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Data-driven nonlinear frequency response method for control-oriented design of forced periodic operation and operating conditions

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ABSTRACT

The optimal design of forced periodic operation and associated operating conditions has received notable attention due to the potential to improve conversion rates through the intrinsic nonlinear dynamics of chemical reactions. However, the limited capacity of analysing higher-order nonlinearities, especially under varying operating conditions, poses significant challenges. To tackle these difficulties, the Nonlinear Frequency Response (NFR) method and computer-aided approaches have been proposed and applied to different reaction processes. Nevertheless, due to reliance on the first principle model, current methods are difficult to be literally applied in practice to perform the designs. To address this limitation, the present study proposes an integrated data-driven design approach that can perform effective quantitative analysis and integrated design of both forced periodic operation parameters and operating conditions for the effective control and design of the underlying chemical reaction process. From the input–output data obtained from either simulations or experimental measurements, the proposed method builds a data-driven optimization-oriented model that can, for the first time, be used for both quantitative analysis and design of forced periodically operated reaction processes. This resolves the challenges with applying the existing NFR-based methods and provides an effective solution practically applicable to a wide range of complex chemical reaction processes. Simulation studies on a non-isothermal continuous stirred tank reactor (CSTR) and an experimental investigation on a small-scale CO₂ absorption device have verified the effectiveness of the proposed method and demonstrated its potential in real-world applications.

1. Introduction

In the chemical industry, reaction processes are often expected to continue in a homeostatic manner under the given optimal steady state control strategies [1]. This is because the primary role of these control strategies often lies in suppressing the impact of interference to maximize the percentage of reactants converted into products, that is the rate of reactants converted into products, and increase profits [2]. However, with the increasing demand of productivity, how to further improve the conversion rate on the existing basis has become a critical focus of attention [3].

A possibility of improvement lies in the nonlinearity induced from kinetics behaviors [4]. Forced periodic operation is such an effective attempt that utilizes the system nonlinearities to achieve performance enhancement. This is often achieved by artificially forcing the chemical reaction process input into a periodic form around its steady state to produce a dynamic output response represented by the reactant or product yield of concern [5]. Thanks to the nonlinear behaviors, the time-averaged dynamic output response may perform better than the output under steady-state operation.

Forced periodic operation has drawn considerable interest from researchers due to its advantages and has been

extensively studied in the past few decades. Wilhite et al. [6] experimentally studied phenylacetylene hydrogenation process in a trickle-bed reactor, demonstrating that the selectivity of styrene can increase by up to 45% under liquid-limited reaction. Pioneer research teams also explored the advantages of forced periodic operation through experiments from the enhancement perspective of reaction rates [7], energy efficiency [8], selectivity [9] and so on. However, the forcing frequency and amplitude are often repeatedly adjusted based on observations, which cannot fully utilize the benefits of forced periodic operation and may even result in inferior performance to steady-state operations.

To provide an objective reference for experimental works, researchers also proposed rigorous process modeling and model-based nonlinear analysis. Zhai et al. [10] proposed a Laplace-Borel transform method which combines shuffle product operation to decompose system analysis into transient dynamics and steady-state solutions. However, the decoupling and expression of first order nonlinear terms are complicated. In addition, π -criterion [11], first-harmonic [12], extremum-seeking control [13], model predictive control [14, 15] and sequential quadratic programming [16] are also developed for nonlinear analytical studies. These methods are often model-dependent, which is a challenge when applied to complex practical processes.

In addition, recent studies have also attempted to apply machine-learning-based methods to the optimization of forced periodic operation. Park et al. [17] developed an artificial neural network–genetic algorithm (ANN–GA)

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optimization framework and experimentally investigated renewable ammonia synthesis under low-pressure conditions. Although this machine-learning-assisted method can provide favorable operating designs, it essentially relies on a black-box relationship between operating variables and performance indicators, which does not explicitly preserve an interpretable framework for the quantitative analysis of forced periodic operation and is susceptible to overfitting, particularly when data are limited. Therefore, the method generally provides limited insight into how the forced periodic operation frequency and amplitude contribute to the output response.

In contrast to the black-box optimization strategies, a method known as NFR has been proposed and widely applied to analyze the performance of chemical systems with either single or multiple input periodic modulations [18]. Building upon this method, hybrid NFR approaches were also proposed to optimize the benefits of forced periodic operation [19–23]. However, the reliance of the NFR method on the first principle models of the underlying chemical reaction processes has limited its practical applicability to complex systems, particularly when quantitative-analysis-based optimal design is required.

To resolve this difficulty, a data-driven NFR approach was proposed in a previous study [24]. The approach identifies a data-driven NFR model directly from process data acquired from experiments to enable quantitative analysis and optimal design of forced periodic operation under fixed operating conditions. However, the earlier work focused only on data-driven analysis and the optimal design of periodic operation in chemical reaction processes, without considering the influence of operating conditions. Specifically, the operating conditions were treated as fixed parameters rather than design variables, and the coupled effects of the forcing frequency, amplitude, and operating conditions could not be systematically quantified or exploited in the design. In chemical reaction processes, operating conditions such as temperature, flow rate, and pressure define the environment in which reactions occur. These conditions are typically determined during process design and can significantly affect the performance of forced periodic operation.

To address this challenge and fully exploit forced periodic operation for the effective control and design of chemical reaction processes, the present study extends our previously proposed data-driven optimal design approach to enable the systematic joint design of forced periodic operation and operating conditions. Starting from an initial design, the proposed approach alternately designs the forced periodic operation parameters and a single operating condition, allowing the coupled effects on the chemical reaction performance to be quantified. The procedure continues until either the prescribed stopping criterion is satisfied or a predetermined number of iterations is reached, resulting in an integrated design. This integrated design approach is applied to both a simulated non-isothermal CSTR process and a laboratory-scale experimental CO₂ absorption device.

The results validate the effectiveness of the proposed approach and demonstrate its practical significance in chemical reaction applications. Although a single operating condition is considered in the present study, the framework can, in principle, be extended to multiple operating conditions according to the design requirements of the process. To the best of our knowledge, this represents the first comprehensive solution for the integrated data-driven design of forced periodic operation and operating conditions in chemical reaction processes. The main contributions of the present study are summarized as follows:

- (1) Develop an integrated data-driven method for the simultaneous design of forced periodic operation and operating conditions based on the physically interpretable nonlinear frequency response framework;
- (2) Develop an effective design framework to address the coupled effects and iteratively design the forced periodic operation frequency, amplitude, and operating conditions;
- (3) Demonstrate the effectiveness and practical applicability of the proposed data-driven method through simulation studies on a non-isothermal CSTR and experimental validation on a laboratory-scale CO₂ absorption process.

The basic principles of the proposed method can be extended to more complex chemical reaction systems operating under multiple operating conditions, thereby offering broad potential for industrial applications.

2. The NFR model of chemical systems

2.1. Volterra-series-based NFR model and its DC component

The NFR model is a systematic description of forced periodically operated chemical reaction systems based on the Volterra series [25]. In cases where the systems exhibit stability at the zero equilibrium, which is inherently satisfied in forced periodic operation processes, the dynamics can be effectively captured by the Volterra series as [26]

$$y(t, p) = y_0(p) + \sum_{n=1}^N \int_{-\infty}^{\infty} \cdots \int_{-\infty}^{\infty} h_n(\tau_1, \dots, \tau_n, p) \prod_{i=1}^n u(t - \tau_i) d\tau_i \quad (1)$$

where p denotes the operating conditions, $u(t)$ and $y(t, p)$ are the time series of the forced periodic operation input and output, respectively, $y_0(p)$ is the steady-state output when $u(t) = 0$, N is the maximum nonlinearity order, and $h_n(\tau_1, \dots, \tau_n, p)$ is the n^{th} order Volterra kernel.

When the nonlinear system (1) is subjected to an external forced multitone excitation

$$u(t) = \sum_{i=1}^K A_i \cos(\omega_i t + \angle A_i) = \sum_{\substack{i=-K \\ i \neq 0}}^K \frac{A_i}{2} \exp(j\omega_i t) \quad (2)$$

where $A_{-i} = A_i^*$ and $\omega_{-i} = -\omega_i$, the output spectrum $Y(j\omega)$ has been well studied and can be represented as [27]

$$Y(j\omega) = \begin{cases} Y_0(p) + \frac{1}{2^n} \sum_{\omega_{k_1} + \dots + \omega_{k_n} = 0} A_{k_1} \dots A_{k_n} \times H_n(j\omega_{k_1}, \dots, j\omega_{k_n}, p), & \omega = 0, \\ \frac{1}{2^{n-1}} \sum_{\omega_{k_1} + \dots + \omega_{k_n} = \omega} A_{k_1} \dots A_{k_n} \times H_n(j\omega_{k_1}, \dots, j\omega_{k_n}, p), & \omega > 0, \end{cases} \quad (3)$$

$$k_l \in \{-K, \dots, -1, 1, \dots, K\}, \quad l = 1, \dots, n$$

where $Y_0(p) = y_0(p)$, and

$$H_n(j\omega_{k_1}, \dots, j\omega_{k_n}, p) = \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} h_n(\tau_1, \dots, \tau_n, p) \times \exp(-j(\omega_{k_1}\tau_1 + \dots + \omega_{k_n}\tau_n)) d\tau_1 \dots d\tau_n \quad (4)$$

is the n^{th} order generalized frequency response function (GFRF) under the operating conditions p [28].

