

Evaluation of the potential of Periodic Reactor Operations Based on the Second Order Frequency Response Function

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## Evaluation of the Potential of Periodic Reactor Operations Based on the Second Order Frequency Response Function

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### Abstract

A new, fast and easy method for analysing the potential for improving reactor performance by replacing steady state by forced periodic operation is presented. The method is based on Volterra series, generalized Fourier transform and the concept of higher-order frequency response functions (FRFs). The second order frequency response function, which corresponds to the dominant term of the non-periodic (DC) component,  $G_2(\omega, -\omega)$ , is mainly responsible for the average performance of the periodic processes. Based on that, in order to evaluate the potential of periodic reactor operation, it is enough to derive and analyze  $G_2(\omega, -\omega)$ . The sign of this function defines the sign of the DC component and reveals whether the performance improvement by cycling is possible. The method is used to analyze the periodic performance of a continuous stirred tank reactor (CSTR), plug flow tubular reactor (PFTR) and dispersive flow tubular reactor (DFTR), after introducing periodic change of the input concentration. Simple homogeneous, isothermal,  $n$ -th order reaction mechanism is studied.

**Keywords:** Forced periodic operation, Frequency response functions, Non-periodic (DC) component, Continuous stirred tank reactor, plug flow tubular reactor, dispersive flow tubular reactor,  $n$ -th order reaction

### 1. Introduction

Periodic operations of different chemical engineering processes, especially of chemical reactors, have been attracting attention of a number of research groups in the

last 20-30 years (Schlädlich et al., 1983; Nappi et al., 1985; Chanchlani et al., 1994; Silveston, 1998; Aida and Silveston, 2005). The attractiveness of the periodic operations lies in the fact that the average process performance corresponding to the periodic operation can be superior to the optimal steady-state operation, i.e., the conversion can be increased by cycling one or more inputs. In order to explain the possibility of conversion improvement, Figure 1 demonstrates the differences between steady state and periodic operation, for a simple reaction mechanism  $A \rightarrow \text{products}$ .

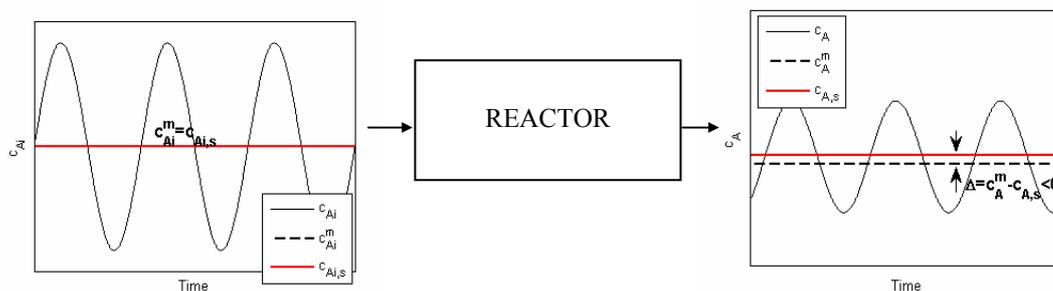


Figure 1. A simplified representation of a favourable periodic reactor operation

Let us assume that when the reaction is performed in a steady state operation  $c_{Ai,s}$  and  $c_{As}$  are the input and output concentrations of the reactant A, respectively. If the input concentration is modulated periodically (e.g. in a co-sinusoidal way) around its steady-state value, the outlet concentration will also oscillate. If the reactor is a nonlinear system, the mean value of the outlet concentration  $c_A^m$  will in principle be different from  $c_{A,s}$ . The difference  $\Delta = c_A^m - c_{A,s}$  can be negative, zero or positive, depending on the type of nonlinearity. If  $\Delta < 0$ , the periodic operation can be considered as favourable, as it corresponds to increased conversion, in comparison to the steady-state operation.

Testing whether a periodic operation is favourable, i.e., whether it results with increased productivity, generally demands long and tedious experimental and/or numerical work. In this paper we present a new, fast and easy method for testing periodic processes, based on the Volterra series approach (Volterra 1959), nonlinear frequency response and the concept of higher order frequency response functions (Weiner and Spina, 1980). In Section 2 we give a brief overview of these tools. More details about the theoretical background can be found in (Petkovska, 2005).

## 2. Frequency response method

Frequency response (FR) is one of the most commonly used methods for investigation of process dynamics. It actually represents a quasi-stationary response of the system to periodic (sinusoidal or co-sinusoidal) input modulation. Contrary to FR of a linear

system, which is a periodic function of the same shape and frequency as the input, FR of a nonlinear system also contains a non-periodic (DC) component and an indefinite sequence of higher harmonics:

$$y(t) = y_s + y_{DC} + y_I + y_{II} + \dots = y_s + y_{DC} + B_I \cos(\omega t + \varphi_I) + B_{II} \cos(2\omega t + \varphi_{II}) + \dots \quad (1)$$

A convenient way to treat weakly nonlinear systems with polynomial nonlinearities in the frequency domain is to replace the nonlinear model  $\mathbf{G}$  with a sequence of frequency response functions (FRFs) of the first, second, third, etc., order ( $G_1(\omega)$ ,  $G_2(\omega_1, \omega_2)$ ,  $G_3(\omega_1, \omega_2, \omega_3), \dots$ ) (Weiner and Spina, 1980).

In general, the output from a weakly nonlinear system can be represented in the Volterra series form (Volterra, 1959):

$$y = y_s + \sum_{i=1}^{\infty} y_m(t) \quad (2)$$

where  $y_1$  corresponds to the response of the linearised model and  $y_2, y_3$ , etc. are correction functions of different orders. If the input is defined as a single harmonic periodic function with amplitude  $A$  and frequency  $\omega$ :

$$x(t) = x_s + A \cos(\omega t) = x_s + \frac{A}{2} e^{j\omega t} + \frac{A}{2} e^{-j\omega t} \quad (3)$$

the correction function of the  $m$ -the order  $y_m(t)$  can be represented in the following way:

$$y_m(t) = {}_m C_0 G_{m,0} \left(\frac{A}{2}\right)^m e^{jm\omega t} + {}_m C_1 G_{m,1} \left(\frac{A}{2}\right)^m e^{j(m-2)\omega t} + \dots = \sum_{i=0}^m {}_m C_i G_{m,i} \left(\frac{A}{2}\right)^m e^{j(m-2i)\omega t} \quad (4)$$

where:

$$G_{m,i} = G_m(\underbrace{\omega, \dots, \omega}_{m-i}, \underbrace{-\omega, \dots, -\omega}_i) \quad (5)$$

and  ${}_m C_i$  is a binomial coefficient defined as:

$${}_m C_i = \frac{m!}{i!(m-i)!} \quad (6)$$

Hence, the Volterra series of the system output for a single harmonic input can be written as:

$$y(t) = y_s + \sum_{m=1}^{\infty} y_m(t) = \sum_{m=1}^{\infty} \sum_{i=0}^m {}_m C_i G_{m,i} \left(\frac{A}{2}\right)^m e^{j(m-2i)\omega t} \quad (7)$$

