

# Extent-based reconstruction of the inlet composition matrix in process systems with feed variability and unknown reaction dynamics

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**Abstract:** Extent-based representation is a powerful tool for reaction systems since it decouples the reaction related dynamics and inlet flow dynamics. However it assumes that the inlet flow composition is exactly known. In this paper, we present the design of an estimation procedure to partially reconstruct the approximate inlet composition matrix based on the extent representation of the process. This is especially necessary when process systems have recycle streams or the inlet composition matrix contains traces of other species. The estimation is done by transforming the measured moles to the extent basis based on a nominal but incorrect inlet composition. The use of this incorrect composition will reveal the difference between the true process and the nominal model. The error between these two can be exploited to be cast a constrained linear optimization problem to estimate the uncertainty in the inlet composition. The correction of the inlet composition matrix will be crucial in obtaining an appropriate extent-based representation that can be used for control, and state and parameter estimation approaches. The use of extents is motivated because it allows to represent the system with a set of decoupled dynamics, avoiding the necessity of the reaction dynamics in the estimation procedure. The techniques developed in this paper are ultimately tested in a simple case study of a CSTR with a recycle stream from a flash evaporator.

*Keywords:* extent representation, parameter estimation, model update, uncertainty

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## 1. INTRODUCTION

Reaction systems are usually modeled using conservation laws described by mass and energy balance equations. These equations represent different phenomena acting on the system, namely reaction, and transport dynamics (Skogestad (2008)). The particular structure in the balance equations has been exploited by decoupling the process dynamics in variants and invariants of reaction by means of a diffeomorphic linear transformation. The resulting dynamics is described in terms of extents (Asbjørnsen (1972)). This decomposition approach has been extended to include a more general representation of the reaction systems, such as systems with multiple phases, mass transfer, and non-isothermal dynamics (Amrhein et al. (2010), Bhatt et al. (2010), Hoang et al. (2020)), and even used for control design purposes (Márquez-Ruiz et al. (2019)). There has also been substantial effort in using this decomposition for control, and state and parameter estimation purposes. In particular, the estimation of kinetic parameters has been addressed via the extent representation using incremental estimation or graph-based techniques (Márquez-Ruiz et al. (2018), Villez et al. (2019)). Extent-based incremental parameter estimation refers to a two-step estimation procedure. First, the concentration/mole measurement is transformed into extent-based variables to decouple the effects. Secondly, the parameters affecting each dynamic are computed separately, which can lead to better parameter identifiability conditions. However, the extent-based incremental identification has

been applied mainly for batch reaction systems. This limits the applicability of the incremental identification approach for semi-batch or continuous operations. Additionally, a strong assumption in semi-batch and continuous process operations is the exact knowledge of the feed stock or raw material used. The feed could perhaps be adjusted in case of a batch operation but in a CSTR connected to upstream processes or with a recycle stream, the feed composition might be varying. This poses a problem when applying the linear transformations to compute the extents for these two cases. Furthermore, the subsequent kinetic parameter estimation is not reliable due to the incorrect extent calculation as a consequence of the uncertainty in the inlet composition. Hence, knowing a correct value of the inlet composition matrix is crucial because this information will lead to a reliable extent-based representation that can be used for control design, and state and parameter estimation. In this paper, we propose a method to estimate the inlet uncertainty using an extent-based approach to circumvent the problem of the unknown reaction dynamics, which limits the use of classical methods. The uncertainty is used to correct a nominal model such that it describes the process behavior. The inlet composition uncertainty matrix is calculated solving a linear constrained optimization.

The paper is organized as follows: Section 2 treats the notion of the extent representation, and the conditions for existence of a linear diffeomorphism between the mole and the extent space. Section 3 introduces the inlet composition uncertainty matrix, as well as the restrictions

it must satisfy to ensure physical interpretation of the extent-based model. Theorems on the necessity of measuring the inverse residence time to correctly estimate the uncertainty are also introduced in this section. Section 4 presents the problem set-up and the solution to recover an approximate inlet composition matrix based on full mole measurement. Section 5 presents a simple example of a CSTR with a recycle coming from a flash evaporator used as a demonstrator for the techniques developed in the previous section. Finally, section 6 contains the conclusions derived from this work.

## 2. EXTENT-BASED REPRESENTATION

The reaction variants coincide with the extent of reaction if and only if the initial conditions of the former are strictly zero. Moreover, if the process contains an inlet stream, then the change in time of moles is affected by two independent dynamics, reaction and inlet flow. Under this situation, the reactor dynamics cannot be expressed in terms of the extent of reaction directly. To circumvent this situation, the concept of extent is extended to extents of reaction and inlet flows.

Consider the mole balance equation for CSTR with a well-stirred mixture of  $S$  species,  $N_r$  independent reactions,  $N_l$  independent inlet flows, and **one** outlet flow given by:

$$\dot{\mathbf{n}} = \mathbf{N}^\top \mathbf{r} + \mathbf{X}_{\text{in}} \mathbf{F}_{\text{in}} - \frac{F_{\text{out}}}{n_L} \mathbf{n}, \quad \mathbf{n}(0) = \mathbf{n}_0 \quad (1)$$

where  $\mathbf{n} \in \mathbb{R}^S$  is the vector of moles,  $\mathbf{r} \in \mathbb{R}^{N_r}$  is the (unknown) vector of chemical independent reactions,  $\mathbf{F}_{\text{in}} \in \mathbb{R}_{\geq 0}^{N_l}$  is the molar inlet flow vector,  $\mathbf{N} \in \mathbb{R}^{N_r \times S}$  is the stoichiometric matrix,  $\mathbf{X}_{\text{in}} \in \mathbb{R}_{[0,1]}^{S \times N_l}$  is the inlet molar fraction matrix,  $F_{\text{out}} \in \mathbb{R}$  the molar outlet flow, and  $n_L$  is the total number of moles in the liquid reacting mixture.