Equation (3) is recognized as the NFR model in the research field of forced periodic operation, which reflects the functional dependence among the forcing frequency ω , amplitude A , operating conditions p and the spectrum of the output forced periodic response. Especially, the output spectrum at zero frequency, $Y(j\omega) = Y(0)$, known as the DC component [29], has received wide attention for its ability to quantify the gain of forced periodic operation [30].

$$y_{DC} = Y_0(p) + \sum_{n=1}^N \frac{1}{2^n} A_{k_1} \dots A_{k_n} H_n(j\omega_{k_1}, \dots, j\omega_{k_n}, p) \quad (5)$$

In the case where the system is excited by a general square-wave input

$$u(t) = \frac{4Au_0}{\pi} \sum_{i=1,3}^{\infty} \frac{\cos\left(i\omega t - \frac{\pi}{2}\right)}{i} \quad (6)$$

where u_0 is the steady-state input, Eq. (5) becomes

$$y_{DC} = Y_0(p) + A^2 \left[2 \left(\frac{2u_0}{\pi} \right)^2 H_2(j\omega, -j\omega, p) + 2 \left(\frac{2u_0}{3\pi} \right)^2 H_2(3j\omega, -3j\omega, p) + \dots \right] + A^4 \left[6 \left(\frac{2u_0}{\pi} \right)^4 H_4(j\omega, j\omega, -j\omega, -j\omega, p) + 6 \left(\frac{2u_0}{3\pi} \right)^4 H_4(3j\omega, 3j\omega, -3j\omega, -3j\omega, p) + \frac{4}{3} \left(\frac{2u_0}{\pi} \right)^4 H_4(j\omega, j\omega, j\omega, -3j\omega, p) + \frac{4}{3} \left(\frac{2u_0}{\pi} \right)^4 H_4(-j\omega, -j\omega, -j\omega, 3j\omega, p) + \frac{24}{32} \left(\frac{2u_0}{\pi} \right)^4 H_4(j\omega, -j\omega, 3j\omega, -3j\omega, p) + \dots \right] + \dots$$

Equation (7) indicates that once the amplitude and the GFRFs are determined, the performance gain achieved by forced periodic operation can be evaluated, which has stimulated many recent NFR-based studies [31–33].

2.2. The NFR model-based analysis of a non-isothermal CSTR

To elucidate the role of the DC component in analyzing nonlinear forced periodic operation chemical reactors, consider a non-isothermal CSTR system governed by the following ODEs [34]:

$$V \frac{dy_c(t)}{dt} = F u_p(t) - F y_c(t) - k e^{-\frac{E_A}{RT}} (y_c(t))^n V \quad (8)$$

$$V \rho C_P \frac{dT}{dt} = F \rho C_P T_i - F \rho C_P T - \Delta H_R k e^{-\frac{E_A}{RT}} (y_c(t))^n V - U A_w (T - T_J) \quad (9)$$

where t is time, n is the reaction order, V is the reactor volume, F and T_i are the flow rate and temperature of the inlet stream, k is the pre-exponential factor, E_A is the activation energy, R is the gas constant, ρC_P is the heat capacity, ΔH_R is the heat of reaction, $U A_w$ is the heat-transfer coefficient and area, T_J is the coolant temperature, $u_p(t)$ and $y_c(t)$ are the forced periodic operated reactants concentration at the inlet and outlet and T is the output temperature of the reactants.

Equations (8) and (9) are also known as the first principle model. Under the square-wave input modulation

$$u_p(t) = u_0 + u(t) = u_0 + \frac{4Au_0}{\pi} \sum_{i=1,3}^{\infty} \frac{\cos\left(i\omega t - \frac{\pi}{2}\right)}{i} \quad (10)$$

where u_0 represents the steady-state inlet concentration of the reactants. The steady-state output y_{c0} and T_0 can also be determined by rewriting models (8) and (9) under steady-state conditions as

$$F y_{c0} - F u_0 + k e^{-\frac{E_A}{RT_0}} (y_{c0})^n V = 0 \quad (11)$$

$$F \rho C_P T_0 - F \rho C_P T_i + \Delta H_R k e^{-\frac{E_A}{RT_0}} (y_{c0})^n V + U A_w T_0 - U A_w T_J = 0 \quad (12)$$

From the Volterra-series (1) and the NFR method [34], the DC component (7) can be derived and simplified as [34]

$$y_{DC} = Y_0(p) + A^2 \left[\frac{-4\Lambda(\omega)u_0^2\alpha Y_0(p)(1+\alpha)^2(1+St)}{\pi^2 B_{ps} (4A_{ps}^2\omega^2 + (B_{ps} - \omega^2)^2)} + \frac{-4\Lambda(3\omega)u_0^2\alpha Y_0(p)(1+\alpha)^2(1+St)}{9\pi^2 B_{ps} (36A_{ps}^2\omega^2 + (B_{ps} - 9\omega^2)^2)} + \dots \right] + \dots \quad (13)$$

Table 1A comparison of $y_{DC}(\omega, A, F)_{num}$ and $y_{DC}(\omega, A, F)_{NFR}$ of the non-isothermal CSTR

Frequency ω	Square wave forced periodic operation of inlet concentration					
	$y_{DC}(\omega, A, F)$ ($F = 1 \text{ m}^3/\text{min}$)					
	Amplitude $A = 15\%$			Amplitude $A = 50\%$		
	Numerical result	NFR Method	$\delta_{NFR_ \omega A}$	Numerical result	NFR Method	$\delta_{NFR_ \omega A}$
4.25	0.3417	0.3360	-1.7%	0.2934	0.1955	-33.4%
5.25	0.3346	0.3044	-9.0%	0.2948	-0.1553	-152.7%
5.53	0.3340	0.2977	-10.9%	0.2971	-0.2301	-177.5%
6.25	0.3371	0.3276	-2.8%	0.3055	0.1025	-66.5%
7.25	0.3453	0.3446	-0.2%	0.3180	0.2910	-8.5%
8.25	0.3489	0.3479	-0.3%	0.3313	0.3281	-1.0%
9.25	0.3496	0.3490	-0.2%	0.3416	0.3395	-0.6%

where

$$\alpha = k \exp\left(-\frac{E_A}{RT}\right) y_c(t)^{n-1} \frac{V}{F}, \gamma = \frac{E_A}{RT_0}, St = \frac{U A_w}{\rho C_p F},$$

$$\beta = \frac{\Delta H_R k_0 \exp\left(-\frac{E_A}{RT_0}\right) y_c(t)^n V}{\rho C_p T_0 F}$$

$$A_{ps} = -\frac{2 + n\alpha + St + \beta\gamma}{2},$$

$$B_{ps} = 1 + n\alpha + \beta\gamma + n\alpha St + St,$$

$$\Lambda(\omega) = n(n-1)\omega^2 + n^2[(1+St)^2 - 2\beta^2\gamma] - n(1+St + \beta\gamma)^2$$

To facilitate rapid analysis of forced periodic operation, the idea of truncating (13) up to the second order was proposed in [34] under the following operating conditions:

$$n = 1, k = 10^{10} \text{ min}^{-1}, V = 1 \text{ m}^3, E_A = 69256 \text{ kJ/kmol},$$

$$\Delta H_R = 543920 \text{ kJ/kmol}, T_i = 323 \text{ K}, T_j = 365 \text{ K},$$

$$\rho C_p = 4.184 \times 10^3 \text{ kJ/K/m}^3, u_0 = 2 \text{ kmol/m}^3,$$

$$U A_w = 27337 \text{ kJ/K/min}, R = 8.314 \text{ J/(mol} \cdot \text{K)}$$

Tables 1 and 2 show the system-analysis results at $\{F = 1 \text{ m}^3/\text{min}, A = 15\% \text{ and } 50\%, \omega = [4.25, \dots, 9.25] \text{ rad/min}\}$, and at $\{\omega = 4.9877 \text{ rad/min}, A = 49.98\%, F = [0.35, \dots, 0.95] \text{ m}^3/\text{min}\}$. Moreover, the corresponding results obtained by direct simulation of the first principle model (8) and (9) are also shown in the Tables for comparison. Here

$$\delta_{NFR_ \omega A} = \frac{y_{DC}(\omega, A, F)_{NFR} - y_{DC}(\omega, A, F)_{num}}{y_{DC}(\omega, A, F)_{num}} \quad (14)$$

and

$$\delta_{NFR_ F} = \frac{\left(\frac{y_{DC}(\omega, A, F) - Y_0(F)}{Y_0(F)}\right)_{NFR} - \left(\frac{y_{DC}(\omega, A, F) - Y_0(F)}{Y_0(F)}\right)_{num}}{\left(\frac{y_{DC}(\omega, A, F) - Y_0(F)}{Y_0(F)}\right)_{num}} \quad (15)$$

are the relative errors between the NFR method results denoted by the subscript NFR and the numerical results denoted by the subscript num.

Table 2A comparison of $\left(\frac{y_{DC}(\omega, A, F) - Y_0(F)}{Y_0(F)}\right)_{NFR}$ and $\left(\frac{y_{DC}(\omega, A, F) - Y_0(F)}{Y_0(F)}\right)_{num}$

Flow rate F	$\{\omega, A\} = \{4.9877 \text{ rad/min}, 49.98\%\}$		
	$\frac{y_{DC}(\omega, A, F) - Y_0(F)}{Y_0(F)}$		Relative error
	Numerical solution	NFR method	
0.35	-0.0364	-0.1259	245.7%
0.45	-0.0755	-0.1159	53.5%
0.55	-0.1387	-0.1109	-20.1%
0.65	-0.1989	-0.1381	-30.6%
0.75	-0.2120	-0.2081	-1.8%
0.85	-0.2019	-0.3790	87.7%
0.95	-0.1746	-0.7837	348.8%

It can be observed from the results in Tables 1 and 2 that the NFR method can capture the overall dynamic trends of the system outputs. This implies that the method can qualitatively determine whether forced periodic operation is superior to steady-state operation. However, there exist three obvious problems in quantitative analysis. First, both the sharp increase in relative error at the resonant frequency $\omega = 5.53 \text{ rad/min}$ and the incorrect sign of $y_{DC}(\omega, A, F)$ at high amplitude A highlight the insufficient quantitative accuracy of the method. Second, and more critically, the relative error arising from the frequency analysis as shown in Table 1 may affect the analysis of the system performance and further complicate the flow-rate design. Finally, the conventional NFR method relies heavily on the first principle model. Therefore, for complicated processes that cannot be effectively modeled, the qualitative analysis becomes difficult.

