On the use of shape constraints for state estimation in reaction systems

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Abstract: State estimation techniques are used for improving the quality of measured signals and for reconstructing unmeasured quantities. In chemical reaction systems, nonlinear estimators are often used to improve the quality of estimated concentrations. These nonlinear estimators, which include the extended Kalman filter, the receding-horizon nonlinear Kalman filter and the moving-horizon estimator, use a state-space representation in terms of concentrations. An alternative to the representation of chemical reaction systems in terms of concentrations consists in representing these systems in terms of extents. This paper formulates the state estimation problem in terms of extents, which allows imposing *additional shape constraints* on the sign, monotonicity and concavity/convexity properties of extents. The addition of shape constraints often leads to significantly improved state estimates. A simulated example illustrates the formulation of the state estimation problem in terms of concentrations and extents, and the use of shape constraints.

Keywords: State estimation, receding-horizon nonlinear Kalman filter, vessel extents, shape constraints.

1. INTRODUCTION

Many processes in the (bio-)chemical industry utilize chemical reactions to convert feed materials into intermediate or final products. The quality of these products depends on the quality of the data used for monitoring, control and optimization. Measurements made during the course of a reaction are often limited in number and usually corrupted with noise. The field of state estimation focuses on both improving the accuracy of the measured signals and reconstructing unmeasured signals by enforcing their consistency with a given process model (Simon, 2006). For the static case, state estimation is referred to as data reconciliation (Narasimhan and Jordache, 1999).

The models of chemical reaction systems are most often derived from first principles and written as differential-algebraic equations (DAE), with concentrations, temperatures, pressures and possibly other quantities as state variables. These equations are nonlinear and highly coupled, since each state variable is influenced by multiple rate processes such as reactions, mass transfers, and flows. An alternative representation of reaction systems in terms of "vessel extents" has been proposed by Amrhein et al. (2010) and reformulated by Rodrigues et al. (2015). Vessel extents are to open reactors (reactors with inlet and outlet streams) what batch extents are to batch reactors. In the extent formulation, each state variable is influenced by a single rate process, which considerably simplifies the analysis. In turn, the original states (concentrations) can be represented as linear combinations of these vessel extents.

Several state estimators are available for nonlinear dynamic systems. Among these estimators, the most commonly used is probably the extended Kalman filter (EKF) (Jazwinski, 1970). EKF is recursive by nature and thus can easily be implemented in real time. The major drawback of EKF lies in its inability to handle bounds and algebraic constraints, which are common in the representation of chemical reaction systems. The moving-horizon estimator (MHE) constitutes an alternative that can handle constraints on the estimated states (Rao et al., 2001, 2003). A constrained optimization problem is formulated at each sampling time using a time window of past measurements. This allows incorporating shape constraints (such as sign, monotonicity and concavity/convexity) in the estimation problem for the given window. The drawback of the MHE method is the need to solve differential equations within the optimization loop, which can become a computational issue for real-time estimation.

The receding-horizon nonlinear Kalman filter (RNK) is another nonlinear state estimator. It is based on the prediction and update steps of the Kalman filter (Rengaswamy et al., 2013). In the update step, an optimization problem is solved using a time window of past measurements. The RNK method differs from the MHE methods in the sense that the optimization problem does not require solving differential equations, which considerably reduces the computational burden.

This paper formulates the state estimation problem in terms of vessel extents, which allows exploiting additional shape constraints associated with the extents. In certain cases, the shapes are known a priori, while for other cases,

a data-driven approach can be used to formulate appropriate constraints. The objective of the paper is to compare state estimation in the (original) concentration domain with state estimation in terms of extents, in particular the advantage that results from being able to use additional shape constraints. Since the objective is not to compare the performance of various nonlinear estimators, the RNK method is chosen here for its computational simplicity.

This paper is organized as follows. Section 2 briefly reviews the representation of chemical reaction systems in terms of both numbers of moles and vessel extents. In Section 3, the shape properties of extents are discussed. Section 4 formulates the RNK in terms concentrations and extents. In Section 5, the performance of these two estimator formulations are compared via a case study, while Section 6 concludes the paper.

2. SYSTEM REPRESENTATION

In this section, chemical reaction systems are first modeled in terms of numbers of moles and then in terms of extents.

2.1 Numbers of moles

Consider a homogeneous reaction system involving S species, R independent reactions, p inlet streams, and one outlet stream. A dynamic model in terms of the numbers of moles can be written as

$$\dot{\mathbf{n}}(t) = \mathbf{N}^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in}\mathbf{u}_{in}(t) - \omega(t)\mathbf{n}(t), \quad \mathbf{n}(0) = \mathbf{n}_0, \quad (1)$$

