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A novel data-driven approach to analysis and optimal design of forced periodic operation of chemical reactions

Yuhan Dong, Zi-Qiang Lang, Jun Zhao, Senior *Member, IEEE,* Wei Wang, *Senior Member, IEEE,* and Zhong Lan

***Abstract*—Forced periodic operation is a technique that periodically changes the manipulating variable of a chemical reaction system in order to exploit nonlinear dynamics to improve reactant conversion rate. However, the analysis and design of a periodically operated chemical process is a significant challenge. To resolve this problem, recently, Nonlinear Frequency Response (NFR) based methods have been proposed. However, because of the need to derive the NFR from a first principle model, existing NFR methods can only perform qualitative analysis to simple processes and are often difficult to be applied in engineering practice. The present study proposes a novel data driven approach to the analysis and optimal design of forced periodic operation of chemical reactions. From the data generated numerically using the first principle model or experimentally from experimental tests, the approach produces a data-driven NFR model that can readily be used for both quantitative study and optimal design of forced periodic operation of any complexities. This can fundamentally address the challenges faced by the existing NFR methods, and provides an effective approach that can potentially be applied in engineering practice. Simulation studies and experimental works are carried out on the application of the new method to an isothermal CSTR system and a laboratory-scale carbon dioxide absorption process, respectively. The results verify the effectiveness and advantage of the newly proposed data driven approach and demonstrate the potential of the new approach in engineering applications.**

***Index Terms*—Nonlinear chemical system, Forced periodic operation, Data-driven modeling, analysis and optimal design.**

I. Introduction

In chemical productions, the consumption of reactants is usually accompanied. If the ratio of the conversion of reactants to products can be increased not only can more products be obtained, but also the purpose of saving production costs can be achieved. Therefore, how to improve the reactant conversion rate is a key issue in chemical production [1].

In chemical industry, most reactions during chemical production can behave nonlinearly. Forced periodic operation is an approach that exploits the nonlinear behaviors to improve the process performance in terms of reactant conversion rate. This is often achieved by periodically alternating the process input around its steady-state to produce a corresponding periodic variation for the process output represented by reactant conversion rate [2]. Consequently, thanks to the nonlinear behaviors of chemical processes, the average value of the varying process output in terms of the concentration of reactant can be lower than the output under the steady-state operation as shown in Fig. 1. A simple explanation of the nonlinear behavior that is exploited by periodic operations for a better chemical reaction performance is provided in Appendix A.

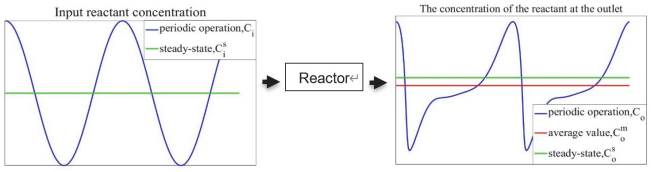

Figure 1 An illustration of a forced periodic operation and its advantage over traditional steady-state operation: Because $C_0^m < C_0^s$, overall, the periodic operation achieves a better performance than traditional steady-state operation.

Forced periodic operation has attracted extensive attention from researchers due to its advantages and potential from 1960s. Rüdiger Lange et al. [3] applied forced periodic operation to chemical system experimental and simulation experiments respectively, proving the superiority of forced periodic operation on alpha-methyl styrene conversion. Y. W. Budhi et al. [4] discussed the influence of hydrogen concentration under square wave forced periodic operation on the hydrogen separation of Pd75-Ag25 membrane by experiments, indicating that the recovery of hydrogen was obviously better than steady-

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Y. Dong, J. Zhao, and W. Wang. are with the School of Control Science and Engineering, Dalian University of Technology, Dalian 116024, China (e-mail: yuhan_dong@mail.dlut.edu.cn; zhaoj@dlut.edu.cn; wangwei@dlut.edu.cn).

Z. Lang is with the Department of Automatic Control and Systems Engineering, University of Sheffield, Sheffield, S1 3JD, U.K. and is associated with East China University of Science and Technology, China (e-mail: z.lang@sheffield.ac.uk).

Z. Lan is with the Institute of Chemical Engineering, Dalian University of Technology, Dalian 116024, China (e-mail: lanzhong@dlut.edu.cn).

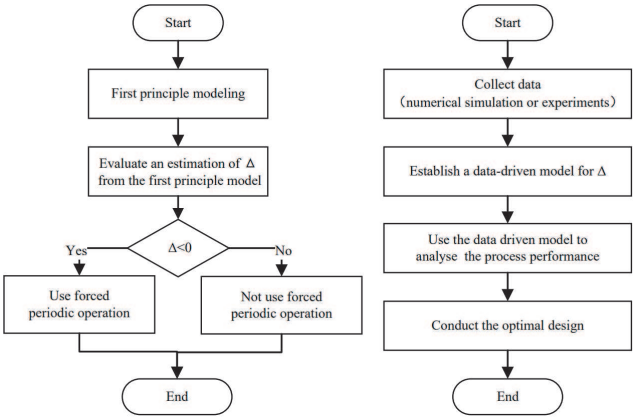
state operation. In addition, many research teams have also carried out research experiment studies on forced periodic operation to improve the conversion rate [5], product yield [6], and selectivity [7]. However, in these works, the selection of the parameters of the forced periodic operational input, such as amplitude and frequency, is all based on try and error or the experience of researchers.

In addition to simplified analysis and experimental works, researchers have also carried out more sophisticated analytical studies on both the condition and the degree of forced periodic operation improvement. In this respect, first-harmonic Fourier series [8] and Pontryagin maximum principle [9] were used to evaluate the gain from the perspective of optimal control. However, this again requires an accurate analytical first principle model, which is difficult to be applied to more complicated systems. S. Varigonda et al. [10] proposed a method that uses differential flatness to simplify the optimal periodic control. However, this is limited on obtaining an optimal control scheme for specific cases.

More recently, in order to determine whether a forced periodic operation can improve the performance of a chemical reaction process, a method called Nonlinear Frequency Response (NFR) was proposed by Nikolić et.al [11]. The NFR had then been applied to a non-isothermal Continuous Stirred Tank Reactor (CSTR) with a single forced periodic operation input [12][13]. Moreover, system analysis on adiabatic CSTR [14] and methanol synthesis [15][16] has also been realized. More recently, by exploiting the computation software, the computer-aided Nonlinear Frequency Response (cNFR) methods [17][18] have been developed.

The basic idea of the NFR method is to determine and analyze the difference between the average value C_o^m of the concentration at the outlet under periodic operation and the concentration value C_o^s under steady state operation as illustrated in Fig. 1, i.e., $\Delta = C_o^m - C_o^s$, using a nonlinear system frequency analysis and the first principle model, which describes the physical and chemical mechanism underlying the chemical reaction process under study [19]. This is implemented by the procedure shown in Fig. 2 (a). However, the difficulties with carrying out frequency analysis for more complicated nonlinear chemical systems imply that the NFR approach can only be used to conduct a qualitative evaluation of whether a beneficial effect can be achieved by the exploitation of a forced periodic operation. As far as we are aware of, the quantitative analysis of the performance of forced periodic operations and the optimal design of periodic operational parameters are still significant challenges to the application of forced periodic operation in practical chemical reaction processes. In response to these challenges, in the present study, a novel data driven approach is developed for the quantitative analysis and optimal design of forced periodic operations of a wide range of chemical reaction processes.

The fundamental idea of the new approach is as illustrated in Fig. 2 (b). It is to use the simulated or experimental data from a periodically operated chemical process to establish a model in a data driven way representing the relationship between the performance index Δ and the operational parameters and then exploit the established model to evaluate the performance and carry out the optimal design of the forced periodic operation. The implementation of a forced periodic operation in actual chemical production process normally requires an actuator, such as the mass flow controller to realize the required periodic input. The data can be collected from either the numerical simulations using a first principle model or experimental studies on the periodically operated chemical process The constructed model of Δ is derived based on the nonlinear frequency response approach and data driven methods, but thanks to its data driven nature, it can be obtained for chemical reaction processes of any complexities. This can fundamentally resolve the challenges to current NFR based techniques and has the potential to be widely applied in engineering practice. The focus of the present study is concerned with the derivation of an algorithm that can implement the novel data driven approach. The algorithm is then applied to a simple *n*th order isothermal CSTR reaction model to validate the effectiveness of the new approach via simulation studies. Afterwards, a laboratory-scale carbon dioxide absorption experiment is conducted to demonstrate the potential of the new approach in chemical engineering applications. The new approach is expected to profoundly resolve the difficulties with current NFR based analyses, produce an innovative method that can facilitate the optimal design of forced periodic operations, and provide an effective technology that can potentially bring about significant economic benefits to a wide range of chemical engineering production processes.



