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FORCED PERIODICALLY OPERATED CHEMICAL REACTORS-EVALUATION AND ANALYSIS BY THE NONLINEAR FREQUENCY RESPONSE METHOD

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PERIODIČNE OPERACIJE HEMIJSKIH REAKTORA-EVALUACIJA I ANALIZA PRIMENOM METODE NELINEARNOG FREKVENTNOG ODZIVA

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Title of Doctoral Dissertation:

FORCED PERIODICALLY OPERATED CHEMICAL REACTORS-EVALUATION AND ANALYSIS BY THE NONLINEAR FREQUENCY RESPONSE METHOD

Abstract

The conventional way to design and operate the processes in chemical engineering is to determine the optimal steady-state design and to operate as close as possible to that steady-state. Nevertheless, many investigations have proven that periodic operations, when one or more inputs are periodically modulated, can result with better process performances, especially for chemical reactors.

The origin of improvement of the reactor performance lies in fact that for nonlinear systems, the periodic modulation of one or more inputs will cause the outputs to change periodically, as well, with the mean value which is, in general, different from their steady-state values.

In this work, we propose and implement the nonlinear frequency response (NFR) method for fast and easy evaluation of possible reactor improvements throughout periodic modulations. The NFR method is a relatively new method, mathematically based on Volterra series, generalized Fourier transform and the concept of higher-order frequency response functions (FRFs).

The change of the reactor performances caused by periodic operations can be evaluated from the DC (non-periodic) component of the frequency response of the reactor, if it is a weakly nonlinear system. The DC component can be calculated exactly as a sum of an indefinite series, with members which are proportional to the asymmetrical even order FRFs. Nevertheless, based on the NFR method, the DC component can be estimated only from the first, dominant term of this series, which is proportional to the asymmetrical second order frequency response function $G_2(\omega,-\omega)$. In that way, for analysis of possible improvements of forced periodically operated chemical reactors, it is enough to derive and analyze asymmetrical second order FRFs $G_2(\omega,-\omega)$. For this reason, the NFR method is essentially approximate.

In this work, the nonlinear frequency response method is applied for evaluation of possible improvements (increase of the reactant conversion or product yield) through periodic modulation of one (single input modulation) and simultaneous modulation of two inputs, when a homogeneous, simple, irreversible nth order reaction takes place in an isothermal, non-isothermal or adiabatic continuously stirred tank reactor (CSTR).

The NFR method is tested on several numerical examples and the results are compared with the results calculated by numerical integration, which as considered as exact. Good agreements between the results of the NFR method and results of numerical integration are obtained, except for highly nonlinear systems around the resonant frequency, when high forcing amplitudes are used.

It is concluded that, whether and to which extend is possible to achieve the improvements of the reactor performance through periodic operations, can be evaluated by the nonlinear frequency response method. The influence of the forcing parameters (frequency, amplitudes and phase shift of the input modulations) on the possible improvement can also be determined by the nonlinear frequency response method.

Keywords: Nonlinear frequency response method, Higher order frequency response functions, Volterra series, Periodically operated chemical reactors, Single input modulation, Two-input modulation, Forcing parameters, Isothermal CSTR, Non-isothermal CSTR, Adiabatic CSTR

Scientific area: Chemistry and Chemical Technology

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PERIODIČNE OPERACIJE HEMIJSKIH REAKTORA-EVALUACIJA I ANALIZA PRIMENOM METODE NELINEARNOG FREKVENTNOG ODZIVA

Rezime

Uobičajen način projektovanja procesa u hemijskom inženjerstvu podrazumeva određivanje optimalnog stacionog stanja i upravljanje procesom na način koji odezbeđuje da se uslovi održavaju što je moguće bliže tom optimalnom stacionarnom stanju. Ipak, mnoga istaživanja su pokazala da se performanse procesa, pogotovo hemijskih reaktora, mogu poboljšati ukoliko se jedan ili više ulaza periodično menja.

Poboljšanje performansi hemijskih reaktora pri periodičnom režimu rada je posledica nelinearnosti sistema. Kod nelinearnih sistema, kada se periodično menja jedan ili više ulaza, izlazi iz sistema se takođe periodično menjaju, a njihova srednja vrednost se, u opštem slučaju, razlikuje od stacionarnih vrednosti.

Methoda nelinearnog frekventnog odziva (NFO) je u ovom radu predložena i primenjena za brzo i lako određivanje mogućeg poboljšanja performansi reaktora primenom periodičnog režima rada. Metoda NFO je relativno nova metoda i ona je matematički bazirana na Voltera redovima, generalizovanoj Furijeovoj transformaciji i na konceptu frekventnih prenosnih funkcija (FPF) višeg reda.

Uticaj periodičnih operacija na performanse reaktora se može odrediti preko DC komponente (neperiodičnog člana) frekventnog odziva nelinearnog sistema. DC komponenta se može tačno prikazati beskonačnim redom čiji su članovi proporcionalni asimetričnim FPF parnih redova. Medjutim, u predloženoj metodi NFO DC komponenta se procenjuje samo na osnovu svog dominantnog člana koji je proporcionalan asimetričnoj FPF drugog reda $G_2(\omega,-\omega)$, tako da je za analizu mogućeg poboljšanja performansi reaktora pri periodičnom režimu rada dovoljno izvesti i analizirati samo ovu funkciju. Zbog toga je metoda NFO po svojoj suštini približna.

U ovom radu, metoda NFO je primenjena za procenu mogućeg poboljšanja (povećenja konverzije reaktanta ili prinosa proizvoda) pri periodičnoj promeni jednog ili dva ulaza

izotermnih, neizotermnih ili adijabatskih protočnih reaktora sa idealnim mešanjem (PRIM) sa homogenom, jednostavnom, nepovratnom reakcijom *n*-tog reda.

Methoda nelinearnog frekventnog odziva je primenjena na nekoliko numeričkih primera, a dobijeni rezultati su upoređeni sa rezultatima koji su izračunati primenom numeričke integracije, koji se smatraju za tačne. Postignuto je dobro slaganje između rezultata koji su dobijeni primenom metode NFO i rezultata numeričke integracije, osim u slučajevima izrazito nelinearnih sistema u okolini rezonantne frekvencije, kada su korišćene jako velike amplitude.

Zaključeno je da određivanje da li je, i u kojoj meri, moguće postići poboljšanje performansi hemijskih reaktora primenom periodičnih operacija moguće primenom metode nelinearnog frekventnog odziva. Primenom ove metode se takođe može odrediti uticaj parametara periodičnih operacija (frekvencija, amplitude i fazne razlike ulaznih promenljivih) na moguće poboljšanje i usvojiti opseg ovih parametara koji treba koristiti za uspešne periodične procese.

Ključne reči: Metoda nelinearnog frekventnog odziva, Frekventne prenosne funkcije višeg reda, Volterra redovi, Periodične operacije hemijskih reaktora, Periodična promena jednog ulaza, Periodična promena dva ulaza, Parametri periodične promene, Izotermni PRIM, Neizotermni PRIM, Adijabatski PRIM

Naučna oblast: Hemija i hemijska tehnologija

CONTENT

I Introduction

1.1 Periodic processes

The periodically operated processes are a class of processes which are, in general, non-stationary. The periodically operated processes can be divided into two major classes, deliberate periodic processes and inherent periodic processes. The deliberate periodic processes can operate either under steady-state conditions or under periodic forcing of one or more inputs. The deliberate periodic processes are caused by forced periodic modulation of one or more inputs and their implementation is justified and imposed only if they lead to improvement of the system performance (*Petkovska and Seidel-Morgenstern*, *2012*). On the other hand, the nature of the inherent periodic processes is periodic and they cannot operate under steady-state conditions. Examples of inherent periodic processes are all processes which include adsorption, because the sorbent should be regenerated or replaced after a certain time. Separation reactors are also inherently periodic (*Silveston and Hudgins*, *2012*).

In this work, the investigation of periodic processes is limited to the deliberate periodic processes.

The conventional way of designing processes in chemical engineering is to determine the optimum steady-state. Control systems are then designed in a way to compensate for any fluctuation of the inputs and to make that the system operates as close as possible to the optimum steady-state. In this way, the controlled system is forced to have a relatively constant output which corresponds to the desired optimum steady-state conditions (*Douglas*, *1967*).

Nevertheless, many theoretical and experimental investigations of periodic processes in chemical engineering, especially reactors, in the last 50 years, showed that periodic operation in some cases can be superior to the optimal steady-state design and that one way to achieve process intensification is to operate the process in a periodic way, in order to obtain better average performance compared to the optimal steady-state operation (*Douglas and Rippin 1966; Douglas 1967; Horn and Lin 1967; Bailey and Horn 1971; Renken 1972; Bailey 1973; Watanabe et al. 1981; Schadlich et al. 1983; Silveston 1987; Sterman 1990a, 1990b, 1991; Silveston 1998*).

Forced periodic operations can be applied to a wide variety of plant units.

The source of the possible improvement through forced periodic operation lies in the process nonlinearity. Nevertheless, the improvement is obtained only in some cases, while in some others the periodic operation can be unfavourable, depending on the system nonlinearity. In general, for forced periodically operated nonlinear system, the average value of the output is different from the steady-state value and as a result, the system performance can be improved or deteriorated (*Douglas and Rippin*, *1966*).

The magnitude of the difference between the average value of the output of interest and its steady-state value depends on the degree of system nonlinearity. This difference is small for mild nonlinearities, but for highly nonlinear systems or those which exhibit resonance, it might be significant (*Douglas*, *1967*).

Considering that most chemical processes are nonlinear in nature, the nonlinear behaviour offers the opportunity to improve the time-averaged performance, such as conversion, selectivity, yield and production rates of chemical processes by unsteady-state periodic operations *(Chen et al., 1994)*. Both the experiments and the numerical simulation studies confirmed that it is often advantageous to exploit the nonlinear behaviour of chemical reactors and operate in a dynamic regime by forced periodic cycling of one or more inputs *(Sterman and Ydstie, 1991)*.

There are many ways of operating a system periodically. It is possible to periodically modulate one or more input variables with different forcing parameters i.e. frequency, wave shape, amplitudes and phase differences. It is this richness of different forcing strategies that makes it possible to find at least one mode that will achieve the chosen objectives (for reactor systems: increased conversion, improved selectivity, increased catalyst activity etc). On the other hand, this very richness presents a challenge how to decide which forcing strategy to use and how to find it efficiently *(Silveston at al., 1995)*.

The investigations of Parulekar (*Parulekar*, *2003*) have shown that the higher the number of inputs subject to periodic forcing, the better the process (reactor) performance could be achieved and that an increase in the number of modulated inputs would lead to broadening of the regions in the operating parameter space where forced periodic operations are superior to the corresponding optimal steady state operations.

As concluded by Sterman ans Ydstie, multi-input periodic modulation can lead to improvement of the steady-state performance even when single-input modulation have a negligible or detrimental effect on the system performance i.e. significant improvements

can be obtained using multi-input perturbations even when single-input perturbations produce little or no effect (*Sterman and Ydstie, 1990b*).

Previous investigations showed that the benefit of the interaction between two inputs can be realized only if the forcing frequencies for the two inputs are equal as well as the fact that difference between synchronized inputs is an important variable. The phase difference is the dominant parameter of the influence of the periodic operations and its appropriate choice may result in significant modifications in the behaviour of a system under forced periodic operation (*Parulekar, 2003*).

Periodic operations of chemical reactors attract attention of researches with various goals where some of them are, improvement of heterogeneous catalyzed reactors (*Barto et al.*, *1994*; *Matros*, *1996*), improvement of a continuous fermentation processes (*Ruan and Chen*, *1996*; *Nguang and Chen*, *1998*), modulation as a stabilizing factor for exothermic CSTRs (*Cinar et al.*, *1987*) or even for kinetic study in order to determine the reaction order and both parameters in Arrhenius equation (activation energy and pre-exponential parameter) (*Jaree* and *Nuammaneerat*, *2010*).

It is also necessary to point out that periodic operations are more complex and more costly to develop and only significant improvements of certain objectives, compared to the classical steady-state operations, will justify their application (*Markovic et al., 2008*).

1.1.1. Process improvements through periodic operation – Short literature review

Theoretical and experimental investigation of possible improvement of forced periodically operated reactors in comparison to the optimal steady-state has been a research topic of many investigation groups world-wide for over fifty years.

Many investigators concluded that the periodic operations can be superior than the steady-state operation, for homogeneous continuous stirred tank reactors (*Renken*, *1972*; *Douglas*, *1972*; *Lee and Bailey*, *1979*; *Lee et al.*, *1980*; *Farhadpour and Gibilaro*, *1981*; *Watanabe et al.*, *1981*; *Schadlich et al.*, *1983*; *Sterman and Ydstie 1990a*, *1990b*, *1991*; *Suman 2004*; *Sidhu*, *2007*) as well as for heterogeneous catalytic reactors (*Thullie et al.*, 1986; *Barto et al.*, *1994*; *Matros*, *1994*; *Silveston et al.*, *1995*; *Silveston*, *1998*; *Reshetnkov et al.*, *2003*; *Silveston and Hudgins*, *2004a*, *2004b*; *Zahn et al.*, *2009*; *Reshetnikov*, *2010*).

In the late sixties of the previous century, Douglas with his co-authors (*Douglas and Rippin*, *1966*; *Douglas*, *1967*; *Ritter and Douglas*, *1970*; *Douglas*, *1972*) theoretically investigated the periodic operations of chemical reactors, with a focus on isothermal and non-isothermal CSTRs, and concluded that, in some cases, the reactor performance was improved by unsteady state operations.

Renken (*Renken*, *1972*) investigated theoretically the influence of forced periodic modulation of inlet concentration of the reactant on the reactor performance when irreversible consecutive-competing reaction occurred in a CSTR and concluded that both yield and selectivity of the intermediate product can be improved in this way. Afterwards, Lee and Bailey (*Lee at al. 1980*; *Lee and Bailey*, *1980*) investigated, both theoretically and experimentally, the forced periodically operated CSTR with a homogeneous liquid phase consecutive-competitive reaction (saponification of diethyl adipate). Both theoretical and experimental investigations showed that significant increase of intermediate product yield was obtained by forced cycling of the feed composition and insignificant improvement by forced periodic cycling of the temperature in the jacket (*Lee at al.*, *1980*). Farhadpour and Gibilaro (*Farhadpour and Gibilaro*, *1981*) investigated development of the optimal modes of periodic operations of CSTRs with a consecutive-competitive reaction.

A review of theoretical investigations of periodic operation of chemical reactors was given by Bailey (*Bailey*, *1973*), in which it was recommended that more experiments must be done in order to prove the improvements which were predicted by surprisingly plenty theoretical studies.

Later on, an extensive review of experimental investigations of periodic operations of chemical reactors were given in (*Silveston*, *1987*) where it was pointed out that most of the investigations of the periodically operated chemical reactors in the decades 1970-1980 were focused on the periodic modulation of the reactant compositions, usually in a square wave form. All experimental studies described in (*Silveston*, *1987*) showed that increase in catalytic activity was obtained by periodic operations. Then, updated reviews of both theoretical and experimental investigations of periodically operated catalytic reactors were given in (*Silveston et al.*, *1995* and *Silveston 1998*).

Sterman and Ydstie (*Sterman and Ydstie 1990a*, *1990b*, *1991*) theoretically analyzed the periodically operated CSTRs with square-wave input modulations, both for single and multi-input modulations for parallel, reversible, consecutive and consecutive-

competitive reactions. They defined the conditions which need to be satisfied in order to achieve improvement.

In (*Silveston and Hudgins*, *2004a*), the use of total pressure modulation of catalytic reactions with mass transfer limited rates has been analyzed in detail, in order to increase the mass transfer rates and thus enhance the mass transfer in porous catalytic particles. The same authors pointed out that the temperature modulation might have significant influence on the reactor performance through increase of the reaction rate, and therefore significant improvement could be expected as a result of temperature modulations (*Silveston and Hudgins, 2004b*).

Investigation of forced periodic operations of a cascade of adiabatic fixed-bed reactors with catalytic total oxidation showed that higher conversion and better utilization of the catalytic beds was obtained with this mode of operation (*Zahn et al.*, *2009*).

A comprehensive up-to-day review of periodic operations of chemical reactors can be found in a book edited by Silveston and Hudgins (*Silveston and Hudgins*, *2012*).

While numerous theoretical and experimental investigations have been carried out to demonstrate the ability of performance improvements via forced periodical operations, practical industrial applications of periodic operation were rarely found in the past. Nevertheless, considering serious increasing requirements of resource and energy conservation, it is expected that the economic importance of the periodic operation of chemical processes will be much increased. It is therefore highly desirable to investigate the dynamic behaviour and the performance of the periodic operation of chemical processes *(Petkovska and Seidel-Morgenstern, 2012)*.

1.1.2. Methods for evaluation of periodic operations – Short literature review

Evaluating the effects of the forced periodic operation of chemical processes on the process performance can be carried out by experimental studies. However, the experimental approach is rather time consuming and costly considering that forcing parameters and forcing strategy which should be used are completely unknown. It is therefore of economic importance to carry out theoretical studies alternatively for assessing the effects of periodic operations of chemical processes and then selecting the optimal forcing inputs before any experimental study (*Chen et al.*, *1994*).

Previously, three major approaches for theoretical analysis of forced periodic operations were suggested. First, it was the Hamilton-Jacobi approach based on the maximum

principle or relaxed steady state analysis (*Bailey and Horn*, *1971*; *Bailey*, *1973*), the application which is limited on high forcing frequencies. The second approach, the frequency-domain approach using the second-variation methods (*Watanabe et al.*, *1981*) which was suitable for low and intermediate forcing frequencies. The third approach, the π-criterion, provided the sufficient condition for performance improvement around the optimal steady-state for a broad forcing frequency range (*Sterman and Ydstie*, *1990a*, *1990b*, *1991*).

Nevertheless, the previously suggested theoretical methods for evaluation of possible performance enhancement through periodic operations have not been widely applied, owing to the complexity of their application and some uncertainty about their reliability. Therefore, there is still a need for developing a simple and reliable general method which would enable to evaluate quantitatively the possibility of process improvements through periodic operations, quickly and in early development stages *(Petkovska and Morgenstern, 2012).*

A general theoretical method for analysis of forced periodically operated chemical reactor, which will give the answers on the following questions:

- whether the reactor performance can be improved by periodic input modulation or not;
- which conditions needs to be satisfied in order to achieve the improvement, (determining the forcing strategy i.e. defining the forcing input(s), forcing amplitude(s), forcing frequency and phase difference for two-input modulation which should be used in order to achieve satisfactory improvement),
- what would be the magnitude of the possible enhancements

will be presented in this work. This method is based on the analysis of the frequency response of nonlinear systems and it is named the Nonlinear Frequency Response (NFR) method.

1.2. Frequency response of weakly nonlinear systems and the concept of higher order frequency response functions

Frequency response (FR) is a quasi-stationary response of a stable system to a periodic (sinusoidal or co-sinusoidal) input modulation around the steady-state, which is achieved when the transient response becomes negligible (theoretically for infinite time) (*Douglas, 1972*).

FR of a linear system is a periodic function of the same shape and frequency as the input modulation but with different amplitude and a phase shift. The mean value of this periodic function is equal to its steady-state value. Frequency response function (FRF) of a linear system is defined by the amplitude ratio and the phase difference of the output and input in the quasi-stationary state (*Douglas, 1972*).

1.2.1. Single input modulation

For a stable linear system with a single input $x(t)$ and a single output $y(t)$, the dynamic response to an arbitrary input $x(t)$ can be defined using a convolution integral:

$$y(t) = \int_{-\infty}^{\infty} g(\tau)x(t-\tau)d\tau$$

$$(1.1)$$

where $g(\tau)$ is the so-called impulse-response function of the system, or its kernel (*Douglas, 1972*).

By applying Fourier transform to the function $g(\tau)$, where τ represents time, the frequency response function of a linear system is obtained

$$G(\omega) = \int_{-\infty}^{\infty} g(\tau)e^{-j\omega\tau}\,d\tau$$

$$(1.2)$$

The FRF of a linear system is directly related to the amplitude and phase of the quasi-stationary response to a single harmonic input (*Douglas, 1972*):

$$x(t) = A\cos(\omega t) \Rightarrow t \to \infty: y(t) = A|G(\omega)|\cos\big(\omega t + \arg(G(\omega))\big)$$

$$(1.3)$$

The quasi-stationary response of a nonlinear system to a periodic (sinusoidal or co-sinusoidal) input around a steady-state represents the nonlinear frequency response (NFR). Frequency response of the nonlinear system is a complex periodic function and it cannot be represented by a single frequency response function as it was the case for the linear systems (*Weiner and Spina, 1980*). For weakly nonlinear systems, the nonlinear frequency response, in addition to the basic harmonic, which has the same frequency as the input modulation, also contains a non-periodic (DC) component and an infinite number of higher harmonics (*Douglas, 1972; Weiner and Spina, 1980; Petkovska and Seidel-Morgenstern 2012*).

One of the most convenient tools for mathematical analysis of the NFR is the concept of higher order frequency response functions (FRFs) (*Weiner and Spina, 1980*) which is based on Volterra series and the generalized Fourier transform (*Petkovska and Seidel-Morgenstern, 2012*). We refer to the method based on this concept "the Nonlinear Frequency Response (NFR) method."

The response of a weakly nonlinear system, for which the system nonlinearity has a polynomial form or can be expanded into a Taylor series, can be represented in the form of a Volterra series (*Volterra, 1959*):

$$y(t) = y_s + \sum_{n=1}^{\infty} y_n(t)$$

(1.4)

The subscript *s* will be used to denote the steady-state values.

The *n*th element of the Volterra series is defined as:

$$y_n(t) = \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} g_n(\tau_1, \dots, \tau_n) x(t - \tau_1) \dots x(t - \tau_n) d\tau_1 \dots d\tau_n$$

(1.5)

where $g_n(\tau_1, \dots \tau_n)$ is the *n*th order Volterra kernel or generalized impulse response function of order *n* (*Volterra, 1959*).

The first element of the Volterra series, $y_1(t)$ corresponds to the linearized model, while $y_2(t)$, $y_3(t)$,… are the correction functions of the first, second, third…order. The Volterra series of infinite length is necessary to represent exactly a weakly nonlinear system, nevertheless, for practical applications series of finite lengths can be used (*Volterra, 1959; Petkovska and Seidel-Morgenstern, 2012*).

By applying multidimensional Fourier transform on the function $g_n(\tau_1, \dots, \tau_n)$, the *n*th order generalized FRF is obtained (*Weiner and Spina, 1980*):

$$G_n(\omega_1, \dots, \omega_n) = \int_{-\infty}^{\infty} \dots \int_{-\infty}^{\infty} g_n(\tau_1, \dots, \tau_n) e^{j(\omega_1\tau_1 + \dots + \omega_n\tau_n)} d\tau_1 \dots d\tau_n$$

(1.6)

which is directly related to the *n*th element of the output in its quasi-steady periodic state, presented in the Volterra series form (Eq. 1.5) (*Petkovska and Marković, 2006*).

In this way, the nonlinear model G of a weakly nonlinear system with polynomial nonlinearities can be replaced by an infinite sequence of frequency response functions (FRFs) of different orders which are directly related to the DC component and different harmonics of the response (*Weiner and Spina, 1980*), as it is presented in Figure 1.1.

$x(t)$ → $G \equiv G_1(\omega), G_2(\omega_1, \omega_2), G_3(\omega_1, \omega_2, \omega_3), \ldots$ → $y(t)$
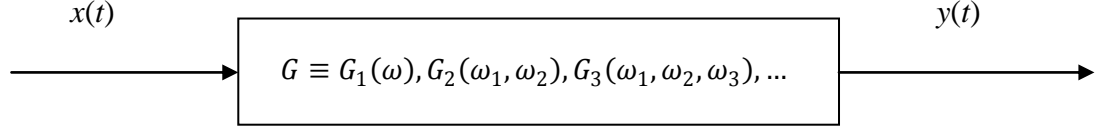
Figure 1.1 Block diagram of a weakly nonlinear system

If the input of the nonlinear system is defined as a periodic function of the general form:

$$x(t) = \sum_{k=1}^{N} A_k e^{j\omega_k t}$$

(1.7)

the nth element of the Volterra series (Eq. 1.5) is (*Volterra, 1959*)

$$y_n(t) = \sum_{k_1=1}^{N} \sum_{k_2=1}^{N} \ldots \sum_{k_n=1}^{N} A_{k_1} A_{k_2} \ldots A_{k_n} G_n(\omega_{k_1}, \omega_{k_2}, \ldots \omega_{k_n}) e^{j(\omega_{k_1} + \omega_{k_2} + \cdots + \omega_{k_n})t}$$

(1.8)

For an input which is defined as a single harmonic periodic function with forcing amplitude A and forcing frequency ω:

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

(1.9)

the first, second and third elements of the Volterra series are:

$$y_1(t) = \frac{A}{2} e^{j\omega t} G_1(\omega) + \frac{A}{2} e^{-j\omega t} G_1(-\omega)$$

(1.10)

$$y_2(t) = \left(\frac{A}{2}\right)^2 e^{2j\omega t} G_2(\omega, \omega) + 2\left(\frac{A}{2}\right)^2 e^0 G_2(\omega, -\omega) + \left(\frac{A}{2}\right)^2 e^{-2j\omega t} G_2(-\omega, -\omega)$$

(1.11)

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$$y_3(t) = \left(\frac{A}{2}\right)^3 e^{3j\omega t} G_3(\omega, \omega, \omega) + 3\left(\frac{A}{2}\right)^3 e^{j\omega t} G_3(\omega, \omega, -\omega)$$

$$+ 3\left(\frac{A}{2}\right)^3 e^{-j\omega t} G_3(\omega, -\omega, -\omega) + \left(\frac{A}{2}\right)^3 e^{-3j\omega t} G_3(-\omega, -\omega, -\omega)$$

$$(1.12)$$

Then, the response of the weakly nonlinear system is:

$$y(t) = y_s + \frac{A}{2} e^{j\omega t} G_1(\omega) + \frac{A}{2} e^{-j\omega t} G_1(-\omega) + \left(\frac{A}{2}\right)^2 e^{2j\omega t} G_2(\omega, \omega)$$

$$+ 2\left(\frac{A}{2}\right)^2 e^0 G_2(\omega, -\omega) + \left(\frac{A}{2}\right)^2 e^{-2j\omega t} G_2(-\omega, -\omega)$$

$$+ \left(\frac{A}{2}\right)^3 e^{3j\omega t} G_3(\omega, \omega, \omega) + 3\left(\frac{A}{2}\right)^3 e^{j\omega t} G_3(\omega, \omega, -\omega)$$

$$+ 3\left(\frac{A}{2}\right)^3 e^{-j\omega t} G_3(\omega, -\omega, -\omega) + \left(\frac{A}{2}\right)^3 e^{-3j\omega t} G_3(-\omega, -\omega, -\omega) + \cdots$$

$$(1.13)$$

By collecting the terms of the same frequency, it can be easily shown that the response of a weakly nonlinear system to a single harmonics input is obtained as a sum of the basic harmonic, which has the same frequency as the input, a DC (non-periodic) term and an infinite number of higher harmonics (*Petkovska and Seidel-Morgenstern, 2012*), as follows

$$y(t) = y_s + y_{DC} + y_I + y_{II} + y_{III} + \cdots$$

$$= y_s + y_{DC} + B_I \cos(\omega t + \varphi_I) + B_{II} \cos(2\omega t + \varphi_{II}) + B_{III} \cos(3\omega t + \varphi_{III}) + \cdots$$

$$(1.14)$$

where subscript DC denotes the DC component, and I, II, III the first, second and third harmonics. B_I, B_{II}, B_{III} are the amplitudes of the corresponding output harmonics and φ_I, φ_{II}, φ_{III} are the phase shifts of the corresponding output harmonic in relation to the input function.

The DC component of the output is obtained by collecting the non-periodic terms (the terms with e^0) from the Volterra series and can be expressed as the following infinite series (*Weiner and Spina, 1980*):

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

$$(1.15)$$

where $G_2(\omega,-\omega)$ represents the asymmetrical second order frequency response function (ASO FRF) and $G_4(\omega,\omega,-\omega,-\omega)$ the asymmetrical fourth order FRF.

After collecting the terms of frequency ω (the terms with $e^{j\omega t}$ and $e^{-j\omega t}$), the first harmonic of output is obtained

$$y_I = B_I \cos(\omega t + \varphi_I)$$

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

$$+ \left\{ \left(\frac{A}{2}\right) G_1(-\omega) + 3\left(\frac{A}{2}\right)^3 G_3(\omega, -\omega, -\omega) + \cdots \right\} e^{-j\omega t}$$

$$(1.16)$$

The second harmonic of the output can be obtained by collecting the terms of frequency 2ω (the terms with $e^{2j\omega t}$ and $e^{-2j\omega t}$)

$$y_{II} = B_{II} \cos(2\omega t + \varphi_{II})$$

$$= \left\{ \left(\frac{A}{2}\right)^2 G_2(\omega, \omega) + 4\left(\frac{A}{2}\right)^4 G_4(\omega, \omega, \omega, -\omega) + \cdots \right\} e^{2j\omega t}$$

$$+ \left\{ \left(\frac{A}{2}\right)^2 G_2(-\omega, -\omega) + 4\left(\frac{A}{2}\right)^4 G_4(\omega, -\omega, -\omega, -\omega) + \cdots \right\} e^{-2j\omega t}$$

$$(1.17)$$

After collecting the terms with frequency 3ω (the terms with $e^{3j\omega t}$ and $e^{-3j\omega t}$), the third harmonic of output is:

$$y_{III} = B_{III} \cos(3\omega t + \varphi_{III})$$

$$= \left\{ \left(\frac{A}{2}\right)^3 G_3(\omega, \omega, \omega) + 5\left(\frac{A}{2}\right)^5 G_5(\omega, \omega, \omega, \omega, -\omega) + \cdots \right\} e^{3j\omega t}$$

$$+ \left\{ \left(\frac{A}{2}\right)^3 G_3(-\omega, -\omega, -\omega) + 5\left(\frac{A}{2}\right)^5 G_5(\omega, \omega, -\omega, -\omega, -\omega) \right.$$

$$\left. + \cdots \right\} e^{-3j\omega t}$$

$$(1.18)$$

etc.

For weakly nonlinear systems, the contributions of the higher harmonics of the output decrease with increasing their order, as well as the contributions of the frequency

response functions of higher order. Thus, the dominant term of the DC component is defined by the asymmetrical second order FRF $G_2(\omega,-\omega)$, the dominant term of the first harmonics by the first order FRF $G_1(\omega)$, the dominant term of the second harmonics by the symmetrical second order FRF $G_2(\omega,\omega)$, the dominant term of the third harmonics by the third order FRF $G_3(\omega,\omega,\omega)$, and so on, (*Petkovska and Seidel-Morgenstern, 2012*).

The DC component of the output is responsible for the time-average performance of periodic process (*Marković et al. 2008*). As in this work the NFR method is used for investigation of the average performance of periodically operated chemical reactors, only the DC component and the asymmetrical second order FRF $G_2(\omega,-\omega)$, which corresponds to its dominant term, are of interest.

The DC component of the output, for a weakly nonlinear system, can be approximately calculated just from the asymmetrical second order FRF $G_2(\omega,-\omega)$

$$y_{DC} \approx 2\left(\frac{A}{2}\right)^2 G_2(\omega,-\omega)$$

(1.19)

Therefore, in order to evaluate the performance of periodically operated chemical reactors for single input modulation, it would be enough to derive and analyze only the ASO FRF $G_2(\omega,-\omega)$.

1.2.2. Multi-input modulation

A dynamic model of a weakly nonlinear system with multiple modulated inputs needs to be represented by several sets of FRFs. How many series of FRFs is needed for describing the system depends on the number of modulated inputs and outputs which are of interest.

For example, a block diagram representing a nonlinear system with two modulated inputs ($x(t)$, $z(t)$) and one output ($y(t)$) is presented in Figure 1.2. For this case, in order to define the complete model, it is necessary to define three sets of FRFs: two of them relating the output to each of the inputs and one set of cross-functions relating the output to both inputs. This third set contains only functions of the second and higher orders (*Petkovska and Seidel-Morgenstern, 2012*).
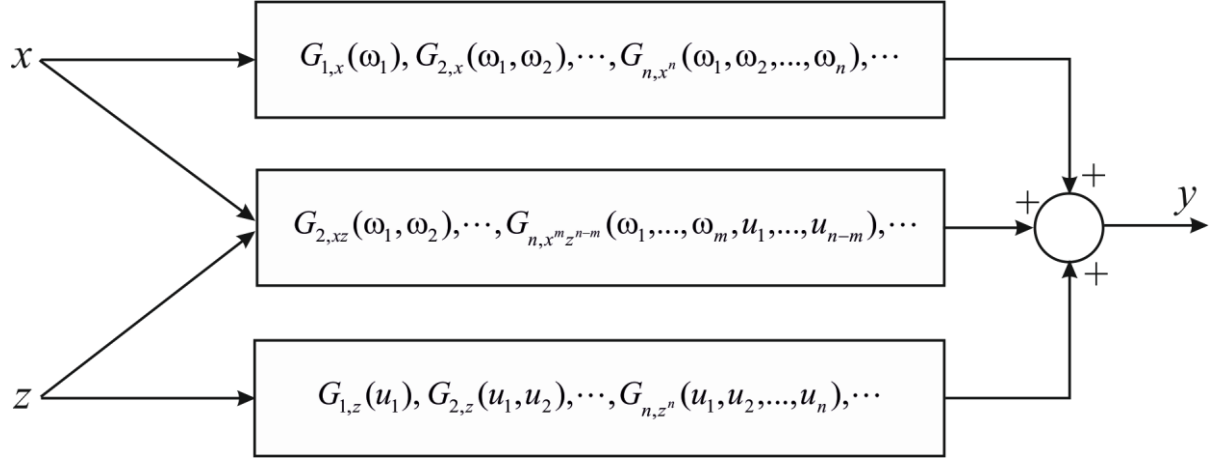
Figure 1.2 Block diagram of a weakly nonlinear system with two inputs and one output

The following notations are used in Figure 1.2: G_{n,x^n} and G_{n,z^n} are the nth order FRFs corresponding to the individual inputs $x(t)$ and $z(t)$, respectively, while $G_{n,x^m z^{n-m}}$ is the nth order cross-function, with order m regarding input $x(t)$ and n-m, regarding input $z(t)$.

For a system which is represented in Figure 1.2, the output is a sum of the contributions of the inputs $x(t)$ and $z(t)$ separately (via the G_x and G_z functions), and the contribution corresponding to the cross-effect of both inputs (via the G_{xz} functions). Each of these contributions can be presented as Volterra series (*Petkovska and Marković, 2006*):

$$y(t) = y_x(t) + y_z(t) + y_{xz}(t) = \sum_{n=1}^{\infty} y_{x,n}(t) + \sum_{n=1}^{\infty} y_{z,n}(t) + \sum_{n=1}^{\infty} y_{xz,n}(t)$$

(1.20)

If the inputs $x(t)$ and $z(t)$ are defined as general periodic functions in the following way:

$$x(t) = \sum_{k=1}^{N} A_k e^{j\omega_k t}$$

(1.21)

$$z(t) = \sum_{k=1}^{N} B_k e^{j u_k t}$$

(1.22)

The nth elements of the Volterra series corresponding to the single inputs $y_{x,n}$ and $y_{z,n}$ can be presented in an analogous way as in Eq. (1.8) and the nth element corresponding to the cross effect of both inputs is (*Petkovska and Marković, 2006; Petkovska and Seidel-Morgenstern, 2013*):

$$y_{xz,n}(t) = \sum_{m=1}^{n} \sum_{k_1=1}^{N} \cdots \sum_{k_n=1}^{M} A_{k_1} \cdots A_{k_m} B_{k_{m+1}} \cdots B_{k_n}$$
$$\times G_{n,x^m z^{n-m}}(\omega_{k_1}, \ldots, \omega_{k_m}, u_{k_{m+1}}, \ldots, u_{k_n})$$
$$\times e^{j(\omega_{k_1} + \cdots + \omega_{k_m} + u_{k_{m+1}} + \cdots + u_{k_n})t}$$

$$(1.23)$$

If the two inputs, $x(t)$ and $z(t)$, are periodically modulated co-sinusoidally, with different frequencies (ω and u), forcing amplitudes A_X and A_Z, respectively, and with a phase difference (φ) between them:

$$x(t) = x_s + A_X \cos(\omega t) \tag{1.24}$$

$$z(t) = z_s + A_Z \cos(ut + \varphi) \tag{1.25}$$

the cross-term of the output is obtained in the following form (*Nikolić Paunić and Petkovska, 2013*):

$$
\begin{aligned}
y_{xz}(t) = \left(\frac{A_x}{2}\right)\left(\frac{A_z}{2}\right)&\Big(e^{j\varphi}\, e^{j(\omega+u)t}\, G_{2,xz}(\omega, u) + e^{-j\varphi}\, e^{-j(\omega+u)t}\, G_{2,xz}(-\omega, -u) \\
&+ e^{-j\varphi}\, e^{j(\omega-u)t}\, G_{2,xz}(\omega, -u) + e^{j\varphi}\, e^{-j(\omega-u)t}\, G_{2,xz}(-\omega, u)\Big) \\
+ \left(\frac{A_x}{2}\right)^2 \left(\frac{A_z}{2}\right)&\Big(e^{j\varphi}\, e^{j(2\omega+u)t}\, G_{3,xxz}(\omega, \omega, u) \\
&+ e^{-j\varphi}\, e^{-j(2\omega+u)t}\, G_{3,xxz}(-\omega, -\omega, -u) \\
&+ e^{-j\varphi}\, e^{j(2\omega-u)t}\, G_{3,xxz}(\omega, \omega, -u) + e^{j\varphi}\, e^{-j(2\omega-u)t}\, G_{3,xxz}(-\omega, \omega, u)\Big) \\
+ \left(\frac{A_x}{2}\right)\left(\frac{A_z}{2}\right)^2 &\Big(e^{2j\varphi}\, e^{j(\omega+2u)t}\, G_{2,xzz}(\omega, u, u) \\
&+ e^{-2j\varphi}\, e^{-j(\omega+2u)t}\, G_{3,xzz}(-\omega, -u, -u) \\
&+ e^{-2j\varphi}\, e^{j(\omega-2u)t}\, G_{3,xzz}(\omega, -u, -u) + e^{2j\varphi}\, e^{-j(\omega-2u)t}\, G_{3,xz}(-\omega, u, u)\Big) \\
+ \cdots
\end{aligned}
$$

$$(1.26)$$

The DC component of the output, which is responsible for the time-average behaviour is also given as a sum of contributions of the modulations of inputs $x(t)$ and $z(t)$ separately and the cross-effect of both inputs:

$$y_{DC} = y_{DC,x} + y_{DC,z} + y_{DC,xz} \tag{1.27}$$

The second order approximations of the DC components corresponding to the individual inputs $x(t)$ and $z(t)$, are defined in the analogous way as in Eq. (1.19)

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

(1.28)

$$y_{DC,z} \approx 2\left(\frac{A_z}{2}\right)^2 G_{2,zz}(u, -u)$$

(1.29)

On the other hand, it is obvious from equation (1.26) that the cross-term will contribute to the DC component only if one frequency is an integer multiple of the other, because only in that case some of the terms in equation (1.26) become time invariant. However, the largest contribution of the cross-effect is defined by the second order terms, which contribute to the DC component only if the input frequencies are equal ($u=\omega$). From that we can conclude that the interaction of the two modulated inputs gives highest contribution to the DC component, and consequently best results regarding process improvement, when the two inputs are modulated with equal frequencies. This conclusion is in accordance with the results of Parulekar, who systematically analyzed the potential improvement of periodic operated systems with multiple input modulations, using the generalized π-criterion *(Parulekar, 2003)*.

For the case of equal input frequencies, the DC component which corresponds to cross-effect of both inputs is:

$$y_{DC,xz} = \left(\frac{A_x}{2}\right)\left(\frac{A_z}{2}\right)\left(e^{-j\varphi} G_{2,xz}(\omega, -\omega) + e^{j\varphi} G_{2,xz}(-\omega, \omega)\right) + \cdots$$

(1.30)

Taking into account only the second order terms and using the fact that

$G_{2,xz}(-\omega, \omega) = conj\left(G_{2,xz}(\omega, -\omega)\right)$, equation (1.30) can be rewritten in the following way:

$$y_{DC,xz} \approx 2\left(\frac{A_x}{2}\right)\left(\frac{A_z}{2}\right)\left(\cos(\varphi) Re\left(G_{2,xz}(\omega, -\omega)\right) + \sin(\varphi) Im\left(G_{2,xz}(\omega, -\omega)\right)\right)$$

(1.31)

If we introduce the cross ASO term, which is a function of both frequency and phase difference between the two inputs:

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

(1.32)

the second order approximation of the DC component of the cross-effect can be written in the following way:

$$y_{DC,xz} \approx 2\left(\frac{A_x}{2}\right)\left(\frac{A_z}{2}\right)G_{2,xz}^*(\omega, \varphi)$$

(1.33)

It is important to notice that the cross-effect of the modulation of two synchronized inputs strongly depends on the phase difference between them. As the matter of fact, the cross term can always be made negative, or positive, whatever is desirable, by a proper choice of the phase difference φ. Furthermore, it is possible to determine the optimal phase difference, for which the first derivative of the cross second order term $\partial G_{2,xz}^*/\partial\varphi$ is equal to zero, and consequently, the DC cross-term has a minimum:

$$\varphi_{opt} = arctang\left(\frac{Im(G_{2,xz}(\omega, -\omega))}{Re(G_{2,xz}(\omega, -\omega))}\right) - \pi$$

(1.34)

or a maximum:

$$\varphi_{opt} = arctang\left(\frac{Im(G_{2,xz}(\omega, -\omega))}{Re(G_{2,xz}(\omega, -\omega))}\right)$$

(1.35)

This optimal phase difference is in principle a function of the forcing frequency ω. Nevertheless, by finding the partial first derivative $\partial G_{2,xz}^*/\partial\omega$ and equating it to zero, it is also possible to find a condition from which the optimal frequency for which $G_{2,xz}^*$ has a minimum or a maximum, can be calculated:

$$Re\left(G_{2,xz}(\omega, -\omega)\right)\frac{\partial Re\left(G_{2,xz}(\omega, -\omega)\right)}{\partial\omega} + Im\left(G_{2,xz}(\omega, -\omega)\right)\frac{\partial Im\left(G_{2,xz}(\omega, -\omega)\right)}{\partial\omega} = 0$$

(1.36)

Finally, when two inputs are modulated with equal frequencies, the DC component can be approximately calculated using the single input and cross ASO FRFs, the forcing amplitudes of the input modulations A_x and A_z and the phase difference φ, using the following expression:

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

$$(1.37)$$

In order to determine whether the periodic operation of a system with two modulated inputs is superior to the optimal steady-state operation, it is necessary to derive all three asymmetrical second order FRFs ($G_{2,xx}(\omega,-\omega)$, $G_{2,zz}(\omega,-\omega)$ and $G_{2,xz}(\omega,-\omega)$) and to calculate the DC component for chosen forcing parameters (frequency, amplitudes and phase difference). It is important to notice that the optimal frequency for which $G_{2,xz}^*$ has a minimum or a maximum (defined by equations (1.34) and (1.35)) can, in principle, be different from the optimal frequency which would minimize the total y_{DC}, because equations (1.34) and (1.35) correspond only to the contribution of the cross-effect.

The procedure for derivation of higher order FRFs is standard and can be found in *(Petkovska, 2001; Petkovska, 2006; Petkovska and Do, 1998; Petkovska and Marković, 2006)*. The derivation process is recurrent, meaning that the first order FRFs have to be derived first, than the second order FRFs, etc. For our current application, we limit our derivations and analysis to the first order and the asymmetrical second order FRFs.

II Nonlinear frequency response for fast estimation of the time-average performance of periodically operated chemical reactors

In this Chapter, it will be explained how the NFR method can be used in order to estimate the time-average performance of periodically operated chemical reactors, when one or more inputs are modulated.

As illustration, in Figure 2.1, a reactor subjected to a periodical modulation of one or more inputs is schematically presented. The difference between steady-state and periodic operation of a chemical reactor for a simple reaction mechanism A→v_PP is presented in this figure, for a case when the mean outlet concentration of the reactant is lower than its steady-state value, which, on the other hand, corresponds to the higher mean outlet concentration of the product.
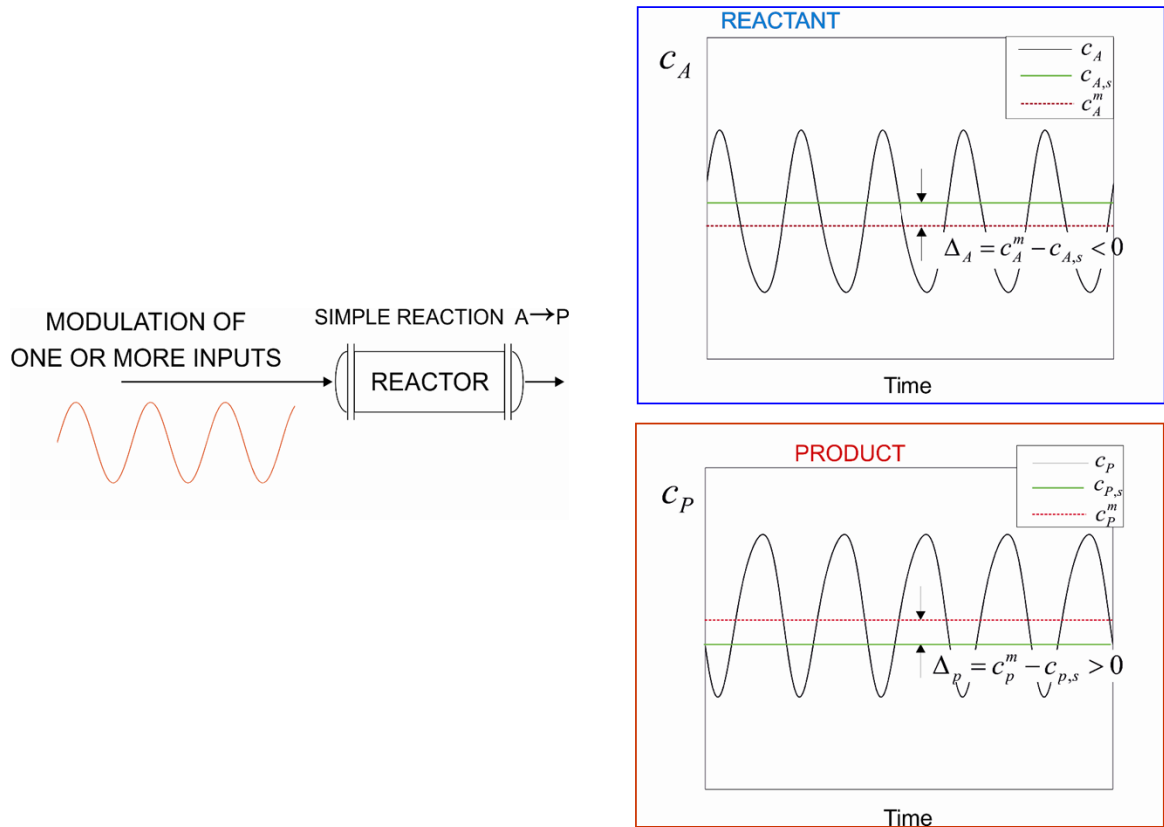
Figure 2.1 Illustration of periodic reactor operation

$c_{A,s}$ is the outlet concentration of the reactant when the process is performed in a steady-state operation. If one or more inputs of the nonlinear reactor is modulated periodically

around its steady-state value, the mean value of the outlet concentration $c_A{}^m$ during periodic operation can be different from the steady-state outlet concentration of the reactant $c_{A,s}$, i.e. the difference, $\Delta c_A = c_A^m - c_{A,s}$ can be negative, zero, or positive depending on the type of nonlinearity.

The mean outlet concentration of the product ($c_P{}^m$), can also be different from its steady-state value ($c_{P,s}$) and the difference of the outlet product concentration subjected to the periodic modulation of one or more inputs, is defined in an analogous way $\Delta c_P = c_P^m - c_{P,s}$.

The change of the reactor performance subjected to periodic modulation can be followed throughout the outlet concentration of the reactant or outlet concentration of the product and in this Chapter both approaches will be explained.

Evaluation of the time-average behavior for cases when the flow-rate is modulated and the case when inlet concentration and flow-rate are simultaneously modulated will be analyzed separately. We are analyzing forced periodically operated CSTRs with constant volume, meaning that, if one of the modulated inputs is flow-rate, the outlet flow-rate will also periodically change in the same way as the inlet. Thus, in these cases the improvement can't be measured only by the outlet concentrations of the reactant and product and the molar flow-rates of the reactant or product should be considered. The method for evaluation of possible improvement when flow-rate is modulated will be also given in this Chapter.

For application of the NFR method, it is convenient to use dimensionless inputs and outputs, so further on we will mainly operate with the dimensionless variables which are defined as relative deviation from the steady-state values.

The dimensionless inputs X and Z are defined as the relative deviations from the previously established steady-state

$$X = \frac{x(t) - x_s}{x_s}$$

(2.1)

$$Z = \frac{z(t) - z_s}{z_s}$$

(2.2)

The dimensionless time (τ) and dimensionless forcing frequency (ω) are defined as follows

$$\tau = \frac{t}{\tau_{res,s}} = \frac{t}{V/F_s}$$

(2.3)

$$\omega = \omega_d \tau_{res,s} = \omega_d \frac{V}{F_s}$$

(2.4)

where $\tau_{res,s} = V/F_s$ is a residence time in the steady-state (t denotes time, V volume of the reactor, F flow-rate, ω_d dimensional frequency and the subscript s steady-state value).

The dimensionless outlet concentrations of the reactant and product, as well as the dimensionless flow-rate are defined as

$$C_A = \frac{c_A(t) - c_{A,s}}{c_{A,s}}$$

(2.5)

$$C_P = \frac{c_P(t) - c_{P,s}}{c_{P,s}}$$

(2.6)

$$\Phi = \frac{F(t) - F_s}{F_s}$$

(2.7)

respectively.

2.1. Forced periodically operated reactor without flow-rate modulation

For the case when flow-rate is not one of the modulated inputs, and it is constant, for $\Delta c_A < 0$, the periodic operation can be considered as favorable, as it corresponds to lower outlet concentration of the reactant and therefore to higher conversion, in comparison to the steady-state operation *(Marković and al. 2008)*.

On the other hand, if $\Delta c_P > 0$ the periodic operation is considered to be favorable since it means that the mean outlet concentration of product ($c_P{}^m$) which corresponds to periodic operation is higher than it is for the steady-state operation, i.e. the product yield increased.

The decrease or increase of the outlet reactant and product concentrations as a consequence of periodic operation, in comparison to the steady-state operation, which

indicates the influence of periodic modulation of one or more inputs on the reactor performance, can be easily estimated by the NFR method. The difference Δc_A is equal to the DC component of the outlet concentration of the reactant A ($c_{A,DC}$) and the difference Δc_P is equal to the DC component of the outlet concentration of the product P ($c_{P,DC}$). Thus, just by estimating the DC components of the outlet concentrations the performance of the periodically operated chemical reactor can be estimated.

2.1.1. DC components of the outlet concentrations

Single input modulation

As stated previously, the difference between the time-average response of outlet concentration of the reactant for a periodically operated reactor and its steady-state value (Δc_A) is equal to the DC component of the outlet concentration of the reactant *(Petkovska et al., 2010)*.

$$\Delta c_A = c_A^m - c_{A,s} \equiv c_{A,DC} \tag{2.8}$$

On the other hand, if one input, e.g. x, is periodically modulated in a cosine way around its steady-state value (x_s), with forcing amplitude A_X, and forcing frequency ω_d

$$x(t) = x_s\big(1 + A_X \cos(\omega_d t)\big) \tag{2.9}$$

the DC component of the outlet concentration of the reactant ($c_{A,DC}$) is approximately proportional to the asymmetrical second order FRF $G_{A2,XX}(\omega,-\omega)$ which correlates the outlet concentration of the reactant with the modulated input, and has been defined in (Eq. (1.19)) *(Petkovska et al, 2010)*

$$c_{A,DC} \approx 2\left(\frac{A_X}{2}\right)^2 G_{A2,XX}\, c_{A,s}$$

$$\tag{2.10}$$

The periodic modulation of input x can be written in dimensionless form, as follows

$$X(\tau) = A_X \cos(\omega\tau) \tag{2.11}$$

Accordingly, the dimensionless DC component of the outlet concentration of the reactant ($C_{A,DC}$) is defined as the relative deviation of the outlet concentration of the reactant owning to periodic modulation of the chosen input:

$$C_{A,DC} = \frac{c_A^m - c_{A,s}}{c_{A,s}}$$

(2.12)

which on the other hand, according to the NFR method can be approximately calculated as

$$C_{A,DC} \approx 2\left(\frac{A_X}{2}\right)^2 G_{A2,XX}(\omega, -\omega)$$

(2.13)

In an analogous way, the dimensionless DC component of the outlet concentration of the product ($C_{P,DC}$) is proportional to the asymmetrical second order FRF $G_{P2,XX}(\omega,-\omega)$ which correlates the dimensionless outlet concentration of product with modulated input $X(\tau)$.

$$C_{P,DC} \approx 2\left(\frac{A_X}{2}\right)^2 G_{P2,XX}(\omega, -\omega)$$

(2.14)

where the dimensionless DC component $C_{P,DC}$ is defined as:

$$C_{P,DC} = \frac{c_P^m - c_{P,s}}{c_{P,s}}$$

(2.15)

Therefore, in order to evaluate the possible improvement of the reactor when only one input ($X(\tau)$) is periodically modulated, two sets of FRFs can be defined:

- Set of FRFs which correlate the outlet concentration of the reactant with the modulated input $X(\tau)$ ($G_{A1,X}(\omega)$, $G_{A2,XX}(\omega,-\omega)$,…);

- Set of FRFs which correlate the outlet concentration of the product with the modulated input $X(\tau)$ ($G_{P1,X}(\omega)$, $G_{P2,XX}(\omega,-\omega)$,…).

Simultaneous modulation of two inputs

Simultaneous modulation of two inputs, $X(\tau)$ and $Z(\tau)$, with same forcing frequency ω, forcing amplitudes A_X and A_Z, respectively and a phase difference φ between the inputs:

$$X(\tau) = A_X \cos(\omega\tau)$$

(2.16)

$$Z(\tau) = A_Z \cos(\omega\tau + \varphi)$$

(2.17)

is analyzed.

In order to evaluate the possible improvement of the reactor performance with simultaneous modulations of the two inputs $X(\tau)$ and $Z(\tau)$, in addition to the above defined sets of FRF for single input modulation of input $X(\tau)$ it is necessary to define two sets of FRFs which correspond to the modulated input $Z(\tau)$:

- Set of FRFs which correlate the outlet concentration of the reactant with the modulated input $Z(\tau)$ ($G_{A1,Z}(\omega)$, $G_{A2,ZZ}(\omega,-\omega)$,…);

- Set of FRFs which correlate the outlet concentration of the product with the modulated input $Z(\tau)$ ($G_{P1,Z}(\omega)$, $G_{P2,ZZ}(\omega,-\omega)$,…);

and two sets of cross-asymmetrical second order FRFs:

- Set of cross FRFs which correlate the outlet concentration of the reactant with both modulated inputs $X(\tau)$ and $Z(\tau)$, ($G_{A2,XZ}(\omega,-\omega)$, $G_{A2,XZ}(-\omega,\omega)$,…);

- Set of cross FRFs which correlate the outlet concentration of the product with both modulated inputs $X(\tau)$ and $Z(\tau)$, ($G_{P2,XZ}(\omega,-\omega)$, $G_{P2,XZ}(-\omega,\omega)$,…).

If two inputs of the chemical reactor are periodically modulated in a cosine way around their steady-state values as defined with (Eqs. (2.16) and (2.17)), the dimensionless DC component of the outlet concentration of the reactant ($C_{A,DC}$), based on equation (1.37), will be:

$$C_{A,DC} \approx 2\left(\frac{A_X}{2}\right)^2 G_{A2,XX}(\omega,-\omega) + 2\left(\frac{A_Z}{2}\right)^2 G_{A2,ZZ}(\omega,-\omega) + 2\left(\frac{A_X}{2}\right)\left(\frac{A_Z}{2}\right) G_{A2,XZ}^*(\varphi,\omega)$$

(2.18)

where the cross ASO term $G^*_{A2,XZ}(\varphi,\omega)$ is a function of phase difference and the cross ASO FRF $G_{A2,XZ}(\omega,-\omega)$ and defined in the following way

$$G_{A2,XZ}^*(\varphi,\omega) = \cos(\varphi)\,Re(G_{A2,XZ}(\omega,-\omega)) + \sin(\varphi)Im(G_{A2,XZ}(\omega,-\omega))$$

(2.19)

$G_{A2,XX}(\omega,-\omega)$ is the ASO FRF which correlates the outlet dimensionless concentration of the reactant to the dimensionless modulated input $X(\tau)$, $G_{A2,ZZ}(\omega,-\omega)$ the ASO FRF which correlates the outlet concentration of the reactant to the modulated input $Z(\tau)$ and $G_{A2,XZ}(\omega,-\omega)$ the cross ASO FRF which correlates the outlet dimensionless concentration of the reactant to both dimensionless modulated inputs $X(\tau)$ and $Z(\tau)$.

In an analogous way, the dimensionless DC component of outlet concentration of the product ($C_{P,DC}$) is also given with (Eq. (1.37))

$$C_{P,DC} \approx 2\left(\frac{A_X}{2}\right)^2 G_{P2,XX}(\omega,-\omega) + 2\left(\frac{A_Z}{2}\right)^2 G_{P2,ZZ}(\omega,-\omega) + 2\left(\frac{A_X}{2}\right)\left(\frac{A_Z}{2}\right) G_{P2,XZ}^*(\varphi,\omega)$$

$$(2.20)$$

where the cross ASO term $G_{P2,XZ}^*(\varphi,\omega)$ is a function of phase difference and the cross ASO FRF $G_{P2,XZ}(\omega,-\omega)$, as follows:

$$G_{P2,XZ}^*(\varphi,\omega) = \cos(\varphi)\,Re(G_{P2,XZ}(\omega,-\omega)) + \sin(\varphi)Im(G_{P2,XZ}(\omega,-\omega))$$

$$(2.21)$$

$G_{P2,XX}(\omega,-\omega)$ is the ASO FRF which correlates the dimensionless outlet concentration of the product to the modulated input $X(\tau)$, $G_{P2,ZZ}(\omega,-\omega)$ the ASO FRF which correlates the dimensionless outlet concentration of product to the modulated input $Z(\tau)$ and $G_{P2,XZ}(\omega,-\omega)$ the cross ASO FRF which correlates the dimensionless outlet concentration of the product to both modulated dimensionless inputs $X(\tau)$ and $Z(\tau)$.