where $\mathbf{n}$ is the S-dimensional vector of numbers of moles, $\mathbf{r}_v := V\mathbf{r}$ with V the volume and $\mathbf{r}$ the R-dimensional vector of reaction rates, $\mathbf{u}_{in}$ is the p-dimensional vector of inlet mass flowrates, $\omega := \frac{u_{out}}{m}$ is the inverse residence time with the mass m and the outlet mass flowrate u_{out}, $\mathbf{N}$ is the $R \times S$ stoichiometric matrix, $\mathbf{W}_{in} = \mathbf{M}_w^{-1}\check{\mathbf{W}}_{in}$ is the $S \times p$ matrix of inlet compositions, with $\mathbf{M}_w$ the S-dimensional diagonal matrix of molecular weights and $\check{\mathbf{W}}_{in} = [\check{\mathbf{w}}_{in}^1 \cdots \check{\mathbf{w}}_{in}^p]$ with $\check{\mathbf{w}}_{in}^j$ the S-dimensional vector of weight fractions of the jth inlet flow, and $\mathbf{n}_0$ is the S-dimensional vector of initial conditions. Note that the mass m can be computed from the numbers of moles $\mathbf{n}$ as $m(t) = \mathbf{1}_S^{\mathrm{T}}\mathbf{M}_w\mathbf{n}(t)$ or through integration of the continuity equation upon knowledge of the inlet and outlet streams: $\dot{m}(t) = \mathbf{1}_p^{\mathrm{T}}\mathbf{u}_{in}(t) - u_{out}(t)$, $m(0) = m_0$.

The concentrations are computed from the numbers of moles as $\mathbf{c}(t) = \frac{\mathbf{n}(t)}{V(t)}$ and the reaction rates $\mathbf{r}(t)$ are typically nonlinear functions of $\mathbf{c}(t)$.

The S-dimensional representation given in Eq. (1) often contains redundancies, as the system evolves in time only due to the R independent reactions, the p independent inlets and the outlet stream. Hence, for a reactor with outlet, there exists $q := S - (R + p + 1)$ invariants, which are identically equal to zero, such that,

$$\mathbf{P}^+\mathbf{n}(t) = \mathbf{0}_q, \quad (2)$$

where the $S \times q$ matrix $\mathbf{P}$ describes the q-dimensional null space of the matrix $[\mathbf{N}^{\mathrm{T}} \ \mathbf{W}_{in} \ \mathbf{n}_0]$, and $\mathbf{P}^+$ is the pseudo-inverse of $\mathbf{P}$. The invariant relationships given in Eq. (2) can be used to rewrite Eq. (1) in terms of $d := R + p +$

1 independent species. The dynamic model can then be rewritten as:

$$\dot{\mathbf{n}}_1(t) = \mathbf{N}_1^{\mathrm{T}}\mathbf{r}_v(t) + \mathbf{W}_{in,1}\mathbf{u}_{in}(t) - \omega(t)\mathbf{n}_1(t), \quad \mathbf{n}_1(0) = \mathbf{n}_{01} \quad (3a)$$

$$\mathbf{n}_2(t) = -\mathbf{P}_2\,\mathbf{P}_1^+\,\mathbf{n}_1(t), \quad (3b)$$

where $\mathbf{n}_1$ is the d-dimensional vector of independent species, $\mathbf{n}_2$ the q-dimensional vector of dependent species, $\mathbf{N}_1$ is the $R \times d$ subset of the stoichiometric matrix, $\mathbf{W}_{in,1}$ the $d \times p$ subset of inlet compositions, $\mathbf{n}_{01}$ the d-dimensional vector of initial conditions, $\mathbf{P}_2$ is the $q \times q$ subset of $\mathbf{P}$ corresponding to the dependent species and $\mathbf{P}_1$ the $d \times q$ subset of $\mathbf{P}$ corresponding to the independent species. Note that the set of independent species are chosen such that rank of the matrix $[\mathbf{N}_1^{\mathrm{T}} \ \mathbf{W}_{in,1} \ \mathbf{n}_{01}] = d$.

2.2 Vessel extents

The reaction system (3a) can be expressed in terms of vessel extents by using the linear transformation (Rodrigues et al., 2015) [1]

$$\mathbf{x}(t) = \mathbf{T}_1\,\mathbf{n}_1(t) = \left[\mathbf{N}_1^{\mathrm{T}} \ \mathbf{W}_{in,1} \ \mathbf{n}_{01}\right]^{-1}\mathbf{n}_1(t). \quad (4)$$

The transformed system reads:

$$\dot{\mathbf{x}}_r(t) = \mathbf{r}_v(t) - \omega(t)\,\mathbf{x}_r(t), \qquad \mathbf{x}_r(0) = \mathbf{0}_R \quad (5a)$$

$$\dot{\mathbf{x}}_{in}(t) = \mathbf{u}_{in}(t) - \omega(t)\,\mathbf{x}_{in}(t), \qquad \mathbf{x}_{in}(0) = \mathbf{0}_p \quad (5b)$$

$$\dot{x}_{ic}(t) = -\omega(t)\,x_{ic}(t), \qquad x_{ic}(0) = 1, \quad (5c)$$

with the reconstruction equations:

$$\mathbf{n}_1(t) = \mathbf{N}_1^{\mathrm{T}}\mathbf{x}_r(t) + \mathbf{W}_{in,1}\mathbf{x}_{in}(t) + \mathbf{n}_{01}\,x_{ic}(t) \quad (6a)$$

$$\mathbf{n}_2(t) = \mathbf{N}_2^{\mathrm{T}}\mathbf{x}_r(t) + \mathbf{W}_{in,2}\mathbf{x}_{in}(t) + \mathbf{n}_{02}\,x_{ic}(t). \quad (6b)$$

