12th IFAC International Symposium on
Advanced Control of Chemical Processes
July 14-17, 2024. Toronto, Canada

Kinetic parameter estimation of reaction systems via dynamic regressor extension and mixing procedure

Thanh Sang Nguyen [*], **Ngoc Ha Hoang**[◇] [**,***], **Chee Keong Tan** [****], **Mohd Azlan Bin Hussain** [****]

[*] *Faculty of Chemical and Food Technology, HCMC University of Technology and Education, 01 Vo Van Ngan Street, Thu Duc City, 71307 Ho Chi Minh City, Vietnam (email: ntsang@hcmute.edu.vn)*
[**] *Institute of Research & Development, Duy Tan University, 550000 Da Nang, Vietnam (email: hoangngocha2@duytan.edu.vn)*
[***] *Faculty of Electrical-Electronic Engineering, Duy Tan University, 550000 Da Nang, Vietnam (email: ngocha.h@gmail.com)*
[****] *Department of Chemical Engineering, Faculty of Engineering, Universiti Malaya, 50603 Kuala Lumpur, Malaysia (email: {tanck,mohd_azlan}@um.edu.my)*

Abstract: This paper revisits two parameter estimation techniques, based on the gradient-descent (GD) and the least-square (LS) methods, to propose two novel estimators usable for estimating kinetic parameters in reaction systems. Typically, the activation energies of reactions appear in exponential terms of reaction rates, thereby resulting in non-separable nonlinearities while making the available techniques possibly worse. In this work, an overparameterized linear regression equation (LRE) is first derived, where reaction rates are computed from the vessel extents of reactions. On the one hand, we apply the dynamic regressor extension and mixing (DREM) procedure with a simple first-order differential operator to the LRE and then obtain the first estimator, called GD+D estimator. On the other hand, we adopt the technique, developed in Ortega *et al.* (2022), to design the second estimator, called LS+D estimator. Interestingly, the proposed estimators can estimate simultaneously all kinetic parameters and their convergence is ensured under the interval exciting condition that is more relaxed than the persistency of excitation. Simulations for the Van de Vusse reaction system illustrate the proposed estimators.

Keywords: Vessel extent, least squares, gradient-descent estimator, system identification, linear regression model.

1. INTRODUCTION

Non-isothermal chemical reactors that can be operated in batch, semi-batch or continuous mode in a process plant have a key role in producing high value products such as polymers and fine chemicals. In fact, from the first-principle modeling, a set of material and energy balance equations that constitutes a full-order lumped-parameter reactor model can be established to express the dynamics of state variables (Bequette, 1998). It should be noted that reaction rates are nonlinear functions of kinetic parameters, reactor temperature and molar concentrations of species (Alonso and Szederkényi, 2016). Since kinetic parameters are often determined from experiments, the reactor, therefore, belongs to a class of nonlinear systems having a large parameter uncertainty (Dochain, 2003). So far the online estimation methods for these parameters were intensively investigated in Dochain (1991, 2018), where the estimators were designed via the dynamics of reaction variants and invariants (Asbjørnsen, 1972). In these studies, only kinetic constants of the reactions were estimated, while their activation energies, appearing in exponential terms as described by the Arrhenius law, were assumed to be known. It is because the reaction rates are not separable, that is, they cannot be straightaway factorized as a product of a function of measurable or computable signals and the one of unknown parameters. As a result, simultaneously estimating both kinetic constants and activation energies is a challenging issue. To the best of our knowledge, there is no existing method applicable to it.

In this work, we shall first transform the original reactor model to an alternative model expressed in terms of vessel extents [1] by utilizing an one-to-one linear time-invariant (LTI) transformation in Hoang *et al.* (2020) (see also Rodrigues *et al.* (2015)). Within the transformed model, the reaction rates can be computed from the vessel extents of reactions. Then, the relationship between each reaction rate and its unknown kinetic parameters is formulated into an *overparameterized* linear regression equation (LRE) using the natural logarithm operator. Unfortunately, it will be shown later that the regressor in the LRE is not persistently exciting (PE), thereby limiting the applica-

[⋆] No funding was received for conducting this work.
[◇] Corresponding author.

[1] This concept can be considered as a generalized version of reaction variants and invariants in Asbjørnsen (1972).

bility of classical gradient method (Ortega *et al.*, 2020b). To circumvent this problem, on the one hand, the dynamic regressor extension and mixing (DREM) method, first introduced in Aranovskiy *et al.* (2017) and latter studied further in Ortega *et al.* (2020a); Korotina *et al.* (2022), is applied to construct a new extended LRE by using a simple first-order differential operator. From this, the first estimator, based on the gradient-descent (GD) technique, can be obtained. We shall, therefore, refer to it as GD+D estimator. On the other hand, the new least-square (LS) technique with time-varying forgetting factor, first reported in Ortega *et al.* (2022), is adopted to the *overparameterized* LRE that allows designing the second estimator, called LS+D estimator. The construction of the two proposed estimators for simultaneously estimating kinetic constants and activation energies is the main contribution of this work. Interestingly, the global asymptotic convergence of estimation error towards zero is ensured with a weaker excitation requirement, namely the interval excitation (IE) (Kreisselmeier and Rietze-Augst, 1990).

The rest of this paper is organized as follows. Section 2 briefly presents the model of Van de Vusse reaction system in a CSTR and its decoupled dynamics expressed in terms of vessel extents. The main results are developed in Section 3, while simulations in Section 4 illustrate the proposed estimators. Finally, the conclusion is given in Section 5.