3. Data-driven NFR approach under fixed operating conditions

3.1. Procedure of the data-driven NFR approach

To quantitatively analyze and optimize forced periodic operation under a prescribed operating condition, a

data-driven NFR algorithm was developed in our previous work [24]. In the present work, this fixed-condition algorithm serves as the basis for the integrated design of both forced periodic operation and operating conditions. The algorithm is summarized in **Algorithm 1** for the case where a general square-wave input is applied.

Algorithm 1: Data-driven NFR method

Input: The square-wave input in Eq. (10) with m different amplitudes and $(n + 1)$ different frequencies, applied to a chemical reaction system under fixed operating conditions p ;

Output: The DC component $\hat{y}_{DC}(\omega, A, p)$ and the optimal design $\{\omega^*, A^*\}$

Step 1: Obtain the steady-state output $Y_0(p)$ and the forced-periodic outputs $y_{DC}(\omega_j, A_M, p)$, $j = 1, \dots, n + 1$, $M = 1, \dots, m$, from simulations or experiments.

Step 2: Rewrite the NFR model (7) as

$$y_{DC}(\omega, A, p) = Y_0(p) + A^2 N_2(\omega, p) + \dots + A^{2N} N_{2N}(\omega, p) \quad (16)$$

where

$$N_2(\omega, p) = 2 \left(\frac{2u_0}{\pi} \right)^2 H_2(j\omega, -j\omega, p) + 2 \left(\frac{2u_0}{3\pi} \right)^2 H_2(3j\omega, -3j\omega, p) + \dots$$

Step 3: Determine $N_{2i}(\omega_j, p)$, $i = 1, \dots, N$ at $n + 1$ different frequencies using

$$\begin{bmatrix} N_2(\omega_j, p) \\ \vdots \\ N_{2N}(\omega_j, p) \end{bmatrix} = (\Phi_A^T \Phi_A)^{-1} \Phi_A^T \begin{bmatrix} y_{DC}(\omega_j, A_1, p) - Y_0(p) \\ \vdots \\ y_{DC}(\omega_j, A_m, p) - Y_0(p) \end{bmatrix} \quad (17)$$

where

$$\Phi_A = \begin{bmatrix} A_1^2 & \dots & A_1^{2N} \\ \vdots & \ddots & \vdots \\ A_m^2 & \dots & A_m^{2N} \end{bmatrix}$$

For a data-driven NFR model that considers the nonlinearities up to the $2N$ th order, it is usually appropriate to consider $2N = 4-8$ for the quantitative analysis of nonlinear chemical reaction systems [24].

Step 4: Approximate $\hat{N}_{2i}(\omega, p)$, $i = 1, \dots, N$, within the considered frequency range using cubic-spline interpolation and the results obtained in **Step 3** to construct the data-driven NFR model

$$\hat{y}_{DC}(\omega, A, p) = Y_0(p) + A^2 \hat{N}_2(\omega, p) + \dots + A^{2N} \hat{N}_{2N}(\omega, p) \quad (18)$$

Step 5: Determine possible designs of $\{\omega, A\}$ from the coupled equations $\left\{ \frac{\partial(\hat{y}_{DC}(\omega, A, p) - Y_0(p))}{\partial A} = 0, \frac{\partial(\hat{y}_{DC}(\omega, A, p) - Y_0(p))}{\partial \omega} = 0 \right\}$.

Step 6: Compare the designs in **Step 5** with the boundary designs to determine the optimal design of $\{\omega^*, A^*\}$ within the design ranges, such that the desired $\hat{y}_{DC}(\omega^*, A^*, p) - Y_0(p)$ is obtained.

3.2. Optimal design of forced periodic operation parameters

To determine the square-wave forced periodic operation parameters that provide an initial design for the integrated framework, consider the CSTR system described by (8) and

(9) under the same operating conditions as those used in Tab. 1. When the system is subjected to square-wave inputs with 9 amplitudes and 13 frequencies

$$A = (10\%, 15\%, \dots, 50\%), \omega = (4, 4.5, \dots, 10) \text{ rad/min} \quad (19)$$

Following **Algorithm 1**, the data-driven NFR model is constructed under the consideration of 8th-order nonlinearity as

$$\hat{y}_{DC}(\omega, A, F) = Y_0(F) + A^2 \hat{N}_2(\omega, F) + \dots + A^8 \hat{N}_8(\omega, F) \quad (20)$$

where the inlet flow rate F is the operating condition of concern, and is fixed at $F = 1 \text{ m}^3/\text{min}$ in this section, and the steady-state output $Y_0(F) = 0.3499 \text{ kmol/m}^3$ is obtained from the steady-state model (11) and (12).

Table 3 shows the analysis results of $y_{DC}(\omega, A, F)$ obtained from the first principle model and the data-driven NFR model for the same cases as shown in Tab. 1. The purpose of this comparison is to verify whether the fixed-condition data-driven NFR model (20) can provide a reliable quantitative basis for the integrated design. Here

$$\delta_{\text{DATA-} \omega A} = \frac{\hat{y}_{DC}(\omega, A, F)_{\text{DATA}} - y_{DC}(\omega, A, F)_{\text{num}}}{y_{DC}(\omega, A, F)_{\text{num}}} \times 100\% \quad (21)$$

It can be observed from the results in Tab. 3 that, compared with the current model-based NFR method results in Table 1, the results obtained from the fixed-condition data-driven NFR model (20) are in close agreement with the numerical results for all the considered frequencies and amplitudes, even around the resonant frequency $\omega = 5.53 \text{ rad/min}$. The maximum absolute relative error is 0.6%. These results provide a reliable quantitative basis for the design of $\{\omega, A\}$.

Based on this validated data-driven NFR model, the optimal forcing parameters are then determined by comparing the solutions obtained from the coupled equations $\{\partial(\hat{y}_{DC}(\omega, A, F) - Y_0(F))/\partial A = 0, \partial(\hat{y}_{DC}(\omega, A, F) - Y_0(F))/\partial \omega = 0\}$ with the boundary designs, yielding

$$\{\omega^*, A^*\} = \{4.9877 \text{ rad/min}, 49.98\% \} \quad (22)$$

and the expected change in the residual concentration of the reactant relative to the steady-state operation is

$$\hat{y}_{DC}(\omega^*, A^*, F) - Y_0(F) = -0.0567 \text{ kmol/m}^3 \quad (23)$$

which is in close agreement with the numerical results obtained from (8) and (9), namely, $\{\omega^*, A^*\} = \{4.8350 \text{ rad/min}, 50\% \}$ and $y_{DC}(\omega^*, A^*, F) - Y_0(F) = -0.0582 \text{ kmol/m}^3$.

The data-driven NFR model (20) under the fixed inlet flow rate F provides an initial design for the integrated design procedure introduced in the following sections.

4. Optimal design of operating conditions for forced periodically operated chemical reaction systems

4.1. Data-driven model of operating conditions

To optimally design the operating conditions using a data-driven approach, a straightforward strategy is to apply

Table 3A comparison of $y_{\text{DC}}(\omega, A, F)_{\text{num}}$ and $\hat{y}_{\text{DC}}(\omega, A, F)_{\text{DATA}}$ for the non-isothermal CSTR

Frequency ω	Square wave forced periodic operation of inlet concentration					
	$y_{\text{DC}}(\omega, A, F)$ ($F = 1 \text{ m}^3/\text{min}$)					
	Amplitude $A = 15\%$			Amplitude $A = 50\%$		
	Numerical result	Data-driven method	$\delta_{\text{DATA-}\omega A}$	Numerical result	Data-driven method	$\delta_{\text{DATA-}\omega A}$
4.25	0.3417	0.3420	0.1%	0.2934	0.2952	0.6%
5.25	0.3346	0.3365	0.6%	0.2948	0.2939	-0.3%
5.53	0.3340	0.3360	0.6%	0.2971	0.2967	-0.1%
6.25	0.3371	0.3378	0.2%	0.3055	0.3064	0.3%
7.25	0.3453	0.3458	0.1%	0.3180	0.3186	0.2%
8.25	0.3489	0.3485	-0.1%	0.3313	0.3309	-0.1%
9.25	0.3496	0.3493	-0.1%	0.3416	0.3418	0.1%

the data-driven NFR approach under different operating conditions. However, this strategy cannot directly provide a unified model that reveals the coupled influence of both the operating condition p and the forced periodic operation on the system performance. Therefore, an operating-condition-dependent model is required.

Consider the case where a nonlinear chemical reaction process is subject to a forced periodic operation input with operational parameters $\{\omega, A\}$, and a single operating condition p is selected as the condition to be designed. Denote the steady-state output and the DC component of the forced-periodic output response to the operating condition p under k distinct values as $Y_0(p_l)$ and $y_{\text{DC}}(\omega, A, p_l)$, $l = 1, \dots, k$. It follows from the data-driven NFR model (18) that

$$\hat{y}_{\text{DC}}(\omega, A, p) = \hat{Y}_0(p) + A^2 \hat{N}_2(\omega, p) + \dots + A^{2N} \hat{N}_{2N}(\omega, p) \quad (24)$$

Since the forced periodic operation parameters $\{\omega, A\}$ are prescribed during the operating-condition design, the contributions of the higher-order nonlinearities can be incorporated into an effective nonlinear response function with respect to the operating condition p as

$$\hat{y}_{\text{DC}}(\omega, A, p) = \hat{Y}_0(p) + A^2 \hat{N}_{\text{eff}}(\omega, A, p) \quad (25)$$

where

$$\begin{aligned} \hat{N}_{\text{eff}}(\omega, A, p) &= \hat{N}_2(\omega, p) + \dots + A^{2N-2} \hat{N}_{2N}(\omega, p) \\ &= \sum_{i=1}^N A^{2i-2} \hat{N}_{2i}(\omega, p) \end{aligned} \quad (26)$$

It should be noted that this equivalent second-order form does not imply that the higher-order nonlinearities are neglected. Instead, under the prescribed forced periodic operation parameters $\{\omega, A\}$, the higher-order effects are incorporated into the effective function $\hat{N}_{\text{eff}}(\omega, A, p)$.