The vessel extent of reaction $x_{r,i}(t)$ expresses the amount of material produced or consumed by the ith reaction that is still in the reactor at time t, the negative term on the right-hand side accounting for what has left the reactor. Similarly, the vessel extent of inlet expresses the amount of material loaded by the jth inlet that is still in the reactor at time t. Finally, $x_{ic}(t)$ indicates the fraction of the initial conditions that is still in the reactor at time t. The various extents can be grouped in the extent vector $\mathbf{x} := [\mathbf{x}_r^{\mathrm{T}} \ \mathbf{x}_{in}^{\mathrm{T}} \ x_{ic}]^{\mathrm{T}}$. Note that Eqs (6a) and (6b) can be written together as:

$$\mathbf{n}(t) = \mathbf{N}^{\mathrm{T}}\mathbf{x}_r(t) + \mathbf{W}_{in}\mathbf{x}_{in}(t) + \mathbf{n}_0\,x_{ic}(t). \quad (7)$$

3. STATE CONSTRAINTS

Constraints on state estimates can be formulated based on either the numbers of moles or the extents. Furthermore, these constraints are either known a priori because they are generally valid or they can be inferred from measured data. Section 3.1 introduces constraints on the numbers of moles and on the extents based on prior knowledge. Section 3.2 introduces a procedure for estimating shape constraints on the numbers of moles and on the extents based on measurements.

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[1] The $(S \times S)$-dimensional transformation matrix in Rodrigues et al. (2015) reads $\mathbf{T} := \left[\mathbf{N}^{\mathrm{T}} \ \mathbf{W}_{in} \ \mathbf{n}_0 \ \mathbf{P}\right]^{-1}$. Here $\mathbf{T}_1$ is a submatrix of dimension $d \times d$.

Concentrations

The numbers of moles of all species are nonnegative at all sampling times,

$$\mathbf{n}(t_h) \geq \mathbf{0}_S, \qquad \forall h = 0, 1, \ldots, H. \qquad (8)$$

Since the numbers of moles are affected by various rate processes, it is difficult to impose generally valid shape constraints except for few special cases:

- If a species in a batch reactor appears only as reactant (product) in one or more irreversible reactions, then the corresponding number of moles is monotonically decreasing (increasing).
- If a species in a semi-batch reactor appears only as reactant (product) in one or more irreversible reactions and is not added via an inlet stream, then the corresponding number of moles is monotonically decreasing (increasing).

Extents

In the extent domain, the constraints (8) can be enforced at all sampling times t_h ($\forall h = 0, 1, \ldots, H$) as:

$$\mathbf{N}^{\mathrm{T}} \mathbf{x}_r(t_h) + \mathbf{W}_{in}\mathbf{x}_{in}(t_h) + \mathbf{n}_0 \, x_{ic}(t_h) \geq \mathbf{0}_S. \qquad (9)$$

Furthermore, since each extent expresses the effect of a single rate process, it is possible in certain cases to impose additional constraints on their time evolution. The shape constraints that one can impose *a priori* on vessel extents are described next, first for reactors without outlet and then for reactors with outlet.

<u>Batch and semi-batch reactors</u>

Without outlet ($\omega = 0$), the model (5) reduces to:

$$\dot{\mathbf{x}}_r(t) = \mathbf{r}_v(t) \qquad\qquad \mathbf{x}_r(0) = \mathbf{0}_R \qquad (10a)$$
$$\dot{\mathbf{x}}_{in}(t) = \mathbf{u}_{in}(t) \qquad\qquad \mathbf{x}_{in}(0) = \mathbf{0}_p, \qquad (10b)$$

and $x_{ic}(t) = 1$, for which we can propose the following properties.

Lemma 1: (Extents of inlet) *The extents of inlet are:*

(a) nonnegative monotonically increasing functions,
(b) convex (concave) if the corresponding inlet flowrates are monotonically increasing (decreasing)[2].

Proof: The proof of (a) follows from

$$\mathbf{x}_{in}(t_{h+1}) = \mathbf{x}_{in}(t_h) + \int_{t_h}^{t_{h+1}} \mathbf{u}_{in}(t)dt \qquad (11)$$
$$\forall h = 0, 1, \ldots, H-1,$$

and the fact that $\mathbf{u}_{in}(t) \geq \mathbf{0}_p$ on $t \in [t_0, t_H]$.