2.1.2. Conversion of the reactant and yield of the product

The reactor performance subjected to periodic input modulation can be evaluated by the conversion of the reactant or the product yield and from their relative changes in comparison to the steady-state values.

The conversion of the reactant in the steady-state

$$x_{A,s} = \frac{c_{Ai,s} - c_{A,s}}{c_{Ai,s}}$$

$$(2.22)$$

and the yield of the product in the steady-state

$$Y_{P,s} = \frac{1}{\nu_P}\frac{c_{P,s}}{c_{Ai,s}}$$

$$(2.23)$$

are equal ($x_{A,s}=Y_{P,s}$).

The conversion of the reactant and yield of the product for periodically operated chemical reactors, for constant flow-rate, can be defined as follows

$$x_{A,po} = \frac{(c_{Ai})^m - c_A^m}{(c_{Ai})^m} = \frac{c_{Ai,s} - c_A^m}{c_{Ai,s}}$$

$$(2.24)$$

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

<div align="right">(2.25)</div>

In should be noticed that the mean inlet concentration is equal to steady-state inlet concentration, i.e. $(c_{Ai})^m = c_{Ai,s}$.

The reactant conversion for a periodically operated chemical reactor can be written as a function of the dimensionless DC component of the reactant ($C_{A,DC}$) and the conversion of the reactant in the steady-state

$$x_{A,po} = x_{A,s} - C_{A,DC}(1 - x_{A,s})$$

<div align="right">(2.26)</div>

while the yield of product can be expressed as a function of dimensionless DC component of product ($C_{P,DC}$) and the yield of the product in the steady-state:

$$Y_{P,po} = Y_{P,s}(1 + C_{P,DC})$$

<div align="right">(2.27)</div>

The relative changes of the reactant conversion and product yield can be expressed in the following way:

$$\Delta x_A = \frac{x_{A,po} - x_{A,s}}{x_{A,s}} = -\frac{1 - x_{A,s}}{x_{A,s}} C_{A,DC}$$

<div align="right">(2.28)</div>

$$\Delta Y_P = \frac{Y_{P,po} - Y_{P,s}}{Y_{P,s}} = C_{P,DC}$$

<div align="right">(2.29)</div>

From these equations (2.26-2.29), it can be concluded that from the dimensionless DC components of the outlet concentrations of the reactant ($C_{A,DC}$) or product ($C_{P,DC}$), the reactant conversion or product yield for periodic operation and their relative changes can be easily evaluated.

2.1.3. Identifying possible process improvements by sign analysis of the ASO FRFs

Single input modulation

The improvement of the reactor performance will be achieved if the DC component of outlet reactant concentration is negative ($C_{A,DC}<0$) or the DC component of the product outlet concentration is positive ($C_{P,DC}>0$).

<div align="right">25</div>

Based on this and equations ((2.13) and (2.14)), it can be concluded that for single input modulation, the sign of the corresponding ASO FRF will define the sign of the DC component of the outlet concentration which is of interest. Thus, in order to analyze the influence of the periodic operation on the performance of the reactor, it is enough to derive and evaluate only the corresponding ASO FRF, $G_{A2,XX}(\omega,-\omega)$ or $G_{P2,XX}(\omega,-\omega)$ (*Petkovska and Seidel-Morgenstern, 2012*).

It can been concluded, that for $G_{A2,XX}(\omega,-\omega)<0$ or $G_{P2,XX}(\omega,-\omega)>0$, the periodic operation is superior to the steady-state operation for $G_{A2,XX}(\omega,-\omega)=0$ or $G_{P2,XX}(\omega,-\omega)=0$ the periodic operation has no influence on the reactor performance, and for $G_{A2,XX}(\omega,-\omega)>0$ or $G_{P2,XX}(\omega,-\omega)<0$ the periodic operation is inferior to the steady-state operation.

Simultaneous modulation of two-inputs

For simultaneous modulation of two-inputs, in order to conclude whether improvement of the reactor performance will be achieved ($C_{A,DC}<0$ or $C_{P,DC}>0$), the situation is more complex in comparison to single input modulation.

In this case, the dimensionless DC components of outlet concentrations depend on the ASO FRFs which correlate the outlet concentration with the two separate modulated inputs and the cross effect of both modulated inputs (Eqs. (2.18) and (2.20)).

Nevertheless, it is always possible to achieve that the cross ASO terms $G_{A2,XZ}^{*}(\varphi,\omega)$ and $G_{P2,XZ}^{*}(\varphi,\omega)$ which correspond to the DC components originating from the cross-effect of both inputs have desirable signs, by appropriate choice of the phase difference (Eqs. (2.19) and (2.21)).

Considering that it is desirable that the cross ASO terms $G_{A2,XZ}^{*}(\varphi,\omega)$ is negative, in Table 2.1, the recommended phase differences which ensure the negative sign of this cross ASO term is given, depending on the signs of the real and imaginary parts of the cross ASO FRF $G_{A2,XZ}(\omega,-\omega)$.

Table 2.1 The range of the phase difference which assures negative sign of the cross ASO term $G^*_{A2,XZ}(\varphi,\omega)$

$Re(G_{A2,XZ}(\omega,-\omega))$	$Im(G_{A2,XZ}(\omega,-\omega))$	Range of φ (rad)
positive	positive	$-\pi<\varphi<-\pi/2$
positive	negative	$\pi/2<\varphi<\pi$
negative	positive	$-\pi/2<\varphi<0$
negative	negative	$0<\varphi<\pi/2$
positive	zero	$\pi/2<\varphi<\pi \vee -\pi<\varphi<-\pi/2$
zero	positive	$-\pi<\varphi<0$
negative	zero	$-\pi/2<\varphi<\pi/2$
zero	negative	$0<\varphi<\pi$

On the other hand, it is desirable the cross ASO term $G^*_{P2,XZ}(\varphi,\omega)$ be positive, and the recommended phase differences which should be used in order to obtain this goal are given in Table 2.2, depending on the signs of the real and imaginary parts of the cross ASO FRF $G_{P2,XZ}(\omega,-\omega)$.

Table 2.2 The range of the phase difference which assures positive sign of the cross term $G^*_{P2,XZ}(\varphi,\omega)$

$Re(G_{P2,XZ}(\omega,-\omega))$	$Im(G_{P2,XZ}(\omega,-\omega))$	Range of φ (rad)
positive	positive	$0<\varphi<\pi/2$
positive	negative	$-\pi/2<\varphi<0$
negative	positive	$\pi/2<\varphi<\pi$
negative	negative	$-\pi<\varphi<-\pi/2$
positive	zero	$-\pi/2<\varphi<\pi/2$
zero	positive	$0<\varphi<\pi$
negative	zero	$\pi/2<\varphi<\pi \lor -\pi<\varphi<-\pi/2$
zero	negative	$-\pi<\varphi<0$

Furthermore, it is possible to obtain the optimal phase difference, which will always give the minimal possible value of the cross ASO term $G^*_{A2,XZ}(\varphi,\omega)$, (from Eq. (1.34)):

$$\varphi_{opt,A}(\omega) = arctang\left(\frac{Im(G_{A2,XZ}(\omega,-\omega))}{Re(G_{A2,XZ}(\omega,-\omega))}\right) - \pi$$

(2.30)

or which will always give the maximal possible value of the cross ASO term $G^*_{P2,XZ}(\varphi,\omega)$

$$\varphi_{opt,P}(\omega) = arctang\left(\frac{Im(G_{P2,XZ}(\omega,-\omega))}{Re(G_{P2,XZ}(\omega,-\omega))}\right)$$

(2.31)

Thus, the value of the optimal phase difference $\varphi_{opt,A}(\omega)$ will always be in the recommended range of the phase difference given in the Table 2.1, and optimal phase difference $\varphi_{opt,P}(\omega)$ in the recommended range of the phase difference given in the Table 2.2.

If the ASO FRFs corresponding to the separate inputs $X(\tau)$ and $Z(\tau)$, $G_{A2,XX}(\omega,-\omega)$ and $G_{A2,ZZ}(\omega,-\omega)$, are both negative, as the cross ASO term $G^*_{A2,XZ}(\varphi,\omega)$ can always be made

negative by appropriate choice of the phase difference, it is obvious that simultaneous modulation of both inputs will result with even higher improvement in comparison to the separate modulations of these inputs. On the other hand if one or both of these FRFs are positive, than only evaluation of the overall DC component of the outlet concentration of the reactant given with equation (2.18), can clarify the overall effect of the periodic operation on the reactor performance.

In an analogous way, if the ASO FRFs $G_{P2,XX}(\omega,-\omega)$ and $G_{P2,ZZ}(\omega,-\omega)$ are positive, the simultaneous modulation of both inputs will lead to even higher improvement, while if one or both of these ASO FRF are negative, the overall DC component of the outlet concentration of the product (Eq. (2.20)) needs to be evaluated.

2.2. Forced periodically operated reactor with flow-rate modulation

For the case when flow-rate is input which is modulated, besides the outlet concentrations of the reactant and the product (Figure 2.1) the outlet flow-rate will also be a periodical function. Thus, the DC components of the outlet concentrations are not enough for evaluation of possible improvement of the reactor.

In order to estimate the improvement we should compare the mean outlet molar flow-rate of the reactant $((Fc_A)^m)$ owing to periodic operation to the outlet molar flow-rate of the reactant in steady-state $(F_s c_{A,s})$. In the case when flow-rate is periodically modulated, the difference which is given with the following expression:

$$\Delta(Fc_A) = (Fc_A)^m - F_s c_{A,s} \tag{2.32}$$

is an indicator of the possible reactor improvement. If the change of the outlet molar flow-rate of the reactant is negative, i.e. $\Delta(Fc_A) < 0$, the improvement is achieved.

In an analogous way, the change of the mean outlet molar flow-rate of the product, as a result of periodic modulation of the flow-rate, in comparison to the outlet steady-state molar flow-rate of the product, can be defined as follows:

$$\Delta(Fc_P) = (Fc_P)^m - F_s c_{P,s} \tag{2.33}$$

If the change of the outlet molar flow-rate of the product is positive, i.e. $\Delta(Fc_P) > 0$, the periodic modulation of the flow-rate will lead to improvement of the reactor performance.

Considering all presented above, the outputs of interest in the case when the flow-rate is modulated is molar flow-rate of the reactant or the product, which will be marked as N_A and N_P, respectively.

The dimensionless outlet molar flow-rate of the reactant can be defined as the relative deviation from its steady-state value:

$$N_A = \frac{F(t)c_A(t) - F_s c_{A,s}}{F_s c_{A,s}}$$

(2.34)

In a similar way the dimensionless outlet molar flow-rate of the product is defined as:

$$N_P = \frac{F(t)c_P(t) - F_s c_{P,s}}{F_s c_{P,s}}$$

(2.35)

2.2.1. DC components of the outlet molar flow-rates

The dimensionless DC components of outlet molar flow-rate of the reactant and product are defined as follows:

$$N_{A,DC} = \frac{(Fc_A)^m - F_s c_{A,s}}{F_s c_{A,s}}$$

(2.36)

$$N_{P,DC} = \frac{(Fc_P)^m - F_s c_{P,s}}{F_s c_{P,s}}$$

(2.37)

Based on the NFR method, the dimensionless DC components of outlet molar flow-rates of the reactant and product can be approximately estimated from the corresponding ASO FRFs

$$N_{A,DC} \approx 2\left(\frac{A_F}{2}\right)^2 H_{A2,FF}(\omega, -\omega)$$

(2.38)

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

(2.39)

where the ASO FRF $H_{A2,FF}(\omega,-\omega)$ correlates the outlet molar flow-rate of the reactant to modulated flow-rate and the ASO FRF $H_{P2,FF}(\omega,-\omega)$ correlates the outlet molar flow-rate of the product to the modulated flow-rate. These H ASO FRFs can be determined from the G ASO FRFs corresponding to the outlet concentrations, which will be explained in the following text.

2.2.2. Derivation of the H-FRFs from the G-FRFs

When the flow-rate is the input which is periodically modulated in a cosine way with forcing frequency ω_d and forcing frequency A_F, around previously established steady-state flow-rate (F_s)

$$F(t) = F_s(1 + A_F \cos(\omega_d t)) \tag{2.40}$$

and if the dimensionless flow-rate is defined with Eq (2.7), in the dimensionless form:

$$\Phi(\tau) = A_F \cos(\omega\tau) = \frac{A_F}{2} e^{j\omega\tau} + \frac{A_F}{2} e^{-j\omega\tau} \tag{2.41}$$

The dimensionless outlet concentrations of the reactant and product expressed in the Volterra series forms are, respectively

$$C_A(\tau) = \frac{A_F}{2} e^{j\omega\tau} G_{A1,F}(\omega) + \frac{A_F}{2} e^{-j\omega\tau} G_{A1,F}(-\omega) + \cdots + 2\left(\frac{A_F}{2}\right)^2 G_{A2,FF}(\omega,-\omega) + \cdots \tag{2.42}$$

$$C_P(\tau) = \frac{A_F}{2} e^{j\omega\tau} G_{P1,F}(\omega) + \frac{A_F}{2} e^{-j\omega\tau} G_{P1,F}(-\omega) + \cdots + 2\left(\frac{A_F}{2}\right)^2 G_{P2,FF}(\omega,-\omega) + \cdots \tag{2.43}$$

where $G_{A1,F}(\omega)$ is first order FRF which correlates the outlet concentration of the reactant with modulated flow-rate and $G_{A1,F}(-\omega)$ is its conjugate, while $G_{P1,F}(\omega)$ is first order FRF which correlates the outlet concentration of the product with the modulated flow-rate and $G_{P1,F}(-\omega)$ is its conjugate.

On the other hand, after introducing the dimensionless flow-rate and outlet reactant concentration into the definition of the dimensionless outlet molar flow-rate of the reactant N_A, it can be presented as a function of the dimensionless flow-rate (Φ) and the dimensionless outlet concentration of the reactant (C_A):

$$N_A = \Phi + C_A + \Phi C_A \tag{2.44}$$

and, in an analogous way, the dimensionless outlet molar flow-rate of the product is a function of the dimensionless flow-rate (Φ) and the dimensionless outlet concentration of the product (C_P):

$$N_P = \Phi + C_P + \Phi C_P \tag{2.45}$$

The dimensionless DC components of the outlet molar flow-rates of the reactant and product are then:

$$N_{A,DC} = C_{A,DC} + (\Phi C_A) \tag{2.46}$$

$$N_{P,DC} = C_{P,DC} + (\Phi C_P) \tag{2.47}$$

and finally,

$$N_{A,DC} \approx 2 \left(\frac{A_F}{2}\right)^2 \left(G_{A2,FF}(\omega,-\omega) + \frac{1}{2}\Big(G_{A1,F}(\omega) + G_{A1,F}(-\omega) \Big) \right)$$

$$\tag{2.48}$$

$$N_{P,DC} \approx 2 \left(\frac{A_F}{2}\right)^2 \left(G_{P2,FF}(\omega,-\omega) + \frac{1}{2}\Big(G_{P1,F}(\omega) + G_{P1,F}(-\omega) \Big) \right)$$

$$\tag{2.49}$$

The ASO FRF $H_{A2,FF}(\omega,-\omega)$ can be determined from the first order FRF $G_{A1,F}(\omega)$ and the ASO FRF $G_{A2,FF}(\omega,-\omega)$

$$H_{A2,FF}(\omega,-\omega) = G_{A2,FF}(\omega,-\omega) + \frac{1}{2}\Big(G_{A1,F}(\omega) + G_{A1,F}(-\omega) \Big)$$

$$\tag{2.50}$$

In the same way the ASO FRF $H_{P2,FF}(\omega,-\omega)$ can be obtained from the first order FRF $G_{P1,F}(\omega)$ and the ASO FRF $G_{P2,FF}(\omega,-\omega)$.

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

$$\tag{2.51}$$

2.2.3. Conversion of the reactant and yield of the product

The reactant conversion and the product yield, for forced periodically operated reactor with flow-rate modulation, can be defined in the following way:

$$x_{A,po} = \frac{\left(Fc_{Ai,s}\right)^m - \left(Fc_A\right)^m}{\left(Fc_{Ai,s}\right)^m} = \frac{F_s c_{Ai,s} - \left(Fc_A\right)^m}{F_s c_{Ai,s}}$$

$$(2.52)$$

$$Y_{P,po} = \frac{1}{\nu_P} \frac{\left(Fc_P\right)^m}{\left(Fc_{Ai,s}\right)^m} = \frac{1}{\nu_P} \frac{\left(Fc_P\right)^m}{F_s c_{Ai,s}}$$

$$(2.53)$$

In this case, the reactant conversion can be expressed as a function of dimensionless DC component of the molar flow rate of the reactant ($N_{A,DC}$) and the product yield as a function of dimensionless DC component of molar flow-rate of the product ($N_{P,DC}$)

$$x_{A,po} = x_{A,s} - N_{A,DC}(1 - x_{A,s}) \tag{2.54}$$

$$Y_{P,po} = Y_{P,s}(1 + N_{P,DC}) \tag{2.55}$$

The relative changes of the reactant conversion and the product yield caused by forced periodic modulation of the flow-rate are:

$$\Delta x_A = \frac{x_{A,po} - x_{A,s}}{x_{A,s}} = -\frac{1 - x_{A,s}}{x_{A,s}} N_{A,DC}$$

$$(2.56)$$

$$\Delta Y_P = \frac{Y_{P,po} - Y_{P,s}}{Y_{P,s}} = N_{P,DC}$$

$$(2.57)$$

From these equations it can be concluded that, for the case when flow-rate is periodically modulated, the reactant conversion or the product yield and their relative changes can be evaluated from the dimensionless DC components of the outlet molar flow-rate of the reactant ($N_{A,DC}$) or product ($N_{P,DC}$).

2.2.4. Identifying possible process improvements by sign analysis of the ASO FRFs

For the case when the flow-rate is periodically modulated, the improvement of the reactor performance, i.e. the increase of the reactant conversion or the product yield will be achieved if the dimensionless DC component of outlet molar flow-rate of the reactant

is negative ($N_{A,DC}$<0) or the dimensionless DC component of outlet molar flow-rate of the product is positive ($N_{P,DC}$>0).

Thus, the signs of the ASO FRFs $H_{A2,FF}(\omega,-\omega)$ and $H_{P2,FF}(\omega,-\omega)$ will define the signs of the dimensionless DC components of outlet molar flow-rates, which indicate if the improvement is possible. The improvement will be possible if the ASO FRF $H_{A2,FF}(\omega,-\omega)$ is negative or if the ASO FRF $H_{P2,FF}(\omega,-\omega)$ is positive.

It is important to point out that, all above expressions and conclusions for single input modulation of flow-rate are also valid for the case when flow-rate is simultaneously modulated with another input, except with the inlet concentration. The analysis of simultaneous modulation of inlet concentration and flow-rate is given in the following Section.

2.3. Forced periodically operated reactors with simultaneous modulation of inlet concentration and flow-rate

For forced periodically operated reactor when inlet concentration and flow-rate are periodically modulated, in order to evaluate the possible improvement it is necessary to determine the DC components of the outlet molar flow-rates of reactant or product, as well as the inlet molar flow-rate of the reactant.

The outlet molar flow-rates of the reactant and the product are defined in the same way as for single modulation of flow-rate (Eqs. (2.44) and (2.45)) and the inlet molar flow-rate of the reactant is also a periodic function.

The dimensionless inlet molar flow-rate of the reactant is defined as the relative deviation of the inlet molar flow-rate from its steady-state value

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

(2.58)

The dimensionless inlet molar flow-rate can be expressed as a function of the dimensionless flow-rate (Φ) and dimensionless inlet concentration (C_{Ai})

$$N_{Ai} = \Phi + C_{Ai} + \Phi C_{Ai} \tag{2.59}$$

If the inlet concentration and flow-rate are modulated in a cosine way with forcing amplitudes A_C and A_F with phase difference φ between them, the mean value of the inlet molar flow-rate of the reactant is

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

$$(2.60)$$

and it depends on the forcing amplitudes and phase difference between modulated inputs (φ).

2.3.1. DC components of the outlet molar flow-rates

Based on the NFR method, considering that two-inputs are periodically modulated, the dimensionless DC components of outlet molar flow-rate of the reactant and product can be written as

$$N_{A,DC} \approx 2\left(\frac{A_C}{2}\right)^2 G_{A2,CC}(\omega,-\omega) + 2\left(\frac{A_F}{2}\right)^2 H_{A2,FF}(\omega,-\omega) + 2\left(\frac{A_C}{2}\right)\left(\frac{A_F}{2}\right)H_{A2,CF}^*(\varphi,\omega)$$

$$(2.61)$$

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

$$(2.62)$$

where the $H_{A2,CF}^*(\varphi,\omega)$ is the cross ASO term which correlates the outlet molar flow-rate of the reactant with both modulated inputs:

$$H_{A2,CF}^*(\varphi,\omega) = \cos(\varphi)\,Re(H_{A2,CF}(\omega,-\omega)) + \sin(\varphi)\,Im(H_{A2,CF}(\omega,-\omega))$$

$$(2.63)$$

and $H_{P2,CF}^*(\varphi,\omega)$ is the cross ASO term which correlates the outlet molar flow-rate of the product with both modulated inputs

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

$$(2.64)$$

2.3.2. Derivation of the *H*-FRFs from the *G*-FRFs

When the inlet concentration and flow-rate are periodically modulated in a cosine way with forcing frequency ω_d and forcing amplitudes A_C and A_F respectively, with phase difference φ, around previously established steady-state (defined with $c_{Ai,s}$ and F_s), as follows:

$$c_{Ai}(t) = c_{Ai,s}(1 + A_C \cos(\omega_d t)) \tag{2.65}$$

$$F(t) = F_s(1 + A_F \cos(\omega_d t + \varphi)) \tag{2.66}$$

the input modulations can be written in the dimensionless form

$$C_{Ai}(\tau) = A_C \cos(\omega\tau) = \frac{A_C}{2} e^{j\omega\tau} + \frac{A_C}{2} e^{-j\omega\tau} \tag{2.67}$$

$$\Phi(\tau) = A_F \cos(\omega\tau + \varphi) = \frac{A_F}{2} e^{j(\omega\tau + \varphi)} + \frac{A_F}{2} e^{-j(\omega\tau + \varphi)} \tag{2.68}$$

The dimensionless outlet concentrations of the reactant and product expressed in the Volterra series form are, respectively

$$C_A(\tau) = \frac{A_C}{2} e^{j\omega\tau} G_{A1,C}(\omega) + \frac{A_C}{2} e^{-j\omega\tau} G_{A1,C}(-\omega) + \cdots$$

$$+ 2\left(\frac{A_C}{2}\right)^2 G_{A2,CC}(\omega, -\omega) + \ldots \frac{A_F}{2} e^{j\omega\tau} G_{A1,F}(\omega) + \frac{A_F}{2} e^{-j\omega\tau} G_{A1,F}(-\omega)$$

$$+ \cdots + 2\left(\frac{A_F}{2}\right)^2 G_{A2,FF}(\omega, -\omega) + \cdots + \frac{A_C}{2} \frac{A_F}{2} e^{-j\varphi} G_{A2,CF}(\omega, -\omega)$$

$$+ \frac{A_C}{2} \frac{A_F}{2} e^{j\varphi} G_{A2,CF}(-\omega, \omega) + \cdots \tag{2.69}$$

$$C_P(\tau) = \frac{A_C}{2} e^{j\omega\tau} G_{P1,C}(\omega) + \frac{A_C}{2} e^{-j\omega\tau} G_{P1,C}(-\omega) + \cdots$$

$$+ 2\left(\frac{A_C}{2}\right)^2 G_{P2,CC}(\omega, -\omega) + \ldots \frac{A_F}{2} e^{j\omega\tau} G_{P1,F}(\omega) + \frac{A_F}{2} e^{-j\omega\tau} G_{P1,F}(-\omega)$$

$$+ \cdots + 2\left(\frac{A_F}{2}\right)^2 G_{P2,FF}(\omega, -\omega) + \cdots + \frac{A_C}{2} \frac{A_F}{2} e^{-j\varphi} G_{P2,CF}(\omega, -\omega)$$

$$+ \frac{A_C}{2} \frac{A_F}{2} e^{j\varphi} G_{P2,CF}(-\omega, \omega) + \cdots \tag{2.70}$$

From (Eqs.(2.67)-(2.70)) and expression for dimensionless DC component of outlet molar flow-rate of the reactant (Eqs. (2.61)), the following expression for evaluating the cross ASO FRF $H_{A2,CF}(\omega,-\omega)$ from the cross ASO FRF $G_{A2,CF}(\omega,-\omega)$ and the first order FRF $G_{A1,C}(\omega)$ is derived

$$H_{A2,CF}(\omega, -\omega) = G_{A2,CF}(\omega, -\omega) + G_{A1,C}(\omega) \tag{2.71}$$

In the some way, the cross ASO FRF $H_{P2,CF}(\omega,-\omega)$ can be derived from the cross ASO FRF $G_{P2,CF}(\omega,-\omega)$ and the first order FRF $G_{P1,C}(\omega)$

$$H_{P2,CF}(\omega, -\omega) = G_{P2,CF}(\omega, -\omega) + G_{P1,C}(\omega) \tag{2.72}$$

2.3.3. Conversion of the reactant and yield of the product

The reactant conversion and the product yield for the case when inlet concentration and flow-rate in the reactor are simultaneously modulated, are defined as follows

$$x_{A,po} = \frac{(Fc_{Ai})^m - (Fc_A)^m}{(Fc_{Ai})^m} \tag{2.73}$$

$$Y_{P,po} = \frac{1}{\nu_P}\frac{(Fc_P)^m}{(Fc_{Ai})^m} \tag{2.74}$$

After incorporating the dimensionless DC components of the outlet molar flow-rates of the reactant and product as well as the expression for the mean inlet molar flow-rate of the reactant, the reactant conversion and product yield can be presented in following way

$$x_{A,po} = 1 - (1 - x_{A,s})\frac{\left(1 + N_{A,DC}\right)}{\left(1 + 2\left(\frac{A_C}{2}\right)\left(\frac{A_F}{2}\right)\cos(\varphi)\right)} \tag{2.75}$$

$$Y_{P,po} = Y_{P,s}\frac{\left(1 + N_{P,DC}\right)}{\left(1 + 2\left(\frac{A_C}{2}\right)\left(\frac{A_F}{2}\right)\cos(\varphi)\right)} \tag{2.76}$$

The relative changes of the reactant conversion and the product yield caused by simultaneous modulation of inlet concentration and flow-rate are:

$$\Delta x_A = \frac{x_{A,po} - x_{A,s}}{x_{A,s}} = -\frac{1 - x_{A,s}}{x_{A,s}}\frac{\left(N_{A,DC} - 2\left(\frac{A_C}{2}\right)\left(\frac{A_F}{2}\right)\cos(\varphi)\right)}{\left(1 + 2\left(\frac{A_C}{2}\right)\left(\frac{A_F}{2}\right)\cos(\varphi)\right)} \tag{2.77}$$

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

(2.78)

2.3.4. Estimating possible improvements

The estimation of the possible improvement for the case when inlet concentration and flow-rate are simultaneously modulated is not possible throughout the sign analysis of the individual ASO and the cross ASO FRFs and the outlet DC component of the molar flow-rates of the reactant or the product, concerning that the inlet molar flow-rate also depends on the forcing parameters (forcing amplitudes and phase difference), (Eq. (2.74)):

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

$$\times \left(1 + 2\left(\frac{A_C}{2}\right)^2 H_{P2,CC}(\omega, -\omega) + 2\left(\frac{A_F}{2}\right)^2 H_{P2,FF}(\omega, -\omega)\right.$$

$$\left. + 2\left(\frac{A_C}{2}\right)\left(\frac{A_F}{2}\right)\left(\cos(\varphi)\,Re(H_{P2,CF}(\omega, -\omega)) + \sin(\varphi)\,Im(H_{P2,CF}(\omega, -\omega))\right)\right)$$

(2.79)

Nevertheless, it is possible to derive the optimal phase difference, for defined forcing amplitudes (A_C, A_F), which should be used in order to maximize the reactant conversion or product yield, by deriving the first derivative of product yield and equating it to zero:

$$\frac{\partial Y_{P,po}(\omega, A_C, A_F)}{\partial \varphi} = 0$$

(2.80)

which gives:

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$$\frac{\partial Y_{P,po}(\omega, A_C, A_F)}{\partial \varphi}$$

$$= Y_{P,S} \frac{2\left(\frac{A_C}{2}\right)\left(\frac{A_F}{2}\right)}{1 + 2\left(\frac{A_C}{2}\right)\left(\frac{A_F}{2}\right)\cos(\varphi)} \left(Im\left(H_{P2,CF}(\omega, -\omega)\right)\cos(\varphi) \right.$$

$$+ \left(1 + 2\left(\frac{A_C}{2}\right)^2 G_{P2,CC}(\omega, -\omega) + 2\left(\frac{A_F}{2}\right)^2 H_{P2,FF}(\omega, -\omega) \right.$$

$$\left. - Re\left(H_{P2,CF}(\omega, -\omega)\right)\right)\sin(\varphi) + 2\left(\frac{A_C}{2}\right)\left(\frac{A_F}{2}\right)Im\left(H_{P2,CF}(\omega, -\omega)\right) \right) = 0$$

$$(2.81)$$

In order to define the solution of the optimal phase difference which maximizes the product yield for defined forcing amplitudes analytically, Eq. (2.81) can be reduced to following trigonometric equation

$$a\sin(\varphi) + b\cos(\varphi) = c \tag{2.82}$$

with parameters which are defined as

$$a = 1 + 2\left(\frac{A_C}{2}\right)^2 G_{P2,CC}(\omega, -\omega) + 2\left(\frac{A_F}{2}\right)^2 H_{P2,FF}(\omega, -\omega) - Re\left(H_{P2,CF}(\omega, -\omega)\right)$$

$$(2.83)$$

$$b = Im\left(H_{P2,CF}(\omega, -\omega)\right)$$

$$(2.84)$$

$$c = -2\left(\frac{A_C}{2}\right)\left(\frac{A_F}{2}\right)Im\left(H_{P2,CF}(\omega, -\omega)\right)$$

$$(2.85)$$

The analytical solution for optimal phase difference for defined forcing amplitudes is then obtained as:

$$\varphi_{opt}(\omega, A_C, A_F) = arctan\left(2\frac{a \pm \sqrt{a^2 - c^2 + b^2}}{c + b}\right)$$

$$(2.86)$$

This solution can be also determined numerically from equations (2.79) and (2.81).

On the other hand, in order to evaluate the maximal value of the product yield, it is possible to estimate the optimal forcing amplitudes ($A_{C,opt}(\omega)$, $A_{F,opt}(\omega)$) and the optimal

phase difference ($\varphi_{opt}(\omega,A_{C,opt},A_{F,opt})$) corresponding to them by solving numerically the equation (2.79) and finding the values of the forcing parameters when the product yield is maximized.

It should be pointed out that optimization of the forcing parameters for simultaneous modulation of any two inputs can also be done. In the case when inlet concentration and flow-rate are periodically modulated, the optimal phase difference depends on the forcing amplitudes, and they have to be optimized together. Nevertheless, for any two other simulated inputs, the optimal phase difference is independent of the forcing amplitudes, and their optimization can be done separately.

2.4. Procedure for applying the nonlinear frequency response method for estimation of the time average performance of periodic processes

The procedure for applying the NFR method for estimating the time average performance of a periodic process of a chemical reactor is rather standard, and can be summarized in next steps:

1. Postulating the nonlinear mathematical model of the reactor. The model equations are the starting point of our analysis. For applying the NFR method, all nonlinear terms in the model equations need to be represented in the polynomial form (by expanding into the corresponding Taylor series).

2. Defining the input or inputs that are modulated and the output(s) of interest.

3. Deriving the needed FRFs. How many and which FRFs need to be derived depends on the choice of the output and the modulated input(s). For our application, it is enough to derive only the first and the asymmetrical second order FRFs for single input modulation and additionally the cross ASO FRFs for simultaneous modulation of two inputs. The derivation procedure is standard and it has been described in detail in several publications (*Marković et al., 2008; Petkovska et al. 2010; Petkovska and Seidel-Morgenstern, 2012; Nikolić Paunić and Petkovska, 2013; Nikolić et al., 2014a, 2014b; Nikolić et al., 2015*).

4. Analysis of the derived asymmetrical second order FRF(s). The sign analysis of the ASO FRFs can give a direct answer whether the improvement can be achieved, except for the case when inlet concentration and flow-rate are simultaneously modulated.

For single input modulation, the sign of the ASO FRF defines the sign of the DC component, and, accordingly, gives a direct answer whether the improvement of reactor performance is obtainable or not.

For periodic operations with two modulated inputs, direct conclusion about the sign of the DC component and favorability of the periodic operation can be drawn only if both ASO FRFs corresponding to the single inputs correspond to favorable periodic operations. In that case, it is always possible to choose the phase difference in such a way that the cross-effect also contributes to the favorability of the periodic operation. If the signs of one or both single ASO FRFs imply unfavorable periodic operations, it is not possible to draw a definite conclusion on the favorability of the periodic operation when both inputs are modulated simultaneously, only based on their sign. As explained previously, in that case it is necessary to calculate the overall DC component, in order to get the answer whether the improvement can be obtained.

5. Defining the forcing parameters which will be used (forcing frequency, forcing amplitude(s) and phase difference for simultaneous modulation of two inputs). The forcing parameters can be chosen arbitrary or optimized by determining the parameters which maximize or minimize the chosen objective function (such as conversion of the reactant, yield of the product, etc).

6. Approximate calculation of the output DC component of interest and then the reactant conversion or the product yield for periodic operation. Using the derived ASO FRFs, it is possible to approximately calculate the DC component of the chosen output, for defined values of frequency, amplitude(s) and phase difference (for the case of two modulated inputs), for single input modulation by using the Eq. (1.19) or for simultaneous modulation of two inputs by using the Eq. (1.37). The reactant conversion can be calculated by using the equations (2.26, 2.54 or 2.75) and product yield from equations (2.27, 2.55 or 2.76).

2.5. Conditions which need to be satisfied for implementation of the nonlinear frequency response method

Implementation of periodic operations has sense only for stable systems, so the NFR method can only be applied for such systems. For that reasons, in order to investigate forced periodically operated reactors, it is first necessary to determine the domain of stability (*Petkovska and Seidel-Morgenstern, 2012*).

The system is stable if finite input changes of the system produce finite changes in the output. On the other hand, if finite changes of system input produce unlimited changes of the system output, the system is unstable. By analysis of the characteristic equation of the system corresponding to the linear model, the domain of the system stability can be determined (*Douglas, 1972*).

The necessary and sufficient condition that a linear system is stable is that all roots of the characteristic equation are negative or have negative real parts. The system is unstable if there is at least one root of the characteristic equation which is positive or has a positive real part. If one root of the characteristic equation or its real part is equal to zero and all the rest are negative or have negative real parts, the system is on the stability limit (*Douglas, 1972*).

This stability condition is valid only for linear systems, but this analysis can provide valuable information for the stability of nonlinear systems, by using the Lyapunov theorem as follows: If the analysis of the linearized model of a nonlinear system around the operating point which is defined by steady state values, indicates that the system is stable, then the nonlinear system is stable around that operating point. If the analysis shows that the linearized model of the system is unstable then the nonlinear system is also unstable around the operating point. If the analysis shows that the linearized model of the system is on the limit of the stability than the conclusions about the stability of the nonlinear system cannot be made (*Douglas, 1972*).

The first order FRF corresponds to linear model and the domain of stability can be determined by the analysis of the characteristic equation which corresponds to the linear model. If $j\omega$ in the first order FRF is replaced with the Laplace complex variable s, the transfer function is obtain. The characteristic equation of the system is obtained by equating the denominator of the transfer function with zero (*Douglas, 1972*). In that way, the conditions which need to be satisfied in order that the investigated nonlinear system is stable can be set. These conditions are also the conditions which need to be fulfilled for implementation of the NFR method.

The NFR method can be applied for weakly nonlinear stable systems (*Petkovska and Seidel-Morgenstern, 2012*). The NFR method is applicable only for a weakly nonlinear system, for which the system nonlinearities have polynomial forms or can be expanded into a Taylor series, since only for such systems the response can be represented in the form of a Volterra series (*Volterra, 1959*).

Additional condition for implementation of the NFR method is that the Volterra series, given with equation (1.4), converges. Some investigation of Volterra series convergence can be found in (*Xiao et al., 2014; Jing and Lang 2015*).

2.6. The advantages of the NFR method

The previous analytical methods related to identification and estimation of improvement of the periodically operated reactors already explained in Section 1.1.3, have not been applied widely in practice probably because of the complexity of their application and insufficient reliability (*Petkovska and Seidel-Morgenstern, 2012*).

The NFR method is a simple and reliable method for evaluation of the possibility of improvement of the forced periodically operated reactors which gives a fast answer on this question. The NFR method can be used as a starting point for further analysis and optimization (*Petkovska and Seidel-Morgenstern, 2012*).

The NFR method is supposed 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 or by numerical integration. It is meant to replace long and tedious numerical investigations. The most difficult and time consuming step of the NFR method is derivation of the needed FRFs, which needs to be performed only once. After that, all computations associated with the NFR method are reduced to simple algebra. So, the computational efforts of the NFR method are much less in comparison to the classical numerical investigations, which demand numerical integration of coupled sets of nonlinear differential equations (*Nikolić et al., 2015*).

Furthermore, and what is more important, 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 cases of multiple modulated inputs) which should be used in order to obtain a favorable periodic operation. This is not possible with the classical numerical method, which gives results only for the defined sets of forcing parameters (frequency, amplitude and phase difference) for which numerical integrations are performed (*Nikolić et al., 2015*).

Nevertheless, considering the fact that the output of the non-linear system, given as a Volterra series is, for practical application, approximated by finite length sum, the use of the NFR method for estimation of possible process improvement throughout periodic operation, is approximate (*Petkovska and Seidel-Morgenstern, 2012*).

2.7. Applications of the nonlinear frequency response method up to now

2.7.1. Other applications of the nonlinear frequency response method

The concept of the higher frequency response functions has been used in many fields of engineering to investigate and study systems behavior. The NFR method is mostly used for evaluating nonlinear frequency response of systems in communication systems in Electrical Engineering (*Lang and Bilings*, *2000*; *Lang et al.*, *2007*; *Rugh 1981*).

Although a powerful tool for treating weakly nonlinear systems, an in spite of the fact that most chemical engineering systems are weakly nonlinear, the concept of higher order FRFs was not widely used in chemical engineering, until recently. Up to now, several applications of this concept have been introduced.

The NFR method is used for developing new experimental techniques for investigating equilibria and kinetics in heterogeneous system, including identification of the kinetic mechanism, with applications on adsorption (*Petkovska 2006*; *Petkovska and Seidel-Morgenstern, 2005*; *Petkovska and Do, 2000*; *Petkovska, 2005*; *Brzić and Petkovska, 2012*; *Brzić and Petkovska, 2013; Petkovska 2014; Brzić and Petkovska 2015a, 2015b*) membrane (*Petkovska and Petkovska, 2006*; *Petkovska et al.*, *2011*) and electrochemical reaction systems (*Bensmann et al.*, *2010*; *Panić et al.*, *2011*; *Vidaković-Koch et al.*, *2011*).

Also, the NFR method is used for developing a computational method for direct calculation of the periodic steady states of inherent periodic processes (*Petkovska and Marković, 2006*).

2.7.2. Application of the nonlinear frequency response method for evaluation of forced periodically operated chemical reactors

The first applications of the NFR method for evaluation of periodically operated reactors were for evaluation of the forced periodically operated isothermal CSTR, isothermal plug flow reactor (PFR) and isothermal dispersed flow tubular reactor (DFTR) with simple nth order reaction, for single input modulation of inlet concentration (*Marković et al., 2008*) and for evaluation of forced periodically operated isothermal CSTR with a simple nth order heterogeneous reaction with inlet concentration modulation (*Petkovska et al., 2010*).

In this work, the NFR method is implemented for evaluation of possible improvement of the forced periodically operated continuous-stirred tank reactors (CSTRs) in which simple, irreversible, homogeneous nth order chemical reaction A $\rightarrow v_P$P takes place.

First, the NFR method is used for evaluation of forced periodically operated isothermal CSTRs for single input modulation of inlet concentration or flow-rate, as well as for simultaneous modulation of these two inputs (Chapter III). Part of the results presented in this work has been published in (*Nikolić Paunić and Petkovska, 2013*). The results obtained are tested on two numerical examples and the simulation results are presented. Numerical example ISO-1 for isothermal CSTR is taken from the previous publication (*Marković et al., 2008*) and the simulation results are presented for five different reaction orders. Numerical example ISO-2 is taken from the literature (*Douglas, 1972*), and it represents the optimized industrial reactor. The results obtained by NFR method are compared with the results of numerical integration of mathematical model, and agreement between these results is obtained.

Furthermore, the NFR method is implemented for evaluation of possible improvement of forced periodically operated non-isothermal CSTRs for single input modulations and simultaneous modulation of two inputs (Chapter IV).

For the non-isothermal CSTR, the possible inputs which can be periodically modulated are: inlet concentration, flow-rate, inlet temperature and temperature of the cooling/heating fluid. The derivation and analysis of the FRFs for single input modulation of inlet concentration and flow-rate has been published in (*Nikolić et al., 2014a*) and for single input modulation of inlet temperature and temperature of the cooling/heating fluid in (*Nikolić et al., 2014b*). The NFR method is also used for the analysis of simultaneous modulation of inlet concentration and inlet temperature, which is published in (*Nikolić et al., 2015*) and simultaneous modulation of inlet concentration and flow-rate (publication in preparation).

The results of the NFR method are tested on numerical examples which are taken from the literature. Numerical example NONISO-1 (*Douglas, 1972*) represents the optimized industrial reactor and Numerical examples NONISO-2(a) (*Marlin, 2000*) highly nonlinear oscillatory system with resonant behavior (*Nikolić et al., 2015*), NONISO-2(b) nonlinear oscillatory system with weak resonant behavior and NONISO-2(c) nonlinear non-oscillatory system. The simulation results are presented, as well as the comparison with the numerical simulation results.

Finally, an adiabatic CSTR is analyzed as a special case of non-isothermal reactor and tested on experimental system which will be used for experimental investigation (Max Planck Institute for Dynamics of Complex Technical Systems, Magdeburg, Germany), for single input modulation of inlet concentration or flow-rate, as well as for simultaneous modulation of inlet concentration and flow-rate (Chapter V).

In Table 2.3, a summary of different cases of the forced periodically operated reactors that will be investigated in this work by the NFR method are given, as well as the references if the results have already been published. In all investigated cases, a simple homogeneous chemical reaction $A \rightarrow v_P P$ takes place in the reactor.

Table 2.3 Summary of periodic operations analyzed by the NFR method in this work

Reactor type	Isothermal/ Non-isothermal	Number of inputs	Modulated input(s)	Reference
CSTR	Isothermal	1	Inlet concentration	*Nikolić Paunić and Petkovska, 2013*
		1	Flow-rate	
		2	Inlet concentration and flow-rate	
CSTR	Non-isothermal	1	Inlet concentration	*Nikolić et al., 2014a*
		1	Flow-rate	
CSTR	Non-isothermal	1	Inlet temperature	*Nikolić et al., 2014a*
		1	Temperature of the cooling/heating fluid	
CSTR	Non-isothermal	2	Inlet concentration and inlet temperature	*Nikolić et al., 2015*
CSTR	Non-isothermal	2	Inlet concentration and flow-rate	Publication in preparation
CSTR	Adiabatic non-isothermal	1	Inlet concentration	Publication in preparation
		1	Flow-rate	
		1	Inlet temperature	
		2	Inlet concentration and inlet temperature	
		2	Inlet concentration and flow-rate	

III Application of nonlinear frequency response method for evaluation of periodically operated isothermal CSTRs

3.1. Forced periodic operations of isothermal CSTRs

In this Chapter, the NFR method is applied for evaluation of possible improvement for forced periodic operation of isothermal CSTRs with simple, irreversible homogeneous nth order chemical reaction.

For isothermal CSTRs, it is possible to periodically modulate two inputs, inlet concentration and flow-rate. These two inputs can be modulated separately (single input modulation) or simultaneously (two input modulation). Part of the analysis presented in this Chapter has been published in (*Nikolić Paunić and Petkovska, 2013*).

3.2. Mathematical model

The NFR method is used to analyze the performance of a forced periodically operated CSTR in which isothermal, liquid homogeneous, irreversible, simple n*th* order reaction A→v_PP takes place, for which the reaction rate is defined with the following law:

$$r = kc_A^n \tag{3.1}$$

where c_A is the reactant concentration, k the reaction rate constant and n the reaction order.

In our analysis, we assume that the volume of the reactor is constant (*V=const*) although the flow-rate is periodically modulated, meaning that the flow-rate of the feed stream is equal with the outlet flow-rate of the reaction stream at any time, i.e., $F_i(t)=F(t)$. In this way the residence time changes periodically.

The mathematical model of this reactor system is given by the material balance of the reactant and the product in a form of a two nonlinear first order ODEs:

$$V\frac{dc_A(t)}{dt} = F(t)c_{Ai}(t) - F(t)c_A(t) - kc_A^n(t)V$$

$$\tag{3.2}$$

$$V\frac{dc_P(t)}{dt} = -F(t)c_P(t) + v_P kc_A^n(t)V$$

$$\tag{3.3}$$

where: t is time, c_A the outlet concentration of the reactant, c_P the outlet concentration of the product, c_{Ai} the inlet concentration of the reactant, F the volumetric flow-rate of the reaction stream and ν_P the stoichiometric coefficient of the product P.

The periodic modulation is performed around a previously established steady-state. The initial steady state is obtained by writing equations (3.1) and (3.2) for steady-state conditions and can be written in the following form:

$$\frac{c_{Ai,s}}{c_{A,s}} = 1 + \alpha$$

(3.4)

$$\frac{c_{P,s}}{c_{A,s}} = \nu_P \alpha$$

(3.5)

where an auxiliary dimensionless parameter α has been introduced

$$\alpha = k c_{A,s}^{n-1} \frac{V}{F_s}$$

(3.6)

Subscript s is used to denote the steady-state values.

It should be noticed that the auxiliary parameter α corresponds to dimensionless Damkohler number which relate the reaction rate to transport phenomena rate occurring in the system, which is widely used in reaction engineering (*Fogler, 2005*).

For analysis in the frequency domain, it is convenient to transform the model equations into dimensionless forms, by introducing dimensionless variables, as explained previously, as their relative deviations from their steady-state values. The definitions of the dimensionless variables and definition of dimensionless frequency (ω) which will be used in the frequency domain for analysis of isothermal CSTR are given in Table 3.1. ω_d denotes the dimensional frequency.

Table 3.1 Definitions of dimensionless variables for isothermal CSTR

Inlet concentration of the reactant	$C_{Ai} = \dfrac{c_{Ai} - c_{Ai,s}}{c_{Ai,s}}$
Outlet concentration of the reactant	$C_A = \dfrac{c_A - c_{A,s}}{c_{A,s}}$
Outlet concentration of the product	$C_P = \dfrac{c_P - c_{P,s}}{c_{P,s}}$
Flow-rate	$\Phi = \dfrac{F - F_s}{F_s}$
Time	$\tau = \dfrac{t}{V/F_s}$
Frequency	$\omega = \omega_d \dfrac{V}{F_s}$

After replacing the dimensional variables ($c_{A,i}$, c_A, c_P, F, t) in the dimensional mathematical model of the isothermal CSTR (Eqs. (3.1) and (3.2)) with the dimensionless variables (C_{Ai}, C_A, C_P, Φ, τ) and incorporating the auxiliary parameter α (Eq. (3.6)), the dimensionless mathematical model of the isothermal CSTR is obtained in the following form:

$$\frac{dC_A}{d\tau} = (1 + \alpha)(\Phi + 1)(C_{Ai} + 1) - (\Phi + 1)(C_A + 1) - \alpha(1 + C_A)^n$$

(3.7)

$$\frac{dC_P}{d\tau} = -(\Phi + 1)(C_P + 1) + (1 + C_A)^n$$

(3.8)

In order to apply the NFR method, it is necessary that all nonlinearities in the model equations are in the polynomial form. Therefore, the nonlinear term $(1+C_A)^n$ is expanded in the Taylor series around the steady-state point (only the first and the second order terms are shown):

$$(1 + C_A)^n = 1 + nC_A + \frac{1}{2}n(n - 1)C_A^2 + \cdots$$

(3.9)

The terms $F(t)c_{Ai}(t)$, $F(t)c_A(t)$ (in Eq. (3.2)) and $F(t)c_P(t)$ (in Eq. (3.3)) are also nonlinear, and their expansion in Taylor series is given in Appendix A.1, and previously incorporated in (Eq. (3.7) and (3.8)).

By incorporating the Taylor series expansion of the nonlinear term $(1+C_A)^n$ in equations (3.7) and (3.8), the model equations are transformed into the following form:

$$\frac{dC_A}{d\tau} = (1 + \alpha)\Phi C_{Ai} + (1 + \alpha)C_{Ai} + \alpha\Phi - \Phi C_A - (1 + n\alpha)C_A - \frac{1}{2}n(n - 1)\alpha C_A{}^2 + \cdots$$

$$(3.10)$$

$$\frac{dC_P}{d\tau} = -\Phi + nC_A - C_P - \Phi C_P + \frac{1}{2}n(n - 1)C_A{}^2 + \cdots$$

$$(3.11)$$

The resulting dimensionless model equations for the isothermal CSTR with simultaneous modulation of the inlet concentration and flow-rate (equations (3.10) and (3.11)) can be reduced to the case of single input modulation of inlet concentration or flow-rate.

When only the inlet concentration is periodically modulated, the dimensionless flow-rate is equal to zero ($\Phi=0$). The resulting dimensionless equations are:

$$\frac{dC_A}{d\tau} = (1 + \alpha)C_{Ai} - (1 + n\alpha)C_A - \frac{1}{2}n(n - 1)\alpha C_A{}^2 + \cdots$$

$$(3.12)$$

$$\frac{dC_P}{d\tau} = nC_A - C_P + \frac{1}{2}n(n - 1)C_A{}^2 + \cdots$$

$$(3.13)$$

For single input modulation of flow-rate, the dimensionless inlet concentration is equated to zero ($C_{Ai}=0$), and the dimensionless mathematical model of the isothermal CSTR is reduced to equations:

$$\frac{dC_A}{d\tau} = \alpha\Phi - \Phi C_A - (1 + n\alpha)C_A - \frac{1}{2}n(n - 1)\alpha C_A{}^2 + \cdots$$

$$(3.14)$$

$$\frac{dC_P}{d\tau} = -\Phi + nC_A - C_P - \Phi C_P + \frac{1}{2}n(n - 1)C_A{}^2 + \cdots$$

$$(3.15)$$

Considering that a representative dimensionless nonlinear model of the isothermal CSTR is postulated with these equations for each case of forced periodic operation (single or two-input modulation), the stability of the isothermal CSTR is the next step which should be considering in the procedure for application of the NFR method, which will be done in the following Section.

3.3. Stability analysis

The linearized model of isothermal CSTRs is obtained when the nonlinear terms in the dimensional model of the isothermal CSTRs (Eqs. (3.2) and (3.3)) are expanded in the Taylor series around the steady-state point and approximated with the first order term.

The linearized dimensionless mathematical model of CSTRs is given with the following equations:

$$\frac{dC_A}{d\tau} = (1 + \alpha)C_{Ai} + \alpha\Phi - (1 + n\alpha)C_A$$

$$\tag{3.16}$$

$$\frac{dC_P}{d\tau} = -\Phi + nC_A - C_P$$

$$\tag{3.17}$$

After implementing the Laplace transformation on the mathematical model corresponding to the linear model, the transfer functions are obtained. The characteristic equation of the isothermal CSTR is obtained by equating the denominator of obtained transfer function with zero:

$$(1 + s)(1 + n\alpha + s) = 0 \tag{3.18}$$

The roots of the characteristic equations (poles) are $p_1 = -1$ and $p_2 = -(1 + n\alpha)$.

The stability condition for the isothermal CSTR is that the pole p_2 is negative (since the pole p_1 is always negative). After introducing an auxiliary stability parameter B_{ps}, the stability condition for the isothermal CSTR can be written as follows:

$$B_{ps} = 1 + n\alpha > 0 \tag{3.19}$$

Thus, the isothermal CSTR will be stable if the stability parameter B_{ps} is positive, i.e. if n>-1/α.

3.4. Definition of the frequency response functions

The isothermal CSTR, for single input modulation, represents a system with one input and two outputs, the outlet concentration of the reactor and the outlet concentration of the product. For simultaneous modulation of the two inputs, the isothermal CSTR represents a nonlinear system with two inputs and two outputs.

Therefore, in order to describe the behavior of the isothermal CSTR when only the inlet concentration is periodically modulated, two sets of FRFs are defined:

- Set of FRFs which correlate the outlet concentration of the reactant with the modulated inlet concentration ($G_{A1,C}(\omega)$, $G_{A2,CC}(\omega,-\omega)$,…)

- Set of FRFs which correlate the outlet concentration of the product with the modulated inlet concentration ($G_{P1,C}(\omega)$, $G_{P2,CC}(\omega,-\omega)$,…)

For the case when only the flow-rate is periodically modulated, two sets of FRFs are defined:

- Set of FRFs which correlate the outlet concentration of the reactant with the modulated flow-rate ($G_{A1,F}(\omega)$, $G_{A2,FF}(\omega,-\omega)$,…)

- Set of FRFs which correlate the outlet concentration of the product with the modulated flow-rate rate ($G_{P1,F}(\omega)$, $G_{P2,FF}(\omega,-\omega)$,…)

Nevertheless, the *H* ASO FRFs which correlate the outlet molar flow-rates of the reactant $H_{A2,FF}(\omega,-\omega)$ and product $H_{P2,FF}(\omega,-\omega)$ to the modulated flow-rate should be derived from the *G* FRFs (Eqs. (2.48) and (2.49)) as it has been explained in detail in the previous Chapter.

In order to describe the behavior of the isothermal CSTR with simultaneous modulations of the inlet concentration and flow-rate, in addition to the above defined sets of FRF for single input modulation, it is necessary to define:

- Set of cross FRFs which correlate the outlet concentration of the reactant with the inlet concentration and the flow-rate, which are simultaneous modulated ($G_{A2,CF}(\omega,-\omega)$, $G_{A2,CF}(-\omega,\omega)$,…)

- Set of cross FRFs which correlate the outlet concentration of the product with the inlet concentration and the flow-rate, which are simultaneous modulated ($G_{P2,CF}(\omega,-\omega)$, $G_{P2,CF}(-\omega,\omega)$,…).

The H cross ASO FRFs which correlate the outlet molar flow-rates of the reactant $H_{A2,CF}(\omega,-\omega)$ and the product $H_{P2,CF}(\omega,-\omega)$ to both modulated inputs, inlet concentration and flow-rate, should be derived from the G-FRFs (Eqs. (2.64) and (2.65)).

3.5. Derivation procedure of the frequency response functions

The next step in our analysis is deriving the defined sets of FRFs. The derivation and analysis will be limited to the first order and the ASO FRFs for single input modulation and, in addition to the cross ASO FRFs for two-input modulation. The basic steps of this procedure are:

1. The dimensionless inlet concentration ($C_{A,i}(\tau)$) or/and flow-rate ($\Phi(\tau)$) is/are defined in the form of co-sinusoidal function(s);

2. The dimensionless outlet concentrations of the reactant ($C_A(\tau)$) and product ($C_P(\tau)$) are expressed in the Volterra series form;

3. The expressions for dimensionless input(s) ($C_{A,i}(\tau)$ or/and $\Phi(\tau)$) and dimensionless outlet concentrations ($C_A(\tau)$ and $C_P(\tau)$), from steps 1 and 2, are substituted into the corresponding dimensionless model equations (for simultaneous modulation in equations (3.10) and (3.11), for single input modulation of inlet concentration in equations (3.12) and (3.13), for single input modulation of flow-rate in equations (3.14) and (3.15));

4. The method of harmonic probing is applied to the equations obtained in step 3 meaning that the terms with the same amplitude and frequency are collected and equated to zero;

5. The equations obtained in step 4 are solved.

The basic steps of the derivation procedure for single input modulation of inlet concentration and flow-rate are given in Appendix A.2 and for simultaneous modulation of inlet concentration and flow-rate in Appendix A.3. The final expressions of the FRFs are given below. The ASO FRFs and the cross ASO FRFs are presented here in their final form but in Appendix A.2 and A.3 they are also given as functions of the first order FRFs.

After deriving the G-FRFs, the reactant and product H-ASO FRFs for flow-rate modulation are derived and given as well as the cross reactant and product H-ASO terms for simultaneous modulation of inlet concentration and flow-rate.

Considering that the ASO FRFs $G_2(\omega,-\omega)$ and $G_2(\omega,-\omega)$ are conjugate-complex function only ASO FRF $G_2(\omega,-\omega)$ will be given here. In a similar way, only $H_2(\omega,-\omega)$ will be given.