(a) The basic idea of the NFR method (b) The idea of the new approach

Figure 2 An illustration of the current NFR method and the proposed new data-driven approach

II. THE NFR MODEL AND EXISTING NFR MODEL-BASED ANALYSIS OF PERIODICALLY OPERATED CHEMICAL REACTION PROCESS

A. DC component of the output response of nonlinear systems to multitone inputs

The fundamental basis of the NFR model of periodically operated chemical reaction processes is the Volterra series approach of nonlinear systems. The Volterra series approach considers nonlinear systems that can be described by the Volterra series [20].

$$y(t)=Y_0+\sum_{n=1}^{N}\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}h_n(\tau_1,\cdots\tau_n)\prod_{i=1}^{n}u(t-\tau_i)d\tau_i \quad (1)$$

where $y(t)$ and $u(t)$ are the output and input of the system, Y_0 is the system's steady-state output, N is the maximum order of the system nonlinearity, and $h_n(\tau_1,\ldots,\tau_n)$ is the n^{th} order Volterra kernel of the system.

For this type of nonlinear systems, when the input is a general multi-tone input such that

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

where $A_{-i}=A_i^*$, $\omega_{-i}=-\omega_i$, Lang [21] has derived the output frequency response $Y(j\omega)$ which reveals the relationship between the system input and output in the frequency domain as follows:

$$\begin{cases} Y(j\omega)=\begin{cases} Y_0+\dfrac{1}{2^n}\displaystyle\sum_{\omega_{k_1}+\cdots+\omega_{k_n}=0}A_{k_1}\ldots A_{k_n}H_n\left(j\omega_{k_1},\ldots,j\omega_{k_n}\right),\omega=0 \\ \dfrac{1}{2^{n-1}}\displaystyle\sum_{\omega_{k_1}+\cdots+\omega_{k_n}=\omega}A_{k_1}\ldots A_{k_n}H_n\left(j\omega_{k_1},\ldots,j\omega_{k_n}\right),\omega>0 \end{cases} \\ k_l\in\{-K,\ldots,-1,1,\ldots,K\},l=1,\ldots,n \end{cases} \quad (3)$$

where $Y_n(j\omega)$ is the n^{th}-order output spectrum of the system, and

$$H_n(j\omega_{k_1},\ldots,j\omega_{k_n})=\int_{-\infty}^{\infty}\cdots\int_{-\infty}^{\infty}h_n(\tau_1,\ldots,\tau_n)e^{-j(\omega_{k_1}\tau_1+\cdots+\omega_{k_n}\tau_n)}d\tau_1\ldots d\tau_n \quad (4)$$

is known as the n^{th}-order Generalized Frequency Response Function (GFRF) [21].

Equation (3) was referred to as NFR model in the area of periodic operation of chemical processes where what is of most concern is the system response at zero frequency known as DC component [22], which can be represented by

$$y_{DC}=Y(0)=Y_0+\sum_{n=1}^{N}\frac{1}{2^n}\sum_{\omega_{k_1}+\cdots+\omega_{k_n}=0}A_{k_1}\ldots A_{k_n}H_n\left(j\omega_{k_1},\ldots,j\omega_{k_n}\right) \quad (5)$$

In the case where the system input is a single tone sinusoidal signal

$$u(t)=Au_0\cos(\omega t)=\sum_{i=-1,i\neq 0}^{1}\frac{Au_0}{2}exp(j\omega t) \quad (6)$$

and when the system input $u(t)$=0 the system output $y(t)$= Y_0 in the steady state, (5) becomes

$$y_{DC}=Y_0+2\left(\frac{u_0}{2}\right)^2A^2H_2(j\omega,-j\omega)+6\left(\frac{u_0}{2}\right)^4A^4H_4(j\omega,j\omega,-j\omega,-j\omega)+\cdots \quad (7)$$

Equation (7) is the very basis of many studies on the analysis of periodic operation of chemical processes [23]-[26].

B. The NFR model of a simple periodically operated chemical process

In order to explain current methods that apply the NFR model of nonlinear systems, consider an ideal weakly nonlinear CSTR described by differential equation [27]

$$V\frac{dy(t)}{dt}=Fu_p(t)-Fy(t)-k\left(y(t)\right)^nV \quad (8)$$

where V (m^3) is the constant volume of the reactor, F (m^3/s) is the flow rate, k ($s^{-1}mol^{-1}$) is the reaction rate, $u_p(t)$ and $y(t)$ are the real-time concentrations of the reactants at the inlet and outlet, respectively, with unit mol/m^3. Equation (8) is basically the 1^{st} principle model of the chemical reaction process, which was obtained to describe the isothermal CSTR from the perspective of material balance. Denote

$$u_p(t)=u_0+u(t)=u_0+Au_0\cos(\omega_d t) \quad (9)$$

where u_0 represents the steady state concentration of the reactant at the inlet. The steady state output Y_0 of the process under u_0 can be determined by solving the algebraic equation

$$0=Fu_0-FY_0-k\left(Y_0\right)^nV \quad (10)$$

Around the steady state thus determined, the chemical process can be represented by a Volterra series model as illustrated in Fig. 3 providing a basis for the analysis of the chemical process using the NFR approach.

Following the existing NFR method, the DC component of concern in (7) can be derived as [27]

$$y_{DC}=Y_0+\frac{y_0C_2A^2F^2\left(1+kV\left(Y_0\right)^{n-1}/F\right)^2}{2V^2\left(1+n\alpha\right)\left(\left((1+n\alpha)F/V\right)^2+\omega_d^2\right)}+\frac{A^4\left(u_0\right)^4\left(\Sigma_1+\Sigma_2+\Sigma_3+\Sigma_4\right)}{16(1+n\alpha)F/V}+\cdots \quad (11)$$

where

$$\alpha=kV\left(Y_0\right)^{n-1}/F$$

$$\Sigma_1=2C_2F\left(H_2(j\omega,j\omega)H_2(-j\omega,-j\omega)+2\left(H_2(j\omega,-j\omega)^2\right)\right)/Y_0V$$

$$\Sigma_2=6C_2F\left(H_1(j\omega)H_3(j\omega,-j\omega,-j\omega)+H_1(-j\omega)H_3(j\omega,j\omega,-j\omega)\right)/Y_0V$$

$$\Sigma_3=3C_3F\left(\left(H_1(j\omega_d)\right)^2H_2(-j\omega_d,-j\omega_d)+\left(H_1(-j\omega_d)\right)^2H_2(j\omega_d,j\omega_d)+4H_1(j\omega_d)H_1(-j\omega_d)H_2(j\omega_d,-j\omega_d)\right)/\left(Y_0\right)^2V$$

$$\Sigma_4=6C_4F\left(H_1(j\omega)\right)^2\left(H_1(-j\omega)\right)^2/\left(Y_0\right)^3V$$

Equation (11) is the NFR model of system (8) under input (9).

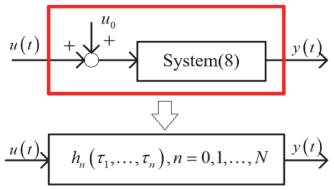


Figure 3 Volterra series representation of isothermal CSTR system (8)

C. Existing NFR based analysis of periodically operated chemical processes

In [27], (11) truncated up to the 2^{nd} order nonlinearity was used to analyze the performance of the periodically operated process (8) with k=0.01 $s^{-1}mol^{-1}$, u_0=1 mol/m^3, V/F=1000 s. The objective was to evaluate the advantage of a sinusoidal signal driven periodic operation of the inlet concentration over traditional static operation. Table 1 shows a comparison of the result from this NFR based analysis at ω_d =0.0009 *rad/s* where

$$\delta_{NFR}=\frac{\left(y_{DC}(\omega_d,A)-Y_0\right)_{NFR}-\left(y_{DC}(\omega_d,A)-Y_0\right)_{num}}{\left(y_{DC}(\omega_d,A)-Y_0\right)_{num}} \quad (12)$$

showing the relative error between the NFR analysis ($y_{DC}(\omega_d$, $A)$-$Y_0)_{NFR}$ and numerical results ($y_{DC}(\omega_d$, $A)$-$Y_0)_{num}$.

It can be found from the comparisons in Table 1 is that the sign of the results determined using the NFR method is always correct. This implies that the existing NFR method is capable to qualitatively determine whether a periodical operation has an advantage over a traditional operation or not for system (8). However, there exists two obvious problems with the qualitative analysis. First, the considerable relative error δ_{NFR}

when amplitude A is significant implies that the NFR method can't be applied to perform quantitively analysis. Secondly, the method depends on the availability of a 1^{st} principle model under study. Therefore, if there is no an applicable 1^{st} principle model, which is the case in most practical systems, one even can't carry out a qualitative analysis as shown in Table 1.

