

Design of Kinetic Parameter Estimators for Reaction Systems: A Dynamic Regressor Extension and Mixing Procedure Approach

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Abstract. This paper aims to design a globally convergent estimator for estimating kinetic parameters of reaction rates, namely activation energies and kinetic constants, using a dynamic regressor extension and mixing (DREM) procedure approach. It is important to note that the appearance of activation energies in exponential terms, from the modeling perspective of the Arrhenius law, leads to non-separable nonlinearities, thereby limiting the applicability of the standard gradient-descent (SGD) estimator. To address this challenging issue, we first propose an overparameterized linear regression equation, where reaction rates are computed using the extent-based reactor model. The DREM procedure with a second-order differential operator is then applied to this equation for designing a modified gradient-descent (MGD) estimator. Interestingly, all kinetic parameters can be estimated simultaneously under an interval excitation condition, which is weaker than the persistently exciting condition. Simulations of the reaction system that synthesizes glycerol ($C_3H_8O_3$) via the hydration of 2-3-epoxy-1-propanol ($C_3H_6O_2$) in a non-isothermal continuous stirred tank reactor illustrate the proposed MGD estimator.

Keywords: Chemical Reactor, Gradient-descent Estimator, Interval Excitation, Linear Regression Model, System Identification, Vessel Extent

INTRODUCTION

In industry, high-value products such as fine chemicals and polymers are synthesized from raw materials in non-isothermal reactors, which can be operated in batch, semi-batch, or continuous mode to meet

customer demands. To ensure safe and efficient operation, it is vitally necessary to construct a reliable mathematical model of reaction systems that complies with control requirements and safety specifications. According to the first principles of process modeling, a full-order reactor model is

developed from material and energy balance equations, which are of differential and play a key role in describing the mutual interactions between reaction progress and thermal effects over a wide range of operating conditions (Bequette, 1998). Within this framework, reaction rates are nonlinear functions expressed in terms of kinetic parameters, molar concentrations of components, and reactor temperature (Dochain, 2003; Levenspiel, 1998). Since kinetic parameters, including kinetic constants and activation energies, are typically determined experimentally, they introduce substantial uncertainty into the reactor model (Fogler *et al.*, 2025), thereby making accurate online estimation of these parameters a critical and practically relevant problem.

A key mathematical obstacle arises from the Arrhenius law, describing the temperature-dependent part of each reaction rate as an exponential function of the activation energy. This, therefore, renders the reaction rate functions non-separable; that is, they cannot be expressed as a product of a function of measurable or computable signals and another function that depends solely on unknown parameters (Ortega *et al.*, 2024). Due to this non-separability, online estimation methods in the previous studies (Dochain, 1991, 2003, 2018; Pyrkin *et al.*, 2023), which exploit the dynamics of reaction variant and invariant states (Asbjørnsen, 1972), are constrained to treat activation energies as a priori known parameters, leaving only the kinetic constants to be estimated. To the best of the authors' knowledge, the concurrent estimation of both kinetic constants and activation energies remains an open, challenging issue.

To overcome this bottleneck, the present paper proposes a new estimation framework

that unfolds in three steps. In the first step, we transform the original reactor model into an equivalent model, expressed in terms of vessel extents by using a one-to-one linear time-invariant (LTI) transformation (Hoang *et al.*, 2020; Rodrigues *et al.*, 2015). It is worth noting that the concept of vessel extents can be regarded as a generalization of the reaction variant and invariant states introduced by Asbjørnsen (1972). Additionally, the LTI transformation decouples the state dynamics. It enables the explicit computation of reaction rates, since each vessel extent variable, which has a clear physical meaning, depends on a single respective rate process. In the second step, by applying the natural logarithm operator to the relationship between each reaction rate and the unknown kinetic parameters yields an overparameterized linear regression equation (LRE) that can be formulated into a compact matrix form. Nevertheless, it is shown later that the regressor of this LRE does not satisfy the persistently exciting (PE) condition required by standard gradient-descent (SGD)-based estimators (Ortega *et al.*, 2020; Pyrkin *et al.*, 2023; Barabanov & Ortega, 2017; Efimov *et al.*, 2019). To address this limitation, in the third step, the dynamic regressor extension and mixing (DREM) procedure (Aranovskiy *et al.*, 2017; Korotina *et al.*, 2022; Ortega *et al.*, 2020) is adopted with a second-order differential operator to construct an extended set of LREs. From this, a modified gradient-descent (MGD) estimator is designed to estimate kinetic parameters simultaneously. Crucially, the proposed MGD estimator guarantees the global asymptotic convergence of estimated parameters, namely kinetic constants and activation energies, to their true values under a weaker condition, which is the interval excitation (IE) (Kreisselmeier & Rietze-Augst, 1990), rather

than the PE one.

The remainder of this paper is organized as follows. Preliminaries section presents the mathematical model of the CSTR and the vessel extent framework. Next, the Results & Discussions Section formulates the overparameterized LRE and establishes the non-PE property of the resulting regressor. The theoretical development of a DREM-based MGD estimator with convergence under the IE condition is also presented in this section. In the Simulations section, simulation results for the synthesis of glycerol ($C_3H_8O_3$) from the hydration of 2,3-epoxy-1-propanol ($C_3H_6O_2$) in a non-isothermal CSTR are provided to illustrate the performance of the proposed estimator. The last section concludes the paper.

PRELIMINARIES

Mathematical Model of CSTR

We considered here a general open non-isothermal reaction system, taking place in a continuous stirred tank reactor (CSTR) and involving S chemical species and R independent reactions. Its stoichiometry was given as follows:

$$\sum_{s=1}^S v_{rs} M_s = 0, \quad r = 1, 2, 3, \dots, R, \quad (1)$$

where M_s was the molar mass of the s^{th} species, v_{rs} was the (suitably signed) stoichiometric coefficient of the s^{th} species with respect to the r^{th} reaction. Then, the following assumptions, which were detailed in Nguyen *et al.* (2021), were made throughout the paper for reactor modeling, and thus delimited the class of reaction systems for which all subsequent results were valid.

(A1) The mixing process in the CSTR was perfect, and the reaction mixture was homogeneous, incompressible, and ideal.

(A2) The CSTR was operated under isobaric conditions with p inlet streams and one outlet stream.

(A3) The rate of heat exchange between the vessel jacket and the reaction mixture, denoted by $q_{ex}(t)$ was modeled by the following equation:

$$q_{ex}(t) = \lambda (T_j(t) - T(t)), \quad (2)$$

where λ was the heat transfer coefficient, $T_j(t)$ and $T(t)$ corresponded to the jacket temperature and the reaction temperature.

