

Analysis and experimental demonstration of forced periodic operation of an adiabatic stirred tank reactor: Simultaneous modulation of inlet concentration and total flow-rate

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ABSTRACT

It is well known, that forced periodic operation possesses the potential for process improvements. Nevertheless, only a small number of applications is reported, due to complex realization, limited predictability and high inertia of larger units.

Nonlinear frequency response (NFR) analysis has proven to predict efficiently time-averaged performance of reactor effluent streams originating from forced periodic changes of one or several input(s).

Focus of this paper was an experimental demonstration of forced periodic operation applied to the hydrolysis of acetic anhydride carried out in an adiabatic CSTR. Theoretical results provided a guideline for experiments exploiting simultaneous sinusoidal modulations of the anhydride inlet concentration and the total volumetric flow-rate. Influences of the forcing parameters (amplitudes and the phase difference) were also studied. Confirming the predictions of NFR analysis a significantly higher time-averaged product yields were

experimentally achieved compared to conventional steady-state operation with simultaneous modulation of two inputs using an optimized phase shift.

Keywords

Dynamic reactor operation, forced periodic modulation, nonlinear frequency response analysis, modulation of two inputs, acetic anhydride hydrolysis

Highlights

- Forced dynamic operation exploiting modulation of two phase-shifted inputs.
- Prediction of mean output properties using the Nonlinear Frequency Response method.
- Experimental validation of predicted performance improvements in an adiabatic CSTR.
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1) Introduction

Continuously operated reactors are usually designed and optimized to operate, after completing a start-up phase, under steady-state conditions. The idea to improve reactor performance by applying a forced dynamic operation altering certain parameters periodically at the reactor inlet was studied for the first time systematically by Horn and Bailey [1-5]. Substantial early contributions to this field were made by Douglas and Rippin [6, 7] and by Renken [8, 9].

Between 1980-1990 numerous theoretical investigations have been carried out to explain and to quantify possible performance improvements due to forced periodic operation, to optimize such regimes and to control them [10-17]. Nevertheless, although there are mathematical proofs that the implementation of forced dynamic regimes is capable to outperform optimized steady-state operation, such advanced concepts were not implemented on an industrial scale. In a review paper published in 1995 as major drawbacks of forced periodic operation were identified (a) increased complexity of the overall process and (b) insufficient quantitative predictability of the process outcome [18]. Furthermore, larger units are often characterized by significant inertia, which can be an obstacle for exploiting rapid changes of inlet perturbations.

Despite the more complex control and operation of the process caused by the periodical changes of certain inputs, there are numerous examples of successful periodic operation of industrially relevant reactions and separation processes, which cannot be operated continuously under steady-state conditions. One example is the reversed flow tubular reactor suggested by Matros, which traps a hot zone within the central reactor region [19]. This periodic operation regime is based on feeding cold gaseous reactant streams in an alternating manner from both reactors ends. Before the reaction is ignited in the central part of the reactor, the feed mixture is heated up periodically in the two entrance zones. Other

examples are Chemical Looping processes [20] or the Catofin Process for alkane dehydrogenation [21]. Forced periodic processes applied on a large scale to perform dedicated separation processes are Pressure Swing Adsorption (PSA) [22] and Simulated Moving Bed (SMB) adsorption [23]. In these cases, several fixed-beds are connected and operated in a cyclic regime realizing distinct sub-steps to fulfill process-specific tasks, including the unavoidable regeneration of adsorbents or catalysts. Some of the separation processes mentioned exploit rather high shifting frequencies. The hardware required to impose such regimes is nowadays readily available and does not cause any more restrictions for implementing periodic operation regimes.

Related to the lack of easy and reliable methods to screen for promising reaction systems and to identify suitable forcing parameters, the comprehensive book edited by Silveston and Hudgins [24] describes the potential of Nonlinear Frequency Response (NFR) analysis for efficiently predicting mean values of the reactor outlet stream [25]. The two ingredients required to apply this method are the provision of a reliable kinetic model for quantifying the reaction rates and a valid reactor model. In [24] much more case studies and successful examples are discussed, compared to [18]. However, it is evident that empirical design approaches dominate and a more rigorous application of theoretical concepts to optimize forced periodic operation is exceptional.

Experimental results of investigating a hydrolysis reaction carried out in an adiabatic continuously stirred tank reactor (CSTR) reactor will be presented in this paper. This reactor type was selected for this conceptionally oriented study devoted to demonstrate the potential of joint concentration and flow-rate modulations. When process enhancement exploiting forced dynamic operation is achievable for this reactor, which is characterized by a broad residence time distribution, there should be potential also for other reactor types, which provide narrower residence time distributions. The Nonlinear Frequency Response (NFR) method is used to identify promising process conditions for single and simultaneous

modulation of two phase-shifted input variables. Based on previously reported research [25] there is not yet a systematic experimental study available in literature for the latter case, which is based on theoretically predicted forcing parameters.

This paper is structured as follows. The idea of forced periodic reactor operation and a summary of the key features of the NFR method will be first illustrates briefly. Then, the reaction system studied will be described along with essential physical and chemical properties including the reaction rate model and the essential balance equations describing an adiabatic CSTR. With this quantitative characterization of both reaction and reactor, the NFR method can offer parameter ranges and forcing conditions for which improved performance is likely. These predictions provided the frame for the experimental analysis. In the main part of the paper, the results of NFR predictions are compared with experimental observations. Finally, a comment on the application of the general concept and the NFR method to evaluate more complex reaction systems is made.

2) Principle and potential of forced dynamic operation

The key idea of dynamic operation of continuously operated flow reactors is the implementation of a forced periodic modulation of one or several input variables (c , T , F) of the inlet stream. This causes non-constant outputs of the outputs at the reactor outlet, which settle down after the completion of a start-up period into a periodic regime. This regime is designated as the cyclic steady-state.

Of practical relevance for economically attractive reaction processes are mean values of case-specific product stream outputs. Conversion of a key reactant is considered frequently as a performance criterion [24]. However, other outputs, such as e.g. yield or space-time-yields, are often more meaningful and important. For the forced periodic operation to be

attractive, the specific performance criterion evaluated should outperform the value achievable by optimized steady-state operation.

In studies reported in the literature [2, 9, 12], typically the analysis of perturbation of just one input is given. Due to the results of our preliminary work (see next section), Figure 1 illustrates the simultaneous implementation of a periodic modulation for two input variables ($x(t)$ and $z(t)$) introduced into a not further specified reactor. The application of two inputs provides more degrees of freedom and increases the potential of periodic operation. After completion of the start-up period, the cyclic regime is characterized by periodic profiles of the numerous outputs, $y_i(t)$. Figure 1 also depicts the mean value of a specific output ($y_{i,p,av}$), together with the corresponding steady-state value ($y_{i,s}$), which results from applying time-averages of $x(t)$ and $z(t)$ at the reactor inlet.

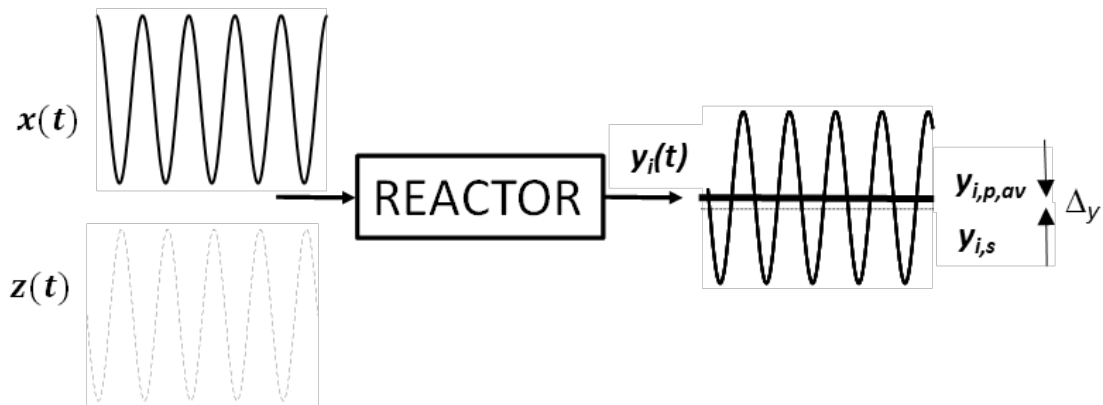


Figure 1: Dynamic operation of a reactor with one (x) or two (x and z) periodically modulated inputs triggering periodic output. Just a single output y_i is illustrated along with its time-averaged mean value $y_{i,p,av}$. In addition is shown a steady-state operation output value, $y_{i,s}$, which results when constantly imposing the mean values of the inputs. Depending on the specific output of the system evaluated, y_i , the marked difference, Δ_y , can be positive or negative.

For a selected objective function quantifying the reactor performance, the corresponding mean value $y_{i,p,av}$ should deviate in the desired direction away from the optimized steady-state value, $y_{i,s,opt}$.

In the next section, key features of the NFR method will be summarized and highlight its ability to efficiently generate an approximation for the mean output $y_{i,p,av}$.

3) NFR method and evaluation of mean values of the periodic output

The Nonlinear Frequency Response (NFR) method is based on Volterra's control theory [26], on the analysis of weakly nonlinear systems [27] and on determining and evaluating higher-order frequency response functions (FRF). The details of the method were provided in recent publications [25, 28, 30-32] and will not be repeated here. In preliminary theoretical investigations, NFR predictions of time-average values have been successfully compared with corresponding results of additionally generated numerical solutions [30].

Of ample relevance for the topic of this paper is the fact, that time-average of the reactor output can be determined by evaluating the non-periodic term of the FRF characterizing the periodic outlet profile, the so-called DC component [25]. It should be mentioned, that the NFR method can be applied only for systems characterized by a stable steady-state, which is frequently encountered.

The NFR method can be easily used to evaluate the impact of the available degrees of freedom (mean value of the modulated input, forcing amplitude, forcing frequency) for modulating just one single input (inlet concentration, total flow-rate, inlet temperature, ...).

However, as exploited in this paper, the method can be extended straightforwardly to analyze the joint effect of simultaneously varying multiple inputs. Then, possible phase differences between the individual inputs offer additional degrees of freedom for optimizing the periodic process regime [30, 33, 34].