The mole balance in a CSTR shown in (1) is in general nonlinear due to the reaction kinetics contained in the vector  $\mathbf{r}$ . It is possible to find a linear diffeomorphism  $\mathbf{T}$  such that the system can be re-expressed in terms of new states that each of them only evolves with respect to the reaction and the inlet flow as follows (Amrhein et al. (2010))

$$\mathbf{n} \mapsto \begin{bmatrix} \mathbf{x}_r \\ \mathbf{x}_{\text{in}} \\ \mathbf{x}_{\text{inv}} \\ x_\lambda \end{bmatrix} = \underbrace{\begin{bmatrix} \mathbf{T}_{1_0}^\top \\ \mathbf{T}_{2_0}^\top \\ \mathbf{T}_{3_0}^\top \\ \mathbf{T}_{4_0}^\top \end{bmatrix}}_{\mathbf{T}_0} \mathbf{n} \quad (2)$$

where  $\mathbf{x}_r$  is the extent of reaction,  $\mathbf{x}_{\text{in}}$  is the extent of inlet flow,  $\mathbf{x}_{\text{inv}}$  is the extent of reaction and inlet flow invariants and  $x_\lambda$  is the initial conditions discounting factor,  $\mathbf{T}_{1_0}$  is the transformation matrix of the reaction space,  $\mathbf{T}_{2_0}$  is the transformation matrix of the inlet space,  $\mathbf{T}_{3_0}$  is the transformation matrix of the reaction and inlet flow invariant space, all with discounted initial conditions  $\mathbf{n}_0$  and  $\mathbf{T}_{4_0}$  portion of the reaction and inlet invariant spaces occupied by the initial conditions  $\mathbf{n}_0$ .

The existence of the aforementioned linear diffeomorphism  $\mathbf{T}_0$  is guaranteed if the following conditions hold:

- (1) The stoichiometric matrix  $\mathbf{N}^\top$  is full column rank, i.e.  $\text{rank}(\mathbf{N}^\top) = N_r$
- (2) The inlet molar fraction matrix  $\mathbf{X}_{\text{in}}$  is full column rank, i.e.  $\text{rank}(\mathbf{X}_{\text{in}}) = N_l$
- (3)  $\text{rank}(\begin{bmatrix} \mathbf{N}^\top & \mathbf{X}_{\text{in}} \end{bmatrix}) = N_r + N_l \leq S$  for  $\mathbf{n}_0 = 0$
- (4)  $\text{rank}(\begin{bmatrix} \mathbf{N}^\top & \mathbf{X}_{\text{in}} & \mathbf{n}_0 \end{bmatrix}) = N_r + N_l + 1 \leq S$  for  $\mathbf{n}_0 \neq 0$

As noted in Márquez-Ruiz et al. (2020), the existence of the linear map  $\mathbf{T}_0$  can be viewed as an input/disturbance-to-state decoupling problem. In this sense,  $\text{col}(\mathbf{N}^\top) \oplus \text{col}(\mathbf{X}_{\text{in}}) \oplus \text{col}(\mathbf{n}_0) \subseteq \mathbb{R}^S$ , guarantees uniqueness of the decomposition, where  $\oplus$  is the direct sum. Additionally,  $\ker(\mathbf{N}) \cap \ker(\mathbf{X}_{\text{in}}^\top) = \mathcal{I}$ , which guarantees the existence of trajectories in the moles space that are reaction and inlet invariant. Finally,  $\text{col}(\mathbf{n}_0) \subseteq \mathcal{I}$ , which implies that the initial conditions must lie in the reaction and inlet invariant subspace, providing independent information about the trajectories in the mole space. If these conditions are satisfied, then the reaction, inlet, and invariant subspaces can be generated performing an orthogonal decomposition of the moles space.

The linear diffeomorphism  $\mathbf{T}_0$  satisfies the following condition:

$$\begin{bmatrix} \mathbf{T}_{1_0}^\top \\ \mathbf{T}_{2_0}^\top \\ \mathbf{T}_{3_0}^\top \\ \mathbf{T}_{4_0}^\top \end{bmatrix} \begin{bmatrix} \mathbf{N}^\top & \mathbf{X}_{\text{in}} & \mathbf{n}_0 \end{bmatrix} = \begin{bmatrix} \mathbf{I}_{N_r+N_l+1} \\ \mathbf{0}_{1 \times N_r+N_l+1} \end{bmatrix} \quad (3)$$