(A4) The r^{th} reaction rate, denoted by $r_{v,r}(t)$, could be represented as a product of a temperature-dependent function and another function of S -dimensional vector of molar concentration of species, denoted by $\mathbf{c}(t)$, as follows:

$$r_{v,r}(\mathbf{c}(t), T(t)) = V(t) k_r(T(t)) \psi_r(\mathbf{c}(t)), \quad (3)$$

where $V(t)$ denoted the time-dependent volume of the reaction mixture and $k_r(T(t))$ was described by the Arrhenius equation as follows:

$$k_r(T(t)) = k_{0,r} \exp\left(\frac{-E_{a,r}}{RT(t)}\right), \quad (4)$$

with $k_{0,r}$, $E_{a,r}$ and R being the kinetic constant, activation energy, and the ideal gas constant, respectively, while $\psi_r(\mathbf{c}(t))$ was given by the mass-action law, i.e.

$$\psi_r(\mathbf{c}(t)) = \prod_{s=1}^S c_s^{|\nu_{rs}|}(t). \quad (5)$$

The mathematical model of the CSTR was expressed in a compact form using the $(S+1)$ -dimensional vector $\mathbf{z}(t) = \begin{bmatrix} \mathbf{n}(t) \\ Q(t) \end{bmatrix}$ as

follows (Hoang *et al.*, 2020):

$$\frac{d\mathbf{z}(t)}{dt} = \mathbf{A} \mathbf{r}_v(t) + \mathbf{b} q_{ex}(t) + \mathbf{C} \mathbf{u}_{in}(t) - \omega(t) \mathbf{z}(t), \quad (6)$$

with

$$\mathbf{A} \equiv \begin{bmatrix} \mathbf{N}^T \\ \Delta H_{ref} \end{bmatrix}_{(S+1) \times R}, \quad \mathbf{b} = \begin{bmatrix} \mathbf{0}_S \\ 1 \end{bmatrix},$$

$$\mathbf{C} \equiv \begin{bmatrix} \mathbf{W}_{in} \\ \tilde{\mathbf{q}}_{in}^T \end{bmatrix}_{(S+1) \times p} \quad \text{and} \quad \mathbf{z}_0 = \begin{bmatrix} \mathbf{n}(0) \\ Q(0) \end{bmatrix}_{(S+1) \times 1}$$

being the constant matrices and $\omega(t) := \frac{u_{out}(t)}{m(t)} > 0$ being the dilution rate,

where

- $Q(t)$ denoted the amount of heat inside the CSTR and it was calculated by $Q(t) = \mathbf{c}_p^T \mathbf{n}(t) (T(t) - T_{ref})$ with $\mathbf{c}_p$ being the S -dimensional vector of molar specific heat capacities of components,
- $\mathbf{r}_v(t) = [\mathbf{r}_{v,1}(t) \quad \mathbf{r}_{v,2}(t) \quad \dots \quad \mathbf{r}_{v,R}(t)]^T$ was the R -dimensional vector of reaction rates,
- $\mathbf{u}_{in}(t) = [\mathbf{u}_{in,1}(t) \quad \mathbf{u}_{in,2}(t) \quad \dots \quad \mathbf{u}_{in,p}(t)]^T$ denoted the p -dimensional vector of inlet mass flowrates,
- $u_{out}(t)$ denoted the outlet mass flowrate,
- $\mathbf{W}_{in}$ denoted the $S \times p$ constant inlet-composition matrix,

- $\tilde{\mathbf{q}}_{in} = [\tilde{q}_{in,1} \quad \tilde{q}_{in,2} \quad \dots \quad \tilde{q}_{in,p}]^T$ denoted the constant vector of inlet specific heat with each element computed by

$$\tilde{q}_{in,i} = c_{p,in,i} (T_{in,i} - T_{ref}), \quad (7)$$

with $c_{p,in,i}$ and $T_{in,i}$ corresponding to the constant heat capacity and the temperature of the i^{th} inlet stream,

- $m(t)$ was the total mass of the reaction mixture.

Decoupled Dynamics with Vessel Extents

It was proved by Hoang *et al.* (2020) that if the inequality $S \geq R + p + 1$ held, and the matrix $\mathbf{W}_{in}$ and the vector $\mathbf{z}_0$ satisfied $\text{rank}([\mathbf{A} \quad \mathbf{b} \quad \mathbf{C} \quad \mathbf{z}_0]) = R + p + 2$, there existed an invertible square matrix defined by:

$$\mathbf{T} = [\mathbf{A} \quad \mathbf{b} \quad \mathbf{C} \quad \mathbf{z}_0 \quad \mathbf{P}], \quad (8)$$

with $\mathbf{P}_{(S+1) \times q}$ ($q = S - R - p - 1 \geq 0$) fulfilling $[\mathbf{A} \quad \mathbf{b} \quad \mathbf{C} \quad \mathbf{z}_0] \mathbf{P} = \mathbf{0}_{(R+p+2) \times q}$. On this basis, the vector $\mathbf{z}(t)$ could be transformed to the space of vessel extents, denoted by $\mathbf{x}(t)$, using the one-to-one LTI transformation $\mathbf{T}$ as follows:

$$\mathbf{x}(t) := [\mathbf{x}_r^T(t), \mathbf{x}_{ex}(t), \mathbf{x}_{in}^T(t), \mathbf{x}_{ic}(t), \mathbf{x}_{iv}^T(t)]^T = \mathbf{T} \mathbf{z}(t), \quad (9)$$

where $\mathbf{x}_r(t) \in \mathbb{R}_{\geq 0}^R$ represented the R -dimensional vector of vessel extents of reaction at time t , $\mathbf{x}_{in}(t) \in \mathbb{R}_{\geq 0}^p$ represented the p -dimensional vector of vessel extents of inlet at time t , $\mathbf{x}_{ex}(t)$ and $\mathbf{x}_{ic}(t)$ were the

scalar vessel extents of heat exchange and initial condition, respectively, at time t . Also, $\mathbf{x}_{iv}$ was the true invariant part with the dimension of q , i.e., $\mathbf{x}_{iv} = \mathbf{0}_q$. Moreover, the original dynamic model was transformed into a decoupled dynamics expressed in terms of $\mathbf{x}(t)$ as follows:

$$\frac{d\mathbf{x}_r(t)}{dt} = \mathbf{r}_v(t) - \omega(t)\mathbf{x}_r(t), \quad (10a)$$

$$\frac{d\mathbf{x}_{ex}(t)}{dt} = \mathbf{q}_{ex}(t) - \omega(t)\mathbf{x}_{ex}(t), \quad (10b)$$

$$\frac{d\mathbf{x}_{in}(t)}{dt} = \mathbf{u}_{in}(t) - \omega(t)\mathbf{x}_{in}(t), \quad (10c)$$

$$\frac{d\mathbf{x}_{ic}(t)}{dt} = -\omega(t)\mathbf{x}_{ic}(t), \quad (10d)$$

$$\mathbf{x}_{iv} = \mathbf{0}_q. \quad (10e)$$

It was important to note that the original state $\mathbf{z}(t)$ could be reconstructed from the vessel extents $\mathbf{x}(t)$ via the following equation:

$$\mathbf{z}(t) = \mathbf{A}\mathbf{x}_r(t) + \mathbf{b}\mathbf{x}_{ex}(t) + \mathbf{C}\mathbf{x}_{in}(t) + \mathbf{z}_0\mathbf{x}_{ic}(t), \quad (11)$$

Remark 1: Due to its physical meaning, the quantity of $\omega(t)$ represented the dilution rate, i.e., the inverse of the residence time of the reactor, and was always positive, i.e., $\omega(t) > 0$. Therefore, $\mathbf{x}_{ic}(t)$ always asymptotically converged to zero as time went to infinity, i.e., $\lim_{t \rightarrow \infty} \mathbf{x}_{ic}(t) = 0$.