The situation of perturbing two inputs periodically around given mean values, $x(t)$ and $z(t)$, is illustrated in Fig. 2. For such a forced periodic regime, there are seven degrees of freedom available, namely two mean inlet values (x_s, z_s), two frequencies (ω_x and ω_z), two amplitudes (A_x and A_z) and a phase difference φ . Previous theoretical studies have shown that best results can be achieved when both inputs are varied using the same forcing frequency, i.e.

$\omega_x = \omega_z = \omega$ [34]. This uniform frequency case with six degrees of freedom is depicted in

Figure 2 and will be further considered below.

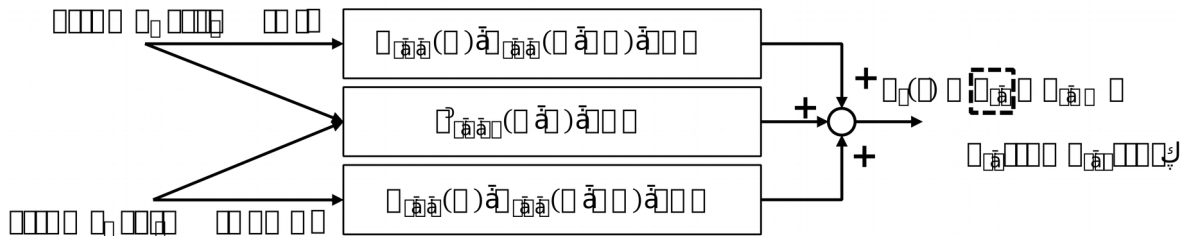


Figure 2: Diagram illustrating the connection between two harmonically modulated inputs $x(t)$ and $z(t)$ with mean values x_s and z_s , forcing amplitudes (A_x, A_z), a uniform forcing frequency (ω) and a phase shift (φ) and a resulting periodic output $y_i(t)$. Indicated are the first terms of the involved transfer functions G (lumping terms of higher-order into THO). The time-averaged mean value of $y_i(t)$ can be approximated by determining just the non-periodic DC component of the output, $y_{i,DC}$, neglecting the higher-order periodic terms.

The calculation of the different terms of the overall transfer function G needs the provision of a dynamic process model for the process of interest. Thus, for analyzing a chemical reaction system both a model for the reaction rates and a model characterizing the specific reactor are required. Furthermore, the output of interest, y_i , which is case-specific and depends on the process goal, needs to be specified. Regarding this latter selection, it is possible to select also functions aggregating several outputs as demonstrated below.

Exploiting Taylor series linearization and the technique of “Harmonic probing” the different order terms of the transfer function can be determined in a straightforward way following the standard procedure described in [25, 34]. A detailed derivation of the different terms of the various process specific functions is provided in [35].

As mentioned above, for evaluating periodic operation, the most essential part is the DC component. For a single input modulation exploiting $x(t, A_x, \omega)$ the relation given in eq. 1 connects the second-order asymmetric function $G_{i,2,x}$ with the DC-component, $y_{i,DC}$, as a measure for the difference between the periodic regime and the corresponding steady-state operation (see Fig. 1):

$$y_{i,DC} = \Delta_y = y_{i,p,av} - y_{i,s} \cong \left(\frac{A_x}{2}\right)^2 G_{i,2,x}(\omega, -\omega) \quad (1)$$

As shown earlier [14, 25], forced periodic operation modulating just a single input can be attractive. However, it may also cause detrimental behavior compared to conventional steady-state operation.

For simultaneous modulation of two inputs (as illustrated in Fig. 2), predictions are slightly more complicated but still straightforward. In this case, each output is connected with a modulated input by a transfer function, namely $G_{i,2,x}$ and $G_{i,2,z}$. Also, an important asymmetrical second-order cross term function arises, namely $G_{i,2,xz}^i$. The DC component of interest then depends on three contributions as exemplified in eq. 2.

$$y_{i,DC} = y_{i,DC,x} + y_{i,DC,z} + y_{i,DC,xz}^i \quad (2)$$

The two straight contributions of each individual input to the DC component can be calculated in full analogy to eq. 1. The additional second-order cross term $G_{i,2,xz}^i$ constitutes of two complex conjugates. This provides for eq. 2 into the following more specific form:

$$y_{i,DC} = \Delta_y \approx 2 \left(\frac{A_x}{2} \right)^2 G_{i,2,x}(\omega, -\omega) + 2 \left(\frac{A_z}{2} \right)^2 G_{i,2,z}(\omega, -\omega) + 2 \left(\frac{A_x}{2} \right) \left(\frac{A_z}{2} \right) (\Re(G_{i,2,xz}^i(\omega, -\omega)) \cos(\cdot) + \Im(G_{i,2,xz}^i(\omega, -\omega)) \sin(\cdot)) \quad (3)$$

It can be proven, that in case of perturbing two inputs simultaneously always optimal phase differences can be found, which generate a beneficial effect compared to conventional steady-state operation [30]. Eq. 4 illustrates the structure of the relation available for the

identification of optimal phase differences $\varphi_{i,opt}$, which maximize the cross-term effect and, thus, the overall performance of the dynamically operated reaction system [25, 30, 34].

$$\varphi_{i,opt} = f\left(\Re\left(G_{i,2,xz}^i(\omega, -\omega)\right), \Im\left(G_{i,2,xz}^i(\omega, -\omega)\right)\right) \quad (4)$$

Details for the specific case considered in this work and corresponding analytical expressions will be presented below and further in the Appendix (eq. A11). More general details regarding the application of the NFR method for systems with two modulated inputs are given in [30]. The functions of interest for the investigated specific application will be discussed in section 5 and provided in the Appendix.

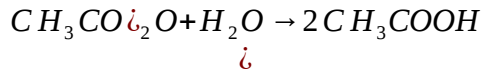
Before describing the experimental study carried out, the next section demonstrates the concept of forced periodic operation to validate the theory.

4) Reaction system

In this section, first the necessary kinetic and thermodynamic parameters of the applied reaction are presented (section 4.1). Then the used reactor model (section 4.2) and the functions for the input flows are given. Then the boundary conditions of the experimental study are derived (section 4.3).

4.1) Reaction: Kinetic model and thermodynamic parameters

The simple model reaction investigated is the liquid phase water hydrolysis of acetic anhydride to acetic acid (eq. 5), which provides a single product and does not change the number of moles.



(5)

The three components are abbreviated below as R (the main reactant anhydride, $M_R=102$ g/mol), W (water, $M_W=18$ g/mol) and P (the produced acid, $M_P=60$ g/mol).

In preliminary investigations, a larger number of continuous steady-state experiments was carried out in a lab-scale reactor and the following simplified n^{th} order power-law model was found capable to describe the kinetics of this reaction in a temperature range between 20 and 40 °C in case of an excess of water:

$$r(T, c_R) = k_0 \exp\left(\frac{-E_A}{RT}\right) c_R^n$$

(6)

Table 1 provides the values estimated for the three free parameters of eq. 6. This table contains also physical and thermodynamic data relevant to quantify the course of this reaction. Of specific relevance for the sake of this study is the miscibility limit of acetic anhydride (R) in water. Around ambient temperature this limit is reported to be 1.4 mol/L [29].

Table 1: Kinetic and thermodynamic parameters of the model reaction investigated (eq. 5).

Parameter	Symbol	Value and unit
Reaction order	n	0.66
Collision factor	k_0	904 L ^{0.34} / (s·mol ^{0.34})
Activation energy	E_A	34.06 kJ/mol
Heat of reaction	$\Delta_R H$	-55.5 kJ/mol
Miscibility limit for R in W (around $T_{ambient}$) [29]	$c_{R,max}$	1.4 mol/L
Product of “density · heat capacity” (Averaged value for W)	ρc_p	4.186 kJ/(K · L)
Density of R at $T_{ambient}$	ρ_R	1082 g/L

4.2) Reactor model: Adiabatic CSTR

The reaction represented by eq. 5 was studied in a continuously operated laboratory-scale stirred tank reactor (CSTR), which was assumed to work close to adiabatic behavior. The dynamic reactor model used to quantify the reaction process consisted of two well-known balance equations. Eq. 7 is the mass balance equation for reactant R and eq. 8 is the energy balance.

$$V \frac{dc_R}{dt} = F_{tot}(t)(c_R^i(t) - c_R) - Vr \quad (7)$$

$$V\rho c_P \frac{dT}{dt} = F_{tot}(t)\rho c_P(T^i(t) - T) + (-\Delta_R H)V \cdot r$$

(8)

The assumptions underlying these equations are an ideal and incompressible liquid phase, no difference between incoming and outgoing total volumetric liquid phase flow-rates, F_{tot} , constant mean values for the fluid phase density (ρ) and the fluid phase heat capacity (c_P). In the two balance equations, V designates the volume of the reaction mixture, T is the temperature and $\Delta_R H$ is the reaction enthalpy. Eq. 6 and the parameters provided in Table 1 are capable to capture the concentration and temperature dependence of the reaction rate r .

Several options of periodically modulating inputs can be implemented in the two balance equations 7 and 8. Exploitable inputs are e.g. the total volumetric flow-rate, $F_{tot}(t)$, the reactant inlet concentration, $c_R^i(t)$, and the inlet temperature, $T^i(t)$. In this paper, only the first two options will be investigated. The attractive impact of an inlet temperature modulation was recently evaluated theoretically [32, 33].

For the inlet reactant concentration and the total flow-rate the following harmonic perturbations are considered:

$$c_R^{\dot{}}(t) = x(t) = c_{R,S}^{\dot{}}(1 + A_C \cos(\omega t)) \quad (9)$$

$$F_{tot}^{\square}(t) = z(t) = F_{tot,S}^{\square}(1 + A_F \cos(\omega t + \varphi)) \quad (10)$$

In the above equations the subscript *s* designates the steady-states (mean) values of the two transient inlet parameters, A_C is the forcing amplitude of the inlet concentration modulation, A_F is the forcing amplitude of the total volumetric flow-rate modulation, ω is the forcing frequency and φ is a phase difference, which can be exploited in case of modulating simultaneously both inputs.