Since  $\mathbf{x}_{\text{inv}}(0) = 0 \implies \mathbf{x}_{\text{inv}}(t) = 0 \forall t \geq 0$ , therefore it can be left out. The model of the CSTR in terms of extents is:

$$\begin{aligned} \dot{\mathbf{x}}_r &= \mathbf{r} - \frac{F_{\text{out}}}{n_L} \mathbf{x}_r, & \mathbf{x}_r(0) &= \mathbf{0}_{N_r} \\ \dot{\mathbf{x}}_{\text{in}} &= \mathbf{F}_{\text{in}} - \frac{F_{\text{out}}}{n_L} \mathbf{x}_{\text{in}}, & \mathbf{x}_{\text{in}}(0) &= \mathbf{0}_{N_l} \\ \dot{x}_\lambda &= -\frac{F_{\text{out}}}{n_L} x_\lambda, & x_\lambda(0) &= 1 \end{aligned} \quad (4)$$

Notice the decoupling effect that the extent of reaction and inlet has on the system dynamics. Under this representation, the independent evolution of the reaction, the inlet and outlet can be easily observed. Finally, the moles can be calculated using the inverse mapping  $\mathbf{T}_0^{-1}$ :

$$\mathbf{n} = \mathbf{T}_0^{-1} \begin{bmatrix} \mathbf{x}_r \\ \mathbf{x}_{\text{in}} \\ x_\lambda \end{bmatrix} \quad (5)$$

where  $\mathbf{T}_0^{-1} = \begin{bmatrix} \mathbf{N}^\top & \mathbf{X}_{\text{in}} & \mathbf{n}_0 \end{bmatrix}$ .

*Remark 1.* Both of the mole basis and extent basis representations exist individually. This implies that one can choose to work on either basis without any restriction. However, the existence of the linear diffeomorphism  $\mathbf{T}_0 : \mathcal{M} \subseteq \mathbb{R}_{\geq 0}^S \mapsto \mathcal{X} = \mathbb{R}^{N_r} \oplus \mathbb{R}^{N_l} \oplus \mathbb{R}^{N_\varepsilon}$  is only guaranteed if the rank conditions 1–4 are satisfied. If the linear diffeomorphism  $\mathbf{T}_0$  does not exist, then the spaces  $\mathcal{M}$  and  $\mathcal{X}$  are not homeomorphic, which implies that the extent and mole dynamics cannot be related in a one-to-one manner.

### 3. EXTENT REPRESENTATION WITH UNCERTAIN INLET COMPOSITION

Each of the blocks of  $\mathbf{T}$  and  $\mathbf{T}_0$  require perfect knowledge of  $\mathbf{N}$ ,  $\mathbf{X}_{\text{in}}$ , and  $\mathbf{n}_0$ . However, in many practical situations, these matrices are not known exactly, as the reaction stoichiometry might not be fully known, and inlet flows might be contaminated with other species. In this section, we address the second case, i.e. the stoichiometric matrix  $\mathbf{N}$  is completely known, while  $\mathbf{X}_{\text{in}}$  has some uncertainty. Furthermore, in order to give some structure to the analysis and results, we take the following assumption as valid:

*Assumption 1.* The inlet composition matrix is uncertain with respect to known species in the process, i.e. the contamination cannot be a result of mixing the inlet with species not contained in the chemical reaction at hand.

Let us define the "assumed" inlet composition matrix as  $\mathbf{X}_{\text{in}}^\circ$ . On the other hand, the "true" inlet composition matrix is  $\mathbf{X}_{\text{in}} = \mathbf{X}_{\text{in}}^\circ + \Delta\mathbf{X}_{\text{in}}$ . Furthermore, due to some physical constraints, both the true inlet composition matrix  $\mathbf{X}_{\text{in}}$ , and  $\mathbf{X}_{\text{in}}^\circ$  satisfy the following properties:

- (1)  $\mathbf{X}_{\text{in}}$  is always a positive matrix.<sup>1</sup>
- (2)  $\mathbf{1}_S^\top \mathbf{X}_{\text{in}} = \mathbf{1}_{1 \times N_L} \Rightarrow \|\mathbf{X}_{\text{in}}\|_1 = 1$
- (3)  $0 \leq x_{i,j} \leq 1 \quad \forall i = 1, \dots, S. \quad \forall j = 1, \dots, \ell$ , where  $x_{i,j}$  is the  $i$ -th species composition in the  $j$ -th inlet stream.

As a consequence of the properties of the inlet composition matrix, it follows that

- (1)  $\mathbf{1}_S^\top \Delta\mathbf{X}_{\text{in}} = \mathbf{0}_{1 \times N_L}$
- (2)  $|\delta x_{i,j}| \leq 1 \quad \forall i = 1, \dots, S. \quad \forall j = 1, \dots, \ell$ , where  $\delta x_{i,j}$  is the perturbation to  $i$ -th species composition in the  $j$ -th inlet stream.

In the following, we assume that the balance equation of a reaction process system in the mole basis is given by

$$\dot{\mathbf{n}} = \mathbf{N}^\top \mathbf{r} + \mathbf{X}_{\text{in}} \mathbf{F}_{\text{in}} - \zeta \mathbf{n}, \quad \mathbf{n}(0) = \mathbf{n}_0 \quad (6)$$

and the model describing the process is

$$\dot{\mathbf{n}}^\circ = \mathbf{N}^\top \mathbf{r}^\circ + \mathbf{X}_{\text{in}}^\circ \mathbf{F}_{\text{in}} - \zeta^\circ \mathbf{n}^\circ, \quad \mathbf{n}^\circ(0) = \mathbf{n}_0 \quad (7)$$

where  $\zeta = \frac{F_{\text{out}}}{n_L}$  and  $\zeta^\circ = \frac{F_{\text{out}}}{n_L^\circ}$  are the inverse the residence time of the system and the model. Notice that  $\zeta$  is a time-varying function.