RESULTS & DISCUSSIONS

Problem Formulation

In this paper, the kinetic parameters of the reaction system, namely $k_{0,r}$ and $E_{a,r}$ with $R = 1, 2, \dots, R$, are treated as unknown, and the goal is to design an estimator to estimate them simultaneously.

Before proceeding, we shall briefly outline the theoretical development of the estimator design in this work. First of all, *Lemma 1* establishes an overparameterized LRE, showing a mathematical relationship between the unknown parameters $\boldsymbol{\theta}_r$ and the measurable/computable signals $y_r(t)$, and proves that its regressor is not PE. Then, Proposition 1 is derived to explain why a SGD estimator consequently fails to drive the estimation error towards the zero equilibrium. As a result, in the final step, we shall apply the DREM procedure under the weaker excitation condition, as expressed in Assumption (A5), to develop a MGD estimator that converges in Proposition 2.

Lemma 1.

Consider a reaction system satisfying Assumptions (A1)-(A4). Then there exist the LREs of the following form:

$$y_r(t) = \boldsymbol{\phi}^T(t)\boldsymbol{\theta}_r, r = 1, 2, 3, \dots, R, \quad (12)$$

where

- $y_r(t) = \ln\left(\frac{\mathbf{r}_{v,r}(t)}{V(t)\psi_r(t)}\right)$ is a computable signal with respect to the r^{th} reaction,
- $\boldsymbol{\phi}(t) := [\phi_1 \quad \phi_2(t)]^T = \left[1 \quad \frac{-1}{T(t)}\right]^T$ is a regressor,

$$\bullet \theta_r = [\theta_{r,1} \quad \theta_{r,2}]^T = \left[\ln(k_{0,r}) \quad \frac{E_{a,r}}{R} \right]^T \text{ is}$$

an unknown constant vector of the r^{th} reaction.

Moreover, the regressor $\phi(t)$ does not fulfill the condition of persistency of excitation, that is, there do not exist the positive constants t_r and δ_r such that the following inequality:

$$\int_t^{t+t_r} \phi^T(\tau) \phi(\tau) d\tau \geq \delta_r \mathbf{I}_2, \quad (13)$$

holds for all $t \geq 0$.

Proof.

From (4), we can clearly see that the function $k_r(T(t))$ can be represented in the following form:

$$k_r(T(t)) = \frac{r_{v,r}(t)}{V(t)\psi_r(t)}, \quad (14)$$

Then, by substituting (4) into (14) and applying the natural logarithm operator to both sides, one can obtain the following equation:

$$\ln\left(\frac{r_{v,r}(t)}{V(t)\psi_r(t)}\right) = \ln(k_{r,0}) - \frac{1}{T(t)} \frac{E_{a,r}}{R}, \quad (15)$$

which can be reformulated into the form of (12) as a result.

Furthermore, by letting $\bar{T}$ be the steady-state value of $T(t)$, i.e. $\lim_{t \rightarrow \infty} T(t) = \bar{T}$, the following equality:

$$\begin{aligned} \lim_{t \rightarrow \infty} (\phi^T(t) \phi(t)) &= \lim_{t \rightarrow \infty} \begin{bmatrix} 1 & \frac{-1}{T(t)} \\ \frac{-1}{T(t)} & \frac{1}{T^2(t)} \end{bmatrix} \\ &= \begin{bmatrix} 1 & \frac{-1}{\bar{T}} \\ \frac{-1}{\bar{T}} & \frac{1}{\bar{T}^2} \end{bmatrix}, \end{aligned} \quad (16)$$

holds, leading to:

$$\lim_{t \rightarrow \infty} \int_t^{t+t_r} \phi^T(\tau) \phi(\tau) d\tau - \delta_r \mathbf{I}_2 = \begin{bmatrix} t_r - \delta_r & \frac{-t_r}{\bar{T}} \\ \frac{-t_r}{\bar{T}} & \frac{t_r}{\bar{T}^2} - \delta_r \end{bmatrix}. \quad (17)$$

Essentially, the matrix on the right-hand side of (17) is positive semi-definite if and only if all of its (leading and non-leading) principal minors are non-negative (Shores, 2018), that is, all the following conditions:

$$t_r - \delta_r \geq 0, \quad (18a)$$

$$(t_r - \delta_r) \left(\frac{t_r}{\bar{T}^2} - \delta_r \right) - \frac{t_r^2}{\bar{T}^2} \geq 0, \quad (18b)$$

$$\frac{t_r}{\bar{T}^2} - \delta_r \geq 0, \quad (18c)$$

must be fulfilled for some positive constants $t_r > 0$ and $\delta_r > 0$. However, it can be verified that they contradict each other. As a result, there are no positive constants t_r and δ_r such that the inequality (13) is satisfied, that is, the regressor $\phi(t)$ is not PE. The latter concludes with proof. $\square$

In the following proposition, we shall construct a standard gradient-descent (SGD) estimator. However, its convergence is based on the PE condition for the regressor $\phi(t)$, which is not satisfied by the reaction systems, as shown in *Lemma 1*.

Proposition 1.

Consider the LRE (12) with the SGD estimator, expressed by:

$$\frac{d\hat{\theta}_r(t)}{dt} = \Upsilon_r \phi(t) (y_r(t) - \phi^T(t) \hat{\theta}_r(t)), \quad (19)$$

with the matrix $\Upsilon_r \in \mathbb{R}^{2 \times 2}$ being the adaptation gain. The following claims hold.

- (i) The parameter estimation error, defined as $\tilde{\theta}_r(t) := \theta_r - \hat{\theta}_r(t)$, is governed by the following differential equation:

$$\frac{d\tilde{\theta}_r(t)}{dt} = -\Upsilon_r \phi(t) \phi^T(t) \tilde{\theta}_r(t), \quad (20)$$

- (ii) The zero equilibrium of (20) is globally asymptotically stable if and only if the regressor $\phi(t)$ is PE.

Proof.