3.6. *G* frequency response functions

3.6.1. Inlet concentration modulation

The first order FRFs $G_{A1,C}(\omega)$ and $G_{P1,C}(\omega)$

$$G_{A1,C}(\omega) = \frac{1+\alpha}{B_{ps}+j\omega}$$

(3.20)

$$G_{P1,C}(\omega) = \frac{n}{1+j\omega} \times \frac{1+\alpha}{B_{ps}+j\omega}$$

(3.21)

The asymmetrical second order FRFs $G_{A2,CC}(\omega,-\omega)$ and $G_{P2,CC}(\omega,-\omega)$

$$G_{A2,CC}(\omega,-\omega) = -\frac{\alpha(1+\alpha)^2}{2B_{ps}} \times \frac{n(n-1)}{(\omega^2+B_{ps}^2)}$$

(3.22)

$$G_{P2,CC}(\omega,-\omega) = \frac{(1+\alpha)^2}{2B_{ps}} \times \frac{n(n-1)}{(\omega^2+B_{ps}^2)}$$

(3.23)

3.6.2. Flow-rate modulation

The first order FRFs $G_{A1,F}(\omega)$ and $G_{P1,F}(\omega)$

$$G_{A1,F}(\omega) = \frac{\alpha}{B_{ps}+j\omega}$$

(3.24)

$$G_{P1,F}(\omega) = \frac{-1}{B_{ps}+j\omega}$$

(3.25)

The asymmetrical second order FRFs $G_{A2,FF}(\omega,-\omega)$ and $G_{P2,FF}(\omega,-\omega)$

$$G_{A2,FF}(\omega,-\omega) = -\frac{\alpha}{2B_{ps}} \times \frac{n(n-1)\alpha^2 + 2(1+n\alpha)}{(\omega^2 + B_{ps}^2)}$$

(3.26)

$$G_{P2,FF}(\omega,-\omega) = \frac{1}{2B_{ps}} \times \frac{n(n-1)\alpha^2 + 2(1+n\alpha)}{(\omega^2 + B_{ps}^2)}$$

(3.27)

3.6.3. Simultaneous modulation of inlet concentration and flow-rate

The cross asymmetrical frequency response functions $G_{A2,CF}(\omega,-\omega)$ and $G_{P2,CF}(\omega,-\omega)$

$$G_{A2,CF}(\omega,-\omega) = \frac{(1+\alpha)}{B_{ps}} \times \frac{(\omega^2 + n\alpha(1+\alpha) + j\omega)}{(\omega^2 + B_{ps}^2)}$$

(3.28)

$$\begin{aligned}
G_{P2,CF}(\omega,-\omega) = \frac{n(1+\alpha)}{B_{ps}} &\frac{1}{(\omega^2+1)(\omega^2 + B_{ps}^2)}\big((\omega^4 \\
&+ \omega^2((1+n\alpha)^2 + (1+n\alpha) + 1 - (\alpha+1)) - (\alpha+1))) \\
&+ j\omega(\omega^2 + (1+n\alpha)^2 + (1+n\alpha) + 1)\big)
\end{aligned}$$

(3.29)

3.7. The H-asymmetrical second order frequency response functions

Considering that the H-FRFs need to be defined only in the cases when the flow-rate is periodically modulated, the H-FRFs for single input modulation of the flow-rate and for simultaneous modulation of the inlet concentration and flow-rate are derived from the G-FRFs (Eqs. (2.48), (2.49), (2.69) and (2.70)) and given in this Section. For inlet concentration modulation the H-ASO FRFs are equal to the G-ASO FRFs.

3.7.1. Flow-rate modulation

The asymmetrical second order FRFs $H_{A2,FF}(\omega,-\omega)$ and $H_{P2,FF}(\omega,-\omega)$

$$H_{A2,FF}(\omega,-\omega) = -\frac{\alpha}{2B_{ps}} \frac{(n(n-1)\alpha^2 - 2n\alpha(1+n\alpha))}{(\omega^2 + B_{ps}^2)}$$

(3.30)

$$H_{P2,FF}(\omega, -\omega) = \frac{1}{2B_{ps}} \frac{(n(n-1)\alpha^2 - 2n\alpha(1 + n\alpha))}{(\omega^2 + B_{ps}^2)}$$

(3.31)

3.7.2. Simultaneous modulation of inlet concentration and flow-rate

The cross asymmetrical second order FRFs $H_{A2,CF}(\omega,-\omega)$ and $H_{P2,CF}(\omega,-\omega)$

The cross ASO FRF $H_{A2,CF}(\omega,-\omega)$

$$H_{A2,CF}(\omega, -\omega) = \frac{(1 + \alpha)}{B_{ps}} \times \frac{(\omega^2 + n\alpha(1 + \alpha) + (1 + n\alpha)^2 - n\alpha j\omega)}{(\omega^2 + B_{ps}^2)}$$

(3.32)

is also given in the following form

$$H_{A2,CF}(\omega, -\omega) = Re\left(H_{A2,CF}(\omega, -\omega)\right) + jIm\left(H_{A2,CF}(\omega, -\omega)\right)$$

(3.33)

where the real and imaginary parts of the cross ASO FRF $H_{A2,CF}(\omega,-\omega)$ are, respectively

$$Re\left(H_{A2,CF}(\omega, -\omega)\right) = \frac{(1 + \alpha)}{B_{ps}} \times \frac{\omega^2 + n\alpha(1 + \alpha) + (1 + n\alpha)^2}{(\omega^2 + B_{ps}^2)}$$

(3.34)

$$Im\left(H_{A2,CF}(\omega, -\omega)\right) = -\frac{n\alpha(1 + \alpha)}{B_{ps}} \times \frac{\omega}{(\omega^2 + B_{ps}^2)}$$

(3.35)

The cross ASO FRF $H_{P2,CF}(\omega,-\omega)$

$$H_{P2,CF}(\omega, -\omega) = \frac{n(1 + \alpha)}{B_{ps}} \times \frac{(\omega^2 + (1 + n\alpha)^2 - (\alpha + 1) + j\omega)}{(\omega^2 + B_{ps}^2)}$$

(3.36)

can also be written in following form

$$H_{P2,CF}(\omega, -\omega) = Re\left(H_{P2,CF}(\omega, -\omega)\right) + jIm\left(H_{P2,CF}(\omega, -\omega)\right)$$

(3.37)

where the real and imaginary parts of the cross ASO FRF $H_{P2,CF}(\omega,-\omega)$ are, respectively

$$Re\left(H_{P2,CF}(\omega,-\omega)\right) = \frac{n(1+\alpha)}{B_{ps}} \times \frac{\omega^2 + (1+n\alpha)^2 - (\alpha+1)}{\left(\omega^2 + B_{ps}^2\right)}$$

(3.38)

$$Im\left(H_{P2,CF}(\omega,-\omega)\right) = \frac{n(1+\alpha)}{B_{ps}} \times \frac{\omega}{\left(\omega^2 + B_{ps}^2\right)}$$

(3.39)

The cross ASO terms $H^*_{A2,CF}(\varphi,\omega)$ and $H^*_{P2,CF}(\varphi,\omega)$

$$H^*_{A2,CF}(\varphi,\omega) = \cos(\varphi)\,Re\left(H_{A2,CF}(\omega,-\omega)\right) + \sin(\varphi)Im\left(H_{A2,CF}(\omega,-\omega)\right) \qquad (3.40)$$

$$H^*_{P2,CF}(\varphi,\omega) = \cos(\varphi)\,Re\left(H_{P2,CF}(\omega,-\omega)\right) + \sin(\varphi)Im\left(H_{P2,CF}(\omega,-\omega)\right) \qquad (3.41)$$

3.8. Correlations between the reactant and product asymmetrical frequency response functions and terms

Single input modulation

The reactant and product ASO FRFs for modulation of the inlet concentration, $G_{A2,CC}(\omega,-\omega)$ and $G_{P2,CC}(\omega,-\omega)$ (Eqs. (3.22) and (3.23)), are correlated in the following way:

$$G_{P2,CC}(\omega,-\omega) = -\frac{1}{\alpha}G_{A2,CC}(\omega,-\omega)$$

(3.42)

Similarly, the reactant and product H ASO FRFs for modulation of flow-rate, $H_{A2,FF}(\omega,-\omega)$ and $H_{P2,FF}(\omega,-\omega)$ (Eqs. (3.30) and (3.31)) are correlated in an analogous way:

$$H_{P2,FF}(\omega,-\omega) = -\frac{1}{\alpha}H_{A2,FF}(\omega,-\omega)$$

(3.43)

Thus, for single input modulation, the product ASO FRF ($G_{P2,CC}(\omega,-\omega)$ and $H_{P2,FF}(\omega,-\omega)$) and the corresponding reactant ASO FRF ($G_{A2,CC}(\omega,-\omega)$ and $H_{A2,FF}(\omega,-\omega)$) are proportional and they have opposite signs.

Therefore, the dimensionless DC components of outlet reactant and product concentrations for periodical modulation of the inlet concentration are also proportional and have opposite signs

$$C_{P,DC} = -\frac{1}{\alpha}C_{A,DC}$$

$$(3.44)$$

as well as dimensionless DC components of outlet reactant and product molar flow-rates for periodical modulation of the flow-rate

$$N_{P,DC} = -\frac{1}{\alpha}N_{A,DC}$$

$$(3.45)$$

As a consequence it can be concluded that the conversion of the reactant and yield of the product for single input modulation are equal ($x_{A,po}=Y_{P,po}$) as well as their relative changes ($\Delta x_{A,po}=\Delta Y_{P,po}$) owing to periodic operation of inlet concentration (from equations (2.24)-(2.27)) or flow-rate (from equations (2.52)-(2.55)). This lead to conclusion that, the effect of improvement or deterioration of the reactor performance owing to periodic operation can be determined just based on one of these ASO FRFs, for the reactant or for the product.

Simultaneous modulation of inlet concentration and flow-rate

The correlations between the cross H-ASO FRFs ($H_{A2,CF}(\omega,-\omega)$ and $H_{P2,CF}(\omega,-\omega)$) is

$$H_{P2,CF}(\omega,-\omega) = -\frac{1}{\alpha}H_{A2,CF}(\omega,-\omega) + \frac{1+\alpha}{\alpha}$$

$$(3.46)$$

and between the cross ASO terms $H^*_{A2,CF}(\varphi,\omega)$ and $H^*_{P2,CF}(\varphi,\omega)$

$$H^*_{2,CFP}(\varphi,\omega) = -\frac{1}{\alpha}H^*_{2,CFA}(\varphi,\omega) + \frac{1+\alpha}{\alpha}\cos(\varphi)$$

$$(3.47)$$

Therefore, the dimensionless DC components of outlet reactant and product molar flow-rates are correlated as follows

$$N_{P,DC} = -\frac{1}{\alpha}N_{A,DC} + 2\left(\frac{A_C}{2}\right)\left(\frac{A_F}{2}\right)\frac{1+\alpha}{\alpha}\cos(\varphi)$$

$$(3.48)$$

It can be easily shown that the reactant conversion and the yield of the product are equal ($x_{A,po}=Y_{P,po}$) for this case, as well, based on equation (3.48) and the definitions of the reactant conversion and product yield (Eqs. (2.73) and (2.74)). It can be shown that the same is valid for their relative changes ($\Delta x_{A,po}=\Delta Y_{P,po}$). This also leads to a conclusion

that in order to evaluate the effect of simultaneous modulation of inlet concentration and flow-rate it is enough to analyze just one of the derived sets of the ASO FRFs, for the reactant or for the product.

3.9. Estimating the possible improvement throughout the sign analysis of the asymmetrical second order frequency response functions

For single input modulation it can be concluded whether it is possible to achieve improvement by forced periodic modulation in comparison to the optimal steady-state operation just from the sign of the corresponding ASO FRF. For the sign analysis, it is important to notice that the auxiliary parameter α (Eq. (3.6)) is always positive which can be concluded from its definition. Also, for a stable isothermal CSTR the stability parameter B_{ps} (Eq. (3.19)) is also always positive.

As already explained in Chapter II, for simultaneous modulation of inlet concentration and flow-rate, the sign analysis of the ASO and cross ASO FRFs will not lead to conclusions about the possible improvement, considering that the inlet molar flow-rate depends on the forcing amplitudes and phase difference.

3.9.1. Asymmetrical second order frequency response functions for inlet concentration modulation

From the expressions of the ASO FRFs $G_{A2,CC}(\omega,-\omega)$ (Eq. (3.22)) and $G_{P2,CC}(\omega,-\omega)$ (Eq. (3.22)) for single input modulation of inlet concentration, it can be concluded that the signs of these functions depend only on the reaction order n. The signs of the ASO FRFs $G_{A2,CC}(\omega,-\omega)$ and $G_{P2,CC}(\omega,-\omega)$ are always opposite (Eq.(3.42)). The results of the sign analysis are given in Table 3.2.

Table 3.2 The summary of the sign analysis results for the ASO FRFs $G_{A2,CC}(\omega,-\omega)$ and $G_{P2,CC}(\omega,-\omega)$

Reaction order, n	$G_{A2,CC}(\omega,-\omega)$ (negative is desirable)	$G_{P2,CC}(\omega,-\omega)$ (positive is desirable)
$n < 0 \ \lor n > 1$	**negative**	**positive**
$0 < n < 1$	positive	negative
$n = 0 \ \lor n = 1$	0	0

Based on the above presented results of the sign analysis of the ASO FRFs for single input modulation of inlet concentration, it is obvious that improvement (increase of the reactant conversion as well as increase of the product yield) will be always achieved for reaction orders $n<0$ and $n>1$, while for $n=0$ and $n=1$ periodic operation has no effect on the improvement and for $0<n<1$, the reactor performance will be deteriorated.

3.9.2. Asymmetrical second order frequency response functions for flow-rate modulation

The signs of the ASO FRFs $H_{A2,FF}(\omega,-\omega)$ (Eq. (3.32)) and $H_{P2,FF}(\omega,-\omega)$ (Eq. (3.36)), corresponding to modulation of the flow-rate, depend only on the term in the numerator of these FRFs:

$$n(n-1)\alpha^2 - 2n\alpha(1+n\alpha) \tag{3.49}$$

This term can be positive or negative and it changes it sign for $n=0$ and n_F which depends on the value of the auxiliary parameter α, in the following way:

$$n_F = -1 - \frac{2}{\alpha}$$

$$\tag{3.50}$$

The summary of the sign analysis of the ASO FRFs $H_{A2,FF}(\omega,-\omega)$ and $H_{P2,FF}(\omega,-\omega)$, depending on the reaction order, are given in the Table 3.3.

Table 3.3 The summary of the sign analysis results for the ASO FRFs $H_{A2,FF}(\omega,-\omega)$ and $H_{P2,FF}(\omega,-\omega)$

Reaction order, n	$H_{A2,FF}(\omega,-\omega)$ (negative is desirable)	$H_{P2,FF}(\omega,-\omega)$ (positive is desirable)
$n=n_F$ or $n=0$	zero	zero
$n<n_F$ or $n>0$	positive	negative
$n_F<n<0$	**negative**	**positive**

For single input modulation of the flow-rate, the improvement will be achieved when the reaction order is in the range $n_F<n<0$, for the reaction orders $n=n_F$ and $n=0$ the periodic modulation of flow-rate has no effect on the reactor performance and for positive reaction orders, $n>0$ and for $n<n_F$ the periodic modulation of the flow-rate will deteriorate the reactor performance throughout the conversion and yield decrease.

3.10. Numerical examples for isothermal CSTRs

The results of the NFR method are tested on two numerical examples of isothermal CSTRs, Numerical example ISO-1 and Numerical example ISO-2.

Numerical example ISO-1 represents an isothermal CSTR which is taken from the previous publication (*Marković et al.*, *2008*) and it includes analysis of forced periodically operated isothermal reactor for different reaction orders. For this Numerical example, only the product ASO FRFs for single input modulation ($G_{P2,CC}(\omega,-\omega)$ and $H_{P2,FF}(\omega,-\omega)$) will be analyzed, in order to verify the results of the sign analysis of these ASO FRFs.

Numerical example ISO-2 corresponds to an optimized industrial reactor which was used as an example in the literature (*Douglas*, *1972*). The analysis is performed for the inlet concentration and flow-rate modulations, separately and simultaneously. The results obtained by the NFR method are compared with the results of numerical integration of the model equations, and good agreements between these results are obtained. The results of numerical simulations obtained in MATLAB, will also be given in this Section.

3.10.1. Numerical example ISO-1

Definition

Numerical example ISO-1 is defined with the same parameter values which were used in (*Marković et al., 2008*):

k=0.001 s^{-1} mol^{1-n}, $c_{Ai,s}$= 1 mol/m^3, $\tau_{res,s}$=100 s

for five different reaction orders (n=-2, -1, 0.5, 1, 2). The example which includes different reaction orders is used in order to test the results of the sign analysis of the ASO FRFs, which mainly depend on the reaction order.

Simulation results

In Figure 3.1, the ASO FRFs $G_{P2,CC}(\omega,-\omega)$ for five different reaction orders are presented vs. dimensionless frequency.
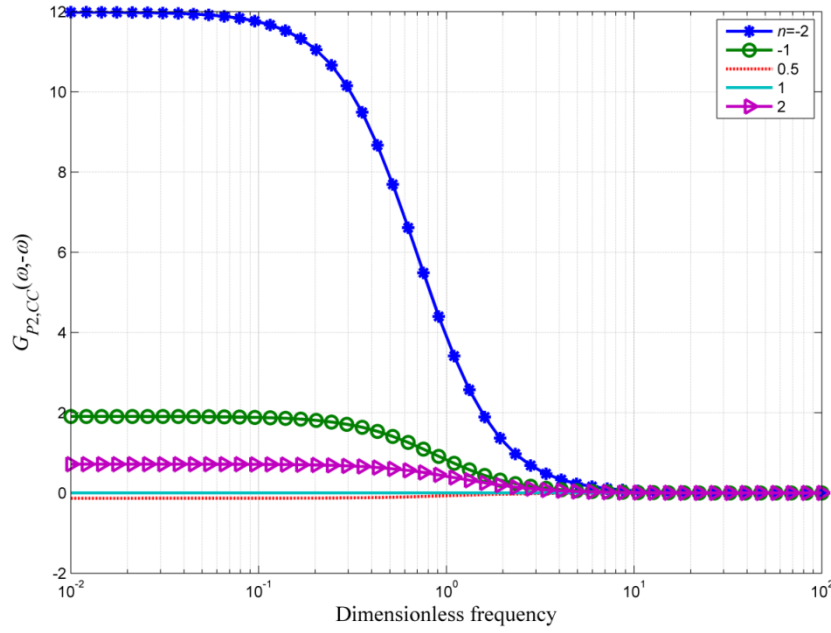
Figure 3.1 The ASO FRFs $G_{P2,CC}(\omega,-\omega)$ for different reaction orders, as functions of the dimensionless forcing frequency

As it can be seen from Figure 3.1:

- The ASO FRFs $G_{P2,CC}(\omega,-\omega)$ tend to asymptotic values for low-forcing frequencies. The low-frequency asymptote is a function of the reaction order and parameter α:

$$\lim_{\omega \to 0} G_{P2,CC}(\omega,-\omega) = \frac{n(n-1)(1+\alpha)^2}{2(1+n\alpha)^3}$$

(3.51)

- High-frequency periodic modulation of the inlet concentration has no effect on the reactor performance, as for all reaction orders

$$\lim_{\omega \to \infty} G_{P2,CC}(\omega,-\omega) = 0$$

(3.52)

- The simulation results are in accordance with the results of the sign analysis for the ASO FRF $G_{P2,CC}(\omega,-\omega)$. For $n=-2$, -1, 2 ($n<0$ or $n>1$) (Table 3.2) $G_{P2,CC}(\omega,-\omega)>0$, meaning that improvement (increased yield of product) will be obtained with periodic modulation of the inlet concentration in comparison to the steady-state. For $n=1$, $G_{P2,CC}(\omega,-\omega)=0$, i.e. the periodic modulation of the inlet

concentration has no influence on the reactor performance and for $n=0.5$ ($0<n<1$) $G_{P2,CC}(\omega,-\omega)<0$, i.e., the reactor performance will be deteriorated.

The ASO FRFs $H_{P2,FF}(\omega,-\omega)$ are graphically presented in Figure 3.2 for different reaction orders ($n=-2, -1, 0.5, 1, 2$), as functions of the dimensionless forcing frequency.
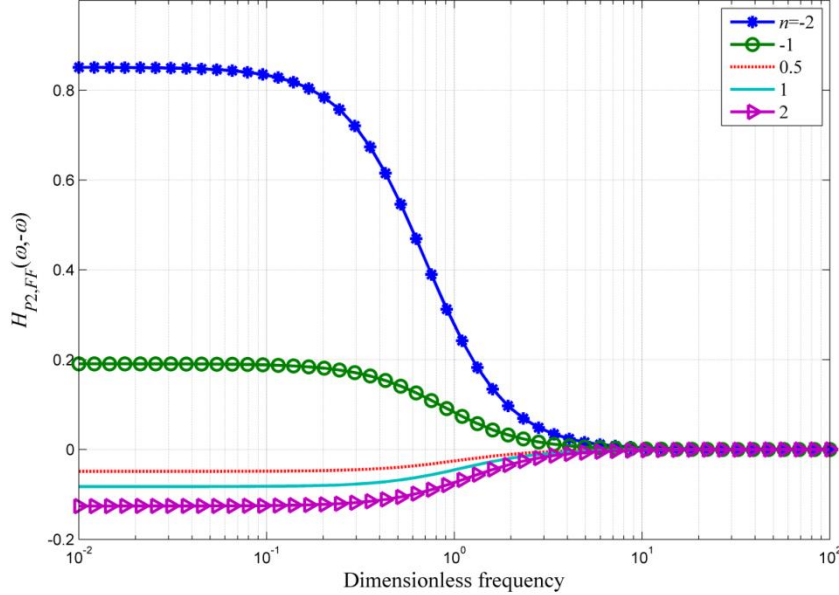
Figure 3.2 The ASO FRFs $H_{P2,FF}(\omega,-\omega)$ as functions of the dimensionless frequency for different reaction orders

As it can be seen from Figure 3.2:

- For low-forcing frequencies the ASO FRFs $H_{P2,FF}(\omega,-\omega)$ tend to asymptotic values for all investigated reaction orders. The low-frequency asymptotic value of this function can be determined from (Eq.(3.30)), and becomes:

$$\lim_{\omega \to 0} H_{P2,FF}(\omega, -\omega) = \frac{n(n-1)\alpha^2 - 2n\alpha(1 + n\alpha)}{2(1 + n\alpha)^3}$$

(3.53)

- In the case of periodic modulation of the flow-rate, the high-frequency modulation again has no effect on the reactor performance, as for all reaction orders

$$\lim_{\omega \to \infty} H_{P2,FF}(\omega, -\omega) = 0$$

(3.54)

- The simulation results are in accordance with the sign analysis results which were presented in Table 3.3. From the sign analysis, considering that the auxiliary parameter n_F is -2.09 (Eq. (3.50)), for the reaction orders n=-2 and -1 ($n_F < n < 0$), the ASO FRF $H_{P2,FF}(\omega,-\omega)$ is expected to be positive. Furthermore, for n=0.5, 1 and 2 ($n>0$), the ASO FRF $H_{P2,FF}(\omega,-\omega)$ is expected to be negative. These results have been confirmed by the simulation results presented in the Figure 3.2. Periodic modulation of the flow-rate will lead to improvement in comparison to the steady-state operation for reaction orders n=-2 and -1, while for n=0.5, 1 and 2 it leads to deterioration of the reactor performance.

3.10.2. Numerical example ISO-2

Definition

Analysis of the periodically operated isothermal CSTR by the NFR method is also done for the Numerical example ISO-2 taken from the literature (*Douglas, 1972*), for the periodic modulation of inlet concentration and flow-rate, separately and simultaneously, around the optimal steady-state. This example corresponds to an industrial isothermal CSTR with a simple, second-order (n=2), irreversible chemical reaction, with a rate constant k=1.248×10^{-3} m^3/kmol/min. The optimal design has been defined with the following values (*Douglas, 1972*)

V=28.32 m^3, F_s=2.832 m^3/h, $c_{Ai,s}$=16.02 kmol/m^3.

The conversion of the reactant and yield of product for the optimal steady-state is 75% ($c_{A,s}$=4.01kmol/m^3, $c_{P,s}$=12.01 kmol/m^3), and the auxiliary parameter α=3.00.

The rector performance will be followed by analyzing the product ASO FRFs and the change of the product yield. For single input modulation, only the product ASO FRFs $G_{P2,CC}(\omega,-\omega)$ and $H_{P2,FF}(\omega,-\omega)$ will be analyzed, considering that they are proportional to the reactant ASO FRFs $G_{A2,CC}(\omega,-\omega)$ and $H_{A2,FF}(\omega,-\omega)$, respectively. For simultaneous modulation of the inlet concentration and flow-rate the yield of product will be evaluated from the product ASO FRFs $G_{P2,CC}(\omega,-\omega)$ and $H_{P2,FF}(\omega,-\omega)$ and the product cross ASO FRF $H^*_{P2,CF}(\omega,-\omega)$.

Simulation results for single input modulation

The ASO FRF $G_{P2,CC}(\omega,-\omega)$ vs. dimensionless forcing frequency is given in Figure 3.3 and the ASO FRF $H_{P2,FF}(\omega,-\omega)$ in Figure 3.4.
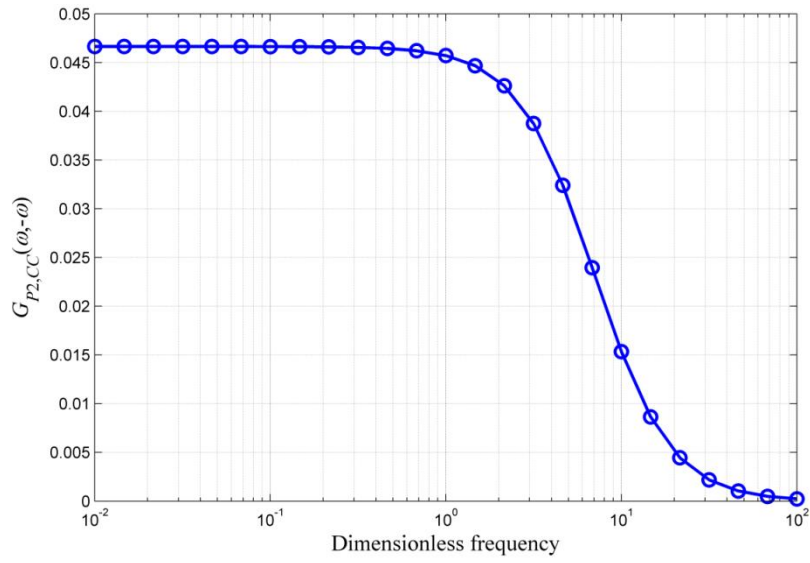
Figure 3.3 The ASO FRF $G_{P2,CC}(\omega,-\omega)$ as a function of dimensionless forcing frequency
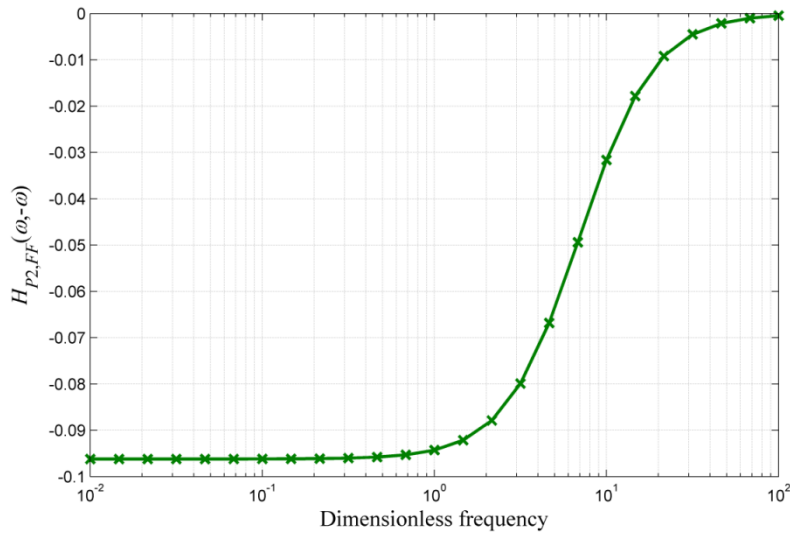
Figure 3.4 The ASO FRF $H_{P2,FF}(\omega,-\omega)$ as a function of dimensionless forcing frequency

As expected from the sign analysis (Tables 3.2 and 3.3), the simulation results presented in Figures 3.3 and 3.4 confirm that the improvement for the reaction order $n=2$ ($n>0$), will be obtained for single input modulation of the inlet concentration ($G_{P2,CC}(\omega,-\omega)>0$) and deterioration for single input modulation of the flow-rate ($H_{P2,FF}(\omega,-\omega)<0$). The highest improvement for single input modulation of inlet concentration modulation can be achieved for low-forcing frequencies, where ASO FRF $G_{P2,CC}(\omega,-\omega)$ tends to an asymptotic value. Nevertheless, the highest value of this ASO FRF is still low (Figure 3.3).

As illustration, in Figure 3.5, the yields of product are graphically presented for single input modulation of inlet concentration with forcing amplitude A_C=100% and for single input of flow-rate with forcing amplitude A_F=75%. For comparison, the yield in steady-state is also given in Figure 3.5.
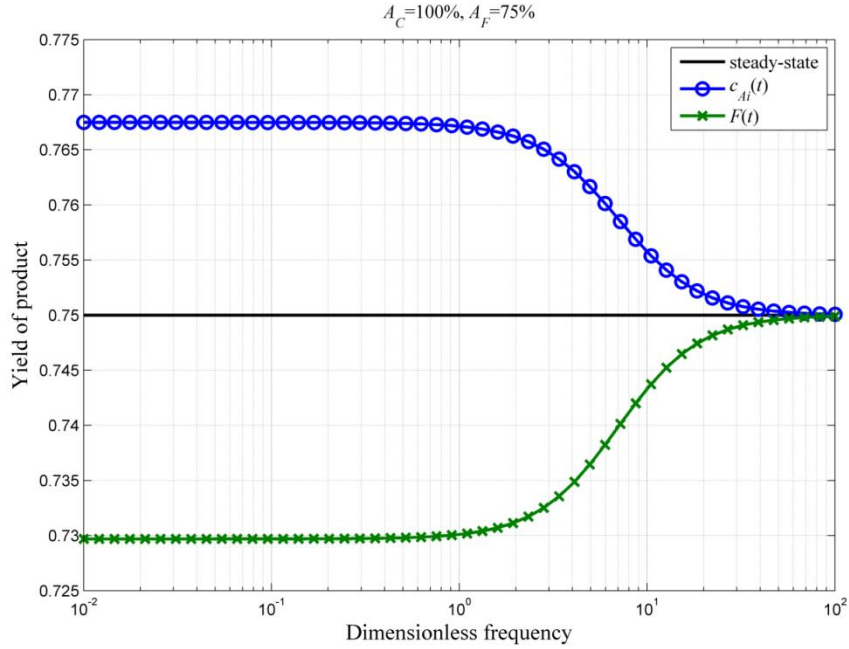
Figure 3.5 Yield of product for the steady-state operation, for single input modulation of inlet concentration with forcing amplitude A_C=100% and for single input modulation of flow-rate with forcing amplitude A_F=75% as functions of dimensionless forcing frequency

Despite the fact that inlet concentration modulation will lead to increase of the product yield, even for the highest forcing amplitude (A_C=100%), this increase is still low, with highest relative increase of 2.33% at low frequencies.

Simulation results for simultaneous modulation of inlet concentration and flow-rate

In order to simulate the case when inlet concentration and flow-rate are simultaneously modulated, arbitrary forcing amplitudes are chosen, for the inlet concentration A_C=100% and for the flow-rate A_F=75%.

The optimal phase difference which maximizes the product yield $\varphi_{opt}(\omega)$ as a function of the dimensionless forcing frequency for defined forcing amplitudes (A_C=100% and A_F=75%) is graphically presented in Figure 3.6.
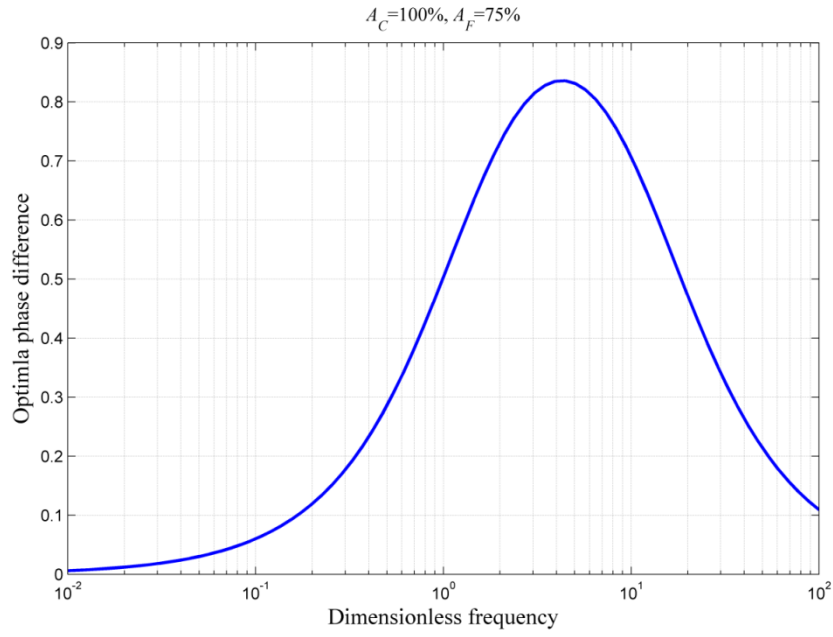
Figure 3.6 The optimal phase difference $\varphi_{opt}(\omega)$ which maximizes the product yield for forcing amplitudes A_C=100% and A_F=75%, vs. dimensionless forcing frequency

In Figure 3.7, the product yields are graphically presented for: steady-state operated reactor, for single input modulation of inlet concentration with forcing amplitude A_C=100%, for flow-rate modulation with forcing amplitude A_F=75% and for simultaneous modulation of these two inputs with optimal phase difference $\varphi_{opt}(\omega)$, all as functions of the dimensionless forcing frequency.
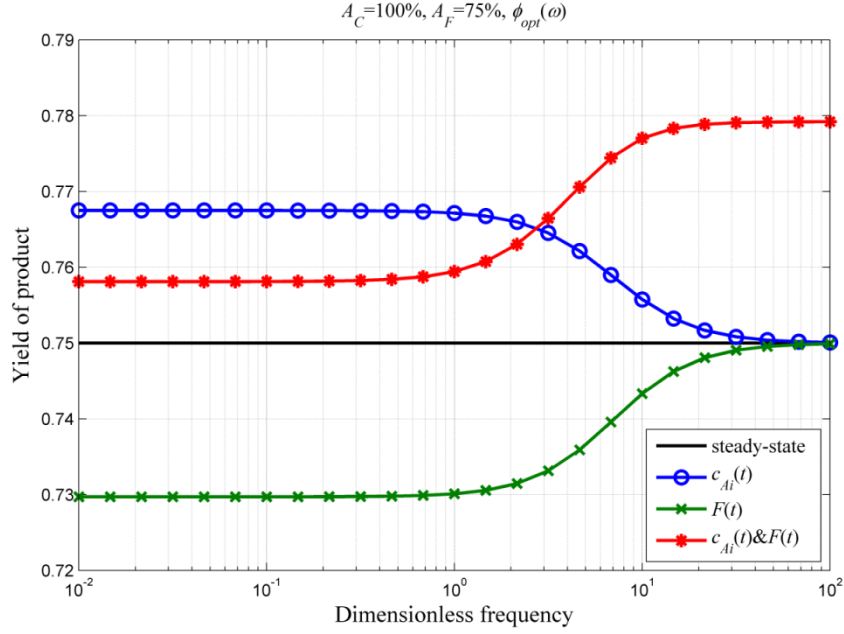
Figure 3.7 The product yield for steady-state operation, for periodic modulation of inlet concentration (A_C=100%), for flow-rate modulation (A_F=75%) and for simultaneous modulation of these two inputs with optimal phase difference ($\varphi_{opt}(\omega)$, A_C=100%, A_F=75%) vs. dimensionless forcing frequency

The simultaneous modulation of the inlet concentration and flow-rate, for these forcing amplitudes and phase difference, for low-forcing frequency is inferior than the single input modulation of inlet concentration, i.e. the increase of the product yield is obtained but for low-forcing frequency this increase is lower than for single input modulation of inlet concentration (Figure 3.7).

On the other hand, for high-forcing frequencies the situation is completely different. Despite the fact that for high-forcing frequency single input modulations have no effect on the reactor performance, the simultaneous modulation of the two inputs will cause increase of the product yield. This increase is even higher than for the low-frequency single input of inlet concentration.

This phenomena is a result of the fact that the real part of the cross ASO FRF $H_{P2,CF}(\omega,-\omega)$ and therefore the cross ASO FRF $H_{P2,CF}(\omega,-\omega)$ for high-frequency modulation tend to following asymptotic value, which is different from zero:

$$\lim_{\omega \to \infty} Re\left(H_{P2,CF}(\omega,-\omega)\right) = \lim_{\omega \to \infty} H_{P2,CF}(\omega,-\omega) = \frac{n(1+\alpha)}{B_{ps}}$$

(3.55)

which leads to a conclusion that the cross ASO FRF $H^*_{P2,CF}(\varphi,\omega)$ and, therefore, the dimensionless outlet molar flow-rate of the product for high-forcing frequencies also tend to corresponding asymptotic values, as follows:

$$\lim_{\omega\to\infty} H^*_{P2,CF}(\varphi,\omega) = \frac{n(1+\alpha)}{B_{ps}} \cos(\varphi)$$

(3.56)

$$\lim_{\omega\to\infty} N_{P,DC} = 2\left(\frac{A_C}{2}\right)\left(\frac{A_F}{2}\right)\frac{n(1+\alpha)}{B_{ps}} \cos(\varphi)$$

(3.57)

Therefore, the product yield for high-forcing frequencies is given with the following expression

$$\lim_{\omega\to\infty} Y_{P,po} = Y_{P,s} \frac{1 + 2\left(\frac{A_C}{2}\right)\left(\frac{A_F}{2}\right)\frac{n(1+\alpha)}{B_{ps}}\cos(\varphi)}{1 + 2\left(\frac{A_C}{2}\right)\left(\frac{A_F}{2}\right)\cos(\varphi)}$$

(3.58)

Thus, the product yield for high-frequencies simultaneous modulation of inlet concentration and flow-rate depends on the forcing amplitudes, phase difference between modulated inputs and the characteristics of the system (throughout reaction order n and auxiliary parameter α). The reactor performance for high-forcing frequency modulations of the inlet concentration and flow-rate depends only on the cross effect of two modulated inputs.

For the isothermal CSTR analyzed in Numerical example ISO-2, the optimal forcing amplitudes $A_{C,opt}(\omega)$ and $A_{F,opt}(\omega)$, and the optimal phase difference $\varphi_{opt}(\omega)$ are numerically determined in Matlab by using standard *fminmax* function and graphically presented in Figure 3.8, as functions of the dimensionless forcing frequency. The optimal forcing parameters which correspond to maximal product yield are determined from equation (2.77).
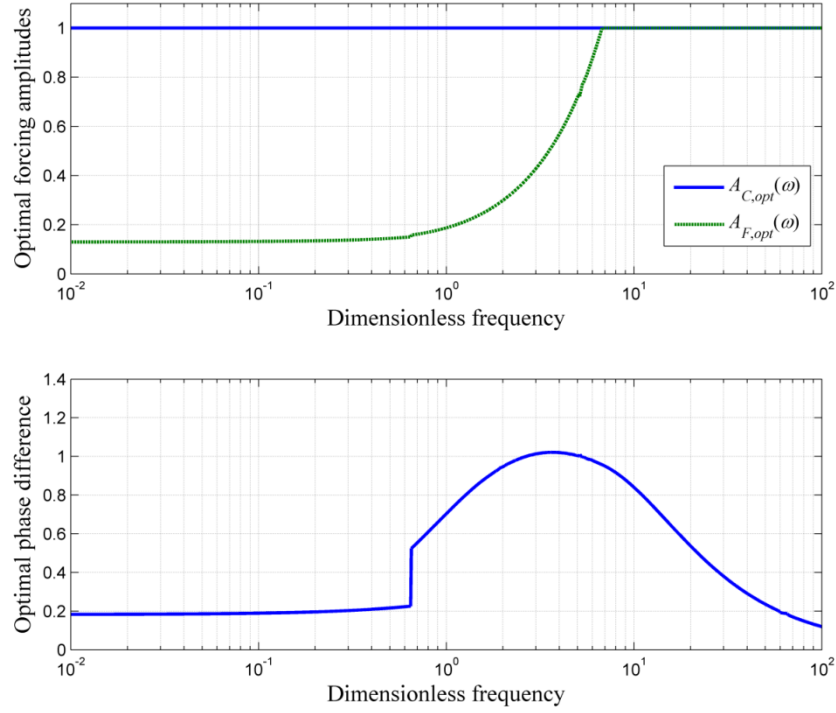
Figure 3.8 The optimal forcing amplitudes $A_{C,opt}(\omega)$, $A_{F,opt}(\omega)$, and the optimal phase difference $\varphi_{opt}(\omega)$ which maximize the product yield for simultaneous modulation of inlet concentration and flow-rate, vs. dimensionless forcing frequency

The optimal forcing amplitude for inlet concentration modulation is $A_{C,opt}(\omega)=100\%$ in the whole frequency range, which is expected concerning that the ASO FRF $G_{P2,CC}(\omega,-\omega)$ is positive. On the other hand, for flow-rate modulation, the optimal forcing amplitude is small for low-forcing frequencies where the ASO FRF $H_{P2,FF}(\omega,-\omega)$ is negative, while for high forcing frequencies where the ASO FRF $H_{P2,FF}(\omega,-\omega)$ tends zero the optimal forcing amplitudes is $A_{F,opt}(\omega)=100\%$.

Then, the product yield for simultaneous modulation of inlet concentration and flow-rate with the optimal forcing amplitudes and optimal phase difference is graphically presented in Figure 3.9. In the same Figure, the product yields for single input modulations with same forcing amplitudes, as well as for steady-state operation, are also given.
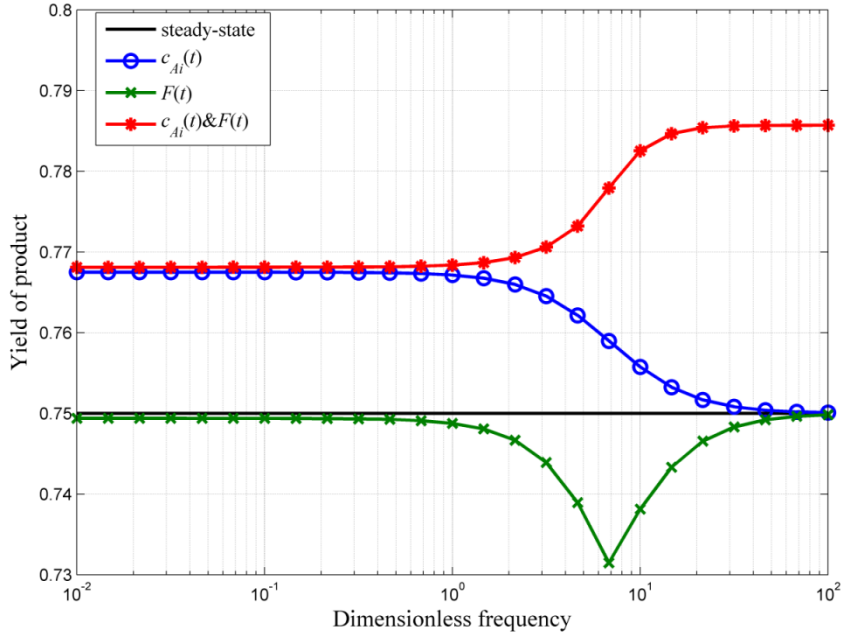
Figure 3.9 The yield of the product for steady-state operation, for periodic modulation of inlet concentration ($A_{C,opt}(\omega)$), for flow-rate modulation ($A_{F,opt}(\omega)$) and for simultaneous modulation of these two inputs with optimal forcing amplitudes and optimal phase difference $\varphi_{opt}(\omega)$ corresponding to them, vs. dimensionless forcing frequency

When the optimal forcing amplitudes and phase difference are used, the yield of the product for low-forcing frequencies is insignificantly higher than for the single input modulation of inlet concentration. For high-forcing frequencies, the increase of yield is higher when the optimal forcing parameters are used in comparison to the previous investigated case, and again higher than for low-frequency single input modulation of inlet concentration. When both optimal forcing amplitudes and optimal phase difference are used, the increase of the product yield is higher than for arbitrary chosen forcing amplitudes (Figure 3.7).

Comparison with the results obtained by numerical integration

In order to prove the effectiveness of the NFR method, the approximate values of the product yields, calculated by the NFR method are compared with the results obtained by numerical simulations, for periodic modulation of the inlet concentration and flow-rate, separately and simultaneously, around the previously established steady-state. The numerical integration was performed by using the dimensional mathematical model of the isothermal CSTR (Eqs. ((3.2) and (3.3)), for the system defined in Numerical

example ISO-2. The model equations were solved by using a standard Matlab function *ode15s.*

Comparison of the product yields estimated by the NFR method and calculated by numerical simulation is shown in Tables 3.4, 3.5 and 3.6. The results obtained for single input modulation of the inlet concentration with forcing amplitude A_C=100% and for single input modulation of the flow-rate with forcing amplitude A_F=75%, for dimensionless forcing frequencies ω=0.1, 1, and 10 are given in Table 3.4. In Tables 3.5 and 3.6, the numerical results are compared with results of NFR method for simultaneous modulation of inlet concentration and flow-rate. In Table 3.5, the product yields are determined for the case when arbitrary forcing amplitudes (A_C=100% and A_F=75%) and optimal phase difference corresponding to them are used $\varphi_{opt}(\omega)$ for dimensionless forcing frequencies ω=0.1, 1, and 10. In Table 3.6, the results are given for the optimal forcing amplitudes $A_{C,opt}(\omega)$ and $A_{F,opt}(\omega)$ and the optimal phase differences $\varphi_{opt}(\omega)$ corresponding to them.

The relative changes of product yield owning to the periodic operation were also calculated,

$$\Delta Y_{P,po}(\%) = \frac{Y_{P,po} - Y_{P,s}}{Y_{P,s}} \, 100$$

(3.59)

and they are given in Tables 3.4-3.6, in percentages.

In order to compare the agreement between the approximate results obtained by the NFR method with the results of numerical integration, which are considered to be exact, the relative errors for product yields were calculated in the following way:

$$\delta_Y(\%) = \frac{Y_{P,po}(NFRM) - Y_{P,po}(num)}{Y_{P,po}(num)} 100$$

(3.60)

and they are also given in Tables 3.4-3.6.

Table 3.4 Yields of the product and their relative changes for single input modulation of the inlet concentration and the flow-rate, estimated by numerical simulation and by the NFR method, and the relative errors

Inlet concentration modulation, A_C=100%					
ω	$Y_{P,po}$ (%)		δ_Y (%)	$\Delta Y_{P,po}$ (%)	
	num	NFRM		num	NFRM
0.1	77.62	76.75	-1.16	+3.49	+2.33
1	77.33	76.71	-0.80	+3.11	+2.28
10	75.59	75.57	-0.03	+0.79	+0.76
Flow-rate modulation, A_F=75%					
ω	$Y_{P,po}$ (%)		δ_Y (%)	$\Delta Y_{P,po}$ (%)	
	num	NFRM		num	NFRM
0.1	72.89	72.97	+0.11	-2.81	-2.71
1	72.95	73.01	+0.08	-2.73	-2.65
10	74.37	74.33	-0.05	-0.84	-0.89

Table 3.5 Yields of the product and their relative changes for simultaneous modulation of the inlet concentration and the flow-rate with optimal phase differences, estimated by numerical simulation and by the NFR method, and the relative errors

Simultaneous modulation of inlet concentration and flow-rate, A_C=100%, A_F=75%, $\varphi=\varphi_{opt}$						
ω	φ_{opt} (rad)	$Y_{P,po}$ (%)		δ_Y (%)	$\Delta Y_{P,po}$ (%)	
		num	NFRM		num	NFRM
0.1	0.0600	75.77	75.81	+0.05	+1.03	+1.08
1	0.5035	75.87	75.98	+0.14	+1.16	+1.31
10	0.7063	77.84	77.88	+0.05	+3.79	+3.84

Table 3.6 Yields of the product and their relative changes for simultaneous modulation of the inlet concentration and the flow-rate with optimal forcing amplitudes and phase differences, estimated by numerical simulation and by the NFR method, and the relative errors

Simultaneous modulation of inlet concentration and flow-rate
ω	$A_{C,opt}$ (%)	$A_{F,opt}$ (%)	φ_{opt} (rad)		$Y_{P,po}$ (%)	δ_Y (%)		$\Delta Y_{P,po}$ (%)
				num	NFRM		num	NFRM
0.1		13.20	0.1892	77.41	76.81	-0.78	+3.21	+2.41
1	100	18.73	0.7038	77.22	76.84	-0.49	+2.96	+2.45
10		100	0.8394	78.18	78.25	+0.09	+4.24	+4.33

From the results which are given in Tables 3.4, 3.5 and 3.6, it can be concluded that good agreement between the approximate results (product yield and their relative change) estimated by the NFR method with the results obtained by numerical integration (which are considered to be exact) for periodic modulation of the inlet concentration or/and flow-rate is obtained. The relative errors are less than $\pm 1.2\%$, which leads to a conclusion that the NFR method, based on the second order approximation, gives excellent prediction of the magnitude of the product yield for the periodically operated isothermal CSTR.

As expected, from the NFR analysis, the improvement (higher yield) can be obtained with single input modulation of the inlet concentration and for simultaneous modulation of both inputs, which was confirmed with the results of numerical integration given in Tables 3.4-3.6.

3.11. Summary of Chapter III

In this Chapter, the nonlinear frequency response method was used for evaluation of possible improvement of forced periodically operated isothermal CSTR in which homogeneous, irreversible simple nth order reaction A→v_PP takes place, when inlet concentration and flow-rate were modulated separately (single input modulation) or simultaneously (two-input modulation).

The general methodology of the derivation procedure was used for derivation of the necessary ASO FRFs which determine the outlet reactant and product DC components, and thus the yield of the product or conversion of the reactant:

- The asymmetrical frequency response functions which correlate the outlet concentration of the reactant and the product with the modulated inlet concentration ($G_{A2,CC}(\omega,-\omega)$ and $G_{P2,CC}(\omega,-\omega)$)
- The asymmetrical frequency response function which correlate the outlet molar flow-rates of the reactant and the product to the modulated flow-rate ($H_{A2,FF}(\omega,-\omega)$ and $H_{P2,FF}(\omega,-\omega)$)
- The cross asymmetrical frequency response function which correlates the outlet molar flow-rates of the reactant and the product to modulated inputs, inlet concentration and flow-rate ($H_{A2,CF}(\omega,-\omega)$ and $H_{P2,CF}(\omega,-\omega)$).

From the expression of the ASO FRFs, it was concluded that the high-frequency single input modulation had no influence on the reactor performance and that for the low-frequency modulation the ASO FRFs tended to asymptotic values. On the contrary, simultaneous modulation of inlet concentration and flow-rate had influence on the reactor performance in the whole frequency range.

From the correlations between the reactant and product asymmetrical frequency response functions for each case of periodic modulation, it was concluded that the analysis of one of them (reactant or product ASO FRFs) was enough, considering that both approaches lead to the same conclusions.

The sign analysis of the ASO FRFs which correspond to the single input modulation of the inlet concentration or flow-rate was performed. It was concluded that for single input modulation of the inlet concentration the improvement would always be obtained for negative reaction orders ($n<0$) and for reaction orders higher than 1 ($n>1$), while for the reaction orders between 0 and 1 ($0<n<1$), the reactor performance would be deteriorated. For reaction orders $n=1$ and $n=0$, the modulation of inlet concentration would not influence the reactor performance. On the other hand, for single input modulation of the flow-rate, an auxiliary parameter n_F exists, which depends on the characteristics of reactor system which needs to be evaluated in order to predict the sign of the corresponding ASO FRF, and thus the possible improvement. Nevertheless, positive reaction orders ($n>0$) will always lead to deterioration of the reactor performance and for $n=0$, the periodic modulation of flow-rate will not influence the reactor performance. If reaction order is negative, than it was shown that the reactor performance would be improved for $n_F<n<0$ and deteriorated for $n<n_F$.

The results of the NFR method were tested on two numerical examples, Numerical example ISO-1 and Numerical example ISO-2. The Numerical example ISO-1 included analysis for different reaction orders. The prediction of the sign analysis for single input modulations was confirmed with simulations of the ASO FRFs. Therefore, it can be decided whether to operate in the periodic regime or not, based only on the sign analysis of the corresponding ASO FRF.

For Numerical example ISO-2, which corresponds to an optimized industrial reactor taken from the literature, separate and simultaneous modulation of inlet concentration and flow-rate were analyzed by the NFR method, and it was concluded that:

- Single input modulation of the inlet concentration will lead to increase of the product yield, which is highest for low-forcing frequencies, but is still low (for maximal forcing amplitude $A_C=100\%$, the relative increase of the product yield was $\Delta Y_P=2.33\%$;

- Single input modulation of the flow-rate will cause the product yield decrease;

- The results of the sign analysis again gave correct predictions of the signs of ASO FRFs for single input modulations;

- The forcing amplitudes and phase difference for simultaneous modulation of the two inputs have a decisive role on the reactor performance;

- For simultaneous modulation of the inlet concentration and flow-rate, when the optimal forcing parameters (which maximize the product yield) were used, the yield of product could be increased. For low-forcing frequencies this increase was insignificantly higher than for single input modulation of the inlet concentration, but for high-forcing frequencies modulations, this increase is higher;

- Still, the highest increase of the product yield which can be achieved for this industrial reactor system is modest, and the highest increase of $\Delta Y_P \approx 4.76\%$ can be obtained for high-forcing frequency simultaneous modulation of inlet concentration and flow-rate, with maximal forcing amplitudes ($A_C=A_F=100\%$) and the corresponding optimal phase difference.

- The results of the NFR method were compared with the results of numerical integration and very good agreement was obtained, both for separate and for simultaneous modulations of the inlet concentration and flow-rate.

IV Application of nonlinear frequency response method for evaluation of periodically operated non-isothermal CSTRs

4.1. Forced periodic operations of non-isothermal CSTRs

In this Chapter, the NFR method is applied for evaluation of periodically operated non-isothermal CSTRs. Besides the two inputs which can be modulated for isothermal CSTRs, the concentration of the feed steam and its flow-rate, for the case of a non-isothermal CSTRs two additional inputs can also be periodically modulated: the temperature of the feed stream and the temperature of the cooling/heating fluid (*Nikolić and Petkovska, 2014a*).

It can be expected to obtain much higher difference between the periodic and optimal steady-state operation for a non-isothermal reactors, because the equations used to describe the non-isothermal system contain exponential nonlinearity in the reactor temperature, so that nonlinear behavior often becomes visible even for small input disturbances. In addition, the system equations can have complex conjugate roots and, if the damping coefficient of the linearized equations is less than 0.707, the system can exhibit resonance. In this case, the reactor tends to amplify the effect of disturbances in the neighborhood of the resonant frequency and the larger deviations from the steady-state conditions will cause the nonlinear phenomena to become more pronounced (*Douglas, 1972*).

Since the potential for improvement through periodic operation strongly depends on the degree of the nonlinearity of the system, it is expected that the non-isothermal CSTR, which is highly nonlinear, would offer a lot of potential for process improvement. Also, the non-isothermal CSTR is a good test for the NFR method considering that the method is valid for weakly nonlinear systems (*Nikolić and Petkovska, 2014a*).

Considering that the NFR method is applicable only for stable systems and the fact that a non-isothermal CSTR can in principle exhibit unstable behavior (*Douglas, 1972*), the stability analysis is very important.

In this Chapter, the NFR method is applied for evaluation of periodic operations of non-isothermal CSTRs in which a simple *n*th order, irreversible, homogeneous chemical reaction takes place for single input modulation of the concentration of the reactant in the feed stream, the flow-rate, the temperature of the feed stream and the temperature of the cooling/heating fluid. Part of these results has been published in (*Nikolić et al.,*

2014a, 2014b). The analysis of forced periodic operation of non-isothermal CSTRs is also performed for the case of simultaneous modulation of two inputs, inlet concentration and inlet temperature (part of this investigation has been published in (*Nikolić et al.,* 2015) as well as inlet concentration and flow-rate (publication in preparation).

In principle, six combinations are possible for simultaneous modulation of two inputs, as four inputs can be modulated, but, in this work, we limited our investigation just on two combinations for two input modulation, as stated above.

4.2. Mathematical model

The non-isothermal CSTR is considered in which a simple, irreversible, liquid homogeneous *n*th order chemical reaction, $A \longrightarrow \nu_P P$, takes place, with a rate law

$$r = k_o e^{-\frac{E_A}{RT}} c_A^n$$

(4.1)

where c_A is the reactant concentration, T the temperature, k_o the pre-exponential factor in the Arrhenius equation, E_A activation energy and R the universal gas constant.

The mathematical model consists of the material balances of the reactant:

$$V \frac{dc_A(t)}{dt} = F(t)c_{A,i}(t) - F(t)c_A(t) - k_o e^{-\frac{E_A}{RT(t)}} c_A^n(t) V$$

(4.2)

material balance of the product

$$V \frac{dc_P(t)}{dt} = -F(t)c_P(t) + \nu_P k_o e^{-\frac{E_A}{RT(t)}} c_A^n(t) V$$

(4.3)

and the energy balance

$$V \rho c_p \frac{dT(t)}{dt} = F(t)\rho \bar{c}_p T_i(t) - F(t)\rho \bar{c}_p T(t) + (-\Delta H_R) k_o e^{-\frac{E_A}{RT(t)}} c_A^n(t) V$$
$$- U A_w \big(T(t) - T_J(t) \big)$$

(4.4)

The notations used for the isothermal CSTR are also used for the non-isothermal CSTR. The new notations used in the mathematical model of the non-isothermal CSTR are: ΔH_R heat of reaction, U the overall heat transfer coefficient, A_w the surface for heat

exchange, ρ density and $\overline{c}_p$ heat capacity. The subscript i which is used in the balance equations denotes the inlet, and the subscript J the heating/cooling fluid in the reactor jacket.

The mathematical model of the non-isothermal CSTR is based on the following assumptions: all physical and chemical properties are constant, independent on temperature (ρ, $\overline{c}_p$, ΔH_R, k_o, E_A, U), the volume of the reactor is constant, (meaning that inlet flow-rate is equal to outlet flow-rate ($V=const$, $F_i(t)=F(t)$), and the flow-rate of the cooling/heating fluid is sufficiently high to ensure that the inlet temperature in the jacket is equal to outlet temperature from the jacket.

