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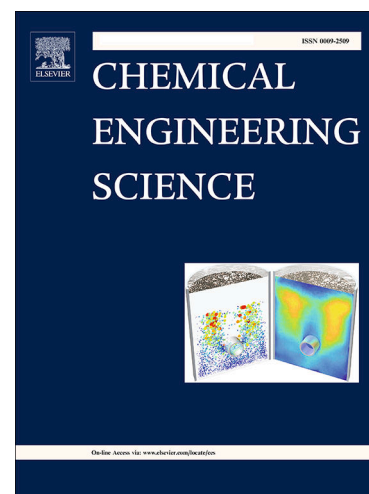
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Forced periodic operations of a chemical reactor for methanol synthesis - the search for the best scenario based on Nonlinear Frequency Response Method.

Part II Simultaneous modulation of two inputs

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Abstract

The analysis of the potential to improve performance of a methanol synthesis reactor through forced periodical operations by Nonlinear Frequency Response method is presented. The methanol synthesis in an isothermal and isobaric lab-scale CSTR is considered. First, the analysis was performed for single input modulations (in Part I), which showed that significant improvements can't be achieved. Here, the study is extended to analysis of simultaneous modulations of two inputs. All possible input combinations (6 cases) are analysed and the optimal forcing parameters, maximizing the time-average methanol production, were determined. For all combinations the improvement is possible, but for some cases it is not significant. The highest improvement is predicted for simultaneous modulation of the inlet partial pressure of CO and the inlet volumetric flow rate. This case, for which it is possible to achieve up to 33.51 % of methanol production, is analysed in detail and optimized using multi-objective optimization.

Keywords: Forced periodic operation, Methanol synthesis, Non-linear frequency response, Process improvement, Simultaneous modulation of two inputs, Multi-objective optimization

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I Introduction

Forced periodic operations, performed by forced periodic modulations of one or more inputs, can be considered as intensified processes, which, by proper choice of the modulated inputs and forcing parameters, could lead to significant process improvements (*Van Gerven and Stankiewicz, 2009; Petkovska and Seidel-Morgenstern, 2013*). The investigation of forced periodic operations in the field of chemical engineering, especially reactor engineering, became an attractive topic for researchers worldwide. Previous investigations showed that different reactor performances (e.g. conversion, selectivity, productivity...etc.) can be improved by implementation of forced periodic operations (*Bailey 1973; Chen et al., 1994; Douglas 1972; Renken 1972; Schadlich et al. 1983; Silveston 1987; Silveston et al., 1995; Silveston 1998; Silveston and Hudgins, 2013; Sterman 1990a, 1990b, 1991*). Simultaneous modulation of two inputs had been investigated by many research groups and the details could be found in, for example (*Chen et al. (1994), Parulekar (2003), Sterman et al. (1990b), Silveston and Hudgins (2013)*). Although the fact that simultaneous modulation of two inputs, which is the subject of the analysis in this manuscript, has a significant potential for improvement, to our knowledge, it has not been implemented industrially yet. Some of the reasons for the lack of industrial applications can be found in (*Stankiewicz and Kuczynski, 1995*).

Nevertheless, in some cases, forced periodic operations could lead to deterioration of time-average process performances. Therefore, theoretical prediction and evaluation of possible process improvement, prior to any experimental investigation, is an important task (*Petkovska and Seidel-Morgenstern, 2013*). In our previous work we introduced the Nonlinear Frequency Response (NFR) method for evaluation of possible improvements owing to periodic operations, as well as for evaluation of optimal forcing parameters and conditions which should be satisfied in order to obtain the highest possible improvement (*Currie et al., 2018; Marković et al. 2008; Nikolić-Paunić and Petkovska, 2013; Nikolić et al., 2014a, 2014b, 2015, 2016a, 2016b, 2020; Nikolić, 2016; Nikolić and Petkovska, 2016; Petkovska et al., 2010, 2018; Petkovska and Seidel-Morgenstern, 2013; Živković et al. 2020a; 2020b*).

In this two-part manuscript, the NFR method is used to perform a systematic search for the periodic process which provides the highest improvements, considering a well-mixed reactor in which heterogeneously catalysed methanol synthesis takes place. In Part I of this work, the NFR analysis was used for evaluating possible improvements in cases of single input modulations, with the main conclusion that this approach was not attractive. In this manuscript (Part II), it is shown that significant improvements are possible for some cases of simultaneous modulations of two inputs.

2. Nonlinear frequency response method for simultaneous modulation of two inputs

Frequency response of a nonlinear system is a complex periodic function (Douglas, 1972). In this study, the frequency response of a nonlinear system is analysed using the Nonlinear Frequency Response (NFR) method. This method uses the concept of higher order frequency response functions (FRFs), which is based on Volterra series and the generalized Fourier transform (Marković et al, 2006, Petkovska and Seidel-Morgenstern, 2013; Volterra, 1959; Winer and Spina, 1980). The NFR method can be applied to stable weakly nonlinear systems (Petkovska and Seidel-Morgenstern, 2013; Volterra, 1959; Winer and Spina, 1980). In Part I of this paper, the implementation of the NFR method for periodic operations with single input modulations was explained, and here we give the basic facts of its implementation for the cases of simultaneous modulations of two inputs. More details can be found in our previous publications (e.g. Nikolić and Petkovska, 2013; Petkovska et al., 2018).

If one or more inputs of a weakly nonlinear systems is/are periodically modulated around a previously established steady-state, the frequency response of the system output is obtained as a sum of the output steady-state value (y_s), the basis harmonic (y_I), an infinite number of higher harmonics (y_{II}, y_{III}, \dots) and a non-periodic (DC) term (y_{DC}) (Marković et al, 2006, Petkovska and Seidel-Morgenstern, 2013; Petkovska et al., 2018):

$$y(t) = y_s + y_{DC} + y_I + y_{II} + y_{III} + \dots \quad (1)$$

In order to evaluate the potential of a forced periodical operation of a system, it is only necessary to predict the DC component of the output of interest, as it determines the time-average performance of the analysed system.

The DC component of an output y , for the case when two inputs (e.g. x and z) are periodically modulated, can be given as a sum of the contributions of the DC component related to the single inputs (x and z) separately and the contribution of the DC component originating from the cross-effect of both inputs (Nikolić and Petkovska, 2013):

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

For co-sinusoidal modulations of inputs x and z , with equal frequencies ω , input amplitudes A_x and A_z , respectively and phase difference φ between them, the separate contributions of the two inputs to the DC component can be approximately evaluated from the corresponding asymmetrical second order (ASO) FRFs, in the same way as explained in Part I:

$$y_{DC,in} \approx 2 \left(\frac{A_{in}}{2} \right)^2 G_{y,in,in}^{(2)}(\omega, -\omega) \quad in=x \text{ or } z \quad (3)$$

while the contribution of the cross-effect can be approximately evaluated in the following way (Nikolić and Petkovska, 2013; Petkovska et al., 2018):

$$y_{DC,xz} \approx 2\left(\frac{A_x}{2}\right)\left(\frac{A_z}{2}\right)G_{y,x,z}^{*(2)}(\omega,\varphi) \quad (4)$$

$G_{y,x,z}^{*(2)}(\omega,\varphi)$ is the so-called cross ASO term, which correlates the output y with both modulated inputs (x and z). It is a function of both frequency and phase difference between the two modulated inputs, and is evaluated based on the cross asymmetrical second order FRF ($G_{y,x,z}^{(2)}(\omega, -\omega)$), in the following way:

$$G_{y,x,z}^{*(2)}(\omega,\varphi) = \cos(\varphi)\text{Re}(G_{y,x,z}^{(2)}(\omega, -\omega)) + \sin(\varphi)\text{Im}(G_{y,x,z}^{(2)}(\omega, -\omega)) \quad (5)$$

Thus, for the case of modulation of two inputs (x and z), in order to evaluate the possible improvement of the output y , it is necessary to derive three ASO FRFs: two of them correlating the output to each of the inputs ($G_{y,x,x}^{(2)}(\omega, -\omega)$ for input x and, $G_{y,z,z}^{(2)}(\omega, -\omega)$ for input z) and one cross ASO function ($G_{y,x,z}^{(2)}(\omega, -\omega)$, correlating the output to both modulated inputs) (Nikolić Paunić and Petkovska, 2013, Petkovska et al., 2018). The overall DC component of the output y , written as follows:

$$y_{DC} \approx 2\left(\frac{A_x}{2}\right)^2 G_{y,x,x}^{(2)}(\omega, -\omega) + 2\left(\frac{A_z}{2}\right)^2 G_{y,z,z}^{(2)}(\omega, -\omega) + 2\left(\frac{A_x}{2}\right)\left(\frac{A_z}{2}\right)G_{y,x,z}^{*(2)}(\omega,\varphi) \quad (6)$$

should be calculated for a chosen set of forcing parameters (forcing frequency, forcing amplitudes and phase difference) (Nikolić and Petkovska, 2013; Nikolić et al., 2015; Nikolić et al., 2016a; 2016b). In principle, it is possible find a set of forcing parameters resulting the periodic operation with highest improvement (Nikolić and Petkovska, 2013, Nikolić, 2016, Petkovska et al, 2016).

The phase difference is a crucial parameter for a periodic operation with simultaneous modulations of two inputs, considering that its appropriate choice guaranties that the cross term of the DC component has the desirable sign. Furthermore, by choosing the optimal phase difference, the cross-effect can be maximized (Felischak 2020; Felischak et al. 2021; Nikolić, 2016; Nikolić and Petkovska, 2013; Petkovska et al., 2018). The optimal phase difference, maximizing the DC component can be determined based only on the cross ASO FRF, in the following way (Nikolić and Petkovska, 2013):

$$\varphi_{opt} = \arctan\left(\frac{\text{Im}(G_{y,x,z}^{(2)}(\omega, -\omega))}{\text{Re}(G_{y,x,z}^{(2)}(\omega, -\omega))}\right) \quad (7)$$

The derivation procedure of the FRFs is standard and it can be found in our previous publications (*Marković et al.*, 2008; *Petkovska and Seidel-Morgenstern*, 2013; *Nikolić Paunić and Petkovska*, 2013; *Nikolić et al.*, 2014a; 2014b; 2015; 2016a; 2016b; *Nikolić and Petkovska*, 2016; *Petkovska et al.*, 2010; 2018, *Petkovska and Seidel-Morgenstern* 2013). The derivation procedure is recurrent, so the first order FRFs should be derived first and then the asymmetrical second order FRFs.

3 Methanol synthesis reaction

The performance of a forced periodically operated chemical reactor in which methanol is produced from synthesis gas (mixture of CO, CO₂ and H₂), through hydrogenation of CO and CO₂, using a commercial Cu/ZnO/Al₂O₃ catalyst, is analysed. The hydrogenation reactions are (*Graaf et al.* (1988)):



In addition, the reverse water-gas shift reaction (RWGS) is taking place according to:



The analysis of forced periodic operation of methanol synthesis is based on the kinetic model presented in (*Seidel et al.*, 2018; 2020). This model was derived evaluating results of numerous steady state and dynamic experiments described in (*Vollbrecht*, 2007). Key features of the model are the quantitative incorporation of a) the rate of altering the amounts of reduced and oxidized surface sites upon changing the gas phase composition and b) the dynamically changing amounts stored in both phases. With respect to the second feature the model assumes that the time constants for adsorption and desorption are much faster than the time constants for the chemical reactions, the imposed periodic modulation and the residence in the reactor. Based on typical sticking coefficients and adsorption rate constants predicted for similar systems for example in (*Panczyk*, 2006; *Yhang et al.*, 2020) this assumption is well fulfilled for the heterogeneously catalyzed methanol synthesis studied in this work and the modulation frequencies, flow-rates and reactor sizes considered below. This assumption allows simplifying the model and assuming permanently established adsorption equilibria. The kinetic model and parameters used in this study were given in Part I of this work.

It is important to point out again that the main prerequisite for reliable predictions of possible improvements owing to forced periodic operation is to have a reliable mathematical model of both the reaction kinetics and the reactor. Hereby, a good kinetic model and accurate values of

its parameters is of particular importance. The mathematical structure of the model, more precisely its nonlinearities will influence the outcome of the analysis of forced periodic operation. Below we will “trust” the kinetic model and postpone a quantitative analysis of the impact of unavoidable remaining model deficits to a forthcoming future study.

4. Evaluation of possible performance improvements of methanol synthesis reactor with simultaneous periodic modulations of two inputs

In this Section, the NFR method is applied for analysis and evaluation of possible improvements of methanol production for forced period operations with simultaneous modulation of two inputs. The analysis is performed for a laboratory-scale uniformly mixed Micro-Berty reactor, which was used for kinetic measurements (*Vollbrecht, 2007*). It is planned that the results of the theoretical analysis, presented below, will be experimentally validated using this same reactor type.

4.1. Mathematical model

The starting point for application of the NFR method is the mathematical model of the analysed system, which has been given in Part I of this paper. We repeat here just the main facts regarding the model. The mathematical model is based on the following assumptions: the reaction of methanol synthesis occurs in an isothermal and isobaric CSTR, the gas phase is ideal in the range of operation parameters, the adsorption equilibrium between the solid and the fluid phase exists, the adsorption processes follow the Langmuir-Hinshelwood mechanism, the catalyst deactivation can be neglected and only the reactions defined in equations (8-10) take place.

The mathematical model of the analysed system can be described with eight ordinary differential equations: the material balances for each of the six components present in the system (CH_3OH , CO_2 , CO , H_2 , H_2O and N_2 (inert)), the total material balance (from which the volumetric flow rate of the outlet stream is evaluated) and an equation which describes the catalyst dynamics.

It has to be pointed out that for a complex nonlinear system such as the one investigated in our work, the heterogeneously catalysed synthesis of methanol carried out in a well-mixed isothermal reactor (CSTR type), the overall effect of a periodic input modulation on the reactor performance is a results of a number of coupled nonlinear phenomena and their combined effects at different time scales, which all change with the steady-state point around which the system is modulated. The nonlinear effects which are included and have effect on the prediction of possible improvements are nonlinearities related to: rate of reaction rates, adsorption isotherms, interaction between flow-rate and concentration, dynamics of catalysis (conversion between the

reduction and oxidized active centres, in detail described in Part I of this two-part manuscript), and coupled effects of all previous listed nonlinearities.

Considering that for the NFR analysis it is convenient to use a dimensionless mathematical model, the dimensionless variables are defined as relative deviations from the corresponding steady-state values (Appendix A) and incorporated into the starting model equations. Afterwards, all nonlinear terms in the mathematical model are expanded into Taylor series form around the steady-state point, as already presented in Part I of this paper.

4.2. Inputs, outputs and frequency response functions (FRFs)

For the analysed system, it is possible to modulate periodically four different inputs: the partial pressures of all reactants in the feed stream (CO_2 , CO , H_2) and the volumetric flow-rate of inlet steam. The outputs are: the partial pressures of all components in the outlet stream (of the reactants and products, i.e. CH_3OH , CO_2 , CO , H_2 , H_2O), the fraction of reduced active centres on the catalyst surface and the volumetric flow-rate of the outlet stream.