From the data $Y_0(p_l)$ and $y_{\text{DC}}(\omega, A, p_l)$, $l = 1, \dots, k$, the effective nonlinear response function $\hat{N}_{\text{eff}}(\omega, A, p)$ in (25) at these k distinct sampled values of the operating condition p can be determined as

$$\begin{bmatrix} \hat{N}_{\text{eff}}(\omega, A, p_1) \\ \vdots \\ \hat{N}_{\text{eff}}(\omega, A, p_k) \end{bmatrix} = \frac{1}{A^2} \begin{bmatrix} y_{\text{DC}}(\omega, A, p_1) - Y_0(p_1) \\ \vdots \\ y_{\text{DC}}(\omega, A, p_k) - Y_0(p_k) \end{bmatrix} \quad (27)$$

To extend $\hat{N}_{\text{eff}}(\omega, A, p_l)$, $l = 1, \dots, k$ to any value of the operating condition p within the design range $p \in [p_1, p_k]$, an approximation of $\hat{N}_{\text{eff}}(\omega, A, p)$ can be obtained directly by cubic-spline interpolation as

$$\begin{cases} \hat{N}_{\text{eff}}(\omega, A, p) = a_j + b_j(p - p_j) + c_j(p - p_j)^2 + d_j(p - p_j)^3 \\ p \in [p_j, p_{j+1}], \quad j = 1, \dots, k-1 \end{cases} \quad (28)$$

and the steady-state output $Y_0(p_l)$, $l = 1, \dots, k$, is similarly approximated as

$$\begin{cases} \hat{Y}_0(p) = a_{j0} + b_{j0}(p - p_j) + c_{j0}(p - p_j)^2 + d_{j0}(p - p_j)^3 \\ p \in [p_j, p_{j+1}], \quad j = 1, \dots, k-1 \end{cases} \quad (29)$$

where a_j, b_j, c_j, d_j and $a_{j0}, b_{j0}, c_{j0}, d_{j0}$ are all polynomial coefficients of cubic-spline functions and can be determined as described in [35]. It should be noted that cubic-spline interpolation is not the only possible approximation method for constructing the data-driven model, and other suitable interpolation methods can also be used when appropriate.

This makes it possible to construct a data-driven model for operating-condition design under the prescribed forced periodic operation parameters $\{\omega, A\}$ as

$$\hat{y}_{\text{DC}}(\omega, A, p) = \hat{Y}_0(p) + A^2 \hat{N}_{\text{eff}}(\omega, A, p) \quad (30)$$

for quantitative analysis of how the operating condition p affects the behavior of forced periodically operated chemical reaction processes.

4.2. Optimal design of operating conditions

To fully exploit the advantages of the operating condition, the data-driven NFR model (30) is further applied to the design of the chemical reaction system. Denote

$$\hat{\gamma}(\omega, A, p) = \frac{\hat{y}_{\text{DC}}(\omega, A, p) - \hat{Y}_0(p)}{\hat{Y}_0(p)} \quad (31)$$

which quantifies the improvement rate of forced periodic operation relative to steady-state operation under the same operating condition and can be evaluated for any operating condition of concern using (30). Thus, over each segment of the operating range, the designs can be obtained by solving

$$\frac{d\hat{\gamma}(\omega, A, p)}{dp} = \frac{d}{dp} \left(\frac{A^2 \hat{N}_{\text{eff}}(\omega, A, p)}{\hat{Y}_0(p)} \right) = 0 \quad (32)$$

where $p \in [p_j, p_{j+1}]$, $j = 1, \dots, k-1$. The possible designs of p for the **periodically operated** process can be identified as

$$\{(\omega, A, p_1^*), (\omega, A, p_2^*), \dots, (\omega, A, p_L^*)\} \quad (33)$$

where L is the total number of solutions obtained from (32) and the corresponding improvement rates are given by:

$$\hat{\gamma}(\omega, A, p_1^*), \hat{\gamma}(\omega, A, p_2^*), \dots, \hat{\gamma}(\omega, A, p_L^*) \quad (34)$$

Moreover, by comparing the results in (34) with those at the **boundaries of all interpolation segments**

$$\hat{\gamma}(\omega, A, p_1), \hat{\gamma}(\omega, A, p_2), \dots, \hat{\gamma}(\omega, A, p_k) \quad (35)$$

the operating-condition design p^* can be determined according to the following criteria:

- For reactant-residual-focused outputs

$$\hat{\gamma}(\omega, A, p^*) = \min \left(\{ \hat{\gamma}(\omega, A, p_1^*), \dots, \hat{\gamma}(\omega, A, p_L^*) \} \cup \{ \hat{\gamma}(\omega, A, p_1), \dots, \hat{\gamma}(\omega, A, p_k) \} \right) \quad (36)$$

- For product-focused outputs

$$\hat{\gamma}(\omega, A, p^*) = \max \left(\{ \hat{\gamma}(\omega, A, p_1^*), \dots, \hat{\gamma}(\omega, A, p_L^*) \} \cup \{ \hat{\gamma}(\omega, A, p_1), \dots, \hat{\gamma}(\omega, A, p_k) \} \right) \quad (37)$$

Through **this design procedure**, the operating condition that **minimizes or maximizes** the improvement rate, **according to the output of interest**, can be determined **within the prescribed design range**.

4.3. Application to flow rate optimization

To quantitatively evaluate how the varying operating condition affects the system performance and to carry out the **flow-rate design based** on the designed forcing input in (22), consider the CSTR system under the forcing input with the optimally designed **forcing parameters** $\{\omega^*, A^*\} = \{4.9877 \text{ rad/min}, 49.98\%\}$ and take the inlet flow rate F as the operating condition of concern. In the case where the flow rate F is varied over 9 values

$$F = \{0.3, 0.4, \dots, 1.1\} \text{ m}^3/\text{min} \quad (38)$$

Using the equivalent form in Eq. (30), in which the **higher-order nonlinear effects are incorporated into** $\hat{N}_{\text{eff}}(\omega, A, F)$, the data-driven model can be constructed as

$$\hat{y}_{\text{DC}}(\omega^*, A^*, F) = \hat{Y}_0(F) + (A^*)^2 \hat{N}_{\text{eff}}(\omega^*, A^*, F) \quad (39)$$

Fig. 1 shows the reduction rate of the residual reactant concentration at the outlet $\hat{\gamma}(\omega^*, A^*, F)$ evaluated from (31)

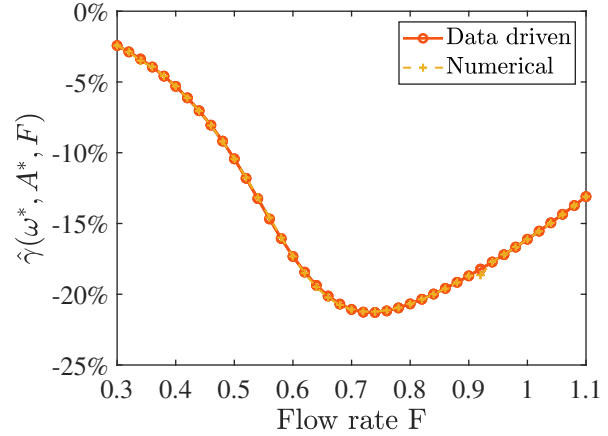


Fig. 1: Reduction rate of the residual reactant concentration under $\{\omega^*, A^*\} = \{4.9877 \text{ rad/min}, 49.98\%\}$ and $F \in [0.3, 1.1] \text{ m}^3/\text{min}$.

and (39) for $F \in [0.3, 1.1] \text{ m}^3/\text{min}$. **As shown in the figure**, compared with the results obtained by the current NFR method in Tab. 2, the data-driven model (39) accurately captures the reduction rate of the residual reactant concentration **achieved by the optimal design of the flow rate F** .

Moreover, from (32)–(36), the optimal design of the flow rate occurs at $F^* = 0.733 \text{ m}^3/\text{min}$ and the expected reduction rate is

$$\begin{aligned} \hat{\gamma}(\omega^*, A^*, F^*) &= \frac{\hat{y}_{\text{DC}}(\omega^*, A^*, F^*) - \hat{Y}_0(F^*)}{\hat{Y}_0(F^*)} \times 100\% \\ &= -21.295\% \end{aligned} \quad (40)$$

which **indicates** a further decrease in the residual reactant concentration through the optimal design of the **inlet flow rate**, compared with the independent optimal design of the forced periodic operation in (22) as

$$\begin{aligned} \hat{\gamma}(\omega^*, A^*, F) \big|_{F=1 \text{ m}^3/\text{min}} &= \frac{\hat{y}_{\text{DC}}(\omega^*, A^*, F) - \hat{Y}_0(F)}{\hat{Y}_0(F)} \times 100\% \\ &= \frac{-0.0567}{0.3499} \times 100\% = -16.205\%. \end{aligned} \quad (41)$$

5. Integrated design of both forced periodic operation and operating conditions

5.1. The overall framework

It has been demonstrated that the optimal designs of external forced periodic operation inputs and the operating condition can exploit process nonlinearities to improve the process performance. Since the two designs are **coupled but non-conflicting**, an iterative joint data-driven design approach that extends the original data-driven NFR method by incorporating operating-condition design is developed and summarized as follows:

Step 1: Determine an initial operating condition $p^{(0)}$ from the selected k distinct operating condition **values** p_l , $l = 1, \dots, k$;

Step 2: Construct square-wave inputs with known operational parameters $\{\omega_j, A_M\}$, $j = 1, \dots, n+1$, $M = 1, \dots, m$ and set the initial iteration cycle number to $r = 0$ and let q denote the index of the accepted-design sequence, with $q = 0$ corresponding to the first accepted design;

