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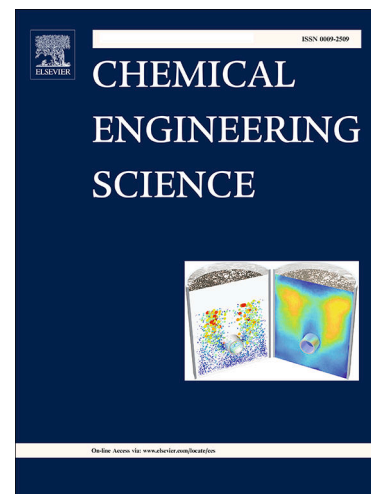
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Forced periodic operations of a chemical reactor for methanol synthesis – the search for the best scenario based on Nonlinear Frequency Response Method.

Part I Single input modulations

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Abstract

In this two-part paper a comprehensive study of the potential to improve performance criteria of a methanol synthesis reactor through forced periodical operations is presented. The study uses the Nonlinear Frequency Response method, a powerful analytical and approximate tool which gives an answer whether and under which conditions certain periodic operation would lead to improvement of process performance. To demonstrate the method, isothermal and isobaric methanol synthesis in a lab-scale CSTR is considered. In Part I, the analysis is performed for single input modulations. Partial pressures of each reactant in the feed stream and the total inlet volumetric flow-rate are considered as possible modulated inputs. The results show that modulations of single inputs essentially do not provide potential for significant improvements. In Part II, the study will be extended to analysis of periodic operations with simultaneous modulations of two inputs and conditions offering significant performance enhancements will be identified.

Keywords: Forced periodic operations, Methanol synthesis, Nonlinear frequency response, Process improvement, Single input modulations

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Operating processes in forced periodic mode is one way of Process Intensification (PI), which represents a set of innovative principles in process or equipment design leading to significant process improvements (*Van Gerven and Stankiewicz, 2009*). The term forced periodic operation refers to a case when one or more inputs of a system are periodically modulated around their corresponding steady-state value(s) (*Petkovska and Seidel-Morgenstern, 2013*). In chemical engineering, the standard way to design and operate continuous processes is based on the optimal steady-state design and a control system which keeps all outputs as close as possible to their optimal steady-state values. Nevertheless, it is a known fact that perturbing the system periodically can sometimes result in better performance than the optimal steady-state operation (*Silveston and Hudgins, 2013*). Forced periodic operations of chemical reactors have been of interest for many research groups worldwide, involved in numerous theoretical, numerical or experimental studies (*Armstrong and Teixeira, 2020; Bailey 1973; Douglas and Rippin 1966; Douglas 1967; Douglas 1972; Renken 1972; Schadlich et al. 1983; Silveston 1987; 1998; Silveston and Hudgins, 2013; Sterman and Ydstie 1990a, 1990b, 1991; Chen et al., 1994*). These studies showed that the time-average indicators of chemical reactor performance, such as conversion, selectivity, production rates, productivity, could be improved by implementing forced periodic operations.

Although the physical reasons can be different, it could be said that the process improvement owing to forced periodic operations is always a consequence of process nonlinearity (*Petkovska and Seidel-Morgenstern, 2013*). For simple cases with only one nonlinear effect, it is usually explained based on the convexity of the nonlinear term. Nevertheless, in the cases such as investigated in this work, with a heterogeneously catalysed complex reaction scheme, there are a large number of coupled nonlinear effects, which do not just add up, but also have combined effects. The contributions of these nonlinear effects and their combinations change from one steady-state to another. Also, it is important to know that the resulting performances could be improved, deteriorated or unchanged, in comparison to the steady-state performance (*Douglas and Rippin, 1966*). The specific response to forced periodic input modulations of the system considered in our study, for the heterogeneously catalysed synthesis of methanol carried out in a well-mixed isothermal reactor (CSTR type), is due to a number of nonlinear phenomena and time scales. For a complex nonlinear system such as the one investigated in our work, a simple interpretation of the lack of improvement for single input modulation cannot be given with any scientific certainty.