Notation. $\mathbb{R}^n_{\geq 0}$ is the set of n-dimensional vectors of non-negative real elements. $\mathbf{0}_{m\times n}$ and $\mathbf{0}_m$ symbolize an $m \times n$ zero matrix and an m-dimensional zero column vector, respectively. Also, $\mathbf{I}_m$ is an identity matrix of dimension m. For any matrix $\mathbf{A}$, $\|\mathbf{A}\|, \det(\mathbf{A})$ and $\operatorname{adj}(\mathbf{A})$ denote the Euclidean norm, the determinant and the adjugate (or adjoint) of $\mathbf{A}$, i.e. $\mathbf{A}\operatorname{adj}(\mathbf{A}) = \det(\mathbf{A})\mathbf{I}$, respectively.

2. PRELIMINARIES

2.1 Vessel-extent-based reactor model

We consider here the Van de Vusse reaction system occurring in a non-isothermal continuous stirred tank reactor (CSTR). The system involves $S = 6$ species and $R = 3$ independent reactions. Its reaction stoichiometry is expressed as follows (Nguyen *et al.*, 2021) :

$$\mathrm{C_5H_6}\ (S_1) \xrightarrow[+\mathrm{H_2O}\ (S_5)]{\mathrm{r}_{v,1}} \mathrm{C_5H_7OH}\ (S_2) \xrightarrow[+\mathrm{H_2O}\ (S_5)]{\mathrm{r}_{v,2}} \mathrm{C_5H_8(OH)_2}\ (S_3)$$

$$2\mathrm{C_5H_6}\ (S_1) \xrightarrow{\mathrm{r}_{v,3}} \mathrm{C_{10}H_{12}}\ (S_4),$$

where H_2SO_4 as the 6^{th} component (S_6) is the catalyst of the reaction network. Besides, the CSTR is operated with $p = 2$ independent inlet streams and one outlet stream, whose the mass flowrates are denoted by $\mathbf{u}_{in}(t) = [\mathrm{u}_{in,1}(t), \mathrm{u}_{in,2}(t)]^{\mathrm{T}}$ and $\mathrm{u}_{out}(t)$. The following assumptions are made throughout the paper (we refer the readers to Nguyen *et al.* (2021); Bequette (1998) for a detailed interpretation of these assumptions).

- **A1** The reacting mixture is homogeneous, incompressible and ideal.
- **A2** The operation of the CSTR is under isobaric conditions.
- **A3** The rate of heat flow between the jacket and the reaction mixture is modeled by the constitutive heat-transfer equation as follows :

$$q_{ex}(t) = \lambda(T_J(t) - T(t)), \tag{1}$$

where λ is the heat exchange coefficient, $T_J(t)$ and $T(t)$ are the jacket temperature and the reactor one, respectively.

- **A4** The rate of the r^{th} reaction, denoted by $\mathrm{r}_{v,r}(t)$ with $r = 1, 2, 3$, is a separable function of $T(t)$ and the S-dimensional vector of concentrations of species, denoted by $\mathbf{c}(t)$. In other words, it can be factored into the following form (Alonso and Szederkényi, 2016) :

$$\mathrm{r}_{v,r}\big(\mathbf{c}(t), T(t)\big) = V(t)\,\mathrm{k}_r\big(T(t)\big)\,\psi_r\big(\mathbf{c}(t)\big), \tag{2}$$

where $V(t)$ is the time-dependent volume of the mixture (assumed to be available via measurements) and the function $\mathrm{k}_r(T(t))$ is given by the Arrhenius equation as follows :

$$\mathrm{k}_r(T(t)) = \mathrm{k}_{0,r}\exp\left(\frac{-E_{a,r}}{\mathrm{R}\,T(t)}\right), \tag{3}$$

with $\mathrm{k}_{0,r}$ the kinetic constant, $E_{a,r}$ the activation energy and R the ideal gas constant, while the function $\psi_r(\mathbf{c}(t))$ obeys the mass-action law, i.e.

$$\psi_r(\mathbf{c}(t)) = \prod_s \mathrm{c}_s^{|\nu_{rs}|}(t) \tag{4}$$

with ν_{rs} being the (suitably signed) stoichiometric coefficient of Species (i.e. Reactants) s in Reaction r.

Essentially, the mathematical model of the CSTR, including mole balance and enthalpy balance equations, can be written in a compact form using the $(S+1)$-dimensional vector $\mathbf{z}(t) = \begin{bmatrix}\mathbf{n}(t)\\ H(t)\end{bmatrix}$ as follows (Hoang *et al.*, 2020) :

$$\dot{\mathbf{z}}(t) = \mathcal{A}\,\mathbf{r}_v(t) + \mathbf{b}\,q_{ex}(t) + \mathcal{C}\,\mathbf{u}_{in}(t) - \omega(t)\,\mathbf{z}(t), \quad \mathbf{z}(0) = \mathbf{z}_0 \tag{5}$$

with the constant matrices $\mathcal{A} = \begin{bmatrix}\mathbf{N}^{\mathrm{T}}\\ 0\end{bmatrix}_{(S+1)\times R}$, $\mathbf{b} = \begin{bmatrix}\mathbf{0}_S\\ 1\end{bmatrix}$, $\mathcal{C} = \begin{bmatrix}\mathbf{W}_{in}\\ \check{\mathbf{h}}_{in}^{\mathrm{T}}\end{bmatrix}_{(S+1)\times p}$ and $\mathbf{z}_0 = \begin{bmatrix}\mathbf{n}_0\\ H_0\end{bmatrix}$, where