Likewise, the balance equation can be written in the extent basis for both the system and the model. In the case of the system, we have

$$\begin{aligned} \dot{\mathbf{x}}_r &= \mathbf{r}(\mathbf{x}) - \zeta \mathbf{x}_r, & \mathbf{x}_r(0) &= \mathbf{0}_{N_r} \\ \dot{\mathbf{x}}_{\text{in}} &= \mathbf{F}_{\text{in}} - \zeta \mathbf{x}_{\text{in}}, & \mathbf{x}_{\text{in}}(0) &= \mathbf{0}_{N_L} \\ \dot{\mathbf{x}}_{\text{inv}} &= -\zeta \mathbf{x}_{\text{inv}}, & \mathbf{x}_{\text{inv}}(0) &= \mathbf{0}_{N_e} \\ \dot{x}_\lambda &= -\zeta x_\lambda, & x_\lambda(0) &= 1 \end{aligned} \quad (8)$$

Similarly, the extent representation is

$$\begin{aligned} \dot{\mathbf{x}}_r^\circ &= \mathbf{r}^\circ(\mathbf{x}^\circ) - \zeta^\circ \mathbf{x}_r^\circ, & \mathbf{x}_r^\circ(0) &= \mathbf{0}_{N_r} \\ \dot{\mathbf{x}}_{\text{in}}^\circ &= \mathbf{F}_{\text{in}} - \zeta^\circ \mathbf{x}_{\text{in}}^\circ, & \mathbf{x}_{\text{in}}^\circ(0) &= \mathbf{0}_{N_L} \\ \dot{\mathbf{x}}_{\text{inv}}^\circ &= -\zeta^\circ \mathbf{x}_{\text{inv}}^\circ, & \mathbf{x}_{\text{inv}}^\circ(0) &= \mathbf{0}_{N_e} \\ \dot{x}_\lambda^\circ &= -\zeta^\circ x_\lambda^\circ, & x_\lambda^\circ(0) &= 1 \end{aligned} \quad (9)$$

Recall that in Remark 1, mole and extent basis dynamics exist individually but can be related by a linear diffeomorphism  $\mathbf{T}_0$ . In this sense, the invertible linear map  $\mathbf{T}_0^\circ$  relating (7) and (9) can be found because  $\mathbf{N}$ ,  $\mathbf{X}_{\text{in}}^\circ$ , and  $\mathbf{n}_0$  are known. However, the computation of the linear diffeomorphism between (6) and (8) cannot be done because  $\mathbf{X}_{\text{in}}$  is not known. Nonetheless, since  $\mathbf{X}_{\text{in}} = \mathbf{X}_{\text{in}}^\circ + \Delta\mathbf{X}_{\text{in}}$ , the estimation of  $\mathbf{X}_{\text{in}}$  is addressed with the estimation of  $\Delta\mathbf{X}_{\text{in}}$ .

On the other hand, from (8) and (9), it is clear to see that the equivalence of part of these representations depends on the values of  $\zeta$  and  $\zeta^\circ$ . This is formalized in the following theorem

*Theorem 1.* Let  $\mathbf{F}_{\text{in}} > \mathbf{0}_{N_L}$  and let  $F_{\text{out}} > 0$  be known and equal for both the system and the model, then the extent of inlet  $\mathbf{x}_{\text{in}}$ ,  $\mathbf{x}_{\text{inv}}$ , and  $x_\lambda$  in the representations (8) and (9) are equivalent if and only if  $\zeta = \zeta^\circ \quad \forall t \in (0, \infty)$ .

The proof is omitted due to space constraints.

Theorem 1 holds trivially for  $F_{\text{out}} = 0$  because  $\zeta = \zeta^\circ = 0$  irrespective of the values of  $n_L$  and  $n_L^\circ$  is satisfied or not. Additionally, it is possible to delineate the conditions when  $\zeta = \zeta^\circ \neq 0$ . This is outlined in the following Lemma

*Lemma 1.* Let the stoichiometric  $\mathbf{N} \in \mathbb{R}^{N_r \times S}$  be full row rank, i.e.  $\text{rank}(\mathbf{N}) = N_r$ . If the  $S$ -dimensional column vector of ones  $\mathbf{1}_S$  is in the null space of  $\mathbf{N}$ , then the total number of moles is conserved by the chemical reaction, and the model and system inverse residence times  $\zeta^\circ$  and  $\zeta$  are equal  $\forall t \in (0, \infty)$ .

The proof follows from the comparison of the global mole balances based on (6) and (7).