Considering that there are many ways to apply forced periodic operations, e.g.: different inputs which can be modulated, different shapes of the modulated input(s), different values of the forcing parameters (amplitude(s), frequency, phase difference, etc.), it is a challenging task to find the mode which would lead to the highest improvement (*Parulekar, 2003; Silveston et al., 1995*). It is therefore of economic importance to carry out theoretical studies for assessing the effects of forced periodic operations of chemical processes, before any experimental studies (*Chen et al., 1994*). In our previous work (*Marković et al., 2008; Nikolić, 2016; Petkovska and Seidel-Morgenstern, 2013; Petkovska et al., 2018*) we introduced the Nonlinear Frequency Response (NFR) method as a reliable analytical tool for evaluating possible improvements and finding the best forcing parameters (*Nikolić, 2016; Živković et al., 2020b*).

The Nonlinear Frequency Response (NFR) method is based on the analysis of the frequency response of weakly nonlinear systems (*Nikolić, 2016; Petkovska and Seidel-Morgenstern, 2013; Petkovska et al., 2018*). It is a general, mathematically based theoretical and approximate method which answers the following questions (*Nikolić, 2016; Petkovska and Seidel-Morgenstern, 2013; Petkovska et al., 2018*):

- Can the process performance be improved by periodic input modulations or not?
- Which input(s) should be periodically modulated in order to improve the process performance?
- Which forcing parameters (amplitude(s) and frequency of the input modulations, as well as the phase difference in the case of simultaneous modulation of two inputs) should be used?
- What would be the extent of the possible improvement?

Until now, the NFR method has been applied for studying forced periodic operations of several different reactor systems. Simple irreversible n^{th} order reactions were considered in continuous stirred tank reactor (CSTR) (*Marković et al., 2008; Nikolić-Paunić and Petkovska, 2013; Nikolić and Petkovska, 2016; Nikolić et al., 2014a, 2014b, 2015; Nikolić, 2016; Nikolić et al., 2016a, 2016b, 2020; Petkovska et al., 2010;*), plug flow reactor (PFR) and dispersed flow tubular reactor (DFTR) (*Marković et al., 2008*). Different thermal regimes were studied: isothermal (*Marković et al., 2008; Nikolić-Paunić and Petkovska, 2013; Nikolić and Petkovska, 2016; Petkovska et al., 2010*), general non-isothermal (*Nikolić-Paunić and Petkovska, 2013; Nikolić et al., 2014a, 2014b, 2015, 2016*) and adiabatic (*Nikolić, 2016; Nikolić et al., 2016b; Nikolić et al., 2020*). Single input modulation of different input shapes: general (*Nikolić and Petkovska, 2016; Nikolić et al., 2020*), sinusoidal (*Marković et al., 2008; Nikolić-Paunić and Petkovska, 2013; Nikolić and Petkovska, 2016; Nikolić et al., 2014a, 2014b, 2015; Nikolić, 2016; Nikolić et al., 2016a, 2016b;*

Petkovska et al., 2010;), square-wave (*Nikolić and Petkovska*, 2016; *Nikolić et al.*, 2020), for inlet reactant concentration (*Marković et al.*, 2008; *Nikolić-Paunić and Petkovska*, 2013; *Nikolić and Petkovska*, 2016; *Nikolić et al.*, 2014a, 2014b, 2015; *Nikolić*, 2016; *Petkovska and Seidel-Morgenstern*, 2013; *Petkovska et al.*, 2010;), flow-rate (*Nikolić-Paunić and Petkovska*, 2013; *Nikolić*, 2016; *Nikolić et al.*, 2016a, 2016b), inlet temperature and temperature of the cooling/heating medium modulation (*Nikolić et al.*, 2014b, 2015), as well as simultaneous modulation of two inputs (*Nikolić-Paunić and Petkovska*, 2013; *Nikolić et al.*, 2015; 2016a, 2016b, 2020; *Nikolić*, 2016) were considered. The NFR method was also used for analysis of forced periodic operation for Sabatier reaction (*Currie et al.*, 2018).

