \mu_{max}\frac{S}{\left(K_{S_1} + S + \frac{S^2}{K_I}\right)}\frac{K_P}{(K_P + P)}\left(1 - \frac{P}{P_f}\right),$$
$$\nu = \nu_m ax\frac{S}{(K_{S_2} + S)}.$$

Figures 2-3 show the true and noisy measurements. The corresponding dilution rate D varies as a trapezoidal signal from 0.1 to $0.2/h$.

Instead of assuming kinetic models for μ and ν, these are regarded as unknown inputs w_1 and w_2 to a nonlinear dynamic system with the states $x_1 = X$ $x_2 = P$ and $x_3 = S$:

$$\dot{x}_1 = -Dx_1 + x_1 w_1 \quad (24)$$

$$\dot{x}_2 = -Dx_2 + x_1 w_2 \quad (25)$$

$$\dot{x}_3 = D(S_{in} - x_3) - \eta_1 x_1 w_1 - \eta_2 x_1 w_2. \quad (26)$$

$$y_1 = x_1 \quad (27)$$

$$y_2 = x_2 \quad (28)$$

The inverse system is then

$$\dot{z}_1 = \dot{y}_1 \quad (29)$$

$$\dot{z}_2 = \dot{y}_2 \quad (30)$$

$$w_1 = D + \frac{1}{z_1}\dot{y}_1 \quad (31)$$

$$w_2 = D\frac{z_2}{z_1} + \frac{1}{z_1}\dot{y}_2 \quad (32)$$

The results of the estimation are shown in Figures 4-7. Although the noise is relatively small, the calculated inputs are without regularization, as expected, not useful (Figures 4,5). A regularization with the approach described above results in reasonable estimates, as shown in Figures 6,7. The simulation was done with a second order transfer function G_f with a regularization parameter determined by the L-curve criterion.

6. CONCLUSIONS

We have considered, in this work, the estimation of unknown reaction rates based on the theory of inverse problems. The proposed estimator does not assume or require any model for the reaction rates. The method is based on system inversion and filtering. The design has been achieved for MIMO linear and nonlinear systems. The results obtained show that efficient and satisfactory estimations could be achieved.

As seen from our problem formulation, the method is not restricted to the estimation of reaction rates. It is applicable to problems where unknown inputs w are determined from measurements of other quantities using the considered model structure. Some other examples from chemical engineering are estimation of heat fluxes, heat of reaction or interphase mass transfer. Similar problems appear also in other engineering and science areas. Moreover, different types of system uncertainties such as nonlinearities, parameter changes, faults and unknown external excitation can be conveniently represented as unknown inputs. Therefore, the unknown input estimation method is of great interest for system supervision and robust or fault-tolerant control.

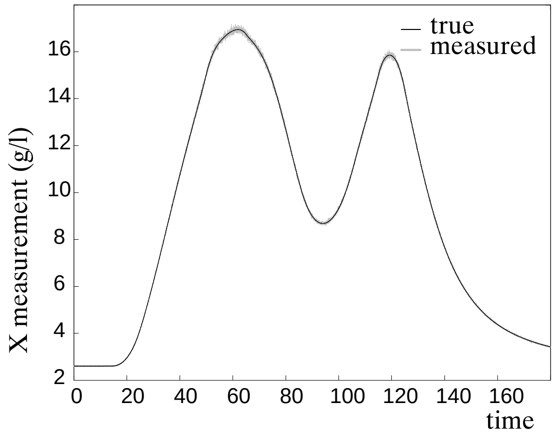

Fig. 2. Biomass concentration measurements

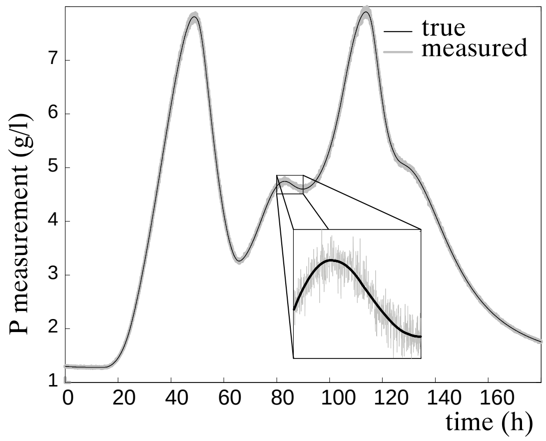

Fig. 3. Product concentration measurements

This work may be extended by considering other classes of systems where the inverse system may be determined.