To prove the claim (i), we first note that $\frac{d\tilde{\theta}_r(t)}{dt} = -\frac{d\hat{\theta}_r(t)}{dt}$, which can be clearly seen from the definition of $\tilde{\theta}_r(t)$. Then, by substituting the expression of $y_r(t)$, given by (12), into the dynamics of $\hat{\theta}_r(t)$, given by (19), one can obtain the dynamics of $\tilde{\theta}_r(t)$ as shown in (20).

Moreover, the differential equation (20) can be solved analytically to obtain a solution, expressed as follows:

$$\tilde{\theta}_r(t) = \tilde{\theta}_r(0) \exp\left(-\Gamma_r \int_0^t (\phi^T(\tau) \phi(\tau)) d\tau\right). \quad (21)$$

Based on this, one can conclude that the global asymptotic convergence of $\tilde{\theta}_r(t)$ towards the zero equilibrium, i.e. $\lim_{t \rightarrow \infty} \tilde{\theta}_r(t) = \mathbf{0}_2$, is ensured only if the following inequality: $\int_0^t (\phi^T(\tau) \phi(\tau)) d\tau > 0$, holds for all time, that is, the regressor $\phi(t)$ is PE, thereby proving the claim (ii). The latter concludes with proof. $\square$

From the viewpoint of Proposition 1 and Lemma 1, it is important to emphasize that the SGD estimator, given by (19), cannot successfully estimate the unknown constant

vector θ_r since the regressor $\phi(t)$ does not satisfy the PE requirement, which is known to be restrictive in this setting. Fundamentally, it has been proved in Wang et al. (2023) (see also Yi & Ortega (2022)) that the LRE (12) is *identifiable*, which is instrumental for the simultaneous estimation problem of kinetic parameters, provided the regressor $\phi(t)$ satisfies the interval excitation (IE) condition. This condition is indeed weaker than the PE one. We, therefore, shall impose it in the following assumption.

(A5) The regressor is bounded and interval exciting, that is, the following inequality:

$$\int_0^{t_r} \phi^T(\tau) \phi(\tau) d\tau \geq \delta_r \mathbf{I}_2, \quad (22)$$

holds for some $t_r > 0$ and $\delta_r > 0$ (Kreisselmeier & Rietze-Augst, 1990).

The Construction of MGD Estimator with the Second-order Operator

Under Assumption (A5), we can estimate the unknown constant vector θ_r . In the first step, the DREM procedure is applied to the LRE (12) to generate an extended set of LREs, which allows the design of a modified gradient-descent (MGD) estimator in the following proposition.

Proposition 2.

Consider the LRE (12) with the regressor $\phi(t)$ verifying Assumption (A5), and define the

matrix $\Phi^T(t) = \begin{bmatrix} \phi_1 & \phi_2(t) \\ \phi_{f,1}(t) & \phi_{f,2}(t) \end{bmatrix}$ and the

vector $\mathbf{Y}_r(t) = \begin{bmatrix} y_r(t) \\ y_{f,r1}(t) \end{bmatrix}$, where the signals

$y_{f,r1}(t)$, $\phi_{f,1}(t)$ and $\phi_{f,2}(t)$ are bounded and generated by the following differential equations:

$$\frac{d^2 y_{f,r1}(t)}{dt} = -\gamma_r \frac{d y_{f,r1}(t)}{dt} - \beta_r y_{f,r1}(t) + \alpha_r y_r(t), \quad (23a)$$

$$\frac{d^2 \phi_{f,1}(t)}{dt} = -\gamma_r \frac{d \phi_{f,1}(t)}{dt} - \beta_r \phi_{f,1}(t) + \alpha_r \phi_1(t), \quad (23b)$$

$$\frac{d^2 \phi_{f,2}(t)}{dt} = -\gamma_r \frac{d \phi_{f,2}(t)}{dt} - \beta_r \phi_{f,2}(t) + \alpha_r \phi_2(t), \quad (23c)$$

with the initial conditions given as follows:

$$y_{f,r1}(0) = y_{0f,r1}, \quad \phi_{f,1}(0) = \phi_{0f,1},$$

$$\phi_{f,2}(0) = \phi_{0f,2}, \quad \frac{dy_{f,r1}(0)}{dt} = 0, \quad \frac{d\phi_{f,1}(0)}{dt} = 0,$$

$$\frac{d\phi_{f,2}(0)}{dt} = 0 \text{ and the tuning parameters}$$

$\alpha_r \neq 0$, β_r and γ_r . Then, the following claims hold:

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

$$\mathbf{Y}_r(t) = \mathbf{\Phi}_r^T(t) \boldsymbol{\theta}_r. \quad (24)$$

- (ii) The MGD estimator, given by the following differential equation:

$$\frac{d\hat{\boldsymbol{\theta}}_r(t)}{dt} = \Gamma_r \Delta_r(t) (\mathbf{Y}_r(t) - \Delta_r(t) \hat{\boldsymbol{\theta}}_r(t)), \quad (25)$$

with $\hat{\boldsymbol{\theta}}_r(0) = \hat{\boldsymbol{\theta}}_{r,0}$, $\mathbf{Y}_r(t) = \text{adj}(\mathbf{\Phi}_r^T(t)) \mathbf{Y}_r(t)$

and $\Delta_r(t) = \det(\mathbf{\Phi}_r^T(t))$, where $\Gamma_r \in \mathbb{R}^{2 \times 2}$ is

an adaptation gain matrix, guarantees the global and asymptotic convergence of $\hat{\boldsymbol{\theta}}_r(t)$

to its true value, i.e. $\lim_{t \rightarrow \infty} \hat{\boldsymbol{\theta}}_r(t) = \boldsymbol{\theta}_r$, if $\Delta_r(t)$ is

not square-integrable over $\mathbb{R}_{\geq 0}$, that is,

$$\int_0^{+\infty} |\Delta_r^2(\tau)| d\tau = +\infty \text{ over } \mathbb{R}_{\geq 0}.$$

Proof.

To prove the claim (i), the second-order differential operator $H_r(p)$, defined as

$$H_r(p) := \frac{\alpha_r}{p^2 + \gamma_r p + \beta_r} \text{ with } p := \frac{d}{dt}, \text{ is}$$

applied to both sides of the LRE (12), thereby yielding the following LRE:

$$y_{f,r1}(t) = \phi_{f,r}^T(t) \boldsymbol{\theta}_r, \quad (26)$$

with $\phi_{f,r}(t) = [\phi_{f,r1}(t) \ \phi_{f,r2}(t)]^T$, where

the signals $y_{f,r1}(t)$, $\phi_{f,r1}(t)$ and $\phi_{f,r2}(t)$ are generated by (23a), (23b) and (23c), respectively. Then, by writing this equation in matrix form, the system of linear regression equations given by (24) can be obtained, thereby proving claim (i).