- $\mathbf{n}(t)$ is the S-dimensional vector of molar numbers, computed as $\mathbf{n}(t) = V(t)\,\mathbf{c}(t)$,
- $H(t)$ is the enthalpy of reacting mixture, given by $H(t) = \mathbf{h}^{\mathrm{T}}(t)\mathbf{n}(t)$ with $\mathbf{h}(t)$ being the vector of S component molar enthalpies of the outlet stream,
- $\mathbf{r}_v(t) = [\mathrm{r}_{v,1}(t)\ \mathrm{r}_{v,2}(t)\ \mathrm{r}_{v,3}(t)]^{\mathrm{T}}$ represents the vector of R reaction rates,
- $\mathbf{N} = \begin{bmatrix}-1 & 1 & 0 & 0 & -1 & 0\\ 0 & -1 & 1 & 0 & -1 & 0\\ -2 & 0 & 0 & 1 & 0 & 0\end{bmatrix}$ is the stoichiometric matrix,
- $\mathbf{W}_{in}$ is the $S \times p$ constant inlet-composition matrix,
- $\check{\mathbf{h}}_{in}^{\mathrm{T}}$ is the p-dimensional vector of inlet specific enthalpies,
- $\mathbf{n}_0$ and H_0 are the initial conditions of $\mathbf{n}(t)$ and $H(t)$, respectively,
- $\omega(t) := \frac{\mathrm{u}_{out}(t)}{m(t)} > 0$ is the dilution rate of the reaction system with $m(t)$ being the mass of reacting mixture.

In fact, Hoang *et al.* (2020) proved that if the conditions of $S \geq R + p + 1$ and $\operatorname{rank}([\mathcal{A}\ \mathbf{b}\ \mathcal{C}\ \mathbf{z}_0]) = R + p + 2$ hold, there exists a non-singular square matrix, defined as :

$$\mathcal{T} := [\mathcal{A}\ \mathbf{b}\ \mathcal{C}\ \mathbf{z}_0\ \mathbf{P}]^{-1}, \tag{6}$$

with the matrix $\mathbf{P}_{(S+1)\times q}$ (with $q := S - R - p - 1 \geq 0$) satisfying $[\mathcal{A}\ \mathbf{b}\ \mathcal{C}\ \mathbf{z}_0]^{\mathrm{T}}\mathbf{P} = \mathbf{0}_{(R+p+2)\times q}$. More importantly, the constant matrix $\mathcal{T}$ implies an one-to-one LTI transformation from $\mathbf{z}(t)$ to $\mathbf{x}(t)$, the space of vessel extents, as recalled in the following lemma.

Lemma 1. (Hoang *et al.*, 2020) The transformation from $\mathbf{z}(t)$ to $\mathbf{x}(t)$ via $\mathcal{T}$ is expressed by :

$$\mathbf{x}(t) := [\mathbf{x}_r^{\mathrm{T}}(t)\ \mathrm{x}_{ex}(t)\ \mathbf{x}_{in}^{\mathrm{T}}(t)\ \mathrm{x}_{ic}(t)\ \mathbf{x}_{iv}^{\mathrm{T}}]^{\mathrm{T}} = \mathcal{T}\,\mathbf{z}(t), \quad (7)$$

that brings the dynamic reactor model (5) to the following decoupled form :

$$\dot{\mathbf{x}}_r(t) = \mathbf{r}_v(t) - \omega(t)\,\mathbf{x}_r(t), \qquad \mathbf{x}_r(0) = \mathbf{0}_R, \quad (8a)$$

$$\dot{\mathrm{x}}_{ex}(t) = q_{ex}(t) - \omega(t)\,\mathrm{x}_{ex}(t), \qquad \mathrm{x}_{ex}(0) = 1, \quad (8b)$$

$$\dot{\mathbf{x}}_{in}(t) = \mathbf{u}_{in}(t) - \omega(t)\,\mathbf{x}_{in}(t), \qquad \mathbf{x}_{in}(0) = \mathbf{0}_p, \quad (8c)$$

$$\dot{\mathrm{x}}_{ic}(t) = -\omega(t)\,\mathrm{x}_{ic}(t), \qquad \mathrm{x}_{ic}(0) = 1, \quad (8d)$$

$$\mathbf{x}_{iv} = \mathbf{0}_q, \quad (8e)$$

where $\mathbf{x}_r(t) \in \mathbb{R}^R_{\geq 0}$ and $\mathbf{x}_{in}(t) \in \mathbb{R}^p_{\geq 0}$ correspond to the vector of vessel extents of reactions and inlet flows at time t, while $\mathrm{x}_{ex}(t) \in \mathbb{R}$ and $\mathrm{x}_{ic}(t) \in \mathbb{R}_{\geq 0}$ represent the vessel extent of heat exchange and the dimensionless vessel extent of initial conditions at time t, respectively. Additionally, $\mathbf{x}_{iv}$ is the remaining invariant part with the dimension of q. Furthermore, from $\mathbf{x}(t)$, the original state vector $\mathbf{z}(t)$ can be reconstructed as follows :

$$\mathbf{z}(t) = \mathcal{A}\,\mathbf{x}_r(t) + \mathbf{b}\,\mathrm{x}_{ex}(t) + \mathcal{C}\,\mathbf{x}_{in}(t) + \mathbf{z}_0\,\mathrm{x}_{ic}(t). \quad (9)$$

Remark 1. The dynamics of $\mathrm{x}_{ic}(t)$ (8d) is exponentially stabilized at zero due to $\omega(t) > 0$, and the invariant part $\mathbf{x}_{iv}$ (8e) is identical to $\mathbf{0}_q$.

Remark 2. Without the knowledge of the kinetic parameters, the vector of reaction rates $\mathbf{r}_v(t)$ can be calculated from the partial measurements of $R - 1$ mole numbers and the reactor temperature $T(t)$ via an extent-based procedure as proposed in Nguyen *et al.* (2021). On this basis, $\mathbf{r}_v(t)$ can be considered as a computable signal to estimate all unknown kinetic parameters.

2.2 Problem formulation

In this work, the kinetic parameters of reactions, i.e. $k_{0,r}$ and $E_{a,r}$ with $r = 1, 2, 3$, are considered to be unknown. And, we are interested in simultaneously estimating them. The following lemma gives a set of *overparameterized* LREs that shows the relationship between these unknown parameters and the computable signals.