The material and energy balances in the steady-state are reduced to the following equations

$$\frac{c_{Ai,s}}{c_{A,s}} = 1 + k_o e^{-\frac{E_A}{RT_s}} c_{A,s}^{n-1} \frac{V}{F_s}$$

(4.5)

$$c_{P,s} = \nu_P k_o e^{-\frac{E_A}{RT_s}} c_{A,s}^{n} \frac{V}{F_s}$$

(4.6)

$$\frac{T_{i,s}}{T_s} = 1 - \frac{(-\Delta H_R) k_o e^{-\frac{E_A}{RT_s}} c_{A,s}^{n}}{\rho \overline{c}_p T_s} \frac{V}{F_s} + \frac{UA_w}{F_s \rho \overline{c}_p} - \frac{UA_w T_{J,s}}{F_s \rho \overline{c}_p T_s}$$

(4.7)

The following dimensionless auxiliary parameters can be introduced

$$\alpha = k_o e^{-\frac{E_A}{RT_s}} c_{A,s}^{n-1} \frac{V}{F_s}, \quad \beta = \frac{\Delta H_R k_o e^{-\frac{E_A}{RT_s}} c_{A,s}^{n}}{\rho \overline{c}_p T_s} \frac{V}{F_s}, \quad \delta = \frac{UA_w T_{J,s}}{F_s \rho \overline{c}_p T_s}, \quad \gamma = \frac{E_A}{RT_s}, \quad St = \frac{UA_w}{F_s \rho \overline{c}_p}$$

(4.8)

and incorporated in the steady-state material and energy balances, they lead to:

$$\frac{c_{Ai,s}}{c_{A,s}} = 1 + \alpha$$

(4.9)

$$\frac{c_{P,s}}{c_{A,s}} = \nu_P \alpha$$

(4.10)

$$\frac{T_{i,s}}{T_s} = 1 + \beta + St - \delta$$

$$(4.11)$$

The introduced dimensionless auxiliary parameters (α, β, δ, γ and St) depend on:

- the kinetic and thermodynamic data of the chemical reaction (n, k_o, E_A, ΔH_R),

- the physical and thermodynamic parameters of the reactor system (V, ρ, $\overline{c_p}$, U, A_w)

- the steady-state reactant concentration ($c_{A,s}$), temperature in the reactor (T_s), flow-rate (F_s) and the temperature of the cooling/heating fluid ($T_{J,s}$).

Again, the model equations are transformed into dimensionless form for easier analysis in the frequency domain. Besides the dimensionless variables defined in the previous Chapter, for the isothermal CSTR (Table 3.1) which have been defined as relative deviations from their steady-state values, additional dimensionless variables for the non-isothermal CSTR are given in Table 4.1.

Table 4.1 Definitions of additional dimensionless variables for non-isothermal CSTR

Inlet temperature	$\theta_i = \dfrac{T_i - T_{i,s}}{T_{i,s}}$
Temperature in the reactor	$\theta = \dfrac{T - T_s}{T_s}$
Temperature of the heating/cooling fluid	$\theta_J = \dfrac{T_J - T_{J,s}}{T_{J,s}}$

The dimensionless variables (Tables 3.1 and 4.1) and the auxiliary parameters (Eq. (4.8)) are introduced in the model equations (Eqs. (4.2)-(4.4)) and the following dimensionless equations are obtained:

$$\frac{dC_A}{d\tau} = (1 + \alpha)(\Phi + 1)(C_{Ai} + 1) - (\Phi + 1)(C_A + 1) - k_o c_{A,s}^{n-1} \frac{V}{F_s} e^{-\frac{E_A}{RT_s(\theta+1)}}(1 + C_A)^n$$

$$(4.12)$$

$$\frac{dC_P}{d\tau} = -(\Phi + 1)(C_P + 1) + k_o \frac{c_{A,s}^n}{c_{P,s}} \frac{V}{F_s} e^{-\frac{E_A}{RT_s(\theta+1)}}(1 + C_A)^n$$

$$(4.13)$$

$$\frac{d\theta}{d\tau} = (1 + \beta + St - \delta)(\Phi + 1)(\theta_i + 1) - (\Phi + 1)(\theta + 1) - St(\theta + 1) - \delta(\theta_J + 1)$$

$$- \frac{\Delta H_R k_o c_{A,s}^n V}{\rho \overline{c_p} T_s F_s} e^{-\frac{E_A}{RT_s(\theta+1)}}(1 + C_A)^n$$

(4.14)

Since, for application of the NFR method all nonlinearities should be given in the polynomial form, the nonlinear terms in the dimensionless model equations $e^{-\frac{E_A}{RT_s(\theta+1)}}$ and $(1 + C_A)^n$ are expanded in the Taylor series form, around the steady-state point. For our analysis only the first and second order terms are shown. The Taylor series expansions of these nonlinear terms are given in Appendix B1. The terms $F(t)c_{Ai}(t)$, $F(t)c_A(t)$ (in Eq. (4.2)), $F(t)c_P(t)$ (in Eq. (4.3)) and $F(t)T_i(t)$, $F(t)T(t)$ (in Eq. (4.4)) are also nonlinear, and their expansion in Taylor series is done in an analogy as for isothermal CSTR (given in Appendix A.1).

The Taylor series expansions of the nonlinear terms are incorporated into equations ((4.12)-(4.14)), and the following final form of the dimensionless model equations is obtained:

$$\frac{dC_A}{d\tau} = (1 + \alpha)C_{Ai} + (1 + \alpha)\Phi C_{A,i} - (1 + n\alpha)C_A - \alpha\gamma\theta + \alpha\Phi - \Phi C_A$$

$$- \alpha\left(n\gamma C_A\theta + \left(\frac{\gamma^2}{2} - \gamma\right)\theta^2 + \frac{1}{2}n(n-1)C_A^2 + \cdots\right)$$

(4.15)

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

(4.16)

$$\frac{d\theta}{d\tau} = (1 + \beta + St - \delta)\Phi\theta_i + (1 + \beta + St - \delta)\theta_i - (1 + St + \beta\gamma)\theta - n\beta C_A$$

$$+ (\beta + St - \delta)\Phi - \Phi\theta + \delta\theta_J$$

$$- \beta\left(n\gamma C_A\theta + \left(\frac{\gamma^2}{2} - \gamma\right)\theta^2 + \frac{1}{2}n(n-1)C_A^2 + \cdots\right)$$

(4.17)

Equations ((4.15)-(4.17)) represent the dimensionless model equations of the non-isothermal CSTR for the general case, i.e. simultaneous modulation of all possible modulated inputs: inlet concentration (C_{Ai}), flow-rate (Φ), inlet temperature (θ_i) and

temperature of the cooling/heating fluid (θ_J). These equations can be easily reduced for each specific case of the forced periodic modulation of the non-isothermal CSTR. For instance, for single input modulation all dimensionless inputs which are not subject of the periodic modulation are set to zero. For simultaneous modulation of two-inputs, all others dimensionless inputs except modulated ones, should be set to zero and so on.

4.3. Stability analysis

As already stated, the NFR method is applicable only for stable systems while the non-isothermal CSTR can be unstable. Because of that, it is important to analyze the stability of the reactor and to determine the domain in which the non-isothermal CSTR is stable first. By analyzing the characteristic equation which corresponds to the linearized model, the stability and oscillatory domains of the system can be easily determined.

The characteristic equation of the system can be obtained after applying Laplace transform on the linearized mathematical model of the non-isothermal CSTR:

$$\frac{dC_A}{d\tau} = (1 + \alpha)C_{Ai} - (1 + n\alpha)C_A - \alpha\gamma\theta + \alpha\Phi$$

(4.18)

$$\frac{dC_P}{d\tau} = nC_A - C_P + \gamma\theta - \Phi$$

(4.19)

$$\frac{d\theta}{d\tau} = (1 + \beta + St - \delta)\theta_i - (1 + St + \beta\gamma)\theta - n\beta C_A + (\beta + St - \delta)\Phi + \delta\theta_J$$

(4.20)

after equating the denominator of the transfer functions to zero.

The characteristic equation of the non-isothermal CSTR defined with model equations ((4.2)-(4.4)) is

$$(s + 1) \times \left(s^2 + s(2 + \beta\gamma + St + n\alpha) + (1 + n\alpha + \beta\gamma + n\alpha St + St)\right) = 0 \qquad (4.21)$$

The roots of this characteristic equation, i.e. the poles of the non-isothermal CSTR, are:

$$p_1 = -1$$

(4.22)

$$p_{2,3} = A_{ps} \pm \sqrt{A_{ps}^2 - B_{ps}}$$

(4.23)

where the following stability parameters A_{ps} and B_{ps} have been introduced

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

(4.24)

$$B_{ps} = (1 + n\alpha + \beta\gamma + n\alpha St + St)$$
(4.25)

As $p_1=-1$ is always negative, the analysis of the roots of characteristic equation shows that the non-isothermal CSTR will be stable if p_2 and p_3 have negative real parts, i.e., if the following conditions are met (*Nikolić et al., 2014a*):

$$A_{ps} < 0 \text{ and } B_{ps} > 0$$
(4.26)

Thus, the NFR method and the concept of higher frequency response functions can be applied for a forced periodically operated non-isothermal CSTR only if $A_{ps}<0$ and $B_{ps}>0$, i.e. in the domain of the reactor stability.

The oscillatory domain can also be determined by analyzing the roots of the characteristic equation. If all roots of the characteristic equation are real the system is non-oscillatory, otherwise, if the roots of the characteristic equation are conjugate-complex, the system will be oscillatory (*Douglas, 1972*).

Therefore, the system is oscillatory for $A_{ps}^2<B_{ps}$, and otherwise, if $A_{ps}^2 \geq B_{ps}$ the system is non-oscillatory.

The stability and oscillatory domains for the non-isothermal CSTR, depending on the auxiliary parameters A_{ps} and B_{ps}, are graphically presented in Figure 4.1.
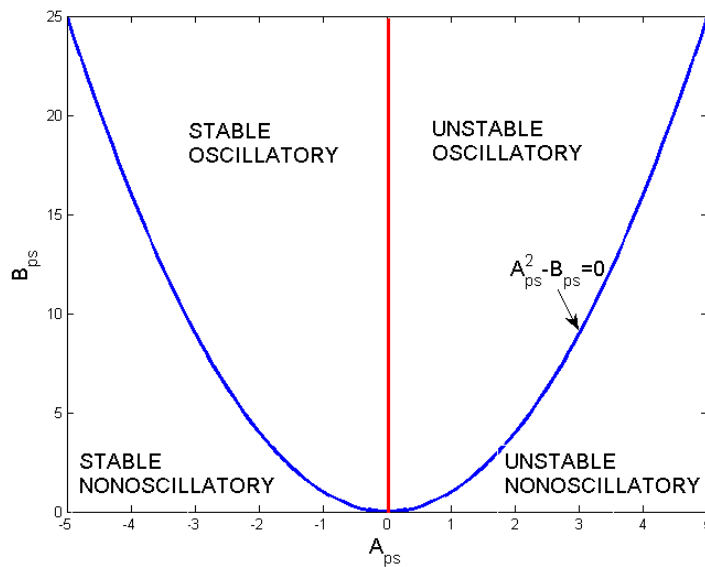
Figure 4.1 Areas of stability and oscillatory for a non-isothermal CSTR, depending on the stability parameters A_{ps} and B_{ps}

If the characteristic equation of the non-isothermal CSTR is given in the standard form of a second order system (*Douglas, 1972*)

$$s^2 + 2\xi\omega_n s + \omega_n^2 = 0 \qquad (4.27)$$

the damping coefficient (ξ) and the natural frequency (ω_n) can also be determined from the auxiliary stability parameters A_{ps} and B_{ps}:

$$\xi = -\frac{A_{ps}}{\sqrt{B_{ps}}}$$

$$\qquad (4.28)$$

$$\omega_n = \sqrt{B_{ps}} \qquad (4.29)$$

It is well known that a stable oscillatory system with damping coefficient less than 0.707 exhibits resonance, i.e., amplification of the inlet modulation for some input frequencies (*Douglas, 1972*). The frequency at which the amplitude of the outlet is maximal is called resonant frequency (*Douglas, 1972*).

For the non-isothermal CSTR which exhibits resonant behavior, the resonant frequency can also be determined form the auxiliary parameters A_{ps} and B_{ps} from the following equation:

$$\omega_r = \sqrt{B_{ps} - 2A_{ps}^2} \qquad (4.30)$$

4.4. Definition of the frequency response functions

Single input modulation

For single input periodic modulations, the non-isothermal CSTR represents a nonlinear system with one modulated input and three outputs, since modulation of each input will cause change of the reactant concentration, the product concentration and the temperature in the reactor.

Therefore, in order to describe the forced periodically operated non-isothermal CSTR for single input modulation, it is necessary to derive three sets of FRFs for modulated input.

For the general case of single input modulation, if the dimensionless input which is periodically modulated is defined as $X(\tau)$, in order to describe the system it is necessary to derive three sets of FRFs which correlate three outputs and the input $X(\tau)$

- Set 1: $G_{A1,X}(\omega)$, $G_{A2,XX}(\omega,-\omega)$,… - FRFs which correlate the dimensionless outlet concentration of the reactant $C_A(\tau)$ with the modulated dimensionless input $X(\tau)$;

- Set 2: $G_{P1,X}(\omega)$, $G_{P2,XX}(\omega,-\omega)$,… - FRFs which correlate the dimensionless outlet concentration of the product $C_P(\tau)$ with the modulated dimensionless input $X(\tau)$;

- Set 3: $F_{1,X}(\omega)$, $F_{2,XX}(\omega,-\omega)$,… - FRFs which correlate the dimensionless outlet temperature $\theta(\tau)$ with the modulated dimensionless input $X(\tau)$.

If flow-rate is the input which is modulated, in order to evaluate the possible improvement, the reactant H ASO FRF ($H_{A2,FF}(\omega,-\omega)$) should be derived from the reactant G-FRFs $G_{A1,F}(\omega)$ and $G_{A2,FF}(\omega,-\omega)$ (Eq. (2.44)) and the product H ASO FRF ($H_{P2,FF}(\omega,-\omega)$) should be derived from the product G-FRFs $G_{P1,F}(\omega)$ and $G_{P2,FF}(\omega,-\omega)$ (Eq. (2.45)).

Simultaneous modulation of two inputs

When two inputs of the non-isothermal CSTR are simultaneously periodically modulated, it represents a nonlinear system with two modulated inputs and three outputs: the outlet concentration of the reactant, the outlet concentration of the product and the outlet temperature.

If the dimensionless inputs which are periodically modulated are denoted as $X(\tau)$ and $Z(\tau)$, in order to describe the system, it is necessary to derive nine sets of FRFs: three sets of FRFs which correspond to the single input modulation of input $X(\tau)$ (listed above), three sets of FRFs which correspond to single input modulation of input $Z(\tau)$:

- Set 4: $G_{A1,Z}(\omega)$, $G_{A2,ZZ}(\omega,-\omega)$,…- FRFs which correlate the dimensionless outlet concentration of the reactant $C_A(\tau)$ with the modulated dimensionless input $Z(\tau)$;

- Set 5: $G_{P1,Z}(\omega)$, $G_{P2,ZZ}(\omega,-\omega)$,…- FRFs which correlate the dimensionless outlet concentration of the product $C_P(\tau)$ with the modulated dimensionless input $Z(\tau)$;

- Set 6: $F_{1,Z}(\omega)$, $F_{2,ZZ}(\omega,-\omega)$,… - FRFs which correlate the dimensionless outlet temperature $\theta(\tau)$ with the modulated dimensionless input $Z(\tau)$;

and three sets of cross FRFs, which correspond to simultaneous modulation of both inputs, $X(\tau)$ and $Z(\tau)$

- Set 7: $G_{A2,XZ}(\omega,-\omega)$, $G_{A2,XZ}(-\omega,\omega)$,… - The cross FRFs which correlate the dimensionless outlet concentration of the reactant $C_A(\tau)$ with the modulated dimensionless inputs $X(\tau)$ and $Z(\tau)$;

- Set 8: $G_{P2,XZ}(\omega,-\omega)$, $G_{P2,XZ}(-\omega,\omega)$,… - The cross FRFs which correlate the dimensionless outlet concentration of the product $C_P(\tau)$ with the modulated dimensionless inputs $X(\tau)$ and $Z(\tau)$;

- Set 9: $F_{2,XZ}(\omega,-\omega)$, $F_{2,XZ}(-\omega,\omega)$,… -The cross FRFs which correlate the dimensionless outlet temperature $\theta(\tau)$ with the modulated dimensionless inputs $X(\tau)$ and $Z(\tau)$.

For the case when the flow-rate and inlet concentration are simultaneously modulated, the reactant cross H ASO FRF $H_{A2,CF}(\omega,-\omega)$ should be derived from the reactant first order G-FRF $G_{A1,C}(\omega)$ and the reactant cross ASO FRF $G_{A2,CF}(\omega,-\omega)$ (Eq. (2.69)) and the product cross H ASO FRF $H_{P2,CF}(\omega,-\omega)$ needs to be derived from the product first order G FRF $G_{P1,C}(\omega)$ and the product cross ASO FRF $G_{P2,CF}(\omega,-\omega)$ (Eq. (2.70)).

Since we are interested in the improvement of the reactor performance, i.e. increase of reactant conversion or product yield, the outlet temperature is not of interest. Nevertheless, if it is necessary to follow the temperature in the reactor from the aspect of safety and equipment limitations, the mean outlet temperature can be estimated in an analogous way as the outlet concentrations, from the ASO FRFs $F_{2,XX}(\omega,-\omega)$ or/and $F_{2,ZZ}(\omega,-\omega)$ (and the cross ASO FRF $F_{2,XZ}(\omega,-\omega)$ for simultaneous modulation of two inputs), which correlate the outlet temperature with the modulated input(s).

The derivation of the F-FRFs will be give, since they need to be derived in the process of the derivation of the G-FRFs, but without their further analysis. The final expressions for the F FRFs will be given in Appendix B.2, B.3 and B.4.

4.5. Derivation procedure of the FRFs

The basic steps of the procedure for derivation of the frequency response functions for forced periodically operated non-isothermal CSTRs, similar as for the isothermal CSTRs, are:

1. For single input modulation, the modulated dimensionless input $X(\tau)$ (inlet concentration $C_{Ai}(\tau)$, flow-rate $\Phi(\tau)$, inlet temperature $\theta_i(\tau)$ or temperature of the heating/cooling fluid $\theta_J(\tau)$) is defined in the form of a co-sinusoidal function, while for simultaneous modulation of two-inputs, the two inputs are defined in the form of co-sinusoidal functions with equal frequencies, different amplitudes and a phase shift between them,

2. The outputs: the dimensionless outlet concentration of the reactant $C_A(\tau)$, the dimensionless outlet concentration of the product $C_P(\tau)$ and the dimensionless outlet temperature $\theta(\tau)$, are expressed in the Volterra series form,

3. The expressions for the dimensionless modulated input(s), from step 1 and dimensionless outputs, from step 2, are substituted into the corresponding dimensionless model equations (Eqs. (4.15)-(4.17)) while all dimensionless inputs which are not modulated should be equated to zero,

4. The method of harmonic probing is applied to the equations obtained in step 3, i.e., the terms with the same amplitude and frequency are collected and equated to zero,

5. The equations obtained in step 4 are solved.

As a result of the derivation procedure the final expressions for the ASO FRFs ($G_{A2,XX}(\omega,-\omega)$, $G_{P2,XX}(\omega,-\omega)$, $G_{A2,ZZ}(\omega,-\omega)$, $G_{P2,ZZ}(\omega,-\omega)$) and the cross ASO FRFs (($G_{A2,XZ}(\omega,-\omega)$, $G_{A2,XZ}(-\omega,\omega)$, $G_{P2,XZ}(\omega,-\omega)$ and $G_{P2,XZ}(-\omega,\omega)$)) will be obtained. Additionally, the H ASO FRFs should be derived for flow-rate modulation ($H_{A2,FF}(\omega,-\omega)$, $H_{P2,FF}(\omega,-\omega)$) and cross H ASO FRFs for simultaneous modulation of inlet concentration and flow-rate ($H_{A2,CF}(\omega,-\omega)$, $H_{P2,CF}(\omega,-\omega)$) from some of the derived G FRFs. Considering that the ASO FRFs $G_2(\omega,-\omega)$ is a conjugate complex function of $G_2(-\omega,\omega)$, which is also valid for cross ASO FRFs as well as for the H ASO FRFs, only one of them will be given ($G_2(\omega,-\omega)$ or $H_2(\omega,-\omega)$).

For single input modulation, the final expressions for the first and the ASO FRFs which correlate the outlet concentrations of the reactant and the product with each modulated input (inlet concentration, flow-rate, inlet temperature and temperature of the cooling/heating fluid), the G-functions, are obtained and given below, as well as the H-functions for flow-rate modulation. The basic steps of the derivation procedure for each modulated input are given in Appendix B.2. The ASO FRFs, expressed based on the first order FRFs are also given in Appendix B.2.

Furthermore, the cross ASO FRFs for simultaneous modulation of the inlet concentration and inlet temperature, as well as, both the G and the H cross ASO FRFs for simultaneous modulation of inlet concentration and flow-rate, are derived and given below. The basic steps of the derivation procedure for simultaneous modulation of the inlet concentration and inlet temperature are given in Appendix B.3, for simultaneous

modulation of the inlet concentration and flow-rate in Appendix B.4. Here, only the final expressions are given.

4.6. The *G*-frequency response functions

4.6.1. Inlet concentration modulation

The first order FRFs $G_{A1,C}(\omega)$ and $G_{P1,C}(\omega)$

$$G_{A1,C}(\omega) = \frac{(1+\alpha)(1+St+\beta\gamma+j\omega)}{B_{ps}-\omega^2-2A_{ps}\omega j}$$

(4.31)

$$G_{P1,C}(\omega) = \frac{n(1+\alpha)(1+St+j\omega)}{(1+j\omega)(B_{ps}-\omega^2-2A_{ps}\omega j)}$$

(4.32)

The ASO FRFs $G_{A2,CC}(\omega,-\omega)$ and $G_{P2,CC}(\omega,-\omega)$

$$G_{A2,CC}(\omega,-\omega) = -\frac{\alpha(1+\alpha)^2(1+St)}{2B_{ps}} \times \frac{\Lambda}{\left(B_{ps}-\omega^2\right)^2+4A_{ps}^2\omega^2}$$

(4.33)

$$G_{P2,CC}(\omega,-\omega) = \frac{(1+\alpha)^2(1+St)}{2B_{ps}} \times \frac{\Lambda}{\left(B_{ps}-\omega^2\right)^2+4A_{ps}^2\omega^2}$$

(4.34)

In the expressions of the ASO FRFs $G_{A2,CC}(\omega,-\omega)$ and $G_{P2,CC}(\omega,-\omega)$, an auxiliary parameter (Λ) is introduced

$$\Lambda = \Lambda_1\omega^2+\Lambda_2$$

(4.35)

where the Λ_1 and Λ_2 are defined as:

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

(4.36)

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

(4.37)

4.6.2. Flow-rate modulation

The first order FRFs $G_{A1,F}(\omega)$ and $G_{P1,F}(\omega)$

$$G_{A1,F}(\omega) = \frac{\alpha(1+St-\gamma(St-\delta)+j\omega)}{B_{ps}-\omega^2-2A_{ps}\omega j}$$

(4.38)

$$G_{P1,F}(\omega) = -\frac{(1 + St - \gamma(St - \delta) + j\omega)}{B_{ps} - \omega^2 - 2A_{ps}\omega j}$$

(4.39)

The ASO FRFs $G_{A2,FF}(\omega,\text{-}\omega)$ and $G_{P2,FF}(\omega,\text{-}\omega)$

$$G_{A2,FF}(\omega, -\omega) = -\frac{\alpha}{2B_{ps}} \times \frac{\Omega}{\left(B_{ps} - \omega^2\right)^2 + 4A_{ps}^2\omega^2}$$

(4.40)

$$G_{P2,FF}(\omega, -\omega) = \frac{1}{2B_{ps}} \times \frac{\Omega}{\left(B_{ps} - \omega^2\right)^2 + 4A_{ps}^2\omega^2}$$

(4.41)

An auxiliary parameter Ω was introduced in the numerators of the final expressions of the ASO FRFs $G_{A2,FF}(\omega,\text{-}\omega)$ and $G_{P2,FF}(\omega,\text{-}\omega)$:

$$\Omega = \Omega_1\omega^2 + \Omega_2 \tag{4.42}$$

Ω_1 and Ω_2 are functions of the reaction order n and all auxiliary parameters, which can be presented with the following expressions:

$$\Omega_1 = n(n-1)\alpha^2(1 + St) + 2n\alpha(1 + St)(1 + \gamma(\beta + St - \delta))$$
$$+ (2(1 + St + \beta\gamma) + \gamma(\gamma - 2)(1 + St)(\beta + St - \delta)^2)$$

(4.43)

$$\Omega_2 = n(n-1)\alpha^2(1 + St)\left(1 + St - \gamma(St - \delta)\right)^2$$
$$+ \gamma(\gamma - 2)(1 + St)\left(\beta + (St - \delta)(1 + n\alpha)\right)^2$$
$$+ 2n\alpha\gamma(1 + St)(\beta + (St - \delta)(1 + n\alpha))\left(1 + St - \gamma(St - \delta)\right)$$
$$+ 2\left(1 + St + \beta\gamma + n\alpha(1 + St)\right)\left((1 + \beta\gamma + St)(1 + St - \gamma(St - \delta))\right)$$
$$- \gamma(\beta + (St - \delta)(1 + n\alpha))\Big)$$

(4.44)

4.6.3. Modulation of inlet temperature

The first order FRFs $G_{A1,T}(\omega)$ and $G_{P1,T}(\omega)$

$$G_{A1,T}(\omega) = \frac{-\alpha\gamma(1 + \beta + St - \delta)}{B_{ps} - \omega^2 - 2A_{ps}\omega j}$$

(4.45)

$$G_{P1,T}(\omega) = \frac{\gamma(1 + \beta + St - \delta)}{B_{ps} - \omega^2 - 2A_{ps}\omega j}$$

(4.46)

The ASO FRFs $G_{A2,TT}(\omega,\text{-}\omega)$ and $G_{P2,TT}(\omega,\text{-}\omega)$

$$G_{A2,TT}(\omega, -\omega) = -\frac{\alpha\gamma(1 + St)(1 + \beta + St - \delta)^2}{2B_{ps}} \times \frac{\Psi}{\left(B_{ps} - \omega^2\right)^2 + 4A_{ps}^2\omega^2}$$

(4.47)

$$G_{P2,TT}(\omega, -\omega) = \frac{\gamma(1 + St)(1 + \beta + St - \delta)^2}{2B_{ps}} \times \frac{\Psi}{\left(B_{ps} - \omega^2\right)^2 + 4A_{ps}^2\omega^2}$$

(4.48)

The auxiliary parameter Ψ used, in the numerators of the ASO FRFs $G_{A2,TT}(\omega,\text{-}\omega)$ and $G_{P2,TT}(\omega,\text{-}\omega)$ is defined as:

$$\Psi = \Psi_1\omega^2 + \Psi_2$$

(4.49)

where the parameters Ψ_1 and Ψ_2 are defined as follows:

$$\Psi_1 = (\gamma - 2)$$

(4.50)

$$\Psi_2 = -2n^2\alpha^2 - \alpha(4 + \alpha\gamma)n + (\gamma - 2)$$

(4.51)

4.6.4. Modulation of temperature of the cooling/heating fluid

The first order FRFs $G_{A1,J}(\omega)$ and $G_{P1,J}(\omega)$

$$G_{A1,J}(\omega) = \frac{-\alpha\gamma\delta}{B_{ps} - \omega^2 - 2A_{ps}\omega j}$$

(4.52)

$$G_{P1,J}(\omega) = \frac{\gamma\delta}{B_{ps} - \omega^2 - 2A_{ps}\omega j}$$

(4.53)

The ASO FRFs $G_{A2,JJ}(\omega,\text{-}\omega)$ and $G_{P2,JJ}(\omega,\text{-}\omega)$

$$G_{A2,JJ}(\omega, -\omega) = -\frac{\alpha\gamma\delta^2(1 + St)}{2B_{ps}} \times \frac{\Psi}{\left(B_{ps} - \omega^2\right)^2 + 4A_{ps}^2\omega^2}$$

(4.54)

$$G_{P2,JJ}(\omega, -\omega) = \frac{\gamma \delta^2 (1 + St)}{2B_{ps}} \times \frac{\Psi}{\left(B_{ps} - \omega^2\right)^2 + 4A_{ps}^2 \omega^2}$$

<div align="right">(4.55)</div>

The auxiliary parameter which figures in the expressions in the ASO FRFs $G_{A2,JJ}(\omega,-\omega)$ and $G_{P2,JJ}(\omega,-\omega)$ is the same as in the ASO FRFs $G_{A2,TT}(\omega,-\omega)$ and $G_{P2,TT}(\omega,-\omega)$, defined with Eqs. ((4.49)-(4.51)).

4.6.5. Simultaneous modulation of inlet concentration and inlet temperature

The cross ASO FRFs $G_{A2,CT}(\omega,-\omega)$ and $G_{P2,CT}(\omega,-\omega)$

The cross ASO FRF $G_{A2,CT}(\omega,-\omega)$

$$G_{A2,CT}(\omega, -\omega)$$
$$= -\frac{n\alpha\gamma(1 + \alpha)(1 + St)(1 + \beta + St - \delta)}{B_{ps}}$$
$$\times \frac{\left((1 + St + \alpha(1 + St + \beta\gamma) + 2\beta(1 + n\alpha) + \omega^2) + j\omega(\alpha - 2\beta - St)\right)}{\left(B_{ps} - \omega^2\right)^2 + 4A_{ps}^2 \omega^2}$$

<div align="right">(4.56)</div>

can be written in the following form

$$G_{A2,CT}(\omega, -\omega) = Re\left(G_{A2,CT}(\omega, -\omega)\right) + jIm\left(G_{A2,CT}(\omega, -\omega)\right) \qquad (4.57)$$

where the real and imaginary parts of the cross ASO FRF $G_{A2,CT}(\omega,-\omega)$ are defined as:

$$Re\left(G_{A2,CT}(\omega, -\omega)\right)$$
$$= -\frac{n\alpha\gamma(1 + \alpha)(1 + St)(1 + \beta + St - \delta)}{B_{ps}}$$
$$\times \frac{(1 + St + \alpha(1 + St + \beta\gamma) + 2\beta(1 + n\alpha) + \omega^2)}{\left(B_{ps} - \omega^2\right)^2 + 4A_{ps}^2 \omega^2}$$

<div align="right">(4.58)</div>

$$Im\left(G_{A2,CT}(\omega, -\omega)\right) = -\frac{n\alpha\gamma(1 + \alpha)(1 + St)(1 + \beta + St - \delta)}{B_{ps}} \times \frac{\omega(\alpha - 2\beta - St)}{\left(B_{ps} - \omega^2\right)^2 + 4A_{ps}^2 \omega^2}$$

<div align="right">(4.59)</div>

In analogy, the cross ASO FRF $G_{P2,CT}(\omega,-\omega)$

$$G_{P2,CT}(\omega, -\omega)$$

$$= \frac{n\gamma(1 + \alpha)(1 + St)(1 + \beta + St - \delta)}{B_{ps}}$$

$$\times \frac{\left((1 + St + \alpha(1 + St + \beta\gamma) + 2\beta(1 + n\alpha) + \omega^2) + j\omega(\alpha - 2\beta - St)\right)}{\left(B_{ps} - \omega^2\right)^2 + 4A_{ps}^2\omega^2}$$

(4.60)

can be written in the form

$$G_{P2,CT}(\omega, -\omega) = Re\left(G_{P2,CT}(\omega, -\omega)\right) + jIm\left(G_{P2,CT}(\omega, -\omega)\right)$$ (4.61)

where the real and imaginary parts of the cross ASO FRF $G_{P2,CT}(\omega, -\omega)$ are defined as:

$$Re\left(G_{P2,CT}(\omega, -\omega)\right)$$

$$= \frac{n\gamma(1 + \alpha)(1 + St)(1 + \beta + St - \delta)}{B_{ps}}$$

$$\times \frac{(1 + St + \alpha(1 + St + \beta\gamma) + 2\beta(1 + n\alpha) + \omega^2)}{\left(B_{ps} - \omega^2\right)^2 + 4A_{ps}^2\omega^2}$$

(4.62)

$$Im\left(G_{P2,CT}(\omega, -\omega)\right) = \frac{n\gamma(1 + \alpha)(1 + St)(1 + \beta + St - \delta)}{B_{ps}} \times \frac{\omega(\alpha - 2\beta - St)}{\left(B_{ps} - \omega^2\right)^2 + 4A_{ps}^2\omega^2}$$

(4.63)

The cross ASO terms $G^*_{A2,CT}(\varphi, \omega)$ and $G^*_{P2,CT}(\varphi, \omega)$

$$G^*_{A2,CT}(\varphi, \omega) = \cos(\varphi)\,Re\left(G_{A2,CT}(\omega, -\omega)\right) + \sin(\varphi)\,Im\left(G_{A2,CT}(\omega, -\omega)\right)$$ (4.64)

$$G^*_{P2,CT}(\varphi, \omega) = \cos(\varphi)\,Re\left(G_{P2,CT}(\omega, -\omega)\right) + \sin(\varphi)\,Im\left(G_{P2,CT}(\omega, -\omega)\right)$$ (4.65)

The optimal phase differences

$$\varphi_{opt,A}(\omega) = \arctan\left(\frac{Im\left(G_{A2,CT}(\omega, -\omega)\right)}{Re\left(G_{A2,CT}(\omega, -\omega)\right)}\right) - \pi$$

(4.66)

$$\varphi_{opt,P}(\omega) = \arctan\left(\frac{Im\left(G_{P2,CT}(\omega, -\omega)\right)}{Re\left(G_{P2,CT}(\omega, -\omega)\right)}\right)$$

(4.67)

4.6.6. Simultaneous modulation of inlet concentration and flow-rate

The cross ASO FRFs $G_{A2,CF}(\omega,-\omega)$ and $G_{P2,CF}(\omega,-\omega)$

The cross ASO FRF $G_{A2,CF}(\omega,-\omega)$, can be written in the following way

$$G_{A2,CF}(\omega,-\omega) = \frac{(1+\alpha)}{B_{ps}} \times \frac{(\Pi_R + j\omega\Pi_I)}{\left(B_{ps} - \omega^2\right)^2 + 4A_{ps}^2\omega^2}$$

(4.68)

where two additional auxiliary parameters have been introduced, Π_R and Π_I.

The auxiliary parameter Π_R can be written in the polynomial form:

$$\Pi_R = \Pi_{R1}\omega^4 + \Pi_{R2}\omega^2 + \Pi_{R3}$$

(4.69)

with

$$\Pi_{R1} = 1 + \beta\gamma + St$$

(4.70)

$$\Pi_{R2} = n^2\alpha^2\beta\gamma$$
$$+ n\alpha\big(2(1+\beta\gamma+St)^2 + (1+\beta\gamma+St) - 2(1+St)(1+\beta\gamma+St)$$
$$+ \beta\gamma + \alpha(1+St) - \gamma(\beta+St-\delta)(1+St)\big) + (1+\beta\gamma+St)^3$$

(4.71)

$$\Pi_{R3} = n^2\alpha^2\beta\gamma(1+St)\big(1+St-(1+2(St-\delta))\big)$$
$$+ n\alpha\Big((1+St)(1+\beta\gamma+St)^2 - \beta\gamma(1+\beta\gamma+St)$$
$$+ \alpha(1+\beta\gamma+St)\big((1+St)-\gamma(St-\delta)\big) - \gamma(\beta+St-\delta)(1+St)(1$$
$$+ St + 2\beta)\Big)$$

(4.72)

Π_{R1}, Π_{R2} and Π_{R3} are functions of the reaction order and parameters α, β, γ, δ and St.

The auxiliary parameter Π_I can also be given in the polynomial form

$$\Pi_I = \Pi_{I1}\omega^2 + \Pi_{I2}$$

(4.73)

where the parameter Π_{I1} is a function of auxiliary parameters β, γ and St (and is equal to Π_{R1})

$$\Pi_{I1} = 1 + \beta\gamma + St$$

(4.74)

and Π_{I2} is a function of the reaction order and all auxiliary parameters (α, β, γ, δ and St)

$$\Pi_{I2} = n^2\alpha^2\beta\gamma$$
$$+ n\alpha((1 + \beta\gamma + St)^2 + \beta\gamma(1 + \beta\gamma + St) + \beta\gamma$$
$$- (1 + St)(1 + \beta\gamma + St) - \gamma(\beta + St - \delta)(1 + St)(\alpha - St - 2\beta))$$
$$+ (1 + \beta\gamma + St)^3$$

(4.75)

The cross ASO FRF $G_{P2,CF}(\omega,-\omega)$ can be written in the following way:

$$G_{P2,CF}(\omega, -\omega) = \frac{(1 + \alpha)}{\alpha B_{ps}} \times \frac{(\Gamma_R + j\omega\Gamma_I)}{(\omega^2 + 1)\left(\left(B_{ps} - \omega^2\right)^2 + 4A_{ps}^2\omega^2\right)}$$

(4.76)

by introducing the auxiliary functions Γ_R and Γ_I

$$\Gamma_R = B_{ps}\left(\left(B_{ps} - \omega^2\right)^2 + 4A_{ps}^2\omega^2\right)\omega^2 - (\omega^2 + 1)\Pi_R$$

(4.77)

$$\Gamma_I = B_{ps}\left(\left(B_{ps} - \omega^2\right)^2 + 4A_{ps}^2\omega^2\right) - (\omega^2 + 1)\Pi_I$$

(4.78)

The auxiliary functions Γ_R and Γ_I can also be presented in their developed polynomial forms which are, owing to their complexity, given in Appendix B5.

4.7. The *H*-asymmetrical second order frequency response functions

4.7.1. Flow-rate modulation

The ASO FRFs $H_{A2,FF}(\omega,-\omega)$ and $H_{P2,FF}(\omega,-\omega)$

$$H_{A2,FF}(\omega, -\omega) = -\frac{\alpha}{2B_{ps}} \times \frac{\Omega_H}{\left(B_{ps} - \omega^2\right)^2 + 4A_{ps}^2\omega^2}$$

(4.79)

$$H_{P2,FF}(\omega, -\omega) = \frac{1}{2B_{ps}} \times \frac{\Omega_H}{\left(B_{ps} - \omega^2\right)^2 + 4A_{ps}^2\omega^2}$$

(4.80)

The auxiliary parameter Ω_H, introduced in the numerator of the ASO FRFs $H_{A2,FF}(\omega,-\omega)$ and $H_{P2,FF}(\omega,-\omega)$ is:

$$\Omega_H = \Omega_{1H}\omega^2 + \Omega_{2H}$$

(4.81)

where Ω_{1H} and Ω_{2H} are functions of the auxiliary functions Ω_1 and Ω_2, respectively and, therefore of the reaction order n and all auxiliary parameters (α, β, γ, δ and St):

$$\Omega_{1H} = \Omega_1 + 2B_{ps}\big(1 + St - \gamma(St - \delta)\big) + 4A_{ps}B_{ps} \tag{4.82}$$

$$\Omega_{2H} = \Omega_2 - 2\big(1 + St - \gamma(St - \delta)\big)B_{ps}^2 \tag{4.83}$$

4.7.2. Simultaneous modulation of inlet concentration and flow-rate

The cross ASO FRFs $H_{A2,CF}(\omega,\text{-}\omega)$ and $H_{P2,CF}(\omega,\text{-}\omega)$

The cross ASO FRF $H_{A2,CF}(\omega,\text{-}\omega)$ can be written in the following way:

$$H_{A2,CF}(\omega, -\omega) = \frac{1 + \alpha}{B_{ps}} \times \frac{(\Pi_{RH} + j\omega\Pi_{IH})}{\big(B_{ps} - \omega^2\big)^2 + 4A_{ps}^2\omega^2}$$

$$\tag{4.84}$$

with the newly introduced auxiliary functions Π_{RH} and Π_{IH}:

$$\Pi_{RH} = \Pi_R + B_{ps}\big(B_{ps} - \omega^2\big)(1 + St + \beta\gamma) - 2A_{ps}B_{ps}\omega^2 \tag{4.85}$$

$$\Pi_{IH} = \Pi_I + B_{ps}\big(B_{ps} - \omega^2\big) + 2A_{ps}B_{ps}(1 + St + \beta\gamma) \tag{4.86}$$

Their developed polynomial forms are given in Appendix B6.

The cross ASO FRF $H_{A2,CF}(\omega,\text{-}\omega)$ can also be given in the following form:

$$H_{A2,CF}(\omega, -\omega) = Re\left(H_{A2,CF}(\omega, -\omega)\right) + jIm\left(H_{A2,CF}(\omega, -\omega)\right) \tag{4.87}$$

where its real and imaginary parts are defined as follows

$$Re\left(H_{A2,CF}(\omega, -\omega)\right) = \frac{1 + \alpha}{B_{ps}} \times \frac{\Pi_{RH}}{\big(B_{ps} - \omega^2\big)^2 + 4A_{ps}^2\omega^2}$$

$$\tag{4.88}$$

$$Im\left(H_{A2,CF}(\omega, -\omega)\right) = \frac{1 + \alpha}{B_{ps}} \times \frac{\omega\Pi_{IH}}{\big(B_{ps} - \omega^2\big)^2 + 4A_{ps}^2\omega^2}$$

$$\tag{4.89}$$

The cross ASO FRF $H_{P2,CF}(\omega,\text{-}\omega)$ can be expressed in the following way:

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

$$\tag{4.90}$$

where:

$$\Gamma_{RH} = \Gamma_R + n\alpha B_{ps}\Big((1 + St + \beta\gamma)\big(B_{ps} - \omega^2 + 2A_{ps}\omega^2\big) + \omega^2\big(B_{ps} - \omega^2\big) - 2A_{ps}\omega^2\Big)$$

$$\tag{4.91}$$

$$\Gamma_{IH} = \Gamma_I + n\alpha B_{ps}\left(B_{ps} - \omega^2 + 2A_{ps}\omega^2 + (1 + St + \beta\gamma)\left(2A_{ps} - \left(B_{ps} - \omega^2\right)\right)\right)$$

$$(4.92)$$

(The auxiliary functions Γ_{RH} and Γ_{IH} are also given in their developed polynomial form in Appendix B7).

The cross ASO FRF $H_{P2,CF}(\omega,-\omega)$ can also be given in the following form:

$$H_{P2,CF}(\omega,-\omega) = Re\left(H_{P2,CF}(\omega,-\omega)\right) + jIm\left(H_{P2,CF}(\omega,-\omega)\right)$$

$$(4.93)$$

where its real and imaginary parts are defined as:

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

$$(4.94)$$

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

$$(4.95)$$

The cross ASO terms $H^{*}_{A2,CF}(\varphi,\omega)$ and $H^{*}_{P2,CF}(\varphi,\omega)$

$$H^{*}_{A2,CF}(\varphi,\omega) = \cos(\varphi)\,Re\left(H_{A2,CF}(\omega,-\omega)\right) + \sin(\varphi)\,Im\left(H_{A2,CF}(\omega,-\omega)\right) \quad (4.96)$$

$$H^{*}_{P2,CF}(\varphi,\omega) = \cos(\varphi)\,Re\left(H_{P2,CF}(\omega,-\omega)\right) + \sin(\varphi)\,Im\left(H_{P2,CF}(\omega,-\omega)\right) \quad (4.97)$$

4.8. Correlations between the reactant and product asymmetrical frequency response functions and terms

Single input modulation

For single input modulation of the inlet concentration, inlet temperature and temperature of the cooling/heating fluid, the reactant G-ASO FRFs and product G-ASO FRFs are correlated as follows

$$G_{P2,XX}(\omega,-\omega) = -\frac{1}{\alpha}G_{A2,XX}(\omega,-\omega) \quad X = C, T, J$$

$$(4.98)$$

For flow-rate modulation, the reactant H-ASO FRF and product H-ASO FRF are correlated in an analogous way

$$H_{P2,FF}(\omega, -\omega) = -\frac{1}{\alpha} H_{A2,FF}(\omega, -\omega)$$

(4.99)

In a similar way as for the isothermal CSTR, for single input modulation of the inlet concentration, inlet temperature, and temperature of the cooling/heating fluid of the non-isothermal CSTR, the DC components of the outlet reactant concentration (Eq. (2.12)) and the DC component of outlet concentration of the product (Eq. (2.13)) are always proportional, and have opposite signs.

$$C_{P,DC} = -\frac{1}{\alpha} C_{A,DC}$$

(4.100)

This is also valid for the reactant and product dimensionless DC component of the outlet molar flow-rate (Eqs. (2.36) and (2.37)) when the flow-rate is periodically modulated:

$$N_{P,DC} = -\frac{1}{\alpha} N_{A,DC}$$

(4.101)

As a consequence of these correlations, the reactant conversion and product yield are equal, as well as their relative changes ($x_{A,po} = Y_{P,po}$, $\Delta x_{A,po} = \Delta Y_{P,po}$) (Eqs. (2.24)-(2.27)) and (2.52)-(2.55)). Consequently, it is enough to focus on analysis of either the reactant or product FRFs and DC components, in order to estimate the possible improvements of the periodically operated non-isothermal CSTRs.

Simultaneous modulation of inlet concentration and inlet temperature

When inlet concentration and inlet temperature are simultaneous periodically modulated, the cross ASO FRFs corresponding to the outlet reactant concentration and outlet product concentration are proportional and have the opposite signs (similar as for the single input modulations).

$$G_{P2,CT}(\omega, -\omega) = -\frac{1}{\alpha} G_{A2,CT}(\omega, -\omega)$$

(4.102)

The same is true for their real and imaginary parts

$$Re\left(G_{P2,CT}(\omega, -\omega)\right) = -\frac{1}{\alpha} Re\left(G_{A2,CT}(\omega, -\omega)\right)$$

(4.103)

$$Im\left(G_{P2,CT}(\omega, -\omega)\right) = -\frac{1}{\alpha}Im\left(G_{A2,CT}(\omega, -\omega)\right)$$

<div align="right">(4.104)</div>

and the cross ASO terms

$$G^*_{P2,CT}(\varphi, \omega) = -\frac{1}{\alpha}G^*_{A2,CT}(\varphi, \omega)$$

<div align="right">(4.105)</div>

Considering the correlation between the cross ASO FRFs $G_{A2,CT}(\omega,-\omega)$ and $G_{P2,CT}(\omega,-\omega)$ (Eq. (4.102)) and their real (Eq. (4.103)) and imaginary parts (Eq. (4.104)), it can be concluded that the optimal phase difference which minimizes the outlet concentration of the reactant $\varphi_{opt,A}(\omega)$ (Eq. (2.28)) and the phase difference which maximizes the outlet concentration of the product $\varphi_{opt,P}(\omega)$ (Eq. (2.29)) are equal.

$$\varphi_{opt,A}(\omega) = \varphi_{opt,P}(\omega) = \varphi_{opt}(\omega) \qquad\qquad (4.106)$$

This optimal phase difference in the same time maximizes the reactant conversion reactant and the product yield.

As a consequence of all the facts explained above, the outlet dimensionless DC components of the outlet product (Eq. (2.16)) and reactant (Eq. (2.18)) concentrations, for simultaneous modulation of inlet concentration and inlet temperature, are also proportional and have opposite signs:

$$C_{P,DC} = -\frac{1}{\alpha}C_{A,DC}$$

<div align="right">(4.107)</div>

Therefore, similarly as for single input modulations, it can be shown that the conversion of the reactant and yield of the product are equal ($x_{A,po} = Y_{P,po}$) for this case, as well as, their relative changes owing to periodic operation ($\Delta x_{A,po} = \Delta Y_{P,po}$).

Simultaneous modulation of inlet concentration and flow-rate

For simultaneous modulation of inlet concentration and flow-rate, the cross ASO FRFs $H_{A2,CF}(\omega,-\omega)$ and $H_{P2,CF}(\omega,-\omega)$ and the cross ASO terms $H^*_{A2,CF}(\omega,\varphi)$ and $H^*_{P2,CF}(\omega,\varphi)$ are correlated in same way as for the isothermal CSTR (Eqs. (3.46) and (3.47)):

$$H_{P2,CF}(\omega, -\omega) = -\frac{1}{\alpha}H_{A2,CF}(\omega, -\omega) + \frac{1+\alpha}{\alpha}$$

<div align="right">(4.108)</div>

$$H^*_{P2,CF}(\omega, \varphi) = -\frac{1}{\alpha} H^*_{A2,CF}(\omega, \varphi) + \cos(\varphi) \frac{1 + \alpha}{\alpha}$$

<div align="right">(4.109)</div>

It is important to notice that the correlation between the cross ASO FRFs $H_{A2,CF}(\omega,-\omega)$ and $H_{P2,CF}(\omega,-\omega)$ (Eq. (4.108)) for simultaneous modulation of inlet concentration and flow-rate for the non-isothermal CSTR is reduced to the same correlation as for the isothermal CSTR:

$$N_{P,DC} = -\frac{1}{\alpha} N_{A,DC} + 2 \left(\frac{A_C}{2} \right) \left(\frac{A_F}{2} \right) \cos(\varphi) \frac{1 + \alpha}{\alpha}$$

<div align="right">(4.110)</div>

Consequently, all conclusions given for the isothermal CSTR with simultaneous modulation of the inlet concentration and flow-rate, concerning the equality between the reactant conversion and product yield, as well as theirs relative changes, are also valid for the non-isothermal CSTR.

4.9. Estimating the possible improvement throughout the sign analysis of the asymmetrical second order frequency response functions

The ASO FRFs corresponding to the outlet concentration of the reactant $G_{A2,XX}(\omega,-\omega)$ and the ASO FRFs which correspond to the outlet concentration of the product $G_{P2,XX}(\omega,-\omega)$, for single input modulations always have opposite signs. Therefore, the sign analysis of the ASO FRFs for single input modulations will be performed only for the ASO FRFs $G_{A2,XX}(\omega,-\omega)$ (the desirable sign is negative), and these results will directly be used to predict the sign of $G_{P2,XX}(\omega,-\omega)$.

From the definitions of the dimensionless auxiliary parameters (Eq. (4.8)), it can be concluded that the auxiliary parameters α, γ, δ and St are always positive, while the auxiliary parameter β is positive for endothermic and negative for exothermic reactions. The sign of the stability parameters for stable systems are also defined, $A_{ps}<0$ and $B_{ps}>0$.

Considering that the forcing frequency represents a new variable of the forced periodically operated reactors which can be varied as desired, the sign of the ASO FRFs will be analyzed in respect to the forcing frequency, as for any investigated system, the system parameters are known (*Nikolić et al., 2014a, 2014b*).

The sign analysis of the real and imaginary parts of the cross ASO FRFs for simultaneous modulation of inlet concentration and inlet temperature will also be

analyzed in order to determine the range of phase difference which should be used in order to ensure the desired signs of the cross ASO terms.

4.9.1. Asymmetrical second order FRFs for inlet concentration modulation

The sign analysis of the ASO FRF $G_{A2,CC}(\omega,-\omega)$ (Eq.(4.33)) can be reduced to the sign analysis of the term Λ, since all other terms are positive. The sign of the ASO FRF $G_{A2,CC}(\omega,-\omega)$ depends on the sign of the term Λ in the following way:

$$sign(G_{A2,CC}(\omega,-\omega)) = -sign(\Lambda) \tag{4.111}$$

The term Λ depends on the characteristics of the reactor system (throughout the reaction order n and the auxiliary parameters β, γ and St) and forcing frequency ω, which is a parameter of periodic operation.

In general, the ASO FRF $G_{A2,CC}(\omega,-\omega)$ can change its sign if the following equation:

$$G_{A2,CC}(\omega,-\omega) = 0 \Leftrightarrow \Lambda = 0 \Leftrightarrow$$
$$n(n-1)\omega^2 + n^2((1+St)^2 - 2\beta^2\gamma) - n(1+St+\beta\gamma)^2 = 0 \tag{4.112}$$

has a real solution, which is then given with the following expression

$$\omega_{0,C} = \sqrt{\frac{(1+St+\beta\gamma)^2 - n((1+St)^2 - 2\beta^2\gamma)}{n-1}} \tag{4.113}$$

If Eq. (4.112) has no real solutions, the $G_{A2,CC}(\omega,-\omega)$ has the same sign in the whole frequency range. Eq. (4.112) will have real solutions if the numerator and denominator of the rational function under the square root in Eq. (4.113) have the same sign. The sign in the denominator depends only on reaction order and changes for $n=1$. The sign of the numerator also depends on the reaction order and changes for:

$$n = n_C = \frac{(1+St+\beta\gamma)^2}{(1+St)^2 - 2\beta^2\gamma} \tag{4.114}$$

which can be calculated from the auxiliary parameters β, γ and St.

The results of the sign analysis of the ASO FRF $G_{A2,CC}(\omega,-\omega)$ and $G_{P2,CC}(\omega,-\omega)$ (which has the opposite sign (Eq. (4.98))) are summarized and presented in Table 4.2.

Table 4.2 The summary of the sign analysis results for $G_{A2,CC}(\omega,-\omega)$ and $G_{P2,CC}(\omega,-\omega)$

Condition	Frequency range	$G_{A2,CC}(\omega,-\omega)$ (negative is desirable)	$G_{P2,CC}(\omega,-\omega)$ (positive is desirable)
$n=0$	$\forall\omega$	zero	zero
$n<n_C$ and $n<0$	$\forall\omega$	**negative**	**positive**
$n<n_C$ and $0<n<1$	$\forall\omega$	positive	negative
$n_C<1$ and $n=1$	$\forall\omega$	**negative**	**positive**
$n<n_C$ and $n>1$	$\omega<\omega_{0,C}$	positive	negative
	$\omega>\omega_{0,C}$	**negative**	**positive**
$n>n_C$ and $n<0$	$\omega<\omega_{0,C}$	positive	negative
	$\omega>\omega_{0,C}$	**negative**	**positive**
$n>n_C$ and $0<n<1$	$\omega<\omega_{0,C}$	**negative**	**positive**
	$\omega>\omega_{0,C}$	positive	negative
$\frac{1}{n_C}<1$ and $n=1$	$\forall\omega$	positive	negative
$n>n_C$ and $n>1$	$\forall\omega$	**negative**	**positive**

4.9.2. Asymmetrical second order FRFs for flow-rate modulation

The sign of the ASO FRF $H_{A2,FF}(\omega,-\omega)$ depends on the characteristics of the reactor system (reaction order n and all auxiliary parameters) and the forcing frequency ω.

The sign of ASO FRF $H_{A2,FF}(\omega,-\omega)$ depends on the auxiliary function in the numerator Ω_H in the following way (Eq. (4.79)):

$$sign(H_{A2,FF}(\omega,-\omega)) = -sign(\Omega_H) \qquad (4.115)$$

Therefore, the sign analysis of the ASO FRF $H_{A2,FF}(\omega,-\omega)$ can be reduced to the sign analysis of the function Ω_H, defined by equations ((4.81)-(4.83)).

The frequency for which the function $H_{A2,FF}(\omega,-\omega)$ can change its sign can be determined from the following condition:

$$H_{A2,FF}(\omega,-\omega) = 0 \quad \Leftrightarrow \quad \Omega_H = 0 \Leftrightarrow \Omega_{1H}\omega^2 + \Omega_{2H} = 0 \qquad (4.116)$$

The solution of Eq. (4.116) is real if the complex functions Ω_{1H} and Ω_{2H} have opposite signs

$$\omega_{0,F} = \sqrt{-\frac{\Omega_{2H}}{\Omega_{1H}}}$$

<div align="right">(4.117)</div>

If auxiliary functions Ω_{1H} and Ω_{2H} have the same sign, the ASO FRF $H_{A2,FF}(\omega,-\omega)$ will have the same sign in the whole frequency range.

The results of the sign analysis of the ASO FRFs $H_{A2,FF}(\omega,-\omega)$ and $H_{P2,FF}(\omega,-\omega)$ are summarized in the Table 4.3. As mentioned, these ASO FRFs will always have opposite signs (Eqs. (4.99)).

Table 4.3 The summary of the sign analysis results for $H_{A2,FF}(\omega,-\omega)$ and $H_{P2,FF}(\omega,-\omega)$

Sign of Ω_{1H}	Sign of Ω_{2H}	Range of forcing frequency	$H_{A2,FF}(\omega,-\omega)$ (negative is desirable)	$H_{P2,FF}(\omega,-\omega)$ (positive is desirable)
positive	**negative**	$\omega<\omega_{0,F}$	positive	negative
		$\boldsymbol{\omega>\omega_{0,F}}$	**negative**	**positive**
negative	**positive**	$\boldsymbol{\omega<\omega_{0,F}}$	**negative**	**positive**
		$\omega>\omega_{0,F}$	positive	negative
positive	**positive**	$\forall\boldsymbol{\omega}$	**negative**	**positive**
negative	negative	$\forall\omega$	positive	negative
zero	negative	$\forall\omega$	positive	negative
	positive	$\forall\boldsymbol{\omega}$	**negative**	**positive**
positive	zero	$\forall\boldsymbol{\omega}$	**negative**	**positive**
negative		$\forall\omega$	positive	negative

4.9.3. Asymmetrical second order FRFs for inlet temperature modulation

All terms in the asymmetrical second order FRF $G_{A2,TT}(\omega,-\omega)$ are positive, except the term Ψ which can be positive or negative. Based on this, the sign of ASO FRF $G_{A2,TT}(\omega,-\omega)$ depends on the sign of the term Ψ in the following way:

$$sign(G_{A2,TT}(\omega,-\omega)) = -sign(\Psi) \qquad (4.118)$$

The sign of the term Ψ depends on the reaction order n, auxiliary parameters α and γ, which are characteristic of the investigated system, and the forcing frequency ω.

The ASO FRF for a particular investigated reaction system (with defined values of reaction order n and auxiliary parameters α and γ), can have the same sign in the whole frequency range or it can change the sign, depending on whether the solutions of the following equation:

$$G_{A2,TT}(\omega,-\omega) = 0 \Leftrightarrow \Psi = (\gamma-2)\omega^2 - 2\alpha^2 n^2 - \alpha(4+\alpha\gamma)n + (\gamma-2) = 0$$

$$\qquad (4.119)$$

$$\omega_{0,T} = \sqrt{\frac{2\alpha^2 n^2 + \alpha(4+\alpha\gamma)n - (\gamma-2)}{\gamma - 2}}$$

$$\qquad (4.120)$$

are real or complex-conjugates.