Furthermore, by premultiplying, from the left, both sides of (24) by $\text{adj}(\mathbf{\Phi}_r^T(t))$ and noting that $\Delta_r(t) = \text{adj}(\mathbf{\Phi}_r^T(t)) \mathbf{\Phi}_r^T(t)$ (Shores, 2018), we can obtain the following equation:

$$\mathbf{Y}_r(t) = \Delta_r(t) \boldsymbol{\theta}_r. \quad (27)$$

Substituting $\mathbf{Y}_r(t)$ from (27) into (25)

subsequently leads to the dynamics of $\tilde{\boldsymbol{\theta}}_r(t)$ written by the following differential equation:

$$\frac{d\tilde{\boldsymbol{\theta}}_r(t)}{dt} = -\Gamma_r \Delta_r^2(t) \tilde{\boldsymbol{\theta}}_r(t), \quad (28)$$

having the analytic solution as follows:

$$\tilde{\boldsymbol{\theta}}_r(t) = \tilde{\boldsymbol{\theta}}_r(0) \exp\left(-\Gamma_r \int_0^t \Delta_r^2(\tau) d\tau\right). \quad (29)$$

As a result, if $\lim_{t \rightarrow \infty} \int_0^t \Delta_r^2(\tau) d\tau = +\infty$, i.e.

$\Delta_r(t) \notin L_2$ over $\mathbb{R}_{\geq 0}$, is satisfied, the global

asymptotic convergence of $\hat{\boldsymbol{\theta}}_r(t)$ to $\boldsymbol{\theta}_r$ is ensured, thereby proving the claim (ii). The latter concludes the proof. $\square$

Remark 2: The non-square-integrability condition of $\Delta_r(t)$ holds if $\Delta_r(t) \notin L_2$ over

$\mathbb{R}_{\geq 0}$, which is ensured under Assumption (A5) by the design of the second-order

DREM operator.

Figure 1 illustrates the overall procedure, including the successive steps for designing the proposed MGD estimator. The algorithm begins with the computation of vessel extents $\mathbf{x}(t)$ from $\mathbf{z}(t)$ using the one-to-one LTI transformation $\mathbf{T}$ via (9). For each reaction $r=1,2,\dots,R$, the overparameterized LRE $y_r(t) = \boldsymbol{\phi}^T(t)\boldsymbol{\theta}_r$ with $r=1,2,3,\dots,R$, is then expressed in terms of the computable signals $y_r(t)$ and the unknown kinetic parameters $\boldsymbol{\theta}_r$. Next, the computable signals $y_{f,r1}(t)$, $\phi_{f,r1}(t)$ and $\phi_{f,r2}(t)$ are generated according to (23a), (23b), (23c) with suitable selection of tuning parameters $\alpha_r \neq 0$, β_r and γ_r . From this, the matrices $\mathbf{Y}_r(t)$ and $\Delta_r(t)$ are calculated as $\mathbf{Y}_r(t) = \text{adj}(\boldsymbol{\Phi}_r^T(t))\mathbf{Y}_r(t)$ and $\Delta_r(t) = \det(\boldsymbol{\Phi}_r^T(t))$, respectively. A key condition is then checked: if $\Delta_r(t)$ is square-

integrable, the tuning parameters are adjusted and the signal generation step is repeated; otherwise, the MGD estimator is constructed as (25), whose global asymptotic convergence is guaranteed under the interval-excitation condition, given by Assumption (A5), as established in **Proposition 2**.

Remark 3: Unlike offline non-linear least-squares fitting, which is a batch procedure solving a non-convex problem with no global convergence guarantee (Dattner *et al.*, 2020; Himmelblau *et al.*, 1967), and standard online observers (Dochain, 1991, 2003, 2018; Pyrkin *et al.*, 2023), which estimate only the kinetic constants with the activation energies assumed known a priori, the proposed MGD estimator (25) estimates both simultaneously in an online recursive manner, with proven global asymptotic convergence under the IE condition, given in Assumption (A5). Hence, this feature makes it suitable for adaptive control applications (Romero *et al.*, 2023).

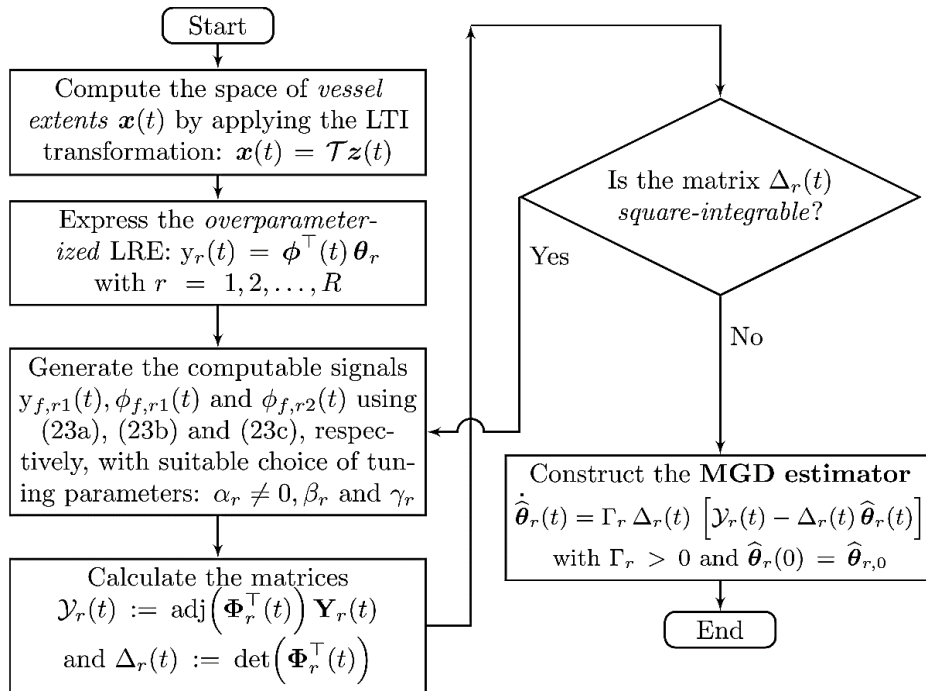
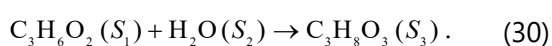


Fig. 1: Procedure to design the MGD estimator.

SIMULATIONS

To illustrate the SGD estimator and the proposed MGD estimator, we consider here the synthesis of glycerol (propane-1,2,3-triol, $C_3H_8O_3$) from the hydration of 2,3-epoxy-1-propanol ($C_3H_6O_2$), taking place in a non-isothermal CSTR, as a case study. Its stoichiometric equation is written as follows (Hoang et al., 2013; Vleeschhouwer & Fortuin, 1990):



Clearly, the system involves $S=4$ components, including 3 active ones and HNO_3 as the 4th component (S_4) as the catalyst, and $R=1$ an independent reaction. Also, $N = [v_1 \ v_2 \ v_3 \ v_4] = [-1 \ -1 \ 1 \ 0]$ is the constant stoichiometric matrix.