To prove convexity in (b), consider the three time points $t_h < t_{h+1} < t_{h+2}$ on the interval $[t_0, t_H]$. From (11) and the fact that the inlet flowrates are monotonically increasing, it follows that

$$\frac{\mathbf{x}_{in}(t_{h+2}) - \mathbf{x}_{in}(t_{h+1})}{t_{h+2} - t_{h+1}} \geq \mathbf{u}_{in}(t_{h+1}) \geq \frac{\mathbf{x}_{in}(t_{h+1}) - \mathbf{x}_{in}(t_h)}{t_{h+1} - t_h},$$

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[2] In practice, it is required to know the monotonic behavior of the inlet flowrates or reaction rates but not their exact numerical values.

which gives the convexity property (Boyd and Vandenberghe, 2004),

$$\frac{\mathbf{x}_{in}(t_{h+2}) - \mathbf{x}_{in}(t_{h+1})}{t_{h+2} - t_{h+1}} \geq \frac{\mathbf{x}_{in}(t_{h+1}) - \mathbf{x}_{in}(t_h)}{t_{h+1} - t_h}.$$

Similar arguments are used to prove concavity. □

Lemma 2: (Extents of irreversible reactions) *The extents of irreversible reactions are:*

(a) nonnegative monotonically increasing functions,
(b) concave (convex) if the corresponding reaction rates are monotonically decreasing (increasing).

Proof: The proof of (a) follows from

$$\mathbf{x}_r(t_{h+1}) = \mathbf{x}_r(t_h) + \int_{t_h}^{t_{h+1}} \mathbf{r}_v(t)dt \qquad (13)$$
$$\forall h = 0, 1, \ldots, H-1,$$

and the fact that $\mathbf{r}_v(t) \geq \mathbf{0}_R$ on $t \in [t_0, t_H]$.

To prove concavity in (b), consider the three time points $t_h < t_{h+1} < t_{h+2}$ on the interval $[t_0, t_H]$. From (13) and the fact that the reaction rates are monotonically decreasing, it follows that

$$\frac{\mathbf{x}_r(t_{h+2}) - \mathbf{x}_r(t_{h+1})}{t_{h+2} - t_{h+1}} \leq \mathbf{r}_v(t_{h+1}) \leq \frac{\mathbf{x}_r(t_{h+1}) - \mathbf{x}_r(t_h)}{t_{h+1} - t_h},$$

which gives the concavity property,

$$\frac{\mathbf{x}_r(t_{h+2}) - \mathbf{x}_r(t_{h+1})}{t_{h+2} - t_{h+1}} \leq \frac{\mathbf{x}_r(t_{h+1}) - \mathbf{x}_r(t_h)}{t_{h+1} - t_h}.$$

Similar arguments are used to prove convexity. □

<u>Reactors with outlet</u>

In the presence of an outlet, the monotonicity and convexity/concavity properties of the extents of inlet and reaction no longer hold. There remains the nonnegative properties of $\mathbf{x}_{in}(t)$, and of $\mathbf{x}_r(t)$ for irreversible reactions. In addition, the following property holds for the extent of initial conditions.

Lemma 3: (Extent of initial conditions) *The extent of initial conditions is a nonnegative monotonically decreasing function.*

Proof: The solution to Eq. (5c) is $x_{ic}(t) = e^{-\int_0^t \omega(t)dt}$. It follows that $x_{ic}(t)$ cannot be negative and, from $\omega(t) \geq 0$, that it is monotonically decreasing. □

3.2 Constraints based on measurements

In certain cases, generic shape constraints cannot be guaranteed, but are nevertheless present in (at least part of) the data. For example, it is common to observe extents of reaction with an inflection point, where the extents change from a convex to a concave shape or conversely.

The procedure for identifying shape constraints on the basis of measurements is presented in the context of the extent domain, but it can also be applied in the concentration domain. The procedure is as follows:

(1) Using Eq. (5) and noting that $\mathbf{r}_v$ is a function of $\mathbf{x}$, express the first and second time derivatives of the extents *analytically* in terms of $\mathbf{x}$, $\mathbf{u}_{in}$ and ω.
(2) Select a time window $\mathscr{T}$ of size N.

(3) Compute the extents $\tilde{\mathbf{x}}(t_h) = \mathbf{T}_1 \tilde{\mathbf{n}}_1(t_h)$ in the time window $\mathscr{T}$ from the *measured* numbers of moles $\tilde{\mathbf{n}}_1(t_h)$ [3].

(4) Estimate the first and second derivatives of each extent using the analytical expressions in Step (1), that is, $\dot{\tilde{x}}_i(t_h)$ and $\ddot{\tilde{x}}_i(t_h)$, $i = 1, \ldots, d$, $t_h \in \mathscr{T}$.

(5) Design shape constraints based on the sign of the estimated second derivatives:
- if $\ddot{\tilde{x}}_i(t_h) \geq 0$, $\forall t_h \in \mathscr{T}$, then $\tilde{x}_i(t)$ is convex on $\mathscr{T}$, and stop the procedure;
- if $\ddot{\tilde{x}}_i(t_h) \leq 0$, $\forall t_h \in \mathscr{T}$, then $\tilde{x}_i(t)$ is concave on $\mathscr{T}$, and stop the procedure;
- if $\ddot{\tilde{x}}_i(t_h)$ changes sign on the time window $\mathscr{T}$, reduce the size of the time window and go back to Step (2); however, if N is already small with regard to the window size that is necessary to handle measurement noise, no convex/concave shape can be imposed and proceed to Step (6) to investigate the existence of monotonicity constraints.