The solution for $\omega_{0,T}$ will be real if the numerator and denominator under the square root have the same signs and complex if these signs are different. Further, the numerator depends on the reaction order, and it will change its sign for

$$n_{T1,T2} = \frac{-(4+\alpha\gamma) \pm \sqrt{\alpha^2\gamma^2 + 8\alpha\gamma + \gamma}}{4\alpha}$$

$$\qquad (4.121)$$

It should be noticed that n_{T1} and n_{T2} are always real. If we choose that the solutions are $n_{T1} < n_{T2}$, the final results of the sign analysis of the ASO FRF $G_{A2,TT}(\omega,-\omega)$ are given in Table 4.4. The sign of the ASO FRF $G_{P2,TT}(\omega,-\omega)$ will be always opposite to the sign of $G_{A2,TT}(\omega,-\omega)$ (Eq. (4.98)).

Table 4.4 The summary of the sign analysis results for $G_{A2,TT}(\omega,-\omega)$ and $G_{A2,JJ}(\omega,-\omega)$ (negative sign is desirable), $G_{P2,TT}(\omega,-\omega)$ and $G_{P2,JJ}(\omega,-\omega)$ (positive sign is desirable)

Reaction order, n	Sign of (γ-2)	Forcing frequency, ω	$G_{A2,TT}(\omega,-\omega)$ and $G_{A2,JJ}(\omega,-\omega)$ (negative is desirable)	$G_{P2,TT}(\omega,-\omega)$ and $G_{P2,JJ}(\omega,-\omega)$ (positive is desirable)
$n<n_{T1}$ or $n>n_{T2}$	**positive**	$\omega<\omega_{0,T}$	positive	negative
		$\omega>\omega_{0,T}$	**negative**	**positive**
	negative or zero	$\forall\omega$	positive	negative
$n_{T1}<n<n_{T2}$	**negative**	$\omega<\omega_{0,T}$	**negative**	**positive**
		$\omega>\omega_{0,T}$	positive	negative
	positive or zero	$\forall\omega$	**negative**	**positive**
$n=n_{T1}$ or $n=n_{T2}$	**positive**	$\forall\omega$	**negative**	**positive**
	negative	$\forall\omega$	positive	negative
	zero	$\forall\omega$	zero	zero

4.9.4. Asymmetrical second order FRFs for modulation of temperature of the cooling/heating fluid

Again, the term Ψ in the numerator is the only one that determines the sign of the ASO FRFs $G_{A2,JJ}(\omega,-\omega)$ and $G_{P2,JJ}(\omega,-\omega)$, and it can change its sign (all other terms are positive). As a result, the sign analysis of the ASO FRF $G_{A2,JJ}(\omega,-\omega)$, is practically identical as in the previous case, for the ASO FRF $G_{A2,TT}(\omega,-\omega)$. Consequently, the signs of the ASO FRFs $G_{A2,JJ}(\omega,-\omega)$ and $G_{P2,JJ}(\omega,-\omega)$ are the same as the signs of $G_{A2,TT}(\omega,-\omega)$ and $G_{P2,TT}(\omega,-\omega)$, respectively, and they can be predicted by using the results given in Table 4.4.

4.9.5. The cross asymmetrical second order terms for simultaneous modulation of inlet concentration and inlet temperature

The sign of the cross ASO term $G^*_{A2,CT}(\varphi,\omega)$ depends on the sign of the real and imaginary parts of the cross ASO FRF $G_{A2,CT}(\omega,-\omega)$ and the phase difference between the two modulated inputs (Eq. (4.64)). As already explained in Chapter II in detail, in this case the cross ASO term can always have the desired sign, by appropriate choice of the phase difference. The sign analysis of the real and imaginary parts of the cross ASO FRF $G_{A2,CT}(\omega,-\omega)$ will be done and the recommended phase difference which will ensure negative sign of the cross ASO term $G^*_{A2,CT}(\varphi,\omega)$ will be given. Based on signs of the real and imaginary parts of the cross ASO FRF $G_{A2,CT}(\omega,-\omega)$, the sign of the real and imaginary parts of the cross ASO FRF $G_{P2,CT}(\omega,-\omega)$ are also determined considering the previously concluded fact that these FRFs have opposite signs, as given with (Eqs. (4.103) and (4.104)). Based on this, and the results given in Tables 2.1 and 2.2, the recommended phase difference which will give the negative value of the cross ASO term $G^*_{A2,CT}(\varphi,\omega)$ will, in the same time, ensure the positive sign of the cross ASO term $G^*_{P2,CT}(\varphi,\omega)$.

Signs of $Re(G_{A2,CT}(\omega,-\omega))$ and $Re(G_{P2,CT}(\omega,-\omega))$

The sign of the real part of the cross ASO FRF $G_{A2,CT}(\omega,-\omega)$ depends on the reaction order n, newly introduced auxiliary parameter in the denominator of the cross ASO FRF $G_{A2,CT}(\omega,-\omega)$:

$$\varepsilon_R = 1 + St + \alpha(1 + St + \beta\gamma) + 2\beta(1 + n\alpha) \tag{4.122}$$

and, in some cases, on the forcing frequency ω.

The real part of the cross ASO FRF $G_{A2,CT}(\omega,-\omega)$ changes its sign if $\varepsilon_R<0$, for a frequency

$$\omega_{0,CT} = \sqrt{-\varepsilon_R} \tag{4.123}$$

otherwise if $\varepsilon_R \geq 0$, it has the same sign in the whole frequency range.

The results of the sign analysis of $Re(G_{A2,CT}(\omega,-\omega))$, as a function of the reaction order n, auxiliary parameter ε_R and forcing frequency, are summarized in Table 4.5. According to equation (4.103), the sign of the real part of the ASO FRF $G_{P2,CT}(\omega,-\omega)$ is always the opposite.

Table 4.5 The summary of the sign analysis results for the real parts of $G_{A2,CT}(\omega,-\omega)$ and $G_{P2,CT}(\omega,-\omega)$

Reaction order, n	ε_R	Forcing frequency, ω	$Re\big(G_{A2,CT}(\omega,-\omega)\big)$	$Re\big(G_{P2,CT}(\omega,-\omega)\big)$
$n=0$	any	$\forall\omega$	zero	zero
$n>0$	positive or zero	$\forall\omega$	negative	positive
	negative	$\omega<\omega_{0,CT}$	positive	negative
		$\omega=\omega_{0,CT}$	zero	zero
		$\omega>\omega_{0,CT}$	negative	positive
$n<0$	positive or zero	$\forall\omega$	positive	negative
	negative	$\omega<\omega_{0,CT}$	negative	positive
		$\omega=\omega_{0,CT}$	zero	zero
		$\omega>\omega_{0,CT}$	positive	negative

Signs of $Im(G_{A2,CT}(\omega,-\omega))$ and $Im(G_{P2,CT}(\omega,-\omega))$

The sign of $Im(G_{A2,CT}(\omega,-\omega))$ depends on the reaction order n and the term:

$$\varepsilon_I = \alpha - 2\beta - St \tag{4.124}$$

The final results of the sign analysis for the imaginary part of FRF $G_{A2,CT}(\omega,-\omega)$, as a function of the reaction order n and the sign of the term ε_I, are given in Table 4.6, as well as the signs of the imaginary part of cross ASO FRF $G_{P2,CT}(\omega,-\omega)$ (Eq. (4.104)).

Table 4.6 The summary of the sign analysis results for the imaginary parts of $G_{A2,CT}(\omega,-\omega)$ and $G_{P2,CT}(\omega,-\omega)$

Reaction order, n	ε_I	$Im\big(G_{A2,CT}(\omega,-\omega)\big)$	$Im\big(G_{P2,CT}(\omega,-\omega)\big)$
n=0	any	zero	zero
n>0	zero	zero	zero
	positive	negative	positive
	negative	positive	negative
n<0	zero	zero	zero
	positive	positive	negative
	negative	negative	positive

After determining the signs of the real and imaginary parts of the cross ASO FRFs $G_{A2,CT}(\omega,-\omega)$ or $G_{P2,CT}(\omega,-\omega)$, from the general case for two-input modulation (Tables 2.1 or 2.2), the final conclusions for the recommended phase difference which should be used in order to obtain the desirable signs can be made.

The optimal phase difference, will always be in the recommended range of the phase difference, which leads to desirable influence of the cross effect.

4.10. Numerical example NONISO-1

In order to illustrate the theoretical results obtained by the NFR method for forced periodically operated non-isothermal CSTRs, a numerical example is chosen for simulation of the ASO FRFs, cross ASO FRFs and analysis of their signs, as well as for comparison of the results obtained by the NFR method with numerical integration. The analysis is performed for single input modulations of the inlet concentration, flow-rate, inlet temperature, temperature of the cooling/heating fluid, for simultaneous modulation of inlet concentration and inlet temperature and for simultaneous modulation of inlet concentration and flow-rate. This numerical example will be referred as NONISO-1.

4.10.1. Definition of the Numerical example NONISO-1

The values of the model parameters used for simulations are given in Table 4.7. The parameters listed in Table 4.7 correspond to an optimized exothermal reactor with a first-order reaction, taken from of a textbook by Douglas (*Douglas, 1972*).

Table 4.7 Parameters for the non-isothermal CSTR named as Numerical example NONISO-1

Parameter	Value
Reaction order, n	1
Stochiometric coefficient, v_P	1
Volume of the reactor, V (m^3)	1.439
Pre-exponential factor of the reaction rate constant, k_o (1/min)	4.3177×10^5
Activation energy, E_A (kJ/kmol)	50242
Heat capacity, $\overline{\rho c_p}$ (kJ/(m^{3}K))	4186.8
Heat of reaction, ΔH_R (kJ/kmol)	-50242
Steady-state flow-rate, F_s (m^3/min)	0.0238
Steady-state inlet concentration, $c_{Ai,s}$ (kmol/m^3)	5
Steady-state inlet temperature, $T_{i,s}$ (K)	300
Steady-state temperature of the coolant, $T_{J,s}$ (K)	400
Overall heat transfer coefficient, U (kJ/(m^{2}Kmin))	101.8
Surface area for heat exchange, A_w (m^2)	1.073

For this numerical example and the steady-state input variables defined in Table 4.7, only one steady-state solution exists, defined by the outlet steady-state concentrations $c_{A,s}=1.50$ kmol/m^3 and $c_{P,s}=3.50$ kmol/m^3 and the outlet steady-state temperature $T_s=372.33$ K. The conversion of the reactant and yield of the product are $x_{A,s}=Y_{P,s}=0.70$.

The residence time for this non-isothermal CSTR corresponding to this steady-state is $\tau_{res,s}$=60.46 min. It should be pointed out that this steady-state has been optimized (*Douglas*, *1972*).

The values of the auxilliary parameters defined with Eq. (4.8) are: α=2.33, β=-0.11, γ=16.23 δ=1.18 and St=1.10. Furthermore, for the investigated non-isothermal CSTR defined as Numerical example NONISO-1, the stability parameters are A_{ps}=-1.80 (Eq. (4.24)) and B_{ps}=5.16 (Eq. (4.25)). Considering that the stability conditions are satisfied for this steady-state (Eq. (4.26)), i.e., A_{ps}<0, B_{ps}>0, the system is stable. This system is oscillatory ($A_{ps}^2 < B_{ps}$) with damping coefficient ξ=0.79 (Eq. (4.28)) and natural frequency ω_n=2.27 (Eq. (4.29)) and it doesn't exhibit resonant behavior (ξ>0.707).

For each case of periodic input modulation, our focus will be on the outlet concentration of the product or outlet molar flow-rate of the product. The improvement or deterioration of the reactor performance will be followed by the change of the product yield.

4.10.2. Simulation results for single input modulation

In Figure 4.2, the ASO FRFs $G_{P2,CC}(\omega,-\omega)$, $H_{P2,FF}(\omega,-\omega)$, $G_{P2,TT}(\omega,-\omega)$ and $G_{P2,JJ}(\omega,-\omega)$ corresponding to the single input modulation of inlet concentration, flow-rate, inlet temperature and temperature of the cooling fluid, respectively, are graphically presented as functions of the dimensionless forcing frequency.
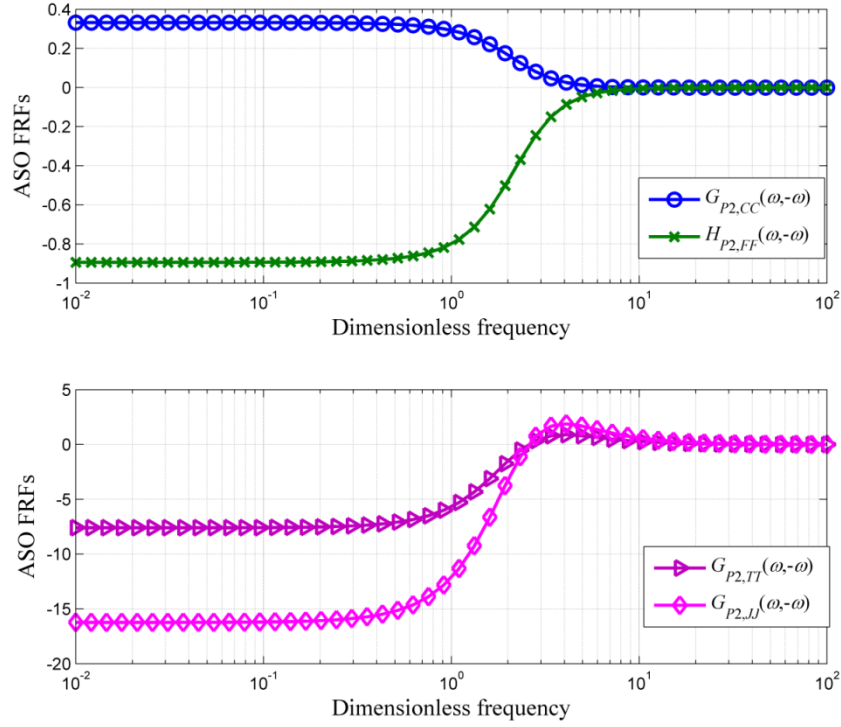
Figure 4.2 The ASO FRFs $G_{P2,CC}(\omega,-\omega)$ and $H_{P2,FF}(\omega,-\omega)$ (up); the ASO FRFs $G_{P2,TT}(\omega,-\omega)$ and $G_{P2,JJ}(\omega,-\omega)$ (down), as functions of the dimensionless forcing frequency

From Figure 4.2, it can be concluded that:

- All ASO FRFs tend to asymptotic values for the low-frequency modulation and tend to zero for high-frequency modulation, which is in accordance with their expressions given with equations (4.34), (4.80), (4.48) and (4.55).

- It is expected to achieve improvement of the reactor performance for the inlet concentration modulation, which is most significant for the low-frequency modulation. The simulation results are in accordance with the results of sign analysis from which it is expected that the ASO FRF $G_{P2,CC}(\omega,-\omega)$ is positive in the whole frequency range (Table 4.2 and Eq. (4.114)) as $n_C=0.018$ ($n_C<1$ and $n=1$).

- Single input modulation of the flow-rate will deteriorate the reactor performance, which is also in accordance with the result of the sign analysis. From Eqs. ((4.82) and (4.83)), $\Omega_{1H}= -4.12<0$ and $\Omega_{2H}=-245.19<0$, and according

to the results presented in Table 4.3, the ASO FRF $H_{P2,FF}(\omega,-\omega)$ is expected to be negative in the whole frequency range, which is confirmed in Figure 4.2.

- Single input modulation of the inlet temperature or temperature in the jacket will cause deterioration of the reactor performance for low-frequency range and only in a narrow range of higher forcing frequency ($\omega>2.57$) it could lead to improvement. The simulation results from Figure 4.2 are in accordance with the results of the sign analysis given in the Table 4.4. From Eqs. ((4.120) and (4.121)), n_{T1}=-8.97, n_{T2}=0.0003, $\omega_{0,T}$=2.57, and the value of the auxiliary parameter γ ((γ-2)=14.23), for $\omega<\omega_{0,T}$=2.57, $G_{P2,TT}(\omega,-\omega)$ and $G_{P2,JJ}(\omega,-\omega)$ are negative while for $\omega>\omega_{0,T}$=2.57, these ASO FRFs are positive (where the improvement can be expected).

As illustration, for arbitrary chosen forcing amplitudes: 100% for the inlet concentration, 50% for the flow-rate and 10% for the inlet temperature and temperature in the jacket, the product yields for all cases of single input modulation, as functions of the dimensionless forcing frequency, are given in Figure 4.3. The product yield for steady-state ($Y_{P,s}$=0.70) is also given in Figure 4.3.
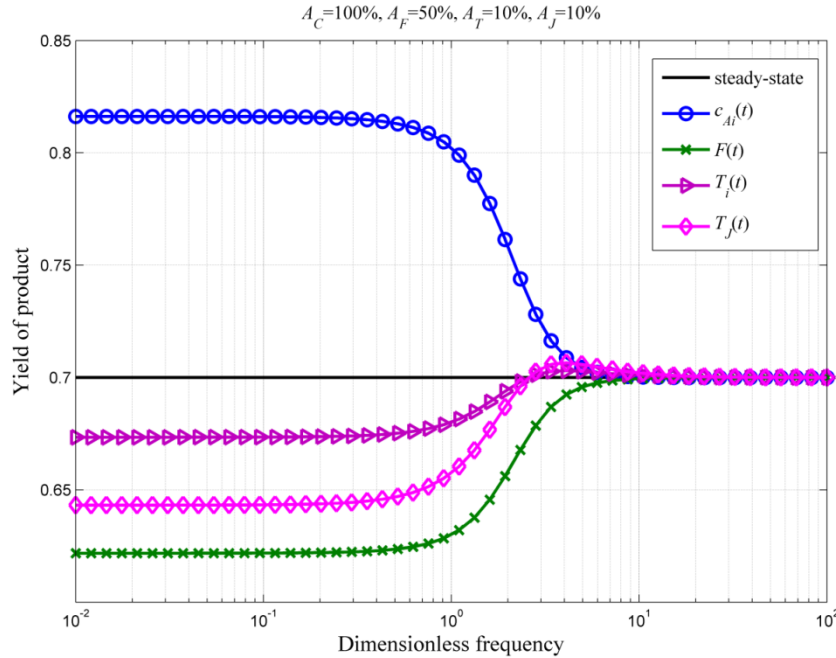
Figure 4.3 Yield of the product for the steady-state operation, for periodic operation with modulation of the inlet concentration (A_C=100%), flow-rate (A_F=50%), inlet temperature and temperature in the jacket (A_T=A_J=10%), as functions of the dimensionless forcing frequency

The highest increase of yield of the product will be obtained for low-frequency inlet concentration modulation when the relative increase is approximately 16.58%. The increase of the product yield for the inlet temperature modulation or temperature of the cooling fluid for the higher forcing frequencies ($\omega > \omega_{0,T} = 2.57$) is practically insignificant.

Comparison with the results obtained by numerical integration

The approximate product yields owing to single input modulation of the inlet concentration, flow-rate, inlet temperature and temperature of the cooling fluid, calculated by the NFR method, are compared with the results of numerical simulation for Numerical example NONISO-1.

In Table 4.8, the results obtained by the NFR method and numerical integration of the model equations are given for forcing frequencies $\omega=0.1$, 1 and 10, forcing amplitudes for the inlet concentration $A_C=100\%$, for the flow-rate $A_F=50\%$ and for the inlet temperature and the temperature of the cooling/heating fluid $A_T=A_J=10\%$. The relative change of the yield and the relative errors (Eq.(3.59)) are also given in Table 4.8.

Table 4.8 The product yield for single input modulations of the inlet concentration, the flow-rate, the inlet temperature or the temperature of the cooling fluid, estimated by numerical simulation and by the NFR method, and the relative errors

Inlet concentration modulation, $A_C=100\%$					
ω	$Y_{P,po}(\%)$		δ_Y (%)	$\Delta Y_{P,po}(\%)$	
	num	NFRM		num	NFRM
0.1	79.92	81.61	+2.11	+14.17	+16.58
1	78.38	80.23	+2.36	+11.97	+14.61
10	70.03	70.03	0	+0.04	+0.04
Flow-rate modulation, $A_F=50\%$					
ω	$Y_{P,po}(\%)$		δ_Y (%)	$\Delta Y_{P,po}(\%)$	
	num	NFRM		num	NFRM
0.1	62.21	62.18	-0.05	-10.54	-11.17
1	63.57	63.00	-0.90	-9.18	-10.00
10	69.95	69.95	0	-0.07	-0.07
Inlet temperature modulation, $A_T=10\%$					
ω	$Y_{P,po}$ (%)		δ_Y (%)	$\Delta Y_{P,po}(\%)$	
	num	NFRM		num	NFRM
0.1	67.52	67.35	-0.25	-3.54	-3.79
1	68.28	68.01	-0.40	-2.46	-2.84
10	70.10	70.10	0	+0.14	+0.14
Modulation of the cooling fluid, $A_J=10\%$					
ω	$Y_{P,po}$ (%)		δ_Y (%)	$\Delta Y_{P,po}$ (%)	
	num	NFRM		num	NFRM
0.1	65.18	64.33	-1.30	-6.88	-8.10
1	66.82	65.76	-1.59	-4.54	-6.06
10	70.21	70.21	0	+0.29	+0.30

The results of the numerical simulations confirmed all above presented conclusions based on the NFR method and the sign analysis of the ASO FRFs. The values of the relative errors show very good agreement between the results of the NFR method and numerical integration, despite the fact that non-isothermal CSTR is a system of significant nonlinearity.

In order to explore the influence of the input amplitude on yield increase and the error of the NFR method for single input modulation of inlet concentration the same results are given in Table 4.9 as in Table 4.8, but with lower forcing amplitude, for A_C=75%. As it can be seen from these results, the relative errors significantly decreased with the decrease of the forcing amplitude. The yield increase is also considerably lower.

Table 4.9 Yields of product for single input modulation of inlet concentration with forcing amplitude A_C=75% estimated by numerical simulation and by the NFR method and the relative errors

	Inlet concentration modulation, A_C=75%				
ω	$Y_{P,po}(\%)$		$\delta_Y\,(\%)$	$\Delta Y_{P,po}(\%)$	
	num	NFRM		num	NFRM
0.1	75.93	76.53	+0.79	+8.47	+9.33
1	75.07	75.75	+0.90	+7.24	+8.21
10	70.02	70.02	0	+0.03	+0.03

4.10.2. Simulation results for simultaneous modulation of inlet concentration and inlet temperature

Furthermore, the data defined for Numerical example NONISO-1 were used for simulations of simultaneous modulation of the inlet concentration and inlet temperature.

For this case, the real and imaginary parts of the cross ASO FRF $G_{P2,CT}(\omega,-\omega)$, (Eqs. (4.62) and (4.63)), are graphically presented in Figure 4.4.
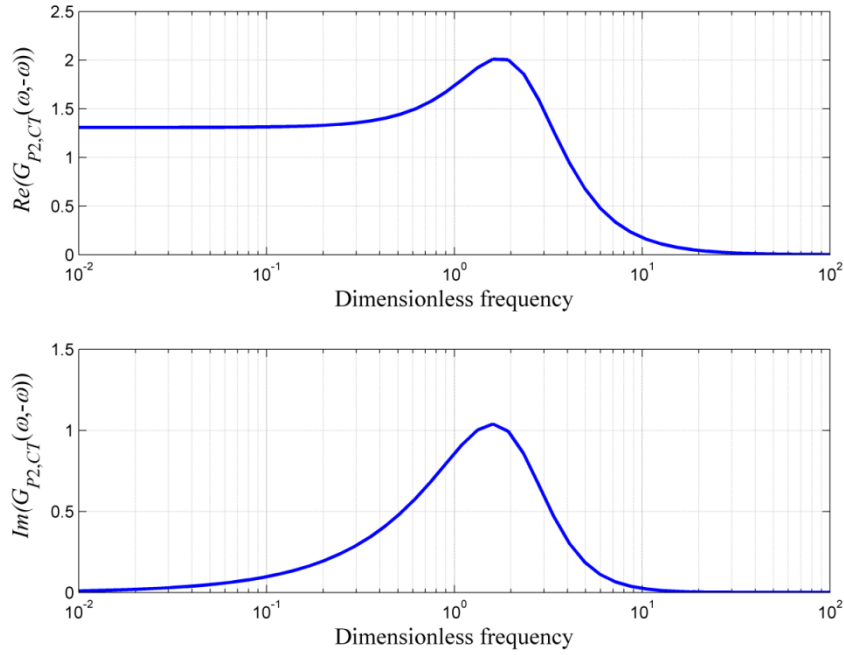
Figure 4.4 The real and imaginary parts of the cross ASO FRF $G_{P2,CT}(\omega,-\omega)$ as functions of the dimensionless forcing frequency

The simulation results are in accordance with the results of the sign analysis (Table 4.5 and 4.6): both the real and the imaginary part of the cross ASO FRF $G_{P2,CT}(\omega,-\omega)$ are positive in the whole frequency range ($n=1$, $\varepsilon_R=1.96>0$, (Eq. (4.122)), $\varepsilon_I=1.46>0$ (Eq. (4.124))). The recommended phase difference which should be used in order to ensure the positive sign of the cross ASO term $G^*_{P2,CT}(\varphi,\omega)$ is between 0 and $\pi/2$ (Table 2.2). The optimal phase difference $\varphi_{opt}(\omega)$ (Eq. (4.67)) is graphically presented in Figure 4.5, and as it can be seen, is in the recommended range.

For low-frequency modulations, the real part of the cross ASO FRF $G_{P2,CT}(\omega,-\omega)$ tends to an asymptotic value and for high-frequency modulations this function tends zero (Eq. (4.62)). On the other hand, the imaginary part of the cross ASO FRF $G_{P2,CT}(\omega,-\omega)$ tends to zero both for low-forcing frequencies and for high-forcing frequencies (Eq. (4.63)). Thus, in the case of simultaneous modulation of the inlet concentration and inlet temperature, the cross ASO FRF $G_{P2,CT}(\omega,-\omega)$ tends to zero for high forcing frequencies (Eq. (4.60)), as well as the cross ASO term $G^*_{P2,CT}(\varphi,\omega)$ (Eq. (4.65)). Therefore, in this case, the high-forcing frequency modulation has no effect on the reactor performance, similarly as for the single input modulations.

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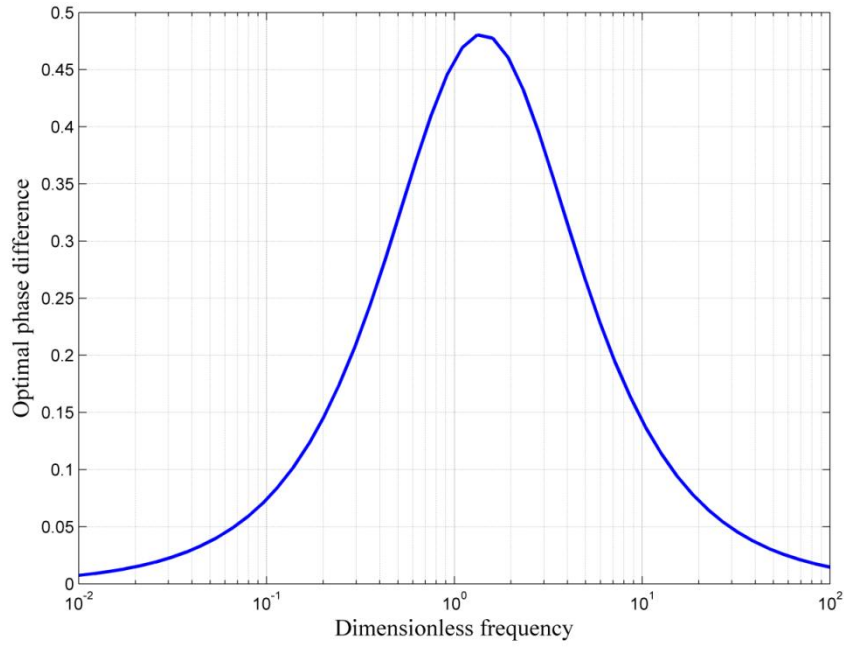
Figure 4.5 The optimal phase difference for simultaneous modulation of the inlet concentration and inlet temperature $\varphi_{opt}(\omega)$ as a function of the dimensionless forcing frequency

The ASO FRFs $G_{P2,CC}(\omega,-\omega)$ and $G_{P2,TT}(\omega,-\omega)$, which correspond to the single input modulation of the inlet concentration and inlet temperature, together with the cross ASO term $G^{*}_{P2,CT}(\varphi_{opt},\omega)$ for these two inputs, vs. forcing frequency, are presented in Figure 4.6.
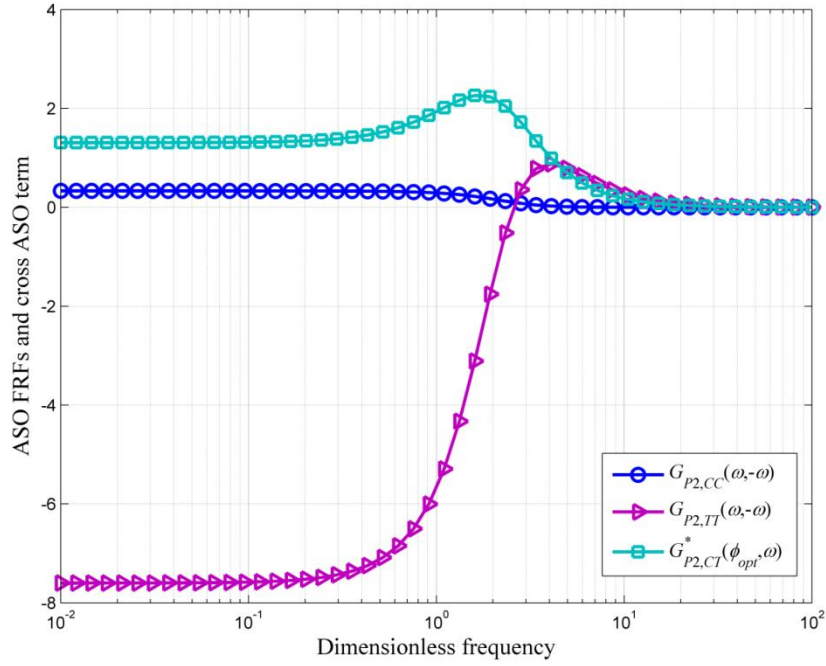
Figure 4.6 The ASO FRFs $G_{P2,CC}(\omega,-\omega)$, $G_{P2,TT}(\omega,-\omega)$ and the cross ASO term $G^{*}_{P2,CT}(\varphi_{opt},\omega)$ as functions of the dimensionless forcing frequency

As expected, the cross ASO term $G^{*}_{P2,CT}(\varphi_{opt},\omega)$, when the optimal phase difference is used, is positive in the whole frequency range, as is the ASO FRF $G_{P2,CC}(\omega,-\omega)$ which corresponds to the inlet concentration modulation. Nevertheless, since the ASO FRF $G_{P2,TT}(\omega,-\omega)$ which corresponds to inlet temperature modulation is negative for $\omega<2.57$, the overall effect of simultaneous modulation of these two inputs on the reactor improvement can be estimated only by evaluation of the overall dimensionless DC component of the outlet product concentration or by evaluation of the product yield.

Finally, in Figure 4.7, the yield of the product, obtained for simultaneous modulation of the inlet concentration and temperature, with optimal phase difference $\varphi_{opt}(\omega)$, and forcing amplitudes $A_C=100\%$ and $A_T=10\%$, is graphically presented. For comparison, in Figure 4.7, the product yields which correspond to the single input modulations of these two inputs with the same forcing amplitudes, as well as for the steady-state operation, are also given.
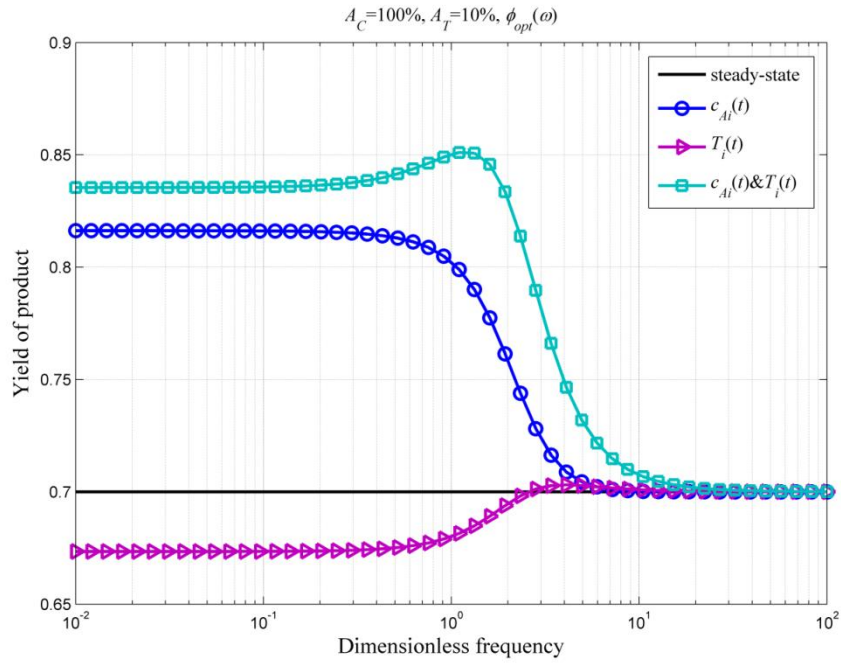
Figure 4.7 Yield of the product for the steady-state operation, for single and simultaneous modulation of the inlet concentration and inlet temperature, with forcing amplitudes A_C=100%, A_T=10% and optimal phase difference, as functions of the dimensionless forcing frequency

Despite the fact that inlet temperature modulation will lead to decrease of the product yield for $\omega<2.57$, simultaneous modulation of the inlet concentration and inlet temperature with appropriate choice of the phase difference and the chosen forcing amplitudes, A_C=100% and A_T=10%, will lead to increase of the product yield, which is higher than for single input modulation of the inlet concentration.

It should be pointed out, that for simultaneous modulation of the inlet concentration and temperature the forcing amplitudes can also be optimized in order to maximize the product yield. Nevertheless, in our analysis we are using arbitrary chosen amplitudes which have physically reasonable values.

Comparison with the results obtained by numerical integration

The approximate product yields calculated by the NFR method are compared with the results of numerical simulation for the Numerical example NONISO-1, for simultaneous modulation of the inlet concentration and inlet temperature.

The comparison is performed for optimal phase differences, for dimensionless forcing frequencies ω=0.1, 1 and 10, forcing amplitudes A_C=100% and A_T=10% (Table 4.10).

The relative changes of the yield owing to simultaneous modulation of the inlet concentration and inlet temperature and the relative errors (Eq. (3.60)) are also given in Table 4.10.

Table 4.10 Yields of the product for simultaneous modulation of the inlet concentration and inlet temperature with forcing amplitudes A_C=100% and A_T=10% with optimal phase differences, estimated by numerical simulation and by the NFR method, and the relative errors

Simultaneous modulation of inlet concentration and inlet temperature, A_C=100%, A_T=10%, φ_{opt}						
ω	φ_{opt} (rad)	$Y_{P,po}$ (%)		δ_Y (%)	$\Delta Y_{P,po}$ (%)	
		num	NFRM		num	NFRM
0.1	0.0740	82.28	83.57	+1.57	+17.54	+19.38
1	0.4586	81.57	85.02	+4.23	+16.53	+21.45
10	0.1425	70.75	70.75	0	+1.07	+1.07

The results of numerical simulation for simultaneous modulation of the inlet concentration and inlet temperature confirmed the conclusions made by the NFR method.

Again, the same results are given in Table 4.11, for lower forcing amplitude of the inlet concentration modulation (A_C=75%), in order to compare the relative errors and the product yield increase.

Table 4.11 Yields of the product for simultaneous modulation of the inlet concentration and inlet temperature with forcing amplitudes A_C=75% and A_T=10%, with optimal phase differences, estimated by numerical simulation and by the NFR method, and the relative error

Simultaneous modulation of inlet concentration and inlet temperature, A_C=75%, A_T=10%, $\varphi_{opt}(\omega)$						
ω	φ_{opt} (rad)	$Y_{P,po}$ (%)		δ_Y (%)	$\Delta Y_{P,po}$ (%)	
		num	NFRM		num	NFRM
0.1	0.0740	77.41	77.34	-0.09	+10.59	+10.48
1	0.4586	77.45	78.85	+1.81	+10.65	+12.64
10	0.1425	70.58	70.58	0	+0.83	+0.83

The values of the relative errors show good agreement between the results of NFR method and numerical integration. The relative errors are lower for lower forcing amplitude of the inlet concentration (Tables 4.10 and 4.11). Lower amplitude also results in lower increase of the product yield.

4.10.3. Simulation results for simultaneous modulation of inlet concentration and flow-rate

The case of periodically operated non-isothermal CSTR when inlet concentration and flow-rate are simultaneously modulated is also tested for the Numerical example NONISO-1.

The simulation results will be first given for arbitrary chosen forcing amplitudes of inlet concentration and flow-rate, when the optimal phase difference which will maximize the product yield is used. Afterwards, the optimal forcing amplitudes and phase difference which maximize the product yield will be determined numerically as functions of the forcing frequency. Then, the simulation results will be given for these optimal forcing parameters.

The optimal phase difference which maximizes the yield of the product $\varphi_{opt}(\omega)$ (Eq. (2.84)) for forcing amplitudes A_C=100% and A_F=50%, is given in Figure 4.8, as a function of the dimensionless forcing frequency.
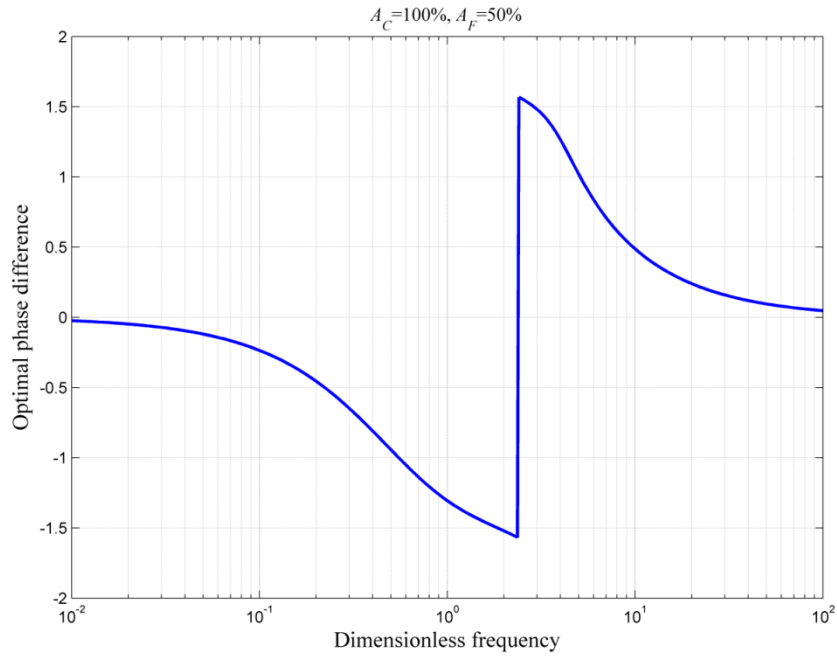
Figure 4.8 The optimal phase difference $\varphi_{opt}(\omega)$ for simultaneous modulation of the inlet concentration and flow-rate with forcing amplitudes A_C=100% and A_F=50%, as a function of the dimensionless forcing frequency

Furthermore, the yield of the product for simultaneous modulation of the inlet concentration and flow-rate with forcing amplitudes A_C=100% and A_F=50% and the corresponding optimal phase difference $\varphi_{opt}(\omega)$ is graphically presented in Figure 4.9, as a function of dimensionless forcing frequency. In the same Figure, the yields of the product corresponding to single input modulations of these two inputs, with the same forcing amplitudes, as well as for the steady-state operation, are given.

Figure 4.9 Yield of the product for the steady-state operation, for single and simultaneous modulation of the inlet concentration and flow-rate with forcing amplitudes A_C=100% and A_F=50%, and the optimal phase difference $\varphi_{opt}(\omega)$, vs. dimensionless forcing frequency

The simulation results in this case showed that simultaneous modulation of the inlet concentration and flow-rate is inferior then the single input modulation of the inlet concentration for low-forcing frequencies. Nevertheless, for high-forcing frequencies, contrary to all previous investigated cases of periodic operations, the simultaneous modulation of the inlet concentration and flow-rate improves the reactor performance.

This can also be confirmed from equation (4.94), as it was shown that the real part of the cross ASO FRF $H_{P2,CF}(\omega,-\omega)$ and the cross ASO FRF $H_{P2,CF}(\omega,-\omega)$ tend to following asymptotic value, for high frequency modulation

$$\lim_{\omega \to \infty} Re\left(H_{P2,CF}(\omega,-\omega)\right) = \lim_{\omega \to \infty} H_{P2,CF}(\omega,-\omega) = \frac{n(1+\alpha)(1+St)}{B_{ps}}$$

(4.125)

From equation (4.97), the cross ASO FRF $H^*_{P2,CF}(\varphi,\omega)$ for high-forcing frequencies will also tend to an asymptotic value:

$$\lim_{\omega \to \infty} H^*_{P2,CF}(\varphi,\omega) = \frac{n(1+\alpha)(1+St)}{B_{ps}} \cos(\varphi)$$

(4.126)

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as well as the outlet dimensionless molar flow-rate of the product

$$\lim_{\omega \to \infty} N_{P,DC} = 2 \left(\frac{A_C}{2}\right) \left(\frac{A_F}{2}\right) \frac{n(1+\alpha)(1+St)}{B_{ps}} \cos(\varphi)$$

$$(4.127)$$

From the above presented, the product yield for high-forcing frequencies is given with the following expression

$$\lim_{\omega \to \infty} Y_{P,po} = Y_{P,s} \frac{1 + 2 \left(\frac{A_C}{2}\right) \left(\frac{A_F}{2}\right) \frac{n(1+\alpha)(1+St)}{B_{ps}} \cos(\varphi)}{1 + 2 \left(\frac{A_C}{2}\right) \left(\frac{A_F}{2}\right) \cos(\varphi)}$$

$$(4.128)$$

It can be seen that in this case the product yield will depend on the forcing amplitudes, phase difference between the modulated inputs and the characteristics of the system (through the reaction order n and auxiliary parameters α, β, γ and St). Also, for high-forcing frequencies, the reactor performance depends only on the cross effect of the simulated inputs. Only in the case of simultaneous modulation of inlet concentration and flow-rate the high forcing frequency will have an influence on the reactor improvement.

Furthermore, for simultaneous modulation of the inlet concentration and flow-rate, the optimal forcing parameters, i.e. the forcing amplitudes and the phase difference which should be used in order to maximize the product yield are graphically presented in Figure 4.10. The optimal forcing amplitudes and phase difference were obtained numerically from equation (2.77) in Matlab (by using standard *fminmax* function).
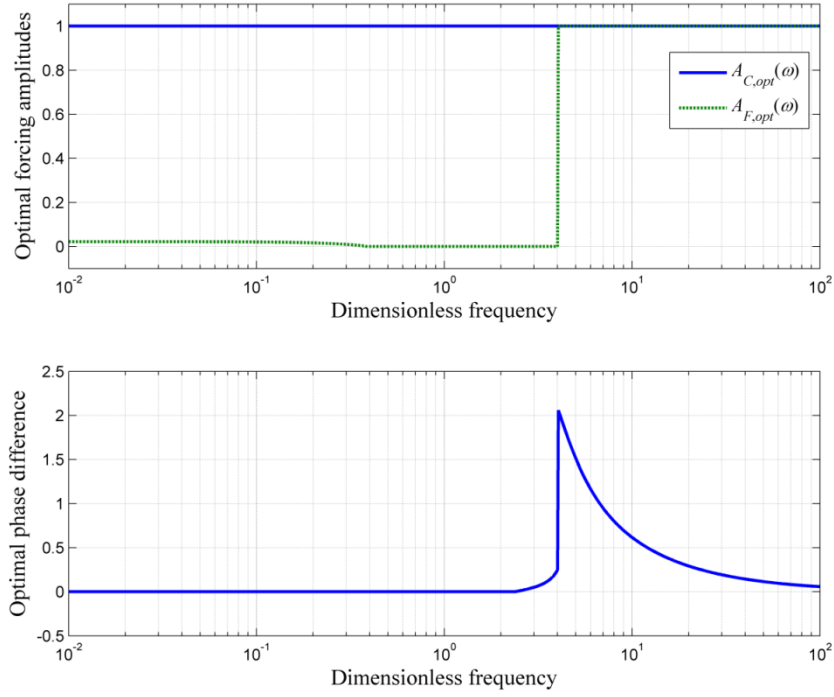
Figure 4.10 The optimal forcing amplitudes (up) and the optimal phase difference
(down) as functions of the dimensionless forcing frequency

For low-forcing frequencies, the optimized forcing parameters indicated that the single input modulation of inlet concentration is recommended, considering that the optimal forcing amplitude for the inlet concentration is 1 and for the flow-rate 0. For high-forcing frequencies, simultaneous modulation of these two inputs is recommended, considering the fact that both optimal forcing amplitudes are 1 (Figure 4.10).

Then, the yield of the product for simultaneous modulation of the inlet concentration and flow-rate with optimal forcing amplitudes $A_{C,opt}(\omega)$, $A_{F,opt}(\omega)$ and optimal phase difference $\varphi_{opt}(\omega)$ is graphically presented in Figure 4.11, as a function of the dimensionless forcing frequency, together with the yields corresponding to single input modulations of the inlet concentration and flow-rate, with the same forcing amplitudes. The yield of the product for steady-state operation is also graphically presented in Figure 4.11.

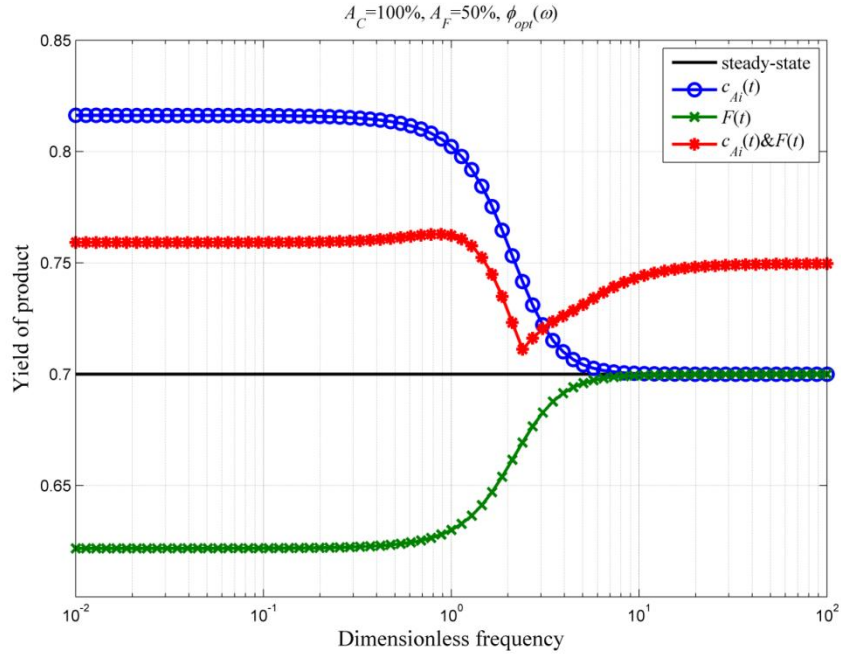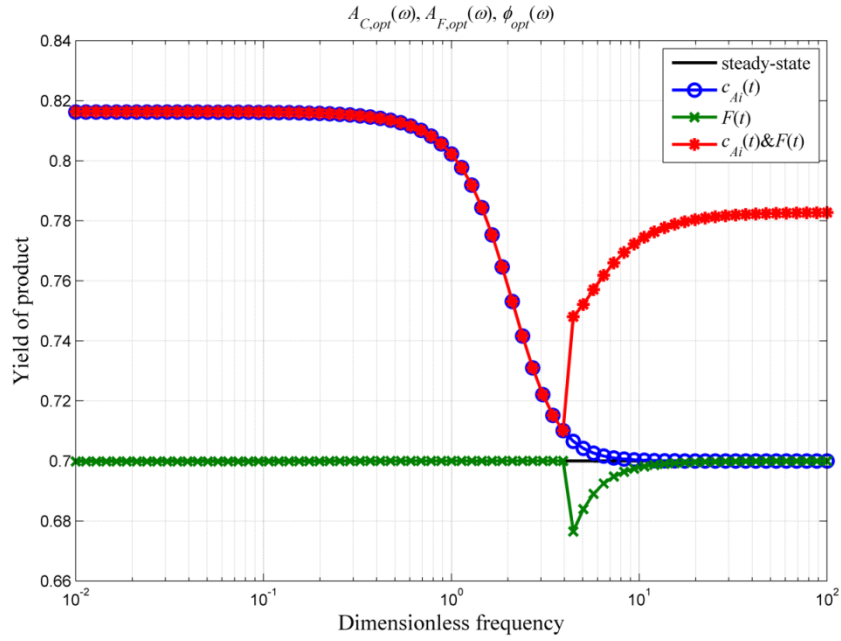Figure 4.11 Yield of the product for the steady-state operation, for single and simultaneous modulation of the inlet concentration and flow-rate with optimal forcing amplitudes $A_{C,opt}(\omega)$, $A_{F,opt}(\omega)$ and optimal phase difference $\varphi_{opt}(\omega)$, vs. dimensionless forcing frequency

Comparison with the results obtained by numerical integration

In Table 4.12, the results of the NFR method are compared with the results of numerical integration for simultaneous modulation of inlet concentration and flow rate with arbitrary chosen forcing amplitudes A_C=100% and A_F=50% and with the corresponding optimal phase difference $\varphi_{opt}(\omega)$ (Eq. (2.84)).

In Table 4.13, the same results are given, but for the optimal forcing amplitudes $A_{C,opt}(\omega)$, $A_{F,opt}(\omega)$ and the corresponding optimal phase difference $\varphi_{opt}(\omega)$ which were numerically obtained in such a way to maximize the product yield.

The results presented in Tables 4.12 and 4.13 are given for dimensionless forcing frequencies 0.1, 1 and 10. The product yields together with their relative changes owing to periodic operation are given. The relative errors of the NFR method, in comparison with the numerical solutions are also given in these Tables.

Table 4.12 Product yields of product for simultaneous modulation of the inlet concentration and flow-rate with forcing amplitudes A_C=100% and A_F=50% with the corresponding optimal phase differences, estimated by numerical simulation and by the NFR method, and the relative errors of the NFR method

Simultaneous modulation of inlet concentration and flow-rate, A_C=100%, A_F=50%, $\varphi_{opt}(\omega)$						
ω	φ_{opt} (rad)	$Y_{P,po}$ (%)		δ_Y (%)	$\Delta Y_{P,po}$ (%)	
		num	NFRM		num	NFRM
0.1	-0.2361	77.09	75.92	-1.52	+10.13	+8.46
1	-1.3066	76.26	76.23	-0.04	+8.94	+8.90
10	0.4867	75.08	74.37	-0.95	+7.26	+6.24

Table 4.13 Product yields for simultaneous modulation of the inlet concentration and flow-rate with optimal forcing amplitudes and optimal phase differences, estimated by numerical simulation and by the NFR method and the relative errors of the NFR method

Simultaneous modulation of inlet concentration and flow-rate								
ω	A_C(%)	A_F (%)	φ_{opt} (rad)	$Y_{P,po}$ (%)		δ_Y (%)	$\Delta Y_{P,po}$ (%)	
				num	NFRM		num	NFRM
0.1		2.05	0	79.92	81.63	+2.14	+14.17	+16.61
1	100	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

As it can be seen from the results given in Tables 4.12 and 4.13, all conclusions and the results obtained by the NFR method are confirmed with the numerical simulation results. The NFR method gives very good predictions, considering low values of the relative errors which are given in Tables 4.12 and 4.13.

As illustration, the simulated outlet concentration of the product, flow-rate and outlet molar flow-rate of the product from the non-isothermal CSTR defined in this example, obtained by numerical integration of the model equations, for simultaneous co-sinusoidal modulation of the inlet concentration and flow-rate, for optimal forcing amplitudes $A_{C,opt}$=100%, $A_{F,opt}$=100%, for forcing frequency ω=10 and optimal phase difference $\varphi=\varphi_{opt}$=0.6151, is given in Figure 4.13. The simulated outlet is given with the start-up period. But first, in Figure 4.12, the modulation of the inlet concentration of the reactant, flow-rate and the inlet molar flow-rate of the reactant are presented for the

defined forcing parameters. In both Figures, the corresponding mean or/and steady-state values are given.
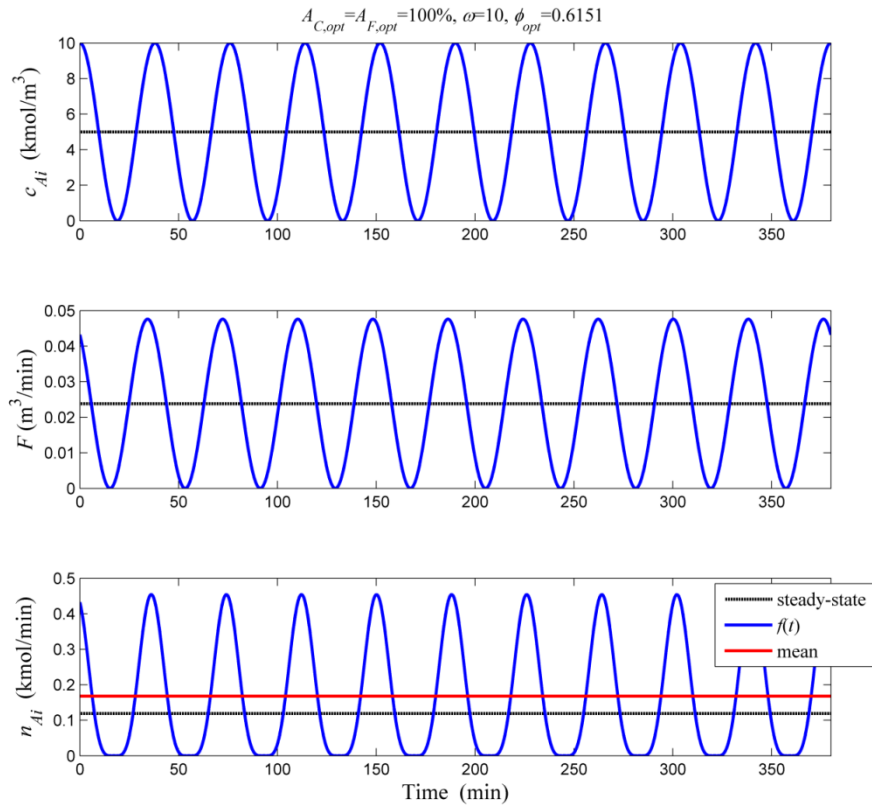
Figure 4.12 The modulated inlet concentration of the reactant (top), and flow-rate (middle), for simultaneous modulation of these two inputs with dimensionless forcing frequency $\omega=10$, optimal forcing amplitudes $A_C=A_F=100\%$, and optimal phase difference $\varphi_{opt}=0.6151$, and the inlet molar flow-rate of the reactant (bottom)
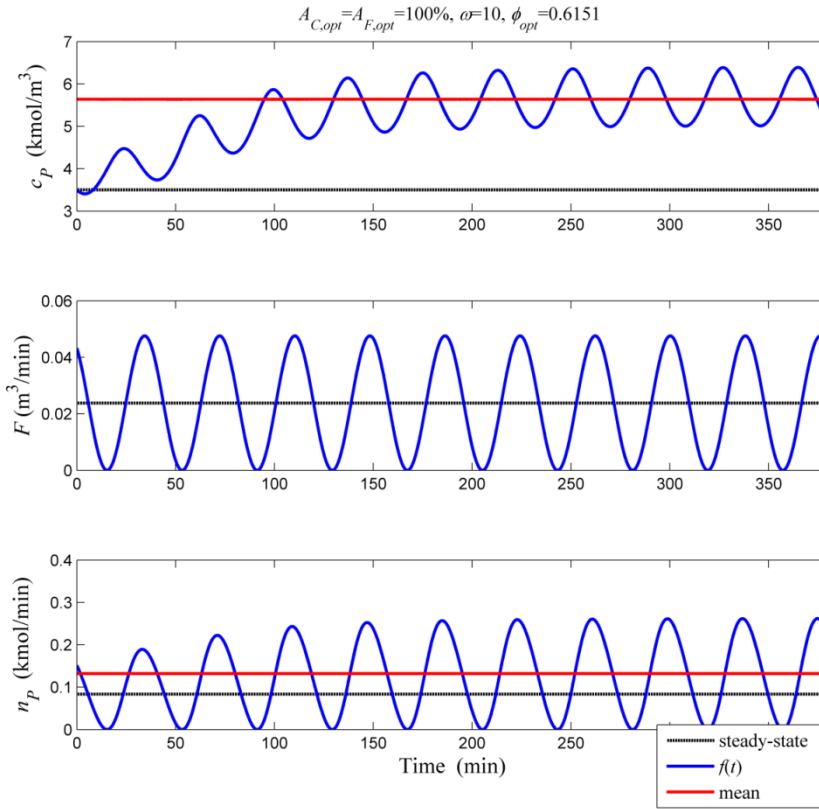
Figure 4.13 The outlet product concentration (top), flow-rate (middle) and the outlet molar flow-rate of the product (bottom) for dimensionless forcing frequency $\omega=10$, optimal forcing amplitudes $A_C=A_F=100\%$, and optimal phase difference $\varphi_{opt}=0.6151$

4.11. Analysis of influence of the system nonlinearity on the results obtained by the NFR method

Considering that the NFR method can be applied only for weakly nonlinear stable systems (*Petkovska and Seidel-Morgenstern*, *2012*) for which the Volterra series is convergent, and the fact that non-isothermal CSTR is in principle a system which is highly nonlinear, in this Section, the NFR method based on the second order approximation will be tested on the systems with different degree of nonlinearity.