Lemma 2. Under Assumption **A4**, the reaction system (5) satisfies the following LREs :

$$\mathrm{y}_r(t) = \boldsymbol{\phi}^{\mathrm{T}}(t)\,\boldsymbol{\theta}_r, \quad r = 1, 2, 3 \quad (10)$$

where $\mathrm{y}_r(t) := \ln\left(\dfrac{\mathrm{r}_{v,r}(t)}{V(t)\,\psi_r(t)}\right)$ is a computable signal, $\boldsymbol{\phi}^{\mathrm{T}}(t) = [\phi_1\ \phi_2(t)]^{\mathrm{T}} := \left[1\ \dfrac{-1}{T(t)}\right]$ is a regressor and $\boldsymbol{\theta}_r = [\theta_{r,1}\ \theta_{r,2}]^{\mathrm{T}} := \left[\ln(k_{0,r})\ \dfrac{E_{a,r}}{\mathrm{R}}\right]^{\mathrm{T}}$ is an unknown constant vector of the r^{th} reaction. Moreover, the regressor $\boldsymbol{\phi}(t)$ is not persistently exciting (PE), that is, there is no positive constant t_r and δ_r such that the inequality :

$$\int_t^{t+t_r} \boldsymbol{\phi}(\tau)\,\boldsymbol{\phi}^{\mathrm{T}}(\tau)d\tau \geq \delta_r\,\mathbf{I}_2, \quad (11)$$

holds for all $t \geq 0$.

Proof. It can be clearly seen from (2) that the function $\mathrm{k}_r(T(t))$ can be expressed as follows :

$$\mathrm{k}_r(T(t)) = \frac{\mathrm{r}_{v,r}(t)}{V(t)\,\psi_r(t)}. \quad (12)$$

Then, by substituting (3) into (12) and applying the natural logarithm operator to its both sides, one obtains :

$$\ln\left(\frac{\mathrm{r}_{v,r}(t)}{V(t)\,\psi_r(t)}\right) = \ln(k_{r,0}) - \frac{1}{T(t)}\,\frac{E_{a,r}}{\mathrm{R}}, \quad (13)$$

which can be subsequently written into the form of (10).

Moreover, let $\overline{T}$ be the steady-state value of $T(t)$ when the time t goes to infinity, i.e. $\lim_{t\to\infty} T(t) = \overline{T}$, the regressor $\boldsymbol{\phi}(t)$ then fulfills the following equality :

$$\lim_{t\to\infty}(\boldsymbol{\phi}(t)\,\boldsymbol{\phi}^{\mathrm{T}}(t)) = \lim_{t\to\infty}\begin{bmatrix} 1 & \dfrac{-1}{T(t)} \\ \dfrac{-1}{T(t)} & \dfrac{1}{T^2(t)} \end{bmatrix} = \begin{bmatrix} 1 & \dfrac{-1}{\overline{T}} \\ \dfrac{-1}{\overline{T}} & \dfrac{1}{\overline{T}^2} \end{bmatrix}. \quad (14)$$

Hence, one can see that

$$\lim_{t\to\infty}\int_t^{t+t_r} \boldsymbol{\phi}(\tau)\,\boldsymbol{\phi}^{\mathrm{T}}(\tau)d\tau - \delta_r\,\mathbf{I}_2 = \begin{bmatrix} t_r - \delta_r & \dfrac{-t_r}{\overline{T}} \\ \dfrac{-t_r}{\overline{T}} & \dfrac{t_r}{\overline{T}^2} - \delta_r \end{bmatrix}, \quad (15)$$

whose right-hand side is positive semi-definite if and only if the following conditions regarding all (leading and non-leading) principal minors :

$$t_r - \delta_r \geq 0, \quad (16a)$$

$$(t_r - \delta_r)\left(\frac{t_r}{\overline{T}^2} - \delta_r\right) - \frac{t_r^2}{\overline{T}^2} \geq 0, \quad (16b)$$

$$\frac{t_r}{\overline{T}^2} - \delta_r \geq 0, \quad (16c)$$

are met for some $t_r, \delta_r > 0$ (Shores, 2007). Nonetheless, it can be verified that they contradict each other, thereby leading to the non-existence of any $t_r, \delta_r > 0$ to fulfill the inequality (11) for t being sufficiently large. As a result, the regressor $\boldsymbol{\phi}(t)$ is not PE (Ortega *et al.*, 2020b). The latter concludes the proof. □

Remark 3. For the case when one of kinetic parameters of reactions, i.e. either $k_{0,r}$ or $E_{a,r}$, is assumed to be known, a set of (standard, that is, the number of equations equals the one of unknowns) LREs can be obtained, which has the same form as given in (10). In this case, the regressor $\phi(t)$ is PE, hence the simplified parameter estimation problem is straightforward (even trivial).

Essentially, Wang *et al.* (2023) proved that the LRE (10) is *identifiable* [2] that allows solving the kinetic estimation problem, if the regressor $\boldsymbol{\phi}(t)$ is interval exciting (IE), which is a *necessary* condition strictly weaker than PE one. Therefore, we shall impose it in the following assumption.

A5 The bounded regressor $\boldsymbol{\phi}(t)$ is IE, that is, there exists a positive scalar δ_r and a time instant t_r such that the following integral inequality :

[2] From the mathematical viewpoint, this term means there exists two different constants t_1 and t_2 such that $\mathrm{rank}\,([\boldsymbol{\phi}(t_1)\,|\,\boldsymbol{\phi}(t_2)]) = 2$.

$$\int_0^{t_r} \boldsymbol{\phi}(\tau)\,\boldsymbol{\phi}^{\mathrm{T}}(\tau)d\tau \geq \delta_r\,\mathbf{I}_2 \tag{17}$$

is satisfied (Kreisselmeier and Rietze-Augst, 1990).