Step 3: Run **Algorithm 1** under the current operating condition $p^{(r)}$ to determine the candidate forced periodic operation design

$$\{\tilde{\omega}^{(r+1)}, \tilde{A}^{(r+1)}\}$$

Step 4: Obtain the steady-state outputs $Y_0(p_l)$, $l = 1, \dots, k$ and the forced-periodic output response $y_{DC}(\tilde{\omega}^{(r+1)}, \tilde{A}^{(r+1)}, p_l)$, $l = 1, \dots, k$;

Step 5: Perform the operating-condition design using (25)–(37) to obtain the candidate operating condition $\tilde{p}^{(r+1)}$. The operating condition for the next alternating cycle is then updated as

$$p^{(r+1)} = \tilde{p}^{(r+1)}$$

irrespective of whether the design is accepted;

Step 6: For reactant-residual-focused outputs, the candidate design

$$\tilde{x}^{(r+1)} = \{\tilde{\omega}^{(r+1)}, \tilde{A}^{(r+1)}, \tilde{p}^{(r+1)}\}$$

is accepted to replace the current accepted design

$$x^{(q)} = \{\omega^{(q)}, A^{(q)}, p^{(q)}\}$$

only if the improvement rate is reduced, that is,

$$\gamma(\omega^{(q)}, A^{(q)}, p^{(q)}) > \gamma(\tilde{\omega}^{(r+1)}, \tilde{A}^{(r+1)}, \tilde{p}^{(r+1)})$$

If this condition is satisfied, set

$$x^{(q+1)} = \tilde{x}^{(r+1)}$$

Otherwise, the candidate design is rejected and the current accepted design retains

$$\{\omega^{(q)}, A^{(q)}, p^{(q)}\}$$

The acceptance rule ensures that the accepted improvement-rate sequence is monotonic non-increasing for reactant-residual-focused outputs. The corresponding convergence justification is provided in Appendix A.

It should be noted that since no accepted integrated design is available before the first alternating cycle, the first feasible candidate design is initialized as the accepted incumbent.

Step 7: For each newly accepted design, check whether the relative change between two consecutive accepted improvement rates satisfies

$$\frac{|\gamma(\omega^{(q+1)}, A^{(q+1)}, p^{(q+1)}) - \gamma(\omega^{(q)}, A^{(q)}, p^{(q)})|}{\max\{|\gamma(\omega^{(q)}, A^{(q)}, p^{(q)})|, \eta\}} \leq \epsilon \quad (42)$$

where ϵ is the prescribed convergence tolerance and $\eta > 0$ is a small constant introduced to avoid division by zero.

If the stopping condition (42) is not satisfied, update the iteration-cycle index by setting

$$r \leftarrow r + 1$$

and return to **Step 3**.

If the stopping condition in Eq. (42) is satisfied, continue the iterative procedure until the next candidate design is obtained. If the stopping condition is also satisfied for this next accepted design, that is,

$$\frac{|\gamma(\omega^{(q+2)}, A^{(q+2)}, p^{(q+2)}) - \gamma(\omega^{(q+1)}, A^{(q+1)}, p^{(q+1)})|}{\max\{|\gamma(\omega^{(q+1)}, A^{(q+1)}, p^{(q+1)})|, \eta\}} \leq \epsilon \quad (43)$$

where the design $\{\omega^{(q+2)}, A^{(q+2)}, p^{(q+2)}\}$ is regarded as a verification to reduce the risk of premature termination caused by an isolated small improvement. The final design can be determined as

$$\{\omega^*, A^*, p^*\} = \{\omega^{(q+1)}, A^{(q+1)}, p^{(q+1)}\}$$

The procedure is also terminated if the iteration index r reaches the prescribed upper limit. In this case, the final accepted $\{\omega, A, p\}$ is regarded as the terminal integrated design.

It should be noted that the alternating design is aimed at reducing the dimensionality and computational burden. For each alternating cycle, the proposed alternating strategy requires $\mathcal{O}((n+1)m + k)$ response evaluations, rather than $\mathcal{O}((n+1)mk)$ required by a direct full-grid search over (ω, A, p) . For multiple operating conditions $p = (p_1, \dots, p_j)$ considered on a joint matrix form, the requirement becomes $\mathcal{O}((n+1)m + \prod_{i=1}^j k_i)$, compared with $\mathcal{O}((n+1)m \prod_{i=1}^j k_i)$ for a direct full-grid search. Moreover, in the numerical case study, the required output responses are generated from the first principle model, while in practical chemical reaction applications, the required input-output data can directly be obtained from experiments and the integrated data-driven design mainly involves low-dimensional computational complexity.

5.2. Application of the integrated data-driven design approach

To demonstrate the effectiveness of the integrated data-driven design approach, the proposed method is first applied to the CSTR system described by (8) and (9) under the same initial parameters. The first alternating design cycle has been described in detail in Sections 3.2 and 4.3.

Building upon the initial design results, an iterative design process is then implemented to reduce the residual reactant concentration at the outlet, with a convergence tolerance of $\epsilon = 0.3\%$. Fig. 2 shows the accepted designs of $\{\omega^*, A^*, F^*\}$ and the improvement rate comparison between $\hat{\gamma}(\omega^*, A^*, F^*)$ obtained from the proposed integrated data-driven method and that evaluated directly from the first principle model (8) and (9), where

$$\delta_{it} = \frac{\hat{\gamma}(\omega^*, A^*, F^*)_{\text{Data}} - \hat{\gamma}(\omega^*, A^*, F^*)_{\text{num}}}{\hat{\gamma}(\omega^*, A^*, F^*)_{\text{num}}} \times 100\% \quad (44)$$

reflects the relative difference between the two performance evaluations.

It can be seen from Fig. 2 that under the prescribed two-stage stopping criterion with $\epsilon = 0.3\%$, the alternating design terminates after 22 cycles and the final design obtained by the data-driven method is

$$\{\omega^*, A^*, F^*\} = \{4.342 \text{ rad/min}, 50\%, 0.6656 \text{ m}^3/\text{min}\} \quad (45)$$

and the reduction rate in residual reactant concentration is

$$\begin{aligned}\hat{\gamma}(\omega^*, A^*, F^*)_{\text{Data}} &= \frac{\hat{y}_{\text{DC}}(\omega^*, A^*, F^*) - \hat{Y}_0(F^*)}{\hat{Y}_0(F^*)} \times 100\% \\ &= \frac{0.2673 - 0.3447}{0.3447} \times 100\% = -22.5\%\end{aligned}\quad (46)$$

Moreover, the total reduction rate with respect to the original steady-state operating condition, $Y_0(F) = 0.3499 \text{ mol/m}^3$, can also be obtained as

$$\begin{aligned}\hat{\gamma}(\omega^*, A^*, F^*)_{\text{Data}_F} &= \frac{\hat{y}_{\text{DC}}(\omega^*, A^*, F^*) - Y_0(F_0)}{Y_0(F_0)} \times 100\% \\ &= \frac{0.2673 - 0.3499}{0.3499} \times 100\% = -23.6\%\end{aligned}\quad (47)$$

which clearly shows the advantage that the integrated data-driven design of forced periodic operation $\{\omega, A\}$ and F brings about to the non-isothermal CSTR system. In addition, the close agreement between the improvement rates obtained from the data-driven model and the first principle model shown in Fig. 2 (e) also supports the effectiveness of the proposed integrated data-driven design strategy within the prescribed design domain.

5.3. Sensitivity analysis of the integrated design results for the non-isothermal CSTR system

Since the inlet flow rate F is the operating condition considered in the non-isothermal CSTR case study, the initial value F_0 defines the starting point of the design procedure. Therefore, F_0 is selected to assess the sensitivity of the proposed method to the initial operating condition. In the case where the initial flow rate F_0 varies over

$$F_0 = \{0.3, 0.6, 1.0\} \text{ m}^3/\text{min} \quad (48)$$

which covers low, intermediate and high values within the design range of the inlet flow rate F . Tab. 4 shows the terminal integrated design results of $\{\omega^*, A^*, F^*\}$ obtained from the different initial inlet flow rates F_0 with respect to the initial inlet flow rate F_0 under the same two-stage stopping criterion and the convergence tolerance $\epsilon = 0.3\%$ as those used in the CSTR case study.

It can be observed from the results shown in Tab. 4 that when the same convergence tolerance $\epsilon = 0.3\%$ is used, the terminal designs obtained from different initial flow rates $F_0 = \{0.3, 0.6, 1.0\} \text{ m}^3/\text{min}$ are highly consistent. Although slight differences can be observed in the terminal design of the forced periodic operation frequency ω^* and the flow rate F^* , all the obtained designs remain close to $\{4.3 \text{ rad/min}, 50\%, 0.66 \text{ m}^3/\text{min}\}$. The corresponding improvement rates $\hat{\gamma}(\omega^*, A^*, F^*)$ remain around -22.5% , and the maximum absolute difference among the $\hat{\gamma}(\omega^*, A^*, F^*)$ results is only 0.01% , which is much smaller than the prescribed convergence tolerance $\epsilon = 0.3\%$. This indicates that the proposed integrated data-driven method exhibits low sensitivity to the initial flow rate within the design range.

Table 4

Sensitivity analysis of the integrated design results to the initial flow rate

F_0 (m ³ /min)	ω^* (rad/min)	A^*	F^* (m ³ /min)	$\hat{\gamma}(\omega^*, A^*, F^*)$
0.3	4.343	50%	0.6660	-22.46%
0.6	4.372	50%	0.6710	-22.45%
1.0	4.342	50%	0.6656	-22.46%

5.4. Comparison with the existing methods

To provide a comparison between the proposed data-driven method and the existing data-driven methods, the results obtained from the conventional NFR method, Gaussian process regression combined with differential evolution (GPR-DE), and artificial neural network combined with genetic algorithm (ANN-GA) [17] are summarized in Tab. 5. Moreover, the output performance under steady-state operation and the results obtained by the direct grid-search design based on the first principle model (8) and (9) are also shown in Tab. 5.