By collecting the constant terms and terms with equal frequencies in equation (7), the DC component and different harmonics of the output (equation (1)) are obtained:

$$y_{DC} = 2\left(\frac{A}{2}\right)^2 G_2(\omega, -\omega) + 6\left(\frac{A}{2}\right)^4 G_4(\omega, \omega, -\omega, -\omega) + \dots \quad (8)$$

$$y_I(t) = \left\{ \frac{A}{2} G_1(\omega) + 3 \left( \frac{A}{2} \right)^3 G_3(\omega, \omega, -\omega) + \dots \right\} e^{j\omega t} + \left\{ \frac{A}{2} G_1(-\omega) + 3 \left( \frac{A}{2} \right)^3 G_3(\omega, -\omega, -\omega) + \dots \right\} e^{-j\omega t} \quad (9)$$

$$y_{II}(t) = \left\{ \left( \frac{A}{2} \right)^2 G_2(\omega, \omega) + 4 \left( \frac{A}{2} \right)^4 G_2(\omega, \omega, \omega, -\omega) + \dots \right\} e^{2j\omega t} + \left\{ \left( \frac{A}{2} \right)^2 G_2(-\omega, -\omega) + 4 \left( \frac{A}{2} \right)^4 G_2(\omega, -\omega, -\omega, -\omega) + \dots \right\} e^{-2j\omega t}, \quad (10)$$

etc.

Equations (8-10) correlate the FRFs of different orders with the DC component and different harmonics of the output, which can be measured experimentally. These equations also show that the first, dominant term of the DC component is defined by the asymmetrical second order FRF  $G_2(\omega, -\omega)$ , the dominant term of the first harmonic by the first order FRF  $G_1(\omega)$  and the dominant term of the second harmonic by the symmetrical second order FRF  $G_2(\omega, \omega)$ .

In this study, we are using the concept of higher order FRFs for investigation of the average performance of periodic processes. For that reason, only the DC component (which is equal to  $\Delta$  defined in the Introduction), and the asymmetrical second order FRF  $G_2(\omega, -\omega)$ , corresponding to its dominant term, are of interest. The sign of the function  $G_2(\omega, -\omega)$  will define the sign of the DC component. In that way, in order to decide on the favourability of a particular periodic operation in comparison with the corresponding steady state operation, it is enough to derive and analyse the function  $G_2(\omega, -\omega)$ .

The objective of this work is to introduce a simple method for evaluation of the periodic reactor operation, based on the analysis of the asymmetrical second order FRF  $G_2(\omega, -\omega)$ . As a first step, in this manuscript the functions  $G_2(\omega, -\omega)$  are derived and analyzed for a simple reaction mechanism and three basic reactor types.

### 3. Model equations

In this work we consider periodic reactor operation for a simple reaction mechanism: isothermal  $n$ -th order reaction of the type  $A \rightarrow \text{products}$ , in the gas phase. We analyse the average periodic performance of three reactor types: a continuous stirred tank reactor (CSTR), a plug flow tubular reactor (PFTR) and a dispersed flow tubular reactor (DSTR) (Levenspiel, 1972).

The mathematical models (non-stationary material balance equations) for all three reactor types are listed below.

### 3.1 CSTR model

For a perfectly mixed reactor in which  $n$ -th order isothermal reaction is taking place, the non-stationary material balance is obtained in the form of a nonlinear first order ODE:

$$V \frac{dc_A}{dt} = F(c_{Ai} - c_A) - kVc_A^n \quad (11)$$

where  $t$  is time,  $c_A$  is the reactant concentration in the reactor and in the outlet stream,  $c_{Ai}$  is the reactant concentration in the feed stream,  $V$  is the reactor volume,  $F$  the flow-rate of the reaction stream and  $k$  the rate constant.

Periodic operation of the reactor around a previously established steady-state is considered. The initial steady-state is defined by the following equation:

$$Fc_{Ai,s} - Fc_{A,s} - kVc_{A,s}^n = 0 \quad (12)$$

For analysis in the frequency domain it is more convenient to transform the model equations into dimensionless form, by defining the concentration variables as relative deviations from their steady-state values. In that case, equation (11) is transformed into:

$$\frac{dC}{d\theta} = (1 + k\tau c_{A,s}^{n-1})(1 + C_i) - (1 + C) - k\tau c_{A,s}^{n-1}(1 + C)^n \quad (13)$$

where  $\tau = \frac{V}{F}$  is the reactor residence time,  $C_i = \frac{c_{Ai} - c_{Ai,s}}{c_{Ai,s}}$  and  $C = \frac{c_A - c_{A,s}}{c_{A,s}}$  are the dimensionless inlet and outlet concentrations, and  $\theta = \frac{t}{\tau}$  is the dimensionless time.

After expanding the nonlinear term  $(1+C)^n$  in the Taylor series form:

$$(1 + C)^n = 1 + nC + \frac{1}{2}n(n-1)C^2 + \dots \quad (14)$$

equation (13) is transformed into:

$$\frac{dC}{d\theta} = (1 + k\tau c_{A,s}^{n-1})C_i - C - k\tau c_{A,s}^{n-1}nC - \frac{1}{2}k\tau c_{A,s}^{n-1}n(n-1)C^2 - \dots \quad (15)$$

### 3.2. PFTR model

For an ideal plug flow reactor with  $n$ -th order reaction mechanism, the model equation is obtained in the form of a nonlinear first order PDE:

$$\frac{\partial c_A}{\partial t} + u \frac{\partial c_A}{\partial z} + kc_A^n = 0 \quad (16)$$

with the following boundary and initial conditions:

$$z = 0 : c_A(0, t) = c_{Ai}(t) \quad \text{and} \quad t \leq 0 : c_A(z, 0) = c_{A,s}(z) \quad \forall z : c_A(z, 0) = c_{A,s}(z) \quad (17)$$

In equations (16) and (17)  $z$  is the axial reactor coordinate,  $c_A$  is the concentration at position  $z$  in the reactor and  $u$  is the reaction stream velocity.