Altering independently the inlet anhydride concentration and the total flow-rate (eqs. 9 and 10) requires calculating the corresponding periodic changes of the individual inlet flow-rates of the two reactants (*R* and *W*), which are supplied in the experiments out of two feed tanks (see section 6). These component-specific inlet flow-rates can be determined from the following mass balance of component *R* (eq. 11) and a total liquid phase mass balance (eq. 12).

$$F_R(t) \frac{\rho_R}{M_R} \dot{=} F_{tot}(t) c_R^{\dot{}}(t) \quad (11)$$

$$F_W(t) + F_R(t) = F_{tot}(t) \quad (12)$$

Together with eqs. 9 and 10 these two equations provide the following explicit expressions characterizing the modulation regime:

$$F_R(t) = c_{R,s} F_{tot,S} \frac{M_R}{\rho_R} (1 + A_C \cos(\omega t))(1 + A_F \cos(\omega t + \varphi)) \quad (13)$$

(13)

$$F_W(t) = F_{tot}(t) - c_{R,s} F_{tot,S} \frac{M_R}{\rho_R} (1 + A_C \cos(\omega t))(1 + A_F \cos(\omega t + \varphi)) \dot{t} \quad (14)$$

For this kind of inlet modulations, the reactor never reaches a steady-state.

4.3) Constraints related to the experimental study

A preliminary theoretical study was carried out for the reaction system considered using the NFR method as a basis for designing the experiments. For this, in addition to the parameters given in Table 1, more parameters or parameter intervals had to be specified within experimentally accessible ranges.

The reactor volume was fixed in the calculations in accordance with the size of the laboratory scale CSTR (see Table 2). The inlet temperature was fixed at $T^n = 294$ K.

To implement the simultaneous forced periodic operation of both the total inlet flow-rate and the inlet concentration of reactant R , it was required to calculate the corresponding transient individual flows of both feed components (R and W) using eqs. 13 and 14. Accepting constraints related to the available laboratory pumps (see section 6), the mean values for the flow-rates given in Table 2 were chosen as a reference situation.

Furthermore, the mentioned miscibility gap between R and W ($c_{R,max}$, Table 1) is required in planning a periodic inlet concentration modulation of R to keep the maximum value below

the thermodynamic limit. Nevertheless, to allow significantly perturbing c_R^i in the periodic regime, i.e. to apply higher forcing amplitudes, A_C , a mean inlet concentration of $c_{R,S}^i = 0.74 \text{ mol/l}$ was chosen as the reference value.

It should be noted, that a simple analysis of mass and energy balances provides the conversion dependent steady-state temperature of an adiabatic CSTR as follows:

$$T = T^i + X_{R,S} * \Delta T_{ad} \quad (15)$$

This equation contains the well-known adiabatic temperature rise, for which holds:

$$\Delta T_{ad} = \frac{(-\Delta H_R) \cdot c_{P,S}^{max}}{\rho c_p} = \frac{(-\Delta H_R) \cdot 2 \cdot c_{R,S}^i}{\rho c_p} \quad (16)$$

The reference conditions reported above provide $\Delta T_{ad} = 19.6 \text{ K}$. The related upper bound of the temperature according to eq. 15 can be used to evaluate the degree of achieving adiabatic conditions in the reactor.

Solving jointly the two balance equations for the adiabatic CSTR (eqs. 7 and 8) with the parameters summarized in Table 2 allows determining the steady-state effluent concentration of R, $c_{R,S}$, and, thus, the steady-state conversion, $X_{R,S}$:

$$X_{R,S} = \frac{\dot{n}_{R,S}^i - \dot{n}_{R,S}}{\dot{n}_{R,S}^i} = \frac{C_{R,S}^i - C_{R,S}}{C_{R,S}^i}$$

(17)

The values of $C_{R,S} = 0.482$ mol/L and $X_{R,S} = 0.349$ are predicted for the reference parameters in steady-state. This corresponds in parallel according to eqs. 15 and 16 to a predicted steady-state temperature of $T_s = 27.8^\circ\text{C}$.

As a suitable alternative to conversion, $X_{R,S}$ (eq. 17), a reference steady-state product yield, $Y_{P,S}$, can be determined. This quantity evaluates the two molar fluxes of the effluent of product P and the inlet of reactant R and respects the corresponding stoichiometric coefficients of the components, ν_k , for $k=R$ and P :

$$Y_{P,S} = 100 \frac{(-\nu_R) \dot{n}_{P,S}}{\nu_P \dot{n}_{R,S}^i} = 100 \cdot \frac{1}{2} \frac{\dot{n}_{P,S}}{\dot{n}_{R,S}^i} = 100 \cdot 0.5 \frac{C_{P,S}}{C_{R,S}^i} \quad (18)$$

For the simple single reaction considered in this investigation (eq. 5) the reference yield agrees with the above-given reference conversion $Y_{P,S} = 34.9$.

It should be finally mentioned, that in conventional steady-state operation performance can be increased e.g. by decreasing the flow-rates (i.e. by offering more residence time) or by

increasing the inlet concentration of R (within the miscibility limit). It is necessary to note again, that the reference situation corresponding to the parameters in Table 2 does not represent a fully optimized steady-state operation. Using slightly different preliminary kinetic parameters first optimization results were described in [30-32]. However, in these calculations an existing miscibility constraint was not respected and the usage of unrealistically high reactant feed concentrations was suggested.

Table 2: Reference parameters of eqs. 7 and 8 in accordance with the constraints and restrictions originating from the reaction system and possibilities for the experimental study.

Parameter	Symbol	Value and unit
Reaction volume	V	0.298 L
Inlet temperature	T^n	294 K
Mean (steady-state) total inlet flow-rate	$\overline{F_{tot}}(t) \dot{=} F_{tot,S}$	0.043 L/min
Mean (steady-state) inlet flow-rate of W	$\overline{F_W}(t) \dot{=} F_{W,S}$	0.040 L/min
Mean (steady-state) inlet flow-rate of R	$\overline{F_R}(t) \dot{=} F_{R,S}$	$3 \cdot 10^{-3}$ L/min
Mean (steady-state) inlet concentration of R	$\overline{c_R}(t) = c_{R,S}$	0.74 mol/L

5) Preliminary analysis of periodic operation: NFR method

After providing the kinetic model and the reactor model as well as suitable realistic parameters, the NFR method can be used to evaluate the possible improvements for forced periodic operation for different scenarios and to suggest promising forcing regimes. To apply the NFR method still a specific objective of the reaction process under consideration needs

to be fixed. In this work, the mean product yield as the objective function of interest is considered. Compared to the corresponding steady-state value defined in eq. 18, periodic operation requires calculating the time-average. Thus, instead of eq. 18 the following equation is now required for performance evaluation:

$$Y_P'(t) = 100 \frac{(-v_R) \dot{n}_P(t)}{v_P \dot{n}_R(t)} = 100 \frac{(-v_R) F_{tot}(t) c_P(t)}{v_P F_{tot}(t) c_R(t)} \approx 100 \frac{(-v_R) \dot{n}_{P,DC}}{v_P \dot{n}_R(t)} \quad (19)$$

Besides providing the known projected temporal input profiles, the determination of the performance criterion requires specifying the time dependence of the outlet product concentration, $c_P(t)$, which provides in combination with the known function $F_{tot}(t)$ the mean molar product flux $\dot{n}_P(t)$ and, thus, $Y_P'(t)$.

To compare between steady-state and periodic operation an absolute yield difference is defined:

$$\Delta Y_P = Y_P'(t) - Y_{P,S} \quad (20)$$

and a normalized criterion will be evaluated below:

$$Y_P^{norm} = \frac{Y_P'(t)}{Y_{P,S}}$$

(21)

A theoretical prediction of these performance criteria, which enter into the NFR method via respecting $y_i(t) \equiv \dot{n}_p(t) = F_{tot}(t) c_p(t)$, needs the derivation of the corresponding asymmetric second-order frequency response functions introduced above. These functions were already derived in [31, 35, 36] for the more general case of a non-isothermal CSTR. The FRFs for the adiabatic reactor considered here can be obtained directly from the available functions for this more general non-isothermal case by setting to zero the overall coefficient for the heat transfer through the reactor wall [37], which is designated in [36] as U . The final functions required for evaluating the molar outlet flux of the product, $\dot{n}_p(t)$, are summarized in the Appendix [36]. With these functions, the DC component can be calculated for the two types of single input modulations and also for the more general case of simultaneous modulation of the two inputs (eq. 3). The following equation illustrates the determination for the latter case based on imposing jointly phase-shifted periodic modulations of the feed concentration ("C") and the total flow-rate ("F"):

$$\dot{n}_{p,DC} \approx 2 \left(\frac{A_C}{2} \right)^2 G_{\dot{n}_p,2,CC}(\omega, -\omega) + 2 \left(\frac{A_F}{2} \right)^2 G_{\dot{n}_p,2,FF}(\omega, -\omega) + 2 \left(\frac{A_C}{2} \right) \left(\frac{A_F}{2} \right) G_{\dot{n}_p,2,CF}(\omega, \omega) \quad (22)$$

The following equation can be efficiently applied to evaluate and optimize the absolute or normalized mean product yields in case of applying periodic operation in comparison to the corresponding steady-state situation (eq. 18):

$$\dot{Y}_P = \frac{Y_{P,s}(1+\dot{n}_{P,DC})}{\left(1+2\left(\frac{A_C}{2}\right)\left(\frac{A_F}{2}\right)\cos(\cdot)\right)}$$

(23)

Figure 3 summarizes the results of three sets of calculations using the NFR method to predict normalized product yields, Y_P^{norm} (eq. 21), namely for applying the two types of single input modulations individually and for the simultaneous modulation of both inputs. In the latter case always the specifically optimized frequency-dependent phase difference, ϕ_{opt} , was applied. During the calculations reported here the amplitudes for the input reactant concentration and the total volume flow were fixed to accessible values ($A_C = 85\%$, $A_F = 55\%$). These rather high amplitudes guarantee to achieve significant effects due to forcing. The two specific values were chosen to agree with preliminary calculations published in [36]. To have a more direct link to the following experimental study the predicted normalized yields are presented in Figure 3 as a function of the period of the modulation P , which is related to the inverse of the frequency ω as follows:

$$P = \frac{1}{\omega}$$

(24)

In the case of applying the two types of single input modulations individually, the periodic regime corresponds for short periods (high frequencies) to the steady-state regime. For periods P longer than 10 minutes the periodic operation performs worse than the steady-state operation. In the case of exclusively applying total flow-rate modulation, this trend levels off at a constant value corresponding to a significant detrimental effect. The modulation of the input concentration has a negative effect, which is most pronounced in a period range around 40 minutes. In both cases, for larger periods the performance comes closer to the steady-state result without being able to reach it.