Simulation of the ASO FRFs and the cross ASO FRFs and the analysis, whether, and to which extent, it would be possible to increase the product yield in a non-isothermal reactor owing to periodic modulation of the inlet concentration and inlet temperature, separately or simultaneously, is performed considering three numerical examples: one which corresponds to an oscillatory stabile system with strong resonant behavior (Numerical example NONISO-2(a)), one which corresponds to an oscillatory stable

system with weak resonant behavior (Numerical example NONISO-2(b)) and one which corresponds to a non-oscillatory stable system (Numerical example NONISO-2(c)).

4.11.1. Numerical examples NONISO-2(a), NONISO-2(b), NONISO-2(c)

The model parameters corresponding to these numerical examples are given in Table 4.14. All parameters have the same values for all three numerical examples, except the heat of reaction. The parameters for Numerical example NONISO-2(a) correspond to a numerical example used in a textbook by Marlin (*Marlin, 2000*).

Table 4.14 Model parameters for the numerical examples

Parameter		Value
Reaction order, n		1
Volume of the reactor, V (m^3)		1
Pre-exponential factor of the reaction rate constant, k_o, (1/min)		$1 * 10^{10}$
Activation energy, E_A (kJ/kmol)		69256
Heat of reaction, ΔH_R (kJ/kmol)	Numerical example NONISO-2(a)	-543920
	Numerical example NONISO-2(b)	-271960
	Numerical example NONISO-2(c)	-54392
Heat capacity, $\overline{\rho c_p}$ (kJ/K/ m^3)		4.184×10^3
Steady-state flow-rate, F_s (m^3/min)		1
Steady-state inlet concentration, $c_{Ai,s}$ (kmol/ m^3)		2
Steady-state inlet temperature, $T_{i,s}$ (K)		323
Steady-state temperature of the coolant, $T_{J,s}$ (K)		365
Overall heat transfer coefficient multiplied by the heat transfer area, UA_w (kJ/K/min)		27337

Furthermore, the steady state point defined with the outlet concentration of the reactant ($c_{A,s}$) and product ($c_{P,s}$), product yield ($Y_{P,s}$) and the outlet temperature (T_s), as well as the stability parameters (A_{ps}, B_{ps}) (Eqs. (4.24) and (4.25)), the damping coefficient (ξ) (Eq. (4.28)), the resonant frequency (ω_r) (if existing) (Eq. (4.30)) and the eigenvalues, are given in Table 4.15, for all three numerical examples.

Table 4.15 The steady-state concentrations, yield and temperature, the stability parameters, damping coefficient, resonant frequency and the eigenvalues for the numerical examples

Numerical example NONISO	Steady-state point				A_{ps}	B_{ps}	ξ	ω_r	The eigenvalues
	$c_{A,s}$ (kmol/m^3)	$c_{P,s}$ (kmol/m^3)	$Y_{P,s}$ (%)	T_s (K)					
2(a)	0.3466	1.6534	82.67	388.1	-0.71	31.59	0.126	5.53	-0.71±5.58i
2(b)	0.7356	1.2644	63.22	370.5	-2.63	15.50	0.669	1.28	-2.63±2.93i
2(c)	1.016	0.9842	49.20	361.3	-4.34	14.02	1.160	/	-2.14, -6.54

The Numerical example NONISO-2(a) is identical to the one used for investigation of single inputs modulations in (*Nikolić et al. 2014a, 2014b*). The reactor is oscillatory stable (A_{ps}<0 and B_{ps}>0, A_{ps}^2<B_{ps}), with a low damping coefficient ξ=0.126 (*Nikolić et al. 2014a*). The non-isothermal CSTR defined as Numerical example NONISO-2(a) is highly nonlinear as a consequence of an extremely high heat of reaction (ΔH_R=-543920 kJ/kmol). Also, concerning that the damping coefficient is quite low, the system is highly oscillatory with pronounced resonant behavior.

For the Numerical example NONISO-2(b) the heat of reaction is 2 times lower than for the system defined as Numerical example NONISO-2(a). The non-isothermal CSTR defined in this way is oscillatory stable with weak resonant behavior with a damping coefficient ξ=0.669. The increase of the damping coefficient for Numerical example NONISO-2(b) in comparison to the Numerical example NONISO-2(a), means that the system is less oscillatory.

Finally, the Numerical example NONISO-2(c) corresponds to a non-isothermal CSTR with heat of the reaction which is 10 times lower than the heat of the reaction for Numerical example NONISO-2(a) (ΔH_R=-54392 kJ/kmol). The system is stable and non-oscillatory with damping coefficient ξ=1.160. The non-isothermal CSTR defined in this way does not exhibit resonant behavior.

The maximal allowed forcing amplitudes of the inlet concentration and inlet temperature are assumed to be the same for all numerical examples, $A_{C,max}$=100%, $A_{T,max}$=15%. The forcing amplitudes are not limited from the aspect of the system stability, but are from the aspect of what could be practically realized. E.g. the maximal

amplitude of the inlet temperature corresponds to absolute maximal change in the inlet temperature of $\Delta T_{i,max}$=48.5 K (*Nikolić et al. 2014a, 2014b*).

The analysis of the periodic operations for these numerical examples is done through simulation and analysis of the product ASO FRFs and product cross ASO FRFs.

4.11.2 Simulation results modulation of the inlet concentration and temperature, separately and simultaneously

In this Section, the simulation results of the product concentration ASO FRFs corresponding to the single input modulation of inlet concentration and temperature, as well as the cross ASO FRFs of product concentration and the yields of product are presented for each numerical example.

In Figure 4.14 the graphical representation of the ASO FRFs $G_{P2,CC}(\omega,-\omega)$ for each numerical example is given vs. dimensionless forcing frequency.
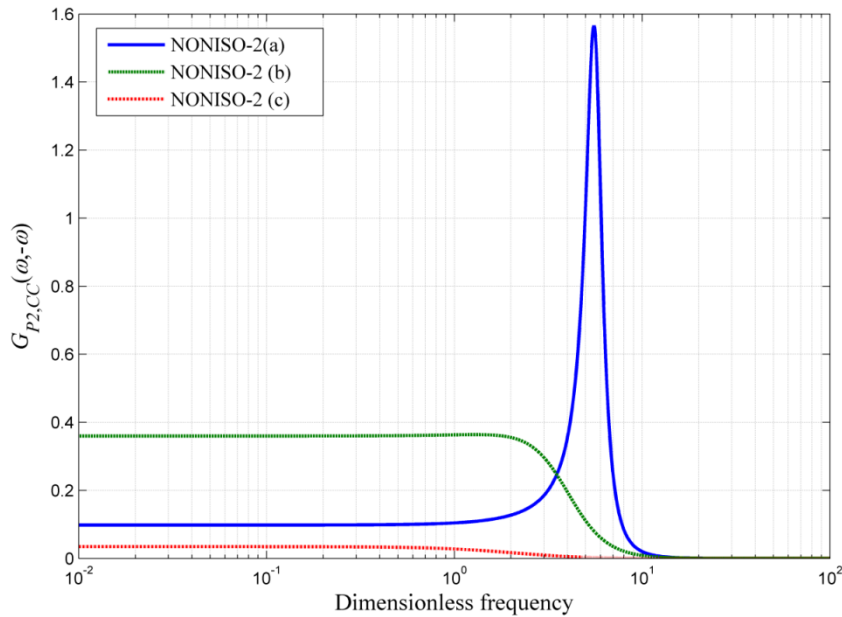
Figure 4.14 The ASO FRFs $G_{P2,CC}(\omega,-\omega)$ vs. dimensionless forcing frequency, for Numerical examples NONISO 2(a), 2(b) and 2(c)

For each numerical example, the ASO FRFs $G_{P2,CC}(\omega,-\omega)$ are positive in the whole frequency range, meaning that the inlet concentration modulation will lead to increase of the product yield in comparison to the steady-state operation. For low-frequencies these ASO FRFs tend to asymptotic values, and for high-forcing frequencies they all tend to zero.

This behavior is in accordance with the sign analysis given in Table 4.2. For reaction order $n=1$ and the values of parameters n_C which are for Numerical examples NONISO-2(a), 2(b) and 2(c), $n_c=0.43$, 0.12 and 0.80, respectively, the positive sign of the $G_{P2,CC}(\omega,-\omega)$ is obtained.

It is interesting to notice, that the ASO FRF $G_{P2,CC}(\omega,-\omega)$ for the highly nonlinear system, Numerical example NONISO-2(a), has an extensive maximum around the corresponding resonant frequency ($\omega_r=5.53$).

In Figure 4.15, the ASO FRFs $G_{P2,TT}(\omega,-\omega)$ for each numerical example is graphically presented vs. dimensionless forcing frequency.
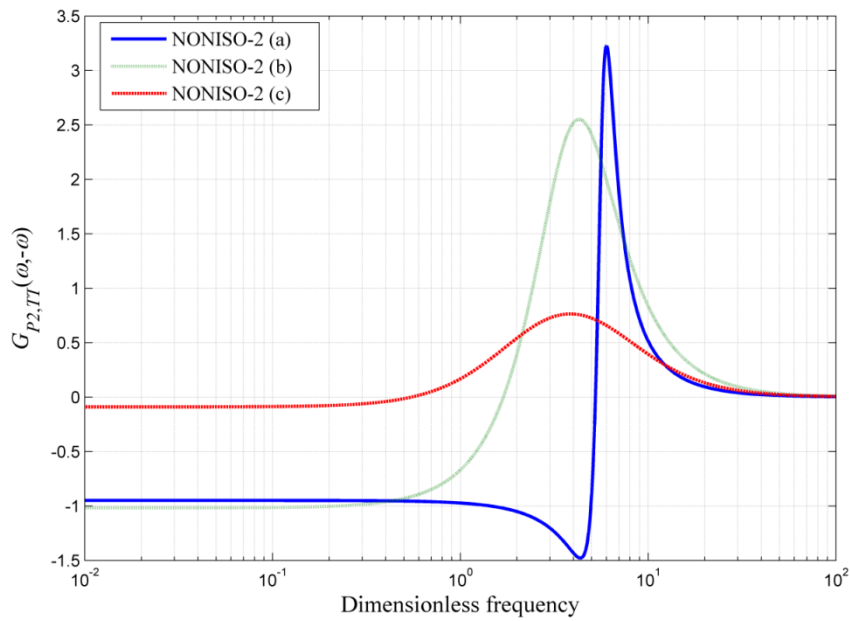
Figure 4.15 The ASO FRFs $G_{P2,TT}(\omega,-\omega)$ vs. dimensionless forcing frequency for Numerical examples NONISO 2(a), 2(b) and 2(c)

From the results of the sign analysis of the ASO FRF $G_{P2,TT}(\omega,-\omega)$ which were given in Table 4.4 and the parameters (Eqs. (4.120) and (4.121)), given in Table 4.16, considering that the reaction order is $n=1$, it can be predicted that the ASO FRFs $G_{P2,TT}(\omega,-\omega)$ for all numerical examples will change the sign from negative to positive, for corresponding forcing frequencies $\omega_{0,T}$ (also given in Table 4.16).

Table 4.16 The parameters necessary for the sign analysis of the ASO FRF $G_{P2,TT}(\omega,-\omega)$

Numerical example NONISO-	n_{T1}	n_{T2}	γ-2	$\omega_{0,T}$
2(a)	-11.15	0.001	19.46	5.24
2(b)	-12.42	0.01	20.48	1.69
2(c)	-13.63	0.03	21.0	0.55

The results of the sign analysis are again confirmed with the simulation results which are given in Figure 4.15. The results of the sign analysis and the simulation results indicate that for each numerical example, the increase of product yield is possible for the forcing frequencies which are higher than corresponding value of forcing frequency $\omega_{0,T}$.

Again, it is interesting to notice the existence of an extensive maximum for Numerical example NONISO-2(a), for the forcing frequency which is near the resonant one (ω_r=5.53). Also, for Numerical example NONISO-2(b), a maximum exists for the forcing frequency which is near to corresponding resonant frequency (ω_r=1.28), but not as extensive as for Numerical example NONISO-2(a).

A graphical representation of the real and imaginary parts of the cross ASO FRFs $G_{P2,CT}(\omega,-\omega)$ as functions of the dimensionless forcing frequency is given in Figure 4.16, for all three numerical examples.
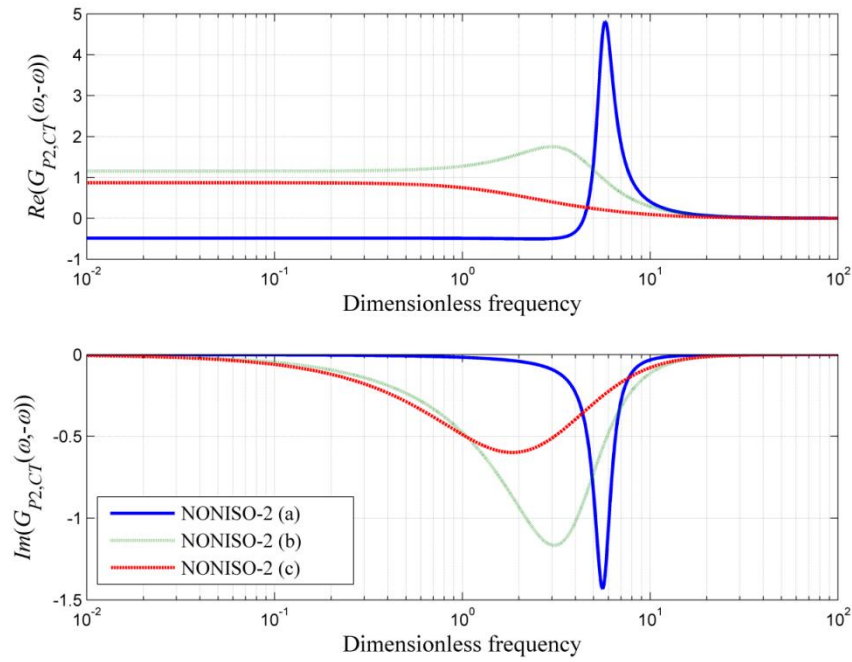
Figure 4.16 The real and imaginary parts of the cross ASO FRF $G_{P2,CT}(\omega,-\omega)$, as functions of the dimensionless frequency, for Numerical examples NONISO-2(a), NONISO-2(b) and NONISO-2(c)

For Numerical example NONISO-2(a), the real and imaginary parts of $G_{P2,CT}(\omega,-\omega)$ both have extensive extremes near the resonant frequency ($\omega_r=5.53$). For Numerical example NONISO-2(b), the real and imaginary parts of $G_{P2,CT}(\omega,-\omega)$ again have extremes near the resonant frequency ($\omega_r=1.28$), but not as extensive as for Numerical example NONISO-2(a). For the non-oscillatory stable non-isothermal CSTR, i.e. Numerical example NONISO-2(c), the real part of the cross ASO FRF $G_{P2,CT}(\omega,-\omega)$ has no extreme values and the imaginary part of this function has a minimum.

The results of the sign analysis, in accordance with Table 4.5 and Table 4.6, as well as the values of the auxiliary parameters ε_R (Eq. (4.122)), $\omega_{0,CT}$ (Eq. (4.123)) and ε_I (Eq.(4.124)) necessary for the sign analysis, are summarized in Table 4.17, with respect that the chemical reaction is first order ($n=1$). The results of the sign analysis of the real and imaginary parts of the cross ASO FRF $G_{P2,CT}(\omega,-\omega)$ are confirmed with the simulation results, presented in Figure 4.16.

Table 4.17 The results of the sign analysis of the real and imaginary parts of $G_{P2,CT}(\omega,-\omega)$, for the three numerical examples

Numerical example NONISO-	ε_R	$\omega_{0,CT}$	Forcing frequency, ω	$Re(G_{P2,CT}(\omega,-\omega))$	ε_I	$Im(G_{P2,CT}(\omega,-\omega))$	Recommended range of φ
2(a)	-19.63	4.43	$\omega<4.43$	negative	-0.65	negative	$-\pi < \varphi < -\dfrac{\pi}{2}$
			$\omega=4.43$	zero			$-\pi < \varphi < 0$
			$\omega>4.43$	positive			$-\dfrac{\pi}{2} < \varphi < 0$
2(b)	10.70	/	$\forall\omega$	positive	-4.37	negative	$-\dfrac{\pi}{2} < \varphi < 0$
2(c)	13.90	/	$\forall\omega$	positive	-5.50	negative	$-\dfrac{\pi}{2} < \varphi < 0$

The phase differences which should be used in order to achieve the positive value of the cross term $G^*_{P2,CT}(\varphi,\omega)$, with respect to the signs of the real and imaginary parts of the cross ASO FRF $G_{P2,CT}(\omega,-\omega)$, according to Table 2.2, are also given in Table 4.17.

The optimal phase differences $\varphi_{opt}(\omega)$ (defined by Eq. (4.67)), for all three numerical examples, are graphically presented in Figure 4.17. The optimal phase differences are in the recommended ranges which are given in Table 4.17.
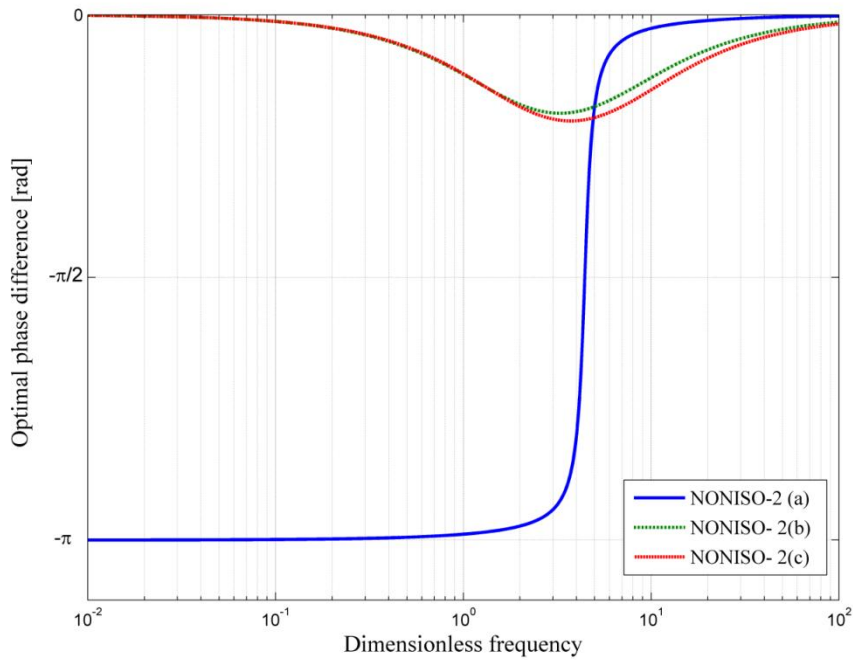
Figure 4.17 The optimal phase differences as functions of the dimensionless forcing frequency, for Numerical examples NONISO-2(a), NONISO-2(b) and NONISO-2(c)

The cross ASO terms corresponding to the optimal phase differences $G^*_{P2,CT}(\varphi_{opt},\omega)$, are graphically presented in Figure 4.18, for Numerical examples NONISO-2(a), NONISO-2(b) and NONISO-2(c), respectively.

$\phi_{opt}(\omega)$
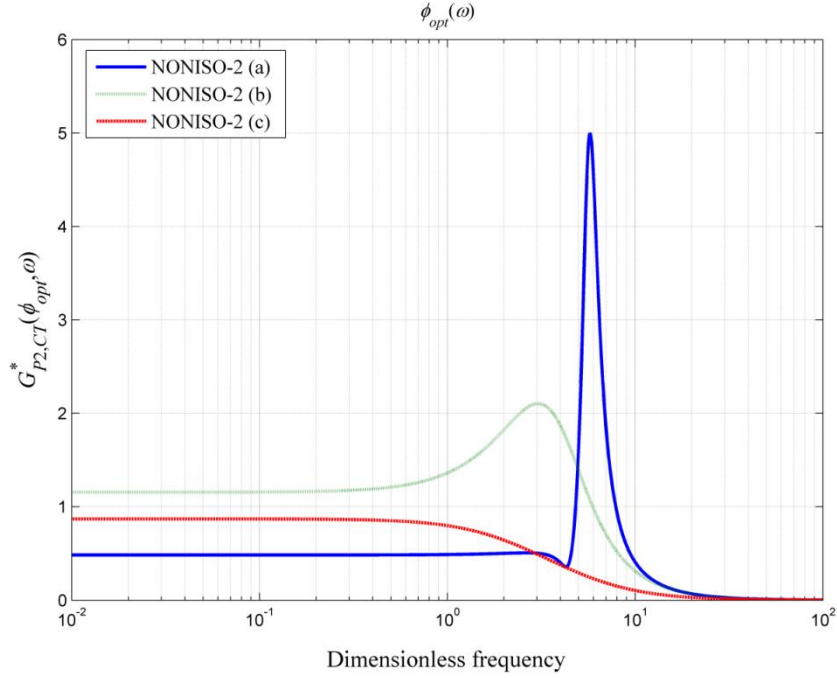
Figure 4.18 The cross ASO terms corresponding to the optimal phase differences, $(G^*_{P2,CT}(\varphi_{opt},\omega))$ as functions of the dimensionless forcing frequency, for Numerical examples NONISO-2(a), NONISO-2(b) and NONISO-2(c)

From Figures 4.14, 4.15 and 4.18 we can conclude the following:

- For Numerical example NONISO-2(a), similarly to the ASO FRFs which correspond to the single input modulations, the cross ASO term $G^*_{P2,CT}(\varphi_{opt},\omega)$ has an extensive maximum close to the resonant frequency ω_r=5.53, where the highest improvement is expected.

- For Numerical example NONISO-2(b), the cross ASO term $(G^*_{P2,CT}(\varphi_{opt},\omega))$ has a maximum in the vicinity of the resonant frequency ω_r=1.28, but not as extensive as for Numerical example NONISO-2(b).

- For the non-oscillatory non-isothermal CSTR defined as Numerical example NONISO-2(c), the cross ASO term $G^*_{P2,CT}(\varphi_{opt},\omega)$ has no extremes.

- For all three numerical examples, the ASO FRFs $G_{P2,CC}(\omega,-\omega)$ are positive in the whole frequency range (*Nikolić et al. 2014a*), while $G_{P2,TT}(\omega,-\omega)$ changes its sign from negative to positive. $G_{P2,TT}(\omega,-\omega)$ is negative for $\omega<\omega_{0,T}$ and positive for $\omega>\omega_{0,T}$ (*Nikolić et al. 2014b*). The forcing frequency for which these ASO

FRFs change its signs is $\omega_{0,T}$=5.24 for Numerical example NONISO-2(a), $\omega_{0,T}$=1.69 for Numerical example NONISO-2(b) and $\omega_{0,T}$=0.55 for Numerical example NONISO-2(c).

- The cross ASO terms for the optimal phase $G^*_{P2,CT}(\varphi_{opt},\omega)$ are, as expected, positive in the whole frequency range for all three numerical examples (Figure 4.19).

- For forcing frequencies $\omega>\omega_{0,T}$ both product ASO FRFs corresponding to the single input modulations $G_{P2,CC}(\omega,-\omega)$ and $G_{P2,TT}(\omega,-\omega)$ are positive, which guaranties that in this frequency range simultaneous modulation of these two inputs will results with yield increase.

- For $\omega<\omega_{0,T}$, since the ASO FRFs $G_{P2,TT}(\omega,-\omega)$ are negative, it is necessary to evaluate the overall DC components of the outlet product concentration or the corresponding yield of the product in order to reveal whether improvement is possible in this frequency range.

The yield of the product for Numerical example NONISO-2(a), obtained when the inlet concentration and inlet temperature are modulated, separately or simultaneously modulated with the optimal phase difference, for forcing amplitudes A_C=50%, A_T=10%, as functions of the dimensionless forcing frequency, are graphically presented in Figure 4.19. The yield of product in steady-state is also given in Figure 4.19 for comparison. The same results are given for the Numerical example NONISO-2(b) in Figure 4.20, and for Numerical example NONISO-2(c), in Figure 4.21.
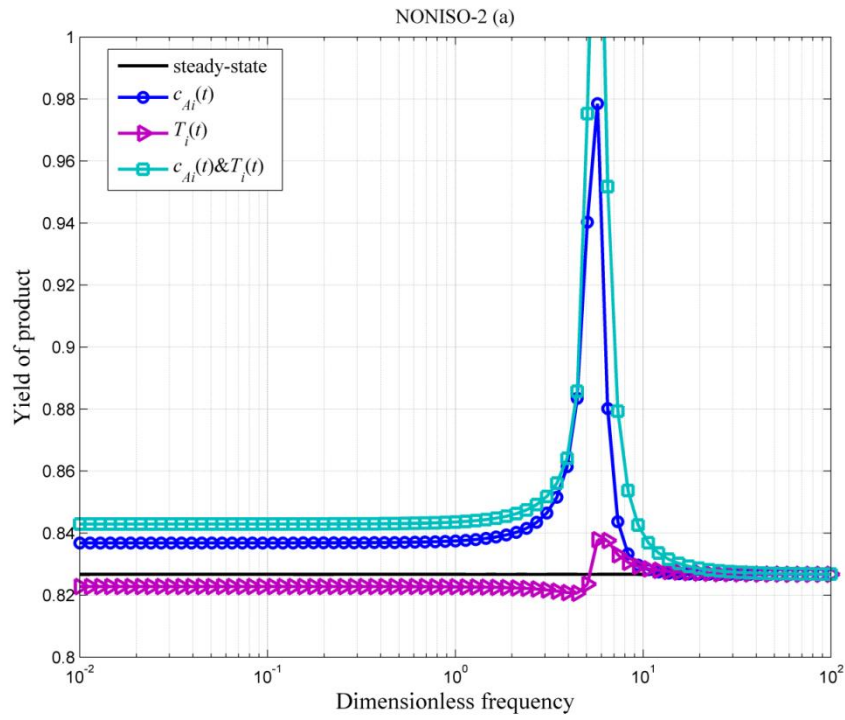
Figure 4.19 The product yield for steady-state operation, for periodic modulation of the inlet concentration with forcing amplitude A_C=50%, for periodic modulation of the inlet temperature with forcing amplitude A_T=10% and for simultaneous modulation of these two inputs with the optimal phase difference, vs. dimensionless forcing frequency, for Numerical example NONISO-2(a)
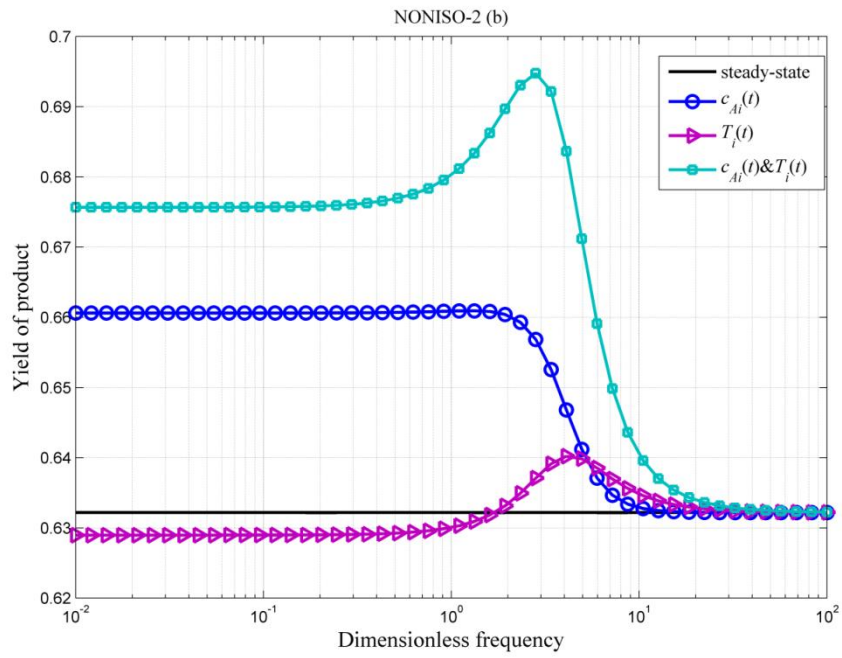
Figure 4.20 The product yield for steady-state operation, for periodic modulation of the inlet concentration with forcing amplitude A_C=50%, for periodic modulation of the inlet temperature with forcing amplitude A_T=10% and for simultaneous modulation of these two inputs with the optimal phase difference, vs. dimensionless forcing frequency, for Numerical example NONISO-2(b)
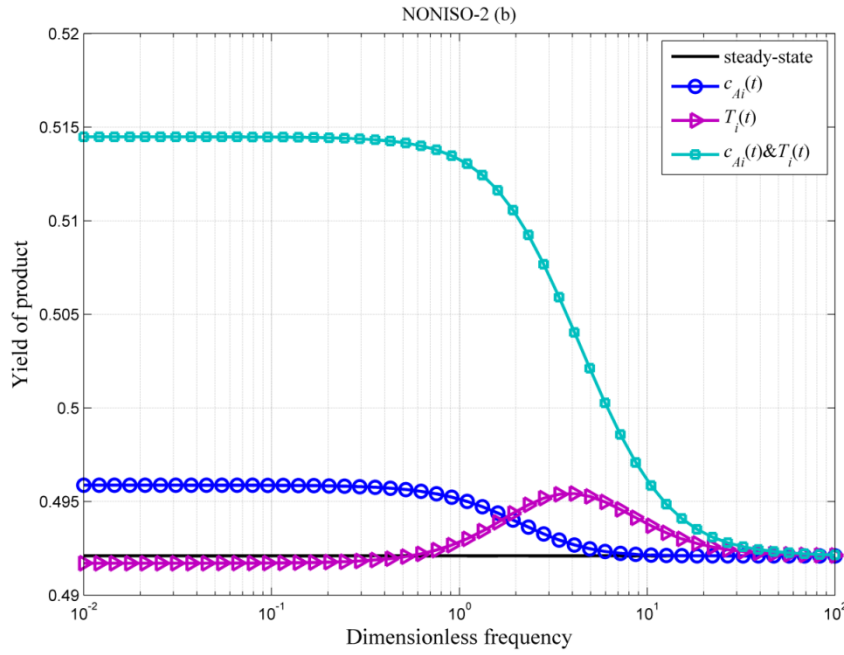
Figure 4.21 The product yield for steady-state operation, for periodic modulation of the inlet concentration with forcing amplitude A_C=50%, for periodic modulation of the inlet temperature with forcing amplitude A_T=10% and for simultaneous modulation of these two inputs with the optimal phase difference, vs. dimensionless forcing frequency, for Numerical example NONISO-2(c)

From Figures 4.19-4.21 it can be concluded that:

- For all three numerical examples, it is possible to achieve higher increase of conversion when both inputs are periodically modulated with optimal phase difference, in comparison to the single input modulations (with same forcing amplitudes).

- Even for forcing frequencies for which it is not possible to achieve higher yield of product by modulation of the inlet temperature ($\omega<\omega_{0,T}$, $G_{P2,TT}(\omega,-\omega)<0$), if inlet concentration and inlet temperature are simultaneously modulated with forcing amplitudes A_C=50%, A_T=10% and the optimal phase difference, it is possible to achieve increase of the product yield. This increase of the product yield is higher in comparison to the single input modulation of inlet concentration.

- The increase of the product yield for two-input modulation around the resonant frequency for Numerical example NONISO-2(b) is significantly lower that it is

for Numerical example NONISO-2(a), around its resonant frequency. Nevertheless, the difference between the product yield increase for Numerical examples NONISO-2(a) and NONISO-2(b) at low-frequencies are much less significant than around the resonant frequency. The increase of the product yield for Numerical example NONISO-2(c) (non-oscillatory CSTR) is lower than for Numerical examples NONISO-2(a) and NONISO-2(b). This means that higher improvement can be expected for the highly nonlinear systems, which is in accordance with the previous investigations (*Ritter and Douglas, 1970*).

- For Numerical example NONISO-2(a), for inlet concentration modulation or simultaneous modulation of inlet concentration and inlet temperature, the product yields have maximums around the resonant frequency (ω_r=5.53). For the case of simultaneous modulation of these two-inputs for the forcing frequency which is near to the resonant one, the product yield, based on the NFR method, is predicted to be higher than 1, which is physically impossible.

- For Numerical example NONISO-2(b), the product yield has a maximum for simultaneous modulation of inlet concentration and inlet temperature for forcing frequencies which are near to the resonant one (ω_r=1.28).

- For Numerical example NONISO-2(b), the product yield for simultaneous modulation of inlet concentration doesn't have any extremes.

4.11.3. Comparison with results obtained by numerical integration

The product yields predicted by application of the NFR method are compared with the results obtained by numerical integration of the model equations, for the periodic modulation of the inlet concentration and inlet temperature, separately and simultaneously (with the optimal phase difference). The model equations were numerically solved in their original, dimensional form (*Nikolić et al, 2014a*) by using a standard Matlab function ode15s. The inputs were modulated in a co-sinusoidal way around the previously established steady-state.

The results of numerical integration and of the NFR method are compared for Numerical examples:

- NONISO-2(a) for 2 different combinations of forcing amplitudes, A_C=50% and 25% for inlet concentration (corresponding to absolute changes of inlet concentration of 1 kmol/m^3 and 0.5 kmol/m^3 respectively) and A_T=10% and 5% for inlet temperature (corresponding to absolute changes of inlet temperature of

32.3 K and 16.2 K respectively) and for 12 different forcing frequencies, including the resonant one.

- NONISO-2(b) for forcing amplitudes A_C=50% and A_T=10% for 8 different forcing frequencies including the resonant one;
- NONISO-2(c) for forcing amplitudes A_C=50% and A_T=10% for 3 different forcing frequencies

In order to compare the agreement between the results obtained by the NFR method and by numerical integration, the relative errors were calculated. The yield of the product obtained by numerical simulation is considered to be exact.

The results of numerical integration and the corresponding results of the NFR method for Numerical example NONISO-2(a) are given in Tables 4.18 and 4.19, for Numerical example NONISO-2(b) in Table 4.20 and for Numerical example NONISO-2(c) in Table 4.21. In Tables 4.18-4.21, the yields of the product and the relative errors δ_Y (Eq. (3.59)) are given in percentages. The steady-state yields were 82.67 %, 63.22 % and 49.20 %, respectively (Table 4.15).

Table 4.18 The product yield for separate and simultaneous modulation of the inlet concentration and temperature with forcing amplitudes A_C=50% and A_T=10%, estimated by numerical simulation and by the NFR method, and the relative errors, for Numerical example NONISO-2(a)

ω	Inlet concentration modulation, A_C=50%			Inlet temperature modulation, A_T=10%			Simultaneous modulation A_C=50%, A_T=10%			
	Y_P		δ_Y	Y_P		δ_Y	φ_{opt}	Y_P		δ_Y
	num	NFRM		num	NFRM			num	NFRM	
0.1	84.05	83.69	-0.43	82.27	82.28	+0.01	-3.14	84.32	84.29	-0.04
1	84.15	83.75	-0.48	82.27	82.27	0	-3.11	84.37	84.36	-0.01
2	84.24	83.99	-0.30	82.24	82.24	0	-3.06	84.32	84.59	+0.32
3	84.25	84.59	+0.40	82.21	82.17	-0.05	-2.96	83.83	85.13	+1.55
4	84.16	86.35	**+2.60**	82.08	82.08	0	-2.52	83.31	86.58	**+3.92**
5	84.51	93.47	**+10.60**	82.15	82.30	0.18	-0.55	84.42	96.51	**+14.32**
5.53	84.58	98.86	**+16.88**	82.42	83.39	+1.18	-0.32	84.83	109	**+28.49**
6	84.53	93.69	**+10.84**	82.77	84.01	+1.50	-0.24	85.06	104.35	**+22.68**
7	84.12	85.19	+1.27	83.22	83.44	+0.26	-0.16	85.25	89.72	**+5.24**
8	83.46	83.53	+0.08	83.08	83.11	+0.04	-0.12	85.04	85.90	+1.01
9	83.05	83.06	+0.01	82.96	82.97	+0.01	-0.10	84.40	84.56	+0.19
10	82.88	82.88	0	82.88	82.88	0	-0.08	83.89	83.93	+0.05

Table 4.19 The product yield for separate and simultaneous modulation of the inlet concentration and temperature with forcing amplitudes A_C=25% and A_T=5%, estimated by numerical simulation and by the NFR method, and the relative errors, for Numerical example NONISO-2(a)

ω	Inlet concentration modulation, A_C=25%			Inlet temperature modulation, A_T=5%			Simultaneous modulation A_C=25%, A_T=5%			
	Y_P		δ_Y	Y_P		δ_Y	φ_{opt}	Y_P		δ_Y
	num	NFRM		num	NFRM			num	NFRM	
0.1	82.95	82.93	-0.02	82.57	82.57	0	-3.14	83.08	83.08	0
1	82.98	82.94	-0.05	82.57	82.57	0	-3.11	83.10	83.09	-0.01
2	83.05	83.00	-0.06	82.56	82.56	0	-3.06	83.15	83.15	0
3	83.05	83.15	+0.12	82.55	82.55	0	-2.96	83.11	83.29	+0.22
4	83.17	83.59	+0.50	82.52	82.52	0	-2.52	83.12	83.65	+0.64
5	83.52	85.37	**+2.21**	82.55	82.58	+0.04	-0.55	83.24	86.13	**+3.47**
5.53	83.65	86.72	**+3.67**	82.68	82.85	+0.20	-0.32	83.59	89.25	**+6.77**
6	83.65	85.43	**+2.13**	82.83	83.01	+0.22	-0.24	83.82	88.09	**+5.09**
7	83.22	83.30	+0.10	82.85	82.86	+0.01	-0.16	83.91	84.43	+0.62
8	82.88	82.89	+0.01	82.78	82.78	0	-0.12	83.43	83.48	+0.06
9	82.77	82.77	0	82.74	82.75	+0.01	-0.10	83.13	83.14	+0.01
10	82.72	82.72	0	82.72	82.72	0	-0.08	82.98	82.99	+0.01

Table 4.20 The product yield for separate and simultaneous modulation of the inlet concentration and temperature with forcing amplitudes A_C=50% and A_T=10%, estimated by numerical simulation and by the NFR method, and the relative errors, for Numerical example NONISO-2(b)

ω	Inlet concentration modulation, A_C=50%			Inlet temperature modulation, A_T=10%			Simultaneous modulation A_C=50%, A_T=10%			
	Y_P		δ_Y	Y_P		δ_Y	φ_{opt}	Y_P		δ_Y
	num	NFRM		num	NFRM			num	NFRM	
0.1	65.97	66.06	+0.14	62.91	62.09	-1.30	-0.04	67.28	67.57	+0.43
1	65.98	66.09	+0.17	63.02	63.01	-0.02	-0.36	67.55	68.03	+0.71
1.28	65.99	66.09	+0.15	63.09	63.08	-0.02	-0.43	67.69	68.29	+0.89
2	66.05	66.03	-0.03	63.34	63.34	0	-0.54	68.22	69.04	+1.20
3	65.66	65.56	-0.15	63.74	63.79	+0.08	-0.59	68.98	69.45	+0.68
4	64.80	64.76	-0.06	63.98	64.02	+0.06	-0.58	68.36	68.50	+0.20
5	64.10	64.09	-0.02	63.96	63.98	+0.03	-0.55	66.99	67.04	+0.07
10	63.29	63.29	0	63.48	63.48	0	-0.38	64.04	64.04	0

Table 4.21 The product yield for separate and simultaneous modulation of the inlet concentration and temperature with forcing amplitudes A_C=50% and A_T=10%, estimated by numerical simulation and by the NFR method, and the relative errors, for Numerical example NONISO-2(c)

ω	Inlet concentration modulation, A_C=50%			Inlet temperature modulation, A_T=10%			Simultaneous modulation A_C=50%, A_T=10%			
	Y_P		δ_Y	Y_P		δ_Y	φ_{opt}	Y_P		δ_Y
	num	NFRM		num	NFRM			num	NFRM	
0.1	49.58	49.59	+0.02	49.17	49.17	0	-0.04	51.43	51.45	+0.04
1	49.51	49.51	0	49.28	49.28	0	-0.35	51.31	51.33	+0.04
10	49.21	49.21	0	49.38	49.38	0	-0.45	49.61	49.61	0

From the results given in Tables 4.18-4.21, it can be concluded that:

- For Numerical example NONISO-2(a), good prediction by the NFR method is obtained only for frequencies which are not near to the resonant frequency. For higher forcing amplitudes (A_C=50%, A_T=10%) the relative errors around the resonant frequency are significant for single input modulation of inlet concentration and for simultaneous modulation of two defined inputs. For lower forcing amplitudes (A_C=25%, A_T=5%) the relative errors are also highest for the forcing frequencies which are near to the resonant one for inlet concentration or simultaneous two-input modulation. Nevertheless, the relative errors for forcing amplitudes (A_C=25%, A_T=5%) are significantly lower than for forcing amplitudes (A_C=50%, A_T=10%) and it can be concluded that the predictions of the NFR method for Numerical example NONISO-2(a) for forcing amplitudes (A_C=25%, A_T=5%) are good.

- For Numerical example NONISO-2(b), excellent agreement between the approximate (NFR method) and exact (numerical) solutions are obtained in the whole frequency range, in spite the fact that the forcing amplitudes are high. The relative errors are higher for forcing frequencies around the resonant one but even in this case the maximal relative error is 1.20%.

- For Numerical example NONISO-2(c), excellent agreement between the approximate (NFR method) and exact (numerical) solutions are obtained in the whole frequency range. The relative errors are insignificant.

- The NFR method based on the second order approximation gives better prediction for the oscillatory stable non-isothermal CSTR with weak resonant

behavior (Numerical example NONISO-2(b)) in comparison to the oscillatory stable non-isothermal CSTR with strong resonant behavior (Numerical example NONISO-2(a)), which is highly nonlinear. The disagreements which were observed for the non-isothermal CSTRs which exhibit resonant behavior (Numerical examples NONISO-2(a) and NONISO-2(b)) disappeared for the non-oscillatory non-isothermal CSTR (Numerical example NONISO-2(c)).

4.11.4. Explanation of the largest disagreement observed around the resonant frequency (Numerical example NONISO-2(a))

The explanation of the disagreement between the results of numerical simulations and the NFR method, for forcing frequencies near the resonant frequency for the Numerical example NONISO-2(a), lies in the fact that the system nonlinearity becomes more pronounced around the resonant frequency *(Ritter and Douglas, 1970)*, and the second order approximation, used in our NFR method (Eq. (1.37)), is not good enough. In the case of more pronounced nonlinearity, a considerable amount of higher harmonics is expected in the system output. In order to investigate the influence of higher order nonlinearities, harmonic analysis of the outlet concentration of the product, obtained by numerical simulation is performed, by Fourier analysis (*Nikolić et al.*, *2014a*).

For illustration, the amplitude spectrum of the outlet product concentration, for the case of simultaneous modulation of inlet concentration and inlet temperature, with a forcing frequency equal the resonant frequency (ω=5.53) and with forcing amplitudes A_C=50% and A_T=10%, is graphically presented in Figure 4.22. In this case, the relative error between the product yield estimated by the NFR method and calculated by numerical integration was high (δ_Y=28.49%, Table 4.18). For comparison, the amplitude spectrum obtained with the same forcing frequency, but with lower forcing amplitudes, A_C=25% and A_T=5%, is also presented in Figure 4.23, for which the relative error was δ_Y=6.77% (Table 4.19).
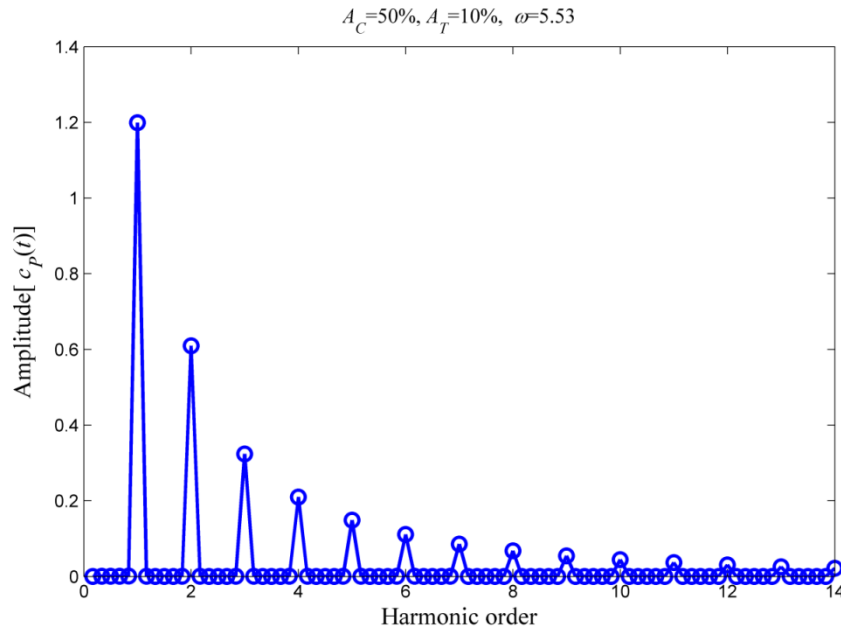
Figure 4.22 Amplitude spectrum of the outlet concentration of the product when the inlet concentration and inlet temperature are periodically modulated in a co-sinusoidal way, with forcing amplitudes A_C=50% and A_T=10%, and for resonant frequency (ω=5.53)
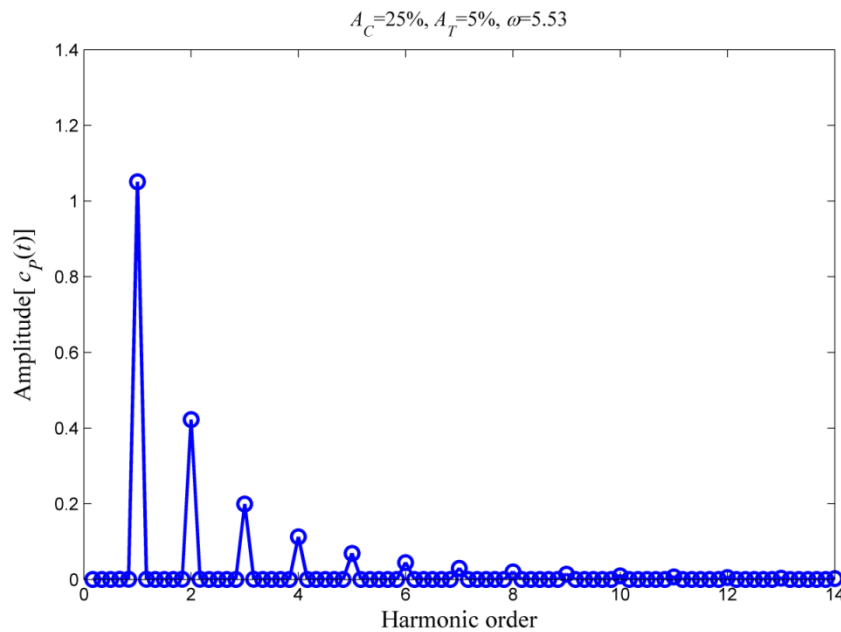
Figure 4.23 Amplitude spectrum of the outlet concentration of the product when the inlet concentration and inlet temperature are periodically modulated in the co-sinusoidal way, with forcing amplitudes A_C=25% and A_T=5% and for resonant frequency (ω=5.53)

From Figure 4.22, it is evident that for the resonant frequency and high forcing amplitudes, the output exhibits a considerable amount of higher harmonics with large

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gains, which means that the nonlinearities of the orders higher than two should not be neglected. In the DC component which is of our interest, these higher nonlinearities are defined by the forth, sixth, etc., ASO FRFs ($G_4(\omega,\omega,-\omega,-\omega)$, $G_6(\omega,\omega,\omega,-\omega,-\omega,-\omega)$,…) (Eq. (1.15)), which were neglected in our approximation of the DC component (Eq. (1.19)). As a consequence, the disagreement between the NFR method and numerical integration is significant. Therefore, in order to evaluate the average output concentration for high amplitudes of highly nonlinear system near the resonant frequency more accurately, for the system which exhibits resonance, it would be necessary to derive the higher order FRFs and take them into account (*Nikolić et al.*, *2014a*).

For the resonant frequency and lower forcing amplitudes (A_C=25% and A_T=5%) the output still exhibits a considerable amount of higher harmonics, but with lower gains in comparison to previous case (Figure 4.23), which results in lower relative error between the results of the NFR method and numerical integration.

In Figure 4.24, the amplitude spectrum of the outlet product concentration for simultaneous modulation of inlet concentration and inlet temperature with high forcing amplitudes (A_C=50% and A_T=10%) but with forcing frequency which is not near to the resonant one (ω=10) is graphically presented. In this case, the relative error between the results of the NFR method and numerical simulation was 0.05% (Table 4.18). As it can be seen, the higher order harmonics are negligible and in this case, Eq. (1.37), which takes into account only the contribution of second order FRFs in the DC component, gives an excellent estimate of the product yield change.
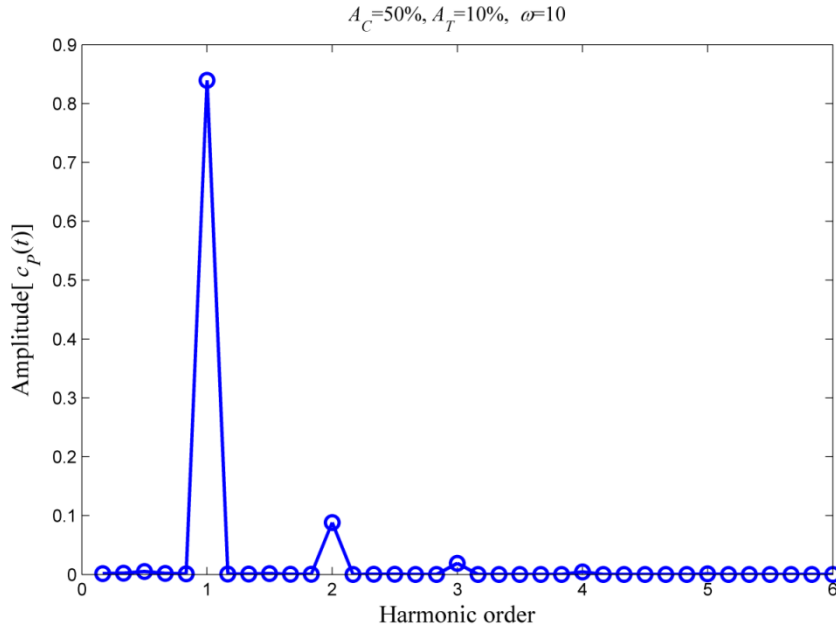
Figure 4.24 Amplitude spectrum of the outlet concentration of the product when the inlet concentration and inlet temperature are periodically modulated in a co-sinusoidal way, with forcing amplitudes A_C=50% and A_T=10% and dimensionless forcing frequency ω=10

As a physical explanation, we can say that, in principle, there are two major sources of nonlinearity in the non-isothermal CSTR: the reaction term, which is a nonlinear function of concentration and temperature, and the coupling between the heat and material balances. In the Numerical example NONISO-2(a), the reaction order is n=1, but, owing to the values of heat of reaction and energy activation (Table 4.14), the temperature dependence of the reaction rate constant and the coupling effect are very strong, resulting with high degree of nonlinearity which can be observed in Figure 4.22. The nonlinearity is more pronounced around the resonant frequency, where the coupling effect is strongest, which explained the results presented in Figures 4.22-4.24 (*Nikolić et al., 2014b*).

Harmonic analysis of the numerical results obtained for single input modulation of inlet concentration modulation for which the relative errors are also significant give very similar results and the same conclusions can be drawn.

4.12. Summary of Chapter IV

In this Chapter, the nonlinear frequency response method was used for evaluation of possible improvements of forced periodically operated non-isothermal CSTRs with homogeneous, irreversible, simple nth order reaction A→v_PP.

Single input modulations were analyzed, when inlet concentration, flow-rate, inlet temperature and temperature of the cooling/heating fluid were modulated. Simultaneous modulation of inlet concentration and inlet temperature and simultaneous modulation of inlet concentration and flow-rate were also investigated.

The asymmetrical second order frequency response functions which correlate the corresponding outlet concentration or molar flow-rate of the reactant and product for each case of single input modulation were derived and analyzed. Then, the cross asymmetrical second order frequency response functions for simultaneous modulation of two inputs were derived and analyzed.

It was concluded that the high-frequency single input modulations had no influence on the reactor performance and that for the low-frequency modulation the ASO FRFs corresponding to single input modulation, tended to asymptotic values. For the simultaneous modulation of inlet concentration and inlet temperature the same conclusions were drawn. Nevertheless, simultaneous modulation of inlet concentration and flow-rate has influence on the reactor performance in the whole frequency range, including the high-frequency modulations. It was concluded that analysis of only the reactant or only product ASO FRFs was enough. Also, it was concluded that the phase difference between the two modulated inputs had an important and decisive influence on the reactor performance. These results are analogous to the ones obtained for isothermal CSTRs (Chapter III).

The sign analysis of the ASO FRFs which correspond to single input modulations of each input, as well as for simultaneous modulation of inlet concentration and inlet temperature, was performed. The summary of the sign analysis of the ASO FRFs were given, in regard to the reactor parameters and the forcing frequency.

The results of the NFR method were tested on several numerical examples, Numerical example NONISO-1 and Numerical example NONISO-2(a), 2(b) and 2(c).
The Numerical example NONISO-1 corresponded to an optimized exothermal reactor with first-order reaction taken from the literature (*Douglas*, 1972). The NFR method predicted that single input modulation of the inlet concentration would lead to increase

of the product yield, while the flow-rate modulation would lead to its decrease. The inlet temperature modulation and modulation of the cooling fluid would lead to insignificant improvement and only in a narrow range of higher forcing frequencies. All conclusions were made by evaluation of the corresponding ASO FRF. The results of the NFR method were compared with numerical integration results and good agreement between them was obtained. The results of the sign analysis have correctly predicted the signs of the ASO FRFs and therefore the possible improvements.

In the second numerical example, NONISO-2, the NFR method was tested on three non-isothermal CSTRs: one oscillatory stable with strong resonant behavior (NONISO-2(a)), one oscillatory stable with weak resonant behavior (NONISO-2(b)) and one non-oscillatory stable (NONISO-2(c)). The analysis was performed for modulation of inlet concentration and inlet temperature, separately and simultaneously. In summary, we could say that the NFR method based on the second order approximation gave satisfactory results for over-damped and under-damped reactors with high and moderate damping coefficients, even for high input amplitudes, while it failed for low damping coefficients. The next step in our research would be to define exact criteria for the range of dumping coefficients for which the method gives reasonable approximations. This issue is directly related to defining the limiting level of non-linearity and the acceptable range of input amplitudes for using the second order approximation of NFR method and finding in which cases it would be necessary to introduce the forth, and possibly higher order FRFs, in order to expand that range. These issues need to be analyzed together with analysis of convergence of the Volterra series *(Nikolić et al., 2015)*.

V Application of nonlinear frequency response method for evaluation of periodically operated adiabatic non-isothermal CSTRs

5.1. Forced periodic operations of adiabatic non-isothermal CSTRs

The adiabatic CSTR is a special case of the non-isothermal CSTR, for which the reactor is operating in adiabatic condition, meaning that there is no heat transfer between the reactor and the environment (*Fogler, 2005*). Therefore, the NFR analysis of the adiabatic CSTR can be derived directly from the already derived FRFs of the non-isothermal CSTR, by setting all the terms and auxiliary parameters which are related to the heat exchange with the cooling/heating medium, i.e., the auxiliary parameters *St* and δ to zero (*St*=0, δ=0).

For the adiabatic non-isothermal CSTR (in further text named only adiabatic CSTR), in comparison to the general non-isothermal CSTR with heat exchange with the cooling/heating fluid, the inputs which can be periodically modulated are the same (inlet concentration, flow-rate, inlet temperature), except the temperature of the cooling/heating fluid.

5.2. Mathematical model

The definitions of the dimensionless variables are the same as they are for the isothermal and general non-isothermal CSTRs (Tables 3.1 and 4.1), except the dimensionless variable for the temperature of the heating/cooling fluid θ_J which can be equated to zero in the dimensionless model equation of energy balance of the non-isothermal CSTR, equation (4.17). The dimensionless mass balance equations for reactant and product are the same as for the general non-isothermal CSTR (given with Eqs. (4.15) and (4.16)) and the dimensionless energy balance is reduced to the following equation:

$$\frac{d\theta}{d\tau} = (1 + \beta)\Phi\theta_i + (1 + \beta)\theta_i - (1 + \beta\gamma)\theta - n\beta C_A + \beta\Phi - \Phi\theta$$

$$- \beta\left(n\gamma C_A\theta + \left(\frac{\gamma^2}{2} - \gamma\right)\theta^2 + \frac{1}{2}n(n-1)C_A{}^2\right)$$

$$(5.1)$$

For the adiabatic CSTR, it is possible to modulate the inlet concentration (C_{Ai}), flow-rate (Φ) and inlet temperature (θ_i), separately and simultaneously, two-by-two. Here the analysis of forced periodically operated adiabatic CSTR by NFR method is done for single input modulation of inlet concentration, flow-rate and inlet temperature, for simultaneous modulation of inlet concentration and inlet temperature and for simultaneous modulation of inlet concentration and flow-rate.

5.3. Stability analysis

The stability parameters for the adiabatic CSTR can be deducted from the stability parameters of the general non-isothermal CSTR, by setting $St=0$, to the following expressions:

$$A_{ps} = -\frac{(2 + n\alpha + \beta\gamma)}{2}$$

(5.2)

$$B_{ps} = 1 + n\alpha + \beta\gamma \tag{5.3}$$

Furthermore, it can be concluded that the adiabatic CSTR will be stable always when the stability parameter B_{ps} is positive ($B_{ps}>0$), considering the fact that stability parameters for the adiabatic CSTR, A_{ps} and B_{ps} are correlated, as follows:

$$A_{ps} = -\frac{(1 + B_{ps})}{2}$$

(5.4)

It can also be concluded that the adiabatic CSTR will be oscillatory for the case when the stability parameter is between 0 and 1 ($0<B_{ps}<1$). Otherwise, for $B_{ps}>1$, the reactor will be non-oscillatory.

The natural frequency (ω_n) is given with the same expression as for the general non-isothermal CSTR (Eq. 4.29) and the damping coefficient (ξ), for adiabatic CSTR becomes:

$$\xi = \frac{1}{2}\frac{\left(1 + B_{ps}\right)}{\sqrt{B_{ps}}}$$

(5.5)

5.4. Definition of the frequency response functions

The definitions of the FRFs are the same as for the general non-isothermal CSTR, except the FRFs which correlate the output with the modulation of the temperature of the cooling/heating fluid, which does not exist.