The CSTR is operated with $p=2$ inlet streams such that the nominal mass flow rates of two inlet streams are $u_{in,1}=0.025$ (kg/s) and $u_{in,2}=0.075$ (kg/s). Also, the total mass of reaction mixture remains unchanged at $m=1.95$ (kg), leading to the operating constraint: $u_{in,1} + u_{in,2} = u_{out} = 0.1$ (kg/s). In

addition, the heat transfer coefficient $\lambda = 0.005$ (kW/K) and the inlet-composition

matrix $W_{in} = \begin{bmatrix} 1/74 & 0 & 0 & 0 \\ 0 & 0.99/18 & 0 & 0.01/63 \end{bmatrix}$ are

selected; the vector $\tilde{q}_{in} = [0 \ 0]$ is computed with $T_{in,1} = T_{in,2} = 298$ (K).

The SGD Estimator

To implement the SGD estimator (19), the adaptation gain matrix Υ and the initial values of parameter estimation errors are chosen as $\Upsilon = \begin{bmatrix} 0.1 & 0 \\ 0 & 0.1 \end{bmatrix}$, $\tilde{\theta}_1(0) = -3$ and $\tilde{\theta}_2(0) = 3$. As shown in Figure 2, the time responses of $\tilde{\theta}(t)$ do not approach the zero equilibrium as time goes to infinity, thereby verifying that the SGD estimator fails to estimate the unknown kinetic parameter vector θ . As explained in Lemma 1 and Proposition 1, the main reason is that the regressor $\phi(t)$ in the LRE (12) does not fulfil the PE requirement, strongly motivating the construction of the MGD estimator in Proposition 2 under the IE condition, which is weaker than the PE one.

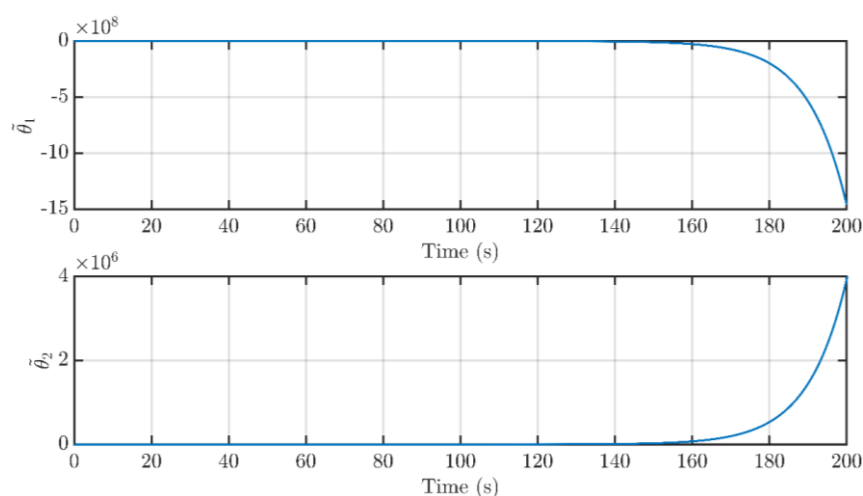


Fig. 2: Estimation errors $\tilde{\theta}(t) = [\tilde{\theta}_1(t) \ \tilde{\theta}_2(t)]$ under the SGD estimator

The MGD Estimator

The MGD estimator in Proposition 2 is implemented with the tuning parameters $\alpha = 0.07$, $\beta = 0.0025$, $\gamma = 0.35$, $y_{0f,1} = 1$, $\phi_{0f,1} = 0$ and $\phi_{0f,2} = 0$; and the gain matrix $\Gamma = \begin{bmatrix} 800 & 0 \\ 0 & 800 \end{bmatrix}$. Moreover, the initial values of parameter estimation errors are taken as $\tilde{\theta}_1(0) = -3.2$ and $\tilde{\theta}_2(0) = -8827$. Figure 3 shows that the mixing signal $\Delta(t)$ sustains a bounded oscillation and its energy $\int_0^{+\infty} \Delta^2(\tau) d\tau$ grows essentially linearly in

time, which, therefore, verifies the non-square integrability of $\Delta(t)$ over the operating horizon. From this, the asymptotic stabilization of $\tilde{\theta}(t)$ towards the zero equilibrium is ensured, as shown in Figure 4. Moreover, the convergence of estimated kinetic parameters from their initial values $k_0(0) = 10^{13}$ and $E_a/R = 8500$ to their corresponding true values: 86×10^{12} and 8827 under the MGD estimator are depicted in Figure 5.

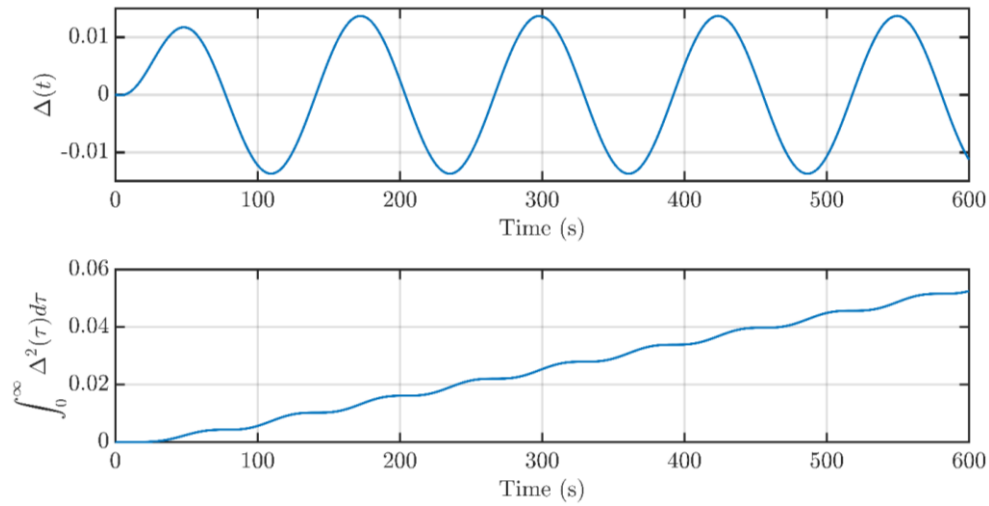


Fig. 3: Mixing signal $\Delta(t)$ and its energy $\int_0^{+\infty} \Delta^2(\tau) d\tau$