Alternatively, an opposite attractive behavior is illustrated in Figure 3 for the case of simultaneously modulating both input parameters in conjunction with always applying the optimal frequency-dependent phase shift (according to eqs. 4 and A11). In this case, the performance of periodic operation is expected to be in the entire period range above the corresponding steady-state values. There are two constant performance regions: a) for periods below 4 minutes with a moderate value of $Y_P^{norm} = 1.05$, and b) for longer periods (above 400 minutes) with a rather high increase ($Y_P^{norm} = 1.26$). In the period range between 10 and 100 minutes, the performance of periodic operation changes rather strongly. This range is well suited for laboratory investigations of liquid-phase reactions. To fix a promising and easy to apply reference period for the experimental study the following aspects were considered. A longer period is for the reaction system considered beneficial to increase the potential of dynamic operation. However, performing experiments with longer periods is time-consuming and causes conflicts with constraints imposed by the lengths of standard working days.

Thus, based on the results of the preliminary theoretical analysis performed together with the mentioned rational considerations, for perturbing simultaneously the total input flow-rate and

the reactant concentration around the mean values given in Table 2 using the two mentioned amplitudes, a reference period P of 40 min was selected. This period corresponds to a frequency of $\omega = 4.167 \cdot 10^{-4}$ Hz. Related to this reference period, an optimal theoretical reference phase shift for modulating both inputs simultaneously could be calculated based on eqs. 4 and A11. The obtained optimal reference phase shift is $\varphi_{opt} = 157^\circ$. The predicted improvement of periodic operation in terms of the normalized product yield (eq. 21) is for the reference condition $Y_P^{norm} = 1.17$. This corresponds according to eq. 20 to an absolute increase of 5.98 %.

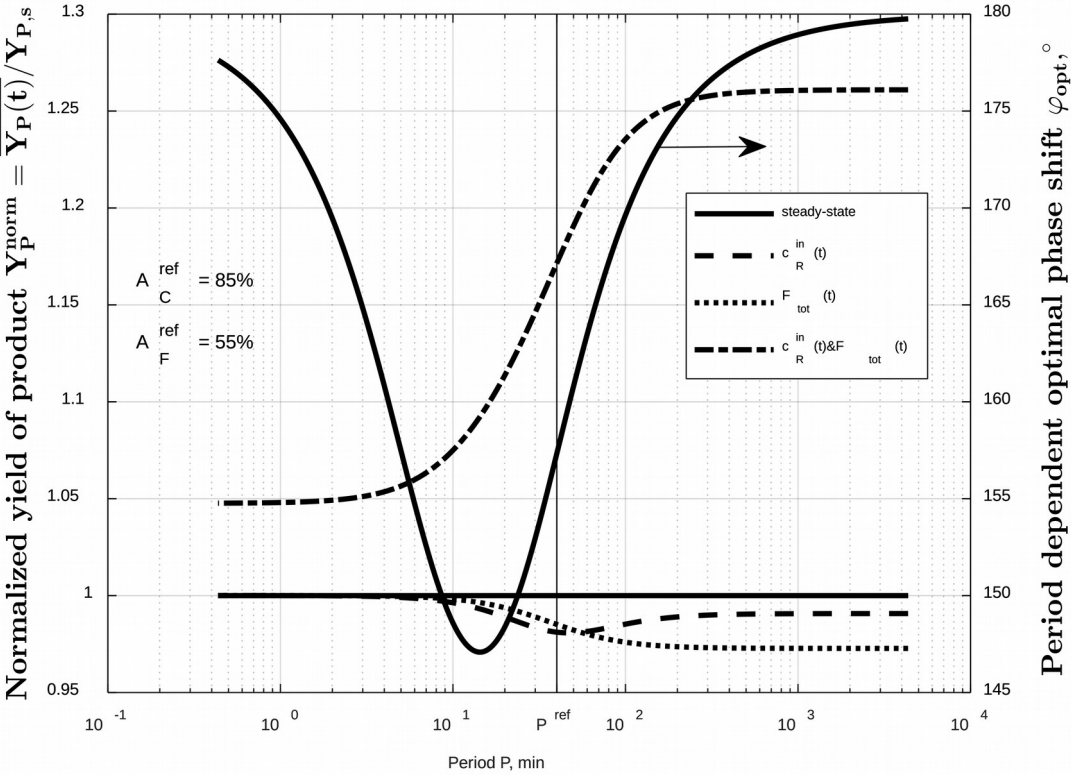


Figure 3: Predictions of the normalized yield of the desired product ($Y_P^{norm} \equiv y(t)$, eq. 21 and

Fig. 1) for single and simultaneous modulation of inlet reactant concentration ($c_R^i \equiv x(t)$) and

total flow ($F_{tot} \equiv z(t)$) as a function of the period P (eq. 24) based on the parameters in Table 1 and 2 in comparison to steady-state operation. The plot is complemented by providing the optimal phase shift for the case of simultaneous modulation (eqs. 4 and A11) and by indicating the selected reference forcing parameters.

At this point, it should be noted that it was not the intention of this project to achieve an overall optimum. Compared to the selected reference situation, conversion in the CSTR could be further improved by simply providing more residence time. However, this would cause a decrease in other performance parameters, as for example the space-time-yield. Regarding the also not fully optimized reactant inlet concentration a further increase is limited by the mentioned miscibility limit.

6) Experimental setup for implementing dynamic operation

For the experimental investigations, a set-up was constructed capable to follow and record continuously the reactor temperature and the product concentration. A schematic representation is given in Fig. 4. To measure the product concentrations a conductivity meter could be used. The set-up was capable of implementing and observing modulations of single parameters and simultaneous modulations of several parameters (including temperature modulations, which were not imposed in this work).

The components of the equipment were a multi-channel peristaltic pump for the water inlet stream (P_1 , *Heidolph Hei-Flow Precision, Germany*), a gear pump for acetic anhydride (P_2 , *ISMATEC BVP-Z, Germany*), two thermostats controlling the inlet temperature (*Huber CC-308 and CC-K12, Germany*), an arbitrary function generator (*Rigol DG-1032z, China*), a custom-made double-jacketed glass vessel (*Witeg Labortechnik, Germany*) and a magnetic stirrer plate (*IKA RCT Basic, Germany*). The jacket of the reactor was not tempered, but only

kept open to the ambient air. Test measurements revealed for low temperature intervals a relatively good adiabatic behavior. The measurements of the product concentration were performed using a calibrated device to record the transient of the conductivity $\kappa(t)$ (*Ahlborn Almemo 2490-1, Germany*). Using a hydrostatic overflow, the volume of the reaction mixture could be kept constant to the value given in Table 2.

Imposing the periodic process regime was automated using *Siemens Simatec S7[®]* and *MATLAB[®]*. For initiation and data collection from the individual units, Siemens control software was used. MATLAB generated the functions for the individual input modulations. The function generator has two separate voltage outlets that can be controlled individually and allow for a reliable and precise setting of the forcing parameters, i.e. the frequencies, amplitudes and phase differences. To check visually the implemented functions, additionally, an oscilloscope was used.

In a start-up phase, before activating a periodic regime, the CSTR was brought into a steady-state operation keeping the input values constant sufficiently long at their mean values. For this, the calibrated pumps were set to constant voltages corresponding to the desired steady-state values of the flow-rate. For the conditions investigated, steady-state operation was reached typically after approximately 90 minutes. Then dynamic voltage changes corresponding to the desired feed flow-rates were activated (eqs. 13 and 14) and the desired periodically changing two reactant inlet flows were pumped for the duration of the experiment (several periods) into the reactor.

During each experiment, the conductivity in the reactor was recorded over time and converted into the transients of the product concentration, $c_P(t)$. Using a standard thermocouple (*Type K Horst, Germany*) the reactor temperature, $T(t)$, could be recorded. To

check the correctness of operation, also the voltages transmitted to the two pumps were recorded.

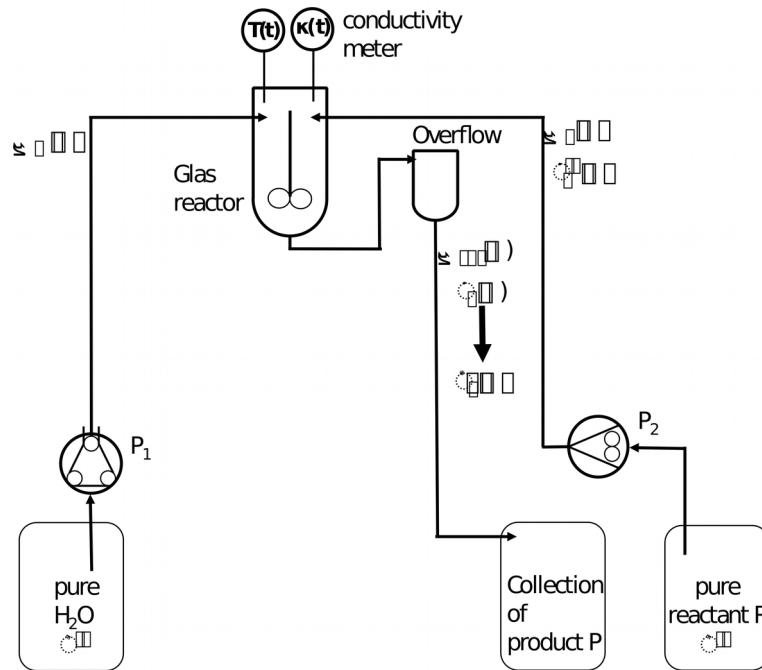


Figure 4: Illustration of experimental set-up capable to implement forced periodic operation of simultaneously modulating reactant concentrations (c_{in} eq. 9) and flow-rates ($F_{tot}(t)$ eq. 10) imposing phase shifts.