(6) Design shape constraints based on the sign of the estimated first derivatives:
- if $\dot{\tilde{x}}_i(t_h) \geq 0$, $\forall t_h \in \mathscr{T}$, then $\tilde{x}_i(t)$ is monotonically increasing on $\mathscr{T}$, and stop the procedure;
- if $\dot{\tilde{x}}_i(t_h) \leq 0$, $\forall t_h \in \mathscr{T}$, $\tilde{x}_i(t)$ is monotonically decreasing on $\mathscr{T}$, and stop the procedure;
- in case $\dot{\tilde{x}}_i(t_h)$ changes sign on the time window $\mathscr{T}$, there are no observable shape constraints; however, the nonnegative properties of $\tilde{\mathbf{x}}_{in}(t)$, $\tilde{x}_{ic}(t)$, and of $\tilde{\mathbf{x}}_r(t)$ for irreversible reactions remain valid.

4. STATE ESTIMATION

In this section, the state estimation problem is formulated for an RNK filter. The formulation is given for the general case of a reactor with outlet. For state estimation in a stochastic framework, it is necessary to extend the system representations given in Section 2 with a measurement equation and both process and measurement noises.

For the system representation in (3a), one has:

$$\dot{\mathbf{n}}_1(t) = \mathbf{N}_1^{\mathrm{T}} \mathbf{r}_v(t) + \mathbf{W}_{in,1} \mathbf{u}_{in}(t) - \omega(t)\mathbf{n}_1(t) + \mathbf{w}_{n1}(t), \quad \mathbf{n}_1(0) = \mathbf{n}_{01} \quad (15a)$$

$$\mathbf{y}(t) = \begin{bmatrix} \mathbf{I}_d \\ -\mathbf{P}_2 \mathbf{P}_1^+ \end{bmatrix} \mathbf{n}_1(t) + \mathbf{w}_y(t) \quad (15b)$$

The S-dimensional measurement vector $\mathbf{y}$ contains the measured numbers of moles. The term $\mathbf{w}_y$ represents Gaussian white measurement noise of covariance $\mathbf{Q}_y$. The term $\mathbf{w}_{n1}$ is a Gaussian random variable with zero-mean and constant variance-covariance matrix $\mathbf{Q}_{n1}$. For the system (5), one can write:

$$\dot{\mathbf{x}}_r(t) = \mathbf{r}_v(t) - \omega(t)\mathbf{x}_r(t) + \mathbf{w}_r(t), \qquad \mathbf{x}_r(0) = \mathbf{0}_R \quad (16a)$$

$$\dot{\mathbf{x}}_{in}(t) = \mathbf{u}_{in}(t) - \omega(t)\mathbf{x}_{in}(t) + \mathbf{w}_{in}(t), \qquad \mathbf{x}_{in}(0) = \mathbf{0}_p \quad (16b)$$

$$\dot{x}_{ic}(t) = -\omega(t)x_{ic}(t) + w_{ic}(t), \qquad x_{ic}(0) = 1 \quad (16c)$$

$$\mathbf{y}(t) = \mathbf{N}^{\mathrm{T}}\mathbf{x}_r(t) + \mathbf{W}_{in}\mathbf{x}_{in}(t) + \mathbf{n}_0 x_{ic}(t) + \mathbf{w}_y(t). \quad (16d)$$

The terms $\mathbf{w}_r$, $\mathbf{w}_{in}$ and w_{ic} are Gaussian random variables with zero-mean and constant variance-covariance $\mathbf{Q}_r$, $\mathbf{Q}_{in}$, and q_{ic}, respectively.

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[3] The extents can also be computed using the data reconciliation procedure described by Srinivasan et al. (2015).

In the next section, the RNK filter equations are developed for the formulation in terms of extents. The corresponding equations in terms of numbers of moles can be written similarly.

4.1 Receding-horizon nonlinear Kalman filter

For the ease of notation, the right-hand sides of Eqs. (16a)–(16c) are defined as $\mathbf{f}_r(\cdot)$, $\mathbf{f}_{in}(\cdot)$ and $f_{ic}(\cdot)$ and are aggregated to the d-dimensional vector $\mathbf{f}(\cdot)$; similarly, the block-diagonal covariance matrix $\mathbf{Q}_x$ is formed:

$$\mathbf{x} = \begin{bmatrix} \mathbf{x}_r \\ \mathbf{x}_{in} \\ x_{ic} \end{bmatrix}, \mathbf{f}_x(\cdot) = \begin{bmatrix} \mathbf{f}_r(\cdot) \\ \mathbf{f}_{in}(\cdot) \\ f_{ic}(\cdot) \end{bmatrix}, \mathbf{Q}_x = \begin{bmatrix} \mathbf{Q}_r & 0 & 0 \\ 0 & \mathbf{Q}_{in} & 0 \\ 0 & 0 & q_{ic} \end{bmatrix}. \quad (17)$$

The RNK filter implements the prediction and update steps over a time window. These steps are briefly discussed next.