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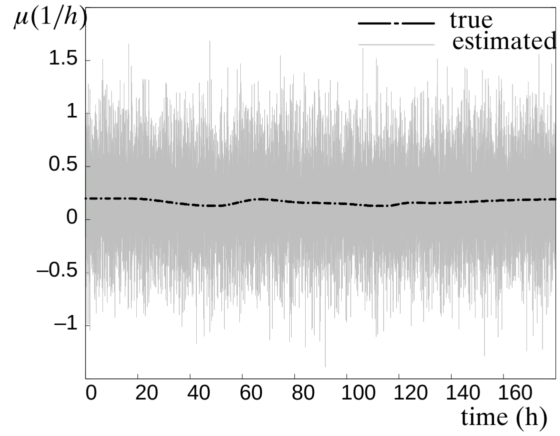

Fig. 4. True and estimated specific reaction rate μ without regularization

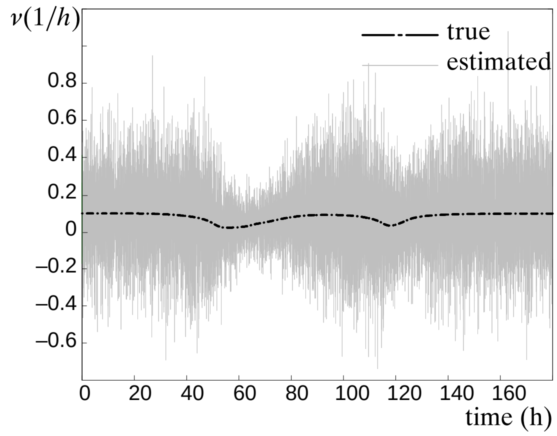

Fig. 5. True and estimated specific reaction rate ν without regularization

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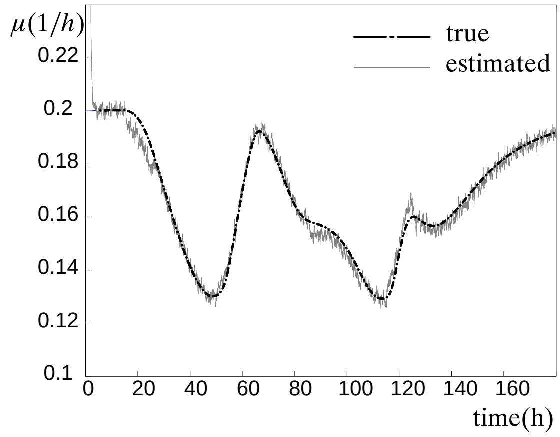

Fig. 6. True and estimated specific reaction rate μ with regularization

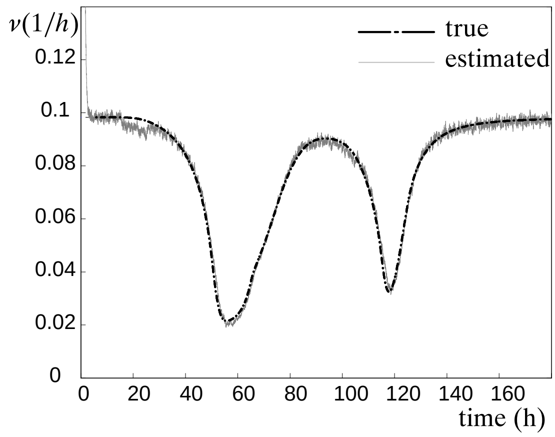

Fig. 7. True and estimated specific reaction rate ν with regularization

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