It can be seen from the results in Tab. 5 that, although the conventional NFR method obtained forced periodic operation parameters $\{\omega^*, A^*\}$ that are similar to those obtained from the grid-search method, the design produces no performance improvements, showing that the conventional NFR method cannot deliver an optimal design in this case.

When the inlet flow rate is incorporated as the operating condition to be designed, it can be observed from the results in Tab. 5 that the proposed data-driven method, ANN-GA and GPR-DE can all provide an integrated design of $\{\omega, A, F\}$. The final design obtained using the proposed data-driven method achieves a 22.46% reduction in the residual reactant concentration, which is close to the 22.5% reduction achieved by the reference design obtained through direct grid-search using the first principle model in (8) and (9). Over the same ranges of design parameters, the performances obtained by ANN-GA and GPR-DE are 22.3% and 21.9%, respectively. These results demonstrate that the proposed method can achieve a performance which is comparable to the designs by the machine-learning-based approaches and closely matches the reference design obtained from the first principle model.

However, there exists a key distinction between the proposed data-driven method and the machine-learning-based methods. Machine-learning-based methods rely on a black-box relationship between operating variables and performance indicators, which lacks physical interpretability and is susceptible to overfitting, particularly when data are limited. In contrast, the proposed method is built upon a physically interpretable nonlinear frequency response framework that explicitly captures the physically interpretable coupled effects of forcing frequency, forcing amplitude, and operating conditions under periodic operations. The proposed data-driven method not only provides an effective integrated design strategy, but also establishes a physically interpretable

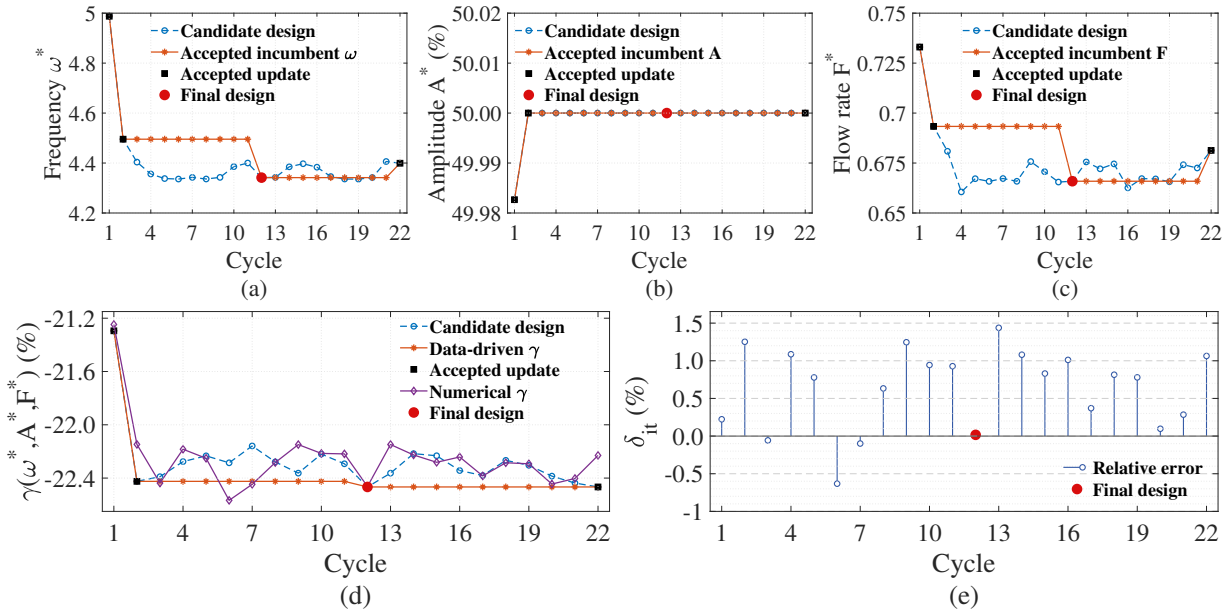


Fig. 2: The evolution process of the proposed iterative designs of $\{\omega^*, A^*, F^*\}$ and a comparison of the reduction rate of reactant concentration with the result of the numerical solution.

Table 5

Results comparison for the non-isothermal CSTR case study

Method	ω^* (rad/min)	A^*	F^* (m ³ /min)	Performance improvement
Steady-state operation	—	—	Fixed	Baseline
Grid-search numerical design of FPO using (8)–(9)	4.8350	50%	Fixed	−0.0582 kmol/m ³
Optimal design of FPO using conventional NFR method	5.4997	50%	Fixed	−0.5799 kmol/m ³
Grid-search integrated design using (8)–(9)	4.3676	49.99%	0.6565	22.5% reduction
Integrated design using data-driven method	4.342	50%	0.6656	22.5% reduction
Integrated design using ANN-GA	4.6142	50%	0.7083	22.3% reduction
Integrated design using GPR-DE	4.1428	50%	0.6601	21.9% reduction

analytical framework for the analysis of periodically forced nonlinear chemical reaction systems.

6. Experimental study and analysis

6.1. Experimental device

To demonstrate the practical applicability of the proposed integrated data-driven method, a reversible reaction between CO₂ and deionized water at room temperature was investigated in this study, with the inlet CO₂ concentration periodically modulated by square-wave inputs. The chemical reaction can be expressed as



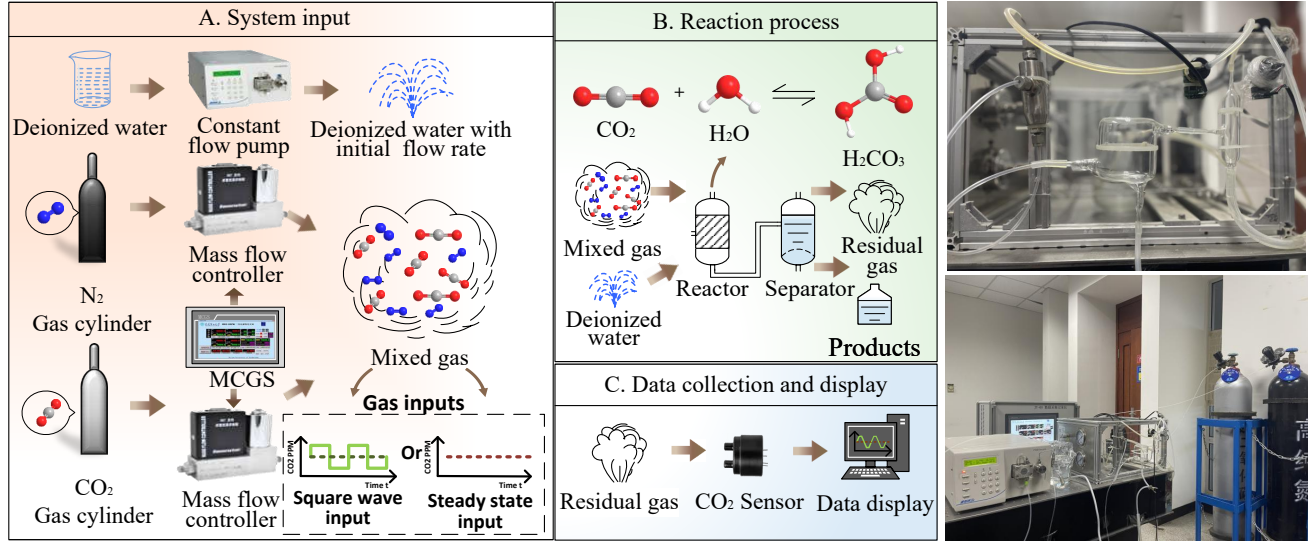
A small-scale chemical experimental device was built for this study, as shown in Fig. 3. The primary objective is to quantify the enhancement in CO₂ absorption by deionized water under different square-wave forced periodic inputs of the inlet CO₂ concentration with the deionized-water flow rate varied as the operating condition, relative to the original steady-state operation.

The experimental rig mainly consists of three components: forced periodic operation input generation, the reaction process, and data collection and visualization. In the input generation unit, the master computer regulates the valve openings of two mass flow controllers for N₂ and CO₂, based on the preset gas flow rates configured through the MCGS interface to enable steady-state or forced periodic operation. For the reaction process, the modulated gas reacts reversibly with deionized water at different constant flow rates at room temperature. The residual gas is then directed to a CO₂ sensor, which measures and visually displays the volume fraction of CO₂ after the reaction.

Prior to the CO₂ absorption experiments, all the sensors and measurement devices were calibrated. The outlet CO₂ concentration was recorded at a sampling interval of 2s. For each combination of forced periodic operation parameters and the deionized-water flow rate, the CO₂ absorption system was operated for at least four complete forcing cycles before periodic steady operation was considered to be reached. The residual concentration of CO₂ at the outlet was then

Table 6Main measurement and control instruments used in the laboratory-scale CO₂ absorption experiment

Equipment	Type	Specification	Accuracy	Repeatability
Mass flow controller	D07	30 sccm	±2% F.S.	±0.2% F.S.
Constant flow pump	P230p	nominal 10 mL/min	±2%	RSD < 0.5%
CO ₂ sensor	SprintIR-6S®	0–100 vol. %	±(70 ppm + 5% rdg) for CO ₂ ≤ 60 vol. % ±(300 ppm + 5% rdg) for CO ₂ > 60 vol. %	–

**Fig. 3:** An illustration of the laboratory scale CO₂ absorption process.

recorded over the subsequent complete forcing cycle. Moreover, the run-to-run and day-to-day variation experiments have been added in the Supplementary Material.