These problems motivate the present study. The aim is to develop an innovative data-driven approach to profoundly resolve these problems with the existing NFR method. The objectives are to

(1) Produce the data-driven NFR model of a chemical reaction process that can take into account system nonlinearity up to any higher order of concern

(2) Carry out quantitative analysis of a periodically operated chemical reaction process, and then

(3) Perform a design of the periodical operation for a desired performance in terms of an optimal reactant conversion rate.

TABLE 1 A COMPARISON OF $(y_{DC}(\omega_d, A) - Y_0)_{NFR}$ AND $(y_{DC}(\omega_d, A) - Y_0)_{num}$ UNDER A SINUSOIDAL OPERATION OF CSTR MODEL (8)

Amplitude A	Frequency ω_d =0.0009 *rad/s*		
	$y_{DC}(\omega_d, A)$-Y_0		Relative error
	Numerical solution	NFR method	δ_{NFR}
15%	-0.00042	-0.00042	0.0%
25%	-0.00118	-0.00117	-0.8%
35%	-0.00235	-0.00229	-2.6%
45%	-0.00395	-0.00378	-4.3%
55%	-0.00605	-0.00565	-6.6%
65%	-0.00872	-0.00789	-9.5%
75%	-0.01208	-0.01051	-13.0%
85%	-0.01635	-0.01349	-17.5%
95%	-0.02190	-0.01686	-23.0%

III. DATA DRIVEN NFR MODEL OF PERIODICALLY OPERATED CHEMICAL REACTION PROCESS

A. Derivation of the data driven NFR model

Under the assumption that a chemical reaction system can be represented by the Volterra Series (1), it is known from (7) that the DC component of the steady-state response of a periodically operated chemical reaction can be described as

$$y_{DC}(\omega, A) = Y_0 + A^2 N_2(\omega) + A^4 N_4(\omega) + \cdots + A^{2N} N_{2N}(\omega) \quad (13)$$

when the system nonlinearity up to the N^{th} order is taken into account. In (13), $N_{2i}(\omega)$, i=1, 2, …, N are the functions of the operational frequency ω and take different forms when different periodic inputs are applied to the system.

In the case of single tone sinusoidal input (6), it can be found by comparing (13) with (7) that

$$N_{2i}(\omega) = \frac{(2i)!}{i!i!} \cdot \left(\frac{u_0}{2}\right)^{2i} H_{2i}\left(\underbrace{j\omega, \ldots, j\omega}_{i}, \underbrace{-j\omega, \ldots, -j\omega}_{i}\right), i = 1, \ldots, N \quad (14)$$

Although (14) implies that (13) is essentially a complicated representation for the DC component of the steady state response of a periodically operated chemical process, the model can readily be determined from the simulated or experimentally obtained data of the process input and output as follows.

Consider the situations where the input and output data of a chemical process periodically operating at n+1 frequencies of ω_{dj}, j=1, …, n+1 are available. From these data, it is known that $N_2(\omega_{dj})$, $N_4(\omega_{dj})$, …, $N_{2N}(\omega_{dj})$, j=1, …, n+1 can be determined as

$$\begin{bmatrix} N_2(\omega_{dj}) \\ \vdots \\ N_{2N}(\omega_{dj}) \end{bmatrix} = \left(\Phi_A^T \Phi_A\right)^{-1} \Phi_A^T \begin{bmatrix} y_{DC}(\omega_{dj}, A_1) - Y_0 \\ \vdots \\ y_{DC}(\omega_{dj}, A_M) - Y_0 \end{bmatrix} \quad (15)$$

where

$$\Phi_A = \begin{bmatrix} A_1^2 & \cdots & A_1^{2N} \\ \vdots & \vdots & \vdots \\ A_M^2 & \cdots & A_M^{2N} \end{bmatrix}$$

Moreover, an approximation for $N_2(\omega)$, $N_4(\omega)$, …, $N_{2N}(\omega)$ with ω being any frequency can be determined using the results obtained by (15) and the cubic spline function as

$$\begin{cases} \hat{N}_{2i}(\omega) = a_{ij} + b_{ij}(\omega - \omega_{dj}) + c_{ij}(\omega - \omega_{dj})^2 + d_{ij}(\omega - \omega_{dj})^3 \\ \omega \in [\omega_{dj}, \omega_{d(j+1)}], i = 1, \ldots, N, j = 1, \ldots, n+1 \end{cases} \quad (16)$$

where a_{ij}, b_{ij}, c_{ij} and d_{ij} are determined as shown in Appendix B.

This allows one to obtain a data driven NFR model of a periodically operated chemical reaction at any frequency ω of interest as follows

$$\hat{y}_{DC}(\omega, A) = Y_0 + A^2 \hat{N}_2(\omega) + A^4 \hat{N}_4(\omega) + \cdots + A^{2N} \hat{N}_{2N}(\omega) \quad (17)$$

where $\hat{y}_{DC}(\omega, A)$ represents an estimate of the DC component of the steady state response of a periodically operated chemical reaction and $\hat{N}_2(\omega), \ldots, \hat{N}_{2N}(\omega)$ are as determined by (16). It can be seen from (17) that the newly proposed data-driven NFR approach allows the approximation of the output response of the nonlinear system up to any order N of system nonlinearity. For an appropriate quantitative analysis, it is often possible to achieve an accurate approximation by taking N as N = 2~4.

Based on (17), the data driven NFR model-based analysis and design of a periodically operated chemical reaction process can, for the first time, be conducted.

B. Data-driven NFR model of a simple periodically operated chemical process

In order to demonstrate the derivation of a specific data driven NFR model, consider the same nonlinear system (8) with n=2, k=0.01 $s^{-1}mol^{-1}$, u_0=1 mol/m^3, V/F=1000 s. From (10), it can be determined that Y_0=0.2702 mol/m^3.

Moreover, 40 simulation studies are carried out on system (8) when the system is subject to 40 single-tone sinusoidal inputs around the steady state input u_0 such that

$$u_p(t) = u_0 + A_m u_0 \cos(\omega_n t), m = 1, \ldots, 10, n = 1, \ldots, 4 \quad (18)$$

where

$$(A_1, A_2, \ldots, A_{10}) = (10\%, 20\%, \ldots, 100\%)$$

$$(\omega_1, \omega_2, \omega_3, \omega_4) = (0.4, 0.6, 0.8, 1.0) \times 10^{-3} \text{ rad/s}$$

producing $y_{DC}(\omega_n, A_m)$, n=1, …, 4, m=1, …, 10.

When the system nonlinearity up to the 4^{th} order is considered, the data driven NFR model of isothermal CSTR system (8) to single tone sinusoidal inputs can be determined as

$$\hat{y}_{DC}(\omega, A) = Y_0 + A^2 \hat{N}_2(\omega) + A^4 \hat{N}_4(\omega) + \cdots + A^8 \hat{N}_8(\omega), \omega \in [\omega_1, \omega_4] \quad (19)$$

with $\hat{N}_2(\omega), \ldots, \hat{N}_8(\omega)$ obtained using (16) and shown in Fig. 4.

Fig.5 shows the DC component of the steady state output response of system (8) evaluated from (19) over the parameters range of $\omega \in [0.0004, 0.001]$ *rad/s* and $A \in [10\%, 100\%]$.

Based on (19), the analysis and design of the forced periodic operation of system (8) under sinusoidal input, will be studied in the next section.

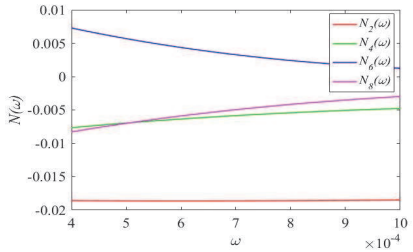


Figure 4 Functions $N_{2N}(\omega), N = 1, 2, 3, 4$ in the data driven NFR model of system (8) under sinusoidal inputs

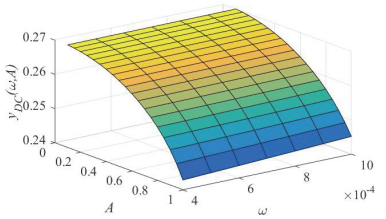


Figure 5 $\hat{y}_{DC}(\omega, A)$ of the isothermal CSTR process under sinusoidal wave operations with $\omega \in [0.4,1] \times 10^{-3}$ *rad/s*, $A \in [10\%,100\%]$

IV. Data driven NFR model based analysis and optimal design of periodically operated chemical reaction processes

A. Analysis

Data driven NFR model-based analysis of periodically operated chemical reaction process is concerned with the evaluation of the DC component of the process steady state response using data driven model (17). Although, in theory, the existing NFR method can also extend the analysis to higher order system nonlinearities as shown in [27], the requirement for the 1st principle model is a fundamental issue that is difficult to be resolved in many engineering practices. However, due to the data driven nature, model (17) can readily be determined from either numerical simulation of an available first principle model or experimental tests on the real chemical process up to any order of system nonlinearities and then applied to evaluate the performance of periodically driven chemical processes.