3. MAIN RESULTS

3.1 The construction of GD+D estimator

In this subsection, the first step to estimate the vectors of unknown parameters $\boldsymbol{\theta}_r$ with $r = 1, 2, 3$ is to apply the DREM procedure to the LRE (10) to generate a new scalar LRE. Then, a GD+D estimator can be constructed as represented in the following proposition.

Proposition 1. Let consider the LRE (10) with $\boldsymbol{\phi}(t)$ verifying Assumption **A5**, and define the vector $\mathbf{Y}_r(t) := \begin{bmatrix} \mathrm{y}_r(t) \\ \mathrm{y}_{f,r1}(t) \end{bmatrix}$ and the matrix $\boldsymbol{\Phi}_r^{\mathrm{T}}(t) := \begin{bmatrix} \phi_1 & \phi_2(t) \\ \phi_{f,r1}(t) & \phi_{f,r2}(t) \end{bmatrix}$, where the signals of $\mathrm{y}_{f,r1}(t)$, $\phi_{f,r1}(t)$ and $\phi_{f,r2}(t)$ are generated by the following differential equations :

$$\dot{\mathrm{y}}_{f,r1}(t) = -\,b_r\,\mathrm{y}_{f,r1}(t) + a_r\,\mathrm{y}_r(t), \quad \mathrm{y}_{f,r1}(0) = 0, \tag{18a}$$

$$\dot{\phi}_{f,r1}(t) = -\,b_r\,\phi_{f,r1}(t) + a_r\,\phi_1, \qquad \phi_{f,r1}(0) = 0, \tag{18b}$$

$$\dot{\phi}_{f,r2}(t) = -\,b_r\,\phi_{f,r2}(t) + a_r\,\phi_2(t), \quad \phi_{f,r2}(0) = 0, \tag{18c}$$

with $a_r \neq 0$ and $b_r \geq 0$ being tuning parameters. Then, the following claims hold

(i) an extended set of two LREs is expressed as follows :

$$\mathbf{Y}_r(t) = \boldsymbol{\Phi}_r^{\mathrm{T}}(t)\,\boldsymbol{\theta}_r, \tag{19}$$

(ii) the GD+D estimator :

$$\dot{\widehat{\boldsymbol{\theta}}}_r(t) = \Gamma_r\,\Delta_r(t)\,\left[\mathcal{Y}_r(t) - \Delta_r(t)\,\widehat{\boldsymbol{\theta}}_r(t)\right], \ \widehat{\boldsymbol{\theta}}_r(0) = \widehat{\boldsymbol{\theta}}_{r,0}, \tag{20}$$

with $\mathcal{Y}_r(t) := \mathrm{adj}\,(\boldsymbol{\Phi}_r^{\mathrm{T}}(t))\,\mathbf{Y}_r(t)$ and $\Delta_r(t) := \det\,(\boldsymbol{\Phi}_r^{\mathrm{T}}(t))$, where $\Gamma_r > 0$ is a gain matrix, ensures that $\lim_{t\to\infty} \widetilde{\boldsymbol{\theta}}_r(t) = \boldsymbol{\theta}_r$, if $\Delta_r(t)$ is not square-integrable over $\mathbb{R}_{\geq 0}$, i.e. $\int_0^{+\infty} |\Delta_r^2(\tau)|d\tau = +\infty$ or $\Delta_r(t) \notin \mathcal{L}_2$ over $\mathbb{R}_{\geq 0}$.

Proof. To prove the claim (i), the first-order differential operator $\mathrm{H}_r(\mathfrak{p})$, given by :

$$\mathrm{H}_r(\mathfrak{p}) = \frac{a_r}{\mathfrak{p} + b_r}, \tag{21}$$

with $\mathfrak{p} := \dfrac{\mathrm{d}}{\mathrm{d}t}$, is applied to both sides of the LRE (10), which yields the following LRE :

$$\mathrm{y}_{f,r1}(t) = \boldsymbol{\phi}_{f,r}^{\mathrm{T}}(t)\,\boldsymbol{\theta}_r, \tag{22}$$

with $\boldsymbol{\phi}_{f,r}^{\mathrm{T}}(t) := [\phi_{f,r1}(t)\ \phi_{f,r2}(t)]$, where $\mathrm{y}_{f,r1}(t)$, $\phi_{f,r1}(t)$ and $\phi_{f,r2}(t)$ are generated from (18a), (18b) and (18c), respectively. Writing the equations (10) and (22) into a compact form then yields a system of two LREs as (19).

Furthermore, we have the following equation :

$$\mathcal{Y}_r(t) = \Delta_r(t)\,\boldsymbol{\theta}_r, \tag{23}$$

by premultiplying from the left both sides of (19) by $\mathrm{adj}\,(\boldsymbol{\Phi}_r^{\mathrm{T}})$ and noting that $\Delta_r(t)\,\mathbf{I}_2 = \mathrm{adj}\,(\boldsymbol{\Phi}_r^{\mathrm{T}})\,\boldsymbol{\Phi}_r^{\mathrm{T}}$. Substituting $\mathcal{Y}_r(t)$ from (23) into (20) subsequently leads to the dynamics of estimation error: $\widetilde{\boldsymbol{\theta}}_r(t) := \widehat{\boldsymbol{\theta}}_r(t) - \boldsymbol{\theta}_r$, as follows :

$$\dot{\widetilde{\boldsymbol{\theta}}}_r(t) = -\Gamma_r\,\Delta_r^2(t)\,\widetilde{\boldsymbol{\theta}}_r(t), \tag{24}$$

which can be solved analytically by :

$$\widetilde{\boldsymbol{\theta}}_r(t) = \widetilde{\boldsymbol{\theta}}_r(0)\exp\left(-\Gamma_r\int_0^t \Delta_r^2(\tau)\mathrm{d}\tau\right). \tag{25}$$

Consequently, if the condition of $\Delta_r(t) \notin \mathcal{L}_2$ over $\mathbb{R}_{\geq 0}$ holds, the global asymptotic convergence of $\widehat{\boldsymbol{\theta}}_r(t)$ to $\boldsymbol{\theta}_r$, i.e. $\lim_{t\to\infty} \widetilde{\boldsymbol{\theta}}_r(t) = \mathbf{0}_2$, is ensured, thereby proving the claim (ii). The latter concludes the proof □

Remark 4. Instead of the operator $\mathrm{H}_r(\mathfrak{p})$ (21), a general single-input single-output operator, introduced in Ortega *et al.* (2020a), can be utilized to generate a scalar LRE having the same form as (22) with more degrees of freedom. But, it certainly requires more computational demands.

