

## Periodic operation with modulation of inlet concentration and flow-rate Part I Non-isothermal CSTR

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### Abstract

Nonlinear frequency response (NFR) method, which is an analytical, fast and easy method for evaluating the performance of forced periodically operated chemical reactors is used in this, two-part paper, for investigation of possible improvements of a non-isothermal continuous stirred tank reactor (CSTR) with simple reaction mechanism, when inlet concentration and flow-rate are periodically modulated, separately or simultaneously. Product yield corresponding to periodic operations is defined, expressions for its estimation, based on the NFR method, are derived for each investigated case and it is used for evaluating the performance improvements achieved through periodic operation. In Part I the general non-isothermal case is considered and in Part II, these results are applied to the case of an adiabatic CSTR and implemented for evaluation of possible improvements for the case of acetic acid anhydride hydrolysis reaction.

Keywords: Non-isothermal CSTR, Non-linear frequency response, Periodic operation, Product yield increase, Two-input modulation

### 1. Introduction

In the last 50 years many theoretical and experimental investigations of periodic operations in chemical engineering showed that periodic operations can, in some cases, lead to better average performance compared to the optimal steady-state operation [1-17]. The source of the possible improvement lies in the process nonlinearity. Chemical reactors have been seen as especially good candidates for periodic operations considering their significant nonlinearity [1-17]. A comprehensive up-to-date review of investigations on periodic operations of chemical reactors can be found in a book edited by Silveston and Hudgins [18].

“(Figure 1)”

In Fig. 1, a schematic representation of forced periodically operated reactor is given in order to explain the possible improvements of reactor performance through periodic operations. When one or more inputs into the reactor are periodically modulated around their steady-state values, owing to

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system nonlinearity, the mean values of the outlet reactant and product concentrations can be different from their steady-state values. In Fig.1,  $c_A$  and  $c_P$  are used to denote the outlet reactant and product concentration, respectively. The superscript  $m$  is used to denote the mean value and subscript  $s$  for steady-state value. The steady-state and periodic operation of a chemical reactor for a simple reaction mechanism  $A \rightarrow P$  is presented, for a case when the mean outlet concentration of the reactant is lower than its steady-state value and the mean outlet concentration of the product is higher (the situation corresponding to higher reactant conversion and product yield). The differences between the mean and the steady-state concentrations  $\Delta_A$  and  $\Delta_P$ , shown in Fig. 1, are measures of the process improvement. Experimental and numerical simulation approaches for investigations of periodically operated processes, which are most commonly used, are rather time consuming and costly, considering the fact that the forcing parameters and forcing strategy which should be used are completely unknown. A number of theoretical approaches have also been established, but they have not been widely applied in practice. Some details about them can be found in [17, 19].

In this work, a theoretical, simple and reliable general method for analysis of forced periodically operated chemical reactors will be presented, which enables quantitative evaluation of the possibility of process improvements through periodic operations, quickly and in early development stages [19]. This method is based on the frequency response analysis of weakly nonlinear systems, and it is named Nonlinear Frequency Response (NFR) method.

The first published applications of the NFR method were to evaluate the performance of forced periodically operated isothermal CSTRs, isothermal plug flow reactors (PFRs) and isothermal dispersed flow tubular reactors (DFTRs) with simple isothermal  $n$ th order reaction [20] and for isothermal CSTRs with a simple  $n$ th order heterogeneous reaction [21], for modulation of the inlet reactant concentration. The NFR method was also used for evaluation of forced periodically operated isothermal CSTRs with simultaneous modulations of inlet concentration and flow-rate [22], as well as non-isothermal CSTRs with single input modulations of inlet concentration and flow-rate [23], inlet temperature and temperature of the heating/cooling fluid [24] and simultaneous modulation of inlet concentration and inlet temperature [25].

The NFR method is meant to be used as a first step for fast screening of possible periodic operations, in order to detect processes which should further be investigated experimentally [19]. Unlike numerical integrations, the NFR method gives a complete overview of the investigated periodic operation, with defined ranges of the forcing parameters (input frequency, amplitude(s) and phase differences for two input modulation) which should be used in order to obtain a reactor performance improvement [25].

In this work, the NFR method is used to investigate the periodic operations of non-isothermal CSTRs with modulation of inlet reactant concentration and flow-rate. In this, Part I, the general non-isothermal case is considered, while in Part II [26] these results are applied to the adiabatic case, with illustration on the reaction of acetic anhydride hydrolysis.

The mathematical foundations and the explanation of the NFR method can be found in our previous publications (e.g. in [20] and [19]). Very short recapitulation of the method is given in the next section.

## 2. The nonlinear frequency response method for fast estimation of the time-average performance of periodically operated chemical reactors

First, let us remind that frequency response is actually the periodic steady-state obtained when one or more inputs into the system are modulated in a sinusoidal or co-sinusoidal way and that frequency response of a weakly nonlinear system (such as a chemical reactor) is a complex periodic function [27], which is a sum of the basic harmonic, higher harmonics and a non-periodic (the so-

called DC) component [4, 27, 19]. The nonlinear model of a weakly nonlinear system can, in the frequency domain, be replaced by a set of linear frequency response functions (FRFs) of different orders [27], which are directly related to the DC component and different harmonics of the response [27, 28]. On the other hand, although the system response contains periodic components, only the DC component of the output is responsible for the time-average performance of the periodic process. Thus, in order to estimate the time-average behavior of a weakly nonlinear system and decide whether the periodic operation is favorable or not, it is enough to evaluate the DC component.

For a single input  $x$  which is defined as a single harmonic periodic function with forcing amplitude  $A_x$  and forcing frequency  $\omega$ , which is modulated around a previously established steady-state value defined with  $x_s$ :

$$x(t) = x_s + A_x \cos(\omega t) = x_s + \frac{A_x}{2} e^{j\omega t} + \frac{A_x}{2} e^{-j\omega t} \quad (1)$$

the DC component of the output  $y$  can be approximately calculated from the asymmetrical second order (ASO) FRF correlating the output and the input  $x$ , which we will denote as  $G_{2,xx}(\omega, -\omega)$ , in the following way [27, 20]

$$y_{DC} \approx 2 \left( \frac{A_x}{2} \right)^2 G_{2,xx}(\omega, -\omega) \quad (2)$$