The implementation of the data driven NFR model-based analysis generally involves:

1) Construct and apply the data driven NFR model
$$\hat{y}_{DC}(\omega, A) = Y_0 + A^2 \hat{N}_2(\omega) + A^4 \hat{N}_4(\omega) + \cdots + A^{2N} \hat{N}_{2N}(\omega)$$
to quantitatively evaluate the advantage of a forced periodic operation over traditional steady state operation for a chemical reaction process;
2) Analyze the accuracy and effectiveness of the newly proposed data driven NFR model-based approach using relative error between the numerically determined and the data driven produced results.

Now consider, as an example, the isothermal CSTR chemical reaction system (8) when the system is subjected to a single-tone sinusoidal input. In this case $N = 4$, and the data driven model has been obtained and shown in (19). The analysis results for the cases where A= (15%, ..., 95%) are shown in Table 2 where

$$\delta_{New\_NFR} = \frac{\left(y_{DC}(\omega_d, A) - Y_0\right)_{New\_NFR} - \left(y_{DC}(\omega_d, A) - Y_0\right)_{num}}{\left(y_{DC}(\omega_d, A) - Y_0\right)_{num}} \quad (20)$$

showing the relative error between the data driven analysis result $(y_{DC}(\omega_d, A)\text{-}Y_0)_{New\_NFR}$ and numerically determined result $(y_{DC}(\omega_d, A)\text{-}Y_0)_{num}$. In comparison with the results in Table 1, it can be observed from the results in Table 2 is that not only the sign of $(y_{DC}(\omega_d, A)\text{-}Y_0)$ determined using the data driven NFR model is correct in all cases but also the value of $(y_{DC}(\omega_d, A)\text{-}Y_0)$ determined using the data driven NFR model is much more accurate. This shows that the data driven NFR model is capable to quantitatively evaluate the performance of a forced periodic operation which is important and necessary for the design of forced periodic operations for chemical reactions.

TABLE 2 A COMPARISON OF $(y_{DC}(\omega_d, A) - Y_0)_{New\_NFR}$ AND $(y_{DC}(\omega_d, A) - Y_0)_{num}$ UNDER A SINUSOIDAL OPERATION OF CSTR MODEL (8)

Amplitude A	Frequency $\omega_d = 0.0009\ rad/s$		
	$(y_{DC}(\omega_d, A)\text{-}Y_0)$		Relative error
	Numerical solution	New method	δ_{New_NFR}
15%	-0.00042	-0.00042	0.00%
25%	-0.00118	-0.00118	0.00%
35%	-0.00235	-0.00235	0.00%
45%	-0.00395	-0.00396	0.25%
55%	-0.00605	-0.00606	0.17%
65%	-0.00872	-0.00872	0.00%
75%	-0.01208	-0.01208	0.00%
85%	-0.01635	-0.01635	0.00%
95%	-0.02190	-0.02192	0.09%

B. Optimal design

Data driven-based analysis can, as demonstrated above, achieve a more accurate quantitative estimation of the system performance, which is dependent on the operational parameters of the forced periodic input, that is, the frequency and amplitude of the forced periodic input. In order to realize the advantages of forced periodic operations over traditional steady-state operations, the proposed data-driven method can be applied to perform an optimal design of the operational parameters to maximize the reactant conversion rate and, consequently, achieve an optimized performance for the chemical reaction process under study.

The optimal design of a forced periodic operation generally involves determining periodic operation frequency and amplitude such that $(y_{DC}(\omega, A)\text{-}Y_0)$ reaches a minimum if an optimal reactant conversion rate is to be achieved.

When the data driven NFR model (17) has been determined, from equations

$$\begin{cases} \dfrac{\partial\left(\hat{y}_{DC}(\omega, A) - Y_0\right)}{\partial A} = 2A\hat{N}_2(\omega) + \ldots + 2NA^{2N-1}\hat{N}_{2N}(\omega) = 0 \\ \dfrac{\partial\left(\hat{y}_{DC}(\omega, A) - \hat{Y}_0\right)}{\partial \omega} = A^2 \dfrac{d\hat{N}_2(\omega)}{d\omega} + \cdots + A^{2N} \dfrac{d\hat{N}_{2N}(\omega)}{d\omega} = 0 \end{cases} \quad (21)$$

possible frequencies and amplitudes that could be used to achieve an optimal forced periodic operation when $\omega \in (\omega_{d1}, \omega_{d2})$ can be determined as

$$\{\omega_{s_1}, A_{s_1}\},\ldots,\{\omega_{s_{k1}}, A_{s_{k1}}\}, \omega_{s_i} \in (\omega_{d_1}, \omega_{d_2}), A_{s_i} \in (A_1, A_M), i = 1,\ldots,k_l \quad (22)$$

where k_l is the total number of the solutions to (21) in this case.

Further, by evaluating

$$\beta = \left(\frac{\partial^2(\hat{y}_{DC}(\omega_{s_i}, A_{s_i}) - \hat{Y}_0)}{\partial\omega^2}\right)\cdot\left(\frac{\partial^2(\hat{y}_{DC}(\omega_{s_i}, A_{s_i}) - Y_0)}{\partial A^2}\right) - \left(\frac{\partial(\hat{y}_{DC}(\omega_{s_i}, A_{s_i}) - Y_0)}{\partial\omega\partial A}\right)^2 \quad (23)$$

and applying the extreme value judgment conditions [28], it is known that

- If $\beta > 0$ and $\frac{\partial^2(\hat{y}_{DC}(\omega_{s_i}, A_{s_i}) - \hat{Y}_0)}{\partial\omega^2} < 0$, $\hat{y}_{DC}(\omega, A)$-Y_0 takes a maximum value at $\{\omega_{si}, A_{si}\}$;
- If $\beta > 0$ and $\frac{\partial^2(\hat{y}_{DC}(\omega_{s_i}, A_{s_i}) - \hat{Y}_0)}{\partial\omega^2} > 0$, $\hat{y}_{DC}(\omega, A)$-Y_0 takes a minimum value at $\{\omega_{si}, A_{si}\}$;
- If $\beta = 0$, $\hat{y}_{DC}(\omega, A)$-Y_0 may take a maximum value or a minimum value, which needs to be discussed separately;
- If $\beta < 0$, $\{\omega_{si}, A_{si}\}$ has nothing to do with an extreme value.

Based on these, the optimal design of ω and A when $\omega \in (\omega_{d1}, \omega_{d2})$ can be determined. Similarly, the optimal designs when ω is in the frequency ranges of $(\omega_{d2}, \omega_{d3})$, …, $(\omega_{dn}, \omega_{dn+1})$ can also be found. Denote these optimal design results as

$$\{\omega_1^*, A_1^*\}, \{\omega_2^*, A_2^*\}, \ldots, \{\omega_n^*, A_n^*\} \quad (24)$$

where n represents the total number of these optimal designs. The final design of a periodically operated chemical process over the considered frequency and amplitude ranges can then be obtained by comparing

$$(\hat{y}_{DC}(\omega_i^*, A_i^*) - Y_0), i = 1,\ldots,n \quad (25)$$

with the optimal design results at the boundary

$$\omega = \omega_{dj}, j = 1,\ldots,n+1,\ A \in [A_1, A_M] \text{ and } A = A_i, n = 1, M,\ \omega \in [\omega_{d1}, \omega_{dn+1}] \quad (26)$$

determined by

$$\frac{\partial(\hat{y}_{DC}(\omega_{dj}, A) - Y_0)}{\partial A} = 2A\hat{N}_2(\omega_{dj}) + \cdots + 2NA^{2N-1}\hat{N}_{2N}(\omega_{dj}) = 0 \quad (27)$$

$$\frac{\partial(\hat{y}_{DC}(\omega, A_n) - \hat{Y}_0)}{\partial\omega} = A_n^2\frac{d\hat{N}_2(\omega)}{d\omega} + \cdots + A_n^{2N}\frac{d\hat{N}_{2N}(\omega)}{d\omega} = 0 \quad (28)$$

and

$$(\hat{y}_{DC}(\omega, A) - Y_0), \omega = \omega_{d1} \text{ or } \omega = \omega_{d(n+1)} \text{ and } A = A_1 \text{ or } A_M \quad (29)$$

This can find a ω^* and A^* such that $(\hat{y}_{DC}(\omega^*, A^*)$-$Y_0)$ reach a minimum if an optimal conversion rate is to be achieved.