Prediction step

Given the state vector $\mathbf{x}(t_h|t_h)$, one computes the *a priori* estimate $\mathbf{x}(t_{h+1}|t_h), \ldots, \mathbf{x}(t_{h+N}|t_h)$ for the time window $\mathscr{T}$ of length N using the state evolution described by Eqs (16a)-(16c). This prediction step is also referred to as 'open-loop' estimation. Let the (Nd)-dimensional vector $\mathbf{x}_{\mathscr{T}|t_h}$ concatenate all these predicted states, i.e. $\mathbf{x}_{\mathscr{T}|t_h} := [\mathbf{x}(t_{h+1}|t_h)^{\mathrm{T}}, \cdots, \mathbf{x}(t_{h+N}|t_h)^{\mathrm{T}}]^{\mathrm{T}}$.

An *a priori* estimate of the covariance matrix $\mathbf{P}_{\mathscr{T}|t_h}$ of dimension $(Nd \times Nd)$ is given by

$$\mathbf{P}_{\mathscr{T}|t_h} = \begin{pmatrix} \mathbf{P}_{t_{h+1}|t_h} & \mathbf{P}_{(t_{h+1}t_{h+2})|t_h} & \cdots & \mathbf{P}_{(t_{h+1}t_{h+N})|t_h} \\ \mathbf{P}_{(t_{h+1}t_{h+2})|t_h} & \mathbf{P}_{t_{h+2}|t_h} & \cdots & \mathbf{P}_{(t_{h+2}t_{h+N})|t_h} \\ \vdots & \vdots & \ddots & \vdots \\ \mathbf{P}_{(t_{h+1}t_{h+N})|t_h} & \cdots & \cdots & \mathbf{P}_{t_{h+N}|t_h} \end{pmatrix},$$

where the diagonal elements represent the variances of the predicted states and the off-diagonal elements represent the covariance between predicted states. The elements of the matrix $\mathbf{P}_{\mathscr{T}|t_h}$ are estimated from $\mathbf{P}(t_h|t_h)$ using the following iterative relationships (Rengaswamy et al., 2013):

$$\mathbf{P}_{t_{h+N}|t_h} = \mathbf{A}_{t_{h+N-1}} \mathbf{P}_{t_{h+N-1}|t_h} \mathbf{A}_{t_{h+N-1}}^{\mathrm{T}} + \mathbf{Q}_x$$

$$\mathbf{P}_{(t_{h+N-1})(t_{h+N})|t_h} = \mathbf{P}_{(t_{h+N-1})(t_{h+N-1})|t_h} \mathbf{A}_{t_{h+N-1}}^{\mathrm{T}}.$$

The recursion is initialized using

$$\mathbf{P}_{t_{h+1}|t_h} = \mathbf{A}_{t_h} \mathbf{P}_{t_h|t_h} \mathbf{A}_{t_h}^{\mathrm{T}} + \mathbf{Q}_x,$$

where $\mathbf{A}_{t_h} := \exp\{\frac{\partial \mathbf{f_x}}{\partial \mathbf{x}}|_{\mathbf{x}(t_h|t_h)}\}$ is the linearization matrix of the differential equations (16a)–(16c).

Update step

Given the N measured outputs $\mathbf{y}_{\mathscr{T}} := [\mathbf{y}(t_{h+1})^{\mathrm{T}}, \ldots, \mathbf{y}(t_{h+N})^{\mathrm{T}}]^{\mathrm{T}}$, the update step of RNK is formulated as a constrained optimization problem, whose solution is the *a posteriori* state estimate $\mathbf{x}_{\mathscr{T}|t_{h+N}} := [\mathbf{x}(t_{h+1}|t_{h+1})^{\mathrm{T}}, \ldots, \mathbf{x}(t_{h+N}|t_{h+N})^{\mathrm{T}}]^{\mathrm{T}}$. With the introduction of the quantities $\boldsymbol{\alpha} := \mathbf{x}_{\mathscr{T}|t_{h+N}} - \mathbf{x}_{\mathscr{T}|t_h}$ and $\boldsymbol{\beta} := \mathbf{y}_{\mathscr{T}} - \mathbf{f}_y(\mathbf{x}_{\mathscr{T}|t_h})$, the update step can be formulated as the following constrained optimization problem:

$$\min_{\mathbf{x}_{\mathscr{T}|t_{h+N}}} \quad \boldsymbol{\alpha}^{\mathrm{T}} \mathbf{P}_{\mathscr{T}|t_h}^{-1} \boldsymbol{\alpha} + \boldsymbol{\beta}^{\mathrm{T}} \mathbf{Q}_y^{-1} \boldsymbol{\beta}$$
$$\text{s.t.} \quad \mathbf{h}(\mathbf{x}_{\mathscr{T}|t_{h+N}}) \leq \mathbf{0}_m$$
$$\mathbf{x}_{\mathscr{T}|t_{h+N}} \geq \mathbf{0}_{Nd},$$

where $\mathbf{h}(\cdot)$ denotes the m applicable shape constraints.