3.2 The construction of LS+D estimator

In this subsection, we shall present the second estimator, called LS+D estimator, to solve the estimation problem for the LRE (10). It is designed by interlacing the LS algorithm with time-varying forgetting factor and the DREM procedure as given in the following proposition. It should be noted that the estimation method was originally published in Ortega *et al.* (2022).

Proposition 2. Let consider the LRE (10) with $\boldsymbol{\phi}(t)$ verifying Assumption **A5**. The LS+D estimator can be then constructed as follows :

$$\dot{\widehat{\boldsymbol{\eta}}}_r(t) = \alpha_r\,\mathbf{F}(t)\,\boldsymbol{\phi}(t)\,(\mathrm{y}_r(t) - \boldsymbol{\phi}^{\mathrm{T}}(t)\,\widehat{\boldsymbol{\eta}}_r(t))\,, \ \widehat{\boldsymbol{\eta}}_r(0) = \widehat{\boldsymbol{\eta}}_{r,0} \tag{26a}$$

$$\dot{\mathbf{F}}(t) = -\,\alpha_r\,\mathbf{F}(t)\,\boldsymbol{\phi}(t)\,\boldsymbol{\phi}^{\mathrm{T}}(t)\,\mathbf{F}(t) + \beta_r(t)\,\mathbf{F}(t), \quad \mathbf{F}(0) = \frac{1}{f_0}\mathbf{I}_2, \tag{26b}$$

$$\dot{\widehat{\boldsymbol{\theta}}'}_r(t) = \mathit{\Gamma}_r\,\mathit{\Delta}_r\left(\mathscr{Y}_r(t) - \mathit{\Delta}_r\,\widehat{\boldsymbol{\theta}'}_r(t)\right), \ \widehat{\boldsymbol{\theta}'}_r(0) = \widehat{\boldsymbol{\theta}'}_{r,0}, \tag{26c}$$

$$\dot{z}_r(t) = \beta_r(t)\,z_r(t), \qquad z_r(0) = 1, \tag{26d}$$

with the definition of :

$$\beta_r(t) := \beta_{r,0}\left(1 - \frac{||\mathbf{F}(t)||}{M}\right), \tag{27a}$$

$$\mathit{\Delta}_r(t) := \det\,(\mathbf{I}_2 - z_r(t) f_0\,\mathbf{F}(t))\,, \tag{27b}$$

$$\mathscr{Y}_r(t) := \mathrm{adj}\,(\mathbf{I}_2 - z_r(t) f_0\,\mathbf{F}(t))\,(\widehat{\boldsymbol{\eta}}_r(t) - z_r(t) f_0\,\mathbf{F}(t)\,\widehat{\boldsymbol{\eta}}_{r,0})\,, \tag{27c}$$

with $r = 1, 2, 3$, where $\alpha_r > 0, \beta_{r,0} > 0, f_0 > 0, M \geq \dfrac{1}{f_0}$ are tuning parameters, and $\mathit{\Gamma}_r > 0$ is an adaption gain matrix. Then, the proposed estimator guarantees that $\lim_{t\to\infty} \widehat{\boldsymbol{\theta}'}_r(t) = \boldsymbol{\theta}_r$ with all signals bounded.

Proof. From the LRE (10), a set of two extended LREs can be constructed as follows :

$$\boldsymbol{Y}_r(t) = \Theta_r(t)\,\boldsymbol{\theta}_r, \tag{28}$$

where $\boldsymbol{Y}_r(t)$ and $\Theta_r(t)$ are expressed by the following differential equations :

$$\dot{\boldsymbol{Y}}_r(t) + \alpha_r\,\mathbf{F}(t)\,\boldsymbol{\phi}(t)\,\boldsymbol{\phi}^{\mathrm{T}}(t)\,\boldsymbol{Y}_r(t) = \alpha_r\,\mathbf{F}(t)\,\boldsymbol{\phi}(t)\,\mathrm{y}_r(t), \tag{29a}$$

$$\dot{\Theta}_r(t) + \alpha_r\,\mathbf{F}(t)\,\boldsymbol{\phi}(t)\,\boldsymbol{\phi}^{\mathrm{T}}(t)\,\Theta_r(t) = \alpha_r\,\mathbf{F}(t)\,\boldsymbol{\phi}(t)\,\boldsymbol{\phi}^{\mathrm{T}}(t), \tag{29b}$$

with $\boldsymbol{Y}_r(0) = \mathbf{0}_2$ and $\Theta_r(0) = \mathbf{0}_{2\times 2}$. It was shown in Ortega *et al.* (2022, Proposition 3) that their analytical solutions are given by :

$$\boldsymbol{Y}_r(t) := \widehat{\boldsymbol{\eta}}_r(t) - z_r(t)\, f_0\, \mathbf{F}(t)\, \widehat{\boldsymbol{\eta}}_{r,0}, \tag{30a}$$

$$\Theta_r(t) := \mathbf{I}_2 - z_r(t)\, f_0\, \mathbf{F}(t). \tag{30b}$$

From this, by premultiplying from the left both sides of (28) by $\mathrm{adj}\,(\Theta_r(t))$, we obtain a new LRE as follows :

$$\mathscr{Y}_r(t) = \Delta_r(t)\, \boldsymbol{\theta}_r, \tag{31}$$

with $\Delta_r(t)$ and $\mathscr{Y}_r(t)$ defined from (27b) and (27c), respectively, that allows designing the estimator (26c). Noting that its stability analysis can be found in Ortega *et al.* (2022, Proposition 1). The latter concludes the proof. □

Remark 5. In this work, the design of the LS-D estimator is different as compared to Pyrkin *et al.* (2023) since kinetic constants, i.e. $\mathrm{k}_{0,r}$, are not assumed to be known. Also, instead of employing the dynamics of chemical invariants, the extent-based reactor model (8) is exploited here to construct the LRE (10) usable for simultaneously estimating all kinetic parameters, i.e. $\mathrm{k}_{0,r}$ and $E_{a,r}$.