For steady state, the reactor material balance reduces to:

$$u \frac{dc_{As}}{dz} = -kc_{As}^n \quad (18)$$

The model equations (16) and (17) are again transformed into dimensionless form:

$$\frac{\partial C}{\partial \theta} + \frac{\partial C}{\partial x} + kc_{A,s}^{n-1} \tau ((1+C)^n - (1+C)) = 0 \quad (19)$$

$$x = 0 : C = C_i(0, \theta) \quad \text{and} \quad \theta \leq 0 : C_i(0) = 0, \quad \forall x : C(x, 0) = 0 \quad (20)$$

The definitions of dimensionless concentrations and time are analogous as for the CSTR. In addition,  $x = \frac{z}{L}$  is the dimensionless axial coordinate of the PFTR reactor,

and the residence time is defined as  $\tau = \frac{L}{u}$  ( $L$  is the reactor length).

After expanding the nonlinear term  $(1+C)^n$  in the Taylor series form, equation (19) is transformed into the following form:

$$\frac{\partial C}{\partial \theta} + \frac{\partial C}{\partial x} + \tau kc_{A,s}^{n-1} (n-1)C + \frac{1}{2} \tau n(n-1)kc_{A,s}^{n-1} C^2 + \dots = 0 \quad (21)$$

### 3.3. DFTR model

This reactor model, which takes into account axial dispersion, corresponds to a more realistic case of non-ideal flow. The material balance equation for this case is obtained in the form of a nonlinear second order PDE:

$$\frac{\partial c_A}{\partial t} + u \frac{\partial c_A}{\partial z} + kc_A^n = D_{eff} \frac{\partial^2 c_A}{\partial z^2} \quad (22)$$

with the following boundary:

$$z = 0 : c_A(0, t) = c_{Ai}(t) + D_{eff} \left. \frac{\partial c_A}{\partial z} \right|_{z=0}, \quad z = L : \left. \frac{\partial c_A}{\partial z} \right|_{z=L} = 0 \quad (23)$$

and initial conditions:

$$t \leq 0 : c_{Ai}(0) = c_{Ai,s}, \quad \forall z : c_A(z, 0) = c_{As}(z) \quad (24)$$

This model has an additional parameter in comparison with the previous one: the axial dispersion coefficient  $D_{eff}$ . The steady state concentration is obtained as a solution of the corresponding steady-state equation:

$$u \frac{\partial c_{A,s}}{\partial z} + kc_{A,s}^n = D_{eff} \frac{\partial^2 c_{A,s}}{\partial z^2} \quad (25)$$

Using the dimensionless variables defined previously, equations (22-24) are transformed into:

$$\frac{\partial C}{\partial \theta} + \frac{\partial C}{\partial x} + kc_{A,s}{}^{n-1} \tau \left( (1+C)^n - (1+C) \right) = \frac{1}{2N} \frac{\partial^2 C}{\partial x^2} \quad (26)$$

$$x = 0: \quad C(0, \theta) = C_i(\theta) + \frac{1}{2N} \frac{\partial C}{\partial x} \Big|_{x=0}, \quad x = 1: \quad \frac{\partial C}{\partial x} \Big|_{x=1} = 0 \quad (27)$$

$$\theta \leq 0: C_i(0) = 0, \quad \forall x: C(x, 0) = 0 \quad (28)$$

In equations (26) and (27)  $N$  is the number of theoretical plates, which is related to the axial dispersion coefficient  $D_{eff}$ :  $N = \frac{uL}{2D_{eff}}$ .

The nonlinear term  $(1+C)^n$  in equation (26) is again expanded in the Taylor series, resulting with the following equation:

$$\frac{\partial C}{\partial \theta} + \frac{\partial C}{\partial x} + \tau kc_{A,s}{}^{n-1} (n-1)C + \frac{1}{2} \tau n(n-1) kc_{A,s}{}^{n-1} C^2 + \dots = \frac{1}{2N} \frac{\partial^2 C}{\partial x^2} \quad (29)$$

#### **4. Frequency response functions for the analysed reactors**

The next step in our procedure is deriving the necessary FRFs for each case under consideration. For estimating the average reaction performance, it is necessary and enough to estimate the DC component. As explained in Section 2, the sign of the DC component is determined by the asymmetrical second order FRF  $G_2(\omega, -\omega)$ . Consequently, we will limit our derivations and analysis to the first ( $G_1(\omega)$ ) and asymmetrical second order FRFs ( $G_2(\omega, -\omega)$ ).

The procedure for deriving the higher order FRFs is rather standard and can be found in our previous papers (Petkovska and Do 1998, 2000; Petkovska 2001; Petkovska and Marković, 2006).

The basic steps of this procedure are as follows:

- 1) Defining the input concentration  $C_i(\theta)$  in the form of a co-sinusoidal function (Eq.(3));
- 2) Expressing the output concentration  $C(\theta)$  in the Volterra series form (Eq. (7));
- 3) Substituting the expressions for  $C_i(\theta)$  and  $C(\theta)$  into the corresponding model equations;
- 4) Applying the method of harmonic probing to the equations obtained in step 3 (collecting the terms with the same amplitude and frequency and equating them to zero);

5) Solving the equations obtained in Step 4.

Some details of the derivation procedure can be found in the Appendix. In the main body of this manuscript, only the final expressions for the first and asymmetrical second order FRFs for the three models under consideration will be presented.

#### 4.1 First order and second order FRFs for the CSTR model

- First order FRF:

$$G_1(\omega) = \frac{1 + k\tau c_{A,s}^{n-1}}{1 + k\tau c_{A,s}^{n-1}n + \omega j} \quad (30)$$

- Second order FRF corresponding to the DC component:

$$G_2(\omega, -\omega) = -\frac{1}{2}n(n-1) \frac{k\tau c_{A,s}^{n-1}(1 + k\tau c_{A,s}^{n-1})^2}{(1 + k\tau c_{A,s}^{n-1}n)((1 + k\tau c_{A,s}^{n-1}n)^2 + \omega^2)} \quad (31)$$

#### 4.2. First and second order FRFs for the PFTR model

a) First order FRF:

$$G_1(\omega) = \frac{1}{1 + k\tau(n-1)c_{Ai,s}^{n-1}} e^{-j\omega} \quad (32)$$

b) Second order FRF corresponding to the DC component:

$$G_2(\omega, -\omega) = -\frac{1}{2}n(n-1) \frac{k\tau c_{Ai,s}^{n-1}}{2(1 + k\tau(n-1)c_{Ai,s}^{n-1})^2} \quad (33)$$