7) Experimental results

7.1 Illustration of steady-state behavior and process dynamics

a) Start-up phase until reaching a steady-state

At first, the approach of the reaction system to steady-state operation was studied. The approach to the steady-state applying the reference parameters is shown in Figure 5. From the results the following conclusions can be drawn:

I) The time required to reach steady-state behavior is approximately 90 minutes.

II) The finally reached steady-state molar product flux of $\dot{n}_{P,S}^{\text{exp}} \approx 0.02$ mol/min shown in

Figure 5 corresponds to a product concentration of $c_{P,S}^{\text{exp}} \approx 0.47$ mol/L. A conversion and a

product yield (eqs. 17 and 18) of $X_{R,S}^{\text{exp}} \approx 0.32$ and $Y_{P,S}^{\text{exp}} \approx 32$. These values are relatively

close to the predicted values $c_{P,S} = 0.516$ mol/L, $X_{R,S} = 0.349$ and $Y_{P,S} = 34.9$.

III) The observed steady-state temperature is approximately $T_s = 27^\circ\text{C}$, which is just slightly below the expected value for completely adiabatic behavior (27.8°C , see below result using eq. 17). Thus, the unavoidable heat losses are not very significant in the laboratory reactor used and the simple adiabatic reactor model is quite accurate. The lower experimentally observed temperature compared to the prediction agrees with the observed lower steady-state conversion and yield.

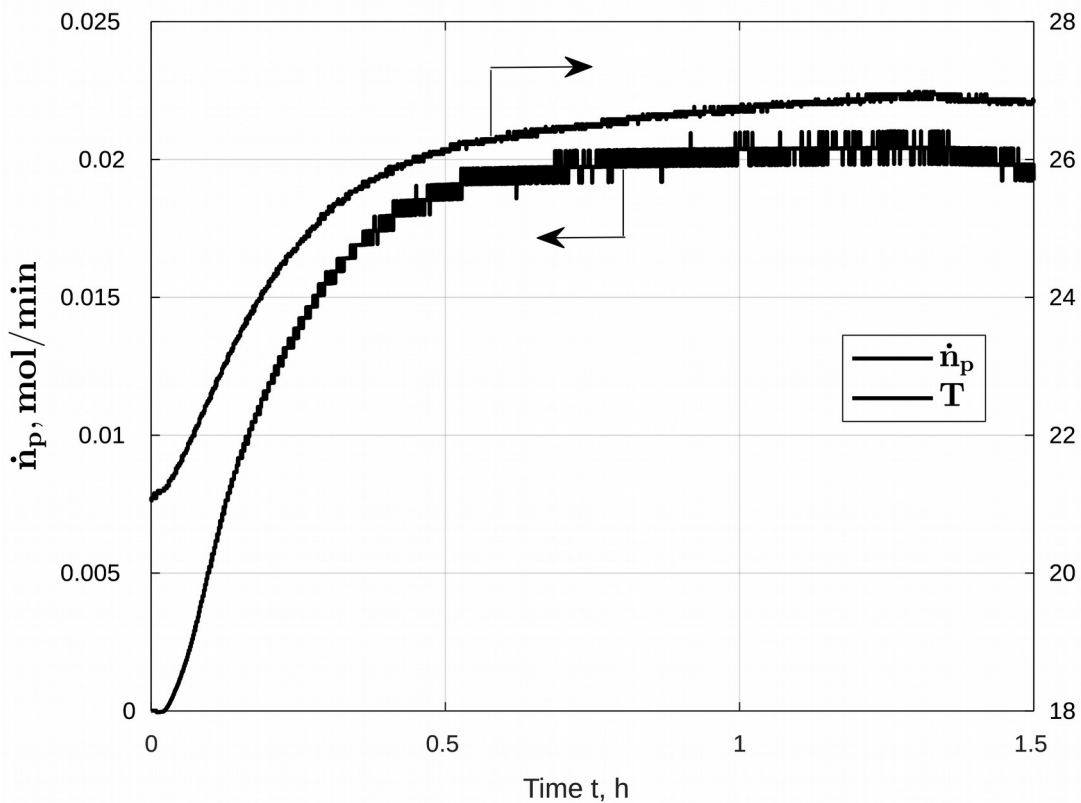


Figure 5: Molar flow-rate of the product P (acetic acid, left axis) and reactor temperature (right axis) during start-up under steady inlet parameters approaching steady-state (reference conditions according to Table 2).

b) Forced periodic operation

In the dynamic experiments, the inlet parameters were modulated as described above always after reaching a steady-state corresponding to the mean inlet values. After starting the regime of using periodic inlet perturbations, the system needed one to two periods to reach a cyclic steady-state.

Figure 6 illustrates first the implemented courses of the modulated inlet parameters for the run belonging to the reference situation.

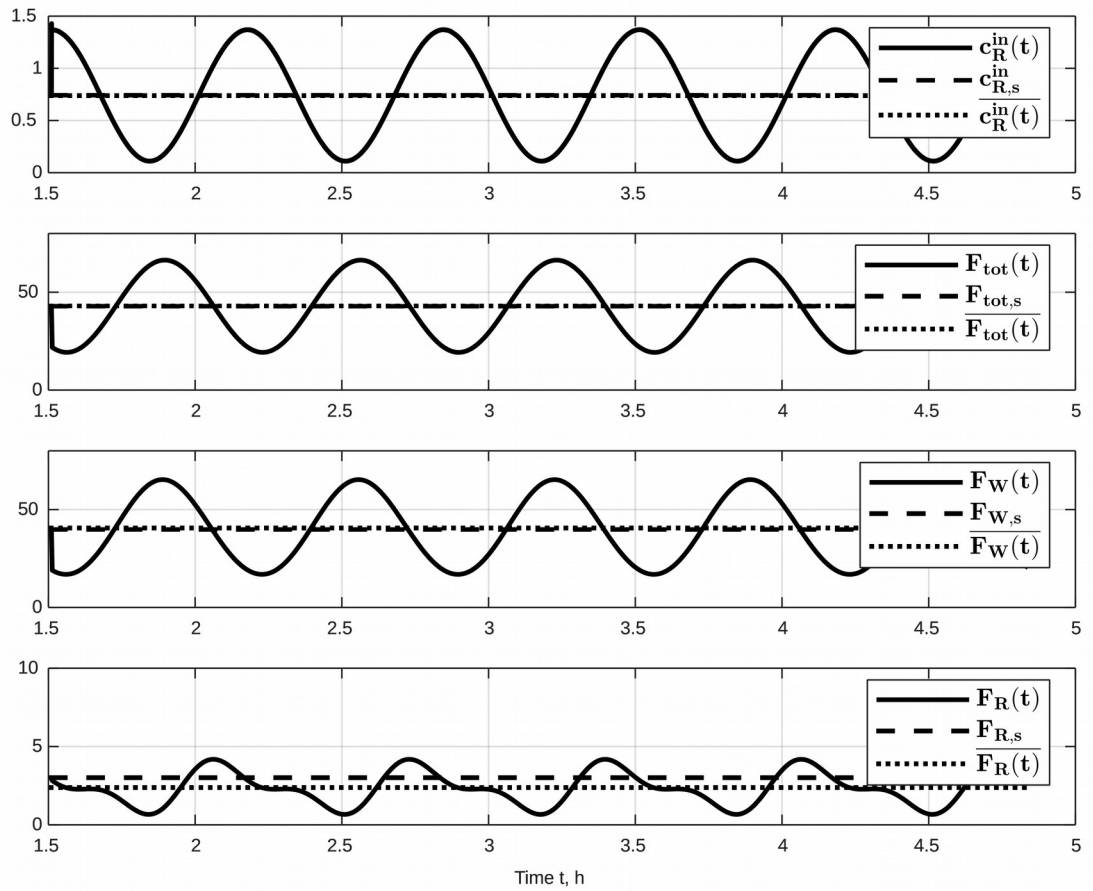


Figure 6: Inputs for forced periodic for simultaneously modulating (a) the inlet concentration of the reactant acetic anhydride (R), (b) the total volumetric flow-rate, (c) the volumetric flow-rate of water (W) and (d) the volumetric flow-rate of R around a previously established steady-state belonging to the reference parameters (Table 2). The forcing parameters are: frequency $\omega=4.167 \cdot 10^{-4}$ Hz (or period: 40 min), amplitude of inlet reactant concentration $A_c=85\%$, (between 0,11 mol/l and 1,37 mol/l) with a mean value of 0,74 mol/L), amplitude of total volumetric flow-rate $A_f=55\%$ (between 19.35 and 66.65 ml/min with a mean of 43 ml/min), predicted optimal phase shift $\varphi=157^\circ$ (eq. A11).

The imposed phase shift between the two modulated input parameters can be recognized in the first two rows of Figure 6 by the different positions of the maxima and minima.

The essential measured output information is the transient of the product concentration

$c_P(t)$. The course for the reference conditions corresponding to the inputs shown in

Figure 6 is given in Figure 7 together with the resulting calculated molar product fluxes,

$$\dot{n}_P(t)$$

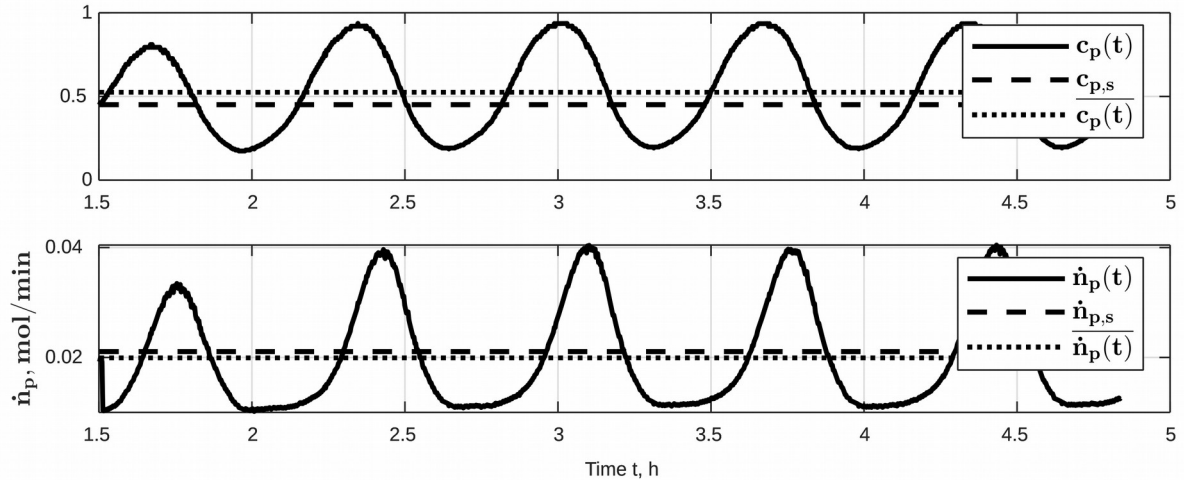


Figure 7: Measured transients of the outlet product concentration and the outlet molar product flux corresponding to the inlet modulations shown in Fig. 6. Mean values both for steady-state and forced periodic operation are shown as lines.