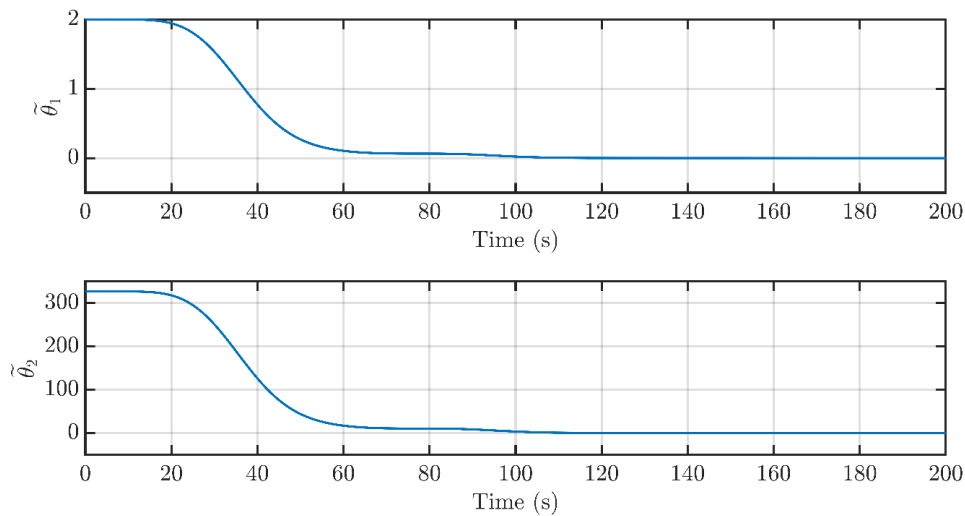


Fig. 4: Estimation errors $\tilde{\theta}(t) = \begin{bmatrix} \tilde{\theta}_1(t) & \tilde{\theta}_2(t) \end{bmatrix}$ under the MGD estimator

The robustness of the proposed MGD estimator is further assessed in the presence of both measurement noise and external disturbance. Specifically, the molar amount $n_1(t)$ is corrupted by additive zero-mean Gaussian noise with standard deviation equal to 1% of its mean value. In contrast, the reactor temperature's measurement is corrupted by additive zero-mean Gaussian noise with the standard deviation $\sigma_T = 0.5(K)$. Also, the second inlet stream is subject to an unmeasured periodic fluctuation, as follows:

$$u_{in,2} = 0.075(1 + 0.15\sin(0.05t)),$$

representing an exogenous disturbance such as upstream flow variability. As shown in Figure 6, the mixing signal $\Delta(t)$ maintains a bounded, non-vanishing oscillation and its energy $\int_0^{+\infty} \Delta_r^2(\tau)d\tau$ grows unboundedly in time; thereby verifying that the non-square-integrability condition, i.e. $\Delta(t) \notin L_2$, is preserved despite the noise and the disturbance.

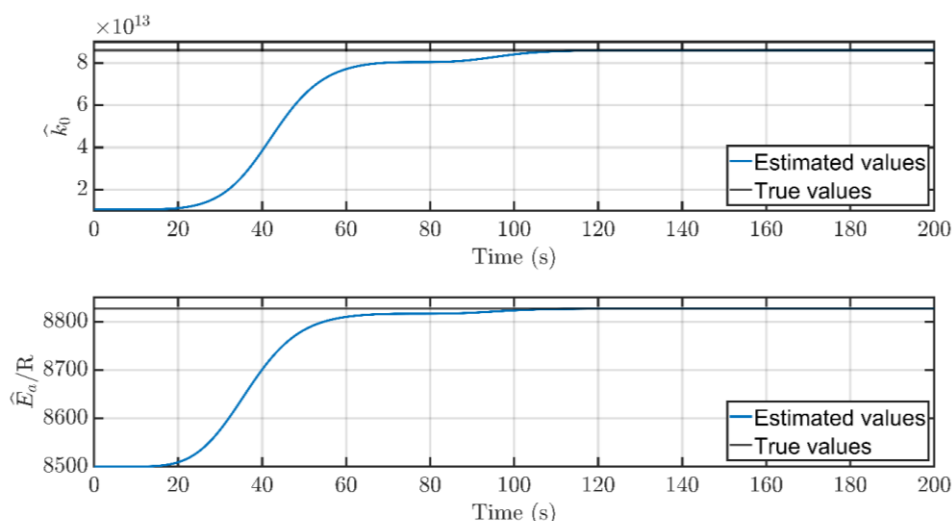


Fig. 5: Estimates k_0 and E_a/R under the MGD estimator

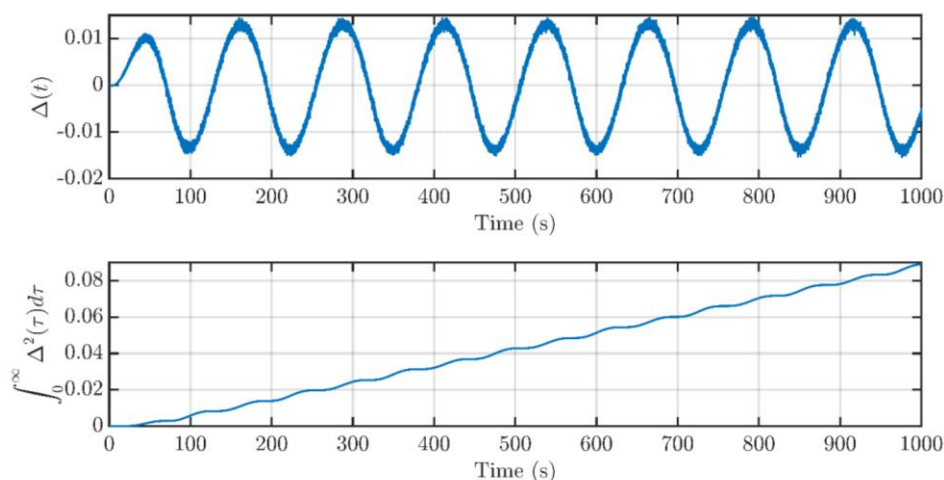


Fig. 6: Mixing signal $\Delta(t)$ and its energy $\int_0^{+\infty} \Delta^2(\tau)d\tau$ under measurement noise and disturbance