If, besides the input  $x(t)$  (Eq. (1)), another input  $z(t)$  is also modulated in a co-sinusoidal way around a previously established steady-state value  $z_s$ , with a forcing amplitude  $A_z$ , with the same forcing frequency  $\omega$  and a phase difference  $\varphi$ :

$$z(t) = z_s + A_z \cos(\omega t + \varphi) \quad (3)$$

the DC component of the output  $y$  is given as a sum of contributions of the modulations of inputs  $x$  and  $z$  separately and the cross-effect of both inputs [22, 25]:

$$y_{DC} \approx 2 \left( \frac{A_x}{2} \right)^2 G_{2,xx}(\omega, -\omega) + 2 \left( \frac{A_z}{2} \right)^2 G_{2,zz}(\omega, -\omega) + 2 \left( \frac{A_x}{2} \right) \left( \frac{A_z}{2} \right) G_{2,xz}^*(\omega, \varphi) \quad (4)$$

where  $G_{2,zz}(\omega, -\omega)$  is the ASO FRF which correlates the output  $y$  to the input  $z$  and  $G_{2,xz}^*(\omega, \varphi)$  is the cross ASO term defined with the following expression,

$$G_{2,xz}^*(\omega, \varphi) = \left( \cos(\varphi) \operatorname{Re} \left( G_{2,xz}(\omega, -\omega) \right) + \sin(\varphi) \operatorname{Im} \left( G_{2,xz}(\omega, -\omega) \right) \right) \quad (5)$$

The cross ASO term  $G_{2,xz}^*(\omega, \varphi)$  is a function of the phase difference and the cross asymmetrical second order frequency response function  $G_{2,xz}(\omega, -\omega)$  which correlates the output with both modulated inputs [22, 25].

Thus, for a weakly nonlinear system with two modulated inputs ( $x(t)$  and  $z(t)$ ) and one output ( $y(t)$ ), the DC component of the output is approximately calculated from the ASO FRFs  $G_{2,xx}(\omega, -\omega)$ ,  $G_{2,zz}(\omega, -\omega)$  and  $G_{2,xz}(\omega, -\omega)$ , the input amplitudes and the phase difference between the inputs [19, 22, 25]. The sign of this DC component shows whether the periodic operation results with process improvement or deterioration, and its magnitude is a quantitative measure of the improvement.

It was shown [22] that interaction of two modulated inputs gives highest contribution and best results regarding process improvement when the two inputs are modulated with equal frequencies [22].

It is also important to notice that the cross-effect of the modulation of two synchronized inputs strongly depends on the phase difference between them and its appropriate choice may result in significant modifications in the behaviour of the system under forced periodic operation [17, 22 and 25].

The procedure for applying the NFR method for estimating the time-average performance of a forced periodically operated chemical reactor is rather standard and it has been defined in our previous publications [19-25]. Here, we apply it to analysis of non-isothermal CSTRs with periodic modulation of the reactant feed concentration and flow-rate. Unlike our previous publications in which the analysis was based on the mean outlet concentration, here we will focus on estimating the product yield and its possible increase owing to periodic operation.

For theoretical analysis and derivation of the necessary FRFs it is best to use co-sinusoidal input modulations. Nevertheless, the NFR method can be used for any shape of periodic input modulation and the derived ASO FRFs can also be used to estimate the output DC component for a general shape of the periodic input modulation. From mathematical point of view, the derivation of the ASO FRFs is much easier for single harmonic input modulation.

### 3. Application of the NFR method on a non-isothermal CSTR with periodic modulation of inlet concentration and flow-rate

In our previous investigations, we used the difference between the mean outlet reactant or product concentration and the corresponding steady-state value, as a measure of the process improvement. Nevertheless, in the cases when the flow-rate of the reaction stream is modulated, the mean outlet molar flow-rate needs to be analyzed in order to get proper information about the performance improvement. Therefore, in this section we are going to derive and analyze the ASO FRFs corresponding to the outlet molar flow-rate of the product, as well as the corresponding DC components. Further, we will define the product yield corresponding to the periodic operations, which will be used for evaluating of the reactor performance improvement.

#### 3.1. Derivation of the ASO FRFs

The starting point of the derivation procedure is setting up the model equations. A general case of a non-isothermal CSTR is considered, with a simple, irreversible, homogeneous  $n$ th order chemical reaction,  $A \rightarrow \nu_P P$  with a rate law

$$r = k_o e^{-\frac{E_A}{RT}} C_A^n \quad (6)$$

In this work we start from the dimensionless form of the mathematical model, which has been developed in our previous publications [23, 24 and 25]. The model consists of the reactant and product material balances and energy balance and, for the case when the only modulated inputs are the inlet concentration and flow-rate it is reduced to the following equations:

$$\begin{aligned} \frac{dC_A}{d\tau} = & (1 + \alpha)C_{A,i} + (1 + \alpha)\Phi C_{A,i} - (1 + n\alpha)C_A - \alpha\gamma\theta + \alpha\Phi - \Phi C_A \\ & - \alpha \left( n\gamma C_A \theta + \left( \frac{\gamma^2}{2} - \gamma \right) \theta^2 + \frac{1}{2} n(n-1) C_A^2 + \dots \right) \end{aligned} \quad (7)$$

$$\frac{dC_P}{d\tau} = nC_A - C_P + \gamma\theta - \Phi - \Phi C_P + \left( n\gamma C_A \theta + \left( \frac{\gamma^2}{2} - \gamma \right) \theta^2 + \frac{1}{2} n(n-1) C_A^2 + \dots \right) \quad (8)$$

$$\begin{aligned} \frac{d\theta}{d\tau} = & -(1 + St + \beta\gamma)\theta - n\beta C_A + (\beta + St - \delta)\Phi - \Phi\theta \\ & - \beta \left( n\gamma C_A \theta + \left( \frac{\gamma^2}{2} - \gamma \right) \theta^2 + \frac{1}{2} n(n-1) C_A^2 + \dots \right) \end{aligned} \quad (9)$$

The dimensionless variables used in Eqs. (7-9) are defined in Tab. 1.

“(Table 1)”

In Eqs. (7, 8 and 9) all nonlinear terms have been replaced by their Taylor series expansions (only the first and second order terms are shown), and a set of auxiliary parameters:

$$\alpha = k_o e^{-\frac{E_A}{RT_s}} c_{A,S}^{n-1} \frac{V}{F_s}, \quad \beta = \frac{\Delta H_R k_o e^{-\frac{E_A}{RT_s}} c_{A,S}^n V}{\rho \bar{c}_p T_s} \frac{V}{F_s}, \quad \delta = \frac{U A_w T_J}{F_s \rho \bar{c}_p T_s}, \quad \gamma = \frac{E_A}{RT_s}, \quad St = \frac{U A_w}{F_s \rho \bar{c}_p} \quad (10)$$

have been introduced. The meanings of the notations used in Tab. 1, Eqs. (6) and (10) are:  $t$  is time,  $\omega_d$  the dimensional frequency of modulated input(s),  $c_{Ai}$ ,  $c_A$  and  $c_P$  are the inlet and outlet reactant concentrations and the outlet product concentration, respectively,  $T$  is temperature in the reactor,  $T_J$  temperature of the cooling/heating fluid in the jacket,  $F$  the flow-rate of reaction stream,  $V$  the reactor volume,  $\Delta H_R$  is the heat of reaction, where  $k_o$  the pre-exponential factor in the Arrhenius equation,  $E_A$  activation energy and  $R$  the universal gas constant,  $U$  the overall heat transfer coefficient,  $A_w$  the heat transfer area,  $\rho$  density and  $\bar{c}_p$  heat capacity. Subscript  $s$  denotes the steady-state values.