Now consider the application of the optimal design discussed above to system (8). In single-tone sinusoidal input cases, it can be found that no solutions to (21) are within the valid ranges of $\omega \in (0.0004, 0.0006), \omega \in (0.0006, 0.0008), \omega \in (0.0008, 0.0010)$ and $A \in [10\%, 100\%]$

Therefore, the optimal design for system (8) can only exist at the boundary where

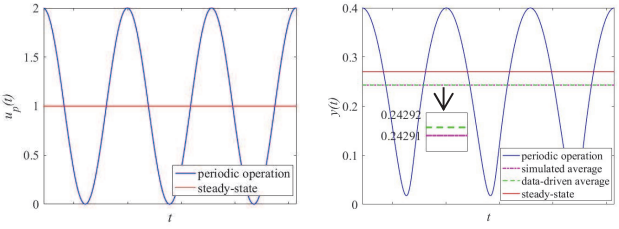
$$\omega = 0.0004, 0.0006, \ldots, 0.0010, A \in [10\%, 100\%] \text{ or } A = 10\%, 100\%, \omega \in [0.0004, 0.0010]$$

Consequently, by comparing the solutions of equations (27)-(29), the optimal design is obtained as $\{\omega^*, A^*\} = \{0.0004$ *rad/s*, 100%$\}$. The expected performance achieved by the design is

$$(\hat{y}_{DC}(\omega^*, A^*) - Y_0) = -0.02724\ mol/m^3 \quad (30)$$

Compared to the numerically simulated result of $(y_{DC}(\omega^*, A^*)$ - $Y_0) = -0.02725$ *mol/m*^{3}, this designed performance only has a difference of 0.14%.

Fig. 6 (a) and (b) show the input and output of system (8) under steady state and optimally designed sinusoidal operations, respectively, clearly demonstrating the advantage of the optimally designed periodic operation over traditional steady state operation.



(a) (b)

Figure 6 Forced periodic operation of inlet concentration for system (8) under optimally designed single tone sinusoidal input

A summary for the detailed implementation of the proposed analysis and design is as follows:

1) Perform a simulation study to obtain the steady state output response Y_0 to the steady state input u_0.
2) Perform simulation studies with the process input alternating around its steady-state u_0 under different frequencies
   $\omega_i, i = 1, \ldots, n+1$
   and amplitudes
   $A_j, j = 1, \ldots, M$
   producing $(y_{DC}(\omega_i, A_j)$-$Y_0)$, $i = 1, \ldots, n+1, j = 1, \ldots, M$;
3) Determine $N_2(\omega)$, $N_4(\omega)$, …, $N_{2N}(\omega)$ using (15) from the input and output data obtained from 1) and 2);
4) Obtain $\hat{N}_2(\omega), \hat{N}_4(\omega) \ldots, \hat{N}_{2N}(\omega)$ at any frequency of interest with the results obtained from 3) using (16);
5) Construct the data-driven NFR model
   $$\hat{y}_{DC}(\omega, A) - Y_0 = A^2\hat{N}_2(\omega) + \cdots + A^{2N}\hat{N}_{2N}(\omega)$$
   and analysis the performance of the nonlinear chemical reaction system under forced periodic operation at different frequencies and amplitudes of interest.
6) Optimally design the forced periodic operational input frequency ω and amplitude A based on the data-driven NFR model obtained in 5). This will be achieved by
   (i) Find the extreme value points of ω and A within the range of
   $$\omega \in (\omega_1, \omega_2), (\omega_2, \omega_3), \ldots, (\omega_n, \omega_{n+1})$$
   and
   $$A \in [A_1, A_M]$$
   using (21) and the judgement condition (23);
   (ii) Find the extreme value points of ω and A at the boundary using (27)-(29);
   (iii) Compare the results of
   $$\hat{y}_{DC}(\omega, A) - Y_0 = A^2\hat{N}_2(\omega) + \cdots + A^{2N}\hat{N}_{2N}(\omega)$$
   at the extreme value points of ω and A obtained in (i) and (ii) and determine ω^* and A^* such that the performance in terms of the value of $(\hat{y}_{DC}(\omega^*, A^*)$ - $Y_0)$ is optimal.

V. Experimental Study

A. Description of the experiment

In order to experimentally demonstrate the effectiveness of the proposed data driven NFR method, a reversible chemical reaction:

$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$

is considered as an exemplification and a laboratory scale carbon dioxide absorption experiment rig was designed and fabricated, as shown in Fig. 7.

The mix of Carbon dioxide and Nitrogen is controlled by an embedded integrated industrial computer with Monitor and Control Generated System (MCGS) such that either a steady-state operation or a forced periodic operation of the chemical reaction process can be implemented. The mixed gas and deionized water controlled by a constant flow pump then undergo a chemical reaction in the reaction tank. Embedded integrated industrial computer is used to continuously record and show the flow rate of the Carbon dioxide and Nitrogen passing into the reaction tank while CO_2 Sensor is used to measure the concentration of carbon dioxide after the reaction. Finally, the liquid after the reaction and remaining gas are separated in the separation tank.

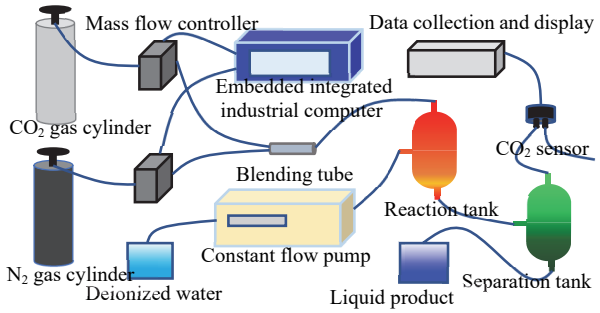


Figure 7 Schematic diagram of the laboratory-scale CO_2 experiment rig

B. Application of the proposed data driven NFR model

In order to apply forced periodic operation to the CO_2 absorption process, a sinusoidally varied CO_2 concentration is generated by the mass flow controllers for Carbon dioxide and Nitrogen gases producing a forced periodic input.

The CO_2 concentration after reaction is measured by CO_2 Sensor and is denoted below as $Vf_{CO2}(t)$. As $Vf_{CO2}(t)$ is measured in terms of the ratio between the volume of CO_2 and the volume of all gasses passing through the sensor [29]. It is known that

$$Vf_{CO_2}(t) = \frac{F_{CO_2}(t) - Abs_{CO_2}(t)}{F_{Gas}(t) - Abs_{CO_2}(t)} \tag{31}$$

where $Abs_{CO2}(t)$ is the flow rate of CO_2 absorbed by the chemical reaction at time t, $F_{Gas}(t)$ is the flow rate of the mixed gas, and $F_{CO2}(t)$ is the flow rate of CO_2 before the chemical reaction. Therefore,

$$Abs_{CO_2}(t) = F_{Gas}(t) - \frac{F_{N_2}(t)}{1 - Vf_{CO_2}(t)} \tag{32}$$

where $F_{N2}(t)$ is the flow rate of nitrogen, and $F_{CO2}(t) = F_{Gas}(t) - F_{N2}(t)$.

In this experimental study, what is interested is the difference between $Abs^m_{CO_2}$ and $Abs^s_{CO_2}$, which are the average of $Abs_{CO2}(t)$ under forced periodic operation and $Abs_{CO2}(t)$ under steady state operation, respectively. In this case

$$y_{DC}(\omega, A) - Y_0 = Abs^m_{CO_2}(\omega, A) - Abs^s_{CO_2} = \frac{1}{t_2 - t_1}\int_{t_1}^{t_2} Abs_{CO_2}(t, \omega, A)dt - Abs^s_{CO_2} \tag{33}$$

where $Abs_{CO2}(t, \omega, A)$ represents $Abs_{CO2}(t)$ obtained from (32) when the chemical reaction process is periodically operated with operating frequency and amplitude being ω and A; t_2-t_1 is a period of time over which the mean of $Abs_{CO2}(t)$ is evaluated. The proposed data driven NFR model-based method can then be applied for the analysis and optimal design of the forced periodic operation.

C. Results of the data-driven NFR model-based analysis

When the experiment was set up as shown in Table 3, it can be obtained from (32) and experimental data that $Y_0 = Abs^s_{CO_2} =$ 1.6349 *ml/min*. 42 experimental tests were conducted in which the sinusoidal input

$$u_p(t) = u_0 + Au_0\cos(\omega t) \tag{34}$$

with different frequencies

$$\omega = \left(\frac{2\pi}{20}, \frac{2\pi}{18}, \frac{2\pi}{16}, \frac{2\pi}{14}, \frac{2\pi}{12}, \frac{2\pi}{8}, \frac{2\pi}{4}\right) rad/\min$$

and amplitudes

$$A = (45\%, 50\%, 60\%, 65\%, 75\%, 80\%)$$

were applied to producing $y_{DC}(\omega_n, A_m)$-Y_0, n=1, …, 7 , m=1, …, 6 using (33) as shown in Table 4.