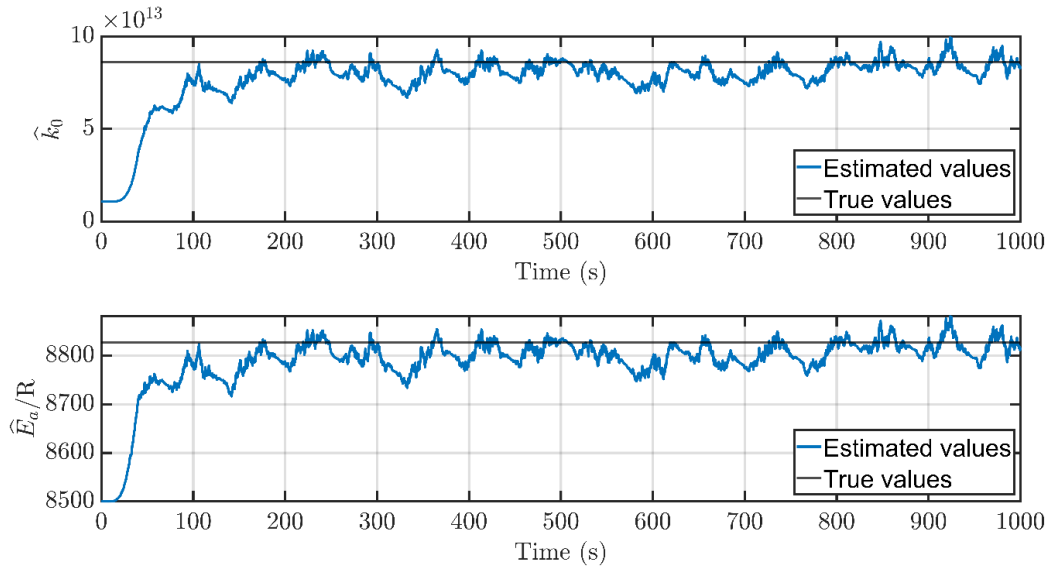


Fig. 7: Estimates k_0 and E_a/R under measurement noise and disturbance

Figure 7 shows that the estimates k_0 and E_a/R converge and thereafter fluctuate within a narrow band around their respective true values. These results demonstrate that, provided the regressor $\phi(t)$ fulfills the IE condition specified in Assumption (A5), the proposed MGD estimator retains its convergence properties and delivers accurate, practically unbiased estimates of the kinetic parameters in the presence of measurement noise and external disturbance.

CONCLUSIONS

This paper has addressed the estimation problem of unknown kinetic parameters, namely the kinetic constant and activation energy. It has been shown that the parameter errors under the SGD estimator fail to converge to the zero equilibrium since the regressor $\phi(t)$ is not PE. By applying the DREM procedure with a second-order differential operator to the LRE (12), an extended set of LREs is obtained, enabling the design of an MGD estimator. The

development of the proposed MGD estimator is indeed independent of the reactor operational modes since its construction relies on the LREs derived from the vessel extent transformation, which is established for general open homogeneous reaction systems. More importantly, convergence is ensured under the IE condition of $\phi(t)$, which is indeed weaker than the PE one.

Numerical simulations were conducted for the synthesis of glycerol from the hydration of 2,3-epoxy-1-propanol in a non-isothermal CSTR. It has been shown that parameter estimation errors under the SGD estimator do not approach the zero equilibrium, thereby confirming the result of Lemma 1 and Proposition 1. In contrast, the MGD estimator effectively drives all parameter estimation errors to the zero equilibrium. Furthermore, simulations show that the MGD estimator remains convergent under realistic perturbations that represent measurement noise and external disturbances encountered in industrial reactors. As future work, we aim to extend the

design of the MGD estimator to heterogeneous reaction systems and to combine it with controllers to develop adaptive control schemes.

NOMENCLATURE

Indices and Dimensions

S	number of chemical species
R	number of independent reactions
P	number of inlet streams
q	dimension of invariant subspace
r	reaction index, $r = 1, 2, \dots, R$
s	species index, $s = 1, 2, \dots, S$
i	inlet stream index, $i = 1, 2, \dots, P$

Reactor Model Variables

$\tilde{\mathbf{c}}_p$	S -dimensional vector of molar specific heat capacities of components
$c_{p,s}$	molar specific heat capacities of s^{th} components
$c_{p,in,i}$	heat capacity of the i^{th} inlet stream
$\mathbf{c}$	S -dimensional vector of molar concentrations of species
$\mathbf{n}$	S -dimensional vector of molar numbers of species
$E_{a,r}$	activation energy of the r^{th} reaction
$k_{0,r}$	kinetic (pre-exponential) constant of the r^{th} reaction
M_s	molar mass of the s^{th} species
m	total mass of the reaction mixture
R	ideal gas constant
Q	amount of heat inside the CSTR
$\mathbf{r}_v$	R -dimensional vector of reaction rates
$r_{v,r}$	reaction rate of the r^{th} reaction (mol/s)
$\tilde{\mathbf{q}}_{in}$	p -dimensional vector of inlet specific heat

$\tilde{q}_{in,1}$	inlet specific heat of the i^{th} inlet stream
q_{ex}	rate of heat exchange between the vessel jacket and the reaction mixture
T	reactor (reaction mixture) temperature
T_j	jacket temperature
V	volume of the reaction mixture
ω	dilution rate (inverse of residence time)
$\mathbf{u}_{in}$	p -dimensional vector of inlet mass flowrates
$u_{in,i}$	scalar mass flowrate of the i^{th} inlet stream
u_{out}	scalar mass flowrate of the outlet stream
$\mathbf{W}_{in}$	$S \times P$ inlet-composition matrix
$T_{in,i}$	temperature of the i^{th} inlet stream
λ	overall heat transfer coefficient
ν_{rs}	stoichiometric coefficient of the s^{th} species with respect to the r^{th} reaction
ψ_r	concentration-dependent part of the r^{th} reaction rate, given by the mass-action law

Vessel Extent Framework

$\mathbf{T}$	square LTI transformation matrix of dimension $(S+1) \times (S+1)$
$\mathbf{x}$	$(S+1)$ -dimensional vector of vessel extents
$\mathbf{x}_r$	R -dimensional vector of vessel extents of reaction
$\mathbf{x}_{in}$	p -dimensional vector of vessel extents of inlet
x_{ex}	scalar vessel extent of heat exchange
x_{ic}	scalar vessel extent of initial condition
$\mathbf{x}_{iv}$	true invariant part of dimension q , i.e., $\mathbf{x}_{iv} = \mathbf{0}_q$

DREM-based Modified Gradient Estimator

Φ	Matrix	defined	by
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$$\Phi^T(t) = \begin{bmatrix} \phi_1 & \phi_2(t) \\ \phi_{f,1}(t) & \phi_{f,2}(t) \end{bmatrix}$$

Y_r Matrix defined by $Y_r(t) = \begin{bmatrix} y_r(t) \\ y_{f,r1}(t) \end{bmatrix}$

Γ_r adaptation gain matrix

Δ_r extended regressor matrix generated by the DREM procedure

Y_r extended output vector generated by the DREM procedure

H_r second-order differential operator applied in the DREM procedure

p derivative operator, i.e. $p := \frac{d}{dt}$

t_r time window length in the PE condition

δ_r positive lower bound constant in the interval excitation (IE) condition

$\bar{T}$ steady-state value of T

Abbreviations

CSTR	continuous stirred tank reactor
DREM	dynamic regressor extension and mixing
IE	interval excitation
LRE	linear regression equation
LTI	linear time-invariant
MGD	modified gradient-descent
ODE	ordinary differential equation
PE	persistently exciting
SGD	standard gradient-descent

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