The nonlinear frequency response method is applicable only for stable systems, so stability analysis needs to be performed before applying it. Some details of the stability analysis for a general case of a non-isothermal reactor can be found in our previous publications [23-25], and here only the final results are given. The non-isothermal CSTR will be stable if the following conditions are met:

$$A_{ps} = -\frac{(2+n\alpha+St+\beta\gamma)}{2} < 0 \quad (11)$$

$$B_{ps} = (1 + n\alpha + \beta\gamma + n\alpha St + St) > 0 \quad (12)$$

The investigated non-isothermal CSTR represents the system with two inputs (inlet reactant concentration and flow-rate) and three outputs (outlet reactant and product concentrations and outlet temperature). The derivation procedure of the ASO FRFs is rather standard [19-25] and for the current case it is very similar to the procedure used in [25]. As a result, several sets of FRFs are obtained, relating the outlet reactant and product concentrations and outlet temperature to the inlet reactant concentration and flow-rate.

In order to analyze the outlet molar flow-rate of the product and its DC component, it is necessary to derive the ASO FRFs corresponding to this output, as well. Using the dimensionless variables defined in Tab. 1, the dimensionless outlet product molar flow-rate can be easily related to the dimensionless outlet product concentration and flow-rate, in the following way:

$$N_p = \Phi + C_p + \Phi C_p \quad (13)$$

Starting from this equation, it is easy to establish the relations between the ASO FRFs corresponding to the product molar flow-rate (which will be denoted as  $H_p$ -functions) and to the product concentration (which will be denoted as  $G_p$ -functions, as in our previous publications):

$$H_{P2,CC}(\omega, -\omega) = G_{P2,CC}(\omega, -\omega) \quad (14)$$

$$H_{P2,FF}(\omega, -\omega) = G_{P2,FF}(\omega, -\omega) + \frac{1}{2} \left( G_{P1,F}(\omega) + G_{P1,F}(-\omega) \right) \quad (15)$$

$$H_{P2,CF}(\omega, -\omega) = G_{P2,CF}(\omega, -\omega) + G_{P1,C}(\omega) \quad (16)$$

In Eqs. (14-16) the subscript  $CC$  corresponds to inlet concentration modulation,  $FF$  to flow-rate modulation,  $CF$  to the cross-effect of both inputs and 1 for the first order FRFs.

Owing to space limitations, here we give only these final ASO FRFs:

$$H_{P2,CC}(\omega, -\omega) = G_{P2,CC}(\omega, -\omega) = \frac{(1 + \alpha)^2(1 + St)}{2B_{ps}} \times \frac{\Lambda_1\omega^2 + \Lambda_2}{(B_{ps} - \omega^2)^2 + 4A_{ps}^2\omega^2} \quad (17)$$

where  $\Lambda_1$  and  $\Lambda_2$  are auxiliary functions defined as:

$$\Lambda_1 = n(n - 1) \quad (18)$$

$$\Lambda_2 = n^2((1 + St)^2 - 2\beta^2\gamma) - n(1 + St + \beta\gamma)^2 \quad (19)$$

$$H_{P2,FF}(\omega, -\omega) = \frac{1}{2B_{ps}} \times \frac{\Omega_{1H}\omega^2 + \Omega_{2H}}{(B_{ps} - \omega^2)^2 + 4A_{ps}^2\omega^2} \quad (20)$$

with the auxiliary functions  $\Omega_{1H}$  and  $\Omega_{2H}$  which are defined as follows

$$\Omega_{1H} = -n\alpha^2(n + 1)(1 + St) - 2n\alpha(1 + St + \beta\gamma) + \gamma(\gamma - 2)(1 + St)(\beta + St - \delta)^2 - 2\gamma(1 + St + \beta\gamma)(\beta + St - \delta) \quad (21)$$

$$\begin{aligned} \Omega_{2H} = & (1 + St) \left( n\alpha(1 + St - \gamma(St - \delta)) + \gamma(\beta + (1 + n\alpha)(St - \delta)) \right)^2 \\ & - 2B_{ps} \left( n\alpha(1 + St - \gamma(St - \delta)) + \gamma(\beta + (1 + n\alpha)(St - \delta)) \right) \\ & - n\alpha^2(1 + St)(1 + St - \gamma(St - \delta))^2 - 2\gamma(1 + St)(\beta + (St - \delta)(1 + n\alpha))^2 \end{aligned} \quad (22)$$

$$H_{P2,CF}(\omega, -\omega) = \frac{n(1 + \alpha)}{B_{ps}} \times \frac{\Gamma_{RH} + j\omega\Gamma_{IH}}{\left( (B_{ps} - \omega^2)^2 + 4A_{ps}^2\omega^2 \right)} \quad (23)$$

with the auxiliary functions  $\Gamma_{RH}$  and  $\Gamma_{IH}$  defined as

$$\begin{aligned} \Gamma_{RH} = & (1 + St) \left( (B_{ps} - \omega^2)^2 + 4A_{ps}^2\omega^2 \right) - (1 + St) \left( (1 + St + \beta\gamma)(B_{ps} - \omega^2) - 2A_{ps}\omega^2 \right) \\ & + \beta\gamma(B_{ps} - \omega^2) \\ & + (1 + St) \left( \omega^2(\gamma(\beta + St - \delta) + \alpha(n - 1)) + n\alpha((1 + St)^2 + 2\beta\gamma(St - \delta)) \right) \\ & - \alpha(1 + \beta\gamma + St)(1 + St - \gamma(St - \delta)) + \gamma(\beta + St - \delta)(1 + St + 2\beta) \end{aligned} \quad (24)$$

$$\Gamma_{IH} = (1 + St)\omega^2 + n\alpha\beta\gamma St + (1 + St)^2 + \beta\gamma St + \gamma(1 + St)(\beta + St - \delta)(\alpha - St - 2\beta) \quad (25)$$

### 3.2. The DC component of the outlet molar flow-rate of the product

The DC component of the dimensionless product molar flow-rate is defined as

$$N_{P,DC} = \frac{(F(t)c_P(t))^m - F_s c_{P,s}}{F_s c_{P,s}} \quad (26)$$

where the superscript  $m$  is used to denote the mean value. The approximations of the DC component of the product molar flow-rate, based on the second order approximation are:

For modulation of the inlet reactant concentration:

$$N_{P,DC} \approx 2 \left(\frac{A_C}{2}\right)^2 H_{P2,CC}(\omega, -\omega) = 2 \left(\frac{A_C}{2}\right)^2 G_{P2,CC}(\omega, -\omega) \quad (27)$$

For modulation of the flow-rate:

$$N_{P,DC} \approx 2 \left(\frac{A_F}{2}\right)^2 H_{P2,FF}(\omega, -\omega) \quad (28)$$

For simultaneous modulation of the inlet concentration and flow-rate:

$$N_{P,DC} \approx 2 \left(\frac{A_C}{2}\right)^2 G_{P2,CC}(\omega, -\omega) + 2 \left(\frac{A_F}{2}\right)^2 H_{P2,FF}(\omega, -\omega) + 2 \left(\frac{A_C}{2}\right) \left(\frac{A_F}{2}\right) H_{P2,CF}^*(\varphi, \omega) \quad (29)$$

where the cross ASO term  $H_{P2,CF}^*(\varphi, \omega)$  is defined as

$$H_{P2,CF}^*(\varphi, \omega) = \cos(\varphi) \operatorname{Re}(H_{P2,CF}(\omega, -\omega)) + \sin(\varphi) \operatorname{Im}(H_{P2,CF}(\omega, -\omega)) \quad (30)$$

### 3.3. Product yield for a periodic process with modulation of the inlet concentration and flow rate

One of the best measures of a reactor performance is the product yield. In general, the product yield for a chemical reaction of the type  $A \rightarrow \nu_P P$ , corresponding to a periodic operation, can be defined in the following way:

$$Y_{P,p0} = \frac{1}{\nu_P} \frac{(F(t)c_P(t))^m}{(F(t)c_{Ai}(t))^m} \quad (31)$$

For periodic operations without flow-rate modulation, this expression reduces to:

$$Y_{P,p0} = \frac{1}{\nu_P} \frac{c_P^m}{c_{Ai,s}^m} \quad (32)$$

while for cases when the flow-rate is the only modulated input, it becomes:

$$Y_{P,p0} = \frac{1}{\nu_P} \frac{(F(t)c_P(t))^m}{F_s c_{Ai,s}^m} \quad (33)$$

For simultaneous modulation of the inlet concentration and flow-rate the general expression (Eq. (31)) needs to be used, as the mean value of the inlet molar flow rate of the reactant can be different than its steady-state value.

The product yield corresponding to a periodic operation can be expressed as a function of the yield corresponding to the steady-state operation ( $Y_{P,s}$ ) and the DC component of the dimensionless product molar flow-rate. For the cases of modulations of single inputs, inlet concentration or flow-rate, the following relation can easily be derived:

$$Y_{P,p0} = Y_{P,s}(1 + N_{P,DC}) \quad (34)$$

For single input modulation of inlet concentration or flow-rate, the increase of the product yield will be achieved if the DC components of the product molar flow-rates are positive, i.e. if the corresponding ASO FRF has a positive sign [19].

Nevertheless, when the inlet concentration and flow-rate are modulated simultaneously, the dimensionless inlet molar flow-rate of the reactant

$$N_{Ai} = \frac{F(t)c_{Ai}(t) - F_s c_{Ai,s}}{F_s c_{Ai,s}} \quad (35)$$

is also a periodic function, with a mean value which is, in principle, different from 0:

$$(N_{Ai})^m = 2 \left(\frac{A_C}{2}\right) \left(\frac{A_F}{2}\right) \cos(\varphi) \quad (36)$$

and depends on the phase difference  $\varphi$ . In that case, the product yield of the periodic process can be evaluated in the following way:

$$Y_{P,po} = Y_{P,s} \frac{(1+N_{P,DC})}{(1+2\left(\frac{A_C}{2}\right)\left(\frac{A_F}{2}\right)\cos(\varphi))} \quad (16)$$

For simultaneous modulation of any two inputs, it is possible to find the optimal phase difference which maximizes or minimizes the DC component of interest, which is a function of frequency [22, 25]. Nevertheless, if the product yield would be maximized for the case with simultaneous modulation of inlet concentration and flow-rate, this optimal phase difference would depend on the chosen input amplitudes. In this case, it is possible to find a set of optimal forcing parameters (both input amplitudes and the phase difference) that maximizes the product yield.

#### 4. Numerical example

As illustration, we show some simulation results, for an exothermal reactor with a first-order reaction, taken from of a textbook by Douglas [4]. This example was already used in [25]. The model parameters are:  $\nu_p=1$ ,  $V=1.439 \text{ m}^3$ ,  $k_o=4.3177 \cdot 10^5 \text{ min}^{-1}$ ,  $E_A=50242 \text{ kJ kmol}^{-1}$ ,  $\overline{\rho c_p}=4186.8 \text{ kJm}^{-3}\text{K}^{-1}$ ,  $\Delta H_R=-50242 \text{ kJ kmol}^{-1}$ ,  $F_s=0.0238 \text{ m}^3 \text{ min}^{-1}$ ,  $c_{A,i,s}=5 \text{ kmol m}^{-3}$ ,

$$T_{i,s}=300 \text{ K}, T_{j,s}=400 \text{ K}, U=101.8 \text{ kJm}^{-2}\text{K}^{-1}\text{min}^{-1}, A_w=1.073 \text{ m}^2.$$

In Fig. 2, the ASO FRFs  $G_{p2,CC}(\omega,-\omega)$  and  $H_{p2,FF}(\omega,-\omega)$  corresponding to the single input modulation of inlet concentration and flow-rate, are graphically presented as functions of the dimensionless forcing frequency.

“(Figure 2)”

It is expected to achieve improvement of the reactor performance for the inlet concentration modulation ( $G_{p2,CC}(\omega,-\omega)>0$ ), which is most significant for the low-frequency modulation. Single input modulation of the flow-rate will deteriorate the reactor performance

( $H_{p2,FF}(\omega,-\omega)>0$ ). From Fig. 2, it can be also seen that both ASO FRFs tend to asymptotic values for the low-frequency modulation and tend to zero for high-frequency modulation.

The real and imaginary parts of the cross ASO FRF  $H_{p2,CF}(\omega,-\omega)$  are graphically presented in Fig. 3 (a) and (b), respectively, as functions of dimensionless forcing frequency.

“(Figure 3)”

The optimal forcing amplitudes and optimal phase difference which maximize the product yield for simultaneous modulation of inlet concentration and flow-rate (Eq. 37) are graphically presented in Fig. 4 (a) and (b), respectively, as functions of dimensionless forcing frequency.