The *a posteriori* covariance matrix $\mathbf{P}_{\mathscr{T}|t_{h+N}}$ is computed as follows (Rengaswamy et al., 2013):

$$\mathbf{K}_{\mathscr{T}|t_{h+N}} = \mathbf{P}_{\mathscr{T}|t_h} \mathbf{C}_{\mathscr{T}|t_h} (\mathbf{C}_{\mathscr{T}|t_h} \mathbf{P}_{\mathscr{T}|t_h} \mathbf{C}_{\mathscr{T}|t_h}^{\mathrm{T}} + \mathbf{Q}_{n1})^{-1} \quad (18)$$

$$\mathbf{P}_{\mathscr{T}|t_{h+N}} = (\mathbf{I} - \mathbf{K}_{\mathscr{T}|t_{h+N}} \mathbf{C}_{\mathscr{T}|t_h}) \mathbf{P}_{\mathscr{T}|t_h}, \quad (19)$$

where $\mathbf{C}_{\mathscr{T}|t_h}$ is the linearized measurement equation obtained at $\mathbf{x}_{\mathscr{T}|t_h}$. At the end of this prediction-update step, the scheme is repeated for the next time window of length N, that is, from t_{h+2} to t_{h+N+1}. Note that, in the absence of constraints, the RNK filter reduces to the EKF filter.

5. SIMULATED CASE STUDY

This section uses a simulated example and the RNK filter to compare the performance of constrained state estimation in terms of numbers of moles and in terms of extents.

Reaction system

Consider the following two-reaction system,

$$R1: \quad A + B \rightarrow C \qquad r_1 = k_1 \, c_A \, c_B \qquad (20)$$
$$R2: \quad A + C \rightarrow D \qquad r_2 = k_2 \, c_A \, c_C. \qquad (21)$$

The reaction system is simulated in a fed-batch reactor with $k_1 = 0.5$ and $k_2 = 0.3$, both in units L mol^{-1} min^{-1}, $V = 1$ L, $n_{A0} = 5$ mol, and $n_{B0} = n_{C0} = 0$ mol. Species B is fed to the reactor with an inlet flowrate of 5 g min^{-1}. Species A, B and D are chosen as the independent species. The numbers of moles of species C are obtained using the invariant relation obtained from Eq. (2):

$$n_C(t) = n_{A0} + n_{C0} + 2 \, n_{D0} - n_A(t) - 2 \, n_D(t).$$

The numbers of moles of species A, B and D are assumed to be measured every minute for 50 minutes. The simulated numbers of moles are corrupted with Gaussian white noise with the variance matrix,

$$\mathbf{Q}_y = \begin{bmatrix} 0.0806 & 0 & 0 \\ 0 & 0.0106 & 0 \\ 0 & 0 & 0.0553 \end{bmatrix}.$$

The flowrate and the volume are assumed to be perfectly known.

RNK filter in terms of numbers of moles

The differential equations in terms of numbers of moles are written as:

$$\dot{n}_A(t) = -\frac{\hat{k}_1}{V(t)} n_A(t) \, n_B(t) - \frac{\hat{k}_2}{V(t)} n_A(t) \, n_C(t) + w_{n,A} \quad (22a)$$

$$\dot{n}_B(t) = -\frac{\hat{k}_1}{V(t)} n_A(t) \, n_B(t) + w_{in,B} u_{in}(t) + w_{n,B} \quad (22b)$$

$$\dot{n}_D(t) = \frac{\hat{k}_2}{V(t)} n_A(t) \, n_C(t) + w_{n,C}, \quad (22c)$$

with the (incorrect) parameter values $\hat{k}_1 = 0.75$ and $\hat{k}_2 = 0.5$. The process noise vector $\mathbf{w}_{n1}$ is assumed to be zero-mean with the variance matrix,

$$\mathbf{Q}_{n1} = \begin{bmatrix} 0.1 & 0 & 0 \\ 0 & 0.025 & 0 \\ 0 & 0 & 0.025 \end{bmatrix}.$$

The following constraints are known from prior knowledge:

- $n_A(t)$ is monotonically decreasing,
- $n_D(t)$ is monotonically increasing.

Furthermore, concave and convex constraints on all independent species are obtained from measurements using a window size $N = 10$.

RNK filter in terms of extents

The differential equations in terms of extents read:

$$\dot{x}_{r,1}(t) = \frac{\hat{k}_1}{V(t)} \left(n_{A0} - x_{r,1}(t) - x_{r,2}(t) \right) \left(w_{in} x_{in}(t) - x_{r,1}(t) \right) + w_{x_{r,1}} \quad (23a)$$

$$\dot{x}_{r,2}(t) = \frac{\hat{k}_2}{V(t)} \left(n_{A0} - x_{r,1}(t) - x_{r,2}(t) \right) \left(x_{r,1}(t) - x_{r,2}(t) \right) + w_{x_{r,2}} \quad (23b)$$

$$\dot{x}_{in}(t) = u_{in}(t) + w_{x_{in}}. \quad (23c)$$

The process noise vector $\mathbf{w}_x$ is zero-mean and has the covariance matrix,

$$\mathbf{Q}_x = \begin{bmatrix} 0.125 & 0.025 & 0 \\ 0.025 & 0.025 & 0 \\ 0 & 0 & \epsilon \end{bmatrix}.$$

Since the flowrate is perfectly known, ϵ is theoretically zero, but it is set to 10^{-5} for numerical reasons. The non-zero part of $\mathbf{Q}_x$ is computed from $\mathbf{Q}_{n1}$ using the transformation (4).