For the evaluation of time-averages of the periodic operation shown in Figure 7 only a few of the final periods (after reaching the cyclic steady-state) were used. In the bottom part of Figure 7 it can be seen, that the mean molar product flux belonging to the periodic operation,

$$\dot{n}_P(t)$$

, is lower than the mean value of the corresponding steady-state operation, $\dot{n}_{P,S}$. To determine the finally relevant product yields (based on eq. 19) the phase-shift between concentrations and flow-rate needs to be respected. If this is done, an improvement in the

normalized product yield of periodic operation (eq. 21) of $\Delta Y_P^{exp} = 4.1\%$ is achieved for

the reference situation. This corresponds to a $Y_P^{norm,exp}$ of 1.11. This improvement is slightly lower than predicted by the NFR method, $\Delta Y_P^{NFR} = 5.98\%$ and $Y_P^{norm,NFR} = 1.17$ (see also Fig. 3 and Fig. 9 below). The reduced experimentally observed yield gain agrees with the fact, that the reactor appears to be not fully adiabatic, which causes a loss of mean conversion. This interpretation is supported also by an inspection of the measured transients of the reactor temperature shown in Figure 8. It can be seen, that the observed mean temperature value of periodic operation is slightly below the predicted one.

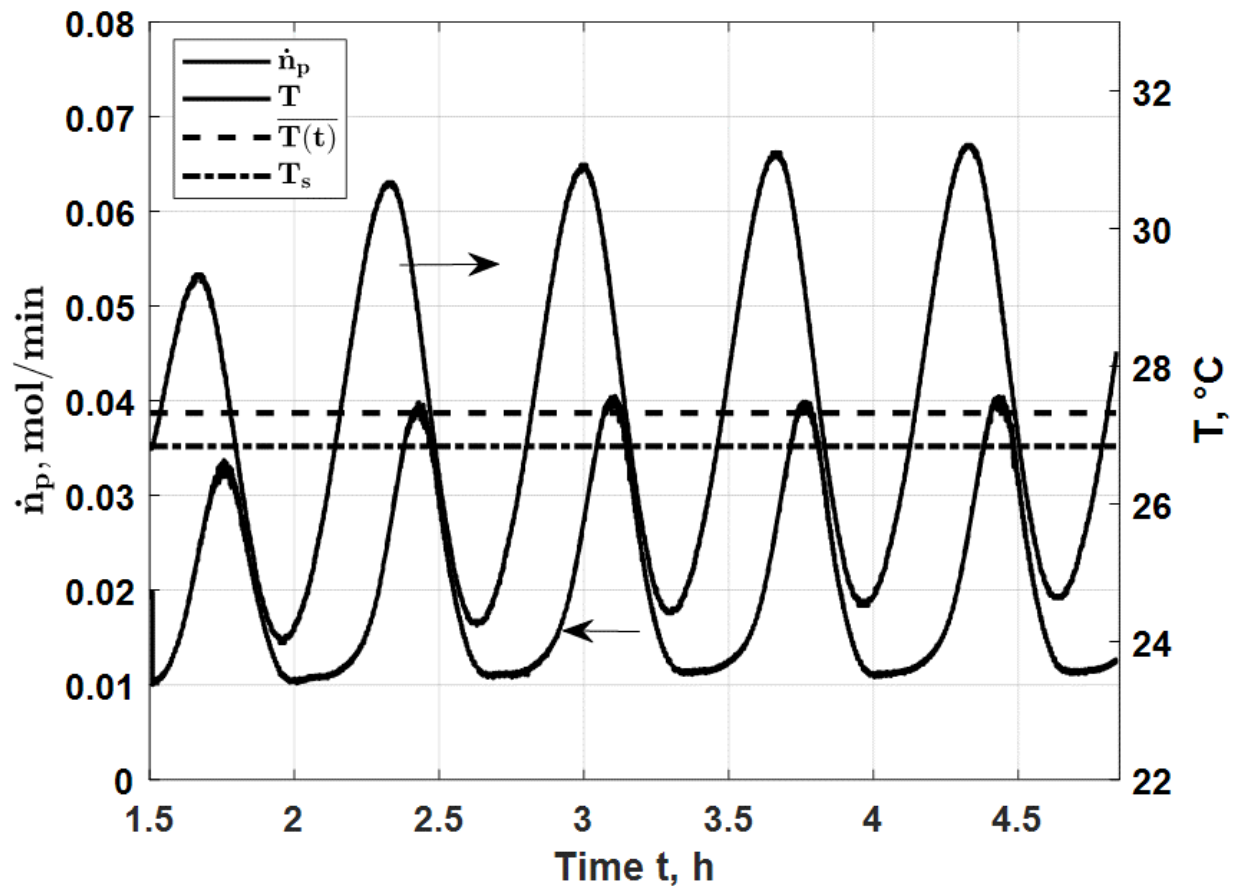


Figure 8: Transient molar flow-rate of the product (left) and transient reactor temperature (right) belonging to the experiment shown in Figs. 6 and 7. The lines indicate the mean of the observed steady-state temperature (dashed-dotted line, see also Fig. 5) and the predicted mean temperature (dashed line).

Summarizing the results related to the reference condition it can be stated, that implementation of simultaneously modulating the two inputs considered in a phase-shifted regime was possible. The predicted improvement of periodic operation could be confirmed. For the reference condition considered an absolute improvement in yield of 4.1 % (eq. 20) was achieved. The gain was found to be close to the predictions of the NFR method (5.98%).

In the next two sections further experimental results are reported, which were performed to study the effect of altering the phase shift and the two forcing amplitudes.

7.2 Influence of the phase shift

The results of studying the influence of exclusively the phase shift in case of simultaneously modulating the two inputs are presented in Figure 9.

If the two inputs are modulated with the same phase (φ_0) the highest reaction rate (due to the highest reactant concentration) acts jointly with the highest flow-rate. Since the latter corresponds to the lowest residence time there is not enough time to exploit the potential of the high rate. This results in low yields. Due to this rationale and according to the theory outlined above, an improvement can be expected with an increasing phase shift. As mentioned already above the optimal theoretical value is found for the system under consideration for an almost complete shift of the extrema of the two input parameters ($\varphi_{optimal} = 157^\circ$, eqs. 4 and A11). In this case, a high reactant concentration is associated with a lower flow-rate and vice versa. Thus, if the reactant inlet concentration is on its way to be reduced the flow-rate will start to be increased, which will trigger faster product removal. This constellation can generate higher mean yields and offers the potential to outperform the

corresponding steady-state operation. An increase of the phase shift beyond the optimum value analogously results in a performance reduction.

The results of the experimental study depicted in Figure 9 together with the NFR method predictions confirm the general trend and very well the position of the optimal phase shift. Evaluating the situation for the optimal phase shift, already in the previous section an overestimation of the periodic performance was reported and arguments for the reason were given. Figure 9 shows that this trend is valid for all phase shifts investigated experimentally.

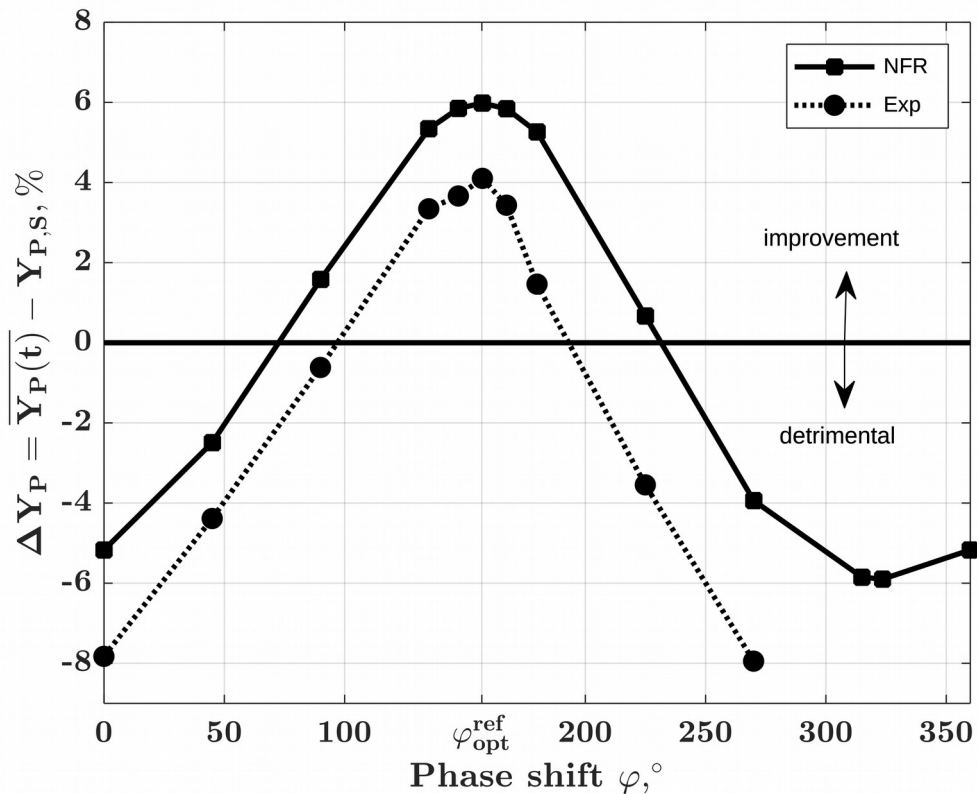


Figure 9: Absolute difference ΔY_P of time-average periodic yield and the corresponding steady-state yield (Eq. 20) for varying the phase shift φ during the exploitation of simultaneously modulating the inlet reactant

concentration (with $A_C^{ref} = 85\%$) and the total volumetric flow (with $A_F^{ref} = 55\%$) for a fixed period of

$P_{\square}^{ref} = 40$ min). Predictions of the NFR method: rectangles. Experimental values: circles.