“(Figure 4)”

As illustration, for optimal forcing parameters, the product yields for separate and simultaneous modulation of inlet concentration and flow-rate are given in Fig. 5 as functions of the dimensionless forcing frequency. Let us remind that the product yield for steady-state is 0.70 ( $Y_{p,s}=0.70$ ).

“(Figure 5)”

The reactor can be improved by simultaneous modulation of inlet concentration and flow-rate when optimal forcing parameters are used in the whole frequency range. The increase of product yield for low-frequency simultaneous modulation of these two-inputs and for single input modulation of inlet concentration is practically identical. On the other hand, for high-forcing frequency, the increase of product yield is obtainable in spite the fact that high-frequency single input modulations have no effect on the reactor performance.



The approximate product yields owing to simultaneous modulation of the inlet concentration and flow-rate with optimal forcing parameters are compared with the results of numerical simulation for forcing frequencies  $\omega=0.1, 1$  and  $10$  and given in Tab. 2. The product yields together with their relative changes ( $\Delta Y_{p,po}$ ) owing to periodic operation are given in Tab. 2 as well as the relative errors ( $\delta_V$ ) of the NFR method.

“(Table 2)”

It can be concluded that the NFR method gives excellent predictions, considering the values of the relative errors (Tab.2).

## 5. Conclusions

The possibility of improvement of a general non-isothermal CSTR with homogeneous, irreversible, simple  $n$ th order reaction  $A \rightarrow \nu_P P$  when inlet concentration and flow-rate are separately or simultaneously modulated can be evaluated from the derived ASO FRFs corresponding to the outlet molar flow rate of the product ( $H_{P2,CC}(\omega, -\omega)$  and  $H_{P2,FF}(\omega, -\omega)$ ) and cross ASO FRF ( $H_{P2,CF}(\omega, -\omega)$ ).

In this work, the product yield is used as a measure of the reactor performance improvement through periodic operation. When the flow-rate is one of the modulated inputs the yield has to be defined as a ratio of the molar flow rates, instead of concentrations. For the case of simultaneous modulation of the inlet concentration and flow-rate, the mean value of the inlet molar flow rate of the reactant is different from its steady-state and depends on the input amplitudes and the phase difference between the inputs. As a consequence, the optimal phase difference depends on the input amplitudes, i.e., an optimal set of forcing parameters (the amplitudes of both inputs and the phase difference) can be found.

The analytical results derived in this work were illustrated using a numerical example of an exothermal reactor, taken from literature. Comparison of the approximate product yields estimated by the NFR method with the values obtained by numerical integration showed excellent agreement.

## Acknowledgement

This work was supported by the Serbian Ministry of Science in the frame of Projects No. 172022 and III45001.

## List of symbols

### Latin symbols

|             |   |
|-------------|---|
| $A$         | input amplitude   |
| $A_{ps}$    | stability parameter                                       |
| $A_w$       | $[m^2]$ heat transfer area                                |
| $B_{ps}$    | stability parameter                                       |
| $c$         | $[kmol\ m^{-3}]$ concentration                            |
| $C$         | dimensionless concentration                               |
| $\bar{c}_p$ | $[kJ\ kg^{-1}K^{-1}]$ heat capacity                       |
| $E_A$       | $[kJ\ kmol^{-1}]$ activation energy                       |
| $F$         | $[m^3\ min^{-1}]$ volumetric flow-rate                    |
| $k_0$       | $[min^{-1}]$ pre-exponential factor in Arrhenius equation |
| $n$         | reaction order  |

|       |   |
|-------|---|
| $N$   | dimensionless molar flow-rate   |
| $R$   | [kJ mol <sup>-1</sup> K <sup>-1</sup> ] universal gas constant                            |
| $St$  | Stanton number  |
| $t$   | [min] time  |
| $T$   | [K] temperature   |
| $U$   | [kJ K <sup>-1</sup> min <sup>-1</sup> m <sup>-2</sup> ] overall heat transfer coefficient |
| $V$   | [m <sup>3</sup> ] volume of the reactor   |
| $x$   | input   |
| $y$   | output  |
| $Y_p$ | [%] yield of product  |
| $z$   | input   |

### Greek symbols

|              |  |
|--------------|--|
| $\Phi$       | dimensionless volumetric flow-rate                   |
| $\alpha$     | auxiliary parameter                                  |
| $\beta$      | auxiliary parameter                                  |
| $\gamma$     | auxiliary parameter                                  |
| $\delta$     | auxiliary parameter                                  |
| $\delta_y$   | [%] relative error                                   |
| $\vartheta$  | dimensionless temperature                            |
| $\nu_p$      | stoichiometric coefficient of the product P          |
| $\rho$       | [kg m <sup>-3</sup> ] density                        |
| $\tau$       | dimensionless time                                   |
| $\tau_{res}$ | [min] residence time                                 |
| $\varphi$    | [rad] phase difference                               |
| $\omega$     | dimensionless forcing frequency                      |
| $\omega_d$   | [rad s <sup>-1</sup> ] dimensional forcing frequency |
| $\Delta H_R$ | [kJ kmol <sup>-1</sup> ] heat of reaction            |

### Subscripts

|         |  |
|---------|--|
| $A$     | reactant   |
| $C, CC$ | corresponding to modulation of the inlet concentration               |
| $CF$    | corresponding to modulation of the inlet concentration and flow-rate |
| $DC$    | non-periodic term  |
| $F, FF$ | corresponding to modulation of flow-rate                             |
| $i$     | inlet  |
| $J$     | heating/cooling fluid in the jacket                                  |

|              |   |
|--------------|---|
| <i>opt</i>   | corresponding to optimal forcing variable     |
| <i>P</i>     | product                                       |
| <i>s</i>     | steady-state                                  |
| <i>x, xx</i> | corresponding to input <i>x</i>               |
| <i>z, zz</i> | corresponding to input <i>z</i>               |
| <i>xz</i>    | corresponding to inputs <i>x</i> and <i>z</i> |

### Superscripts

|          |      |
|----------|------|
| <i>m</i> | mean |
|----------|------|

### Abbreviations

|      |                                 |
|------|---------------------------------|
| ASO  | asymmetrical second order       |
| CSTR | continuous stirred tank reactor |
| FRF  | frequency response functions    |
| NFR  | nonlinear frequency response    |
| num  | numerical                       |