The vectors of all inputs which can be modulated (designated as \mathbf{X} and \mathbf{Z}) and the vector of output variables (designated as \mathbf{Y}), are given in the dimensionless form, as follows:

$$\mathbf{X} = \mathbf{Z} = \begin{bmatrix} P_{\text{CO}_2,0} \\ P_{\text{CO},0} \\ P_{\text{H}_2,0} \\ v_0 \end{bmatrix} \quad \mathbf{Y} = \begin{bmatrix} P_{\text{CH}_3\text{OH}} \\ P_{\text{CO}_2} \\ P_{\text{CO}} \\ P_{\text{H}_2} \\ P_{\text{H}_2\text{O}} \\ \Phi \\ v \end{bmatrix} \quad (11)$$

The analysis for single input modulations, given in Part I of this paper, showed that no significant improvement could be achieved. Therefore, here we give the analysis for simultaneous modulation of all possible combinations of two inputs. Six cases are analysed in total, three combinations when inputs are partial pressures of two reactants:

- partial pressures of CO_2 & CO in the feed stream
- partial pressures of CO_2 & H_2 in the feed stream
- partial pressures of CO & H_2 in the feed stream

and three combinations of the partial pressure of one reactant and the inlet volumetric flow-rate:

- partial pressure of CO_2 in the feed stream and the inlet volumetric flow-rate
- partial pressure of CO in the feed stream and the inlet volumetric flow-rate and
- partial pressure of H_2 in the feed stream and inlet the volumetric flow-rate.

For each of the six cases, the partial pressure of inert (N_2) is also periodically modulated in a way to maintain a constant total pressure (see Appendices B and C). The inert does not participate in the chemical reactions nor in the adsorption on the catalyst surface and its modulation does not influence the reactor outputs. It only influences the value of outlet pressure of inert (N_2) which is not subject of our analysis.

The FRFs, which correlate each output Y_y ($y=1, \dots, 7$) with each modulated input X_x ($x=1, \dots, 4$), for single input modulations: the first order frequency response functions (FRFs), $G_{y,x}^{(1)}(\omega)$ and the asymmetrical second order frequency response functions, $G_{y,x,x}^{(2)}(\omega, -\omega)$ were derived and analysed in Part I of this paper. In this, Part II, the cross ASO FRFs $G_{y,x,z}^{(2)}(\omega, -\omega)$, which correlate the output Y_y to modulated inputs X_x and Z_z (for all six defined combinations) are derived.

The cross asymmetrical second order FRFs are derived by applying the standard derivation procedure (Nikolić and Petkovska, 2013; Nikolić, 2016; Petkovska et al., 2018).

4.3. Derivation of the cross FRFs

In order to derive the cross ASO FRFs for synchronous simultaneous modulations of inputs X_x and Z_z , it is most convenient to define them in the following way:

$$X_x(\tau) = A_x \cos(\omega\tau) = \left(\frac{A_x}{2}\right)e^{j\omega\tau} + \left(\frac{A_x}{2}\right)e^{-j\omega\tau} \quad (12)$$

$$Z_z(\tau) = A_z \cos(\omega\tau + \varphi) = \left(\frac{A_z}{2}e^{j\varphi}\right)e^{j\omega\tau} + \left(\frac{A_z}{2}e^{-j\varphi}\right)e^{-j\omega\tau} \quad (13)$$

In that case, the output Y_y , can be expressed in the form of Volterra series (Volterra, 1959):

$$\begin{aligned} Y_y &= \left(\frac{A_x}{2}\right)e^{j\omega\tau}G_{y,x}^{(1)}(\omega) + \left(\frac{A_x}{2}\right)e^{-j\omega\tau}G_{y,x}^{(1)}(-\omega) + \dots + 2\left(\frac{A_x}{2}\right)^2 e^0 G_{y,x,x}^{(2)}(\omega, -\omega) + \dots + \left(\frac{A_z}{2}\right)e^{j\omega\tau}e^{j\varphi}G_{y,z}^{(1)}(\omega) \\ &+ \left(\frac{A_z}{2}\right)e^{-j\omega\tau}e^{-j\varphi}G_{y,z}^{(1)}(-\omega) + \dots + 2\left(\frac{A_z}{2}\right)^2 e^0 G_{y,z,z}^{(2)}(\omega, -\omega) + \dots + \left(\frac{A_x}{2}\right)\left(\frac{A_z}{2}\right)(e^{-j\varphi}G_{y,x,z}^{(2)}(\omega, \\ &- \omega) + e^{j\varphi}G_{y,x,z}^{(2)}(-\omega, \omega)) + \dots \end{aligned} \quad (14)$$

Following the standard derivation procedure the expressions for the dimensionless inputs (Eqs. (12 and 13)) and outputs (Eq.(14)), are incorporated in the dimensionless mathematical model equations (given in Part I of this paper). The cross ASO FRFs are obtained by collecting the non-periodic terms with $\left(\left(\frac{A_x}{2}\right)\left(\frac{A_z}{2}\right)e^{-j\varphi}\right)$ and equating them with zero.

It is most convenient to present the resulting sets of algebraic equations in the matrix form:

$$\begin{bmatrix} \gamma_{11} & \cdots & \gamma_{17} \\ \vdots & \ddots & \vdots \\ \gamma_{71} & \cdots & \gamma_{77} \end{bmatrix} \times \begin{bmatrix} G_{1,x,z}^{(2)}(\omega, -\omega) \\ G_{2,x,z}^{(2)}(\omega, -\omega) \\ G_{3,x,z}^{(2)}(\omega, -\omega) \\ G_{4,x,z}^{(2)}(\omega, -\omega) \\ G_{5,x,z}^{(2)}(\omega, -\omega) \\ G_{6,x,z}^{(2)}(\omega, -\omega) \\ G_{7,x,z}^{(2)}(\omega, -\omega) \end{bmatrix} = \begin{bmatrix} \Lambda_{1,x,z} \\ \Lambda_{2,x,z} \\ \Lambda_{3,x,z} \\ \Lambda_{4,x,z} \\ \Lambda_{5,x,z} \\ \Lambda_{6,x,z} \\ \Lambda_{7,x,z} \end{bmatrix}, x = 1, 2 \text{ or } 3, z = x + 1, x + 2 \text{ or } x + 3, z \leq 4 \quad (15)$$

The cross ASO FRFs are obtained as the solution of matrix equation (15):

$$\begin{bmatrix} G_{1,x,z}^{(2)}(\omega, -\omega) \\ G_{2,x,z}^{(2)}(\omega, -\omega) \\ G_{3,x,z}^{(2)}(\omega, -\omega) \\ G_{4,x,z}^{(2)}(\omega, -\omega) \\ G_{5,x,z}^{(2)}(\omega, -\omega) \\ G_{6,x,z}^{(2)}(\omega, -\omega) \\ G_{7,x,z}^{(2)}(\omega, -\omega) \end{bmatrix} = \begin{bmatrix} \gamma_{11} & \cdots & \gamma_{17} \\ \vdots & \ddots & \vdots \\ \gamma_{71} & \cdots & \gamma_{77} \end{bmatrix}^{-1} \times \begin{bmatrix} \Lambda_{1,x,z} \\ \Lambda_{2,x,z} \\ \Lambda_{3,x,z} \\ \Lambda_{4,x,z} \\ \Lambda_{5,x,z} \\ \Lambda_{6,x,z} \\ \Lambda_{7,x,z} \end{bmatrix}, x = 1, 2 \text{ or } 3, z = x + 1, x + 2 \text{ or } x + 3, z \leq 4 \quad (16)$$

The definitions of auxiliary functions $\Lambda_{y,x,z}$ ($y=1, \dots, 7, x=1, 2, 3, z=2, 3, 4$) are given in Appendix D.

The auxiliary coefficients $\gamma_{i,j}$ ($i, j=1, \dots, 7$) were defined in Part I of this paper.

4.4. Evaluation of possible improvement

As explained in Part I of this paper, the forced periodic operations are implemented in order to achieve the improvement of different reactor performances, e.g. increase of methanol production, conversion or yield. The increase of all these performances can be evaluated based on time-average outlet molar flow-rate of methanol.

The methanol molar flow-rate can be evaluated from the methanol partial pressure and volumetric flow-rate of the outlet stream:

$$\dot{n}_{CH_3OH} = \frac{p_{CH_3OH}\dot{V}}{RT} \quad (17)$$

or in the dimensionless form:

$$\dot{N}_{CH_3OH} = \frac{\dot{n}_{CH_3OH} - \dot{n}_{CH_3OH,s}}{\dot{n}_{CH_3OH,s}} = \frac{p_{CH_3OH}\dot{V} - p_{CH_3OH,s}\dot{V}_s}{p_{CH_3OH,s}\dot{V}_s} = P_{CH_3OH} + v + P_{CH_3OH}v \quad (18)$$

Using the NFR method, the mean (time-average) value of the outlet molar flow rate of methanol, $(\dot{n}_{CH_3OH})_{mean}$, for simultaneous co-sinusoidal modulations of inputs x and z can be approximately calculated using the following expression:

$$\begin{aligned} (\dot{n}_{CH_3OH})_{mean} &\approx \dot{n}_{CH_3OH,s} \\ &\left(1 + 2\left(\frac{A_x}{2}\right)^2 H_{1,x,x}^{(2)}(\omega, -\omega) + 2\left(\frac{A_z}{2}\right)^2 H_{1,z,z}^{(2)}(\omega, -\omega) + 2\left(\frac{A_x}{2}\right)\left(\frac{A_z}{2}\right) H_{1,x,z}^{*(2)}(\omega, \varphi) \right) \end{aligned} \quad (19)$$

where $H_{1,x,x}^{(2)}(\omega, -\omega)$ and $H_{1,z,z}^{(2)}(\omega, -\omega)$ are the ASO FRFs frequency response functions which correlate the dimensionless outlet molar flow-rate of methanol, separately, to modulated inputs x and z , respectively (both derived and given in Part I of this paper), while $H_{1,x,z}^{*(2)}(\omega, \varphi)$ is the cross ASO term which correlates the outlet molar flow-rate of methanol to both modulated inputs x and z .

$$\dot{n}_{CH_3OH,s} = \frac{(p_{CH_3OH}\dot{V})_s}{RT} \quad (20)$$

is the steady-state value of the outlet molar flow-rate.

This cross ASO term, which is a function of the forcing frequency ω and the phase shift between the two inputs φ , is obtained from the corresponding cross ASO FRF and the phase difference in an analogous way as in eq. (5):

$$H_{1,x,z}^{*(2)}(\omega, \varphi) = \cos(\varphi)Re(H_{1,x,z}^{(2)}(\omega, -\omega)) + \sin(\varphi)Im(H_{1,x,z}^{(2)}(\omega, -\omega)) \quad (21)$$

in Part I of this work we derived the relation between the ASO FRF corresponding to the outlet molar flow rate and input x ($H_{1,x,x}^{(2)}(\omega, -\omega)$) and the FRFs corresponding to the outlet methanol partial pressure and the outlet volumetric flow rate:

$$H_{1,x,x}^{(2)}(\omega, -\omega) = G_{1,x,x}^{(2)}(\omega, -\omega) + G_{7,x,x}^{(2)}(\omega, -\omega) + \frac{1}{2}(G_{1,x}^{(1)}(\omega)G_{7,x}^{(1)}(-\omega) + G_{1,x}^{(1)}(-\omega)G_{7,x}^{(1)}(\omega)),$$

$x = 1, 2, 3 \text{ or } 4$ (22)

In an analogous way, here we derive the relation for the cross ASO FRF $H_{1,x,z}^{(2)}(\omega, -\omega)$:

$$H_{1,x,z}^{(2)}(\omega, -\omega) = G_{1,x,z}^{(2)}(\omega, -\omega) + G_{7,x,z}^{(2)}(\omega, -\omega) + G_{1,x}^{(1)}(\omega)G_{7,z}^{(1)}(-\omega) + G_{1,z}^{(1)}(-\omega)G_{7,x}^{(1)}(\omega)$$

$x = 1, 2 \text{ or } 3, z = x + 1, x + 2 \text{ or } x + 3, z \leq 4$ (23)

Based on the mean value of the methanol outlet molar flow rate, several performance indicators were defined (same as the one used in Part I of this paper):

- normalized methanol production per unit mass of catalyst:

$$(\dot{n}_{CH_3OH}^{norm})_{PO} = \frac{(\dot{n}_{CH_3OH})_{mean}}{m_{cat}} \quad (24)$$

- yield of methanol based of total carbon and

$$(Y_{CH_3OH}^{totC})_{PO} = \frac{(\dot{n}_{CH_3OH})_{mean}}{(\dot{n}_{CO_2} + \dot{n}_{CO})_{0,mean}} \quad (25)$$

- yield of methanol based on hydrogen:

$$(Y_{CH_3OH}^{H_2})_{PO} = 2 \frac{(\dot{n}_{CH_3OH})_{mean}}{(\dot{n}_{H_2,0})_{mean}} \quad (26)$$

For simultaneous modulation of partial pressures of two reactants (CO_2 & CO , CO_2 & H_2 , CO & H_2), the mean values of the molar flow-rates of the reactants in the feed stream are identical to their steady-state values. On the other hand, for simultaneous modulation of partial pressure of one reactant and inlet volumetric flow rate, the mean value of the inlet molar flow-rate of the modulated reactant is different from the corresponding steady-state value, and can be calculated using on the following common equation:

$$(\dot{n}_i)_{0,mean} = (\dot{n}_i)_{0,s} \left(1 + \frac{A_i A_f}{2} \cos(\varphi) \right), \quad i = CO_2, CO \text{ or } H_2 \quad (27)$$

The definitions of the yields for these cases are given in Table 1.

Table 1 The definitions of the yield of methanol based on total carbon and based on hydrogen for simultaneous modulation of the partial pressure of one reactant and the inlet volumetric flow-rate

Modulated inputs x and z	Yield of methanol based on total carbon	Yield of methanol based on hydrogen
Inlet partial pressure of CO ₂ (x) and total inlet volumetric flow-rate (z)	$(Y_{CH_3OH}^{totC})_{PO} = \frac{(\dot{n}_{CH_3OH})_{mean}}{(\dot{n}_{CO_2})_{0,mean} + (\dot{n}_{CO})_{0,s}}$	$(Y_{CH_3OH}^{H_2})_{PO} = 2 \frac{(\dot{n}_{CH_3OH})_{mean}}{(\dot{n}_{H_2})_{0,s}}$
Inlet partial pressure of CO (x) and total inlet volumetric flow-rate (z)	$(Y_{CH_3OH}^{totC})_{PO} = \frac{(\dot{n}_{CH_3OH})_{mean}}{(\dot{n}_{CO_2})_{0,s} + (\dot{n}_{CO})_{0,mean}}$	
Inlet partial pressure of H ₂ (x) and total inlet volumetric flow-rate (z)	$(Y_{CH_3OH}^{totC})_{PO} = \frac{(\dot{n}_{CH_3OH})_{mean}}{(\dot{n}_{CO_2} + \dot{n}_{CO})_{0,s}}$	$(Y_{CH_3OH}^{H_2})_{PO} = 2 \frac{(\dot{n}_{CH_3OH})_{mean}}{(\dot{n}_{H_2})_{0,mean}}$

5. Results and discussion

5.1. Periodic operations around the chosen steady-state point

In this subsection, periodic operations around a chosen steady-state point are analysed, for all six combinations of input modulations. The performance indicator used for evaluation will be the normalized production, defined as the outlet molar flow-rate of methanol per mass of catalyst (Eq. (24)). The chosen reference point was optimized, in such a way to find a compromise between two objective functions, namely the methanol production rate and the methanol yield based on total carbon. Then, the results presented in Section 5 (Table 2 and Figs. 1-4) were obtained by optimizing the forcing parameters (amplitudes, phase shift and frequency) around that steady-state point, in order to maximize one of those objective functions, namely the methanol production rate.