4. SIMULATIONS

In this section, the CSTR is initiated at $T_0 = 388$ (K) and $\mathbf{n}_0 = [1.4\ 1.6\ 11\ 0.4242\ 447\ 5.102]^{\mathrm{T}}$ (kmol) under the operation of $T_J = 370.8$ (K) and $\mathbf{u}_{in} = [12\ 24]^{\mathrm{T}}$ (kg/h). Also, the reactor is operated such that the total mass of reacting mixture is kept unchanged at $m = 10$ (kg), leading to the constraint: $\mathrm{u}_{in,1} + \mathrm{u}_{in,2} = \mathrm{u}_{out} = 36$ (kg/h). Besides, the coefficient $\lambda = 866880$(W/K) and the matrix

$$\mathbf{W}_{in}^{\mathrm{T}} = \begin{bmatrix} \frac{0.3}{66} & 0 & 0 & 0 & \frac{0.7}{18} & 0 \\ 0 & 0 & 0 & 0 & \frac{0.925}{18} & \frac{0.075}{98} \end{bmatrix} \text{(kmol/kg)},$$

are chosen; and the vector $\check{\mathbf{h}}_{in} = [-10269\ -14890]^{\mathrm{T}}$ (kJ/kg) is obtained with $T_{in,1} = T_{in,2} = 403.3$ (K).

4.1 The GD+D estimator

To implement the GD+D estimator in Proposition 1, the tuning parameters and the gain matrix are selected as follows: $a_r = 2000$, $b_r = 0.01$ and $\Gamma_r = \gamma_a \mathbf{I}_2$ with $r = 1, 2, 3$, where $\gamma_a > 0$ is a parameter to adjust Γ_r, i.e. to ensure that $\Gamma_r\, \Delta_r(t)$ is large enough during the operation. From this, the convergence of $\widehat{\boldsymbol{\theta}}_r(t)$ to its exact value can be achieved. Also, initial values of the estimator are taken as $\widehat{\boldsymbol{\theta}}_{1,0} = [10\ 4000]^{\mathrm{T}}$,$\widehat{\boldsymbol{\theta}}_{2,0} = [5\ 3000]^{\mathrm{T}}$, and $\widehat{\boldsymbol{\theta}}_{3,0} = [12\ 2000]^{\mathrm{T}}$.

As represented in Figure 1, all the vectors $\widehat{\boldsymbol{\theta}}_r(t) = \left[\widehat{\theta}_{r,1}(t)\ \widehat{\theta}_{r,2}(t)\right]^{\mathrm{T}}$ with $r = 1, 2, 3$ asymptotically approach their respective exact values without oscillation due to the monotonic non-increase of estimation errors. On this basis, the kinetic constants and the activation energies of three reactions are simultaneously calculated. In addition, as γ_a increases, the rising time of the transient responses diminishes. Hence, the increase in γ_a can accelerate arbitrarily the convergence rate of the GD+D estimator.

4.2 The LS+D estimator

The LS+D estimator in Proposition 2 is implemented with the tuning parameters: $\alpha_r = 30, \beta_{r,0} = 250, f_0 = 0.1$ and $M = 10.5$, and $\mathit{\Gamma}_r = \gamma_b \mathbf{I}_2$ with $r = 1, 2, 3$, where $\gamma_b >$ is a parameter for modifying $\mathit{\Gamma}_r$, i.e. to guarantee that $\mathit{\Gamma}_r\, \Delta_r(t)$ is sufficiently large. From this, the convergence of the estimator is ensured. Moreover, the estimator is initiated at $\widehat{\boldsymbol{\eta}}_{1,0} = \widehat{\boldsymbol{\eta}}_{2,0} = [27\ 9750]^{\mathrm{T}}$,$\widehat{\boldsymbol{\eta}}_{3,0} = [20\ 8500]^{\mathrm{T}}$, $\widehat{\boldsymbol{\theta}'}_{1,0} = [10\ 4000]^{\mathrm{T}}$,$\widehat{\boldsymbol{\theta}'}_{2,0} = [5\ 3000]^{\mathrm{T}}$, and $\widehat{\boldsymbol{\theta}'}_{3,0} = [12\ 2000]^{\mathrm{T}}$.

Figure 2 shows the global asymptotic convergence of $\widehat{\boldsymbol{\theta}'}_r(t) = \left[\widehat{\theta'}_{r,1}(t)\ \widehat{\theta'}_{r,2}(t)\right]^{\mathrm{T}}$ with $r = 1, 2, 3$ towards their respective true values under the LS+D estimator. From this, all the kinetic parameters of three reactions can be estimated simultaneously from $\widehat{\boldsymbol{\theta}'}_r(t)$. Moreover, it can be seen that by increasing γ_b, we can decrease the rising time of $\widehat{\boldsymbol{\theta}'}_r(t)$ that is instrumental in enhancing the transient performance of the proposed estimator.

Note that the convergence time of estimated values under the GD+D estimator (20) is faster than the LS+D estimator (26c). However, the latter estimator seems to be more robust in the presence of noise (Slotine and Li, 1991). This feature is currently under consideration.