#### 4.3. First and second order FRFs for the DFTR model

a) First order FRF:

$$G_1(\omega) = C_1(\omega)e^{\alpha_1(\omega)} + C_2(\omega)e^{\alpha_2(\omega)} + (1 + k\tau(n-1)c_{Ai,s}^{n-1})e^{2N} \quad (34)$$

where  $\alpha_1(\omega)$  and  $\alpha_2(\omega)$  are the characteristic values of the underlying differential equation, while  $C_1(\omega)$  and  $C_2(\omega)$  are the corresponding integration constants, which can be found in Appendix, Eqs. (A-17 – A-19).

b) Second order FRF corresponding to the DC component:

$$G_2(\omega, -\omega) = D_1 + D_2e^{2N} + d_1e^{\alpha_1(\omega)+2N} + d_2e^{\alpha_2(\omega)+2N} + d_3e^{\alpha_1(-\omega)+2N} + d_4e^{\alpha_2(-\omega)+2N} + f_1(1)e^{\alpha_1(\omega)+\alpha_1(-\omega)} + f_2(1)e^{\alpha_1(\omega)+\alpha_2(-\omega)} + f_3(1)e^{\alpha_1(-\omega)+\alpha_2(\omega)} + f_4(1)e^{\alpha_2(-\omega)+\alpha_2(\omega)} \quad (35)$$

where  $D_1, D_2$ , and  $d_1$  to  $d_4$  are integration constants. Their expression can be found in the Appendix, Eqs (A-21,A-23, A-24). Functions  $f_1(1)$  to  $f_4(1)$  are obtained by substituting  $x=1$  in the functions  $f_1(x)$  to  $f_4(x)$  defined in the Appendix (Eq. (A-22)) in order to simplify very cumbersome expressions.

## 5. Discussion with simulations

Analysis of the expressions for the asymmetrical second order FRF  $G_2(\omega, -\omega)$  for the ideal reactors (CSTR - equations (31) and PFTR equation (33)) shows the following:

- (1)  $G_2(\omega, -\omega) < 0$ , for  $n < 0$  and  $n > 1$ . This corresponds to improved reactor performance owing to periodic operation, i.e. to favourable periodic operation.
- (2)  $G_2(\omega, -\omega) = 0$ , for  $n = 0$  and  $n = 1$ . This corresponds to no influence of the periodic operation on reactor performance.
- (3)  $G_2(\omega, -\omega) > 0$ , for  $0 < n < 1$ . This corresponds to worsened reactor performance owing to periodic operation, i.e. to unfavourable periodic operation.

It is important to notice that identical results were obtained for both reactor types. Analysis of equation (35), defining the function  $G_2(\omega, -\omega)$  for the DFTR is not so obvious, nevertheless, it can be shown by numerical analysis that the same conclusions are valid for this reactor type, as well.

As illustration, using the expressions given by equations (31), (33) and (35), the  $G_2(\omega, -\omega)$  functions were simulated for all three reactors and for three different reaction orders ( $n = -1, 0.5$  and  $2$ ), corresponding to the three ranges of interest ( $n < 0, 0 < n < 1$  and  $n > 1$ ). The simulation results are shown in Figures 2 (for the CSTR), 3 (for the PFTR) and 4 (for the DFTR). The parameter values, used for simulation are given in Table 1. For all three reactor types the simulations were performed with the same values of the contact time, rate constant and inlet steady-state concentration.

**Table 1.** Model parameters used for simulations

Rate constant, $k$	$0.001 \text{ s}^{-1} \text{ mol}^{1-n}$
Reaction order, $n$	$[-1, 0.5, 2]$
Steady-state inlet concentration of the reactant A, $c_{Ai,s}$	$1 \text{ mol/m}^3$
Contact time, $\tau$	$100 \text{ s}$
Number of theoretical plates, $N$	$100$

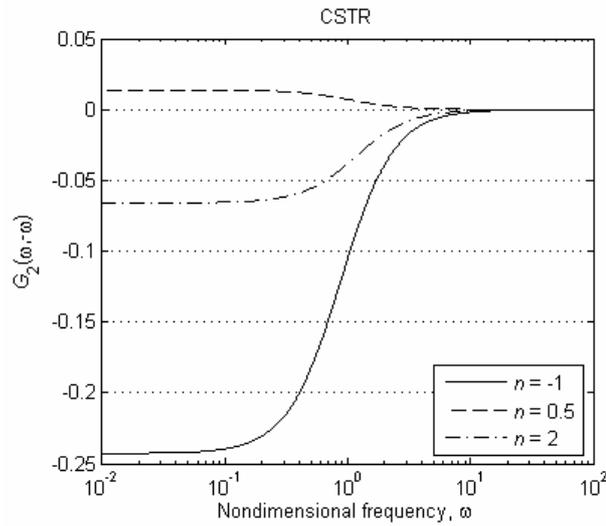


Figure 2. The second order functions  $G_2(\omega, -\omega)$  for CSTR for 3 different reaction orders

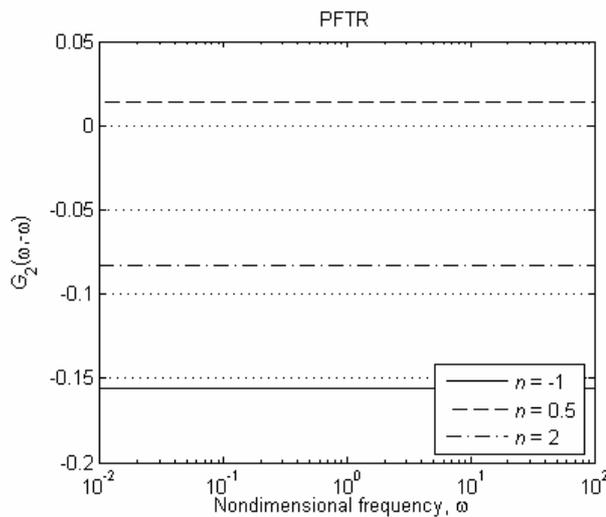


Figure 3. The second order functions  $G_2(\omega, -\omega)$  for PFTR for 3 different reaction orders

The simulation results presented in Figures 2, 3 and 4 confirm the previous conclusions. Negative values of  $G_2(\omega, -\omega)$  are obtained for  $n=-1$  ( $n < 0$ ) and  $n=2$  ( $n > 1$ ), while for  $n=0.5$  ( $0 < n < 1$ )  $G_2(\omega, -\omega)$  is positive. It can also be observed that the asymmetrical second order FRF for the PFTR is independent of frequency, while for the CSTR and DFTR the absolute value of  $G_2(\omega, -\omega)$  decreases with increase of frequency and tends to zero when  $\omega \rightarrow \infty$ .