6.2. Experimental data pre-processing

Since the inlet concentration of the mixed gas before the reaction is determined by the preset flow rates, while the CO₂ sensor measures the outlet volume fraction after the reaction, the dimensions of the two quantities are different. Therefore, an intermediate quantity is introduced to provide a consistent measure of the CO₂ absorption performance. From the working principle of the CO₂ sensors, the measured volume fraction at the outlet can be represented as [36]

$$V_f(t) = \frac{F_{CO_2}(t) - F_{Abs}(t)}{F_{MG}(t) - F_{Abs}(t)} \quad (50)$$

where $V_f(t)$ is the measured CO₂ volume fraction, $F_{CO_2}(t)$ is the flow rate of CO₂ controlled by the master computer, $F_{Abs}(t)$ is the flow rate of CO₂ absorbed by the deionized water, and $F_{MG}(t)$ is the total inlet flow rate of the mixed gas. Consequently, the intermediate measurement is defined as

$$F_{Abs}(t) = F_{MG}(t) - \frac{F_{MG}(t) - F_{CO_2}(t)}{1 - V_f(t)} \quad (51)$$

which has the same unit as the flow rate. For the dynamic operation of the inlet CO₂ concentration, the primary focus

is to enhance the absorption capacity through forced periodic operation, which is quantified as:

$$\begin{aligned} y_{DC}(\omega, A, F_w) - Y_0(F_w) &= F_{Abs}^{fp}(\omega, A, F_w) - F_{Abs}^{ss}(F_w) \\ &= \frac{1}{Q} \sum_{k=1}^Q F_{Abs}(\kappa T) - F_{Abs}^{ss}(F_w) \end{aligned} \quad (52)$$

where $F_{Abs}^{fp}(\omega, A, F_w)$ represents the absorption capacity over a complete square-wave period under forced periodic operation with parameters $\{\omega, A\}$ and deionized water flow rate F_w , $F_{Abs}^{ss}(F_w)$ is the absorption capacity under steady-state operation, Q is the total number of sampling points over one complete forcing cycle, T is the sampling interval.

It should be noted that compared with the CSTR study, the CO₂ absorption experiment focuses on enhancing absorption capacity. Therefore, $y_{DC}(\omega, A, F_w) - Y_0(F_w)$ is expected to take positive values, with larger values indicating greater enhancements in the CO₂ absorption capacity.

6.3. Data-driven design of forced periodic operation

When the initial quantities of the device were preset as in Tab. 7, it can be known from the collected data and (51) that the absorption capacity under steady-state operation with the initial deionized water flow rate was $Y_0(F_{w0}) = 1.8971$ ml/min.

Table 7

Initial quantities of the experiment rig

Quantities	Value	Units
Steady-state N_2 flow rate F_{N_2}	12	mL/min
Steady-state CO_2 flow rate F_{CO_2}	8	mL/min
Initial flow rate of deionized water F_{w0}	8	mL/min

When the inlet CO_2 concentration varied periodically in the form of square waves under 6 different frequencies

$$\omega = \left(\frac{2\pi}{20}, \frac{2\pi}{18}, \frac{2\pi}{14}, \frac{2\pi}{12}, \frac{2\pi}{10}, \frac{2\pi}{8} \right) \text{ rad/min} \quad (53)$$

and 6 different amplitudes

$$A = (50\%, 55\%, 60\%, 65\%, 75\%, 80\%) \quad (54)$$

36 experiments were conducted to obtain $y_{DC}(\omega, A, F_{w0})$ based on Eq. (52), and the corresponding absorption enhancements are listed in Tab. 8.

Considering nonlinearities up to the 8th order, the data driven NFR model at the initial deionized water flow rate F_{w0} can be constructed using **Algorithm 1** as

$$\hat{y}_{DC}(\omega, A, F_{w0}) = Y_0(F_{w0}) + A^2 \hat{N}_2(\omega, F_{w0}) + \dots + A^8 \hat{N}_8(\omega, F_{w0}) \quad (55)$$

Moreover, by simultaneously solving $\partial \hat{y}_{DC}(\omega, A, F_{w0}) / \partial \omega = 0$ and $\partial \hat{y}_{DC}(\omega, A, F_{w0}) / \partial A = 0$ and comparing with the results at the boundaries of the design domain, the design of forced periodic operation parameters within the design domain was determined as

$$\{\omega^*, A^*\} = \{2\pi/20 \text{ rad/min}, 80\%\} \quad (56)$$

and the expected absorption enhancement achieved by this design was

$$\hat{y}_{DC}(\omega^*, A^*, F_{w0}) - Y_0(F_{w0}) = 0.5336 \text{ mL/min} \quad (57)$$

which is only 0.9% different from the experimental result of 0.5286 mL/min.

6.4. Data-driven design of the deionized water flow rate

To further determine the deionized water flow rate through data-driven design and enhance absorption-capacity improvement achieved by forced periodic operation, 7 additional experiments were conducted under 7 deionized water flow rates as

$$F_w = [6.5, 7, 8, 8.5, 9, 9.5, 10] \text{ mL/min} \quad (58)$$

Under the designed square-wave input parameters (56), the steady-state absorption capacity $Y_0(F_w)$ and the forced periodic output $y_{DC}(\omega^*, A^*, F_w)$ were obtained through experiments, with the results summarized in Tab. 9. Using the equivalent form in Eq. (30), the data-driven model at

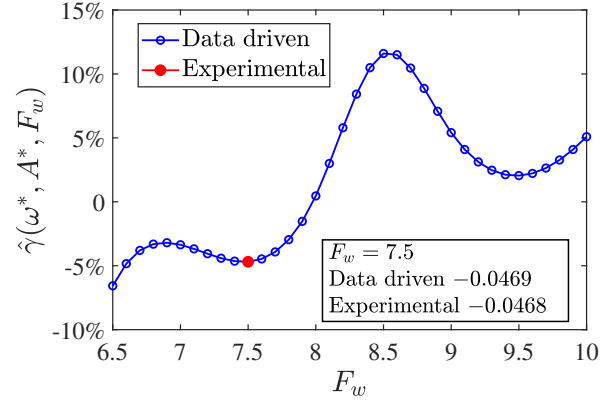


Fig. 4: The enhancement rate of absorption capacity $\hat{\gamma}(\omega^*, A^*, F_w)$ evaluated using (60).

any deionized water flow rate F_w of interest within the investigated range can be constructed using (24)-(30) as

$$\hat{y}_{DC}(\omega^*, A^*, F_w) = \hat{Y}_0(F_w) + (A^*)^2 \hat{N}_{eff}(\omega^*, A^*, F_w) \quad (59)$$

Fig. 4 presents the overall nonlinear relationship between the deionized water flow rate and the absorption capacity enhancement rate, defined as

$$\hat{\gamma}(\omega^*, A^*, F_w) = \frac{\hat{y}_{DC}(\omega^*, A^*, F_w) - \hat{Y}_0(F_w)}{\hat{Y}_0(F_w)} \times 100\% \quad (60)$$

over the range $F_w \in [6.5, 10]$ mL/min. The result for $F_w = 7.5$ mL/min, which was not used in constructing the data-driven model (59), is also highlighted as a validation result. At the validation flow rate $F_w = 7.5$ mL/min, the enhancement rate obtained from the data-driven method is

$$\hat{\gamma}(\omega^*, A^*, F_w) = -4.69\%$$

which differs by only 0.21% from the experimental result of $\gamma(\omega^*, A^*, F_w) = -4.68\%$.

The close agreement in both the sign and the magnitude indicates that the constructed data-driven model (59) can provide a reliable estimation of the performance enhancement.

On this basis, the inlet deionized water flow rate for the CO_2 absorption system can be determined using (31)-(37) as

$$F_w^* = 8.540 \text{ mL/min.} \quad (61)$$

and the expected absorption enhancement rate evaluated by the design is

$$\hat{\gamma}(\omega^*, A^*, F_w^*) = 11.69\% \quad (62)$$

6.5. Integrated design of forced periodic operation and deionized water flow rate

Building upon the individual data-driven designs of square-wave forced periodic operation and the operating condition, i.e., the deionized water flow rate, an alternating

Table 8

The absorption enhancement $(y_{DC}(\omega, A, F_{w0}) - Y_0(F_{w0}))$ transformed from experimental data under square-wave inputs

Amplitude A	$y_{DC}(\omega, A, F_{w0}) - Y_0(F_{w0})$ (mL/min)					
	Frequency ω (rad/min)					
	$2\pi/20$	$2\pi/18$	$2\pi/14$	$2\pi/12$	$2\pi/10$	$2\pi/8$
50%	0.2921	0.2452	0.0116	0.0030	-0.0950	-0.1049
55%	0.4275	0.2662	0.2266	0.1133	-0.0245	-0.1099
60%	0.3571	0.2458	0.0793	0.0250	-0.0781	-0.1110
65%	0.4083	0.3484	0.1987	0.1429	-0.0394	-0.1952
75%	0.5260	0.4028	0.0734	0.0863	-0.1773	-0.1239
80%	0.5286	0.4143	0.2742	0.2961	0.1343	-0.1424

Table 9

Experimental results of $Y_0(F_w)$ and $y_{DC}(\omega^*, A^*, F_w)$ under the designed input with $\{\omega^*, A^*\} = \{2\pi/20 \text{ rad/min}, 80\%\}$

F_w (mL/min)	$Y_0(F_w)$ (mL/min)	$y_{DC}(\omega^*, A^*, F_w)$ (mL/min)
6.5	1.5940	1.4893
7	1.8493	1.7871
8	2.1628	2.1727
8.5	2.2377	2.4972
9	2.4677	2.6013
9.5	2.6105	2.6639
10	2.7462	2.8859

It can be observed from the results shown in Fig. 5 that the integrated design of forced periodic operation and the deionized water flow rate was finally determined as

$$\{\omega^*, A^*, F_w^*\} = \left\{ \frac{2\pi}{20}, 78\%, 8.5 \text{ mL/min} \right\} \quad (63)$$

and the expected absolute absorption capacity improvement relative to the initial steady state operation achieved evaluated by the data-driven model for this design is

$$\hat{y}_{DC}(\omega^*, A^*, F_w^*) - \hat{Y}_0(F_{w0}) = 0.6151 \text{ mL/min} \quad (64)$$

which is only 0.0216 mL/min different from the result

$$y_{DC}(\omega^*, A^*, F_w^*) - Y_0(F_{w0}) = 0.5935 \text{ mL/min.} \quad (65)$$

obtained from the experimental results. Moreover, the expected absorption-capacity enhancement rate evaluated by the data-driven model for this design is

$$\hat{\gamma}(F_w^*) = \frac{\hat{y}_{DC}(\omega^*, A^*, F_w^*) - \hat{Y}_0(F_w^*)}{\hat{Y}_0(F_w^*)} \times 100\% = 11.5\% \quad (66)$$

which is in close agreement with the result

$$\gamma(F_w^*) = \frac{y_{DC}(\omega^*, A^*, F_w^*) - Y_0(F_w^*)}{Y_0(F_w^*)} \times 100\% = 11.9\% \quad (67)$$

obtained from the experimental verification 0.4 percentage points.