## References

- [1] J. M. Douglas, D. W. T. Rippin, *Chem. Eng. Sci.* 1966, 21, 305-315.
- [2] J. M. Douglas, *Ind. Eng. Chem. Proc. DD.* 1967, 6, 43-48.
- [3] A. B. Ritter, J. M. Douglas, *Ind. Eng. Chem. Fund.* 1970, 9(1), 21-27.
- [4] J. M. Douglas, *Process Dynamics and Control*, Prentice-Hall, New Jersey 1972.
- [5] A. Renken, *Chem. Eng. Sci.* 1972, 27, 1925-1932.
- [6] J. E. Bailey, *Chem. Eng. Commun.* 1973,1, 111-124.
- [7] N. Watanabe, K. Onogi, M. Matsubara, *Chem. Eng. Sci.* 1981, 36, 809-818.
- [8] K. Schadlich, U. Hoffmann, H. Hofmann, *Chem. Eng. Sci.* 1983, 38, 1375-1384.
- [9] P. L. Silveston, *Sadhana - Acad. P. Eng S.* 1987, 10, 217-246.
- [10] L. E. Stermann, B. E. Ydstie, *Chem. Eng. Sci.* 1990, 45, 737-749.
- [11] L. E. Stermann, B. E. Ydstie, *Chem. Eng. Sci.* 1990, 45, 721-736.
- [12] L. E. Stermann, B. E. Ydstie, *AIChE Journal* 1991, 37, 986-996.
- [13] P. L. Silveston, *Composition Modulation of Catalytic Reactors*, Gordon and Breach Science Publishers, Amsterdam 1998.
- [14] P. L. Silveston, R. R. Hudgins, *Chem. Eng. Sci.* 2004, 59, 4055-4064.
- [15] P. L. Silveston, R. R. Hudgins, *Chem. Eng. Sci.* 2004, 59, 4043-4053.
- [16] P. Silveston, R. Hudgins, A. Renken, *Catal. Today* 1995, 25, 91-112.
- [17] S. J. Parulekar, *Chem. Eng. Sci.* 2003, 58, 5173-5194.
- [18] P.L. Silveston, R.R. Hudgins, *Periodic Operation of Reactors*, 1<sup>st</sup> ed., Elsevier, Amsterdam 2012.
- [19] M. Petkovska, A. Seidel-Morgenstern, in *Periodic Operation of Reactors*, 1<sup>st</sup> ed. (Eds: P.L. Silveston, R.R. Hudgins), Elsevier, Amsterdam 2012, 14.
- [20] A. Marković, A. Seidel-Morgenstern, M. Petkovska, *Chem. Eng. Res. Des.* 2008, 86, 682-691.
- [21] M. Petkovska, D. Nikolić, A. Marković, A. Seidel-Morgenstern, *Chem. Eng. Sci.* 2010, 65, 3632-3637.
- [22] D. Nikolić-Paunić, M. Petkovska, *Chem. Eng. Sci.* 2013, 104, 208-219.
- [23] D. Nikolić, A. Seidel-Morgenstern, M. Petkovska, *Chem. Eng. Sci.* 2014, 117, 71-84.
- [24] D. Nikolić, A. Seidel-Morgenstern, M. Petkovska, *Chem. Eng. Sci.* 2014, 117, 31-44.
- [25] D. Nikolić, A. Seidel-Morgenstern, M. Petkovska, *Chem. Eng. Sci.* 2015, 137, 40-58.
- [26] D. Nikolić, M. Felischak, A. Seidel-Morgenstern, M. Petkovska, submitted for publication in *Chem. Eng. Technol.*
- [26] D. D. Weiner, J. F. Spina, *Sinusoidal Analysis and Modeling of Weakly Nonlinear Circuits*, 1<sup>st</sup> ed., Van Nostrand Reinhold Company, New York 1980.
- [27] V. Volterra, *Theory of Functionals and Integral and Integrodifferential Equations*, 1<sup>st</sup> ed., Dover, New York 1959.

## Tables with headings

Table 1 Definition of dimensionless variables

| Dimensionless variable                | Definition   |
|---------------------------------------|--|
| Inlet reactant concentration          | $C_{Ai} = \frac{c_{Ai}(t) - c_{Ais}}{c_{Ais}}$       |
| Flow-rate                             | $\Phi = \frac{F(t) - F_s}{F_s}$                      |
| Outlet reactant concentration         | $C_A = \frac{c_A(t) - c_{A,s}}{c_{A,s}}$             |
| Outlet product concentration          | $C_P = \frac{c_P(t) - c_{P,s}}{c_{P,s}}$             |
| Outlet molar flow-rate of the product | $N_P = \frac{F(t)c_P(t) - F_s c_{P,s}}{F_s c_{P,s}}$ |
| Temperature                           | $\theta = \frac{T(t) - T_s}{T_s}$                    |
| Time                                  | $\tau = \frac{t}{V/F_s}$                             |
| Frequency                             | $\omega = \omega_d \frac{V}{F_s}$                    |

Table 2 Product yields for simultaneous modulation of the inlet concentration and flow-rate with optimal forcing parameters estimated by numerical simulation and by the NFR method and the relative errors of the NFR method

| $\omega$ | $A_c(\%)$ | $A_f(\%)$ | $\varphi_{opt}(\text{rad})$ | $Y_{p,po}(\%)$ |       | $\delta_Y(\%)$ | $\Delta Y_{p,po}(\%)$ |        |
|----------|-----------|-----------|-----------------------------|----------------|-------|----------------|-----------------------|--------|
|          |           |           |                             | num            | NFRM  |                | num                   | NFRM   |
| 0.1      | 100       | 2.05      | 0                           | 79.92          | 81.63 | +2.14          | +14.17                | +16.61 |
| 1        |           | 0         | 0                           | 78.38          | 80.23 | +2.36          | +11.97                | +14.61 |
| 10       |           | 100       | 0.6151                      | 79.13          | 77.35 | -2.25          | +13.04                | +10.5  |