### 4. ESTIMATING THE UNCERTAINTY MATRIX FROM MOLE MEASUREMENT IN A CSTR

In this section we present the methodology to estimate the inlet composition uncertainty in a continuous stirred-tank reactor. Due to the presence of an outlet flow ( $F_{\text{out}} > 0$ ),  $\zeta^\circ > 0$  and  $\zeta > 0$ . As per Theorem 1 and Lemma 1, in general both process and model inverse residence times  $\zeta \neq \zeta^\circ \quad \forall t \in (0, \infty)$ , we assume that  $\zeta$  is measured. The stoichiometric matrix  $\mathbf{N}$  and the inlet composition matrix  $\mathbf{X}_{\text{in}}^\circ$  are known, except that the real system has a perturbed inlet composition matrix  $\Delta\mathbf{X}_{\text{in}}$ . Finally, we assume that the reacting mixture is homogeneous and well-stirred. In general, the estimation of  $\Delta\mathbf{X}_{\text{in}}$  can only done using the system's true extent representation in (8) due to Theorem 1. With the exception of specific cases where Lemma 1 holds, inverse residence times of the system and the model are different, and the error convergence to zero cannot be guaranteed.

<sup>1</sup> A positive matrix is a matrix whose elements are all positive. Note that this is different from a Positive Definite Matrix, which only applies to symmetric matrices.

## True extents

$$\dot{\mathbf{x}}_r = \mathbf{r}(\mathbf{x}) - \varsigma \mathbf{x}_r, \quad \mathbf{x}_r(0) = \mathbf{0}_{N_r} \quad (10)$$

$$\dot{\mathbf{x}}_{\text{in}} = \mathbf{F}_{\text{in}} - \varsigma \mathbf{x}_{\text{in}}, \quad \mathbf{x}_{\text{in}}(0) = \mathbf{0}_{N_l} \quad (11)$$

$$\dot{\mathbf{x}}_{\text{inv}} = -\varsigma \mathbf{x}_{\text{inv}}, \quad \mathbf{x}_{\text{inv}}(0) = \mathbf{0}_{N_\varepsilon} \quad (12)$$

$$\dot{x}_\lambda = -\varsigma x_\lambda, \quad x_\lambda(0) = 1 \quad (13)$$

Integrating (11)–(13)

$$\begin{aligned} \mathbf{x}_{\text{in}} &= \int_0^t \Phi_{N_l}(t, \tau) \mathbf{F}_{\text{in}}(\tau) \, d\tau \\ \mathbf{x}_{\text{inv}} &= \mathbf{0}_{N_\varepsilon} \\ x_\lambda &= \Phi(t, 0) \end{aligned}$$

where  $\Phi_{N_l}(t, \tau) = \exp\left(-\int_\tau^t \varsigma(s) \mathbf{I}_{N_l} \, ds\right)$

The linear transformations  $\mathbf{T}_{0_1}^\circ$ ,  $\mathbf{T}_{0_2}^\circ$ ,  $\mathbf{T}_{0_3}^\circ$ , and  $\mathbf{T}_{0_4}^\circ$  are computed based on the model information, and applied to the mole representation of the system in (6) to obtain a pseudo-extent representation:

## Pseudo-extents

$$\dot{\mathbf{w}}_r = \mathbf{r}(\mathbf{w}) + \mathbf{T}_{1_0}^{\circ\top} \Delta \mathbf{X}_{\text{in}} \mathbf{F}_{\text{in}} - \varsigma \mathbf{w}_r, \quad \mathbf{w}_r(0) = \mathbf{0}_{N_r} \quad (14)$$

$$\dot{\mathbf{w}}_{\text{in}} = \mathbf{F}_{\text{in}} + \mathbf{T}_{2_0}^{\circ\top} \Delta \mathbf{X}_{\text{in}} \mathbf{F}_{\text{in}} - \varsigma \mathbf{w}_{\text{in}}, \quad \mathbf{w}_{\text{in}}(0) = \mathbf{0}_{N_l} \quad (15)$$

$$\dot{\mathbf{w}}_{\text{inv}} = \mathbf{T}_{3_0}^{\circ\top} \Delta \mathbf{X}_{\text{in}} \mathbf{F}_{\text{in}} - \varsigma \mathbf{w}_{\text{inv}}, \quad \mathbf{w}_{\text{inv}}(0) = \mathbf{0}_{N_\varepsilon} \quad (16)$$

$$\dot{w}_\lambda = \mathbf{T}_{4_0}^{\circ\top} \Delta \mathbf{X}_{\text{in}} \mathbf{F}_{\text{in}} - \varsigma w_\lambda, \quad w_\lambda(0) = 1 \quad (17)$$

Integrate (15)–(17)

$$\begin{aligned} \mathbf{w}_{\text{in}} &= \underbrace{\int_0^t \Phi_{N_l}(t, \tau) \mathbf{F}_{\text{in}}(\tau) \, d\tau}_{\mathbf{x}_{\text{in}}} \\ &+ \int_0^t \Phi_{N_l}(t, \tau) \mathbf{T}_{2_0}^{\circ\top} \Delta \mathbf{X}_{\text{in}} \mathbf{F}_{\text{in}}(\tau) \, d\tau \end{aligned} \quad (18)$$

$$\mathbf{w}_{\text{inv}} = \int_0^t \Phi_{N_\varepsilon}(t, \tau) \mathbf{T}_{3_0}^{\circ\top} \Delta \mathbf{X}_{\text{in}} \mathbf{F}_{\text{in}}(\tau) \, d\tau \quad (19)$$

$$w_\lambda = \Phi(t, 0) + \int_0^t \Phi(t, \tau) \mathbf{T}_{4_0}^{\circ\top} \Delta \mathbf{X}_{\text{in}} \mathbf{F}_{\text{in}}(\tau) \, d\tau \quad (20)$$

where  $\Phi_{N_\varepsilon}(t, \tau) = \exp\left(-\int_\tau^t \varsigma(s) \mathbf{I}_{N_\varepsilon} \, ds\right)$  and  $\Phi(t, \tau) = \exp\left(-\int_\tau^t \varsigma(s) \, ds\right)$ .