The analysis is performed for the same isothermal, isobaric, lab-scale Micro-Berty reactor, (gas volume 10.3 ml, mass of catalyst 0.00395 kg and total pressure 60 bar) considered in Part I. Also, the same optimal steady-state point used for analysis in Part I is used (temperature 473 K, feed volumetric flow-rate 0.93 ml/min, feed composition: 2.1 % CO₂, 18.5 %, 64.4 % H₂ and 15 % N₂). For the selected optimal steady-state, the normalized outlet molar flow-rate of methanol

is 556.91 mmol/(min kg_{cat}), the yield of methanol based on total carbon 61.05% and the yield of methanol based on hydrogen 39.09%.

As shown in Part I, periodic operations with single input modulations, for all 4 inputs, dominantly lead to reduction of methanol production. As a consequence, in order to maximize the mean normalized outlet molar flow-rate of methanol, it is necessary to optimize, not only the phase difference between modulated inputs and the forcing frequency, but also the forcing amplitudes of the modulated inputs. The optimal phase difference maximizing the methanol outlet molar flow-rate can be calculated analytically, based on the corresponding cross ASO FRF $H_{1,x,z}^{(2)}(\omega, -\omega)$:

$$\varphi_{opt} = \arctan\left(\frac{\text{Im}(H_{1,x,z}^{(2)}(\omega, -\omega))}{\text{Re}(H_{1,x,z}^{(2)}(\omega, -\omega))}\right) \quad (28)$$

Afterwards, the optimal forcing amplitudes are determined numerically, by using a standard Matlab solver (*fminmax*), in order to maximize the mean outlet molar flow rate of methanol (Eq. 19). The amplitude of the volumetric flow-rate can have values up to 1 (100 %), while the amplitudes of the partial pressures are limited with the maximal possible amplitude of the inert partial pressure that needs to be adjusted in order to keep constant total pressure (see Appendices B and C). In principle, the optimal amplitudes and phase difference are frequency dependent.

The results of the NFR analysis for each case of simultaneous modulation of two inputs around the optimal steady state are summarized in Table 2. This table shows the best possible results which can be obtained by each of the 6 possible combinations of inputs. The maximal increase of the normalized methanol production, the corresponding changes of yield of methanol based on total carbon and based on hydrogen, as well as corresponding optimal forcing parameters (amplitudes of both modulated inputs, the dimensionless frequency and the phase difference between the modulated inputs) for which these results are obtained, are presented.

Table 2. The best results which can be obtained by simultaneous modulations of two inputs

Modulated inputs x and z	Maximal increase of $\dot{n}_{CH_3OH}^{norm}$	Change of $Y_{CH_3OH}^{totC}$	Change of $Y_{CH_3OH}^{H_2}$	Optimal forcing parameters			
				A_x (-)	A_z (-)	ω (-)	φ (rad)
Inlet partial pressures of CO ₂ (x) and CO (z)	0.15 %	+0.15%	+0.15 %	1	0.59	1.47	-0.83
Inlet partial pressures of CO ₂ (x) and H ₂ (z)	0.22 %	+0.22 %	+0.22 %	0.36	0.22	1.27	-0.49
Inlet partial pressures of CO (x) and H ₂ (z)	0.45%	+0.45 %	+0.45 %	0.27	0.16	0.01	-0.03

Inlet partial pressure of CO ₂ (x) and total inlet volumetric flow-rate (z)	4.71 %	-0.39 %	+4.71 %	1	1	>30	0.004
Inlet partial pressure of CO (x) and total inlet volumetric flow-rate (z)	33.51 %	-2.12 %	+33.51 %	0.81	1	>30	0.006
Inlet partial pressure of H ₂ (x) and total inlet volumetric flow-rate (z)	5.29 %	+5.29 %	-5.71%	0.23	1	>30	0.01

The relative changes of different performance indicators (normalized outlet molar flow rate of methanol, yield of methanol based on total carbon and yield of methanol based on hydrogen), owing to the periodic input modulations, are calculated using the following generalized equation:

$$Rel. change = \frac{PI_{p0} - PI_{SS}}{PI_{SS}} * 100 (\%) \quad (29)$$

where PI is the general notation for a performance indicator ($PI = \dot{n}_{CH_3OH}^{norm}, Y_{CH_3OH}^{totC}$ or $Y_{CH_3OH}^{totH}$).

Based on the results presented in Table 2, it can be concluded that for all cases with simultaneous modulation of partial pressures of 2 reactants, although possible, the maximal potential improvements are negligible. On the other hand, for the cases with simultaneous modulation of partial pressure of one reactant and the inlet volumetric flow rate, some measurable improvements can be expected. The best case is obviously the one with simultaneous modulation of the inlet partial pressure of CO and inlet volumetric flow rate, with maximal predicted increase of the normalized outlet molar flow-rate of methanol of 33.51%. This case will be presented in detail in the next section and some details for all other cases will be given in Appendix E.

5.2. Detailed results for simultaneous modulations of partial pressure of CO and volumetric flow-rate

Based on the results presented in Table 2, the periodic operation with simultaneous modulations of the inlet partial pressure of CO and volumetric flow-rate of the feed stream was chosen as the best scenario for methanol synthesis. In this section we present this case in more details.

In Figure 1, the optimal forcing parameters, i.e. forcing amplitudes of the inlet partial pressure of CO and inlet volumetric flow-rate, as well as the phase difference between the two modulated inputs which maximize the normalized outlet molar flow rate of methanol, are presented as functions of dimensionless forcing frequency.

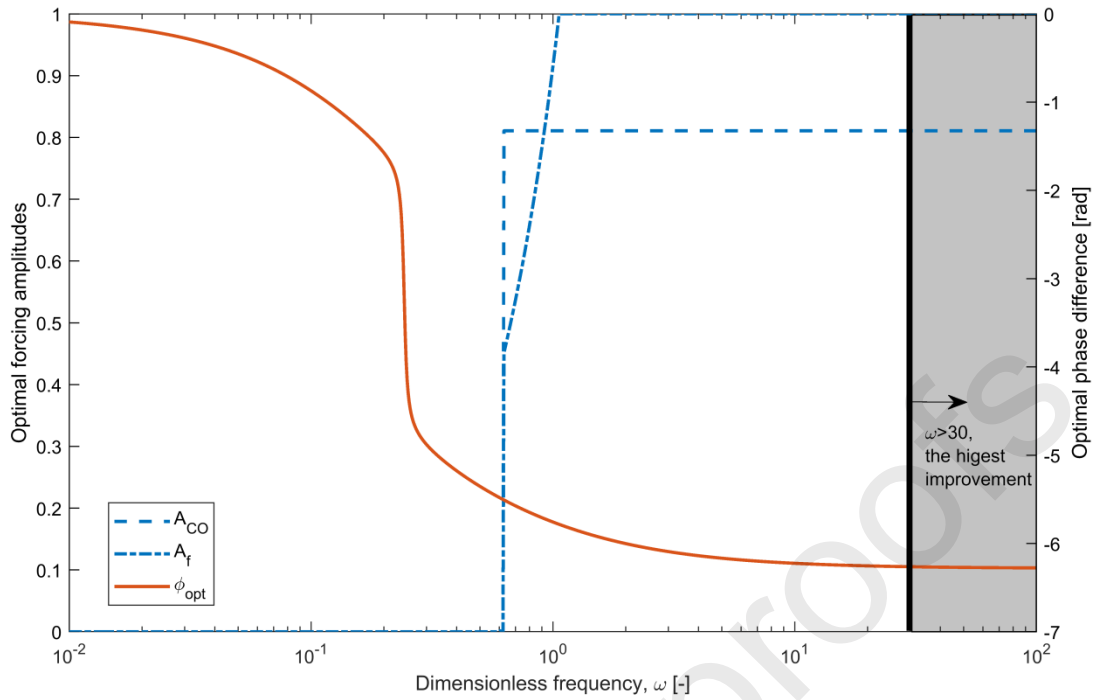


Figure 1. The optimal forcing parameters (forcing amplitudes and phase difference) which maximize the outlet molar flow-rate of methanol for simultaneous modulations of the CO partial pressure and flow-rate of the feed stream, vs. dimensionless forcing frequency

The results presented in Figure 1 shows that the optimal phase difference goes from 0 (for very low frequencies) to -2π (for high frequencies). The optimal inputs amplitudes are zero for all dimensionless frequencies lower than 0.62 (corresponding to period of oscillation of ~ 900 s), meaning that for lower frequencies it is not possible to find a periodic operation with simultaneous modulation of CO partial pressure and flow-rate that would be superior to the steady-state one. For dimensionless frequencies higher than 0.62 the optimal amplitudes rise sharply, reaching their maximal possible values (1 for the inlet volumetric flow-rate and 0.81 for the inlet CO partial pressure) (Figure 1, Table 2).

The ASO FRFs corresponding to the dimensionless outlet molar flow-rate of methanol, for single input modulations of the feed CO partial pressure and feed volumetric flow-rate, as well as the cross ASO term (Eq. 23) (calculated with the optimal phase difference between the two inputs, shown in Figure 1), vs. dimensionless forcing frequency, are presented in Figure 2.

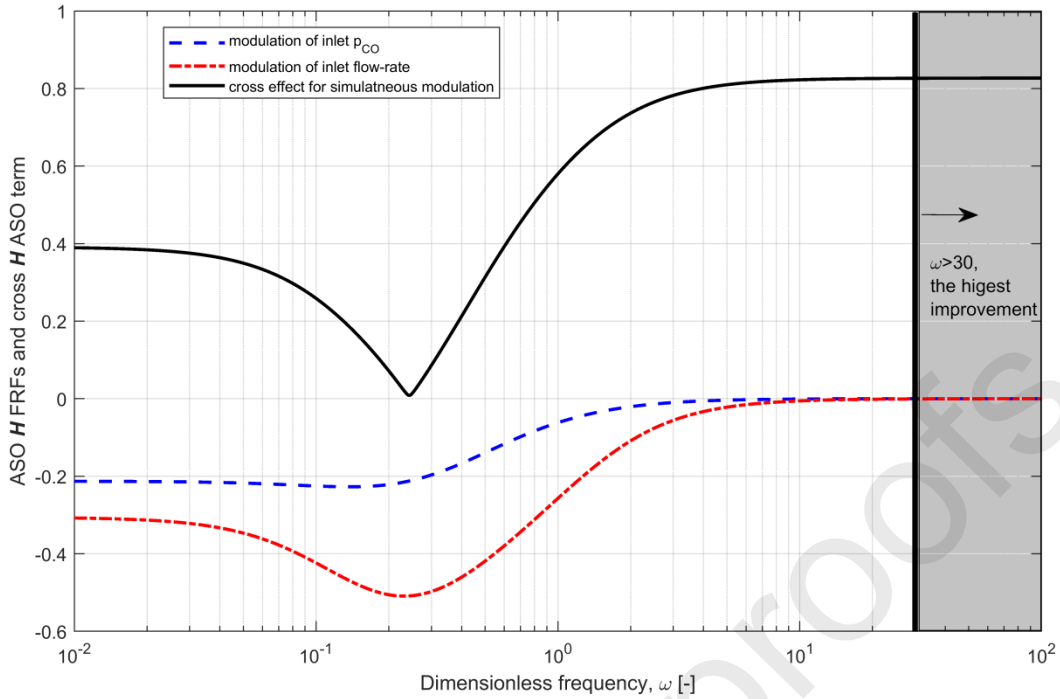


Figure 2. The ASO FRFs corresponding to the dimensionless methanol molar flow-rate for single input modulations of the inlet partial pressure of CO and inlet volumetric flow-rate and the cross ASO term vs. dimensionless forcing frequency

The results given in Figure 2 shows that the ASO FRFs corresponding to the considered inputs are negative in the whole frequency-range, meaning that single input modulations of the inlet partial pressure of CO and inlet volumetric flow-rate would lead to decrease of the normalized outlet molar flow rate of methanol (as already shown in Part I of this paper). On the other hand, the cross effect of simultaneous modulation of these two inputs with optimal phase difference has a positive effect on the desired output (the cross ASO term is positive in whole frequency range). The overall effect of simultaneous modulation of those two inputs will depend on the input amplitudes and it will be desirable only if a set of input amplitudes can be found such that the positive effect of the cross contribution becomes predominant. According to the results presented in Figure 1, such set can be found only for $\omega > 0.62$.

The normalized outlet molar flow-rate of methanol obtained for simultaneous modulation of inlet partial pressure of CO and volumetric flow rate with the optimal forcing parameters (shown in Figure 1) is presented in Figure 3, together with the corresponding optimal steady-state value. The corresponding yields of methanol based on total carbon and based on hydrogen, together with their steady-state values, are presented in Figure 4.