## Figure legends

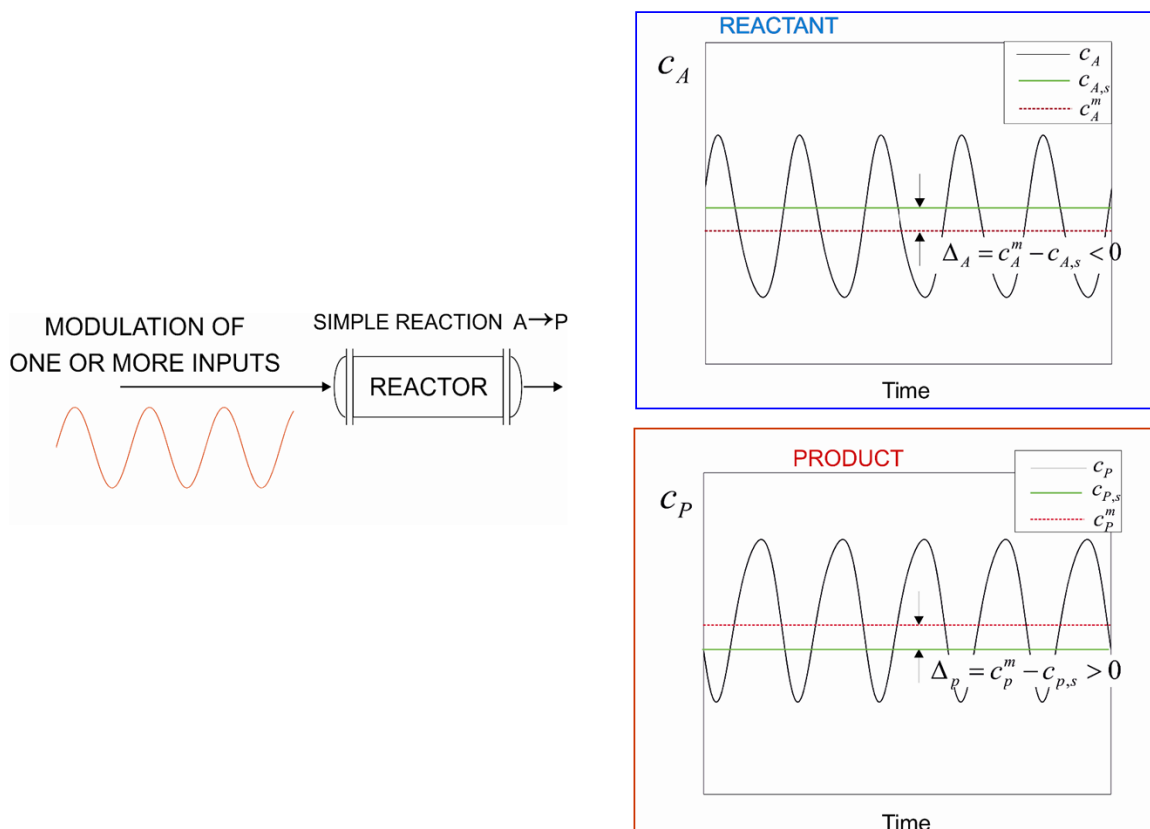


Figure 1 Illustration of a forced periodically operated reactor

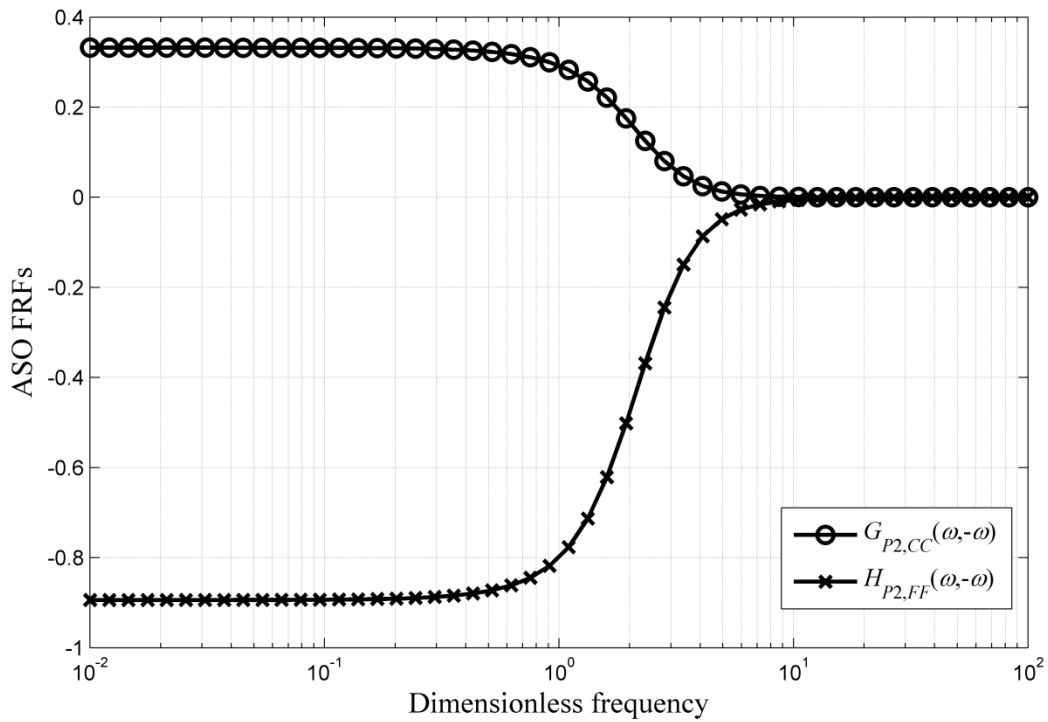


Figure 2 The ASO FRFs  $G_{P2,CC}(\omega, -\omega)$  and  $H_{P2,FF}(\omega, -\omega)$  as functions of the dimensionless forcing frequency

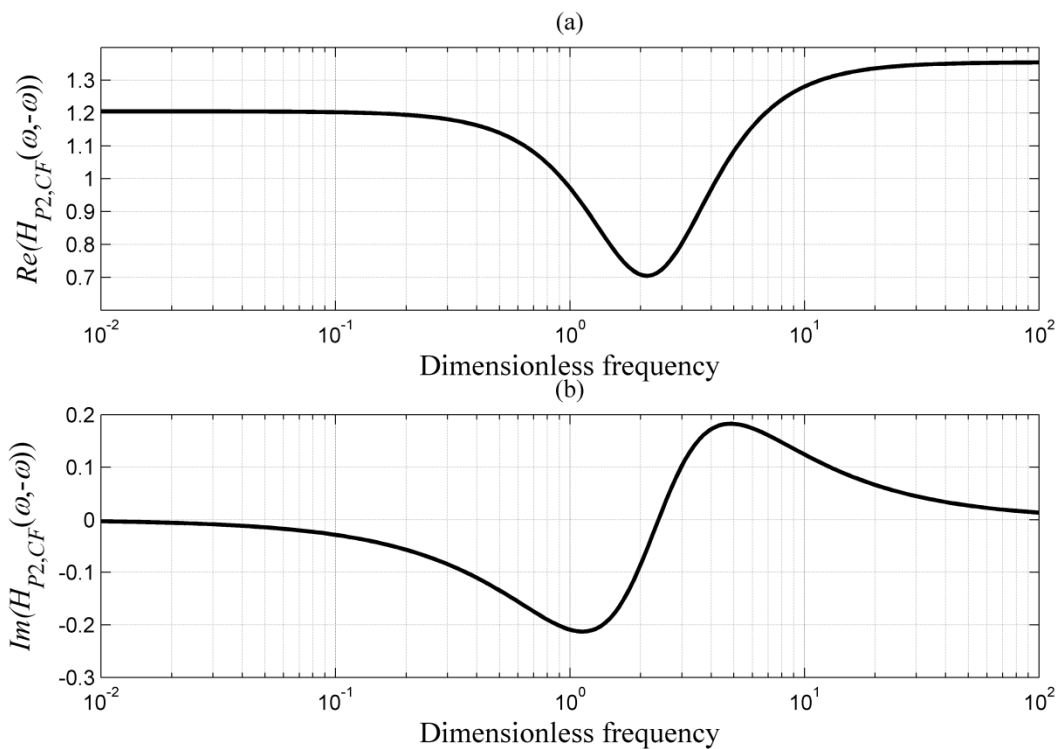


Figure 3 The real (a) and imaginary (b) parts of the cross ASO FRF  $H_{P2,CF}(\omega, -\omega)$  as functions of the dimensionless forcing frequency