The following constraints are known from the reaction system and the operating conditions:

- $x_{r,1}(t)$ is concave,
- $x_{r,2}(t)$ is monotonically increasing,
- $x_{in}(t)$ is monotonically increasing.

Furthermore, concave and convex constraints on $x_{r,2}(t)$ and $\mathbf{x}_{in}(t)$ are obtained from measurements using the window size $N = 10$.

Results and Discussion

First, the performance of the two state estimators is compared using only constraints based on prior knowledge. Table 1 compares the sum of the squared errors for the estimation of the numbers of moles [4] without and with shape constraints, the shape constraints being based exclusively on prior knowlededge. Clearly, the addition of shape constraints improves the estimates. Furthermore, the performance is better via $\mathbf{x}$ than via $\mathbf{n}$, which can be attributed to the fact that more constraints can be placed on $\mathbf{x}$ than on $\mathbf{n}$.

A similar comparison is done for shape constraints determined from both prior knowledge and measurements. Table 2 compares the sum of the squared errors for the estimation of the numbers of moles without and with shape constraints. The performance of both estimators is improved by the addition of shape constraints obtained from

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[4] Since the formulation in terms of extents gives extent estimates, the numbers of moles are reconstructed using Eq. (7).

Species	Unconstrained	RNK estimation	
	via $\mathbf{n}$	via $\mathbf{n}$	via $\mathbf{x}$
A	0.96	0.44	0.10
B	0.19	0.13	0.06
C	1.98	0.63	0.27
D	0.52	0.21	0.12

Table 1. Sum of the squared errors for the estimation of the numbers of moles without and with shape constraints. The RNK estimator is formulated both in terms of numbers of moles ($\mathbf{n}$) and in terms of extents ($\mathbf{x}$), with constraints based exclusively on prior knowledge.

measurements. Fig. 1 shows the corresponding simulated, measured, and estimated numbers of moles of A and D for the formulation of the state estimation problem in terms of extents.
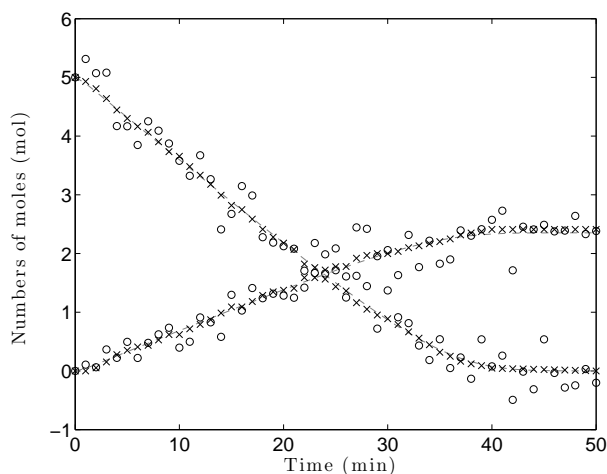

Fig. 1. True (- -), measured ($\circ$) and estimated ($\times$) number of moles of A and D. The RNK filter is formulated in terms of extents, with constraints based on both prior knowledge and measurements.

Species	Unconstrained	RNK estimation	
	via $\mathbf{n}$	via $\mathbf{n}$	via $\mathbf{x}$
A	0.96	0.27	0.06
B	0.19	0.07	0.04
C	1.98	0.37	0.26
D	0.52	0.13	0.10

Table 2. Sum of squared errors for the unconstrained and constrained estimated numbers of moles using an RNK filter formulated in terms of numbers of moles ($\mathbf{n}$) and extents ($\mathbf{x}$), with constraints from both prior knowledge and measurements.

The improvement between Tables 1 and 2 is more pronounced in the case of the formulation via the numbers of moles since more measurement-based constraints are added, or, in other words, fewer constraints were available from prior knowledge. The effectiveness of measurement-based constraints depends on the quality of the measured

data since the procedure relies on the computation of first and second derivatives of noisy measurements. At the limit, when the noise is too large, it might be impossible to apply shape constraints via measurements, and only the constraints from prior knowledge remain valid.

6. CONCLUSION

This paper has compared the formulation of the state estimation problem in terms of numbers of moles and extents. The addition of shape constraints to the state estimation problem has shown to greatly improve the precision of the estimated states. It was also shown that the formulation using extents allows defining additional shape constraints compared to the formulation in terms of the original numbers of moles. A procedure for identifying these shape constraints from measurements has also been introduced. The effectiveness of these measurement-based constraints increases when only a few constraints are available from prior knowledge and the measurement noise is low.

Future work will focus on the combined problem of parameter and state estimation using shape constraints and the extent-based formulation. While this paper has provided detailed conditions about the existence of shape constraints for reactors without outlet, the conditions under which shape constraints can be applied to reactors with outlet are widely unknown. Also, it would be useful to develop a procedure for identifying shape constraints for reversible reactions.

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