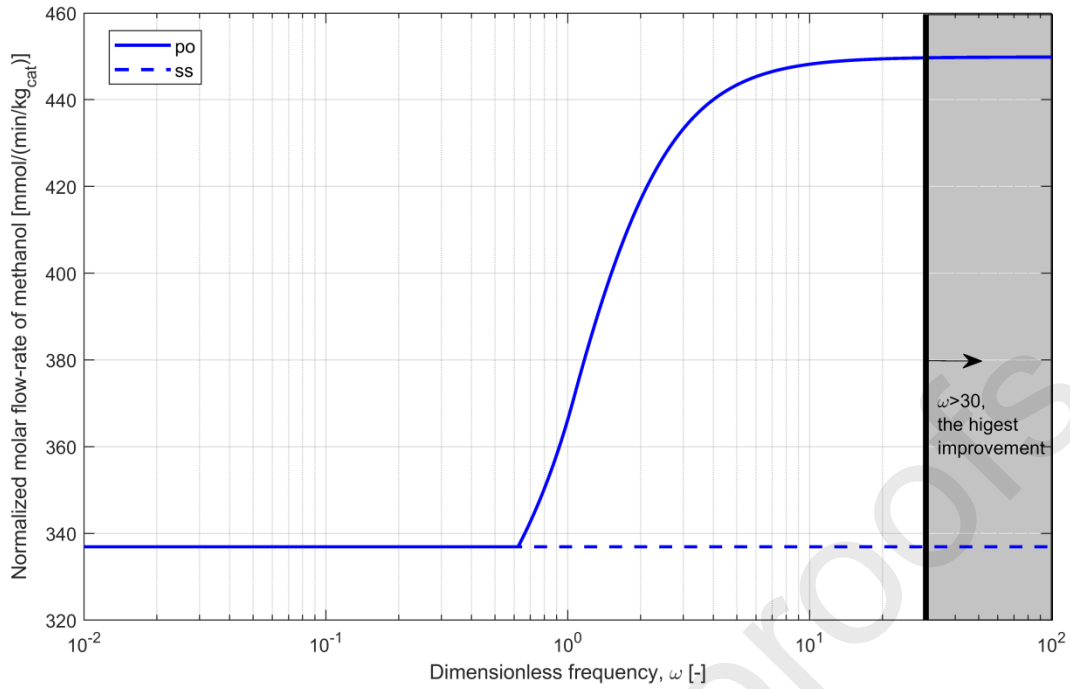


Figure 3. The normalized outlet molar flow-rate of methanol for optimal steady-state (ss) and periodic operation with simultaneous modulation of inlet partial pressure of CO and inlet volumetric flow-rate around the optimal steady-state with optimal forcing parameters (po) vs. dimensionless forcing frequency

The normalized methanol production, shown in Figure 3, is equal to the optimal steady-state value for $\omega < 0.62$. For all frequencies $\omega > 0.62$, the periodic operation with optimal amplitudes and phase difference is superior to the steady-state one. The highest increase or the normalized outlet molar flow rate of methanol is 33.51%. Theoretically, the maximal value is obtained for infinite frequency, but practically it is reached already for $\omega \approx 30$ (corresponding to period of 18.7 s). Increase of normalized outlet molar flow-rate of methanol of around 33% can be obtained already for the $\omega \approx 10$ (correspond to period of 56 s).

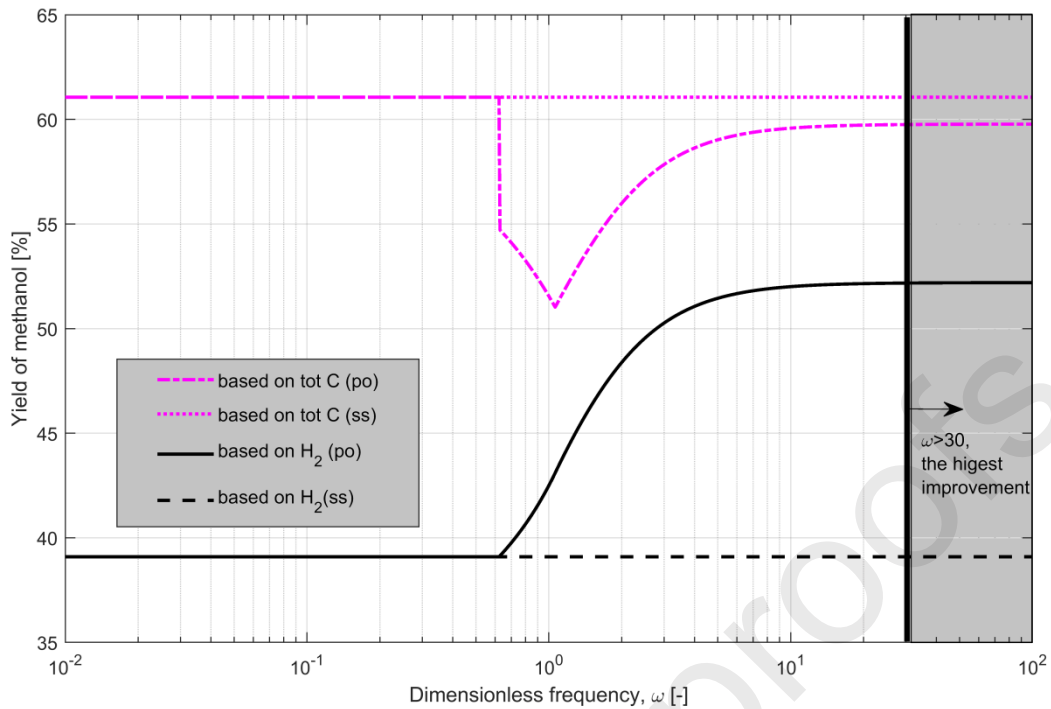


Figure 4 The yields of methanol based on total carbon and based on hydrogen for optimal steady-state (ss) and periodic operation with simultaneous modulation of inlet partial pressure of CO and inlet volumetric flow-rate (po) around the optimal steady-state with optimal forcing parameters (Figure 1), vs. dimensionless forcing frequency

The corresponding yield of methanol based on hydrogen (Figure 4) completely follows the profile of methanol production, which is logical, taking into account its definition in Table 2. On the other hand, for $\omega > 0.62$ the yield of methanol based on total carbon is lower than the corresponding optimal steady-state value. The explanation for this behaviour can be found in the fact that, for the that frequency range and the values of the forcing amplitudes and phase difference (Figure 1), the inlet molar flow-rate of CO (and total carbon) is higher than its corresponding steady state value (according to equation (27)). In order to find the optimal periodic operation which would satisfy all performance criteria, it would be best to use multi-objective optimization. This analysis and its results are shown in the next section.

For the case of simultaneous modulations of the inlet CO partial pressure and flow-rate, both inputs cause oscillations of all process variables, including the surface coverages of all species and reaction rates, but also the residence time. It can be assumed that the change of the CO molar fraction most directly influences the CO surface coverage and the rates of CO hydrogenation and RWG reaction, while the change of the flow rate most directly influences the reactor residence time. By choosing the optimal phase difference, shown in Fig. 1, these changes have a synergetic effect which is best represented by the cross ASO term shown in Fig. 2. This figure and Figure 3

show that the strongest synergistic effect is obtained for relative fast input modulations (for dimensionless frequencies higher than 10).

5.3 Multi-objective optimization

In this work we use a recently developed methodology (Živković *et al*, 2020b) which combines the NFR method with standard multi-objective optimization techniques. In this methodology the objective functions are defined based on the time-average values of the outputs of interest, which are directly related to their DC components. Using the NFR approach, these DC components are approximated by algebraic expressions which are defined based on the corresponding ASO FRFs, input amplitudes and the phase difference between the modulated inputs. As a consequence, the computing time needed for the dynamic optimization of the forced periodic operation is of the same order of magnitude as the computing time needed for the steady-state optimization (Živković *et al*, 2020b) (much shorter than for classical numerical dynamic optimization). Also, all optimization parameters, i.e., the steady-state point and the forcing parameters (frequency, amplitudes, and phase difference), can be determined rapidly in one step. This enables finding an optimal periodic operation around a sub-optimal steady-state point which would be superior to any periodic operation around a previously chosen steady-state point (Živković *et al*, 2020b).

In the current study, we perform multi-objective optimization of a periodic operation with simultaneous modulations the CO partial pressure and volumetric flow-rate of the feed stream. Two objective functions are defined, the yield of methanol based on total carbon and the normalised methanol production:

$$OF1 = (Y_{CH_3OH}^{totC})_{pO} \quad (30)$$

$$OF2 = (\dot{n}_{CH_3OH}^{norm})_{pO} \quad (31)$$

By combining equations (24) and (25) with equation (19) and (27), both objective functions can be approximated by algebraic expressions of frequency, the input amplitudes and the phase difference between the inputs, as well as the steady-state partial variables.

OF1

$$\begin{aligned} & \approx \frac{p_{CH_3OH,s} \dot{V}_s}{p_{CO_2,0,s} \dot{V}_s + p_{CO,0,s} \dot{V}_s \left(1 + \frac{A_{CO} A_f}{2} \cos(\varphi) \right)} \\ & \left(1 + 2 \left(\frac{A_{CO}}{2} \right)^2 H_{1,2,2}^{(2)}(\omega, -\omega) + 2 \left(\frac{A_f}{2} \right)^2 H_{1,4,4}^{(2)}(\omega, -\omega) + 2 \left(\frac{A_{CO}}{2} \right) \left(\frac{A_f}{2} \right) H_{1,2,4}^{*(2)}(\omega, \varphi) \right) \end{aligned} \quad (32)$$

$$\begin{aligned} & \approx \frac{p_{CH_3OH,s} \dot{V}_s}{RT m_{cat}} \\ & \left(1 + 2 \left(\frac{A_{CO}}{2} \right)^2 H_{1,2,2}^{(2)}(\omega, -\omega) + 2 \left(\frac{A_f}{2} \right)^2 H_{1,4,4}^{(2)}(\omega, -\omega) + 2 \left(\frac{A_{CO}}{2} \right) \left(\frac{A_f}{2} \right) H_{1,2,4}^{*(2)}(\omega, \varphi) \right) \end{aligned} \quad (33)$$

In the current multi-objective optimization of the periodic operation the following optimization parameters were determined: inlet partial pressures of CO₂, CO, and H₂ (corresponding to the steady-state point around which the periodic modulations should be performed), the forcing amplitudes of the CO partial pressure and volumetric flow-rate, the forcing frequency and the phase difference. The lower and upper bounds for the optimization variables, as well as defined constraints for the multi-objective optimization are given in Appendix F. The resulting Pareto front is shown. For comparison, the Pareto front obtained by multi-objective optimization of the steady-state operation, obtained in Part I (Appendix G) is also given in Figure 5. The data for each point of both Pareto fronts are given in Appendix F.

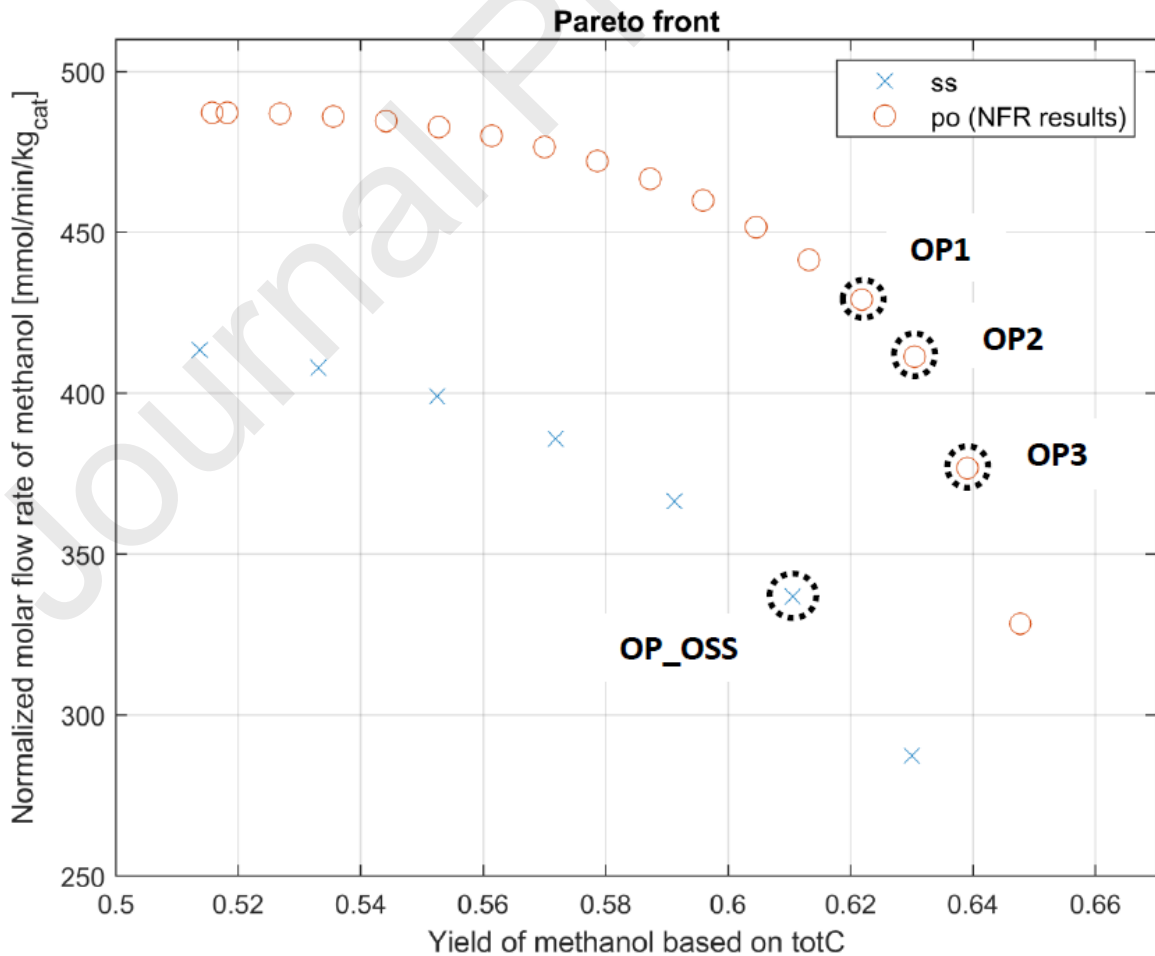


Figure 5 Pareto fronts for multi-objective optimization of Yield of methanol based on total C and normalized methanol production, for steady state (crosses) and periodic operation (circles)

For illustration, four operating points (OP) are selected and marked in Figure 5. The point OP_SS selected on the steady-state Pareto front (point no. 8 in Table F2) is actually the optimal steady-state point that was previously selected for analysis in both parts of this manuscript. Three operating points: OP1, OP2 and OP3 are also selected on the Pareto front for the periodic operation (points no. 16, 17 and 18 in Table F3).

The values of both objective functions corresponding to the four operation points chosen in Figure 5 (OP_OSS from the steady-state Pareto front and OP1, OP2 and OP3 from the periodic operation Pareto front) are given in Table 3. The relative changes of both objective functions between points OP1, OP2 and OP3, on one, and OP_OSS on the other hand, are also given.

As the NFR method is essentially approximate, the values of the objective functions calculated using the results of numerical simulations for the same operation points are also given in Table 3. Although the numerical simulation predictions show somewhat lower improvement than the NFR approximations, the agreement between the numerical and NFR results is very good (the error is around or less than 1.5 %).