Using the properties of the Kronecker product and the vectorization operator, the system of equations in (18)–(20) is equivalent to:

$$\begin{bmatrix} \mathbf{w}_{\text{in}} - \mathbf{x}_{\text{in}} \\ \mathbf{w}_{\text{inv}} \\ w_\lambda - x_\lambda \end{bmatrix} = \int_0^t F_{\text{in}}^\top(\tau) \otimes \Phi_{N_l+N_\varepsilon+1}(t, \tau) \, d\tau \times \left( \mathbf{I}_{N_l} \otimes \begin{bmatrix} \mathbf{T}_{2_0}^{\circ\top} \\ \mathbf{T}_{3_0}^{\circ\top} \\ \mathbf{T}_{4_0}^{\circ\top} \end{bmatrix} \right) \text{vec}(\Delta \mathbf{X}_{\text{in}}) \quad (21)$$

Equation (21) is linear in the vector  $\boldsymbol{\delta} = \text{vec}(\Delta \mathbf{X}_{\text{in}})$ . However, in order to estimate  $\boldsymbol{\delta}$ , it is necessary to calculate the value of the integral. This integral can be expressed in terms of  $\mathbf{x}_{\text{in}}$  as

$$\int_0^t F_{\text{in}}^\top(\tau) \otimes \Phi_{N_l+N_\varepsilon+1}(t, \tau) \, d\tau = (\mathbf{x}_{\text{in}}^\top \otimes \mathbf{I}_{N_l+N_\varepsilon+1}) \quad (22)$$

Replacing (22) in (21), we arrive at the following expression:

$$\begin{bmatrix} \mathbf{w}_{\text{in}} - \mathbf{x}_{\text{in}} \\ \mathbf{w}_{\text{inv}} \\ w_\lambda - x_\lambda \end{bmatrix} = \left( \mathbf{x}_{\text{in}}^\top \otimes \begin{bmatrix} \mathbf{T}_{2_0}^{\circ\top} \\ \mathbf{T}_{3_0}^{\circ\top} \\ \mathbf{T}_{4_0}^{\circ\top} \end{bmatrix} \right) \text{vec}(\Delta \mathbf{X}_{\text{in}}) \quad (23)$$

A constrained optimization is set up based on (23)

$$\begin{aligned} \min_{\boldsymbol{\delta}} \quad & \frac{1}{2} \|\mathbf{E} - \mathbf{D}\boldsymbol{\delta}\|_2 \\ \text{s.t.} \quad & \begin{cases} \mathbf{1}_{SN_l}^\top \boldsymbol{\delta} = 0 \\ \boldsymbol{\delta} \geq -\text{vec}(\mathbf{X}_{\text{in}}^\circ) \\ \boldsymbol{\delta} \leq \mathbf{1}_{SN_l} \end{cases} \end{aligned} \quad (24)$$

where  $\boldsymbol{\delta} = \text{vec}(\Delta \mathbf{X}_{\text{in}})$ ,  $\mathbf{D} = \left( \mathbf{x}_{\text{in}}^\top \otimes \begin{bmatrix} \mathbf{T}_{2_0}^{\circ\top} \\ \mathbf{T}_{3_0}^{\circ\top} \\ \mathbf{T}_{4_0}^{\circ\top} \end{bmatrix} \right)$ , and

$$\mathbf{E} = \begin{bmatrix} \mathbf{w}_{\text{in}} - \mathbf{x}_{\text{in}} \\ \mathbf{w}_{\text{inv}} \\ w_\lambda - x_\lambda \end{bmatrix}$$

whose solution  $\hat{\boldsymbol{\delta}}$  allows us to retrieve the estimate  $\Delta \hat{\mathbf{X}}_{\text{in}}$  based on the estimation of  $\hat{\boldsymbol{\delta}}$  using

$$\Delta \hat{\mathbf{X}}_{\text{in}} = \text{vec}_{S, N_l}^{-1}(\hat{\boldsymbol{\delta}}) \quad (25)$$

where  $\text{vec}^{-1}$  is the inverse vectorization operator defined as

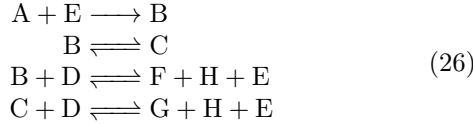
$$\text{vec}_{S, N_l}^{-1}(\hat{\boldsymbol{\delta}}) = \left( \text{vec}^\top(\mathbf{I}_{N_l}) \otimes \mathbf{I}_S \right) (\mathbf{I}_{N_l} \otimes \hat{\boldsymbol{\delta}})$$

The solution to the optimization problem (24) is not unique because the matrix  $\mathbf{D}$  in the optimization problem is not full column rank. This is because we explicitly left out the extents of reaction from the calculation due to the fact that the extent of reaction depends on the vector of unknown chemical rates  $\mathbf{r}$ . The advantage of this approach lies in the fact that we only consider reaction-free dynamics as opposed when we work in the mole basis. This is beneficial because the reaction dynamics are considered to be unknown. Furthermore, the estimation of the inlet

perturbation matrix  $\Delta\mathbf{X}_{\text{in}}$  is cast as a constrained linear optimization, simplifying the estimation procedure.