When the system nonlinearity up to 3rd order is considered, N=3, the data driven NFR model (17) in this case at any frequency of interest can be obtained as

$$\hat{y}_{DC}(\omega, A) = Y_0 + A^2\hat{N}_2(\omega) + A^4\hat{N}_4(\omega) + A^6\hat{N}_6(\omega) \tag{35}$$

with $\hat{N}_2(\omega), \hat{N}_4(\omega), \hat{N}_6(\omega)$ as shown in Fig 8.

Fig. 9 shows $\hat{y}_{DC}(\omega, A)$-Y_0 evaluated using this data driven NFR model over $\omega \in (2\pi/20, 2\pi/4)$ *rad/min*, $A \in$ [45%, 80%].

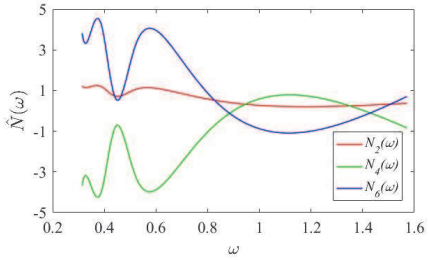


Figure 8 $\hat{N}_2(\omega), \hat{N}_4(\omega)$ and $\hat{N}_6(\omega)$ in the determined data driven NFR model

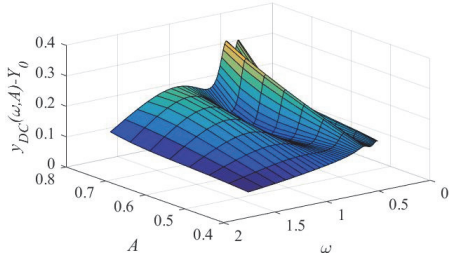


Figure 9 $\hat{y}_{DC}(\omega, A) - Y_0$ evaluated using the data driven NFR model of the periodically operated CO_2 absorption process when $A \in$ [45%,80%], $\omega \in$ [2π/20, 2π/4] *rad/min*

TABLE 3. THE PARAMETERS OF EXPERIMENTAL SETUP

Parameters	Value	Unit
Total flow rate of mixed gas	10	*ml/min*
CO_2 flow rate under steady state operation	4	*ml/min*
N_2 flow rate under steady state operation	6	*ml/min*
Deionized water flow rate	9	*ml/min*

TABLE 4 EXPERIMENTAL RESULTS OF $y_{DC}(\omega_n, A_m) - Y_0$ UNDER A SINUSOIDAL OPERATION OF THE CARBON DIOXIDE ABSORPTION PROCESS

Amplitude A	$y_{DC}(\omega, A) - Y_0$ (*ml/min*) Frequency ω (*rad/min*)						
	2π/4	2π/8	2π/12	2π/14	2π/16	2π/18	2π/20
45%	0.0405	0.0698	0.0963	0.0809	0.1060	0.1165	0.1195
50%	0.0548	0.1018	0.1135	0.1700	0.1235	0.1486	0.1540
60%	0.0600	0.1217	0.1439	0.2181	0.1288	0.1200	0.1214
65%	0.0809	0.1360	0.0942	0.1999	0.1108	0.1417	0.1512
75%	0.0529	0.1317	0.1434	0.2542	0.1744	0.2158	0.2116
80%	0.0952	0.1904	0.2102	0.3166	0.2523	0.2775	0.2728

TABLE 5
A COMPARISON OF $\hat{y}_{DC}(\omega, A)$ AND $y_{DC}(\omega, A)$ WHEN $\omega = 2\pi/12.8\ rad/min$

Amplitude A	Frequency $\omega = 2\pi/12.8\ rad/min$		
	$y_{DC}(\omega, A)$ (ml/min)		Relative error
	Actual experiment	Data driven model	δ_{New_NFR}
45%	1.6894	1.7495	3.6%
50%	1.7085	1.7632	3.2%
60%	1.7696	1.7872	1.0%
65%	1.7748	1.8005	1.4%
70%	1.8145	1.8185	0.2%
75%	1.8387	1.8459	0.4%
80%	1.8740	1.8892	0.8%

TABLE 6 A COMPARISON OF $\hat{y}_{DC}(\omega, A)$ AND $y_{DC}(\omega, A)$ WHEN A=70%

Frequency ω (rad/*min*)	Amplitude A=70%		
	$y_{DC}(\omega, A)$ (ml/min)		*Relative error*
	Actual experiment	New method	δ_{New_NFR}
2π/4	1.6837	1.7028	1.1%
2π/8	1.7459	1.7722	1.5%
2π/12	1.7512	1.7582	0.4%
2π/12.8	1.8145	1.8185	0.2%
2π/14	1.7894	1.8769	4.9%
2π/16	1.7679	1.7712	0.2%
2π/18	1.7741	1.7969	1.3%
2π/20	1.7803	1.7994	1.1%

In order to demonstrate the performance of the data driven NFR model, consider now the evaluation of $\hat{y}_{DC}(\omega, A)$ at $\omega=2\pi/12.8\ rad/min$, shown in Table 5, and $\hat{y}_{DC}(\omega, A)$ at A=70%, shown in Table 6, respectively, using the established the data driven NFR model (35). Note that these results are not available from the experimental data that have been used to construct the data driven model.

Therefore, a comparison of these results with the experimentally measured results under the same periodic operations will be able to show how well the proposed data driven model method can be applied for the analysis of the experimental CO_2 absorption process. In Tables 5 and 6,

$$\delta_{New\_NFR} = \frac{\hat{y}_{DC}(\omega, A) - y_{DC}(\omega, A)}{\hat{y}_{DC}(\omega, A)} \tag{36}$$

with $y_{DC}(\omega, A)$ representing the experimentally measured result.

A common feature that can be seen from the evaluation results in Table 5 and 6 is that not only the sign of $y_{DC}(\omega, A)$ determined using the data driven NFR approach is correct, but also the value of $y_{DC}(\omega, A)$ maintain a high consistency with the results obtained from actual chemical experiments (relative error δ_{New_NFR} below 5%). This implies that even for an actual chemical production process, the data driven NFR approach can also work well when applied to perform the quantitative analysis of the performance of a forced periodic operation of the chemical reaction process.

D. Results of the data-driven NFR model-based optimal design

To optimally design A and ω to achieve a maximum CO_2 absorption compared to the case of steady state operation, first extreme value points of A and ω within $A \in [45\%, 80\%]$ and

$$\omega \in \left[\frac{2\pi}{8}, \frac{2\pi}{4}\right], \left[\frac{2\pi}{12}, \frac{2\pi}{8}\right], \left[\frac{2\pi}{14}, \frac{2\pi}{12}\right], \left[\frac{2\pi}{16}, \frac{2\pi}{14}\right], \left[\frac{2\pi}{18}, \frac{2\pi}{16}\right], \left[\frac{2\pi}{20}, \frac{2\pi}{18}\right] rad/min$$

are evaluated using (21), the judgment condition (23) and boundary judgement equations (27)-(29).

Consequently, by comparing ($\hat{y}_{DC}(\omega, A)$-Y_0), it is known that $\{\omega^*,\ A^*\} = \{0.4453\ rad/min,\ 80\%\}$, and the expected performance achieved by the design is

$$\hat{y}_{DC}\left(\omega^*, A^*\right) - Y_0 = 0.3063\ ml/\min \tag{37}$$

which is only -3.25% different from the practical experiment result ($y_{DC}(\omega^*, A^*)$-Y_0) = 0.3166 *ml/min*.

Fig. 10 shows a comparison of the CO_2 absorption under the optimally designed optimal periodic operation and the CO_2 absorption under steady state operation, Y_0. Both results are experimentally measured. The time average of the CO_2 absorption under the optimally designed periodic operation as well as $\hat{y}_{DC}(\omega^*, A^*)$ evaluated by the data driven model (35) are also shown in Fig. 10 for a comparison. It can be observed that compared to steady state operation, the optimal design has achieved a significant increase in the CO_2 absorption of

$$\frac{y_{DC}\left(\omega^*, A^*\right) - Y_0}{Y_0} = \frac{2.1089 - 1.7921}{1.7921} \times 100\% = 17.6\%$$

The comparisons clearly demonstrate the advantage of the optimally designed periodic operation as well as the accuracy and effectiveness of the data driven NFR model-based analysis and design.