Table 3 The normalized outlet molar flow rate of methanol and yield of methanol based on total carbon for the selected points from the Pareto fronts (Figure 5), based on NFR method and based on numerical simulation

Operating point	Normalized outlet molar flow-rate of methanol [mmol/min/kg _{cat}]		Yield of methanol based on total carbon [%]		Relative change of normalized outlet molar flow-rate of methanol		Relative change of yield of methanol based on total carbon	
	NFR	Num.Sim.	NFR	Num.Sim.	NFR	Num.Sim.	NFR	Num.Sim.
OP_OSS	336.9		61.06		/		/	
OP1	428.96	422.04	62.18	61.18	+27.33%	+25.27%	+1.83%	+0.20%
OP2	411.20	405.34	63.04	62.15	+22.05%	+20.31%	+3.24%	+1.79%
OP3	376.80	373.05	63.91	63.27	+11.84%	+10.73%	+4.67%	+3.62%

From the results presented in Figure 5 and Table 3 it can be concluded that multi-objective optimization enables finding operating points for which the increase of both objective functions is possible. For example, for the operation point OP2 it is possible to achieve increase of methanol production of 22.05 % and increase of yield of methanol based on total carbon of 3.24%. Those results are in good agreement with numerical simulation results presented also in Table 3. It should be noticed that the operating points chosen for comparison lay close to the right lower corner of the Pareto fronts. In this region, the increase of methanol production owing to periodic operation is more significant than the increase of the yield. Nevertheless, if operation points from the left upper corner would be chosen, the situation would be the opposite.

A rigorous numerical optimization based on the full nonlinear model is presented in (Seidel et. al., 2021).

6. Conclusions

In this paper, the NFR analysis was used in order to explore possible improvements of process performances owing to forced periodic operations of a well-mixed reactor in which heterogeneously catalysed methanol synthesis reactor takes, for 6 different cases of simultaneous modulations of two inputs. It was concluded that:

- For all six combinations of input modulations, simultaneous modulations of two inputs can result with improvement, even though the separate input modulations would lead to deterioration of process performances. The appropriate choice of the phase difference between the modulated inputs has a decisive role, but optimization of the input amplitudes is also necessary.
- For the case when an increase of normalized outlet molar flow-rate is set as the main indicator of improvement, for all cases of simultaneous modulation of partial pressures of two reactants the highest possible increase is less than 1%. On the other hand, for simultaneous modulation of the partial pressures of CO₂ or H₂ and inlet volumetric flow-rate, the maximal increase is around 5%. The highest increase of the normalized outlet molar flow rate of methanol of 33.5% is predicted for the case of simultaneous modulation of the inlet partial pressure of CO and inlet volumetric flow-rate, with optimal forcing parameters.
- The NFR analysis also enables fast and easy multi-objective optimization. Multi-objective optimization with two objective functions: yield of methanol based on total carbon and normalised methanol production, which was performed for the most promising case of simultaneous modulations of CO partial pressure and volumetric flow

rate, led to operating points superior to the steady-state operation regarding both indicators of improvement.

- The NFR method was proven as a useful and powerful theoretical tool for analysis, design and optimization of periodic operations, even for the complex case of methanol synthesis reactor.

The theoretical results of the NFR analysis, presented in this work, were used as the basis for full numerical optimization of periodically operated methanol synthesis reactor (*Seidel et al*, 2021). These results will also serve for planning the experimental investigation in a lab-scale Berty type reactor which is planned for near future.

Nomenclature

A	forcing amplitude of input modulation
E	auxiliary parameters for catalyst dynamic equation in dimensionless form
$G_{y,x,\dots,x}^{(n)}(\omega_1, \dots, \omega_2)$	n^{th} order FRF which correlates the output y to modulated input x
$G_{y,x,z}^{(2)}(\omega, -\omega)$	cross ASO FRF which correlates the output y to modulated inputs x and z
ΔG [J/mol]	Gibbs free energy
$H_{i,x,x}^{(2)}(\omega, -\omega)$	ASO FRF which correlates the outlet molar flow-rate of component i to modulated input x
$H_{i,x,z}^{(2)}(\omega, -\omega)$	cross ASO FRF which correlates the outlet molar flow-rate of component i to modulated inputs x and z
J	Jacobian matrix
k_j	reaction rate constant ($j = 1$ for CO hydrogenation, $j = 2$ for CO ₂ hydrogenation, $j = 3$ for RWGS)
k_1^\dagger, k_2^\dagger [s ⁻¹]	reaction rate constant for oxidation-reduction of catalyst
K_i	adsorption constant
K_1, K_2	equilibrium constants for oxidation-reduction of catalyst
K_{p_i} [bar ⁻²]	reaction rate constant for ($i=1$) CO or ($i=2$) CO ₂ hydrogenation
K_{p_3} [—]	reaction rate constant for RWGS
m_{cat} [kg]	mass of catalyst
\dot{n} [mol/s; mmol/min]	molar flow rate
\dot{n}^{norm} [mmol/min/kg _{cat}]	normalized molar flow rate (per unit of mass of catalyst)
\dot{N}	dimensionless molar flow rate
p [bar]	total pressure
p_i [bar]	partial pressure of component i ($i = 1, \dots, 6$)
P_i [bar]	dimensionless partial pressure of component i ($i = 1, \dots, 6$)
q_{sat} [mol/kg]	specific amount of surface centres
q, Q, ϑ, U, s, S	Taylor series coefficients for reaction rates
R [J/mol/K]	gas constant

r_j [mol/kg_{cat}/s] rate of reaction j ($j = 1$ for CO hydrogenation, $j = 2$ for CO₂ hydrogenation, $j = 3$ for RWGS)

t [s] time

T [K] temperature

V_G [m³] volume of gas phase in the reactor

\dot{V} [m³/s] volumetric flow rate

x, z input (general symbol)

\mathbf{X}, \mathbf{Z} vector of dimensionless inputs

y output (general symbol)

\mathbf{Y} vector of dimensionless outputs

y_i molar fraction of component i ($i = 1, \dots, 6$)

$Y_{CH_3OH}^{totC}$ yield of methanol based on total carbon

$Y_{CH_3OH}^{H_2}$ yield of methanol based on hydrogen

Greek letters

γ, Λ cross ASO FRF matrix coefficients and functions

θ relative amount of free active surface centre

ν stoichiometric coefficient

τ dimensionless time

$\tau_{0,s}$ [s] residence time based on the inlet volumetric flow rate

v dimensionless volumetric flow rate

ϕ fraction of reduced centres on catalyst surface

ϕ_{max} maximal value of the fraction of reduced surface centres on catalyst surface

Φ dimensionless total amount of reduced centres on catalyst surface

ω dimensionless frequency

Subscripts

CO modulation of partial pressure of CO in feed stream

CO₂ modulation of partial pressure of CO₂ in feed stream

DC non-periodic component (*direct current*)

i	component ($i=1$ for CH_3OH , $i=2$ for CO_2 , $i=3$ for CO , $i=4$ for H_2 , $i=5$ for H_2O , $i=6$ for N_2)
f	modulation of total inlet volumetric flow rate
H_2	modulation of partial pressure of H_2 in feed stream
j	reaction ($j = 1$ for CO hydrogenation, $j = 2$ for CO_2 hydrogenation, $j = 3$ for RWGS)
0	feed stream
PO, po	periodic operation
SS,ss	steady-state operation
<i>mean</i>	mean value for periodic operation
N_2	modulation of partial pressure of N_2 in feed stream
<i>ref</i>	referent value
s	steady-state
<i>tot C</i>	total carbon

Superscripts

H_2	based on hydrogen
<i>max</i>	maximal value
totC	based on total carbon
*	reduced surface centre
⊙	oxidized surface centre
⊗	surface centre for hydrogen

Abbreviations

AC	<i>Active centres on catalyst surface</i>
ASO	<i>Asymmetrical Second Order</i>
FRF	<i>Frequency Response Functions</i>
NFR	<i>Nonlinear Frequency Response</i>
OP	<i>Operating point</i>
PI	<i>Performance Indicator</i>
RWGS	<i>Reverse water-gas shift</i>

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Appendix**Appendix A The definitions of dimensionless variables****Table A1** The definitions of dimensionless variables

Dimensionless variables	Definitions
Partial pressure of component i	$P_i = \frac{p_i - p_{i,s}}{p_{i,s}}, i = 1,..6$
Partial pressure of component i in the inlet stream	$P_{i,0} = \frac{p_{i,0} - p_{i0,s}}{p_{i0,s}}, i = 1,..6$
Time	$\tau = \frac{t}{\tau_{0,s}} = \frac{t}{V_G/\dot{V}_{0,s}}$
Fraction of reduced centers on the catalyst surface	$\Phi = \frac{\phi - \phi_s}{\phi_s}$
Volumetric flow-rate of the inlet stream	$v_0 = \frac{\dot{V}_0 - \dot{V}_{0,s}}{\dot{V}_{0,s}}$
Volumetric flow-rate of the outlet stream	$u = \frac{\dot{V} - \dot{V}_s}{\dot{V}_s}$
Frequency	$\omega = \omega_d \tau_{0,s}$

The dimensionless frequency (ω) is defined by using the residence time in steady-state calculated based of inlet volumetric flow-rate, defined as:

$$\tau_{0,s} = \frac{V_G}{\dot{V}_{0,s}} \quad (A1)$$

Appendix B The forcing amplitude of inert for simultaneous modulation of partial pressures of two reactants in the feed stream

In order to assure that the total pressure in reactor is constant for simultaneous modulation of partial pressures of two reactants in the feed stream, the inlet pressure of inert (N_2) has to be modulated as follows:

$$P_{N_2,0} = A_{N_2}^{(1)} \cos(\omega\tau - \pi) + A_{N_2}^{(2)} \cos(\omega\tau - \pi + \varphi) \quad (B.1)$$

or presented as

$$P_{N_2,0} = A_{N_2}^{tot} \cos(\omega\tau - \pi + \sigma) \quad (B.2)$$

where $A_{N_2}^{tot}$ is forcing amplitude for partial pressure of inert (N_2) and σ is phase difference

$$A_{N_2}^{tot} = \sqrt{(A_{N_2}^{(1)})^2 + 2A_{N_2}^{(1)}A_{N_2}^{(2)}\cos(\varphi) + (A_{N_2}^{(2)})^2} \quad (B.3)$$

$$\sigma = \arctan\left(\frac{A_{N_2}^{(2)}\sin(\varphi)}{A_{N_2}^{(1)} + A_{N_2}^{(2)}\cos(\varphi)}\right) \quad (B.4)$$

The $A_{N_2}^{(1)}$, $A_{N_2}^{(2)}$ and $A_{N_2}^{tot}$, have to satisfy two equalities and one nonequality

$$A_{N_2}^{(1)} = \frac{y_{z,0,s}}{y_{6,0,s}} A_x \quad A_{N_2}^{(2)} = \frac{y_{z,0,s}}{y_{6,0,s}} A_z \quad (B.5)$$

$$A_{N_2}^{tot} \leq 1 \quad (B.6)$$

in order to assure that total pressure is constant.

Appendix C The forcing amplitude of inert for simultaneous modulation of partial pressure of one reactant and volumetric flow-rate of the feed stream

In this case, the partial pressure of inert (N_2) in feed stream should be modulated out-of-phase to partial pressure of reactant which is modulated, as follows

$$P_{N_2,0} = A_{N_2} \cos(\omega\tau - \pi) \quad (C.1)$$

where the forcing amplitude of inert can be evaluated from following

$$A_{N_2} = \frac{y_{x,0,s}}{y_{6,0,s}} \cdot A_x \quad (C.2)$$

Appendix D Auxiliary functions used in matrix equations for derivation of G cross asymmetrical second order FRFs

The auxiliary functions Λ are defined as follows

$$\Lambda_{i,x,z} = -\frac{\dot{V}_s}{\dot{V}_{0,s}} [G_{i,x}^{(1)}(\omega)G_{7,z}^{(1)}(-\omega) + G_{i,z}^{(1)}(-\omega)G_{7,x}^{(1)}(\omega)] + \frac{RT}{p_{i,s}\dot{V}_{0,s}} m_{cat} \left[\sum_{l=1}^6 \sum_{k=l}^6 (v_{i,1}Q_{lk} + v_{i,2}U_{lk} + v_{i,3}S_{lk})(G_{l,x}^{(1)}(\omega)G_{k,z}^{(1)}(-\omega) + G_{l,z}^{(1)}(-\omega)G_{k,x}^{(1)}(\omega)) \right] \quad (i = 1, \dots, 5; x = 1, z = 2; x = 1, z = 3; x = 2, z = 3) \quad (D.1)$$

$\Lambda_{i,x,z}$

$$= \frac{p_{i,0,s}}{p_{i,s}} - \frac{\dot{V}_s}{\dot{V}_{0,s}} [G_{i,x}^{(1)}(\omega)G_{7,z}^{(1)}(-\omega) + G_{i,z}^{(1)}(-\omega)G_{7,x}^{(1)}(\omega)] + \frac{RT}{p_{i,s}\dot{V}_{0,s}} m_{cat}$$

$$\left[\sum_{l=1}^6 \sum_{k=l}^6 (v_{i,1}Q_{lk} + v_{i,2}U_{lk} + v_{i,3}S_{lk})(G_{l,x}^{(1)}(\omega)G_{k,z}^{(1)}(-\omega) + G_{l,z}^{(1)}(-\omega)G_{k,x}^{(1)}(\omega)) \right]$$

$$(i = 1, \dots, 5; x = 1, z = 4; x = 2, z = 4; x = 3, z = 4) \quad (D.2)$$

 $\Lambda_{6,x,z}$

$$= [-E_2](G_{2,x}^{(1)}(\omega)G_{6,z}^{(1)}(-\omega) + G_{2,z}^{(1)}(-\omega)G_{6,x}^{(1)}(\omega)) + [-E_1]$$

$$(G_{3,x}^{(1)}(\omega)G_{6,z}^{(1)}(-\omega) + G_{3,z}^{(1)}(-\omega)G_{6,x}^{(1)}(\omega)) + [-E_3](G_{4,x}^{(1)}(\omega)G_{6,z}^{(1)}(-\omega) + G_{4,z}^{(1)}(-\omega)$$

$$G_{6,x}^{(1)}(\omega)) + [-E_4](G_{5,x}^{(1)}(\omega)G_{6,z}^{(1)}(-\omega) + G_{5,z}^{(1)}(-\omega)G_{6,x}^{(1)}(\omega))$$

$$(x = k, z = k+1, k+2, k+3 (k = 1, \dots, 3 \text{ and } z \leq 4)) \quad (D.3)$$

$$\Lambda_{7,x,z} = m_{cat} \sum_{i=1}^5 \left[\sum_{l=1}^6 \sum_{k=l}^6 (v_{i,1}Q_{lk} + v_{i,2}U_{lk} + v_{i,3}S_{lk})(G_{l,x}^{(1)}(\omega)G_{k,z}^{(1)}(-\omega) + G_{l,z}^{(1)}(-\omega)G_{k,x}^{(1)}(\omega)) \right]$$

$$(x = k, z = k+1, k+2, k+3 (k = 1, \dots, 3 \text{ and } z \leq 4)) \quad (D.4)$$

Appendix E Results for simultaneous modulation of two inputs (partial pressures (CO_2 & CO , CO_2 & H_2 , CO & H_2) and partial pressure of one reactant (CO_2 or H_2) and inlet volumetric flow-rate)

Appendix E1 Simultaneous modulation of partial pressures of CO_2 and CO in the feed stream