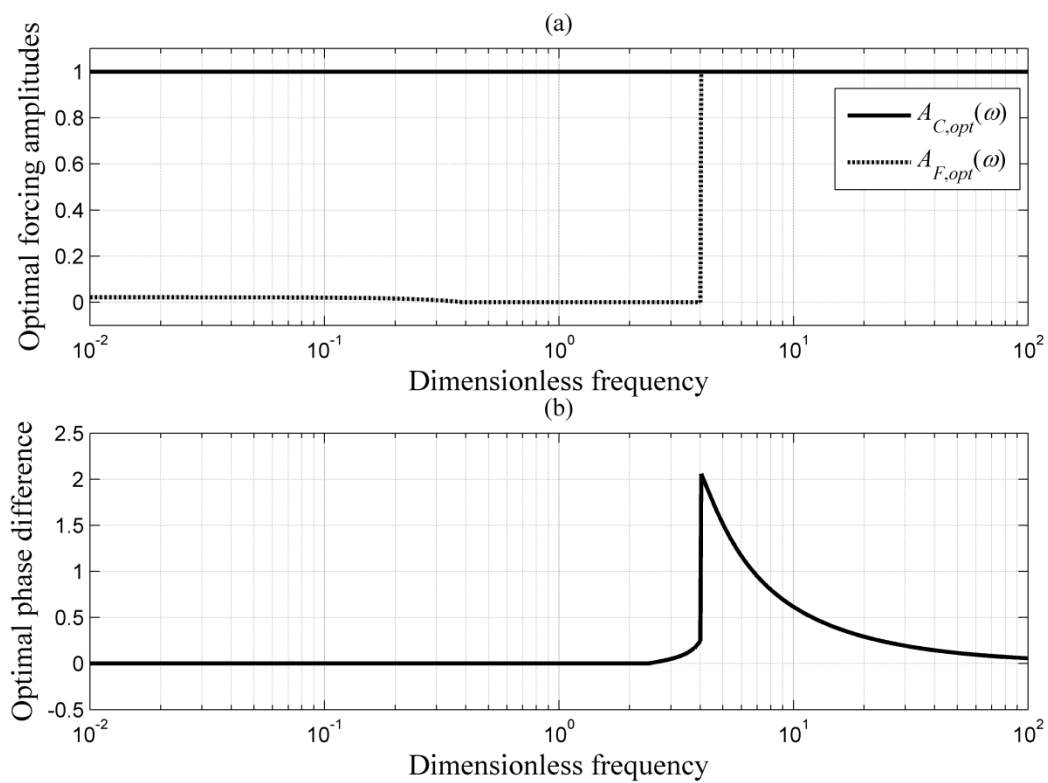


Figure 4 The optimal forcing amplitudes (a) and optimal phase difference (b) for simultaneous modulation of inlet concentration and flow-rate vs. dimensionless forcing frequency



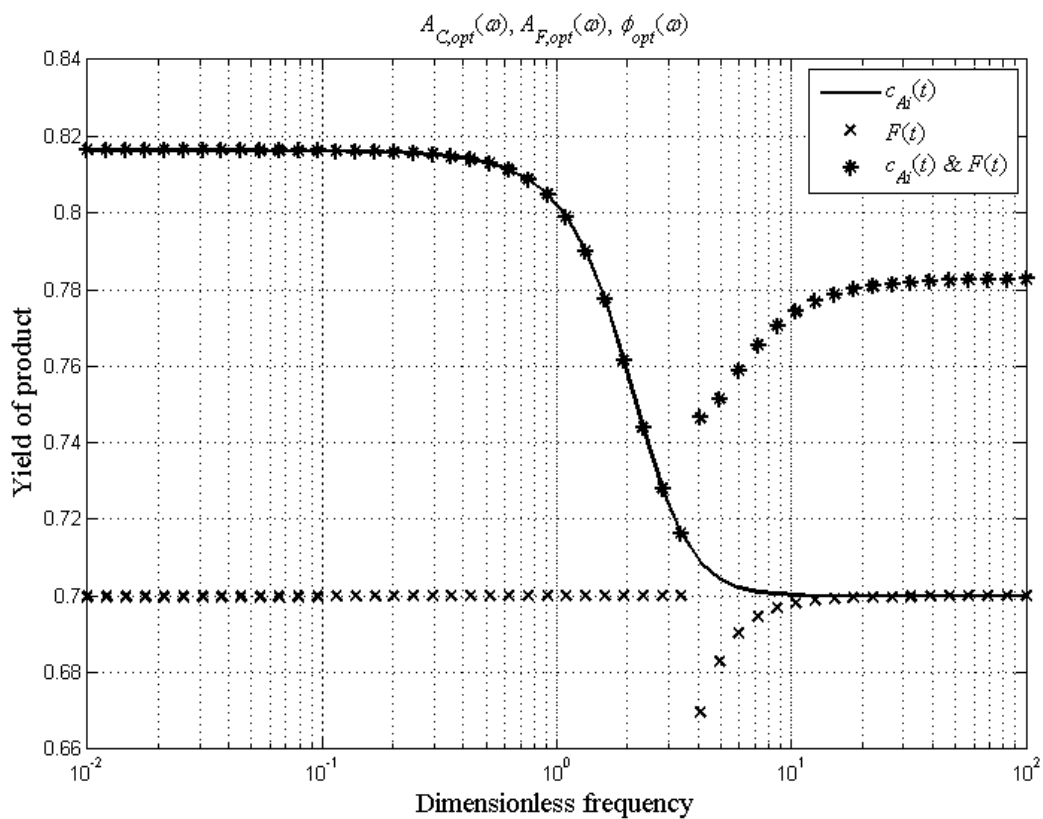


Figure 5 Yields of the product for the steady-state operation and for separate and simultaneous modulation of inlet concentration and flow-rate with optimal forcing parameters as functions of the dimensionless forcing frequency

**TOC**

The nonlinear frequency response method is used for evaluation of possible improvement of a non-isothermal CSTR, through forced periodic operation. It is shown that simultaneous modulation of inlet concentration and flow-rate can lead to significant improvement. Optimal forcing parameters (input amplitudes and phase difference) maximizing the product yield are defined. Significant increase of the product yield for low and high frequencies is obtained.