Additionally, the predicted trend of resulting absolute change in yield illustrates that, according to the second solution of the quadratic equation (eq. A11) for the optimal phase shift, a second value exists which maximizes the detrimental behavior. This point is achieved when the phase shift is further increased to 324° . After increasing the phase shift beyond this minimum, the mean performance is again increasing. For 360° the same change occurs as for 0° .

7.3 Influences of the forcing amplitudes

Figures 10 and 11 present the results of experiments regarding the yield difference between periodic operation modulating the two inputs and the corresponding steady-state operation. Hereby, varying the amplitudes of one of the inputs, while keeping the other amplitude constant at the introduced reference values. In all experiments the specifically predicted optimum phase shift was used. Each experimental series was conducted separately, with the reference case being remeasured each time, which results in deviations in the resulting output changes.

According to the theory, the variation of just a single input variable has a detrimental influence on the desired target for a reaction order between zero and one ([14], Figure 3). This effect is seen in Figure 10 for a vanishing inlet concentration amplitude of 0%. Increasing the amplitudes causes always an enhanced performance of periodic operation. For this system holds: as the amplitude of the input concentration increases, the improvement increases almost linearly. However, case dependent implementable limits should be exploited. Best results are achieved when the optimal phase difference is imposed. It is noteworthy, that the specific optimal phase shift φ varies for changing both amplitudes only slightly in the narrow range between 152° and 162° (Figures 10 and 11).

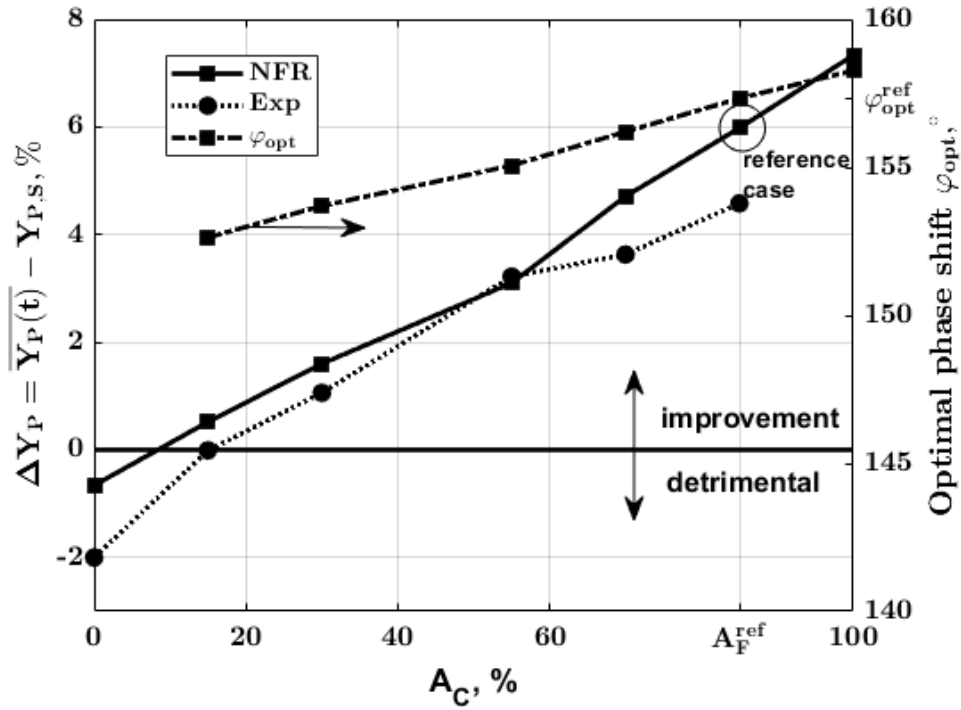


Figure 10: Absolute difference ΔY of time-average periodic yield (eq. 20) and steady-state yield for different amplitudes of the inlet concentration (A_C) with simultaneous modulation of the total volumetric flow-rate (constant amplitude, $A_F^{ref} = 55\%$) and specifically adjusted optimal phase difference φ_{opt} (eqs. 4 and A8): Predictions of the NFR method: rectangles. Experiments: circles. The theoretical reference case for a concentration amplitude of 85% with a corresponding optimal phase shift is marked with an open circle.

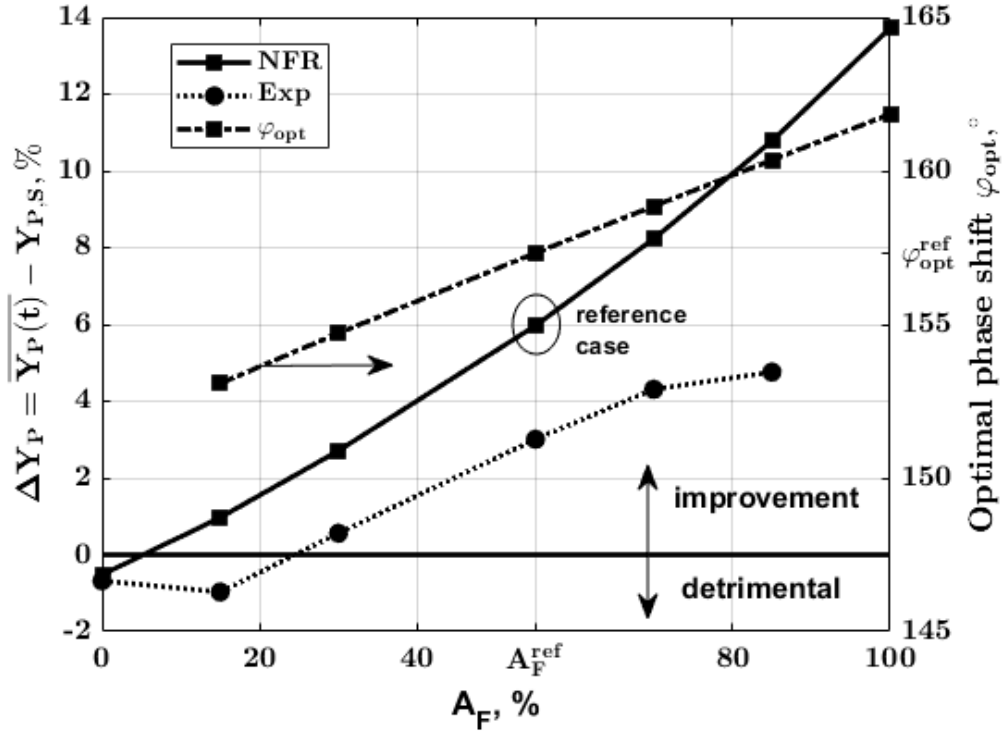


Figure 11: Absolute difference ΔY of time-average periodic yield (eq.20) and steady-state yield for different amplitudes of the total flow-rate (A_F) with simultaneous modulation of the inlet concentration (constant amplitude,

$A_C^{ref} = 85\%$) and specifically adjusted optimal phase difference φ_{opt} (eqs. 4 and A8). Predictions of the NFR method: rectangles. Experiments: circle. The theoretical reference case for a total flow amplitude of 55% with a corresponding optimal phase shift is marked with an open circle.

In Figure 10, for the case of varying the amplitude of the reactant inlet concentration, the absolute yield difference obtained experimentally agree well with the predictions. For the whole amplitude range, in which a detrimental performance of periodic operation is predicted, the experimental results are in rather good agreement with the theory. A similar trend holds for the case of a variation of the amplitude of the total flow-rate (Figure 11). In the interesting range of higher flow-rate amplitudes, the slope of the gain is higher than the slope for the concentration amplitudes shown in Figure 10. Not experimentally validated extrapolations to

amplitudes of 100% suggest that theoretically up to $\Delta Y_P = 13.7\%$ improvement can be achieved using the maximum flow-rate modulation combined with $A_C^{ref} = 85\%$. In comparison to a possible improvement of $\Delta Y_P = 7.3\%$ at a maximum inlet concentration amplitude in combination with an $A_F^{ref} = 55\%$.

As discussed, the predicted improvement of the forced periodic operation is slightly higher, by about 2%, than the observed experimental results. For increasing the flow-rate amplitudes, the course of the experimental results starts deviating more significantly from the predictions. This is due to the fact that for higher amplitudes the pumps applied did not work precisely in the range of the very small flow-rates required temporarily.

Altogether, the results discussed in sections 7.2 and 7.3 confirm the strong predictive potential of the NFR method.

8) Conclusions and outlook

The Nonlinear Frequency Response (NFR) method was applied for evaluation of possible improvements for a forced periodically operated adiabatic continuously stirred tank reactor (CSTR), in which the hydrolysis of acetic anhydride takes place. The method predicted an enhanced performance for the simultaneous modulation of inlet concentration and total flow-rate when an optimal phase difference is applied [37]. The focus of the present work was the experimental validation of these predictions.

Based on preliminary calculations using the NFR method a promising reference condition could be identified, which formed the starting point for the experimental study. As predicted,

the corresponding experiment applying periodic operation with the calculated optimal phase shift provided an improved mean product yield compared to the corresponding steady-state operation (ΔY_p). The gain was only slightly lower than expected, which was found mainly due to the insufficient fulfillment of adiabatic conditions assumed in the prediction and to shortcomings of the simple model for the description of the reaction kinetics.

Further experiments devoted to studying the sensitivity of the reactor performance with respect to the phase shift and the forcing amplitudes confirmed the strength of the NFR method for efficiently predicting main trends connected with forced periodic reactor operation. Here, the predicted maximum and the trend of the absolute change in yield were well represented by the performed experiments. Thus, the method can be recommended as a strong tool ready to be applied for the analysis of other reaction systems. In particular, the derived estimation of an optimal phase shift is seen as a powerful support for process design. This avoids tedious experimental studies. Further investigations are currently devoted to apply and extend the concept and method, e.g. to incorporate non-harmonic perturbations as square waves [38], to analyze kinetically more challenging heterogeneously catalyzed reactions [39, 40], to consider tubular reactors and to apply the NFR method in conjunction with experimental data to estimate or re-estimate model parameters (as e.g. the heat transfer coefficient of the reactor, U , or the reaction order, n).