## 5. EXAMPLE: CSTR WITH RECYCLE

Consider the reaction process system composed of a CSTR and a separation unit. In such a process, the following reactions take place:



The reactant D is fed in excess, while the desired products are F, G, and H. Since the reactant E is also a byproduct in the subsequent reactions, and D is fed in excess, these two components are recycled to the feed of fresh D to ensure complete conversion of A and to promote the formation of the desired products. The recycled stream is cooled down to the same temperature  $T_{\text{in}}$  of the fresh feed. Additionally, the following variables are assumed to be measured: the inlet flow to the reactor  $F_{\text{in}}$ , i.e. the sum of the fresh feed and the recycled streams, all the species, the inverse residence time  $\zeta$ , and the temperature in the process. A representation of the process is illustrated in Figure 1.

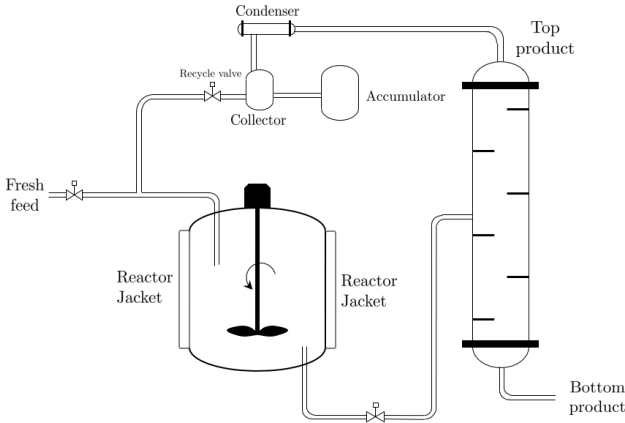


Fig. 1. Reaction process system of a CSTR and a separation unit with a recycle stream.

The stoichiometric matrix, the fresh feed composition matrix, and the initial conditions in the reactor are:

$$\mathbf{N} = \begin{bmatrix} -1 & 1 & 0 & 0 & -1 & 0 & 0 & 0 \\ 0 & -1 & 1 & 0 & 0 & 0 & 0 & 0 \\ 0 & -1 & 0 & -1 & 1 & 1 & 0 & 1 \\ 0 & 0 & -1 & -1 & 1 & 0 & 1 & 1 \end{bmatrix}$$

$$\mathbf{X}_{\text{in}}^{\circ} = [0 \ 0 \ 0 \ 1 \ 0 \ 0 \ 0 \ 0]^{\top}$$

$$\mathbf{n}_0 = [20 \ 0 \ 0 \ 0 \ 10 \ 0 \ 0 \ 0]^{\top} \text{ kmol}$$

After running the optimization (24), we obtain the following uncertainty matrix  $\Delta\mathbf{X}_{\text{in}}$

$$\Delta\hat{\mathbf{X}}_{\text{in}} = \begin{bmatrix} 0.001568 \\ 0.012116 \\ 0.012115 \\ -0.084900 \\ 0.031782 \\ 0.013654 \\ 0.013654 \\ 0.000010 \end{bmatrix} \quad (27)$$

and thus the corrected composition matrix  $\mathbf{X}_{\text{in}}$  is

$$\hat{\mathbf{X}}_{\text{in}} = \mathbf{X}_{\text{in}}^{\circ} + \Delta\hat{\mathbf{X}}_{\text{in}} = \begin{bmatrix} 0.001568 \\ 0.012116 \\ 0.012115 \\ 0.915100 \\ 0.031782 \\ 0.013654 \\ 0.013654 \\ 0.000010 \end{bmatrix} \quad (28)$$

In Figures 2 and 3 a comparison between the real extents computed from the data, the extents computed using  $\mathbf{X}_{\text{in}}^{\circ}$ , and the extents with  $\mathbf{X}_{\text{in}}^{\circ} + \Delta\mathbf{X}_{\text{in}}$ , respectively. The use of the corrected inlet composition matrix allows the extent representation to be approximately equal to the true extents using the actual time-varying inlet composition matrix. One of the reason for the small, though noticeable, differences is that we are trying to approximate a time-varying inlet composition matrix coming from the recycle of material in the process with a single matrix  $\mathbf{X}_{\text{in}} = \mathbf{X}_{\text{in}}^{\circ} + \Delta\mathbf{X}_{\text{in}}$ . This time-invariant corrected matrix will approximate the time variations on average based on the optimization (24). However, if the changes are not too abrupt, the recovery of a global inlet composition matrix can be achieved with the procedure described in the section 4.