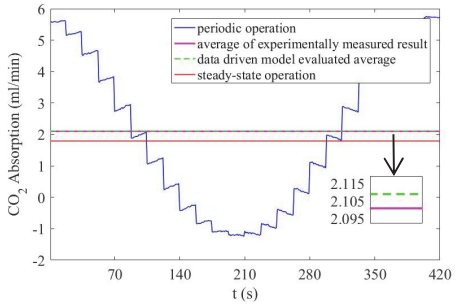


Figure 10 A comparison of experimentally measured CO_2 absorptions under an optimally designed forced periodical operation and its corresponding traditional steady state operation

VI. CONCLUSION

Forced periodic operation can considerably improve the reactant conversion rate associated with many chemical reaction processes. However, the analysis and design of a

forced periodic operation involve the study and exploitation of nonlinear dynamics of the chemical process, which has been a significant challenge. Recently proposed NFR based solutions to the challenge are based on the first principle model and can therefore only be applied to qualitatively evaluate the performance of forced periodic operation systems. In order to fundamentally resolve the problems with existing NFR based methods, the present study has proposed an innovative data-driven approach to the quantitative analysis and optimal design of forced periodic operation of chemical reactions. Because of data-driven nature, the new approach can readily be implemented based on either numerically simulated chemical reaction process responses or experimentally collected data and is applicable to chemical reaction processes of any complexities. Both simulation study and experimental test results have verified the effectiveness and advantage of the new data driven approach and demonstrate the potential of the new approach in engineering applications. Although only single input single output chemical reaction systems are considered in this study, the basic idea can readily be extended to multiple inputs and multi-outputs chemical reaction systems to solve forced periodic operation problems with larger scale and more complicated chemical reaction systems.

APPENDIX A

Consider a simple nonlinear system with model $y(t)=1-x^2(t)$ where $y(t)$ and $x(t)$ are the system output and input, respectively. When $x(t)= x_s(1+A\cos(\omega t))$ that fluctuates around the steady-state input x_s,

$$\begin{aligned} y(t) &= 1-\left(x(t)\right)^2 = 1-\left(x_s\left(1+A\cos\left(\omega t\right)\right)\right)^2 \\ &= 1-x_s{}^2-\frac{x_s{}^2A^2}{2}-2x_s{}^2A\cos\left(\omega t\right)-\frac{x_s{}^2A^2}{2}\cos\left(2\omega t\right) \end{aligned} \tag{A.1}$$

It can be seen from (A.1) that the forced periodic operation produces an averaged system output $1- x_s^2- (x_s^2A^2/2)$ which is different from $1- x_s^2$, that is, the output of the system under the steady input x_s. It is this nonlinear phenomenon/behavior that a forced periodic operation basically exploits to achieve a chemical reaction performance better than traditional steady state operations.

APPENDIX B

According to the properties of the cubic spline functions, over any segment $\omega \in [\omega_j, \omega_{j+1}]$, the second derivative exists, such that

$$\begin{aligned} \hat{N}_{2i}(\omega) &= a_{ij}+b_{ij}\left(\omega-\omega_j\right)+c_{ij}\left(\omega-\omega_j\right)^2+d_{ij}\left(\omega-\omega_j\right)^3 \\ \frac{d\hat{N}_{2i}(\omega)}{d\omega} &= b_{ij}+2c_{ij}\left(\omega-\omega_j\right)+3d_{ij}\left(\omega-\omega_j\right)^2 \\ \frac{d^2\hat{N}_{2i}(\omega)}{d\omega^2} &= 2c_{ij}+6d_{ij}\left(\omega-\omega_j\right) \end{aligned} \tag{B.1}$$

From the continuity of the cubic spline function:

$$N_{2i}\left(\omega_j\right)=a_{ij} \tag{B.2}$$

$$N_{2i}\left(\omega_{j+1}\right)=a_{ij}+b_{ij}\left(\omega_{j+1}-\omega_j\right)+c_{ij}\left(\omega_{j+1}-\omega_j\right)^2+d_{ij}\left(\omega_{j+1}-\omega_j\right)^3 \tag{B.3}$$

From (B.1) and the differential continuity of the cubic spline function:

- First derivative continuity

$$b_{ij}+2c_{ij}\left(\omega_{j+1}-\omega_j\right)+3d_{ij}\left(\omega_{j+1}-\omega_j\right)^2-b_{i(j+1)}=0 \tag{B.4}$$

- Second derivative continuity

$$2c_{ij}+6d_{ij}\left(\omega_{j+1}-\omega_j\right)-2c_{i(j+1)}=0 \tag{B.5}$$

Assume that

$$m_{ij}=\hat{N}_{2i}^{''}\left(\omega_j\right)=2c_{ij} \tag{B.6}$$

So

$$c_{ij}=m_{ij}/2 \tag{B.7}$$

Thereby, b_{ij} and d_{ij} can be obtained from (B.3) and (B.5) as

$$\begin{aligned} b_{ij} &= \frac{N_{2i}\left(\omega_{j+1}\right)-N_{2i}\left(\omega_j\right)}{\omega_{j+1}-\omega_j}-\frac{\omega_{j+1}-\omega_j}{2}m_{ij}-\frac{\omega_{j+1}-\omega_j}{6}\left(m_{i(j+1)}-m_{ij}\right) \\ d_{ij} &= \frac{m_{i(j+1)}-m_{ij}}{6\left(\omega_{j+1}-\omega_j\right)} \end{aligned} \tag{B.8}$$

According to (B.4) and the expressions of b_{ij}, c_{ij}, d_{ij}, it is known that

$$6\left[\frac{z_{j+1}}{h_{j+1}}-\frac{z_j}{h_j}\right]=h_jm_{ij}+2\left(h_j+h_{j+1}\right)m_{i(j+1)}+h_{j+1}m_{i(j+2)} \tag{B.9}$$

where

$$\begin{aligned} h_j &= \omega_{j+1}-\omega_j, j=1,\ldots,n \\ z_j &= N_{2i}\left(\omega_{j+1}\right)-N_{2i}\left(\omega_j\right),\ j=1,\ldots,n \end{aligned}$$

From equation (B.9) and not-a-knot boundary condition, m_{ij} can be shown as

$$\begin{pmatrix} -h_2 & h_1+h_2 & -h_1 & & & & \\ h_1 & 2(h_1+h_2) & h_2 & & & & \\ & h_2 & 2(h_2+h_3) & h_3 & & & \\ & & \ddots & \ddots & \ddots & & \\ & & & h_{n-1} & 2(h_{n-1}+h_n) & h_n & \\ & & & -h_n & h_{n-1}+h_n & -h_{n-1} & \end{pmatrix}\begin{pmatrix} m_{i1} \\ m_{i2} \\ m_{i3} \\ \vdots \\ m_{in} \\ m_{i(n+1)} \end{pmatrix}=6\begin{pmatrix} 0 \\ \frac{z_2}{h_2}-\frac{z_1}{h_1} \\ \frac{z_3}{h_3}-\frac{z_2}{h_2} \\ \vdots \\ \frac{z_n}{h_n}-\frac{z_{n-1}}{h_{n-1}} \\ 0 \end{pmatrix} \tag{B.10}$$

Thus, a_{ij}, b_{ij}, c_{ij}, d_{ij} can all be determined.

REFERENCES

[1] P. L. Silveston, "Periodic operation of chemical reactors-a review of the experimental literature," 1987.

[2] B. Suman, "Study of unsteady state process operation," *Chemical Engineering Journal*, vol. 104, no. 1–3, pp. 63–71, Nov. 2004.

[3] R. Lange, M. Schubert, et al. "Unsteady-state operation of trickle-bed reactors," in *Chemical Engineering Science*, Nov. 2004, vol. 59, no. 22–23, pp. 5355–5361.

[4] Y. W. Budhi, H. Rionaldo, et al. "Forced unsteady state operation for hydrogen separation through Pd-Ag membrane after start-up," *Int J Hydrogen Energy*, vol. 40, no. 32, pp. 10081–10089, Aug. 2015.

[5] S. I. Reshetnikov, E. A. Ivanov, et al. Startsev, "Benzene hydrogenation in the thiophene presence over the sulfide Ni-Mo/γ-Al2O3 catalyst under periodic operation: Kinetics and process modelling," *Chemical Engineering Journal*, vol. 134, no. 1–3, pp. 100–105, Nov. 2007.

[6] Z. Gogová and J. Hanika, "Dynamic modelling of glucose oxidation with palladium catalyst deactivation in multifunctional CSTR: Benefits of periodic operation," *Chemical Engineering Journal*, vol. 150, no. 1, pp. 223–230, Jul. 2009.

[7] B. Munder, L. Rihko-Struckmann, and K. Sundmacher, "Steady-state and forced-periodic operation of solid electrolyte membrane reactors for selective oxidation of n-butane to maleic anhydride," *Chemical Engineering Science*, vol. 62, no. 18–20, pp. 5663–5668, Sep. 2007.