The frequency response functions for periodically operated adiabatic non-isothermal CSTR can be derived by implementing the derivation procedure of the NFR method as for isothermal and non-isothermal CSTR. Nevertheless, it is easier to use already derived expressions for non-isothermal CSTR by equating the above mentioned auxiliary parameters (St and δ) to zero in each expression of frequency response functions and to get the ASO FRFs for adiabatic CSTR.

In the following Section, the final expressions for the reactant and product G FRFs for single input modulation of inlet concentration, flow-rate and inlet temperature, as well as reactant and product cross G ASO FRFs for simultaneous modulation of inlet concentration and inlet temperature and for simultaneous modulation of inlet concentration and flow-rate will be given for adiabatic CSTR. The reactant and product H ASO FRFs will be given for flow-rate modulation as well as reactant and product cross H ASO FRFs for simultaneous modulation of inlet concentration and flow-rate.

5.5. The G-frequency response functions

5.5.1. Inlet concentration modulation

The first order FRFs $G_{A1,C}(\omega)$ and $G_{P1,C}(\omega)$

$$G_{A1,C}(\omega) = \frac{(1+\alpha)(1+\beta\gamma+j\omega)}{B_{ps} - \omega^2 + j\omega(1+B_{ps})}$$

(5.6)

$$G_{P1,C}(\omega) = \frac{n(1+\alpha)}{B_{ps} - \omega^2 + j\omega(1+B_{ps})}$$

(5.7)

The ASO FRFs $G_{A2,CC}(\omega,-\omega)$ and $G_{P2,CC}(\omega,-\omega)$

$$G_{A2,CC}(\omega,-\omega) = -\frac{\alpha(1+\alpha)^2}{2B_{ps}} \times \frac{\Lambda}{(\omega^2+1)(\omega^2+B_{ps}^2)}$$

(5.8)

$$G_{P2,CC}(\omega, -\omega) = \frac{(1 + \alpha)^2}{2B_{ps}} \times \frac{\Lambda}{(\omega^2 + 1)(\omega^2 + B_{ps}^2)}$$

<div align="right">(5.9)</div>

where the same auxiliary parameter Λ (Eq. (4.35)) is used as for the general non-isothermal CSTR, with the same definition of Λ_1 (Eq. (4.36)), while Λ_2 reduces to:

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

<div align="right">(5.10)</div>

5.5.2. Flow-rate modulation

The first order FRFs $G_{A1,F}(\omega)$ and $G_{P1,F}(\omega)$

$$G_{1,FA}(\omega) = \frac{\alpha(1 + j\omega)}{B_{ps} - \omega^2 + j\omega(1 + B_{ps})}$$

<div align="right">(5.11)</div>

$$G_{1,FP}(\omega) = -\frac{(1 + j\omega)}{B_{ps} - \omega^2 + j\omega(1 + B_{ps})}$$

<div align="right">(5.12)</div>

The ASO FRFs $G_{A2,FF}(\omega,-\omega)$ and $G_{P2,FF}(\omega,-\omega)$

$$G_{A2,FF}(\omega, -\omega) = -\frac{\alpha}{2B_{ps}} \times \frac{\Omega_1}{(\omega^2 + B_{ps}^2)}$$

<div align="right">(5.13)</div>

$$G_{P2,FF}(\omega, -\omega) = \frac{1}{2B_{ps}} \times \frac{\Omega_1}{(\omega^2 + B_{ps}^2)}$$

<div align="right">(5.14)</div>

The expression for the ASO FRF $G_{A2,FF}(\omega,-\omega)$ is significantly reduced in comparison to the same function for the general non-isothermal CSTR, considering that for adiabatic CSTR the auxiliary parameters Ω_1 (Eq. (4.43)) and Ω_2 (Eq. (4.44)) are reduced to the same expression:

$$\Omega_1 = \Omega_2 = n(n - 1)\alpha^2 + 2n\alpha(1 + \beta\gamma) + 2(1 + \beta\gamma) + \beta^2\gamma(\gamma - 2)$$

<div align="right">(5.15)</div>

Thus, the auxiliary function Ω (Eq. (4.42)) is reduced to

$$\Omega = \Omega_1(\omega^2 + 1)$$

<div align="right">(5.16)</div>

5.5.3. Modulation of inlet temperature

The first order FRFs $G_{A1,T}(\omega)$ and $G_{P1,T}(\omega)$

$$G_{A1,T}(\omega) = \frac{-\alpha\gamma(1+\beta)}{B_{ps} - \omega^2 + j\omega(1 + B_{ps})}$$

$$(5.17)$$

$$G_{P1,T}(\omega) = \frac{\gamma(1+\beta)}{B_{ps} - \omega^2 + j\omega(1 + B_{ps})}$$

$$(5.18)$$

The asymmetrical second order FRFs $G_{A2,TT}(\omega,-\omega)$ and $G_{P2,TT}(\omega,-\omega)$

$$G_{A2,TT}(\omega, -\omega) = -\frac{\alpha\gamma(1+\beta)^2}{2B_{ps}} \times \frac{\Psi}{(\omega^2 + 1)(\omega^2 + B_{ps}^2)}$$

$$(5.19)$$

$$G_{P2,TT}(\omega, -\omega) = \frac{\gamma(1+\beta)^2}{2B_{ps}} \times \frac{\Psi}{(\omega^2 + 1)(\omega^2 + B_{ps}^2)}$$

$$(5.20)$$

where the auxiliary parameter Ψ is the same as for the general non-isothermal CSTR (Eq.(4.49)), as well as Ψ_1 (Eq. (4.50)) and Ψ_2 (Eq. (4.51)).

5.5.4. Simultaneous modulation of inlet concentration and inlet temperature

The cross ASO FRFs $G_{A2,CT}(\omega,-\omega)$ and $G_{P2,CT}(\omega,-\omega)$

The real part of the FRF $G_{A2,CT}(\omega,-\omega)$ is reduced to

$$Re\big(G_{A2,CT}(\omega, -\omega)\big) = -\frac{n\alpha\gamma(1+\alpha)(1+\beta)}{B_{ps}} \times \frac{\big(\omega^2 + 1 + \alpha(1 + \beta\gamma) + 2\beta(1 + n\alpha)\big)}{(\omega^2 + 1)(\omega^2 + B_{ps}^2)}$$

$$(5.21)$$

and the imaginary part to

$$Im\big(G_{A2,CT}(\omega, -\omega)\big) = -\frac{n\alpha\gamma(1+\alpha)(1+\beta)}{B_{ps}} \times \frac{\omega(\alpha - 2\beta)}{(\omega^2 + 1)(\omega^2 + B_{ps}^2)}$$

$$(5.22)$$

In a similar way, the real and imaginary parts of the cross ASO FRF $G_{P2,CT}(\omega,-\omega)$ are given with:

$$Re\left(G_{P2,CT}(\omega,-\omega)\right) = \frac{n\gamma(1+\alpha)(1+\beta)}{B_{ps}} \times \frac{\left(\omega^2 + 1 + \alpha(1+\beta\gamma) + 2\beta(1+n\alpha)\right)}{(\omega^2+1)(\omega^2+B_{ps}^2)}$$

$$(5.23)$$

$$Im\left(G_{P2,CT}(\omega,-\omega)\right) = \frac{n\gamma(1+\alpha)(1+\beta)}{B_{ps}} \times \frac{\omega(\alpha-2\beta)}{(\omega^2+1)(\omega^2+B_{ps}^2)}$$

$$(5.24)$$

The cross ASO terms $G^*_{A2,CT}(\varphi,\omega)$ and $G^*_{P2,CT}(\varphi,\omega)$ are given with equations (4.64) and (4.65). The optimal phase differences for simultaneous modulation of inlet concentration and inlet temperature are given with equations (4.66) and (4.67).

5.5.5. Simultaneous modulation of inlet concentration and flow-rate

The cross ASO FRFs $G_{A2,CF}(\omega,-\omega)$ and $G_{P2,CF}(\omega,-\omega)$

The cross ASO FRF $G_{A2,CF}(\omega,-\omega)$ is given with

$$G_{A2,CF}(\omega,-\omega) = \frac{(1+\alpha)}{B_{ps}} \frac{(\Pi_R + j\omega\Pi_I)}{(\omega^2+1)(\omega^2+B_{ps}^2)}$$

$$(5.25)$$

where the auxiliary function Π_R is defined in the same way as for the general non-isothermal CSTR, with (Eq. (4.69)), while the auxiliary parameters Π_{R1}, Π_{R2} and Π_{R3} are reduced to the following:

$$\Pi_{R1} = 1 + \beta\gamma \qquad\qquad (5.26)$$

$$\Pi_{R2} = n^2\alpha^2\beta\gamma + n\alpha(2(1+\beta\gamma)^2 - (1+\beta\gamma) + \alpha) + (1+\beta\gamma)^3 \qquad (5.27)$$

$$\Pi_{R3} = n\alpha(1 + \alpha + \beta\gamma(\alpha - 2\beta)) \qquad\qquad (5.28)$$

The auxiliary function Π_I is defined in the same way as for the general non-isothermal CSTR (Eq.(4.73)), but the auxiliary parameters Π_{I1} and Π_{I2} are reduced to:

$$\Pi_{I1} = 1 + \beta\gamma \qquad\qquad (5.29)$$

$$\Pi_{I2} = n^2\alpha^2\beta\gamma + n\alpha(2(1+\beta\gamma)^2 - (1+\beta\gamma) - 1 - \beta\gamma(\alpha - 2\beta)) + (1+\beta\gamma)^3$$

$$(5.30)$$

The cross ASO FRF $G_{P2,CF}(\omega,-\omega)$ is given with

$$G_{P2,CF}(\omega,-\omega) = \frac{(1+\alpha)}{\alpha B_{ps}} \frac{(\Gamma_R + j\omega\Gamma_I)}{(\omega^2+1)(\omega^2+B_{ps}^2)}$$

$$(5.31)$$

where the auxiliary function Γ_R (Eq. (4.77)) for the adiabatic CSTR can be given in a polynomial form:

$$\Gamma_R = \Gamma_{R1}\omega^4 + \Gamma_{R2}\omega^2 + \Gamma_{R3} \tag{5.32}$$

The auxiliary parameters Γ_{R1}, Γ_{R2} and Γ_{R3} are, respectively

$$\Gamma_{R1} = n\alpha \tag{5.33}$$

$$\Gamma_{R2} = n\alpha(B_{ps}^2 + B_{ps} + 1 - (\alpha + 1)) \tag{5.34}$$

$$\Gamma_{R3} = -n\alpha\big(1 + \alpha + \beta\gamma(\alpha - 2\beta)\big) \tag{5.35}$$

The auxiliary function Γ_I (Eq. (4.78)) for the adiabatic CSTR is also given in a polynomial form:

$$\Gamma_I = \Gamma_{I1}\omega^2 + \Gamma_{I2} \tag{5.36}$$

where the auxiliary parameters Γ_{I1} and Γ_{I2} are, respectively

$$\Gamma_{I1} = n\alpha \tag{5.37}$$

$$\Gamma_{I2} = n\alpha\left(B_{ps}^2 + B_{ps} + 1 + \beta\gamma(\alpha - 2\beta)\right) \tag{5.38}$$

5.6. The H-asymmetrical second order frequency response functions

5.6.1. Flow-rate modulation

The ASO FRFs $H_{A2,FF}(\omega,-\omega)$ and $H_{P2,FF}(\omega,-\omega)$

$$H_{A2,FF}(\omega, -\omega) = -\frac{\alpha}{2B_{ps}} \times \frac{\Omega_H}{\left(\omega^2 + B_{ps}^2\right)}$$

$$\tag{5.39}$$

$$H_{P2,FF}(\omega, -\omega) = \frac{1}{2B_{ps}} \times \frac{\Omega_H}{\left(\omega^2 + B_{ps}^2\right)}$$

$$\tag{5.40}$$

The auxiliary parameter Ω_H in the numerator of the ASO FRFs $H_{A2,FF}(\omega,-\omega)$ and $H_{P2,FF}(\omega,-\omega)$ of the adiabatic CSTR is reduced to

$$\Omega_H = -n^2\alpha^2 - n\alpha\big(\alpha + 2(1 + \beta\gamma)\big) + 2(1 + \beta\gamma) - 2(1 + \beta\gamma)^2 + \beta^2\gamma(\gamma - 2)$$

$$\tag{5.41}$$

and, contrary to general case of non-isothermal CSTR (Eq. (4.81)), this auxiliary parameters is not a function of forcing frequency.

5.6.2. Simultaneous modulation of inlet concentration and flow-rate

The cross ASO FRFs $H_{A2,CF}(\omega,-\omega)$ and $H_{P2,CF}(\omega,-\omega)$

For the adiabatic CSTR, the cross ASO FRF $H_{A2,CF}(\omega,-\omega)$ is given as

$$H_{A2,CF}(\omega,-\omega) = \frac{(1+\alpha)}{B_{ps}} \times \frac{(\Pi_{RH} + j\omega\Pi_{IH})}{(\omega^2+1)(\omega^2+B_{ps}^2)}$$

(5.42)

where the auxiliary functions Π_{RH} and Π_{IH}, for the adiabatic CSTR become, respectively:

$$\Pi_{RH} = (\omega^2+1)\left((1+\beta\gamma)(\omega^2+B_{ps}^2) + n\alpha(\alpha+1)\right) + n\alpha\beta\gamma(\alpha-2\beta) \qquad (5.43)$$

$$\Pi_{IH} = -n\alpha\left(\omega^2+1+\beta\gamma(\alpha-2\beta)\right) \qquad (5.44)$$

The cross ASO FRF $H_{P2,CF}(\omega,-\omega)$ for the adiabatic CSTR is given as

$$H_{P2,CF}(\omega,-\omega) = \frac{(1+\alpha)}{B_{ps}} \times \frac{(\Gamma_{RH} + j\omega\Gamma_{IH})}{(\omega^2+1)(\omega^2+B_{ps}^2)}$$

(5.45)

with the auxiliary functions Γ_{RH} and Γ_{IH} which are given with following expressions

$$\Gamma_{RH} = n\left((\omega^2+1)(\omega^2+B_{ps}^2-(\alpha+1)) - \beta\gamma(\alpha-2\beta)\right) \qquad (5.46)$$

$$\Gamma_{IH} = n(\omega^2+1+\beta\gamma(\alpha-2\beta)) \qquad (5.47)$$

The cross ASO terms $H^*_{A2,CF}(\varphi,\omega)$ and $H^*_{P2,CF}(\varphi,\omega)$ for the adiabatic CSTR are given with the same equations as for the general case (equations (4.96) and (4.97)). The optimal phase difference for the adiabatic CSTR, when inlet concentration and flow-rate are periodically modulated, with arbitrary chosen forcing amplitudes, A_C and A_F, is given with equation (2.84).

5.7. Correlations between the reactant and product asymmetrical frequency response functions and terms

All equations and conclusions presented in Section 4.8 for the general non-isothermal CSTR are completely the same and valid for the adiabatic CSTR, both for single input modulation and for simultaneous modulation of two-inputs.

5.8. Estimating the possible improvements throughout the sign analysis of the asymmetrical second order frequency response functions

5.8.1. Asymmetrical second order FRFs for inlet concentration modulation

For the adiabatic CSTR, the results of the sign analysis of the ASO FRFs $G_{A2,CC}(\omega,-\omega)$ and $G_{P2,CC}(\omega,-\omega)$ are the same as they are for the general non-isothermal CSTR, given in Table 4.2 with differently defined $\omega_{0,C}$

$$\omega_{0,C} = \sqrt{\frac{(1 + \beta\gamma)^2 - n(1 - 2\beta^2\gamma)}{n - 1}}$$

(5.48)

and n_C

$$n_C = \frac{(1 + \beta\gamma)^2}{1 - 2\beta^2\gamma}$$

(5.49)

5.8.2. Asymmetrical second order FRFs for flow-rate modulation

For the adiabatic CSTR, the sign analysis of the ASO FRF is simpler than it is the case of the general non-isothermal CSTR. The signs of the ASO FRFs $H_{A2,FF}(\omega,-\omega)$ and $H_{P2,FF}(\omega,-\omega)$ does not depend on the forcing frequency, but they depend only on the sign of the auxiliary parameter Ω_H (Eq. (5.41)) in the following way:

$$sign\left(H_{A2,FF}(\omega,-\omega)\right) = -sign(\Omega_H)$$

(5.50)

The ASO FRF $H_{A2,FF}(\omega,-\omega)$ will have the opposite sign than the auxiliary parameter Ω_H, therefore just by determination of its sign, the sign of the ASO FRF $H_{A2,FF}(\omega,-\omega)$ will be also determined. On the other hand, the ASO FRF $H_{P2,FF}(\omega,-\omega)$ will have the same sign as the auxiliary parameter Ω_H.

5.8.3. Asymmetrical second order FRFs for inlet temperature modulation

The results of the sign analysis of the ASO FRFs $G_{A2,TT}(\omega,-\omega)$ and $G_{P2,TT}(\omega,-\omega)$ for the adiabatic CSTR are completely the same as for the general non-isothermal CSTR, given in Table 4.4. The auxiliary parameters which are necessary to determine the signs of these ASO FRFs $\omega_{0,T}$, n_{T1} and n_{T2} are defined in the same way as in Chapter IV (equations (4.120) and (4.121)).

5.8.4. The cross asymmetrical second order terms for simultaneous modulation of inlet concentration and inlet temperature

The auxiliary parameters ε_R (Eq. (4.122)) and ε_I (Eq. (4.124)), necessary for the sign analysis of the real and imaginary parts of the cross ASO FRFs $G_{A2,CT}(\omega,-\omega)$ and $G_{P2,CT}(\omega,-\omega)$, for the adiabatic CSTR are defined with the following equations:

$$\varepsilon_R = 1 + \alpha(1 + \beta\gamma) + 2\beta(1 + n\alpha) \tag{5.51}$$

$$\varepsilon_I = \alpha - 2\beta \tag{5.52}$$

All other conclusions of the sign analysis of the ASO cross FRFs $G_{A2,CT}(\omega,-\omega)$ and $G_{P2,CT}(\omega,-\omega)$ are the same as for the general non-isothermal CSTR, given in Tables 4.5 and 4.6 and, for the recommended phase difference, in Tables 2.1 and 2.2.

5.9. Numerical example ADIAB-1: Laboratory scale adiabatic CSTR for hydrolysis of acetic acid anhydride to acetic acid

5.9.1. Definition of Numerical example ADIAB-1

As an example for testing the NFR method on the adiabatic CSTR, is a laboratory reactor of volume $V=0.384$ dm^3, in which hydrolysis of acetic acid anhydride to acetic acid takes place (Numerical example ADIAB-1). The overall hydrolysis reaction of acetic acid anhydride (($CH_3CO)_2O$) to acetic acid (CH_3COOH) can be represented as

$(CH_3CO)_2O + H_2O \rightarrow 2\ CH_3COOH$
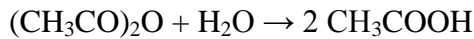
and it is a pseudo-first order reaction in excess of water. The hydrolysis of acetic anhydride is a moderately to highly exothermic, fast reaction (*Hirota et al., 2010*).

The kinetic parameters of acetic acid production, i.e. activation energy (E_A), the pre-exponential factor in the Arrenius equation (k_0) and reaction order (n) were experimentally determined in Max-Plank Institute for Dynamics of Complex Technical Systems (Magdeburg, Germany) and given in Table 5.1. The experimental data agree

quite well with the data in the literature (*Kralj, 2007*).The heat of the reaction and heat capacity, are also given in Table 5.1.

Table 5.1 The parameters for the hydrolysis reaction of acetic acid anhydride

Parameter	Value
Reaction order, n	1
Pre-exponential factor of the reaction rate constant, k_0 (1/s)	139390
Activation energy, E_A (kJ/mol)	44.350
Heat of reaction, ΔH_R (kJ/mol)	-55.500
Heat capacity, $\overline{\rho c_p}$ (kJ/(Kdm^3))	4.186

Before investigating the periodic behavior of the reactor, through simulations of the ASO FRFs, an optimization procedure was performed in order to choose the optimal steady-state around which the reactor would be modulated. The inlet concentration of the acetic acid anhydride and the residence time for a laboratory CSTR in which the room temperature was assumed (T_i=295.15 K), were optimized.

The optimization was done in order to optimize two objective functions: the Space-Time-Yield (*STY*) which is defined as follows

$$STY_s \left(\frac{mol}{sdm^3} \right) = \frac{c_{P,s}}{\tau_{res,s}}$$

(5.53)

and the product yield (or the reactant conversion) (Eqs. (2.20) and (2.21)).

The details about the optimization procedure are given in Appendix C1, and here, in Table 5.1 the solution which was adopted, is defined with the optimized values of inlet concentration ($c_{Ai,s}$) and the residence time ($\tau_{res,s}$) for the inlet temperature ($T_{i,s}$=295.15 K), is given. The Multi-objective optimization using Genetic Algorithm was done in Matlab.

Furthermore, for the adopted optimal steady-state, there is one steady-state solution defined with the concentration of the reactant in the reactor ($c_{A,s}$), concentration of the product in the reactor ($c_{P,s}$) and the temperature in the reactor (T_s) (Table 5.2). The

values of the objective functions (STY_s and $Y_{P,s}$) are also given, as well as the stability parameter (B_{ps}) and the damping coefficient (ξ).

Table 5.2 The steady-state concentrations, temperature and objective functions, the stability parameter and the damping coefficient for the optimal steady-state

$c_{Ai,s}$ (mol/ dm^3)	$T_{i,s}$ (K)	$\tau_{res,s}$ (s)	$c_{A,s}$ (mol/ dm^3)	$c_{P,s}$ (mol/ dm^3)	T_s (K)	STY_s (mol/s/ dm^3)	$Y_{P,s}$ (%)	B_{ps}	ξ
3.640	295.15	218.96	0.8662	5.5477	331.93	0.0253	76.20	2.42	1.099

The adiabatic CSTR in which the hydrolysis of acetic acid anhydride takes place, for the optimal steady-state is stable (B_{ps}=2.42>0) and non-oscillatory, with the damping coefficient ξ=1.099. The values of the auxiliary parameter for the chosen optimal steady-state are: α=3.2024, β= - 0.1108 and γ=16.07.

Considering that the residence time for the optimal steady-state is $\tau_{res,s}$=218.95 s and the fact that the reactor with of volume V=0.384 dm^3 is examined, the steady-state flow rate will be F_s=0.1052 dm^3/min.

Also, the analysis of the periodically operated laboratory adiabatic CSTR, in which the hydrolysis of the acetic anhydride takes place, by the NFR method, showed that the ASO FRF $G_{P2,TT}(\omega,-\omega)$ for modulation of the inlet temperature has very high negative values in the investigated range of inlet concentration and flow-rate (Appendix C2, Figures C1-C2) indicating highly unfavorable periodic operation. Therefore, the modulation of inlet temperature will not be considered and the temperature of the inlet temperature will be assumed to be constant, and modulations of only the inlet anhydride concentration and flow-rate, separately and simultaneously is considered.

5.9.2. Simulation results for single input modulations

The graphical representation of the product (acetic acid) ASO FRF $G_{P2,CC}(\omega,-\omega)$ which correspond to single input modulation of the inlet concentration of acetic acid anhydride, vs. dimensionless forcing frequency is given in Figure 5.1.
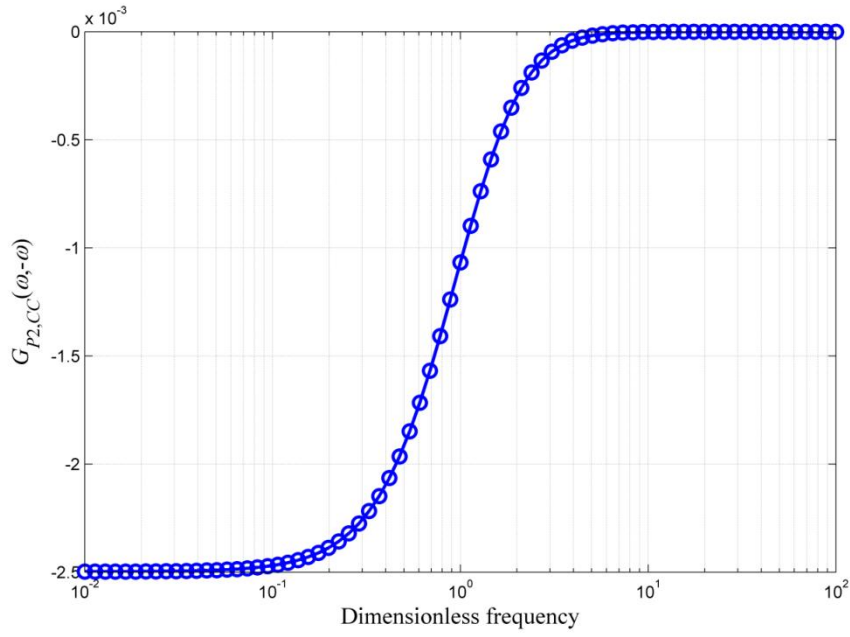
Figure 5.1 The ASO FRF $G_{P2,CC}(\omega,-\omega)$ as a function of the dimensionless forcing frequency

The ASO FRF $G_{P2,CC}(\omega,-\omega)$ is negative in the whole frequency range (Figure 5.1) which indicates that the inlet concentration modulation will lead to deterioration of the reactor performance. The simulation results are in accordance with the sign analysis results, since they lead to a conclusion that the ASO FRF $G_{P2,CC}(\omega,-\omega)$ is negative in whole frequency range (Table 4.2, ($1/n_C<1$ and n=1), $n_C=1.006$ (Eq. (5.49)). Despite the fact that this ASO FRF is negative, its value is quite low, and it can be approximated and accepted that the inlet concentration modulation has no effect on the reactor performance.

The ASO FRF $H_{P2,FF}(\omega,-\omega)$ which correlates the outlet molar flow-rate of the product with modulation of the flow-rate is graphically presented in Figure 5.2, as a function of the dimensionless forcing frequency.
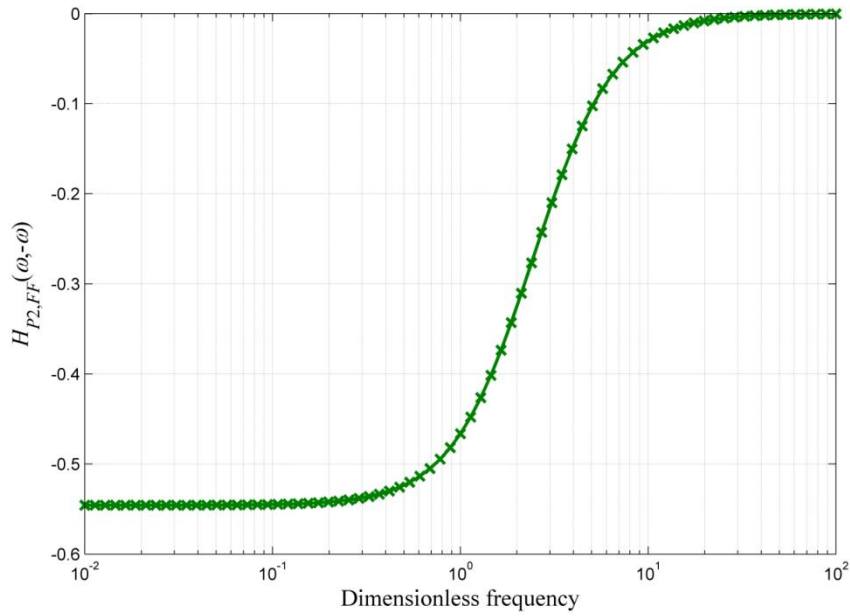
Figure 5.2 The ASO FRF $H_{P2,FF}(\omega,-\omega)$ as a function of the dimensionless forcing frequency

From the sign analysis of the ASO FRF $H_{P2,FF}(\omega,-\omega)$, it is expected this function to be negative in the whole frequency range, since Ω_H=-15.52<0 (Eq. (5.41)). This is confirmed with the simulation results (Figure 5.2). Therefore, the modulation of the flow-rate will lead to deterioration of the reactor performance.

Thus, the NFR method and simulation results for single input modulations of inlet concentration and flow-rate for the examined system showed that the improvement of the reactor performance can not be obtained by single input modulation.

5.9.3. Simulation results for simultaneous modulation of inlet concentration and flow-rate

Despite the fact that the single input modulations of the inlet concentration and flow-rate will lead to deterioration of the reactor performance, simultaneous modulation of these two inputs with appropriate choice of the forcing parameters might have a positive effect on the reactor performance. This analysis will be presented here.

For forcing amplitudes of the inlet concentration and flow-rate, $A_C=A_F=75\%$, the optimal phase difference (Eq. (2.84)) which should be used in order to maximize the product yield is given in Figure 5.3.
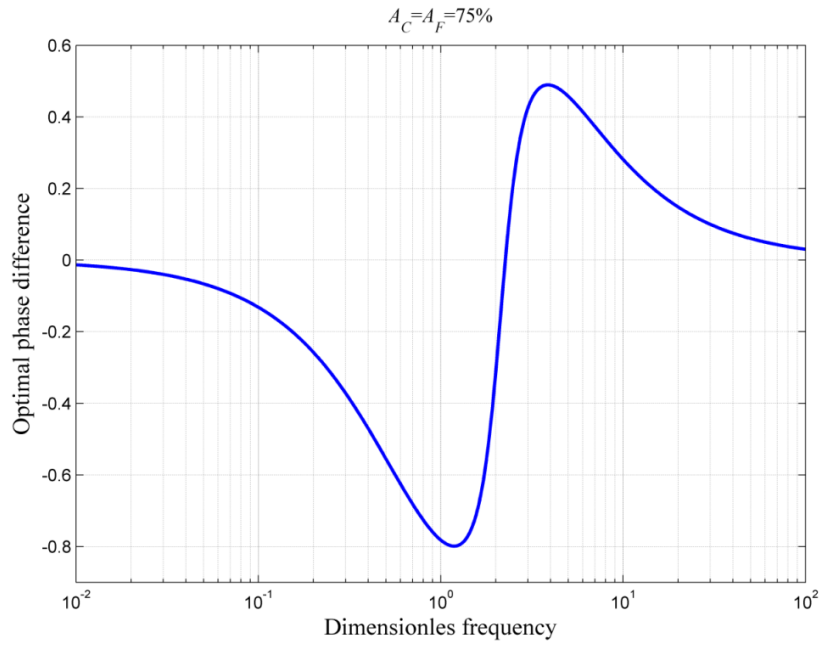
$A_C=A_F=75\%$

Figure 5.3 The optimal phase difference $\varphi_{opt}(\omega)$ for forcing amplitudes $A_C=A_F=75\%$, as a function of the dimensionless forcing frequency

The product yields obtained for single and simultaneous modulations of the inlet concentration and flow-rate, with $A_C=A_F=75\%$ and optimal phase difference presented in Figure 5.3, are shown in Figure 5.4.
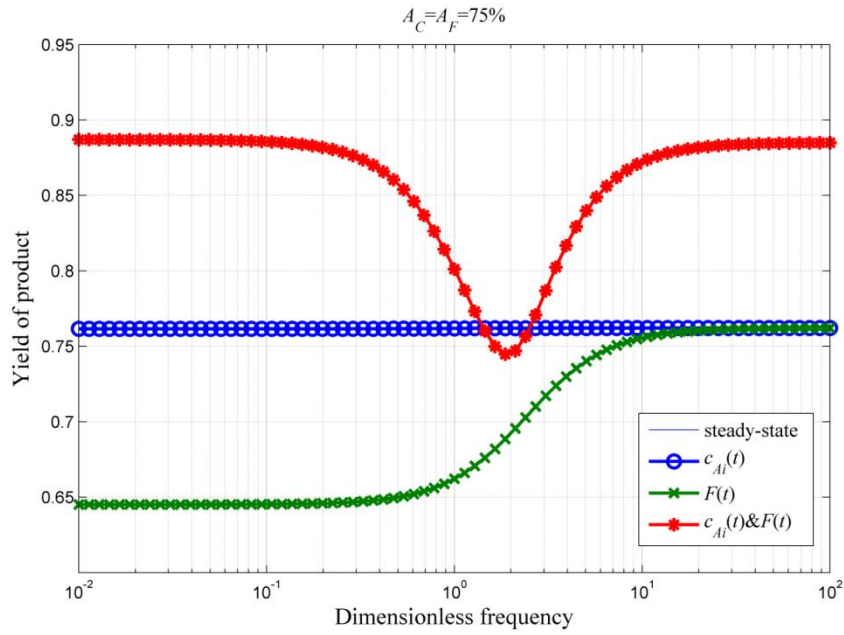
Figure 5.4 The product yields for steady-state operation, for single input modulation of the inlet concentration of acetic anhydride, flow-rate and for simultaneous modulation of inlet concentration and flow-rate, with $A_C=A_F=75\%$ and the optimal phase difference $\varphi_{opt}(\omega)$, as functions of the dimensionless forcing frequency

As expected, based on the results presented in Figure 5.1 and 5.2, the inlet concentration modulation has practically no influence on the reactor performance and the flow-rate modulation will lead to deterioration of reactor performance. Nevertheless, the simultaneous modulation of these two inputs, with forcing amplitudes $A_C=A_F=75\%$ and the corresponding optimal phase difference $\varphi_{opt}(\omega)$ will lead to significant increase of the product yield for low and high forcing frequencies.

Further, the optimal forcing parameters for simultaneous modulation of inlet concentration and flow-rate which maximize the product yield are determined numerically from (Eq. (2.77)) as functions of forcing frequency. They are graphically presented in Figure 5.5.
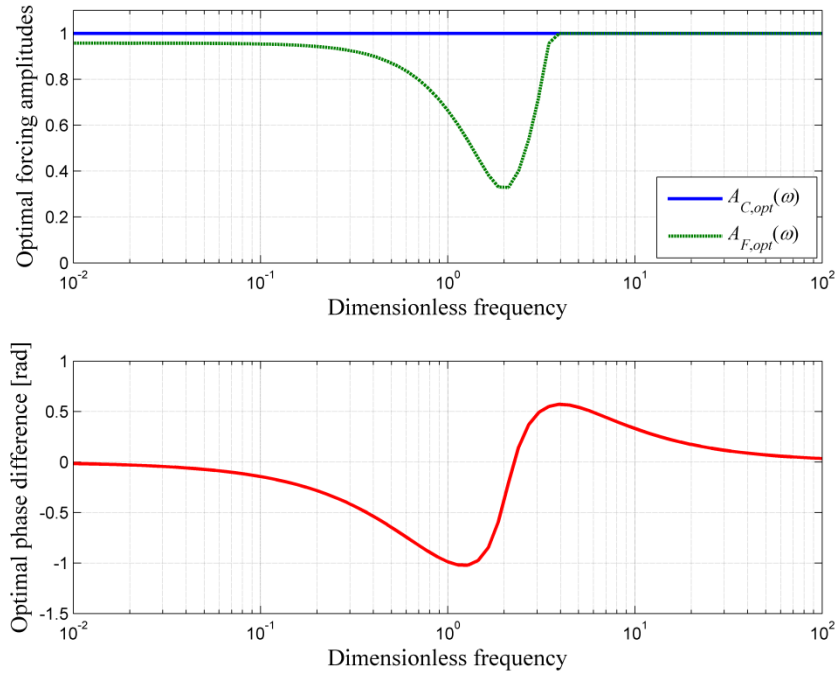
Figure 5.5 The optimal forcing amplitudes $A_{C,opt}(\omega)$, $A_{F,opt}(\omega)$ and the optimal phase difference $\varphi_{opt}(\omega)$, which maximize the product yield for simultaneous modulation of the inlet concentration and flow-rate, vs. dimensionless forcing frequency

The product yield for simulatenous modulation of the inlet concentration and flow-rate with these optimal forcing parameters is graphically presented in Figure 5.6. The product yields for single input modulations with the same forcing amplitudes, as well as for steady-state operation are also given in Figure 5.6.
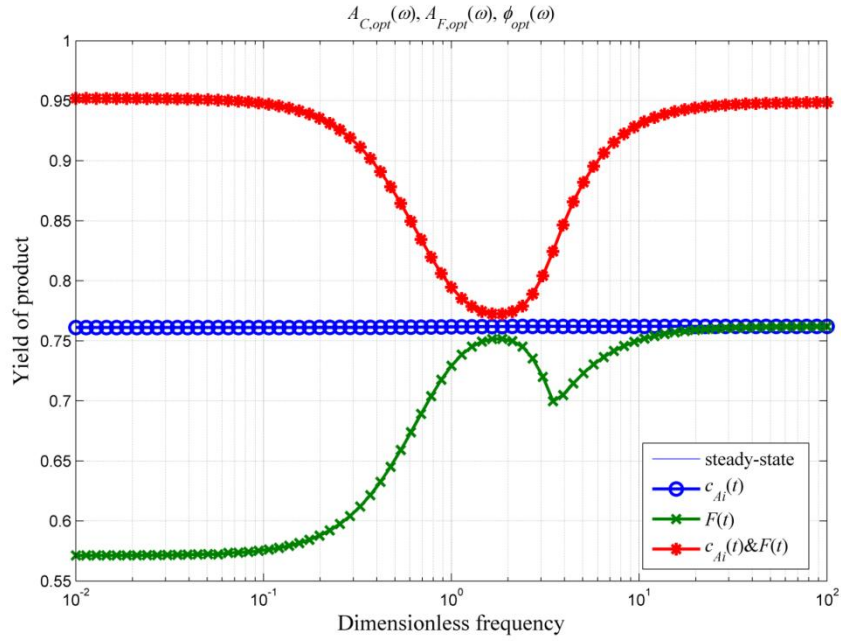
Figure 5.6 The product yields for steady-state operation, for periodic modulation of the inlet concentration with $A_{C,opt}(\omega)$, flow-rate modulation with $A_{F,opt}(\omega)$ and simultaneous modulation of these two inputs with optimal forcing amplitudes and optimal phase difference $\varphi_{opt}(\omega)$ vs. dimensionless forcing frequency

In this case, the increase of product yield is higher than for the previous case shown in Figure 5.4, in whole frequency range. Both low and high-forcing frequency modulations lead to significant increase of the product yield.

The performance of the adiabatic CSTR, when inlet concentration and flow-rate are periodically modulated around previously established steady-state, can be significantly improved from the aspect of product yield increase in comparison to the optimal steady-state, despite the facts that single input modulation of the inlet concentration practically has no influence and single input modulation of the flow-rate will cause the product yield decrease.

5.9.3. Comparison with the results obtained by numerical integration

The approximate results obtained by the NFR method, are compared with the results of numerical integration for simultaneous modulation of the inlet concentration and flow-rate, in a co-sinusoidal way, around the previously established optimal steady-state.

The results of numerical simulations and the NFR method for simultaneous modulation of the inlet concentration and flow-rate with equal forcing amplitudes $A_C=A_F=75\%$ and with the corresponding optimal phase difference $\varphi_{opt}(\omega)$ are given in Table 5.3, for

dimensionless forcing frequencies ω=0.1, 1 and 10. The same results are given for numerically determined optimal forcing parameters (amplitudes and phase difference) for the same frequencies (ω=0.1, 1 and 10), in Table 5.4.

The relative errors for the product yield (δ_Y) are also given in these Tables, in order to compare the results of numerical integration which are considered to be exact, with the estimates from the NFR method.

Table 5.3 The product yields and the relative yield changes, for simultaneous modulation of the inlet concentration and flow-rate with A_C=A_F=75% and the corresponding optimal phase difference, determined by numerical simulation and by the NFR method, and the relative errors

Simultaneous modulation of inlet concentration and flow-rate, A_C=75%, A_F=75%,						
ω	φ_{opt}	$Y_{P,po}$(%)		δ_Y(%)	ΔY_P (%)	
		num	NFRM		num	NFRM
0.1	-0.1321	85.67	85.57	-0.12	+12.43	+12.28
1	-0.7822	79.79	79.99	+0.25	+4.70	+4.96
10	0.2809	85.48	87.23	+2.05	+12.16	+14.46

Table 5.4 The product yields and relative yield changes, for simultaneous modulation of the inlet concentration and flow-rate with optimal forcing parameters (amplitudes and phase differences), determined by numerical simulation and by the NFR method, and the relative errors

Simultaneous modulation of inlet concentration and flow-rate								
ω	$A_{C,opt}$(%)	$A_{F,opt}$ (%)	φ_{opt} (rad)	$Y_{P,po}$(%)		δ_Y(%)	ΔY_P (%)	
				num	NFRM		num	NFRM
0.1		95.45	-0.1437	88.87	95.03	+6.93	+16.62	+24.71
1	100	66.44	-0.9883	81.02	84.01	+3.69	+6.33	+10.23
10		100	0.3323	88.57	93.04	+5.05	+16.22	+22.08

From the values of the relative errors reported in Table 5.4 for forcing amplitudes A_C=A_F=75%,, it can be concluded that the NFR method gives very good predictions of the behavior of the adiabatic CSTR in which hydrolysis of acetic acid anhydride takes place, when the inlet concentration and flow-rate are simultaneously modulated in a co-

sinusoidal way. Thus, the previous conclusions made by NFR method for the forced periodically operated adiabatic CSTR are confirmed.

Nevertheless, for the case when both forcing amplitudes are very high, as given in Table 5.4 for forcing frequencies ω=0.1 and 10, the relative errors increased, as expected for a very high forcing amplitudes.

5.10 Summary of Chapter V

In this Chapter, the nonlinear frequency response method was used for evaluation of possible improvements of forced periodically operated adiabatic non-isothermal CSTRs with liquid homogeneous, irreversible, simple nth order reaction A→v_PP.

Considering that the adiabatic non-isothermal CSTR represents a special case of the general non-isothermal CSTR for, which there is no heat exchange between the reactor and the environment (*Fogler, 2005*), the inputs which can be modulated in this case are: the inlet concentration, flow-rate and inlet temperature. Thus, periodic operations with single input modulations of these three input were analyzed, as well as, periodic operations with simultaneous modulation of inlet concentration and inlet temperature and simultaneous modulation of inlet concentration and flow-rate.

The asymmetrical second order frequency response functions and the cross asymmetrical frequency response functions were obtained by reducing the corresponding functions for the general non-isothermal CSTR, by setting all the terms and auxiliary parameters which were related to the heat exchange with the cooling/heating medium to zero.

The same conclusions, considering the low and high frequency modulation for investigated single or two-input modulations, were drawn as for the isothermal (Chapter III) and general non-isothermal CSTRs (Chapter IV). The sign analysis of the ASO FRFs and cross ASO FRFs was also performed and the summary of the sign analysis of the ASO FRFs was given.

The results of the NFR method were applied here for the analysis of a laboratory scale adiabatic CSTR for hydrolysis of acetic acid anhydride to acetic acid (Numerical example ADIAB-1). The analysis was performed for single and simultaneous modulation of the inlet concentration of acetic acid anhydride and flow-rate. An optimization procedure was performed and the optimal steady-state was adopted. Periodic operations around that optimal steady state were analyzed. The NFR method

predicted that single input modulations of the inlet concentration and flow-rate would lead to decrease of the product yield. Nevertheless, it was shown that simultaneous modulation of these two inputs, with appropriate choice of the forcing parameters, would lead to significant increase of the product yield. Again, good agreement between the results of the NFR method and the results of numerical integration was obtained.

VI Conclusions

In this work, a nonlinear frequency response (NFR) method, based on the second-order approximation, was used for evaluation of influence of forced periodic modulations of one or two inputs on the performance of chemical reactors.

The nonlinear frequency response method was used for evaluation of possible improvements of forced periodically operated continuous stirred tank reactors with liquid homogeneous, irreversible, simple nth order reaction $A \rightarrow v_P P$, for isothermal, non-isothermal and adiabatic conditions. For the isothermal CSTRs, the analysis was performed for single input modulations of the inlet concentration and flow-rate and for simultaneous modulation of these two inputs. For the non-isothermal CSTRs, single input modulations of the inlet concentration, flow-rate, inlet temperature and temperature of the cooling/heating fluid were considered, as well as simultaneous modulations of the inlet concentration and inlet temperature and simultaneous modulation of the inlet concentration and flow-rate. The adiabatic CSTRs where analyzed for single input modulations of the inlet concentration of the reactant, flow-rate and inlet temperature, as well as for simultaneous modulations of the inlet concentration and inlet temperature and simultaneous modulations of the inlet concentration and flow-rate. All investigated cases were summarized in Table 2.3.

The proposed method uses only the asymmetrical second order FRFs, for approximate evaluation of the investigated process. In all investigated cases, a general methodology of the derivation procedure was used for derivation of the necessary asymmetrical second order frequency response functions and cross asymmetrical frequency response functions, defining the outlet reactant and product average concentrations, and thus the product yield and the reactant conversion corresponding to the forced periodically operated reactors.

The derived asymmetrical second order frequency response functions and the cross asymmetrical frequency response functions were analyzed, which included their sign analysis.

The results of the NFR method were tested on several numerical examples: two for the isothermal CSTR (ISO-1 and ISO-2), two for the general non-isothermal CSTR (NONISO-1, and NONISO-2(a) to (c)), and one for the adiabatic non-isothermal CSTR (ADIAB-1).

The main conclusions of this investigation can be summarized as follows:

- The average performance of forced periodically operated chemical reactors can be evaluated from the DC (non-periodic term) component of the output of interest, which, on the other hand, can be approximately estimated from and the corresponding asymmetrical second order FRF(s). In order to determine the influence of the forced periodic operation on the reactor performance for single input modulation, it is enough to derive and analyze only the corresponding asymmetrical second order frequency response function. For evaluation of the reactor performance when two inputs are simultaneously modulated, in addition to the asymmetrical second order FRFs corresponding to each input, the cross asymmetrical second order FRF needs to be derived and analyzed;

- Analysis of either the reactant or the product asymmetrical frequency response functions should be performed, considering the fact that both lead to the same result, regarding the change of the reactant conversion or product yield obtained in the periodic mode of operation.

- For single input modulations, except for the flow-rate modulation, the DC components of the outlet concentrations (reactant or product), estimated from the corresponding asymmetrical second order frequency response functions, can be used to evaluate the possible improvements. For single input modulation of the flow-rate and for simultaneous modulation of the flow-rate with and another input, except the inlet concentration, the DC components of the outlet molar flow-rates (reactant or product) are used in order to determine the possibility of the reactor performance improvements.

- For simultaneous modulation of the inlet concentration and flow-rate, in order to evaluate the possible improvements, besides the DC components of the molar flow-rates (reactant or product), it is necessary to determine the inlet molar flow-rate of the reactant which is not constant and to evaluate the reactant conversion or the product yield corresponding to the periodic operation. The inlet molar flow-rate of the reactant depends directly on the forcing parameters (forcing amplitudes and the phase difference the between modulated inputs);

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- For single input modulations, the sign of the outlet DC component of interest can be determined directly from the sign of the corresponding asymmetrical second order frequency response function, thus giving the answer whether the reactor performance improvements are possible or not,

- For simultaneous modulation of the inlet concentration and temperature, the sign analysis of the real and imaginary parts of the cross asymmetrical second order frequency response will give the recommended phase difference range which should be used in order to obtain the desirable cross effect (positive or negative). If the ASO FRFs corresponding to the single input modulations have desirable signs (negative for the reactant and positive for the product), by appropriate chose of the phase difference the periodic modulation will lead to even higher improvement. If one or both single input ASO FRFs have undesirable signs, the overall DC component of the outlet concentration should be evaluated in order to determine the overall effect on the reactor performance. Also, the forcing amplitudes and the phase difference which optimize the desirable objective function (reactant conversion or product yield) can be determined and used.

- For simultaneous modulation of the inlet concentration and flow-rate, it is not possible to draw a decisive conclusion regarding the reactor performance improvements just on the sign analysis of the ASO FRFs. In this case, the optimal phase difference which optimizes the chosen objective function (reactant conversion or product yield) for defined forcing amplitudes can be determined, or the forcing amplitudes can be optimized together with optimal phase difference.

- High-frequency single input modulations have no influence on the reactor performance, while for the low-frequency modulations the ASO FRFs tend to asymptotic values and the periodic operation, in general, will influence the reactor performance. This is also valid for simultaneous modulation of inlet concentration and inlet temperature;

- Simultaneous modulation of inlet concentration and flow-rate has influence on the reactor performance in the whole frequency range,

- The forcing amplitudes and phase difference for simultaneous modulation of two inputs have a decisive role on the reactor performance;

- The results of the NFR method based on the second order approximation compared with the results of numerical integration, gave a very good agreements. The only exception is a reactor with strong resonance for forcing frequencies which are close to the resonant one when high forcing amplitudes are used. Thus, the NFR method based on the second order approximation gave satisfactory results for over-damped and under-damped reactors with high and moderate damping coefficients, even for high input amplitudes, while it failed for low damping coefficients (*Nikolić et al., 2015*).

- In summary, we could say that the NFR method based on the second order approximation gave satisfactory results for over-damped and under-damped reactors with high and moderate damping coefficients, even for high input amplitudes, while it failed for low damping coefficients. The next step in our research would be to define exact criteria for the range of dumping coefficients for which the method gives reasonable approximations. This issue is directly related to defining the limiting level of non-linearity and the acceptable range of input amplitudes for using the second order approximation of NFR method and finding in which cases it would be necessary to introduce the forth, and possibly higher order FRFs, in order to expand that range. These issues need to be analyzed together with analysis of convergence of the Volterra series *(Nikolić et al., 2015)*. One of the following steps in our research would also be the experimental verification of the theoretical results.

List of symbols

Latin symbols

A input amplitude

A_{ps} stability parameter

A_w surface area for heat exchange

B output amplitude

B_{ps} stability parameter

c_A [mol/m^3]   reactant concentration

C_A dimensionless reactant concentration

c_P [mol/m^3]   product concentration

$\overline{c_P}$ [J/kg/K]   heat capacity

C_P dimensionless product concentration

E_A [J/mol] activation energy

F [m^3/s]   volumetric flow-rate

$G_{An,X}$ n-th order frequency response function which correlate the outlet reactant concentration with modulated input X

$G_{Pn,X}$ n-th order frequency response function which correlate the outlet product concentration with modulated input X

$G_{An,XZ}$ n-th order frequency response function which correlate the outlet reactant concentration with modulated inputs X and Z

$G_{Pn,XZ}$ n-th order frequency response function which correlate the outlet product concentration with modulated inputs X and Z

$G^{*}_{An,XZ}$ the cross term which correlate the outlet reactant concentration with modulated inputs X and Z

$G^{*}_{Pn,XZ}$ the cross term which correlate the outlet product concentration with modulated inputs X and Z

$H_{An,X}$ n-th order frequency response function which correlate the outlet molar flow-rate of the reactant with modulated input X

$H_{Pn,X}$ n-th order frequency response function which correlate the outlet molar flow-rate of the product with modulated input X

$H_{An,XZ}$ n-th order frequency response function which correlate the outlet molar flow-rate of the reactant with modulated inputs X and Z

$H_{Pn,XZ}$ n-th order frequency response function which correlate the outlet molar flow-rate of the product with modulated inputs X and Z

$H^*_{An,XZ}$ the cross term which correlate the outlet molar flow-rate of the reactant with modulated inputs X and Z

$H^*_{Pn,XZ}$ the cross term which correlate the outlet molar flow-rate of the product with modulated inputs X and Z

k reaction rate constant

k_o $[(mol/m^3)^{1-n}/s]$ pre-exponential factor in Arrenius equation

n reaction order

N_A dimensionless molar flow-rate of the reactant

n_A [mol/s] molar flow-rate of the reactant

N_P dimensionless molar flow-rate of the product

n_P [mol/s] molar flow-rate of the product

p_1, p_2, p_3 poles (roots of the characteristic equation)

R [J/mol/K]   universal gas constant

s Laplace complex varible

St Stanton number

STY $[mol/s/m^3]$ Space-Time-Yield

t [s]   time

T [K]   temperature

U $[J/m^2/K/s]$ overall heat transfer coefficient

u, v frequency, general

V $[m^3]$ volume of the reactor

x input

x_A conversion of the reactant

X dimensionless input

y output

Y dimensionless output

Y_P yield of product

z input

Z dimensionless input

Greek symbols

$\Gamma_R, \Gamma_{R1}, \Gamma_{R2}, \Gamma_{R3}$ auxiliary functions in real part of the cross ASO FRF $G_{P2,CF}(\omega,-\omega)$

$\Gamma_{HR}, \Gamma_{HR1}, \Gamma_{HR2}, \Gamma_{HR3} \Gamma_{HR4}$ auxiliary functions in real part of the cross ASO FRF $H_{P2,CF}(\omega,-\omega)$

$\Gamma_I, \Gamma_{I1}, \Gamma_{I2}$ auxiliary functions in imaginary part of the cross ASO FRF

$\qquad\qquad\qquad$ $G_{P2,CF}(\omega,-\omega)$

$\Gamma_{HI}, \Gamma_{HI1}, \Gamma_{HI2}, \Gamma_{HI3}$ auxiliary functions in imaginary part of the cross ASO FRF

$\qquad\qquad\qquad$ $H_{P2,CF}(\omega,-\omega)$

$\Lambda, \Lambda_1, \Lambda_2$ auxiliary functions in expressions of the ASO FRFs $G_{A2,CC}(\omega,-\omega)$

$\qquad\qquad\qquad$ and $G_{P2,CC}(\omega,-\omega)$

$\Pi_R, \Pi_{R1}, \Pi_{R2}, \Pi_{R3}$ auxiliary functions in real part of the cross ASO FRF

$\qquad\qquad\qquad$ $G_{A2,CF}(\omega,-\omega)$

$\Pi_{HR}, \Pi_{HR1}, \Pi_{HR2}, \Pi_{HR3}$ auxiliary functions in real part of the cross ASO FRF

$\qquad\qquad\qquad$ $H_{A2,CF}(\omega,-\omega)$

$\Pi_I, \Pi_{I1}, \Pi_{I2}$ auxiliary functions in imaginary part of the cross ASO

$\qquad\qquad\qquad$ FRF $G_{A2,CF}(\omega,-\omega)$

$\Pi_{HI}, \Pi_{HI1}, \Pi_{HI2}$ auxiliary functions in imaginary part of the cross ASO

$\qquad\qquad\qquad$ FRF $H_{A2,CF}(\omega,-\omega)$

Φ dimensionless volumetric flow-rate

Ψ, Ψ_1, Ψ_2 auxiliary functions in expressions of the ASO FRFs $G_{A2,TT}(\omega,-\omega)$,

$\qquad\qquad\qquad$ $G_{P2,TT}(\omega,-\omega)$, $G_{A2,JJ}(\omega,-\omega)$ and $G_{P2,JJ}(\omega,-\omega)$

$\Omega, \Omega_1, \Omega_2$ auxiliary functions in expressions of the ASO FRFs $G_{A2,FF}(\omega,-\omega)$

$\qquad\qquad\qquad$ and $G_{P2,FF}(\omega,-\omega)$

$\Omega_H, \Omega_{1H}, \Omega_{2H}$ auxiliary functions in expressions of the ASO FRFs $H_{A2,FF}(\omega,-\omega)$

$\qquad\qquad\qquad$ and $H_{P2,FF}(\omega,-\omega)$

α auxiliary parameter

β auxiliary parameter

γ auxiliary parameter

δ auxiliary parameter

δ_Y relative error for product yield

θ dimensionless temperature

v_P stoichiometric coefficient of the product P

ξ damping coefficient

ρ [m^3/kg]   density

τ dimensionless time

τ_{res} [s]   residence time

φ [rad]   phase difference between two modulated inputs

ω dimensionless forcing frequency

ω_d [rad/s]   dimensional forcing frequency

ω_n [rad/s] natural frequency

ω_r [rad/s] resonant frequency

ΔH_R [kJ/mol]   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

CT   corresponding to modulation of the inlet concentration and inlet temperature

DC   non-periodic term

F, FF corresponding to modulation of flow-rate

i   inlet

J   heating/cooling fluid (jacket)

J, JJ   corresponding to modulation of the temperature in the jacket

n   *n*th order

opt   corresponding to optimal forcing variable

P   product

po   periodic operation

s   steady-state

T, TT corresponding to modulation of the inlet temperature

x, *xx*, *X*, *XX*   corresponding to input *x*

z, *zz*, *Z*, *ZZ*   corresponding to input *z*

xz, XZ corresponding to inputs *x* and *z*

I   first harmonic

II   second harmonic

III   third harmonic

Superscripts

m   mean

Abbreviations

ADIAB   adiabatic

ASO   asymmetrical second order

CSTR   continuous stirred tank reactor

FR   frequency response

FRF   frequency response functions

ISO   isothermal

NONISO   non-isothermal

NFR   nonlinear frequency response

num   numerical

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Appendix

A Basic steps of the derivation procedure of the *G*-frequency response function for the isothermal CSTR

A.1. Taylor series expansions of the nonlinear terms in Eqs. ((3.2) and (3.3))

$$F(t)c(t) = F_s c_s + c_s(F - F_s) + F_s(c - c_s) + (F - F_s)(c - c_s) + \cdots \qquad (A1.1)$$

$$c = c_{Ai}, c_A \text{ or } c_P$$

A.2. Derivation of the first order and asymmetrical second order frequency response functions for single input modulation of inlet concentration and flow-rate

Step 1: Defining the dimensionless input $X(\tau)$ ($X=C_{Ai}$ or Φ) in the form of a co-sinusoidal function

$$X(\tau) = A_X cos(\omega\tau) = \frac{A_X}{2}e^{j\omega\tau} + \frac{A_X}{2}e^{-j\omega\tau} \qquad (A2.1)$$

Step 2: Representing the dimensionless outlet concentrations of the reactant and product in the form of Volterra series

$$C_A(\tau) = \left(\frac{A_X}{2}\right)G_{A1,X}(\omega)e^{j\omega\tau} + \left(\frac{A_X}{2}\right)G_{A1,X}(-\omega)e^{-j\omega\tau} + \cdots + 2\left(\frac{A_X}{2}\right)^2 G_{A2,XX}(\omega, -\omega)e^0 + \cdots$$
$$(A2.2)$$

$$C_P(\tau) = \left(\frac{A_X}{2}\right)G_{P1,X}(\omega)e^{j\omega\tau} + \left(\frac{A_X}{2}\right)G_{P1,X}(-\omega)e^{-j\omega\tau} + \cdots + 2\left(\frac{A_X}{2}\right)^2 G_{P2,XX}(\omega, -\omega)e^0 + \cdots$$
$$(A2.3)$$

Step 3: Substituting the expressions for the dimensionless modulated input $X(\tau)$ (Eq. (A2.1)) and dimensionless outlet concentrations defined with equations (A2.2 and A2.3) into the appropriate dimensionless model equations, (for inlet concentration modulation in equations (3.12) and (3.12) and for flow-rate modulation in model equations (3.14) and 3.15)).