5. CONCLUSION

This paper has proposed two different solutions to estimate kinetic constants and activation energies of a reaction system simultaneously. The first one, called the GD+D estimator, is developed by combining the DREM procedure with a simple first-order differential operator and the GD technique. The second one is the LS+D estimator that is designed from the LS technique with time-varying forgetting factor, derived in Ortega *et al.* (2022). It is important to note that the convergence of these two estimators is guaranteed with the IE condition, which is strictly weaker than the PE one. Simulations of the Van de Vusse reaction system illustrate their effectiveness. In addition to a comparative analysis of the two proposed estimators, an extension of the obtained results to heterogeneous reactors and their combination with controllers to design adaptive control systems will be part of our future work.

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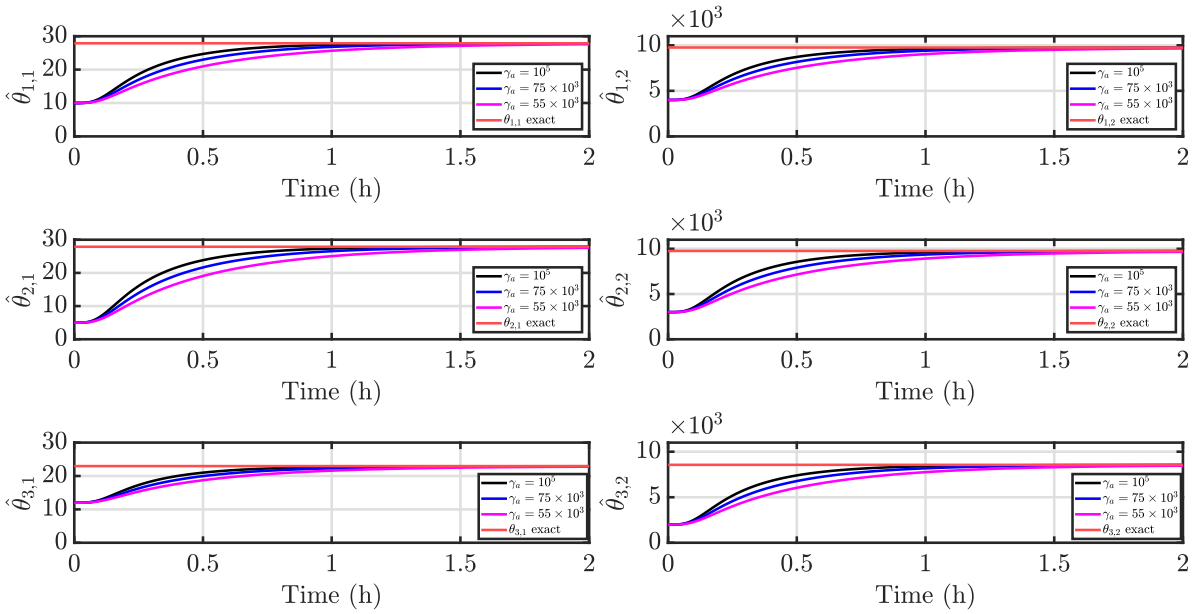

Fig. 1. Time responses of $\widehat{\boldsymbol{\theta}}_r(t)$ with $r = 1, 2, 3$ under the GD+D estimator

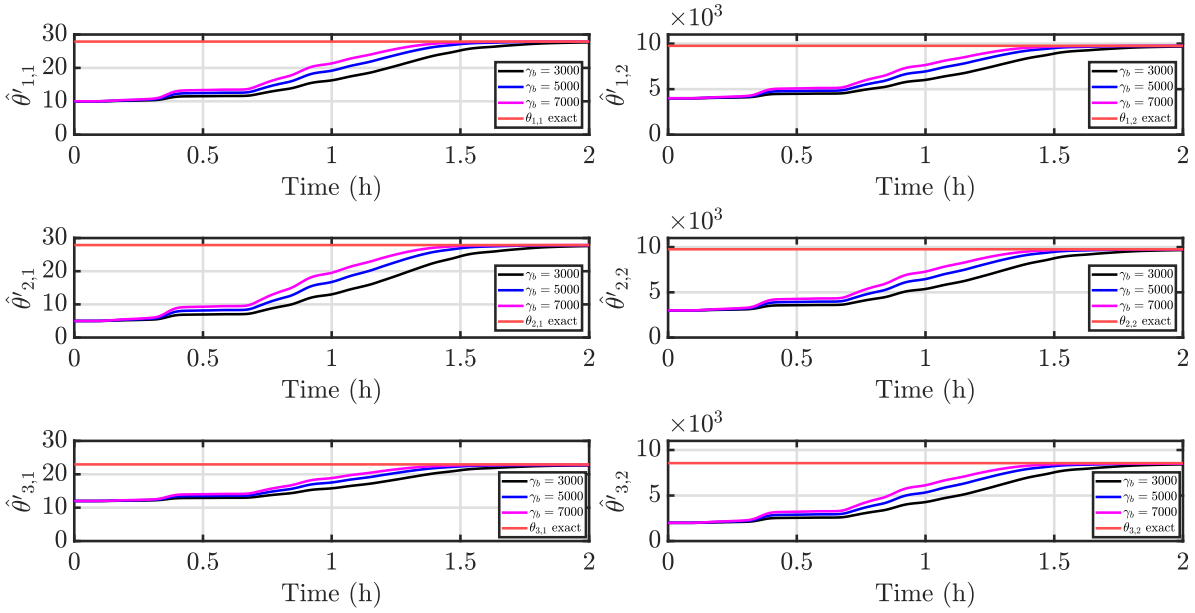

Fig. 2. Time responses of $\widehat{\boldsymbol{\theta}'}_r(t)$ with $r = 1, 2, 3$ under the LS+D estimator

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