[8] J. Alvarez, M. Meraz, F. J. Valdes-Parada, et al. “First-harmonic balance analysis for fast evaluation of periodic operation of chemical processes,” *Chemical Engineering Science*, vol. 74, pp. 256–265, May 2012
[9] A. Zuyev, A. Seidel-Morgenstern, et al. “An isoperimetric optimal control problem for a non-isothermal chemical reactor with periodic inputs,” *Chemical Engineering Science*, vol. 161, pp. 206–214, 2017.
[10] S. Varigonda, T. T. Georgiou and P. Daoutidis, "Numerical solution of the optimal periodic control problem using differential flatness," in IEEE Transactions on Automatic Control, vol. 49, no. 2, pp. 271-275, Feb. 2004
[11] A. Marković, A. S. Morgenstern, and M. Petkovska, “Evaluation of the potential of periodically operated reactors based on the second order frequency response function,” in *Chemical Engineering Research and Design*, 2008, vol. 86, no. 7, pp. 682–691.
[12] D. Nikolić, A. Seidel-Morgenstern, and M. Petkovska, “Nonlinear frequency response analysis of forced periodic operation of non-isothermal CSTR using single input modulations. Part I: Modulation of inlet concentration or flow-rate,” *Chemical Engineering Science*, vol. 117, pp. 71–84, Sep. 2014.
[13] D. Nikolić, A. Seidel-Morgenstern, and M. Petkovska, “Nonlinear frequency response analysis of forced periodic operation of non-isothermal CSTR using single input modulations. Part II: Modulation of inlet temperature or temperature of the cooling/heating fluid,” *Chemical Engineering Science*, vol. 117, pp. 31–44, Sep. 2014
[14] M. Felischak, L. Kaps, *et al.*, “Analysis and experimental demonstration of forced periodic operation of an adiabatic stirred tank reactor: Simultaneous modulation of inlet concentration and total flow-rate,” *Chemical Engineering Journal*, vol. 410, Apr. 2021.
[15] D. Nikolić *et al.*, “Forced periodic operations of a chemical reactor for methanol synthesis – The search for the best scenario based on Nonlinear Frequency Response Method. Part I Single input modulations,” *Chem Eng Sci*, vol. 248, Feb. 2022.
[16] D. Nikolić *et al.*, “Forced periodic operations of a chemical reactor for methanol synthesis – The search for the best scenario based on Nonlinear Frequency Response Method. Part II Simultaneous modulation of two inputs,” *Chem Eng Sci*, vol. 248, Feb. 2022.
[17] L. A. Živković, T. Vidaković-koch, et al. “Computer-aided nonlinear frequency response method for investigating the dynamics of chemical engineering systems,” *Processes*, vol. 8, no. 11, pp. 1–25, Nov. 2020.
[18] L. A. Živković, V. Milić, T. Vidaković-koch, et al. “Rapid multi-objective optimization of periodically operated processes based on the computer-aided nonlinear frequency response method,” *Processes*, vol. 8, no. 11, pp. 1–21, Nov. 2020.
[19] M. Petkovska, D. Nikolić, and A. Seidel-Morgenstern, “Nonlinear Frequency Response Method for Evaluating Forced Periodic Operations of Chemical Reactors,” *Israel Journal of Chemistry*, vol. 58, no. 6. Wiley-VCH Verlag, pp. 663–681, Jun. 01, 2018.
[20] Z. Q. Lang, S. A. Billings, R. Yue, and J. Li, “Output frequency response function of nonlinear Volterra systems,” *Automatica*, vol. 43, no. 5, pp. 805–816, May 2007
[21] Z. Q. Lang and S. A. Billings, “Output frequency characteristics of nonlinear systems,” *International Journal of Control*, vol. 64, no. 6, pp. 1049–1067, 1996.
[22] R. Currie, D. Nikolic, M. Petkovska, and D. S. A. Simakov, “CO2 Conversion Enhancement in a Periodically Operated Sabatier Reactor: Nonlinear Frequency Response Analysis and Simulation-based Study,” *Israel Journal of Chemistry*, vol. 58, no. 6, pp. 762–775, Jun. 2018
[23] H. Shi, Z. Q. Lang, Y. Zhu, D. Yuan, and W. Wang, “Optimal design of the inlet temperature based periodic operation of non-isothermal CSTR using nonlinear output frequency response functions,” *IFAC-Papers Online*, Jan. 2018, vol. 51, no. 18, pp. 620–625.
[24] D. Nikolić, A. Seidel-Morgenstern, and M. Petkovska, “Nonlinear frequency response analysis of forced periodic operations with simultaneous modulation of two general waveform inputs with applications on adiabatic CSTR with square-wave modulations,” *Chemical Engineering Science*, vol. 226, Nov. 2020.
[25] B. Bensmann, M. Petkovska, T., et al. “Nonlinear Frequency Response of Electrochemical Methanol Oxidation Kinetics: A Theoretical Analysis,” *Journal of The Electrochemical Society*, vol. 157, no. 9, p. B1279, 2010.
[26] M. Petkovska and A. Marković, “Fast estimation of quasi-steady states of cyclic nonlinear processes based on higher-order frequency response functions. Case study: Cyclic operation of an adsorption column,” *Industrial and Engineering Chemistry Research*, vol. 45, no. 1, pp. 266–291, Jan. 2006.
[27] D. Nikolić and M. Petkovska, “Evaluation of Performance of Periodically Operated Reactors for Single Input Modulations of General Waveforms,” *Chemie-Ingenieur-Technik*, vol. 88, no. 11, pp. 1715–1722, Nov. 2016.
[28] Bilingual Teaching Group of Advanced Mathematics of Beijing University of Posts and Telecommunications. Advanced Mathematics [M]. 2nd ed. Beijing: Beijing University of Posts and Telecommunications Press, 2017: 153-156.
[29] The manual of SprintIR-6s CO2 sensor. https://www.gassensing.co.uk/products/co2/SprintIR---6S (accessed 2022-04-26).

Yuhan Dong received the B.S. degree in measurement and control technology and instruments from Dalian Maritime University, Dalian, China, in 2018.
She is currently a Ph.D. student in Dalian University of Technology, Dalian, China. Her research interests include analysis and design of nonlinear systems.

Zi-Qiang Lang received the B.S. and M.Sc. degrees in automatic control from Shenyang University and Northeastern University in China, respectively. He received the Ph.D. degree from the Department of Automatic Control and Systems Engineering, University of Sheffield, U.K. He is currently a Chair Professor in complex systems analysis and design with the Department of Automatic Control and Systems Engineering, University of Sheffield. His main expertise relates to the theories and methods for complex systems modelling, analysis, design, signal processing, and the application of these to resolving various scientific and engineering problems. The application areas include smart structures and systems, civil and mechanical structure vibration control, structural health monitoring, condition monitoring and fault diagnosis for wind turbine components and systems, digital manufacturing, and medical diagnosis.

Jun Zhao (SM’19) received the B.S. degree in control theory from Dalian Jiaotong University, Dalian, China, and the Ph.D. degree in engineering from the Dalian University of Technology, Dalian, in 2003 and 2008, respectively. He is currently a Professor with the School of Control Science and Engineering, Dalian University of Technology. He is an associate editor of the IEEE Trans. on Neural Network and Learning Systems, the Control Engineering Practice and the Information Sciences. His current research interests include industrial production scheduling, computer integrated manufacturing, intelligent optimization, and machine learning.

Wei Wang (SM’13) received the B.S., M.S., and Ph.D. degrees from Northeastern University, Shenyang, China, in 1982, 1986, and 1988, respectively, all in industrial automation. He was a Post-Doctoral Fellow with the Division of Engineering Cybernetics, Norwegian Science and Technology University, Trondheim, Norway, from 1990 to 1992, a Professor and Vice Director of the National Engineering Research Center of Metallurgical Automation of China, Beijing, China, from 1995 to 1999, and a Research Fellow with the Department of Engineering Science, University of Oxford, Oxford, U.K., from 1998 to 1999. He is currently a Professor with the School of Control Sciences and Engineering, Dalian University of Technology, Dalian, China. His current research interests include adaptive controls, computer integrated manufacturing, and computer controls of industrial processes.

Zhong Lan received the B.S. degree in Sichuan University, Sichuan, China, and the Ph.D. degree in engineering from the Dalian University of Technology, Dalian, in 2006. He is currently an associate professor with the Institute of Chemical Engineering, Dalian University of Technology. His current research interests include phenomenon on serial surfaces, designing and controlling of nanoscale and microscale structure on solid wall, LiBr heat pump, sea water desalted, CO_2 absorption and fixation, process enhancements and micro systems.