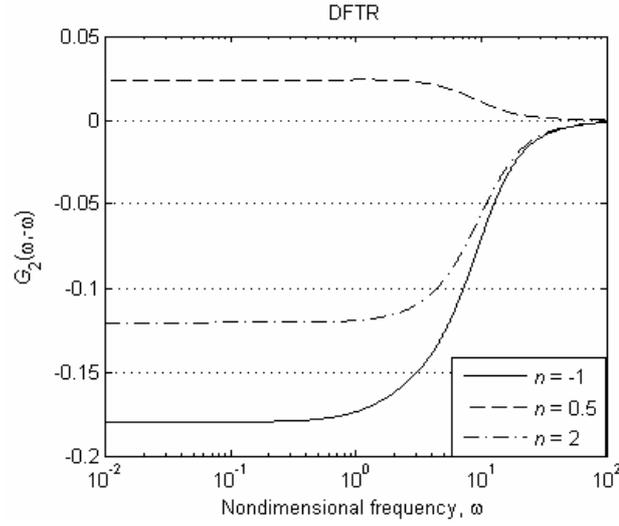


Figure 4. The second order functions  $G_2(\omega, -\omega)$  for DFTR for 3 different reaction orders

As illustration, in Figure 5 we show a quasi-steady state segment of a simulated output concentration from a CSTR (obtained by numerical solution of the model equation (13)), for sinusoidal input concentration change and the following simulation parameters:  $n=-1$ ,  $\tau=100$  s,  $k=0.001$  mol<sup>2</sup>s<sup>-1</sup>,  $c_{A,i,s}=1$  mol/m<sup>3</sup>,  $\omega=0.01$  rad/s and  $A=75\%$ . The corresponding steady-state concentration ( $c_{A,s}=0.8873$  mol/m<sup>3</sup>) and the mean value of the outlet concentration ( $c_A^m=0.8176$  mol/m<sup>3</sup>) are also shown in Figure 5.

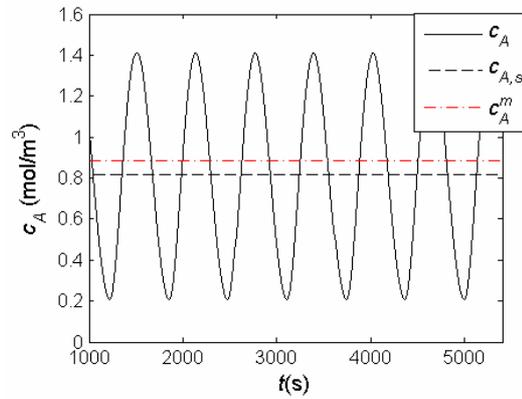


Figure 5. Numerical simulation of the CSTR outlet concentration for a sinusoidal input concentration change, showing the difference between the mean value and the steady-state value

Based on that, we can calculate the reactor performance improvement owing to periodic operation, corresponding to this case:

$$\Delta = c_A^m - c_{A,s} = -0.0697 \text{ mol/m}^3$$

On the other hand, the approximate value of the DC component, calculated based on the second order FRF  $G_2(\omega, -\omega)$  only (only the first term in Eq. (8)), is:

$$y_{DC} \approx 2 \left( \frac{A}{2} \right)^2 G_2(\omega, -\omega) c_{A,s} = -0.0605 \text{ mol/m}^3$$

which is close to the value of  $\Delta$  obtained from the numerical solution. For more precise estimation of the DC component, the contribution of the asymmetrical fourth order FRF  $G_4(\omega, \omega, -\omega, -\omega)$ , and possibly higher order FRFs, would have to be taken into account.

## 6. Conclusions

A new, rather simple method for fast evaluation whether a periodic operation of a reactor has potential for improved performance compared to conventional steady-state operation has been presented. The method is based on frequency response, Volterra series theory and the concept of higher order frequency response functions. A simple example was used for testing the method: isothermal homogeneous  $n$ -th order reaction of the type  $A \rightarrow \text{products}$  and three standard reactor types: CSTR, PFTR and DFTR.

The main conclusions are the following:

1. The average reactor performance in the periodic regime is determined by the DC component of the output, which, on the other hand, is dominantly influenced by the asymmetrical second order FRF  $G_2(\omega, -\omega)$ . Consequently, in order to decide whether a periodic operation would be favourable in comparison with a steady-state one, it is enough to derive  $G_2(\omega, -\omega)$  and analyse its sign.
2. For all three reactor types the same results were obtained: that the periodic operating regime will increase the productivity for reaction order  $n < 0$  or  $n > 1$ . The main consequence of this result is that it would be enough to derive and analyse the  $G_2(\omega, -\omega)$  function for the CSTR in order to decide whether performing the reaction in the periodic regime is worthwhile, or not. Derivation of the  $G_2(\omega, -\omega)$  function for the CSTR is rather simple and fast, compared to other reactor types.
3. The improvement owing to periodic operation can be approximately estimated quantitatively based on the asymmetrical second order FRF  $G_2(\omega, -\omega)$ , only.

Taking all this in account, we believe that the proposed method is very convenient for evaluation of the potential of periodic reactor operations. The method is fast and simple, especially when applied to CSTR. In our future work it will be applied to investigation of more complex reaction mechanisms, including heterogeneous and non-isothermal systems.

## Acknowledgment

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## Appendix: Derivation of the Frequency Response Functions (FRFs) $G_1(\omega)$ and $G_2(\omega, -\omega)$

The final expressions for the first and asymmetric second order FRFs for the three analysed reactor types are given in the main body of this manuscript. Here we give the main points of the derivation procedure, performed in 5 steps.