Step 4: Applying the method of harmonic probing. The terms with $(A_X/2)e^{j\omega\tau}$ corresponding to the first order functions and with $(A_X/2)^2 e^0$ corresponding to the asymmetrical second order function are collected and equated with zero. The resulting equations are presented below:

- For inlet concentration modulation

The equations for the first order frequency response functions

$$(1 + n\alpha + j\omega)G_{A1,C}(\omega) = 1 + \alpha \qquad (A2.4)$$

$$-nG_{A1,C}(\omega) + (1 + j\omega)G_{P1,C}(\omega) = 0 \qquad (A2.5)$$

The equations for the asymmetrical second order frequency response functions

$$2(1 + n\alpha)G_{A2,CC}(\omega, -\omega) = -n(n - 1)\alpha G_{A1,C}(\omega)G_{A1,C}(-\omega) \qquad (A2.6)$$

$$-2nG_{A2,CC}(\omega, -\omega) + 2G_{P2,CC}(\omega) = n(n - 1)G_{A1,C}(\omega)G_{A1,C}(-\omega) \qquad (A2.7)$$

- For flow-rate modulation

The equations for the first order frequency response functions

$$(1 + n\alpha + j\omega)G_{A1,F}(\omega) = \alpha \tag{A2.8}$$

$$-nG_{A1,F}(\omega) + (1 + j\omega)G_{P1,F}(\omega) = -1 \tag{A2.9}$$

The equations for the asymmetrical second order frequency response functions

$$2(1 + n\alpha)G_{A2,FF}(\omega, -\omega) = -\left(G_{A1,F}(-\omega) + G_{A1,F}(\omega)\right) - n(n-1)\alpha G_{A1,F}(\omega)G_{A1,F}(-\omega) \tag{A2.10}$$

$$-2nG_{A2,FF}(\omega, -\omega) + 2G_{P2,FF}(\omega)$$
$$= -\left(G_{P1,F}(-\omega) + G_{P1,F}(\omega)\right) + n(n-1)G_{A1,F}(\omega)G_{A1,F}(-\omega) \tag{A2.11}$$

Step 5: Solving equations obtained in Step 4. As a result, the expressions for the first order FRFs $G_{A1,C}(\omega)$ (Eq. (3.20)), $G_{P1,C}(\omega)$ (Eq. (3.21)) and the asymmetrical second order FRFs $G_{A2,CC}(\omega,-\omega)$ (Eq. (3.22)), $G_{P2,CC}(\omega,-\omega)$ (Eq. (3.23)) for single input modulation of the inlet concentration as well as the first order FRFs $G_{A1,F}(\omega)$ (Eq. (3.24)), $G_{P1,F}(\omega)$ (Eq. (3.25)) and the asymmetrical second order FRFs $G_{A2,FF}(\omega,-\omega)$ (Eq. (3.26)), $G_{P2,FF}(\omega,-\omega)$ (Eq. (3.27)) for single input modulation of the flow-rate. Here the ASO FRFs are given as functions of the first order FRFs, and in the main text their final expressions are given.

$$G_{A2,CC}(\omega, -\omega) = -\frac{n\alpha(n-1)}{2B_{ps}} \times G_{A1,C}(\omega)G_{A1,C}(-\omega) \tag{A2.12}$$

$$G_{P2,CC}(\omega, -\omega) = \frac{n(n-1)}{2B_{ps}} \times G_{A1,C}(\omega)G_{A1,C}(-\omega) \tag{A2.13}$$

$$G_{A2,FF}(\omega, -\omega) = -\frac{1}{2B_{ps}} \times \left(G_{A1,F}(\omega) + G_{A1,F}(-\omega) + n\alpha(n-1)G_{A1,F}(\omega)G_{A1,F}(-\omega)\right) \tag{A2.14}$$

$$G_{P2,FF}(\omega, -\omega) = \frac{1}{2B_{ps}} \times \frac{1}{\alpha}\left(G_{A1,F}(\omega) + G_{A1,F}(-\omega) + n\alpha(n-1)G_{A1,F}(\omega)G_{A1,F}(-\omega)\right) \tag{A2.15}$$

A.3. Derivation of cross asymmetrical second order frequency response functions for simultaneous modulation of inlet concentration and flow-rate

Step 1: Defining the dimensionless inputs $C_{Ai}(\tau)$ and $\Phi(\tau)$ in the form of co-sinusoidal functions

$$C_{Ai}(\tau) = A_C\cos(u\tau) = \frac{A_C}{2}e^{ju\tau} + \frac{A_C}{2}e^{-ju\tau} \tag{A3.1}$$

$$\Phi(\tau) = A_F\cos(v\tau) = \frac{A_F}{2}e^{jv\tau} + \frac{A_F}{2}e^{-jv\tau} \tag{A3.2}$$

Step 2: Representing the dimensionless outlet concentrations of the reactant and product in the form of Volterra series

$$C_A(\tau) = \frac{A_C}{2} G_{1,CA}(u)e^{ju\tau} + \frac{A_C}{2} G_{1,CA}(-u)e^{-ju\tau} + \cdots + 2\left(\frac{A_C}{2}\right)^2 G_{2,CCA}(u,-u)e^0 + \cdots$$

$$+ \frac{A_F}{2} G_{1,FA}(v)e^{jv\tau} + \frac{A_F}{2} G_{1,FA}(-v)e^{-jv\tau} + \cdots + 2\left(\frac{A_F}{2}\right)^2 G_{2,FFA}(v,-v)e^0 + \cdots$$

$$+ \frac{A_C}{2}\frac{A_F}{2} G_{2,CFA}(u,v)e^{j(v+u)\tau} + \cdots$$

(A3.3)

$$C_P(\tau) = \frac{A_C}{2} G_{1,CP}(u)e^{ju\tau} + \frac{A_C}{2} G_{1,CP}(-u)e^{-ju\tau} + \cdots + 2\left(\frac{A_C}{2}\right)^2 G_{2,CCP}(u,-u)e^0 + \cdots$$

$$+ \frac{A_F}{2} G_{1,FP}(v)e^{j\omega\tau} + \frac{A_F}{2} G_{1,FP}(-v)e^{-jv\tau} + \cdots + 2\left(\frac{A_F}{2}\right)^2 G_{2,FFP}(v,-v)e^0$$

$$+ \cdots + \frac{A_C}{2}\frac{A_F}{2} G_{2,CFP}(u,v)e^{j(v+u)\tau} + \cdots$$

(A3.4)

Step 3: Substituting the expressions for the dimensionless inputs (Eqs. (A3.1) and (A3.2)) and dimensionless outlet concentrations defined with equations (A3.3) and (A3.4) into the appropriate dimensionless model equations (Eqs. (3.10) and (3.11)).

Step 4: Applying the method of harmonic probing. The terms with $\frac{A_C}{2}\frac{A_F}{2} e^{j(u+v)\tau}$ corresponding to the cross asymmetrical second order FRFs are collected and equated with zero. The resulting equations are presented below:

$$j(u+v)G_{A2,CF}(u,v) =$$
$$(1+\alpha) - G_{A1,C}(u) - (1+n\alpha)G_{A2,CF}(u,v) - n(n-1)\alpha G_{A1,C}(u)G_{A1,F}(v)$$

(A3.5)

$$j(u+v)G_{P2,CF}(u,v) =$$
$$-G_{P1,C}(u) + nG_{A2,CF}(u,v) - G_{P2,CF}(u,v) + n(n-1)G_{A1,C}(u)G_{A1,F}(v)$$

(A3.6)

Step 5: Solving the equations obtained in Step 4 (Eqs. (A3.5) and (A3.6)) leads to the general expressions for the cross ASO FRFs

$$G_{A2,CF}(u,v) = \frac{1}{(1+n\alpha+j(u+v))}\left((1+\alpha) - G_{A1,C}(u) - n(n-1)\alpha G_{A1,C}(u)G_{A1,F}(v)\right)$$

(A3.7)

$$G_{P2,CF}(u,v) = \frac{1}{(1+j(u+v))}\left(nG_{A2,CF}(u,v) - G_{P1,C}(u) + n(n-1)G_{A1,C}(u)G_{A1,F}(v)\right)$$

(A3.8)

For equal input forcing frequencies ($u = \omega$ and $v = -\omega$) the following relations between the cross ASO FRFs and the first order FRFs are obtained:

$$G_{A2,CF}(\omega,-\omega) = \frac{1}{(1+n\alpha)}\left((1+\alpha) - G_{A1,C}(\omega) - n(n-1)\alpha G_{A1,C}(\omega)G_{A1,F}(-\omega)\right)$$

(A3.9)

$$G_{P2,CF}(\omega, -\omega) = \frac{1}{1 + n\alpha}\Big(n(1 + \alpha) - nG_{A1,C}(\omega) - (1 + n\alpha)G_{P1,C}(\omega)$$
$$- n(n - 1)G_{A1,C}(\omega)G_{A1,F}(-\omega)\Big)$$

<div align="right">(A3.10)</div>

It should be noticed that the cross ASO FRFs $G_{A2,CF}(\omega, -\omega)$ and $G_{A2,CF}(-\omega, \omega)$ are complex-conjugates as well as $G_{P2,CF}(\omega, -\omega)$ and $G_{P2,CF}(-\omega, \omega)$. The final expressions for the cross ASO FRFs $G_{A2,CF}(\omega, -\omega)$ and $G_{P2,CF}(\omega, -\omega)$, after incorporating the expressions for the first order FRFs into equations (A3.9) and (A3.10) are given in the main body of this work, by the Eqs. ((3.28) and (3.29)).

B. Taylor expansions of the nonlinear terms, derivation procedure of asymmetrical frequency response function and some auxiliary functions and parameters for non-isothermal CSTR

B.1.Taylor series expansions of the nonlinear terms in the dimensionless balance equations (4.12-4.14)

$$e^{-\frac{E_A}{RT_s(\theta+1)}} = e^{-\frac{E_A}{RT_s}} + \theta\frac{E_A}{RT_s}e^{-\frac{E_A}{RT_s}} + \theta^2\left(-\frac{E_A}{RT_s}\right)e^{-\frac{E_A}{RT_s}} + \frac{\theta^2}{2}\left(-\frac{E_A}{RT_s}\right)^2 e^{-\frac{E_A}{RT_s}} + \cdots$$

<div align="right">(B1.1)</div>

$$e^{-\frac{E_A}{RT_s(\theta+1)}} = e^{-\gamma}\left(1 + \theta\gamma + \left(\frac{\gamma^2}{2} - \gamma\right)\theta^2 + \cdots\right)$$

<div align="right">(B1.2)</div>

$$(1 + C_A)^n = 1 + nC_A + \frac{1}{2}n(n - 1)C_A^2 + \cdots$$

<div align="right">(B1.3)</div>

$$(1 + C_A)^n e^{-\frac{E_A}{RT_s(\theta+1)}} = e^{-\gamma}\left(1 + \gamma\theta + nC_A + n\gamma C_A\theta + \left(\frac{\gamma^2}{2} - \gamma\right)\theta^2 + \frac{1}{2}n(n - 1)C_A^2 + \cdots\right)$$

<div align="right">(B1.4)</div>

B.2. Derivation of the first order and asymmetrical second order frequency response functions for single input modulation of inlet concentration, flow-rate, inlet temperature and temperature of the cooling/heating fluid

Step 1: Defining the dimensionless input modulation,

$$X(\tau) = A_X cos(\omega\tau) = \frac{A_X}{2}e^{j\omega\tau} + \frac{A_X}{2}e^{-j\omega\tau} \tag{B2.1}$$

where for inlet concentration modulation $X=C_{Ai}$, for flow-rate modulation $X=\Phi$, for inlet temperature modulation $X=T_i$ and for temperature of the cooling/heating fluid $X=T_J$. The corresponding forcing amplitudes are: A_C, A_F, A_T and A_J, respectively.

Step 2: Representing the outlet concentrations of the reactant and product, as well as outlet temperature, in the form of Volterra series:

$$C_A(\tau) = \left(\frac{A_X}{2}\right) G_{A1,X}(\omega)e^{j\omega\tau} + \left(\frac{A_X}{2}\right) G_{A1,X}(-\omega)e^{-j\omega\tau} + \cdots + 2\left(\frac{A_X}{2}\right)^2 G_{A2,XX}(\omega,-\omega)e^0 + \cdots$$

(B2.2)

$$C_P(\tau) = \left(\frac{A_X}{2}\right) G_{P1,X}(\omega)e^{j\omega\tau} + \left(\frac{A_X}{2}\right) G_{P1,X}(-\omega)e^{-j\omega\tau} + \cdots + 2\left(\frac{A_X}{2}\right)^2 G_{P2,XX}(\omega,-\omega)e^0 + \cdots$$

(B2.3)

$$\theta(\tau) = \left(\frac{A_X}{2}\right) F_{1,X}(\omega)e^{j\omega\tau} + \left(\frac{A_X}{2}\right) F_{1,X}(-\omega)e^{-j\omega\tau} + \cdots + 2\left(\frac{A_X}{2}\right)^2 F_{2,XX}(\omega,-\omega)e^0 + \cdots$$

(B2.4)

Step 3: Substituting the expressions for the modulated input, outlet concentrations of the reactant and product and outlet temperature, defined with Eqs. (B2.2-B2.4), into the appropriate model equations (4.15-4.17) (all inputs which are not modulated are set to zero).

Step 4: Collecting the terms with $\left(\frac{A_X}{2}\right) e^{j\omega\tau}$, corresponding to the first order functions, and with $\left(\frac{A_X}{2}\right)^2 e^0$, corresponding to the ASO FRF, and equating them to zero. The resulting equations, which are given in the general form, are for the first order frequency response functions $G_{A1,X}(\omega)$, $G_{P1,X}(\omega)$ and $F_{1,X}(\omega)$

$$[1 + n\alpha + j\omega]G_{A1,X}(\omega) + [0]G_{P1,X}(\omega) + [\alpha\gamma]F_{1,X}(\omega) = k_{X1}$$

$$[-n]G_{A1,X}(\omega) + [1 + j\omega]G_{P1,X}(\omega) + [-\gamma]F_{1,X}(\omega) = k_{X2} \qquad \text{(B2.5)}$$

$$[n\beta]G_{A1,X}(\omega) + [0]G_{P1,X}(\omega) + [1 + St + \beta\gamma + j\omega]F_{1,X}(\omega) = k_{X3}$$

where

for *X=C*: $k_{C1} = 1 + \alpha$, $k_{C2} = k_{C3} = 0$ (B2.6)

for *X=F*: $k_{F1} = \alpha$, $k_{F2} = -1$, $k_{F3} = \beta + St - \delta$ (B2.7)

for *X=T*: $k_{T1} = k_{T2} = 0$, $k_{T3} = 1 + \beta + St - \delta$ (B2.8)

for *X=J*: $k_{J1} = k_{J2} = 0$, $k_{J3} = \delta$ (B2.9)

For the asymmetrical second order frequency response functions: $G_{A2,XX}(\omega)$, $G_{P2,XX}(\omega)$ and $F_{1,XX}(\omega)$, the resulting equations are:

$$[2(1 + n\alpha)]G_{A2,XX}(\omega,-\omega) + [0]G_{P2,XX}(\omega,-\omega) + [2\alpha\gamma]F_{2,XX}(\omega,-\omega) = l_{X1}$$

$$[-2n]G_{A2,XX}(\omega,-\omega) + [2]G_{P2,XX}(\omega,-\omega) + [-2\gamma]F_{2,XX}(\omega,-\omega) = l_{X2} \text{ (B2.10)}$$

$$[2n\beta]G_{A2,XX}(\omega,-\omega) + [0]G_{P2,XX}(\omega,-\omega) + [2(1 + St + \beta\gamma)]F_{2,XX}(\omega,-\omega) = l_{X3}$$

where for *X=C, T* or *J*:

$$l_{X1} = -\alpha P_X; \ l_{X2} = P_X; \ l_{X3} = -\beta P_X \qquad \text{(B2.11)}$$

and for *X=F*:

$$l_{F1} = -G_{1,FA}(\omega) - G_{1,FA}(-\omega) - \alpha P_F \qquad \text{(B2.12)}$$

$$l_{F2} = -G_{1,FP}(\omega) - G_{1,FP}(-\omega) + P_F \tag{B2.13}$$

$$l_{F3} = -F_{1,F}(\omega) - F_{1,F}(-\omega) - \beta P_F \tag{B2.14}$$

where:

$$P_X = n(n-1)G_{1,XA}(\omega)G_{1,XA}(-\omega) + \gamma(\gamma-2)F_{1,X}(\omega)F_{1,X}(-\omega)$$
$$+ n\gamma\left(G_{1,XA}(\omega)F_{1,X}(-\omega) + G_{1,XA}(-\omega)F_{1,X}(\omega)\right) \tag{B2.15}$$

Step 5: After solving the system of equations for the first order FRFs (Eq. (B2.5)) the final expressions for the first order *G* FRFs are given in the main part of this work, and here the $F_{1,X}(\omega)$ are given

$$F_{1,C}(\omega) = \frac{-n\beta\,(1+\alpha)}{B_{ps} - \omega^2 - 2j\omega\,A_{ps}} \tag{B2.16}$$

$$F_{1,F}(\omega) = \frac{(\beta + St - \delta + n\alpha\,(St - \delta)) + j\omega\,(\beta + St - \delta)}{B_{ps} - \omega^2 - 2j\omega\,A_{ps}} \tag{B2.17}$$

$$F_{1,T}(\omega) = \frac{(1 + \beta + St - \delta)(1 + n\alpha + j\omega)}{B_{ps} - \omega^2 - 2j\omega\,A_{ps}} \tag{B2.18}$$

$$F_{1,J}(\omega) = \frac{\delta(1 + n\alpha + j\omega)}{B_{ps} - \omega^2 - 2j\omega\,A_{ps}} \tag{B2.19}$$

The system of equation for the ASO FRFs (Eq. (B2.10)) is solved and the final expressions for the *G*-ASO FRFs are obtained and given in the main part of this work.

Here, the *G*-ASO FRFs given as a function of the first order FRF.

$$G_{A2,CC}(\omega, -\omega) = -\frac{1}{2}\frac{\alpha(1+St)}{B_{ps}}\left(n\gamma G_{A1,C}(\omega)F_{1,C}(-\omega) + n\gamma G_{A1,C}(-\omega)F_{1,C}(\omega)\right.$$
$$\left. + \gamma(\gamma-2)F_{1,C}(\omega)F_{1,C}(-\omega) + n(n-1)G_{A1,C}(\omega)G_{A1,C}(-\omega)\right) \tag{B2.20}$$

$$G_{A2,FF}(\omega, -\omega) = -\frac{1}{2B_{ps}}\left((1 + \beta\gamma + St)\left(G_{A1,F}(\omega) + G_{A1,F}(-\omega)\right)\right.$$
$$- \alpha\gamma\left(F_{1,F}(\omega) + F_{1,F}(-\omega)\right)$$
$$+ \alpha(1+St)\left(n\gamma G_{A1,F}(\omega)F_{1,F}(-\omega) + n\gamma G_{A1,F}(-\omega)F_{1,F}(\omega)\right.$$
$$\left.\left. + \gamma(\gamma-2)F_{1,F}(\omega)F_{1,F}(-\omega) + n(n-1)G_{A1,F}(\omega)G_{A1,F}(-\omega)\right)\right) \tag{B2.21}$$

$$G_{A2,TT}(\omega, -\omega) = -\frac{\alpha(1+St)}{2B_{ps}}\left(\gamma(\gamma-2)F_{1,T}(\omega)F_{1,T}(-\omega) + n\gamma G_{A1,T}(\omega)F_{1,T}(-\omega)\right.$$
$$\left. + n\gamma G_{A1,T}(-\omega)F_{1,T}(\omega) + n(n-1)G_{A1,T}(\omega)G_{A1,T}(-\omega)\right) \tag{B2.22}$$

$$G_{A2,JJ}(\omega, -\omega) = -\frac{\alpha(1 + St)}{2B_{ps}}\Big(\gamma(\gamma - 2)F_{1,J}(\omega)F_{1,J}(-\omega) + n\gamma G_{A1,J}(\omega)F_{1,J}(-\omega)$$
$$+ n\gamma G_{A1,J}(-\omega)F_{1,J}(\omega) + n(n - 1)G_{A1,J}(\omega)G_{A1,J}(-\omega)\Big)$$

(B2.23)

The final expressions for the ASO F FRFs which correspond the outlet temperature with modulated input, are:

$$F_{2,CC}(\omega, -\omega) = -\frac{\beta(1 + \alpha)^2}{2B_{ps}} \times \frac{\Lambda}{(B_{ps} - \omega^2)^2 + 4A_{ps}^2\omega^2}$$

(B2.24)

$$F_{2,FF}(\omega, -\omega) = \frac{1}{2B_{ps}}\frac{1}{(B_{ps} - \omega^2)^2 + 4A_{ps}^2\omega^2} \times$$
$$(2(1 + n\alpha)((\beta + St - \delta + n\alpha(St - \delta))(-\omega^2 + 1 + \beta\gamma + St + n\alpha + n\alpha St)$$
$$+ 2(1 + n\alpha)(\omega^2(\beta + St - \delta)(2 + n\alpha + St + \beta\gamma))$$
$$- 2n\alpha\beta(1 + St - \gamma St + \gamma\delta)(-\omega^2 + 1 + \beta\gamma + St + n\alpha + n\alpha St)$$
$$- 2n\alpha\beta\omega^2(2 + St + \gamma\beta + n\alpha)$$
$$+ \beta\gamma(\gamma - 2)\Big((\beta + St - \delta + n\alpha(St - \delta))^2 + \omega^2(\beta + St - \delta)^2\Big)$$
$$+ n(n - 1)\alpha^2\beta((1 + St - \gamma St + \gamma\delta)^2 + \omega^2)$$
$$+ 2n\alpha\beta\gamma((1 + St - \gamma St + \gamma\delta)(\beta + St - \delta + n\alpha(St - \delta))$$
$$+ \omega^2(\beta + St - \delta)))$$

(B2.25)

$$F_{2,TT}(\omega, -\omega) = -\frac{\beta\gamma(1 + \beta + St - \delta)^2}{2B_{ps}} \times \frac{\Psi}{(B_{ps} - \omega^2)^2 + 4A_{ps}^2\omega^2}$$

(B2.26)

$$F_{2,JJ}(\omega, -\omega) = -\frac{\beta\gamma\delta^2}{2B_{ps}}\frac{\Psi}{(B_{ps} - \omega^2)^2 + 4A_{ps}^2\omega^2}$$

(B2.27)

B.3. Derivation of cross asymmetrical second order frequency response functions for simultaneous modulation of inlet concentration and inlet temperature

Step 1: Defining the dimensionless input modulation,

$$C_{Ai}(\tau) = A_C cos(u\tau) = \frac{A_C}{2}e^{ju\tau} + \frac{A_C}{2}e^{-ju\tau}$$

(B3.1)

$$\theta_i(\tau) = A_T cos(v\tau) = \frac{A_T}{2}e^{jv\tau} + \frac{A_T}{2}e^{-jv\tau}$$

(B3.2)

Step 2: Representing the outlet concentrations of the reactant and product as well as outlet temperature in the form of Volterra series:

$$C_A(\tau) = \frac{A_C}{2} G_{A1,C}(u)e^{ju\tau} + \frac{A_C}{2} G_{A1,C}(-u)e^{-ju\tau} + \cdots + 2\left(\frac{A_C}{2}\right)^2 G_{A2,CC}(u,-u)e^0 + \cdots$$

$$+ \frac{A_T}{2} G_{A1,T}(v)e^{jv\tau} + \frac{A_T}{2} G_{A1,T}(-v)e^{-jv\tau} + \cdots + 2\left(\frac{A_T}{2}\right)^2 G_{A2,TT}(v,-v)e^0 + \cdots$$

$$+ \frac{A_C}{2}\frac{A_T}{2} G_{A2,CT}(u,v)e^{j(v+u)\tau} + \cdots$$

<div align="right">(B3.3)</div>

$$C_P(\tau) = \frac{A_C}{2} G_{P1,C}(u)e^{ju\tau} + \frac{A_C}{2} G_{P1,C}(-u)e^{-ju\tau} + \cdots + 2\left(\frac{A_C}{2}\right)^2 G_{P2,CC}(u,-u)e^0 + \cdots$$

$$+ \frac{A_T}{2} G_{P1,T}(v)e^{jv\tau} + \frac{A_T}{2} G_{P1,T}(-v)e^{-jv\tau} + \cdots + 2\left(\frac{A_T}{2}\right)^2 G_{P2,TT}(v,-v)e^0$$

$$+ \cdots + \frac{A_C}{2}\frac{A_T}{2} G_{P2,CT}(u,v)e^{j(v+u)\tau} + \cdots$$

<div align="right">(B3.4)</div>

$$\theta(\tau) = \frac{A_C}{2} F_{1,C}(u)e^{ju\tau} + \frac{A_C}{2} F_{1,C}(-u)e^{-ju\tau} + \cdots + 2\left(\frac{A_C}{2}\right)^2 F_{2,CC}(u,-u)e^0 + \cdots$$

$$+ \frac{A_T}{2} F_{1,T}(v)e^{jv\tau} + \frac{A_T}{2} F_{1,T}(-v)e^{-jv\tau} + \cdots + 2\left(\frac{A_T}{2}\right)^2 F_{2,TT}(v,-v)e^0 + \cdots$$

$$+ \frac{A_C}{2}\frac{A_T}{2} F_{2,CT}(u,v)e^{j(v+u)\tau} + \cdots$$

<div align="right">(B3.5)</div>

Step 3: Substituting the expressions for the modulated inputs, outlet concentrations of the reactant and product and outlet temperature, defined with Eqs. (B3.3-B3.5), into the appropriate model equations (4.15-4.17) after equated inputs which are not modulated to zero.

Step 4: Collecting the terms with $\frac{A_C}{2}\frac{A_T}{2}e^{j(u+v)\tau}$, corresponding to the cross ASO FRFs, and equating them to zero. The resulting equations are:

$$j(u+v)G_{A2,CT}(u,v)$$
$$= -(1+n\alpha)G_{A2,CT}(u,v) - \alpha\gamma F_{2,CT}(u,v)$$
$$- \alpha\big(\gamma(\gamma-2)F_{1,C}(u)F_{1,T}(v) + n(n-1)G_{A1,C}(u)G_{A1,T}(v)$$
$$+ n\gamma G_{A1,C}(u)F_{1,T}(v) + n\gamma G_{A1,T}(v)F_{1,C}(u)\big)$$

<div align="right">(B3.6)</div>

$$j(u+v)G_{P2,CTP}(u,v)$$
$$= nG_{A2,CT}(u,v) - G_{P2,CT}(u,v) + \gamma F_{2,CT}(u,v)$$
$$+ \big(\gamma(\gamma-2)F_{1,C}(u)F_{1,T}(v) + n(n-1)G_{A1,C}(u)G_{A1,T}(v) + n\gamma G_{A1,C}(u)F_{1,T}(v)$$
$$+ n\gamma G_{A1,T}(v)F_{1,C}(u)\big)$$

<div align="right">(B3.7)</div>

$$j(u+v)F_{2,CF}(u,v)$$
$$= -(1+St+\beta\gamma)F_{2,CT}(u,v) - n\beta G_{A2,CT}(u,v)$$
$$- \beta\big(\gamma(\gamma-2)F_{1,C}(u)F_{1,T}(v) + n(n-1)G_{A1,C}(u)G_{A1,T}(v)$$
$$+ n\gamma G_{A1,C}(u)F_{1,T}(v) + n\gamma G_{A1,T}(v)F_{1,C}(u)\big)$$

<div align="right">(B3.8)</div>

After introducing the $u = \omega$ and $v = -\omega$

$$0 = -(1 + n\alpha)G_{A2,CT}(\omega, -\omega) - \alpha\gamma F_{2,CT}(\omega, -\omega)$$
$$- \alpha\big(\gamma(\gamma - 2)F_{1,C}(\omega)F_{1,T}(-\omega) + n(n - 1)G_{A1,C}(\omega)G_{A1,T}(-\omega)$$
$$+ n\gamma G_{A1,C}(\omega)F_{1,T}(-\omega) + n\gamma G_{A1,T}(-\omega)F_{1,C}(\omega)\big)$$

$$(B3.9)$$

$$0 = nG_{A2,CT}(\omega, -\omega) - G_{P2,CT}(\omega, -\omega) + \gamma F_{2,CT}(\omega, -\omega)$$
$$+ \big(\gamma(\gamma - 2)F_{1,C}(\omega)F_{1,T}(-\omega) + n(n - 1)G_{A1,C}(\omega)G_{A1,T}(-\omega)$$
$$+ n\gamma G_{A1,C}(\omega)F_{1,T}(-\omega) + n\gamma G_{A1,T}(-\omega)F_{1,C}(\omega)\big)$$

$$(B3.10)$$

$$0 = -(1 + St + \beta\gamma)F_{2,CT}(\omega, -\omega) - n\beta G_{A2,CT}(\omega, -\omega)$$
$$- \beta\big(\gamma(\gamma - 2)F_{1,C}(\omega)F_{1,T}(-\omega) + n(n - 1)G_{A1,C}(\omega)G_{A1,T}(-\omega)$$
$$+ n\gamma G_{A1,C}(\omega)F_{1,T}(-\omega) + n\gamma G_{A1,T}(-\omega)F_{1,C}(\omega)\big)$$

$$(B3.11)$$

The system of equation can be written as follows:

$$[(1 + n\alpha)]G_{A2,CT}(\omega, -\omega) + [0]G_{P2,CT}(\omega, -\omega) + [\alpha\gamma]F_{2,CT}(\omega, -\omega) = l_{CT1}$$

$$[-n]G_{A2,CT}(\omega, -\omega) + [1]G_{P2,CT}(\omega, -\omega) + [-\gamma]F_{2,CT}(\omega, -\omega) = l_{CT2} \qquad (B3.12)$$

$$[n\beta]G_{A2,CT}(\omega, -\omega) + [0]G_{P2,CT}(\omega, -\omega) + [(1 + St + \beta\gamma)]F_{2,CT}(\omega, -\omega) = l_{CT3}$$

Where the auxiliary parameters are introduced:

$$P_{CT} = \gamma(\gamma - 2)F_{1,C}(\omega)F_{1,T}(-\omega) + n(n - 1)G_{1,CA}(\omega)G_{1,TA}(-\omega) + n\gamma G_{1,CA}(\omega)F_{1,T}(-\omega) +$$
$$n\gamma G_{1,TA}(-\omega)F_{1,C}(\omega) \qquad (B3.13)$$

$$l_{CT1} = -\alpha P_{CT}, \, l_{CT2} = P_{CT}, \, l_{CT3} = -\beta P_{CT} \qquad (B3.14)$$

Step 5: After solving system of equations (B3.12) the final expressions for the cross ASO FRFs $G_{A2,CT}(\omega,-\omega)$ and $G_{P2,CT}(\omega,-\omega)$ are given in the main part of this work and here only the final of the cross ASO FRF $F_{2,CT}(\omega,-\omega)$ is given:

$$F_{2,CT}(\omega, -\omega) = \frac{n\beta\gamma(1 + \alpha)(1 + \beta + St - \delta)}{B_{ps}} \times$$
$$\frac{(1 + St + \alpha(1 + St + \beta\gamma) + 2\beta(1 + n\alpha) + \omega^2) + j\omega(\alpha - 2\beta - St)}{\left(B_{ps} - \omega^2\right)^2 + 4A_{ps}^2\omega^2}$$

$$(B3.15)$$

The ASO FRFs are here given as a function of the first order FRF, as follows:

$$G_{A2,CT}(\omega, -\omega) = \frac{-\alpha(1 + St)}{B_{ps}}\big(\gamma(\gamma - 2)F_{1,C}(\omega)F_{1,T}(-\omega) + n(n - 1)G_{A1,C}(\omega)G_{A1,T}(-\omega)$$
$$+ n\gamma G_{A1,C}(\omega)F_{1,T}(-\omega) + n\gamma G_{A1,T}(-\omega)F_{1,C}(\omega)\big)$$

$$(B3.16)$$

$$G_{P2,CT}(\omega, -\omega) = \frac{(1 + St)}{B_{ps}} \big(\gamma(\gamma - 2)F_{1,C}(\omega)F_{1,T}(-\omega) + n(n - 1)G_{A1,C}(\omega)G_{A1,T}(-\omega)$$

$$+ n\gamma G_{A1,C}(\omega)F_{1,T}(-\omega) + n\gamma G_{A1,T}(-\omega)F_{1,C}(\omega)\big)$$

<div align="right">(B3.17)</div>

$$F_{2,CT}(\omega, -\omega) = \frac{-\beta}{B_{ps}} \big(\gamma(\gamma - 2)F_{1,C}(\omega)F_{1,T}(-\omega) + n(n - 1)G_{A1,C}(\omega)G_{A1,T}(-\omega)$$

$$+ n\gamma G_{A1,C}(\omega)F_{1,T}(-\omega) + n\gamma G_{A1,T}(-\omega)F_{1,C}(\omega)\big)$$

<div align="right">(B3.18)</div>

B.4. Derivation of cross asymmetrical second order frequency response functions for simultaneous modulation of inlet concentration and flow-rate

Step 1: Defining the dimensionless input modulation,

$$C_{Ai}(\tau) = A_C cos(u\tau) = \frac{A_C}{2} e^{ju\tau} + \frac{A_C}{2} e^{-ju\tau} \tag{B4.1}$$

$$\Phi(\tau) = A_F cos(v\tau) = \frac{A_F}{2} e^{jv\tau} + \frac{A_F}{2} e^{-jv\tau} \tag{B4.2}$$

Step 2: Representing the outlet concentrations of the reactant and product as well as outlet temperature in the form of Volterra series:

$$C_A(\tau) = \frac{A_C}{2} G_{A1,C}(u)e^{ju\tau} + \frac{A_C}{2} G_{A1,C}(-u)e^{-ju\tau} + \cdots + 2\left(\frac{A_C}{2}\right)^2 G_{A2,CC}(u, -u)e^0 + \cdots$$

$$+ \frac{A_F}{2} G_{A1,F}(v)e^{jv\tau} + \frac{A_F}{2} G_{A1,F}(-v)e^{-jv\tau} + \cdots + 2\left(\frac{A_F}{2}\right)^2 G_{A2,FF}(v, -v)e^0 + \cdots$$

$$+ \frac{A_C}{2}\frac{A_F}{2} G_{A2,CF}(u, v)e^{j(v+u)\tau} + \cdots$$

<div align="right">(B4.3)</div>

$$C_P(\tau) = \frac{A_C}{2} G_{P1,C}(u)e^{ju\tau} + \frac{A_C}{2} G_{P1,C}(-u)e^{-ju\tau} + \cdots + 2\left(\frac{A_C}{2}\right)^2 G_{P2,CC}(u, -u)e^0 + \cdots$$

$$+ \frac{A_F}{2} G_{P1,F}(v)e^{jv\tau} + \frac{A_F}{2} G_{P1,F}(-v)e^{-jv\tau} + \cdots + 2\left(\frac{A_F}{2}\right)^2 G_{P2,FF}(v, -v)e^0 + \cdots$$

$$+ \frac{A_C}{2}\frac{A_F}{2} G_{P2,CF}(u, v)e^{j(v+u)\tau} + \cdots$$

<div align="right">(B4.4)</div>

$$\theta(\tau) = \frac{A_C}{2} F_{1,C}(u)e^{ju\tau} + \frac{A_C}{2} F_{1,C}(-u)e^{-ju\tau} + \cdots + 2\left(\frac{A_C}{2}\right)^2 F_{2,CC}(u, -u)e^0 + \cdots$$

$$+ \frac{A_T}{2} F_{1,T}(v)e^{jv\tau} + \frac{A_F}{2} F_{1,F}(-v)e^{-jv\tau} + \cdots + 2\left(\frac{A_F}{2}\right)^2 F_{2,FF}(v, -v)e^0 + \cdots$$

$$+ \frac{A_C}{2}\frac{A_F}{2} F_{2,CF}(u, v)e^{j(v+u)\tau} + \cdots$$

<div align="right">(B4.5)</div>

Step 3: Substituting the expressions for the modulated inputs, outlet concentrations of the reactant and product and outlet temperature, defined with Eqs. (B4.1-B4.5), into the appropriate model equations (4.15-4.17) after equated inputs which are not modulated to zero.

Step 4: Collecting the terms with $\frac{A_C}{2}\frac{A_F}{2}e^{j(u+v)\tau}$, corresponding to the cross ASO FRFs, and equating them to zero. The resulting equations are:

$$[1 + n\alpha + j(v+u)]G_{A2,CF}(v,u) + [0]G_{P2,CF}(v,u) + [\alpha\gamma]F_{2,CF}(v,u)$$
$$= (1+\alpha) - G_{1,CA}(v)$$
$$- \alpha\big[n\gamma G_{A1,C}(v)F_{1,F}(u) + n\gamma G_{A1,F}(u)F_{1,C}(v) + \gamma(\gamma-2)F_{1,C}(v)F_{1,F}(u)$$
$$+ n(n-1)G_{A1,C}(v)G_{A1,F}(u)\big]$$

(B4.6)

$$[-n]G_{A2,CF}(v,u) + [1 + j(v+u)]G_{P2,CF}(v,u) + [-\gamma]F_{2,CF}(v,u)$$
$$= -G_{P1,C}(v)$$
$$+ \big[n\gamma G_{A1,C}(v)F_{1,F}(u) + n\gamma G_{A1,F}(u)F_{1,C}(v) + \gamma(\gamma-2)F_{1,C}(v)F_{1,F}(u)$$
$$+ n(n-1)G_{A1,C}(v)G_{A1,F}(u)\big]$$

(B4.7)

$$[n\beta]G_{A2,CF}(v,u) + [0]G_{P2,CF}(v,u) + [1 + \beta\gamma + St + j(v+u)]F_{2,CF}(v,u)$$
$$= -F_{1,C}(v)$$
$$- \beta\big[n\gamma G_{A1,C}(v)F_{1,F}(u) + n\gamma G_{A1,F}(u)F_{1,C}(v) + \gamma(\gamma-2)F_{1,C}(v)F_{1,F}(u)$$
$$+ n(n-1)G_{A1,C}(v)G_{A1,F}(u)\big]$$

(B4.8)

After introducing the $u = \omega$ and $v = -\omega$ an after introducing the auxiliary parameters (Eqs.(B4.10)-(B4.13)) the system of equations can be written as following:

$$[1 + n\alpha]G_{A2,CF}(\omega,-\omega) + [0]G_{P2,CF}(\omega,-\omega) + [\alpha\gamma]F_{2,CF}(\omega,-\omega) = l_{CF1}$$
$$[-n]G_{A2,CF}(\omega,-\omega) + [1]G_{P2,CF}(\omega,-\omega) + [-\gamma]F_{2,CF}(\omega,-\omega) = l_{CF2} \qquad \text{(B4.9)}$$
$$[n\beta]G_{A2,CF}(\omega,-\omega) + [0]G_{P2,CF}(\omega,-\omega) + [1 + \beta\gamma + St]F_{2,CF}(\omega,-\omega) = l_{CF3}$$
with

$$P_{CF} = n\gamma G_{A1,C}(\omega)F_{1,F}(-\omega) + n\gamma G_{A1,F}(-\omega)F_{1,C}(\omega) + \gamma(\gamma-2)F_{1,C}(\omega)F_{1,F}(-\omega) +$$
$$n(n-1)G_{A1,C}(\omega)G_{A1,F}(-\omega) \qquad \text{(B4.10)}$$
$$l_{CF1} = 1 + \alpha - G_{A1,C}(\omega) - \alpha P_{CF} \qquad \text{(B4.11)}$$
$$l_{CF2} = -G_{P1,C}(\omega) + P_{CF} \qquad \text{(B4.12)}$$
$$l_{CF3} = -F_{1,C}(\omega) - \beta P_{CF} \qquad \text{(B4.13)}$$

Step 5: After solving system of equations the final expressions for the cross ASO FRFs $G_{A2,CF}(\omega,-\omega)$ and $G_{P2,CF}(\omega,-\omega)$ are given in the main part of this work. The cross ASO FRFs are here given as a function of the first order FRFs:

$$G_{A2,CF}(\omega,-\omega) = \frac{1}{B_{ps}}\big((1 + \beta\gamma + St)(1+\alpha) - (1 + \beta\gamma + St)G_{A1,C}(\omega) + \alpha\gamma F_{1,C}(\omega)$$
$$- \alpha(1 + St)\big(n\gamma G_{A1,C}(\omega)F_{1,F}(-\omega) + n\gamma G_{A1,F}(-\omega)F_{1,C}(\omega)$$
$$+ \gamma(\gamma-2)F_{1,C}(\omega)F_{1,F}(-\omega) + n(n-1)G_{A1,C}(\omega)G_{A1,F}(-\omega)\big)\big)$$

(B4.14)

$$G_{P2,CF}(\omega,-\omega) = \frac{1}{B_{ps}}\Big[n(1+\alpha)(1+St) - n(1+St)G_{A1,C}(\omega) - B_{ps}G_{P1,C}(\omega) - \gamma F_{1,C}(\omega)$$

$$+ (1$$
$$+ St)\big(n\gamma G_{A1,C}(\omega)F_{1,F}(-\omega) + n\gamma G_{A1,F}(-\omega)F_{1,C}(\omega)$$
$$+ \gamma(\gamma-2)F_{1,C}(\omega)F_{1,F}(-\omega) + n(n-1)G_{A1,C}(\omega)G_{A1,F}(-\omega)\big)\Big]$$

(B4.15)

$$F_{2,CF}(\omega,-\omega) = \frac{1}{B_{ps}}\Big[-n\beta(1+\alpha) + n\beta G_{A1,C}(\omega) - (1+n\alpha)F_{1,C}(\omega)$$

$$+ \beta\big(n\gamma G_{A1,C}(\omega)F_{1,F}(-\omega) + n\gamma G_{A1,F}(-\omega)F_{1,C}(\omega)$$
$$+ \gamma(\gamma-2)F_{1,C}(\omega)F_{1,F}(-\omega) + n(n-1)G_{A1,C}(\omega)G_{A1,F}(-\omega)\big)\Big]$$

(B4.16)

B.5 The auxiliary functions Γ_R and Γ_I which figure in the cross asymmetrical frequency response function $G_{P2,CF}(\omega,-\omega)$ in polynomial forms

The auxiliary functions Γ_R and Γ_I can be given in polynomial form of forcing frequency

$$\Gamma_R = \Gamma_{R1}\omega^6 + \Gamma_{R2}\omega^4 + \Gamma_{R3}\omega^2 + \Gamma_{R4} \qquad\qquad (B5.1)$$
$$\Gamma_I = \Gamma_{I1}\omega^4 + \Gamma_{I2}\omega^2 + \Gamma_{I3} \qquad\qquad (B5.2)$$

where the auxiliary parameters Γ_{R1}, Γ_{R2}, Γ_{R3} and Γ_{R4} are defined as functions of the stability parameters A_{ps} and B_{ps} and auxiliary parameters Π_{R1}, Π_{R2} and Π_{R3}, respectively in following way:

$$\Gamma_{R1} = B_{ps} - \Pi_{R1} \qquad\qquad (B5.3)$$
$$\Gamma_{R2} = B_{ps}\big(4A_{ps}^2 - 2B_{ps}\big) - \Pi_{R1} - \Pi_{R2} \qquad\qquad (B5.4)$$
$$\Gamma_{R3} = B_{ps}^3 - \Pi_{R2} - \Pi_{R3} \qquad\qquad (B5.5)$$
$$\Gamma_{R4} = -\Pi_{R3} \qquad\qquad (B5.6)$$

and the auxiliary parameters Γ_{I1}, Γ_{I2} and Γ_{I3} which are defined as function of the auxiliary parameters Π_{I1} and Π_{I2} and stability parameters A_{ps} and B_{ps}, as follows:

$$\Gamma_{I1} = B_{ps} - \Pi_{I1} \qquad\qquad (B5.7)$$
$$\Gamma_{I2} = B_{ps}\big(4A_{ps}^2 - 2B_{ps}\big) - \Pi_{I1} - \Pi_{I2} \qquad\qquad (B5.8)$$
$$\Gamma_{I3} = B_{ps}^3 - \Pi_{I2} \qquad\qquad (B5.9)$$

B.6 The auxiliary functions Π_{HR} and Π_{HI} which figure in the cross asymmetrical frequency response function $H_{A2,CF}(\omega,-\omega)$ in polynomial forms

The auxiliary functions Π_{HR} and Π_{HI} can be given in polynomial form of forcing frequency as:
$$\Pi_{HR} = \Pi_{HR1}\omega^4 + \Pi_{HR2}\omega^2 + \Pi_{HR3} \qquad\qquad (B6.1)$$

$$\Pi_{HI} = \Pi_{HI1}\omega^2 + \Pi_{HI2} \qquad\qquad (B6.2)$$

The auxiliary parameters Π_{HR1}, Π_{HR2} and Π_{HR3} are defined as functions of the stability parameters A_{ps} and B_{ps} and auxiliary parameters Π_{R2} and Π_{R3}, in following way:
$$\Pi_{HR1} = \Pi_{R1} = 1 + \beta\gamma + St \qquad\qquad (B6.3)$$
$$\Pi_{HR2} = \Pi_{R2} - (1 + \beta\gamma + St)B_{ps} - 2A_{ps}B_{ps} \qquad\qquad (B6.4)$$

$$\Pi_{HR3} = \Pi_{R3} + (1 + \beta\gamma + St)B_{ps}^2 \tag{B6.5}$$

The auxiliary parameters Π_{HI1} and Π_{HI2} are defined as function of the auxiliary parameters Π_{I1} and Π_{I2} and stability parameters A_{ps} and B_{ps}, as follows:

$$\Pi_{HI1} = \Pi_{I1} - B_{ps} \tag{B6.6}$$

$$\Pi_{HI2} = \Pi_{I2} + B_{ps}^2 + 2(1 + \beta\gamma + St)A_{ps}B_{ps} \tag{B6.7}$$

B.7. The auxiliary functions Γ_{HR} and Γ_{HI} which figure in the cross asymmetrical frequency response function $H_{P2,CF}(\omega,-\omega)$ in polynomial forms

The auxiliary functions Γ_{HR} and Γ_{HI} can be given in polynomial form of forcing frequency as:

$$\Gamma_{HR} = \Gamma_{HR1}\omega^6 + \Gamma_{HR2}\omega^4 + \Gamma_{HR3}\omega^2 + \Gamma_{HR4} \tag{B7.1}$$

$$\Gamma_{HI} = \Gamma_{HI1}\omega^4 + \Gamma_{HI2}\omega^2 + \Gamma_{HI3} \tag{B7.2}$$

The auxiliary parameters Γ_{HR1}, Γ_{HR2}, Γ_{HR3}, and Γ_{HR4}, are defined as functions of the stability parameters A_{ps} and B_{ps} and auxiliary parameters Γ_{R1}, Γ_{R2} and Γ_{R3}, respectively in following way:

$$\Gamma_{HR1} = \Gamma_{R1} \tag{B7.3}$$

$$\Gamma_{HR2} = \Gamma_{R2} - n\alpha \tag{B7.4}$$

$$\Gamma_{HR3} = \Gamma_{R3} + n\alpha(B_{ps} - 2A_{ps}) + n\alpha(1 + St)(2A_{ps} - 1) \tag{B7.5}$$

$$\Gamma_{HR4} = n\alpha(1 + St)B_{ps} \tag{B7.6}$$

and the auxiliary parameters Γ_{HI1}, Γ_{HI2} and Γ_{HI3} which are defined as function of the auxiliary parameters Γ_{I1}, Γ_{I2} and Γ_{I3} and stability parameters A_{ps} and B_{ps}, as follows:

$$\Gamma_{HI1} = \Gamma_{I1} \tag{B7.7}$$

$$\Gamma_{HI2} = \Gamma_{I2} + n\alpha B_{ps}(2A_{ps} - 1) + n\alpha(1 + St)B_{ps} \tag{B7.8}$$

$$\Gamma_{HI3} = \Gamma_{I3} + n\alpha B_{ps}^2 - n\alpha B_{ps}(1 + St)(B_{ps} - 2A_{ps}) \tag{B7.9}$$

C. Optimization procedure and asymmetrical frequency response function $G_{P2,TT}(\omega,-\omega)$ for adiabatic CSTR

C.1. Optimization procedure of the laboratory adiabatic CSTR for hydrolysis of acetic acid anhydride to acetic acid

Two objective functions were defined and the optimal steady-state is obtained in Matlab, by the Multi-objective Genetic Algorithm.

The lower and upper boundary (lb, ub) values for the residence time are set to be, for lower $lb(\tau_{res})$=100 s and for upper $ub(\tau_{res})$=1000 s, considering the volume of the laboratory reactor and the flow-rates of the pumps for water and anhydride of acetic acid.

Two constraints are considered in the optimization procedure:

1. Constraint 1

$$\frac{-\Delta H_r}{\rho cc_p} c_{A,i,s} + T_{i,s} - T_{max} \le 0 \qquad (T_{max}\text{=353.15 K}) \tag{C1.1}$$

Constraint 1 can be reduced to $c_{Ai,s} \le 4.375 \ mol/l$

2. Constraint 2

$$10\,\dot{n}_{A,o} - \dot{n}_{W,o} \leq 0 \tag{C1.2}$$

$$10\,c_{A,i} * F_{tot} - c_{w,i} * F_{tot} \leq 0$$

The constraint 2 can be reduced to $c_{Ai,s} \leq 3.642\ mol/l$. Therefore, the upper boundary value for the inlet concentration is set to be, $ub(c_{Ai,s})$=3.642 mol/l.

The Multi-objective Genetic Algorithm gives the list of recommended solutions depending on the values of two defined objective functions, where the following solution is chosen, for optimal steady-state inlet concentration $c_{Ai,s}$=3.640mol/l and for optimal residence time τ_{res} =218.95 s.

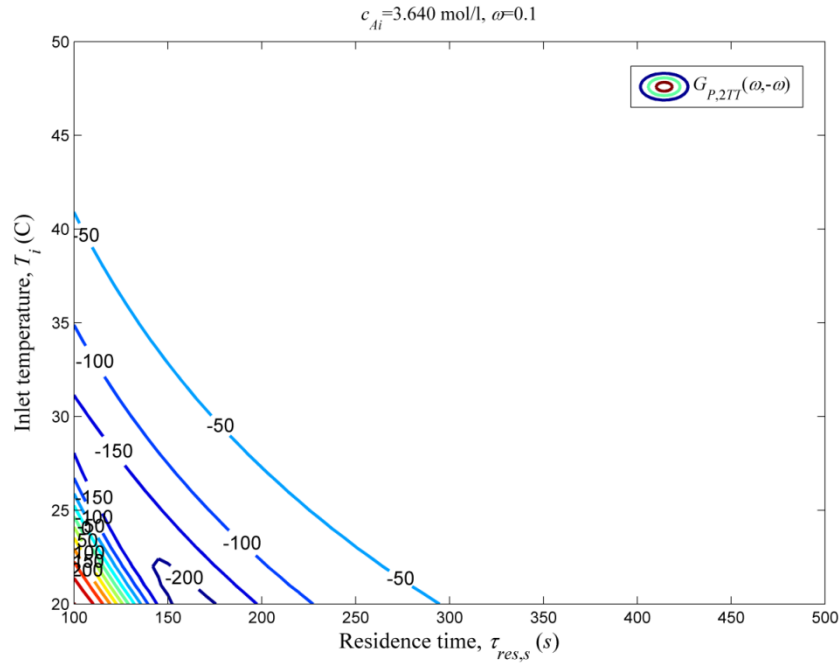## C.2. The asymmetrical second order frequency response function $G_{P2,TT}(\omega,\text{-}\omega)$

Figure C1 The ASO FRF $G_{P2,TT}(\omega,\text{-}\omega)$ as a function of the inlet temperature and residence time for constant inlet concentration $c_{Ai,s}$=3.640 mol/l and dimensionless forcing frequency ω=0.1
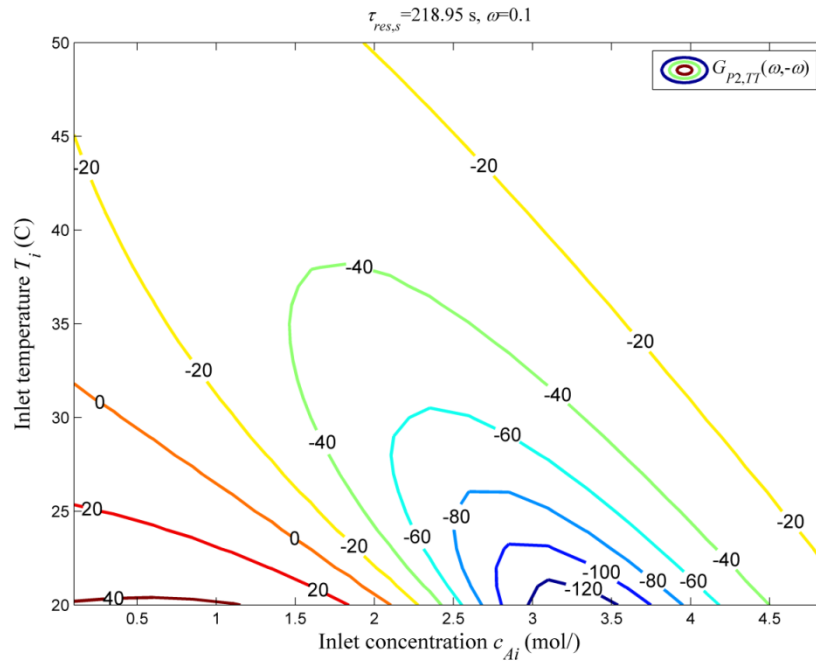
Figure C2 The ASO FRF $G_{P2,TT}(\omega,-\omega)$ as a function of the inlet temperature and inlet concentration of the reactant, for constant residence time $\tau_{res,s}$=218.95 s and dimensionless forcing frequency ω=0.1

Biography of the author

Daliborka Nikolić Paunić was born in Belgrade on 12th April, 1978. She graduated on the Department of Chemical Engineering, on Faculty of Technology and Metallurgy (University of Belgrade), with the average grade 9.24/10. Her final thesis on the undergraduate studies was titled as: "*Theoretical Analysis of Non-linear Frequency Response of Chromatographic Column for Binary Adsorption Systems.*" She got Special annual reward from Serbian Chemical Society in 2004, for excellent achievement in undergraduate studies, as one of the top ten students in the class.

Daliborka Nikolić Paunić is employed in Institute of Chemistry, Technology and Metallurgy (University of Belgrade) from 2005, where she takes a participation in research activities within the projects financed by Ministry for Science and Technology (Republic of Serbia), in sustainable development activities and techno-economical studies. She participated in the international project of bilateral cooperation between Serbia and Germany entitled "Analysis of periodic processes based on non-linear frequency response" in the period from 2010 to 2011. She was on two study visits to the Max-Planck Institute for dynamics of complex technical systems in Magdeburg (Germany).

Daliborka Nikolic Paunić enrolled in doctoral studies at the Faculty of Technology and Metallurgy in the 2005/2006 school year at the Department of Chemical Engineering and passed all the exams with the average grade of 10/10.

Daliborka Nikolic Paunić is the co-author of five papers in leading international journal (M21). She participated in a number of international meetings.

Прилог 1.

Изјава о ауторству

Потписани-а <u>Далиборка Николић Паунић</u>

број индекса ДС-9/2005

Изјављујем

да је докторска дисертација под насловом

Forced periodically operated chemical reactors – Evaluation and analysis by the nonlinear frequency response method (Периодичне операције хемијских реактора – Евалуација и анализа применом методе нелинеарног фреквентног одзива)

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- да нисам кршио/ла ауторска права и користио интелектуалну својину других лица.

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У Београду, 04.04.2016.

Николић Паунић Далиборка

Изјава о истоветности штампане и електронске верзије докторског рада

Име и презиме аутора Далиборка Николић Паунић

Број индекса ДС-9/2005

Студијски програм Хемија и хемијска технологија

Наслов рада Forced periodically operated chemical reactors – Evaluation and analysis by the nonlinear frequency response method (Периодичне операције хемијских реактора – Евалуација и анализа применом методе нелинеарног фреквентног одзива)

Ментор Проф. Др. Менка Петковска

Потписани/а Далиборка Николић Паунић

Изјављујем да је штампана верзија мог докторског рада истоветна електронској верзији коју сам предао/ла за објављивање на порталу **Дигиталног репозиторијума Универзитета у Београду.**

Дозвољавам да се објаве моји лични подаци везани за добијање академског звања доктора наука, као што су име и презиме, година и место рођења и датум одбране рада.

Ови лични подаци могу се објавити на мрежним страницама дигиталне библиотеке, у електронском каталогу и у публикацијама Универзитета у Београду.

Потпис докторанда

У Београду, 04.04.2016

Прилог 3.

Изјава о коришћењу

Овлашћујем Универзитетску библиотеку „Светозар Марковић" да у Дигитални репозиторијум Универзитета у Београду унесе моју докторску дисертацију под насловом:

Forced periodically operated chemical reactors – Evaluation and analysis by the nonlinear frequency response method (Периодичне операције хемијских реактора – Евалуација и анализа применом методе нелинеарног фреквентног одзива) која је моје ауторско дело.

Дисертацију са свим прилозима предао/ла сам у електронском формату погодном за трајно архивирање.

Моју докторску дисертацију похрањену у Дигитални репозиторијум Универзитета у Београду могу да користе сви који поштују одредбе садржане у одабраном типу лиценце Креативне заједнице (Creative Commons) за коју сам се одлучио/ла.

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5. Ауторство – без прераде

6. Ауторство – делити под истим условима

(Молимо да заокружите само једну од шест понуђених лиценци, кратак опис лиценци дат је на полеђини листа).

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Николић Рамић Далиборка

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