The experimental verification in Fig. 5 shows that the integrated design of forced periodic operation and the inlet deionized water flow rate can improve the absorption capacity relative to the initial steady-state operation. The agreement between the results evaluated from the data-driven model and the experimental results validates the effectiveness of the integrated data-driven design method when applied in the laboratory-scale CO₂ absorption system.

Although the proposed data-driven framework has demonstrated its potential through laboratory-scale CO₂ absorption experiments, its industrial adoption still requires systematic validation and engineering extension under practical operating conditions. First, industrial reaction processes often exhibit more complex nonlinearities and dynamic characteristics than the simple CO₂ absorption process,

integrated design was also implemented in the CO₂ experiment to jointly determine the forced periodic operation parameters and the inlet deionized water flow rate, thereby enhancing the absorption capacity. In each alternating design cycle, following the iterative design procedure described in Section 5.1, the forced periodic operation parameters and the inlet deionized water flow rate were updated using the corresponding data-driven models, with the associated CO₂ absorption performance evaluated from the experimental data according to Eq.(52).

Fig. 5 shows the iterative evolution of the candidate designs of the forced periodic operation parameters $\{\omega^*, A^*\}$ and the deionized water flow rate F_w^* . The absolute absorption-capacity improvement relative to the initial steady-state operation

$$\hat{y}_{DC}(\omega^*, A^*, F_w^*) - \hat{Y}_0(F_{w0})$$

and the enhancement rate

$$\hat{\gamma}(\omega^*, A^*, F_w^*) = \frac{\hat{y}_{DC}(\omega^*, A^*, F_w^*) - \hat{Y}_0(F_w^*)}{\hat{Y}_0(F_w^*)} \times 100\%$$

obtained from the data-driven method, together with the corresponding experimental verification results under the data-driven design are also illustrated in Fig. 5. The former evaluates the total improvement achieved by the integrated design relative to the steady-state operation at the initial inlet flow rate F_{w0} , whereas the latter evaluates the improvement achieved by forced periodic operation over steady-state operation under the designed inlet deionized water flow rate F_w^* .

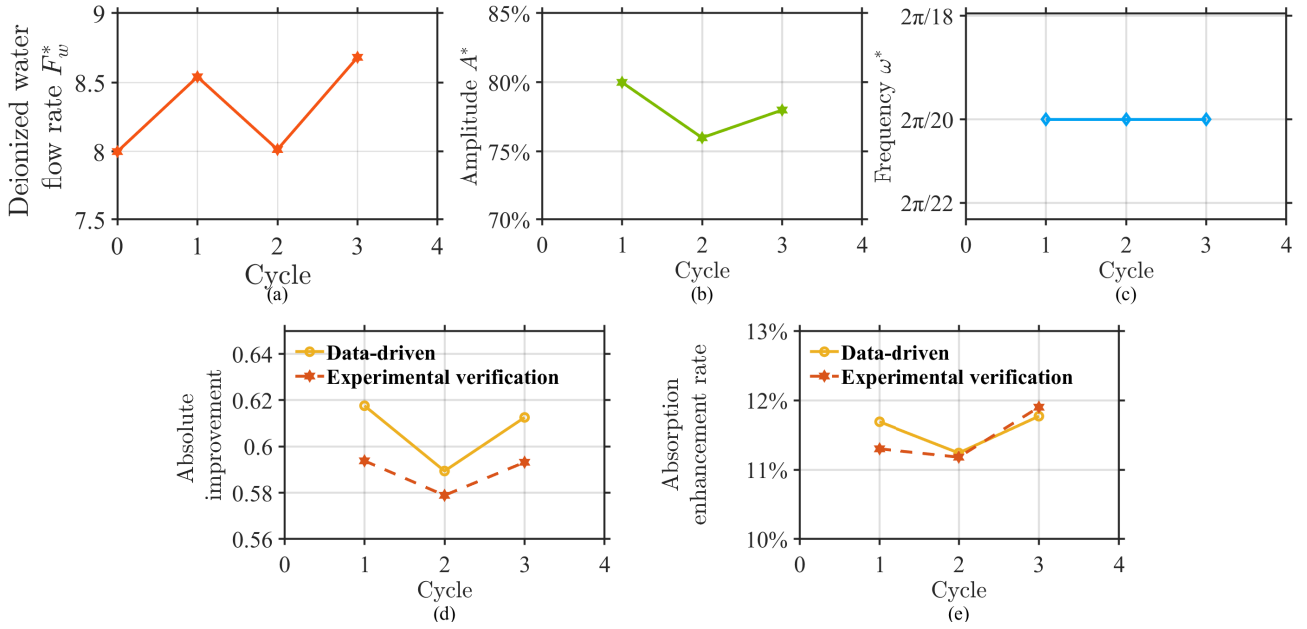


Fig. 5: The evolution process of $\{\omega^*, A^*, F_w^*\}$ and the corresponding enhancement in CO_2 absorption capacity.

including process delays, feed fluctuations and variations in operating conditions. These factors may introduce additional challenges to the proposed method. In addition, the current experimental validation is limited to a single operating condition. When multiple operating conditions must be jointly designed in industrial applications, further experimental and industrial-scale validation is required to verify the applicability and effectiveness of the proposed approach.

7. Conclusion

Enhancing the conversion rate of nonlinear chemical reaction systems can often be achieved through the design of forced periodic operation and the operating conditions. However, analyzing the higher-order nonlinearities inherent in such processes remains a significant challenge. Recently, nonlinear frequency response NFR-based methods have been proposed to address this issue. Nevertheless, because these methods rely on first-principles models, which are often highly complex or unavailable in practice, their application to quantitative analysis and design is substantially constrained.

To overcome these limitations, this study proposes a data-driven method that enables the simultaneous analysis and design of both forced periodic operation and operating conditions. By directly utilizing input–output process data, the proposed approach avoids dependence on first principle models and thereby improves the practical applicability. Furthermore, through an iterative design framework, the method achieves an integrated design of both the forced periodic operation and key operating condition, allowing their synergistic contribution to system performance enhancement.

The proposed method is validated through both numerical simulations and laboratory-scale CO_2 absorption experiments, demonstrating its effectiveness in facilitating process control and the integrated design of forced periodic operation and operating conditions while enhancing the conversion performance of chemical reaction systems. Although the present study focuses on relatively simple reaction systems and considers only a single operating condition as the design variable, the underlying principles of the proposed method are, in principle, applicable to more complex processes involving multiple operating conditions. By incorporating dimensionality-reduction techniques to alleviate the curse of dimensionality, the proposed framework can be extended to high-dimensional design problems, thereby broadening its potential for industrial applications.

Appendix A. Convergence justification of the integrated design algorithm

The convergence analysis is based on the following conditions:

- The feasible design ranges of ω , A , and p are closed and bounded;
- $\hat{y}(\omega, A, p)$ is continuous over the feasible domain $D = \Omega \times \Lambda \times P$, where $\Omega = [\omega_{\min}, \omega_{\max}]$, $\Lambda = [A_{\min}, A_{\max}]$, $P = [p_{\min}, p_{\max}]$;
- $\hat{Y}_0(p) > 0$ over the prescribed operating range.

These conditions are satisfied within the design ranges considered in this study. Therefore, $J(x) = \hat{y}(\omega, A, p)$ is well defined and continuous on the compact feasible design domain D .

According to the acceptance rule of the proposed data-driven method, a newly obtained candidate design at iteration $r + 1$, denoted as $\tilde{x}^{(r+1)} = (\tilde{\omega}^{(r+1)}, \tilde{A}^{(r+1)}, \tilde{p}^{(r+1)})$ is accepted to replace the current accepted design $x^{(q)} = (\omega^{(q)}, A^{(q)}, p^{(q)})$ only when

$$J(\tilde{x}^{(r+1)}) \leq J(x^{(q)}) \quad (\text{A.1})$$

Thus, if the candidate design is accepted, the accepted design is updated as

$$x^{(q+1)} = \tilde{x}^{(r+1)}. \quad (\text{A.2})$$

Otherwise, no new accepted design is generated, the current accepted design $x^{(q)}$ is retained, which means that the accepted objective sequence $\{J(x^{(q)})\}$ is monotonic non-increasing. Since $J(x)$ is continuous on the compact domain D , it attains a finite lower bound $J_{\min}$ on D . Hence,

$$J_{\min} \leq J(x^{(q)}), \quad \forall q \quad (\text{A.3})$$

Therefore, the accepted objective sequence is monotonic non-increasing and bounded below. According to the monotone convergence theorem [37], there exists a finite limit J_{∞} such that

$$\lim_{q \rightarrow \infty} J(x^{(q)}) = J_{\infty} \quad (\text{A.4})$$

Consequently,

$$\lim_{q \rightarrow \infty} |J(x^{(q+1)}) - J(x^{(q)})| = 0 \quad (\text{A.5})$$

CRedit authorship contribution statement

Yuhan Dong: Writing – original draft, Validation, Methodology. **Z.Q. Lang:** Writing – review & editing, Methodology. **Jun Zhao:** Funding acquisition, Project administration. **Wei Wang:** Writing – review & editing, Resources, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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