*Step 1. Defining the input concentration:*

$$C_i(\theta) = \frac{A}{2} e^{j\omega\theta} + \frac{A}{2} e^{-j\omega\theta} \quad (\text{A-1})$$

*Step 2. Representing the output concentration in gas phase in the form of Volterra series:*

$$\begin{aligned} C_{out}(\theta) = & \frac{A}{2} G_1(\omega) e^{j\omega\theta} + \frac{A}{2} G_1(-\omega) e^{-j\omega\theta} + \left(\frac{A}{2}\right)^2 G_2(\omega, \omega) e^{2j\omega\theta} \\ & + 2\left(\frac{A}{2}\right)^2 G_2(\omega, -\omega) e^0 + \left(\frac{A}{2}\right)^2 G_2(-\omega, -\omega) e^{-2j\omega\theta} + \dots \end{aligned} \quad (\text{A-2})$$

For CSTR  $C_{out}(\theta)$  is  $C(\theta)$ , while for PFTR and DFTR it is  $C(x=1, \theta)$ . For the PFTR and DFTR it is convenient to define an auxiliary set of FRFs, e.g.  $H$ -functions, which correspond to the concentration at position  $x$  in the reactor and depend on  $x$ , as well as on  $\omega$ :

$$\begin{aligned} C(x, \theta) = & \frac{A}{2} H_1(x, \omega) e^{j\omega\theta} + \frac{A}{2} H_1(x, -\omega) e^{-j\omega\theta} + \left(\frac{A}{2}\right)^2 H_2(x, \omega, \omega) e^{2j\omega\theta} \\ & + 2\left(\frac{A}{2}\right)^2 H_2(x, \omega, -\omega) e^0 + \left(\frac{A}{2}\right)^2 H_2(x, -\omega, -\omega) e^{-2j\omega\theta} + \dots \end{aligned} \quad (\text{A-3})$$

*Step 3. Substitute the expressions for input concentration and output concentrations defined by Eqs. (A1-A3) into the appropriate model equations*

The resulting equations are too cumbersome and will not be presented.

*Step 4: Collecting the terms with  $Ae^{j\omega\theta}$ , corresponding to the first order functions and with  $2A^2e^0$ , corresponding to the asymmetrical second order function, and equating them to zero.*

The resulting equations for each reactor type are presented below:

#### 4.1 CSTR model

a) First order FRF:

$$j\omega G_1(\omega) = (1 + k\tau c_{As}^{n-1}) - G_1(\omega) - k\tau c_{As}^{n-1} n G_1(\omega) \quad (\text{A-4})$$

b) Second order FRF corresponding to the DC component:

$$0 = 0 - 2G_2(\omega, -\omega) - 2k\tau c_{As}^{n-1} n G_2(\omega, -\omega) - 2k\tau c_{As}^{n-1} \frac{n}{2} (n-1) G_1(\omega) G_1(-\omega) \quad (\text{A-5})$$

#### 4.2 PFTR model

a) First order FRF:

$$\frac{dH_1(x, \omega)}{dx} + \left( j\omega + \frac{\tau k c_{Ai,s}^{n-1} (n-1)}{1 + \tau k c_{Ai,s}^{n-1} (n-1)x} \right) H_1(x, \omega) = 0 \quad (\text{A-6})$$

with the following boundary condition:

$$x = 0: H_1(0, \omega) = 1 \quad (\text{A-7})$$

b) Second order FRF corresponding to the DC component:

$$\frac{dH_2(x, \omega, -\omega)}{dx} + \frac{\tau k (n-1) c_{Ai,s}^{n-1}}{1 + \tau k c_{Ai,s}^{n-1} (n-1)x} H_2(x, \omega, -\omega) + \frac{1}{2} n \frac{\tau k (n-1) c_{Ai,s}^{n-1}}{(1 + \tau k c_{Ai,s}^{n-1} (n-1)x)^3} = 0 \quad (\text{A-8})$$

with the boundary condition:

$$x = 0: H_2(0, \omega, -\omega) = 0 \quad (\text{A-9})$$

#### 4.3 DFTR model

a) First order FRF:

$$\frac{d^2 H_1(x, \omega)}{dx^2} - 2N \frac{dH_1(x, \omega)}{dx} - 2N \left( j\omega + \frac{\tau k c_{Ai,s}^{n-1} (n-1)}{1 + \tau k c_{Ai,s}^{n-1} (n-1)x} \right) H_1(x, \omega) = 0 \quad (\text{A-10})$$

with the following boundary conditions:

$$x = 0: H_1(0, \omega) = 1 + \frac{1}{2N} \left. \frac{dH_1(x, \omega)}{dx} \right|_{x=0}, \quad x = 1: \left. \frac{dH_1(x, \omega)}{dx} \right|_{x=1} = 0 \quad (\text{A-11})$$

b) Second order FRF corresponding to the DC component:

$$\begin{aligned} \frac{d^2 H_2(x, \omega, -\omega)}{dx^2} - 2N \frac{dH_2(x, \omega, -\omega)}{dx} - 2N \frac{\tau k c_{Ai,s}^{n-1} (n-1)}{1 + \tau k c_{Ai,s}^{n-1} (n-1)x} H_2(x, \omega, -\omega) = \\ N \frac{\tau k c_{As}^{n-1} (n-1)n}{1 + \tau k c_{As}^{n-1} (n-1)x} H_1(x, \omega) H_1(x, -\omega) \end{aligned} \quad (\text{A-12})$$

with following boundary conditions:

$$x = 0 : H_2(0, \omega, -\omega) = \frac{1}{2N} \frac{dH_2(x, \omega, -\omega)}{dx} \Big|_{x=0}, \quad x = 1 : \frac{dH_2(x, \omega, -\omega)}{dx} \Big|_{x=1} = 0 \quad (\text{A-13})$$

Step 5. Solving equations obtained in Step 4.

5.1 CSTR model:

Being algebraic, equations (A-4) and (A-5) are easily solved. Their solutions are given Chapter 4.1 in the main body of the manuscript ( Eqs.(30) and (31)).

5.2 PFTR model:

The solutions of the first-order linear differential equations (A-6) and (A-7) are:

a) First order FRF:

$$H_1(x, \omega) = \frac{1}{1 + k\tau(n-1)c_{Ai,s}^{n-1}x} e^{-j\omega x} \quad (\text{A-14})$$

For  $x=1$ , this function becomes equal to the  $G_1(\omega)$  function, corresponding to the concentration at the reactor outlet, given by equation (32).

b) Second order FRF corresponding to the DC component:

$$G_2(\omega, -\omega) = -\frac{k\tau n(n-1)c_{Ai,s}^{n-1}x}{2(1 + k\tau(n-1)c_{Ai,s}^{n-1}x)^2} \quad (\text{A-15})$$

For  $x=1$ , this function becomes equal to the  $G_2(\omega, -\omega)$  function, corresponding to the concentration at the reactor outlet, given by equation (33).

4.3 DFTR model:

In this case, the resulting equations are linear second order homogeneous ODEs with variable coefficients (equations (A-10) and (A-12)). Their solution gives the following results:

a) First order FRF:

$$H_1(x, \omega) = C_1(\omega)e^{\alpha_1(\omega)x} + C_2(\omega)e^{\alpha_2(\omega)x} + (1 + k\tau(n-1)c_{Ai,s}^{n-1}x)e^{2Nx} \quad (\text{A-16})$$

For  $x=1$ , this function becomes equal to the  $G_2(\omega, -\omega)$  function, corresponding to the concentration at the reactor outlet, given by equation (34).