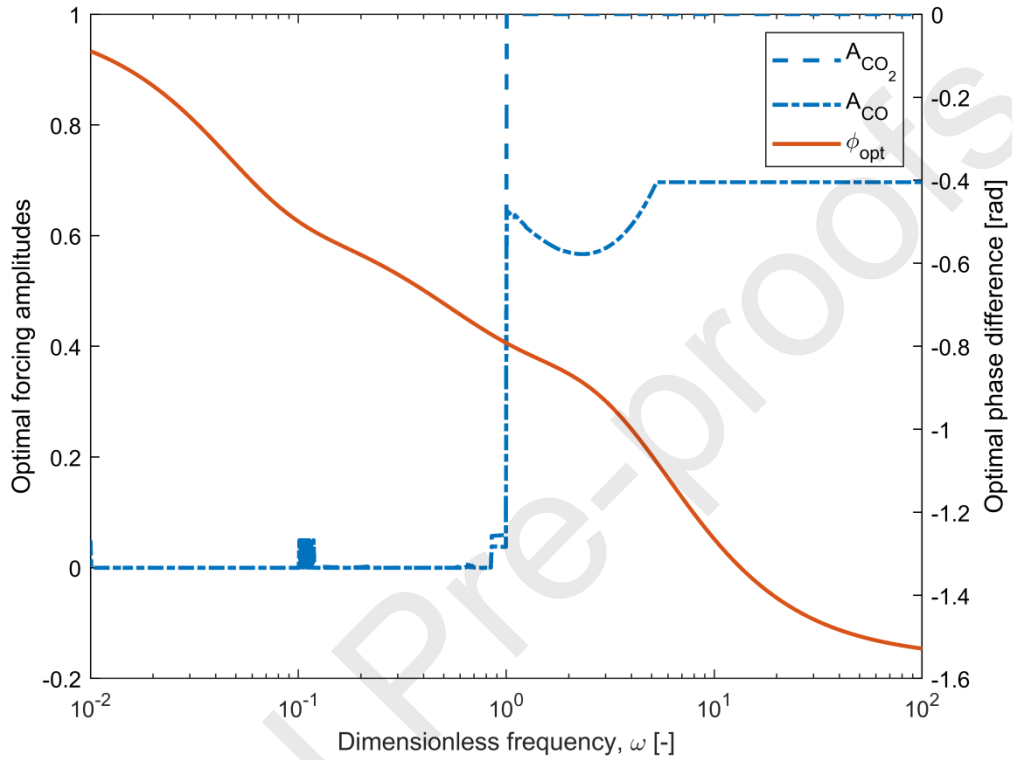


Figure E1.1 The optimal forcing parameters (forcing amplitudes and phase difference between the modulated inputs (partial pressures of CO_2 and CO)) which maximize the normalized outlet molar flow-rate of methanol, vs. dimensionless forcing frequency

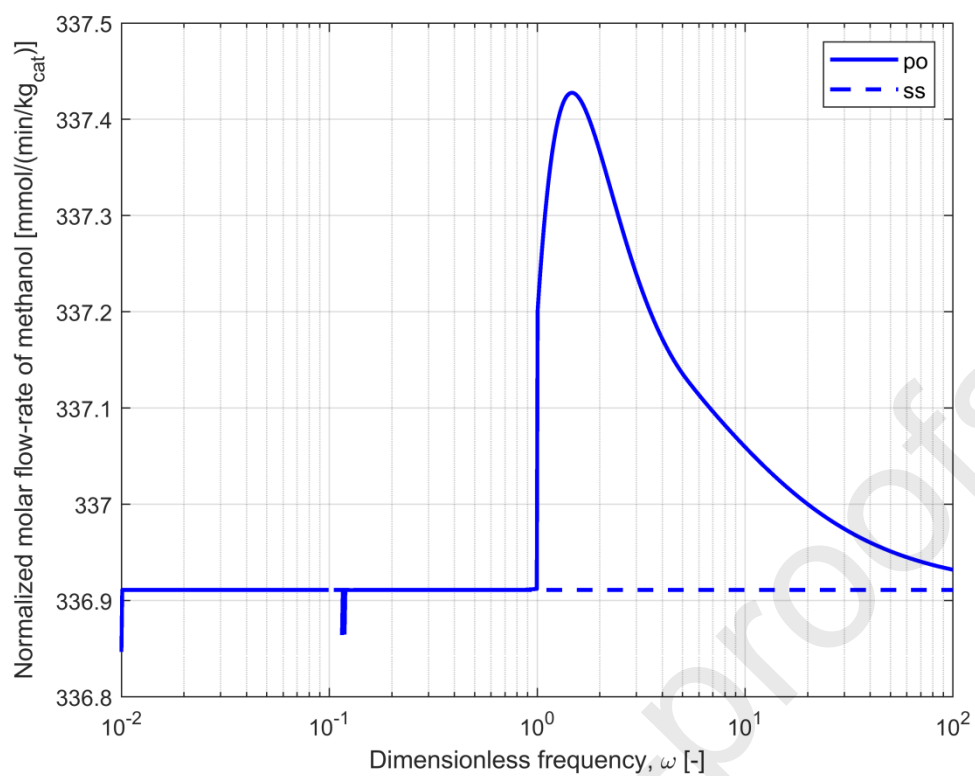


Figure E1.2 The normalized outlet molar flow-rate of methanol for steady-state and for simultaneous modulation of inlet partial pressures of CO_2 and CO around the optimal steady-state modulated using optimal forcing parameters (forcing amplitudes and phase difference, Figure E1.1) vs. dimensionless forcing frequency.

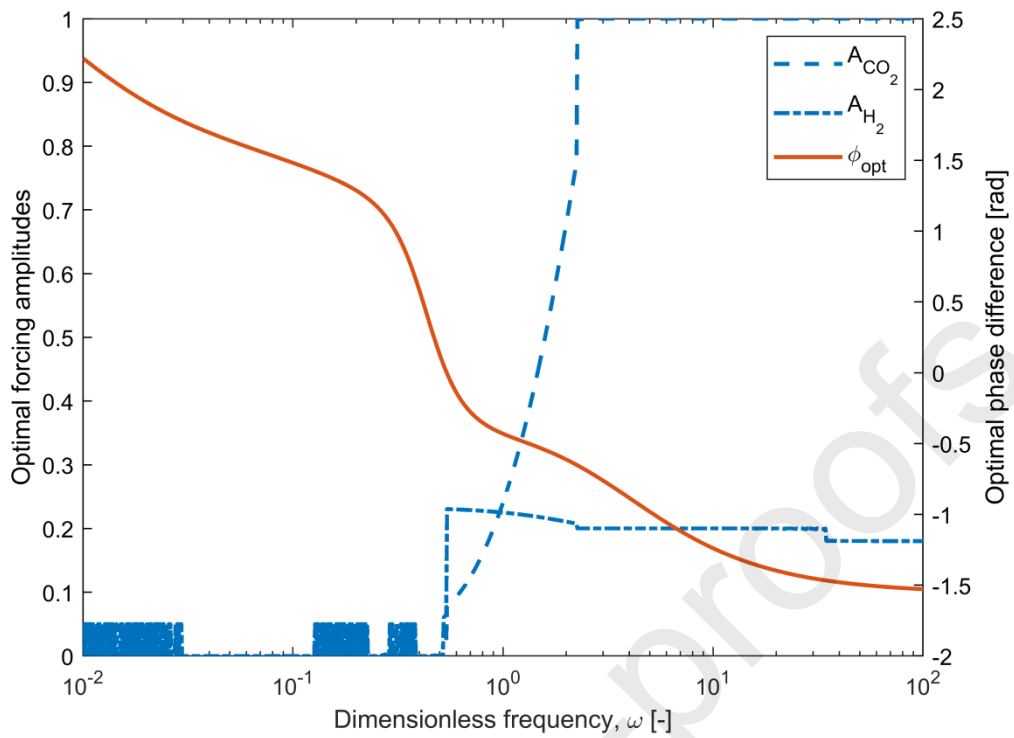


Figure E2.1 The optimal forcing parameters (forcing amplitudes and phase difference between the modulated inputs (partial pressures of CO₂ and H₂)) which maximize the normalized outlet molar flow-rate of methanol, vs. dimensionless forcing frequency

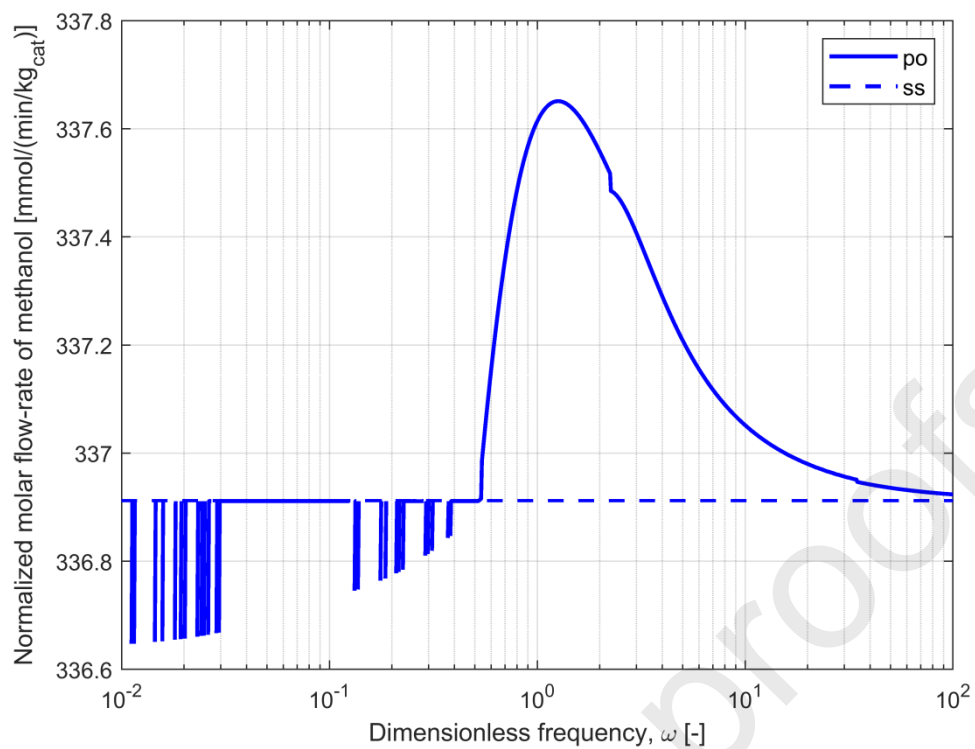


Figure E2.2 The normalized outlet molar flow-rate of methanol for steady-state and for simultaneous modulation of inlet partial pressures of CO₂ and H₂ around the optimal steady-state modulated using optimal forcing parameters (forcing amplitudes and phase difference, Figure E2.1) vs. dimensionless forcing frequency.

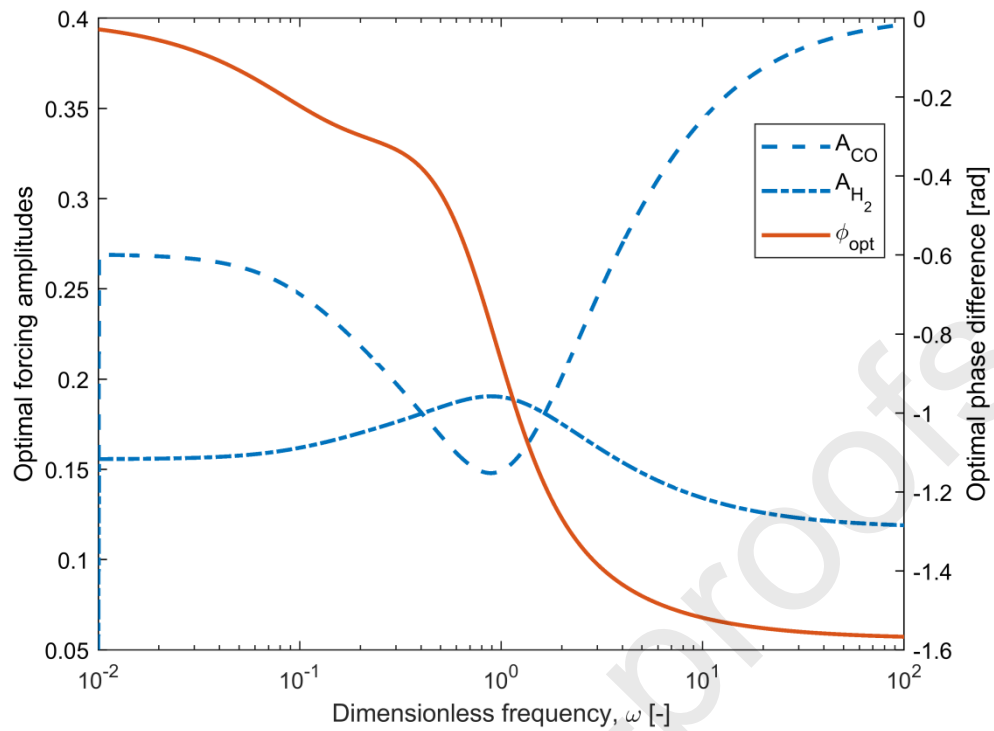


Figure E3.1 The optimal forcing parameters (forcing amplitudes and phase difference between the modulated inputs (partial pressures of CO and H₂)) which maximize the normalized outlet molar flow-rate of methanol, vs. dimensionless forcing frequency

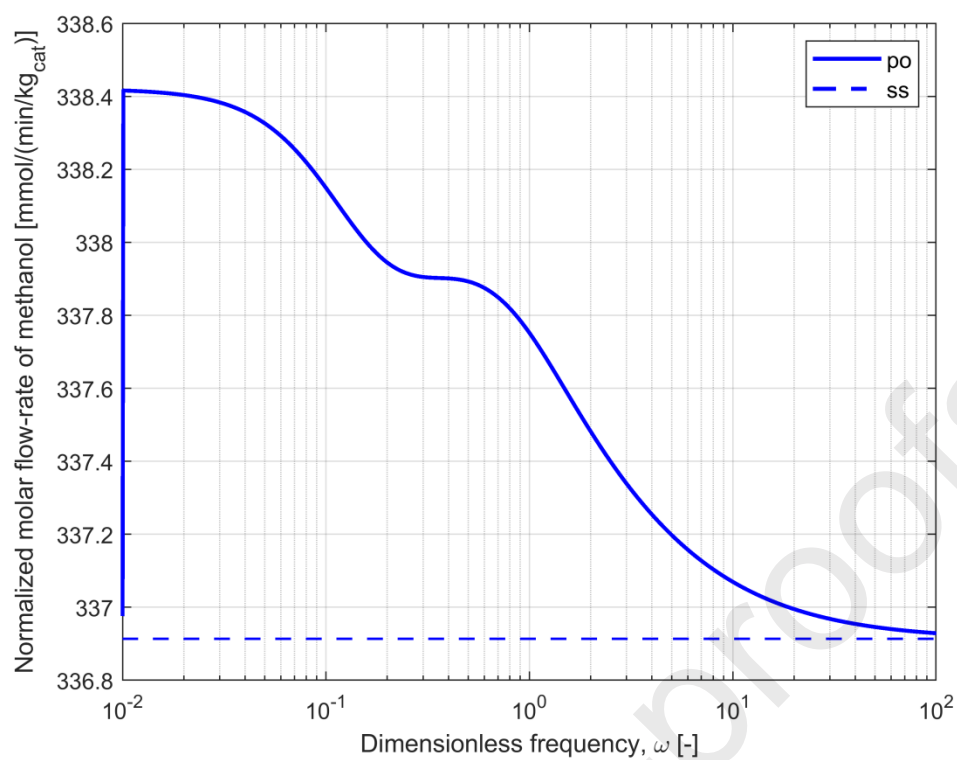


Figure E3.2 The normalized outlet molar flow-rate of methanol for steady-state and for simultaneous modulation of inlet partial pressures of CO and H₂ around the optimal steady-state modulated using optimal forcing parameters (forcing amplitudes and phase difference, Figure E3.1) vs. dimensionless forcing frequency.