Main result of this paper is the successful experimental demonstration of a simultaneous modulation of two phase-shifted inputs and the validation of performance improvements predicted by the Nonlinear Frequency Response (NFR) method.

Authors contributions

This manuscript was written based on the contributions of all authors. All authors have approved the final version of the manuscript.

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Appendix: Relevant functions provided by the NFR method corresponding to the adiabatic CSTR model, the assumed reaction rate model and the evaluated outlet function

The above introduced three asymmetrical second-order FRFs are needed to determine with eq. 22 the DC component of the molar outlet flow of the product P , $\dot{n}_{P,DC} = \dot{n}_P'(t)$, which is then required to quantify the performance of forced periodic operation using for example eqs. 19-21.

Since it is efficient to derive the FRF based on a non-dimensional balance equation [35, 36],

it is convenient to use instead of ω a dimensionless frequency $\tilde{\omega}$ defined as:

$$\tilde{\omega} = \omega \frac{V}{F_{tot}} \quad (A1)$$

The following three functions are valid for the type of modulation investigated in the conjunction with the process goal specified ([35] with $U = 0$):

- a) The asymmetrical second-order FRF for modulation of the inlet reactant concentration,

$$c_R^i(t) :$$

$$G_{\dot{n}_p,2,CC}(\tilde{\omega}, -\tilde{\omega}) = \frac{(1+\alpha)^2}{2B_{P,S}} \cdot \frac{(n(n-1)\tilde{\omega}^2 + n^2(1-2\beta^2\gamma) - n(1+\beta\gamma)^2)}{(\tilde{\omega}^2+1)(\tilde{\omega}^2+B_{P,S}^2)}$$

(A2)

b) The asymmetrical second-order FRF for modulation of the total inlet flow-rate, $F_{tot}^\square(t)$:

$$G_{\dot{n}_p,2,FF}(\tilde{\omega}, -\tilde{\omega}) = \frac{1}{2B_{P,S}} \cdot \frac{(-n^2\alpha^2 - n\alpha(\alpha+2(1+\beta\gamma)) - 2\beta\gamma(1+\beta\gamma) - 2\beta^2\gamma)}{(\tilde{\omega}^2+B_{P,S}^2)}$$

(A3)

c) The asymmetrical second order FRF defining the cross-effect for simultaneous modulation of inlet reactant concentration and total flow-rate:

$$G_{\dot{n}_p,2,CF}^i(\tilde{\omega}, -\tilde{\omega}) = \Re(G_{\dot{n}_p,2,CF}^i(\tilde{\omega}, -\tilde{\omega})) \cos(\varphi) + j \cdot \Im(G_{\dot{n}_p,2,CF}^i(\tilde{\omega}, -\tilde{\omega})) \sin(\varphi) \quad (\text{A4})$$

with

$$\Re(G_{\dot{n}_p,2,CF}^i(\tilde{\omega}, -\tilde{\omega})) = \frac{(1+\alpha)}{B_{P,S}} \cdot \frac{(n((\tilde{\omega}^2+1)(\tilde{\omega}^2+B_{P,S}^2) - (\alpha+1)) - \beta\gamma(\alpha-2\beta))}{(\tilde{\omega}^2+1)(\tilde{\omega}^2+B_{P,S}^2)}$$

(A5)

$$\Im(G_{\dot{n}_p,2,CF}^i(\tilde{\omega}, -\tilde{\omega})) = \frac{(1+\alpha)}{B_{P,S}} \cdot \frac{(j\tilde{\omega}n(\tilde{\omega}^2+1+\beta\gamma(\alpha-2\beta)))}{(\tilde{\omega}^2+1)(\tilde{\omega}^2+B_{P,S}^2)}$$

(A6)

The above applied new four dimensionless parameters α, β, γ and $B_{P,S}^{\square}$ are defined based on the steady-state values of the reactant concentration, $c_{R,S}$, and the temperature, T_S , as follows:

$$\alpha = k_0 \exp\left(\frac{-E_A}{RT_S}\right) c_{R,S}^{n-1} \frac{V}{F_{tot}}$$

(A7)

$$\beta = \frac{\Delta H_R k_0 \exp\left(\frac{-E_A}{RT_S}\right) c_{R,S}^n \frac{V}{F_{tot}}}{\rho c_p T_S}$$

(A8)

$$\gamma = \frac{E_A}{RT_S} \tag{A9}$$

$$B_{P,S} = 1 + n\alpha + \beta\gamma \tag{A10}$$

It should be mentioned, that α corresponds to a characteristic Damköhler number and $B_{P,S}$ is a classical stability parameter, which must be positive to assure a stable steady-state, which is a requirement for the application of the NFR method.

From the real and imaginary parts of $G_{n_p,2,CF}^i$ (eqs. 15 and 16) two phase shifts corresponding to performance extrema can be calculated from the two solutions of the quadratic equation [33] as follows:

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

(A11)

with

$$a = 1 + 2\left(\frac{A_C}{2}\right)^2 G_{\dot{n}_p, 2, CC}(\tilde{\omega}, -\tilde{\omega}) + 2\left(\frac{A_F}{2}\right)^2 G_{\dot{n}_p, 2, FF}(\tilde{\omega}, -\tilde{\omega}) - \Re(G_{\dot{n}_p, 2, CF}(\tilde{\omega}, -\tilde{\omega})) \quad (\text{A12})$$

$$b = \Im(G_{\dot{n}_p, 2, CF}(\tilde{\omega}, -\tilde{\omega})) \quad (\text{A13})$$

$$c = -2\left(\frac{A_C}{2}\right)\left(\frac{A_F}{2}\right) \Im(G_{\dot{n}_p, 2, CF}(\tilde{\omega}, -\tilde{\omega}))$$

(A14)

The values corresponding to the reference situation using the parameters given in Tables 1

and 2 are: $c_{R,S}^{ref} = \dot{i}$ 0.482 mol/L, $T_S^{ref} = 27.8^\circ\text{C}$ (section 4.3). Using the reference

frequency $\omega^{ref} = 4.167 \cdot 10^{-4} \text{ Hz}$ the following values result:

$$\alpha^{ref} = 0.5903, \beta^{ref} = -0.0125, \gamma^{ref} = 13.6126 \wedge B_{P,S}^{ref} = 1.2190, \square_{max}^{ref} = 157^\circ \text{ and } \square_{min}^{ref} = -$$

$36^\circ = 324^\circ$.

For the optimal phase shift $\square_{opt}^{ref} = \square_{max}^{ref}$ eq. (22) leads to a performance improvement,

quantified by the DC component of

$$\dot{n}_{P, DC, max} = \dot{n}_P^{ref}(t) = 0.025 \text{ mol/min} .$$

With this DC component value, the performance criteria $Y_p^{norm}=1.17$ and $\Delta Y_p=5.98$ are obtained using eqs. (20) and (21); see also Figures 3 and 9.

Abbreviations

ASO	–	Asymmetrical Second Order
CSTR	–	Continuously Stirred Tank Reactor
FRF	–	Frequency Response Function
NFR	–	Nonlinear Frequency Response

Nomenclature

a	–	Parameter in eq. A11 (eq. A12)	[–]
A_i	–	Amplitude of input i	[% or –]
b	–	Parameter in eq. A11 (eq. A13)	[–]
$B_{P,s}$	–	Stability parameter	[–]
c	–	Parameter in eq. A11 (eq. A14)	[–]
C_i	–	Concentration of component i	[mol/L]
C_P	–	Heat capacity	[kJ/(kg · K)]
E_A	–	Activation energy	[kJ/mol]
F_i	–	Flow-rate of component i	[ml/min or L/min]
$G_{y,2,xx}$	–	2 nd order FRF for modulated input x and output y	
$G_{y,2,zz}$	–	2 nd order FRF for modulated input z and output y	
$G_{y,2,xz}^i$	–	cross ASO FRF for modulated inputs and output y	
$\Delta_R H$	–	Reaction enthalpy	[kJ/mol]
k	–	Reaction rate constant	[L ^{0,34} / (s·mol ^{0,34})]
k_0	–	Collision factor	[L ^{0,34} / (s·mol ^{0,34})]
n	–	Reaction order	[–]

\dot{n}_i	-	Molar flow of component i	[mol/s]
P	-	Period (eq. 24)	[min]
r	-	Reaction rate	[mol/(s · L)]
R	-	Universal gas constant	[J/(mol · K)]
S	-	Selectivity	[%]
t	-	Time	[s or min]
T	-	Temperature	[K or °C]
ΔT_{ad}	-	Adiabatic Temperature raise	[K or °C]
V	-	Reactor volume	[L]
X	-	Conversion	[%]
x	-	Time-dependent input x	[-]
Y	-	Yield	[%]
y_i	-	Time-dependent output y	[-]
Y^{norm}	-	Normalized Yield	[-]
ΔY_p	-	Absolute Difference in Yield	[%]
z	-	Time-dependent input z	[-]

Greek Letters

α	-	Dimensionless parameter (eq. A7)	[-]
β	-	Dimensionless parameter (eq. A8)	[-]
γ	-	Dimensionless parameter (eq. A9)	[-]

ν	–	Stoichiometric Coefficient	[–]
ω	–	Frequency	[Hz]
$\tilde{\omega}$	–	Dimensionless frequency	[–]
φ	–	Phase shift	[°]
ρ	–	Density	[kg/m ³]

Subscripts

Ambient	–	Ambient condition value
Av	–	Average value
CC	–	Related to single concentration modulation
CF	–	Related to simultaneous concentration and flow-rate modulation
DC	–	non-periodic component
FF	–	Related to single flow-rate modulation
In	–	Inlet/input value
Opt	–	Optimal value
P	–	Product (Acetic Acid)
R	–	Reactant (Acetic Anhydride)
Ref	–	Reference case
S	–	Steady-state
W	–	Water (second reactant)

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