In Eq (A-16)  $\alpha_1(\omega)$  and  $\alpha_2(\omega)$  are the characteristic values:

$$\alpha_{1,2}(\omega) = N \pm \sqrt{N^2 + 4Nj\omega} \quad (\text{A-17})$$

The integration constants  $C_1(\omega)$  and  $C_2(\omega)$  are obtained from the boundary conditions (A-11):

$$C_1(\omega) + C_2(\omega) = 1 + \frac{1}{2N}(\alpha_1(\omega)C_1(\omega) + \alpha_2(\omega)C_2(\omega) + f + 2N) \quad (\text{A-18})$$

$$C_1(\omega)\alpha_1(\omega)e^{\alpha_1(\omega)} + C_2(\omega)\alpha_2(\omega)e^{\alpha_2(\omega)} + (f + 2N(1 + f))e^{2N} = 0 \quad (\text{A-19})$$

b) Second order FRF corresponding to the DC component:

$$\begin{aligned} H_2(x, \omega, -\omega) &= D_1(1 + k\tau(n-1)c_{Ai,s}^{n-1}x) + D_2e^{2Nx} + d_1e^{(\alpha_1(\omega)+2N)x} + d_2e^{(\alpha_2(\omega)+2N)x} \\ &+ d_3e^{(\alpha_1(-\omega)+2N)x} + d_4e^{(\alpha_2(-\omega)+2N)x} + \frac{2Nk\tau(n-1)nc_{Ai,s}^{n-1}}{1 + k\tau(n-1)c_{Ai,s}^{n-1}x} \times \\ &\left( \frac{C_1(\omega)C_1(-\omega)}{f_1(x)} e^{(\alpha_1(\omega)+\alpha_1(-\omega))x} + \frac{C_1(\omega)C_2(-\omega)}{f_2(x)} e^{(\alpha_1(\omega)+\alpha_2(-\omega))x} \right. \\ &\left. + \frac{C_1(-\omega)C_2(\omega)}{f_3(x)} e^{(\alpha_2(\omega)+\alpha_1(-\omega))x} + \frac{C_2(\omega)C_2(-\omega)}{f_4(x)} e^{(\alpha_2(\omega)+\alpha_2(-\omega))x} \right) \end{aligned} \quad (\text{A-20})$$

For  $x=1$ , this function becomes equal to the  $G_2(\omega, -\omega)$  function, corresponding to the concentration at the reactor outlet, given by equation (35).

Integration constants  $d_1 - d_4$  in Eq. (A-20) are defined by the following expressions:

$$\begin{aligned} d_1 &= \frac{2Nk\tau(n-1)nc_{Ai,s}^{n-1}C_1(\omega)}{(\alpha_1(\omega) + 2N)\alpha_1(\omega)}, & d_2 &= \frac{2Nk\tau(n-1)nc_{Ai,s}^{n-1}C_2(\omega)}{(\alpha_2(\omega) + 2N)\alpha_2(\omega)} \\ d_3 &= \frac{2Nk\tau(n-1)nc_{Ai,s}^{n-1}C_1(-\omega)}{(\alpha_1(-\omega) + 2N)\alpha_1(-\omega)}, & d_4 &= \frac{2Nk\tau(n-1)nc_{Ai,s}^{n-1}C_2(-\omega)}{(\alpha_2(-\omega) + 2N)\alpha_2(-\omega)} \end{aligned} \quad (\text{A-21})$$

The functions  $f_1(x)$  to  $f_4(x)$  were introduced in order to simplify Eq. (A-20). They are defined in the following way:

$$\begin{aligned} f_1(x) &= (\alpha_1(\omega) + \alpha_1(-\omega))(2k\tau(n-1)c_{Ai,s}^{n-1} + (1 + k\tau(n-1)c_{Ai,s}^{n-1}x)(\alpha_1(\omega) + \alpha_1(-\omega) - 2N)) \\ f_2(x) &= (\alpha_1(\omega) + \alpha_2(-\omega))(2k\tau(n-1)c_{Ai,s}^{n-1} + (1 + k\tau(n-1)c_{Ai,s}^{n-1}x)(\alpha_1(\omega) + \alpha_2(-\omega) - 2N)) \\ f_3(x) &= (\alpha_1(-\omega) + \alpha_2(\omega))(2k\tau(n-1)c_{Ai,s}^{n-1} + (1 + k\tau(n-1)c_{Ai,s}^{n-1}x)(\alpha_1(-\omega) + \alpha_2(\omega) - 2N)) \\ f_4(x) &= (\alpha_2(\omega) + \alpha_2(-\omega))(2k\tau(n-1)c_{Ai,s}^{n-1} + (1 + k\tau(n-1)c_{Ai,s}^{n-1}x)(\alpha_2(\omega) + \alpha_2(-\omega) - 2N)) \end{aligned} \quad (\text{A-22})$$

$D_1$  and  $D_2$  are obtained from the boundary conditions (A-13):