Appendix E4 Simultaneous modulation of partial pressures of CO₂ in the feed stream and inlet volumetric flow-rate

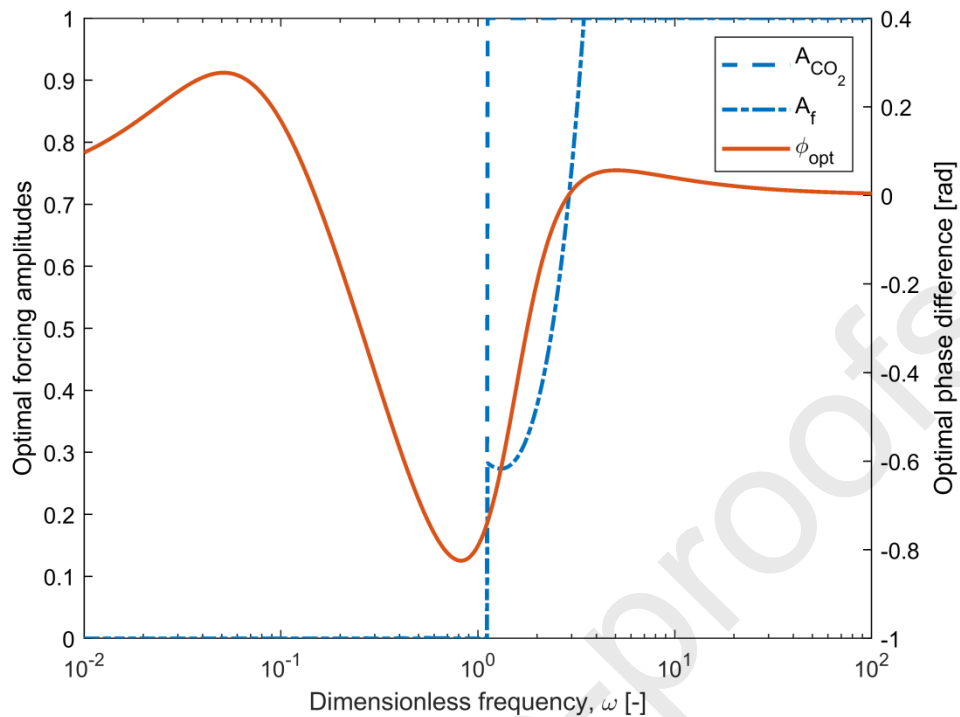


Figure E4.1 The optimal forcing parameters (forcing amplitudes and phase difference between the modulated inputs (partial pressure of CO₂ and inlet volumetric flow-rate)) which maximize the normalized outlet molar flow-rate of methanol, vs. dimensionless forcing frequency

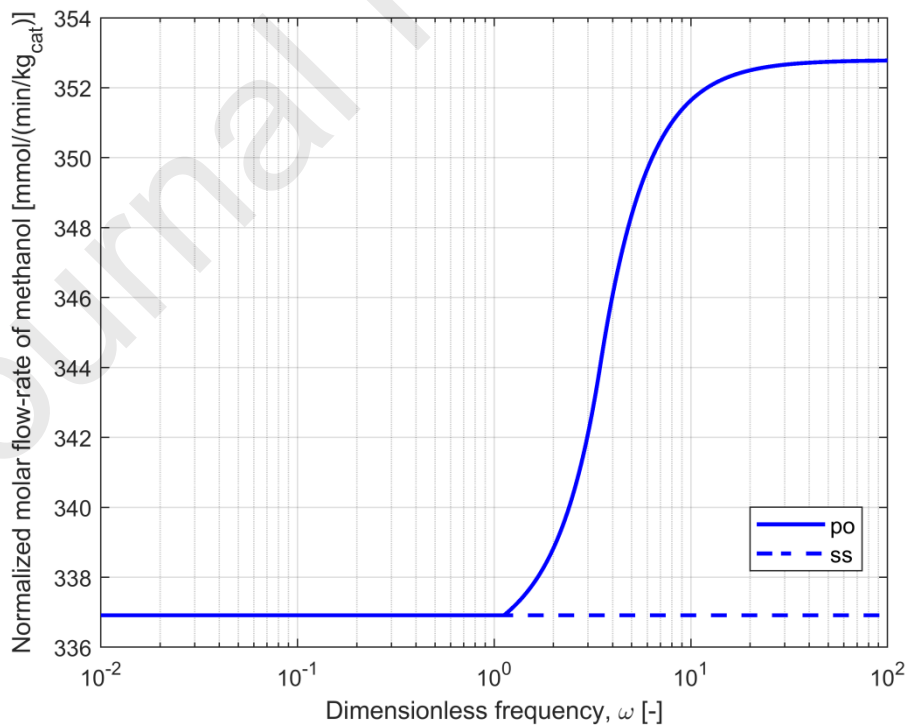


Figure E4.2 The normalized outlet molar flow-rate of methanol for steady-state and for simultaneous modulation of inlet partial pressure of CO₂ and inlet volumetric flow-rate around the optimal steady-state modulated using optimal forcing parameters (forcing amplitudes and phase difference, Figure E4.1) vs. dimensionless forcing frequency.

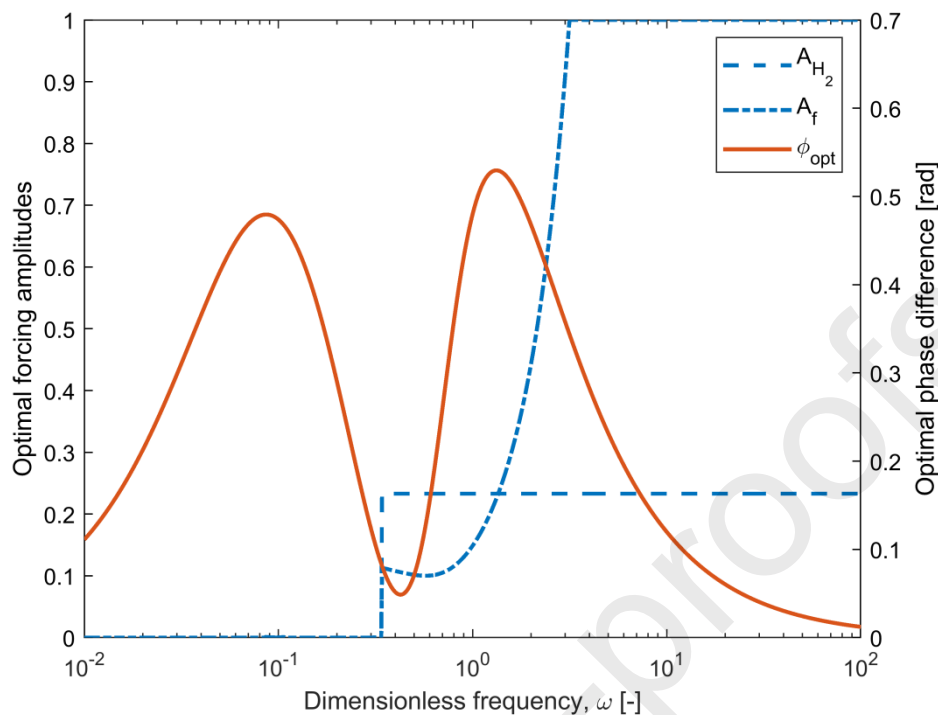


Figure E5.1 The optimal forcing parameters (forcing amplitudes and phase difference between the modulated inputs (partial pressure of H_2 and inlet volumetric flow-rate)) which maximize the normalized outlet molar flow-rate of methanol, vs. dimensionless forcing frequency

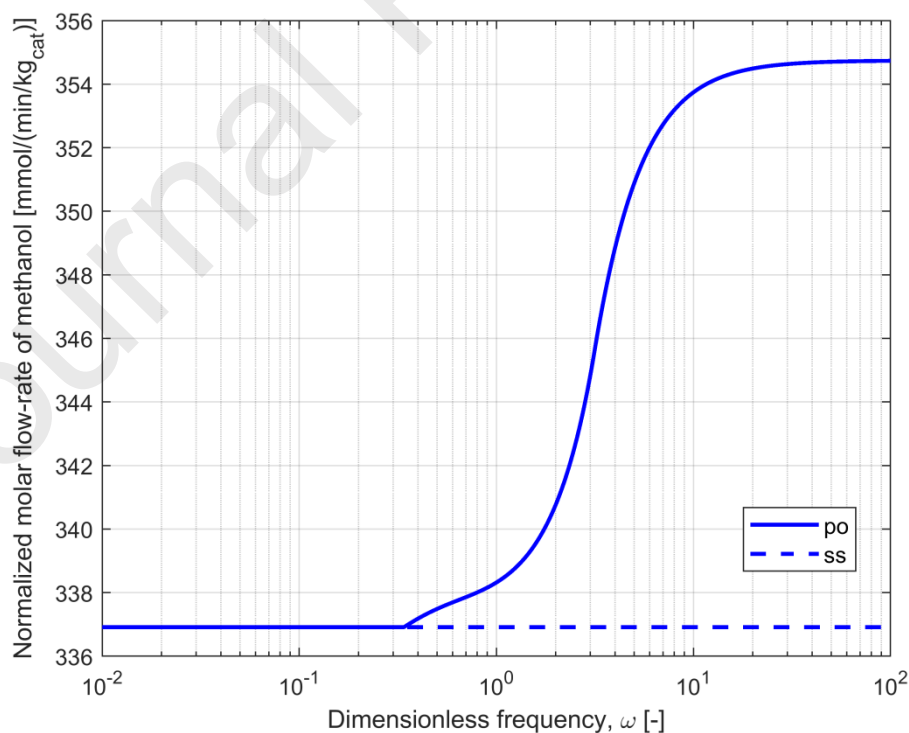


Figure E5.2 The normalized outlet molar flow-rate of methanol for steady-state and for simultaneous modulation of inlet partial pressure of H_2 and inlet volumetric flow-rate around the optimal steady-state modulated using optimal forcing parameters (forcing amplitudes and phase difference, Figure E5.1) vs. dimensionless forcing frequency.

Appendix F Multi-objective optimization

The inlet molar flow-rates of the reactants are defined as

$$y_{R,0} = \frac{p_{R,0}}{p}$$

where R represents the reactant (CO₂, CO or H₂)

Table F.1 Optimization variables with upper and lower boundary values (for operating in steady state regime No.1-3. and for periodic operation No. 1.-7.)

No.	Optimization variable	Boundary values
1.	Inlet molar fraction of CO ₂	0-1
2.	Inlet molar fraction of CO	0-1
3.	Inlet molar fraction of H ₂	0.5-0.85
4.	Forcing amplitude for CO inlet partial pressure modulation	0- 1
5.	Forcing amplitude for flow-rate modulation	0- 1
6.	Forcing frequency	0.01-100
7.	Phase difference between two modulated inputs	(-π)- π

Defined constraints used for Multi-Objective Optimization are:

1. Constraint which assures that carbon exists in feed steam

$$y_{CO_2,0} + y_{CO,0} \geq 0.01$$
2. Constraint which assures constant total pressure

$$y_{CO_2,0} + y_{CO,0} + y_{H_2,0} = 1 - 0.15$$
3. Constraints which bound the maximal possible forcing amplitudes (which assure the constant total pressure (for this case given in Appendix C)

Results of Multi-objective optimization are given in Tables F.2 and F.3.

Table F.2 Results of Multi-objective optimization for steady-state regime (values of objective functions and corresponding optimized variables)

No.	Objective functions		Optimization variables		
	$\dot{n}_{CH_3OH}^{norm}$ [mmol/min/kg(cat) _{cat}]	Yield of methanol based on tot C [-]	Mole fraction of CO ₂ in feed stream [-]	Mole fraction of CO in feed stream [-]	Mole fraction of H ₂ in feed stream [-]
1	417.29	0.4750	0.0351	0.2931	0.5218
2	416.37	0.4943	0.0333	0.2814	0.5353
3	413.39	0.5137	0.0315	0.2691	0.5494
4	407.87	0.5331	0.0296	0.2562	0.5642
5	399.1	0.5524	0.0277	0.2421	0.5801
6	385.97	0.5718	0.0257	0.2264	0.5978
7	366.52	0.5912	0.0236	0.2080	0.6184

δ (OP_OSS)	336.91	0.6106	0.0211	0.1850	0.6439
9	287.37	0.6300	0.0179	0.1525	0.6796

Table F.3 Results of Multi-objective optimization for forced periodic operation regime i.e. for the case of simultaneous modulation of CO and flow-rate optimization (values of objective functions and corresponding optimized variables)

No.	Objective functions		Optimization variables							
	$\dot{n}_{CH_3OH}^{norm}$ [mmol/min/kg(cat)]	Yield of methanol based on tot C [-]	Inlet variables (Mole fractions in feed stream of)			Forcing parameters				
			CO ₂ [-]	CO [-]	H ₂ [-]	Forcing amplitude of			Frequency ω [-]	Phase difference ϕ [rad]
						flow-rate [-]	CO [-]	N ₂ [-]		
1	487.16	0.5157	0.0359	0.2419	0.5722	1	0.6201	-1	100	0.0067
2	487.16	0.5157	0.0359	0.2419	0.5722	1	0.6201	-1	100	0.0067
3	487.16	0.5157	0.0359	0.2419	0.5722	1	0.6201	-1	100	0.0067
4	487.14	0.5182	0.0357	0.2405	0.5739	1	0.6238	-1	100	0.0068
5	486.79	0.5268	0.0347	0.2354	0.5799	1	0.6372	-1	100	0.0072
6	485.95	0.5355	0.0338	0.2302	0.5860	1	0.6516	-1	99.97	0.0076
7	484.57	0.5441	0.0328	0.2248	0.5923	1	0.6672	-1	99.99	0.0080
8	482.59	0.5527	0.0319	0.2192	0.5989	1	0.6842	-1	100	0.0086
9	479.91	0.5614	0.0309	0.2134	0.6057	1	0.7030	-1	100	0.0091
10	476.44	0.5670	0.0300	0.2072	0.6128	1	0.7238	-1	100	0.0098
11	472.06	0.5786	0.0290	0.2007	0.6203	1	0.7473	-1	99.99	0.0105
12	466.62	0.5873	0.0280	0.1938	0.6282	1	0.7741	-1	99.97	0.0115
13	459.9	0.5959	0.0270	0.1863	0.6367	1	0.8052	-1	99.88	0.0125
14	451.64	0.6045	0.0260	0.1781	0.6459	1	0.8421	-1	99.97	0.0138
15	441.5	0.6132	0.0248	0.1691	0.6561	1	0.8870	-1	99.98	0.0153
16 (OP1)	428.96	0.6218	0.0237	0.1590	0.6673	1	0.9432	-1	99.98	0.0173
17 (OP2)	411.22	0.6304	0.0218	0.1479	0.6803	1	1	- 0.9860	99.97	0.0294
18 (OP3)	376.82	0.6391	0.0201	0.1335	0.6964	1	1	- 0.8897	99.96	0.0369
19	328.4	0.6477	0.0186	0.1303	0.7011	1	1	- 0.8684	5.01	0.9000