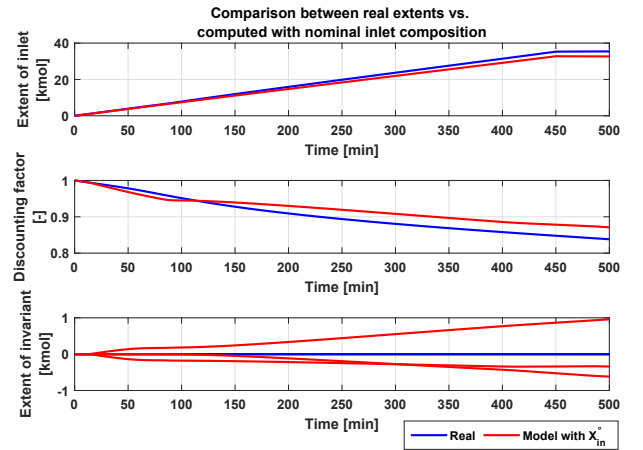


Fig. 2. Extents of inlets, invariant dynamics, and discounting factor computed using the nominal composition matrix  $\mathbf{X}_{\text{in}}^{\circ}$

Furthermore, in Table 1 the root mean-squared error (RMSE) of the corrected extents using  $\hat{\mathbf{X}}_{\text{in}}$  are presented and compared to the RMSE of the extent when the pseudo-extent. The RMSE of the corrected extents are naturally smaller than that of the pseudo-extents. However, these values are rather large because the approach presented here attempts to estimate a time-varying composition with a unique matrix based on recorded data. Nevertheless, the corrected extents  $\hat{\mathbf{x}}$  yields a good agreement with the true extent  $\mathbf{x}$ .

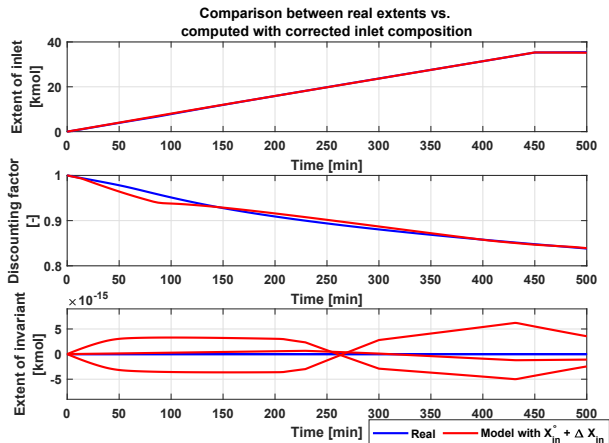


Fig. 3. Extents of inlets, invariant dynamics, and discounting factor computed using the corrected composition matrix  $\hat{\mathbf{X}}_{\text{in}}^{\circ} + \Delta \mathbf{X}_{\text{in}}$

Table 1. RMSE of pseudo-extents and the corrected extents to the true extent  $\hat{\mathbf{X}}_{\text{in}}$  in kmol

Pseudo-extent	Corrected extent
$w_{\text{in}}^{\text{rmse}} = 21.1426$	$\hat{x}_{\text{in}}^{\text{rmse}} = 1.4101$
$w_{\text{inv1}}^{\text{rmse}} = 31.7654$	$\hat{x}_{\text{inv1}}^{\text{rmse}} = 4.3802 \times 10^{-14}$
$w_{\text{inv2}}^{\text{rmse}} = 32.4806$	$\hat{x}_{\text{inv2}}^{\text{rmse}} = 3.7342 \times 10^{-14}$
$w_{\text{inv3}}^{\text{rmse}} = 1.1045$	$\hat{x}_{\text{inv3}}^{\text{rmse}} = 7.3545 \times 10^{-15}$
$w_{\lambda}^{\text{rmse}} = 4.8503$	$\hat{x}_{\lambda}^{\text{rmse}} = 0.4846$

## 6. CONCLUSIONS

The extents of reaction and inlets describe independent dynamics that account for different effects in the process. As such, the extents of reaction depend solely on the reaction, whereas the extents of inlet on the inlet flow going into the process. The mole balance can be independently represented in the mole basis or in the extent basis. However, a linear diffeomorphism that relates both spaces exists under specific rank conditions. If these conditions are not met, then the information obtained in one space cannot be translated into the other. However, the matrices related to the transformation must be well-known in order to obtain a reliable transformation. If part of the information of these matrices is not known, then the transformations will yield an inaccurate representation. Furthermore, a key variable is the inverse residence time, which acts as a time-varying pole of the system Márquez-Ruiz et al. (2020). The knowledge of this quantity is necessary to dynamically compute the extents, and to recover or estimate any information in the mole or extent spaces. One of the most common pieces of missing information is the inlet composition matrix, especially when the process has a recycle stream or a process is fed with the outlet of another process upstream. In such cases, the inlet composition matrix has other components apart from the normal reactants. A different composition matrix will produce different results in term of computation of extents and also in the prediction of the number of moles in the reacting mixture. Moreover, the estimation of the inlet composition uncertainty matrix can be addressed without information about the reaction, which is generally unknown in the process. This is one of the advantages of the extent-based representation. Furthermore, the lack of information in inlet composition will result in the non-uniqueness of the matrix. On the other hand, even when the uncertainty might not be unique, it still allows us to

compute a good estimation of the extent dynamics. The inlet composition uncertainty matrix can be computed solving an optimization problem that minimizes the error between the true extents and those computed using the incorrect inlet composition matrix. This matrix can be used to obtain a corrected inlet composition matrix, which can be employed to estimate other variables in the reaction system. Finally, as observed in the numerical example, the estimation procedure generates satisfactory results recovering extent dynamics very close to the true ones. This is usually the case if the changes in the composition are not too abrupt.

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