$$\begin{aligned}
 & D_1 + D_2 + d_1 + d_2 + d_3 + d_4 + Nn \left( \frac{C_1(\omega)C_1(-\omega)}{(\alpha_1(\omega) + \alpha_1(-\omega))(\alpha_1(\omega) + \alpha_1(-\omega) - 2N)} + \right. \\
 & \frac{C_1(\omega)C_2(-\omega)}{(\alpha_1(\omega) + \alpha_2(-\omega))(\alpha_1(\omega) + \alpha_2(-\omega) - 2N)} + \frac{C_1(-\omega)C_2(\omega)}{(\alpha_1(-\omega) + \alpha_2(\omega))(\alpha_1(-\omega) + \alpha_2(\omega) - 2N)} + \\
 & \left. \frac{C_2(\omega)C_2(-\omega)}{(\alpha_2(\omega) + \alpha_2(-\omega))(\alpha_2(\omega) + \alpha_2(-\omega) - 2N)} \right) = \frac{1}{2N} \left\{ k\tau c_{Ai,s}^{n-1} (n-1)D_1 + 2ND_2 + d_1(\alpha_1(\omega) + 2N) + \right. \\
 & d_2(\alpha_2(\omega) + 2N) + d_3(\alpha_1(-\omega) + 2N) + d_4(\alpha_2(-\omega) + 2N) + 2Nn(n-1)k\tau c_{Ai,s}^{n-1} \times (C_1(\omega)C_1(-\omega) \times \\
 & \left[ C_1(\omega)C_1(-\omega) \left( \frac{\alpha_1(\omega) + \alpha_1(-\omega) - (n-1)k\tau c_{Ai,s}^{n-1}}{f_1(0)} + (n-1)k\tau c_{Ai,s}^{n-1} (\alpha_1(\omega) + \alpha_1(-\omega))(\alpha_1(\omega) + \alpha_1(-\omega) - 2N) \right) \right] \\
 & + C_1(\omega)C_2(-\omega) \left( \frac{\alpha_1(\omega) + \alpha_2(-\omega) - (n-1)k\tau c_{Ai,s}^{n-1}}{f_2(0)} + (n-1)k\tau c_{Ai,s}^{n-1} (\alpha_1(\omega) + \alpha_2(-\omega))(\alpha_1(\omega) + \alpha_2(-\omega) - 2N) \right) \\
 & + C_1(-\omega)C_2(\omega) \left( \frac{\alpha_1(-\omega) + \alpha_2(\omega) - (n-1)k\tau c_{Ai,s}^{n-1}}{f_3(0)} + (n-1)k\tau c_{Ai,s}^{n-1} (\alpha_1(-\omega) + \alpha_2(\omega))(\alpha_1(-\omega) + \alpha_2(\omega) - 2N) \right) \\
 & \left. + C_2(\omega)C_2(-\omega) \left( \frac{\alpha_2(\omega) + \alpha_2(-\omega) - (n-1)k\tau c_{Ai,s}^{n-1}}{f_4(0)} + (n-1)k\tau c_{Ai,s}^{n-1} (\alpha_2(\omega) + \alpha_2(-\omega))(\alpha_2(\omega) + \alpha_2(-\omega) - 2N) \right) \right\} \\
 & \tag{A-23}
 \end{aligned}$$

$$\begin{aligned}
 & k\tau(n-1)c_{Ai,s}^{n-1}D_1 + 2N\beta_2e^{2N} + d_1(\alpha_1(\omega) + 2N)e^{(\alpha_1(\omega)+2N)} + d_2(\alpha_2(\omega) + 2N)e^{(\alpha_2(\omega)+2N)} \\
 & + d_3(\alpha_1(-\omega) + 2N)e^{(\alpha_1(-\omega)+2N)} + d_4(\alpha_2(\omega) + 2N)e^{(\alpha_2(\omega)+2N)} + \frac{2Nk\tau(n-1)c_{Ai,s}^{n-1}}{1+k\tau(n-1)c_{Ai,s}^{n-1}} \times \\
 & \left\{ C_1(\omega)C_1(-\omega)e^{(\alpha_1(\omega)+\alpha_1(-\omega))} \left( \frac{1}{f_1(1)} \left( \alpha_1(\omega) + \alpha_1(-\omega) - \frac{k\tau(n-1)c_{Ai,s}^{n-1}}{1+k\tau(n-1)c_{Ai,s}^{n-1}} \right) + k\tau(n-1)c_{Ai,s}^{n-1} (\alpha_1(\omega) + \alpha_1(-\omega))(\alpha_1(\omega) + \alpha_1(-\omega) - 2N) \right) \right. \\
 & + C_1(\omega)C_2(-\omega)e^{(\alpha_1(\omega)+\alpha_2(-\omega))} \left( \frac{1}{f_2(1)} \left( \alpha_1(\omega) + \alpha_2(-\omega) - \frac{k\tau(n-1)c_{Ai,s}^{n-1}}{1+k\tau(n-1)c_{Ai,s}^{n-1}} \right) + k\tau(n-1)c_{Ai,s}^{n-1} (\alpha_1(\omega) + \alpha_2(-\omega))(\alpha_1(\omega) + \alpha_2(-\omega) - 2N) \right) \\
 & + C_1(-\omega)C_2(\omega)e^{(\alpha_1(-\omega)+\alpha_2(\omega))} \left( \frac{1}{f_3(1)} \left( \alpha_1(-\omega) + \alpha_2(\omega) - \frac{k\tau(n-1)c_{Ai,s}^{n-1}}{1+k\tau(n-1)c_{Ai,s}^{n-1}} \right) + k\tau(n-1)c_{Ai,s}^{n-1} (\alpha_1(-\omega) + \alpha_2(\omega))(\alpha_1(-\omega) + \alpha_2(\omega) - 2N) \right) \\
 & \left. + C_2(\omega)C_2(-\omega)e^{(\alpha_2(\omega)+\alpha_2(-\omega))} \left( \frac{1}{f_4(1)} \left( \alpha_2(\omega) + \alpha_2(-\omega) - \frac{k\tau(n-1)c_{Ai,s}^{n-1}}{1+k\tau(n-1)c_{Ai,s}^{n-1}} \right) + k\tau(n-1)c_{Ai,s}^{n-1} (\alpha_2(\omega) + \alpha_2(-\omega))(\alpha_2(\omega) + \alpha_2(-\omega) - 2N) \right) \right\} = 0 \\
 & \tag{A-24}
 \end{aligned}$$

**Notations:**

- $A$  - input amplitude  
 $B$  – output amplitude, general  
 $c_A$  – concentration of component A ( $\text{molm}^{-3}$ )  
 $c_A^m$  - time-average value of the output concentration  
 $C$  – nondimensional concentration of component A  
 $D_{ax}$  – axial dispersion coefficient ( $\text{cm}^2\text{s}^{-1}$ )  
 $F$  – volumetric flow-rate,  $\text{m}^3\text{s}^{-1}$   
 $G_m$  –  $m$ -th order FRF  
 $H_m$  -  $m$ -th order auxiliary FRF  
 $k$  – rate constant ( $\text{s}^{-1}\text{mol}^{1-n}$ )  
 $L$  – column length (m)  
 $n$  - order of the reaction rate  
 $N$  – number of theoretical plates  
 $t$  – time (s)  
 $u$  – interstitial fluid velocity ( $\text{ms}^{-1}$ )  
 $V$  – reactor volume,  $\text{m}^3$   
 $x$  – input (general), nondimensional axial coordinate  
 $y$  – output (general)  
 $z$  – axial coordinate (m)

**Greek symbols:**

- $\Delta$  - difference between the time-average and the steady-state concentration  
 $\theta$  – dimensionless time  
 $\tau$  – residence time (s)  
 $\varpi$  - frequency ( $\text{rads}^{-1}$ )  
 $\omega$  – dimensionless frequency

**Subscripts:**

- $i$  – inlet  
 $s$  – stationary state

**Abbreviations:**

CSTR- continuous stirred tank reactor  
DC- non-periodic term  
DFTR – dispersed flow tubular reactor  
FR – frequency response  
FRF – frequency response function  
PFTR – plug flow tubular reactor

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