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Menka Petkovska: Theoretical Investigation, Supervision, Reviewing, Conceptualization, Methodology, Reviewing Paper

Highlights

- Forced periodic operation as a potential for reactor improving performance
- Nonlinear frequency response method for evaluation of possible improvement
- Methanol synthesis in isothermal and isobaric lab-scale CSTR
- Simultaneous modulation of two inputs with optimal forcing parameters
- Significant improvement could be obtained

Figure captions

Figure 1. The optimal forcing parameters (forcing amplitudes and phase difference) which maximize the outlet molar flow-rate of methanol for simultaneous modulations of the CO partial pressure and flow-rate of the feed stream, vs. dimensionless forcing frequency

Figure 2. The ASO FRFs corresponding to the dimensionless methanol molar flow-rate for single input modulations of the inlet partial pressure of CO and inlet volumetric flow-rate and the cross ASO term vs. dimensionless forcing frequency

Figure 3. The normalized outlet molar flow-rate of methanol for optimal steady-state (ss) and periodic operation with simultaneous modulation of inlet partial pressure of CO and inlet volumetric flow-rate around the optimal steady-state with optimal forcing parameters (p_o) vs. dimensionless forcing frequency

Figure 4 The yields of methanol based on total carbon and based on hydrogen for optimal steady-state (ss) and periodic operation with simultaneous modulation of inlet partial pressure of CO and inlet volumetric flow-rate (p_o) around the optimal steady-state with optimal forcing parameters (Figure 1), vs. dimensionless forcing frequency

Figure 5 Pareto fronts for multi-objective optimization of Yield of methanol based on total C and normalized methanol production, for steady state (crosses) and periodic operation (circles)

Figure E1.1 The optimal forcing parameters (forcing amplitudes and phase difference between the modulated inputs (partial pressures of CO₂ and CO)) which maximize the normalized outlet molar flow-rate of methanol, vs. dimensionless forcing frequency

Figure E1.2 The normalized outlet molar flow-rate of methanol for steady-state and for simultaneous modulation of inlet partial pressures of CO₂ and CO around the optimal steady-state modulated using optimal forcing parameters (forcing amplitudes and phase difference, Figure E1.1) vs. dimensionless forcing frequency.

Figure E2.1 The optimal forcing parameters (forcing amplitudes and phase difference between the modulated inputs (partial pressures of CO₂ and H₂)) which maximize the normalized outlet molar flow-rate of methanol, vs. dimensionless forcing frequency

Figure E2.2 The normalized outlet molar flow-rate of methanol for steady-state and for simultaneous modulation of inlet partial pressures of CO₂ and H₂ around the optimal steady-state modulated using optimal forcing parameters (forcing amplitudes and phase difference, Figure E2.1) vs. dimensionless forcing frequency.

Figure E3.1 The optimal forcing parameters (forcing amplitudes and phase difference between the modulated inputs (partial pressures of CO and H₂)) which maximize the normalized outlet molar flow-rate of methanol, vs. dimensionless forcing frequency

Figure E3.2 The normalized outlet molar flow-rate of methanol for steady-state and for simultaneous modulation of inlet partial pressures of CO and H₂ around the optimal steady-state modulated using optimal forcing parameters (forcing amplitudes and phase difference, Figure E3.1) vs. dimensionless forcing frequency.

Figure E4.1 The optimal forcing parameters (forcing amplitudes and phase difference between the modulated inputs (partial pressure of CO₂ and inlet volumetric flow-rate)) which maximize the normalized outlet molar flow-rate of methanol, vs. dimensionless forcing frequency

Figure E4.2 The normalized outlet molar flow-rate of methanol for steady-state and for simultaneous modulation of inlet partial pressure of CO₂ and inlet volumetric flow-rate around the optimal steady-state modulated using optimal forcing parameters (forcing amplitudes and phase difference, Figure E4.1) vs. dimensionless forcing frequency.

Figure E5.1 The optimal forcing parameters (forcing amplitudes and phase difference between the modulated inputs (partial pressure of H₂ and inlet volumetric flow-rate)) which maximize the normalized outlet molar flow-rate of methanol, vs. dimensionless forcing frequency

Figure E5.2 The normalized outlet molar flow-rate of methanol for steady-state and for simultaneous modulation of inlet partial pressure of H₂ and inlet volumetric flow-rate around the optimal steady-state modulated using optimal forcing parameters (forcing amplitudes and phase difference, Figure E5.1) vs. dimensionless forcing frequency.

Tables

Table 1 The definitions of the yield of methanol based on total carbon and based on hydrogen for simultaneous modulation of the partial pressure of one reactant and the inlet volumetric flow-rate

Modulated inputs x and z	Yield of methanol based on total carbon	Yield of methanol based on hydrogen
Inlet partial pressure of CO_2 (x) and total inlet volumetric flow-rate (z)	$(Y_{\text{CH}_3\text{OH}}^{\text{totC}})_{PO} = \frac{(\dot{n}_{\text{CH}_3\text{OH}})_{\text{mean}}}{(\dot{n}_{\text{CO}_2})_{0,\text{mean}} + (\dot{n}_{\text{CO}})_{0,s}}$	$(Y_{\text{CH}_3\text{OH}}^{\text{H}_2})_{PO} = 2 \frac{(\dot{n}_{\text{CH}_3\text{OH}})_{\text{mean}}}{(\dot{n}_{\text{H}_2})_{0,s}}$
Inlet partial pressure of CO (x) and total inlet volumetric flow-rate (z)	$(Y_{\text{CH}_3\text{OH}}^{\text{totC}})_{PO} = \frac{(\dot{n}_{\text{CH}_3\text{OH}})_{\text{mean}}}{(\dot{n}_{\text{CO}_2})_{0,s} + (\dot{n}_{\text{CO}})_{0,\text{mean}}}$	
Inlet partial pressure of H_2 (x) and total inlet volumetric flow-rate (z)	$(Y_{\text{CH}_3\text{OH}}^{\text{totC}})_{PO} = \frac{(\dot{n}_{\text{CH}_3\text{OH}})_{\text{mean}}}{(\dot{n}_{\text{CO}_2} + \dot{n}_{\text{CO}})_{0,s}}$	$(Y_{\text{CH}_3\text{OH}}^{\text{H}_2})_{PO} = 2 \frac{(\dot{n}_{\text{CH}_3\text{OH}})_{\text{mean}}}{(\dot{n}_{\text{H}_2})_{0,\text{mean}}}$

Table 2. The best results which can be obtained by simultaneous modulations of two inputs

Modulated inputs x and z	Maximal increase of $\dot{n}_{CH_3OH}^{norm}$	Change of $Y_{CH_3OH}^{totC}$	Change of $Y_{CH_3OH}^{H_2}$	Optimal forcing parameters			
				A_x (-)	A_z (-)	ω (-)	φ (rad)
Inlet partial pressures of CO_2 (x) and CO (z)	0.15 %	+0.15%	+0.15 %	1	0.59	1.47	-0.83
Inlet partial pressures of CO_2 (x) and H_2 (z)	0.22 %	+0.22 %	+0.22 %	0.36	0.22	1.27	-0.49
Inlet partial pressures of CO (x) and H_2 (z)	0.45%	+0.45 %	+0.45 %	0.27	0.16	0.01	-0.03
Inlet partial pressure of CO_2 (x) and total inlet volumetric flow-rate (z)	4.71 %	-0.39 %	+4.71 %	1	1	>30	0.004
Inlet partial pressure of CO (x) and total inlet volumetric flow-rate (z)	33.51 %	-2.12 %	+33.51 %	0.81	1	>30	0.006
Inlet partial pressure of H_2 (x) and total inlet volumetric flow-rate (z)	5.29 %	+5.29 %	-5.71%	0.23	1	>30	0.01

Table 3 The normalized outlet molar flow rate of methanol and yield of methanol based on total carbon for the selected points from the Pareto fronts (Figure 5), based on NFR method and based on numerical simulation

Operating point	Normalized outlet molar flow-rate of methanol [mmol/min/kg _{cat}]		Yield of methanol based on total carbon [%]		Relative change of normalized outlet molar flow-rate of methanol		Relative change of yield of methanol based on total carbon	
	NFR	Num.Sim.	NFR	Num.Sim.	NFR	Num.Sim.	NFR	Num.Sim.
OP_OSS	336.9		61.06		/		/	
OP1	428.96	422.04	62.18	61.18	+27.33%	+25.27%	+1.83%	+0.20%
OP2	411.20	405.34	63.04	62.15	+22.05%	+20.31%	+3.24%	+1.79%
OP3	376.80	373.05	63.91	63.27	+11.84%	+10.73%	+4.67%	+3.62%

Table A1 The definitions of dimensionless variables

Dimensionless variables	Definitions
Partial pressure of component i	$P_i = \frac{p_i - p_{i,s}}{p_{i,s}}, i = 1,..6$
Partial pressure of component i in the inlet stream	$P_{i,0} = \frac{p_{i,0} - p_{i0,s}}{p_{i0,s}}, i = 1,..6$
Time	$\tau = \frac{t}{\tau_{0,s}} = \frac{t}{V_G/\dot{V}_{0,s}}$
Fraction of reduced centers on the catalyst surface	$\Phi = \frac{\phi - \phi_s}{\phi_s}$
Volumetric flow-rate of the inlet stream	$v_0 = \frac{\dot{V}_0 - \dot{V}_{0,s}}{\dot{V}_{0,s}}$
Volumetric flow-rate of the outlet stream	$v = \frac{\dot{V} - \dot{V}_s}{\dot{V}_s}$
Frequency	$\omega = \omega_d \tau_{0,s}$

Table F.1 Optimization variables with upper and lower boundary values (for operating in steady state regime No.1-3. and for periodic operation No. 1.-7.)

No.	Optimization variable	Boundary values
1.	Inlet molar fraction of CO ₂	0-1
2.	Inlet molar fraction of CO	0-1
3.	Inlet molar fraction of H ₂	0.5-0.85
4.	Forcing amplitude for CO inlet partial pressure modulation	0- 1
5.	Forcing amplitude for flow-rate modulation	0- 1
6.	Forcing frequency	0.01-100
7.	Phase difference between two modulated inputs	(-π)- π

Table F.2 Results of multi-objective optimization for steady-state regime (values of objective functions and corresponding optimized variables)

No.	Objective functions		Optimization variables		
	$\dot{n}_{CH_3OH}^{norm}$ [mmol/min/kg(cat) _{cat}]	Yield of methanol based on tot C [-]	Mole fraction of CO ₂ in feed stream [-]	Mole fraction of CO in feed stream [-]	Mole fraction of H ₂ in feed stream [-]
1	417.29	0.4750	0.0351	0.2931	0.5218
2	416.37	0.4943	0.0333	0.2814	0.5353
3	413.39	0.5137	0.0315	0.2691	0.5494
4	407.87	0.5331	0.0296	0.2562	0.5642
5	399.1	0.5524	0.0277	0.2421	0.5801
6	385.97	0.5718	0.0257	0.2264	0.5978
7	366.52	0.5912	0.0236	0.2080	0.6184
8 (OP_OSS)	336.91	0.6106	0.0211	0.1850	0.6439
9	287.37	0.6300	0.0179	0.1525	0.6796

Table F.5 Results of multi-objective optimization for forced periodic operation regime i.e. for the case of simultaneous modulation of CO and flow-rate optimization (values of objective functions and corresponding optimized variables)

No.	Objective functions		Optimization variables							
	$\dot{n}_{CH_3OH}^{norm}$ [mmol/min/kg(cat)]	Yield of methanol based on tot C [-]	Inlet variables (Mole fractions in feed stream of)			Forcing parameters				
			CO ₂ [-]	CO [-]	H ₂ [-]	Forcing amplitude of			Frequency ω [-]	Phase difference ϕ [rad]
						flow-rate [-]	CO [-]	N ₂ [-]		
1	487.16	0.5157	0.0359	0.2419	0.5722	1	0.6201	-1	100	0.0067
2	487.16	0.5157	0.0359	0.2419	0.5722	1	0.6201	-1	100	0.0067
3	487.16	0.5157	0.0359	0.2419	0.5722	1	0.6201	-1	100	0.0067
4	487.14	0.5182	0.0357	0.2405	0.5739	1	0.6238	-1	100	0.0068
5	486.79	0.5268	0.0347	0.2354	0.5799	1	0.6372	-1	100	0.0072
6	485.95	0.5355	0.0338	0.2302	0.5860	1	0.6516	-1	99.97	0.0076
7	484.57	0.5441	0.0328	0.2248	0.5923	1	0.6672	-1	99.99	0.0080
8	482.59	0.5527	0.0319	0.2192	0.5989	1	0.6842	-1	100	0.0086
9	479.91	0.5614	0.0309	0.2134	0.6057	1	0.7030	-1	100	0.0091
10	476.44	0.5670	0.0300	0.2072	0.6128	1	0.7238	-1	100	0.0098
11	472.06	0.5786	0.0290	0.2007	0.6203	1	0.7473	-1	99.99	0.0105
12	466.62	0.5873	0.0280	0.1938	0.6282	1	0.7741	-1	99.97	0.0115
13	459.9	0.5959	0.0270	0.1863	0.6367	1	0.8052	-1	99.88	0.0125
14	451.64	0.6045	0.0260	0.1781	0.6459	1	0.8421	-1	99.97	0.0138
15	441.5	0.6132	0.0248	0.1691	0.6561	1	0.8870	-1	99.98	0.0153
16 (OP1)	428.96	0.6218	0.0237	0.1590	0.6673	1	0.9432	-1	99.98	0.0173
17 (OP2)	411.22	0.6304	0.0218	0.1479	0.6803	1	1	-0.9860	99.97	0.0294
18 (OP3)	376.82	0.6391	0.0201	0.1335	0.6964	1	1	-0.8897	99.96	0.0369
19	328.4	0.6477	0.0186	0.1303	0.7011	1	1	-0.8684	5.01	0.9000

Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

□ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