Recently, the results of NFR analysis of forced periodically operated adiabatic reactor in which hydrolysis of acetic anhydride occurs for simultaneous modulation of two inputs, inlet concentration and flow-rate (*Nikolić*, 2016; *Nikolić et al.*, 2016b), have been experimentally confirmed (*Felischak*, 2020; *Felischak et al.*, 2021).

Also recently, the NFR method was further advanced into the so-called computer-aided Nonlinear Frequency Response (cNFR) method, by developing a user friendly software application for implementing the NFR method, making its application much easier (*Živković et al.*, 2020a). Another recent development was establishing and implementing a new methodology for optimizing forced periodic operations, combining the cNFR approach and multi-objective optimization the one step optimization (*Živković et al.*, 2020b). The main advantage of this approach is that using the NFR approach leads to objective functions which are defined as algebraic expressions of all optimization parameters, which drastically shortens the needed computing time. Also, the optimization is performed in a single step, meaning that all optimization parameters: the steady state point around which the forced periodic operation should be performed and the forcing parameters (frequency, amplitudes and phase difference) are determined at the same time.

In this paper, the NFR method is used for analysing the potential of forced periodical operations of a chemical reactor in which the catalytic methanol synthesis from synthesis gas occurs. Methanol is an important basic chemical which is produced on large scale in chemical industry and used as starting material for production of paraffins, olefins and other organic chemicals, as well as fuel or fuel additives (*Fiedler et al.*, 2000). The important fact is that methanol can be used as an energy carrier (*Olah*, 2004). Excess electrical energy from renewable resources (wind or solar) can be used to generate hydrogen which, combined with CO and/or CO₂ (from biomass or agriculture waste streams) in the presence of a suitable catalyst, can be converted into methanol as a medium for chemical energy storage (*Larsten and Sonderberg*, 2013; *Martin*,

2016; Olan, 2005; Kaeuchle et al., 2016; Seidat et al., 2018). However, methanol production for energy storage using renewable resources deals with unavoidable fluctuations in the supply of hydrogen, CO and/or CO₂. In some cases, these fluctuations could lead to improvement of methanol production. Previous experimental investigations showed that significant improvement in methanol production could be achieved by forced periodic operations (Chanchlani et al., 1992, 1994; Silveston, 1987). Experimental results presented in (Chanchlani et al., 1992, 1994) showed that the improvement of about 35% increase of methanol production relative to steady state is possible (when H₂ and CO₂ in the feed stream are periodically modulated) for an isothermal packed bed reactor when Cu/ZnO and Cu/ZnO/Al₂O₃ were used as catalyst at 225°C and 2.86 MPa.

The NFR method which is used in this work is essentially a mathematical tool which can be used for evaluating forced periodic operations of chemical reactors, as well as any other physical system, without the need to understand the physical reasons for the process improvement or deterioration. As such, this method is very useful to study complex systems, such as the one analysed in our work.

In this two-part manuscript we use the NFR method to perform a systematic search for the best periodic process which would intensify the process of methanol synthesis. In Part I of this work, the NFR analysis is performed for cases of single input modulations. In Part II, the cases of simultaneous modulations of two inputs will be analysed.

2 Nonlinear frequency response method for single input modulations

By definition, frequency response is the quasi-stationary response of a stable system to a periodic (sinusoidal or co-sinusoidal) input modulation around its steady-state value (Douglas, 1972). Frequency response is obtained when the transient response becomes negligible (theoretically for infinite time). For linear systems, frequency response is a periodic function of the same shape and frequency as the input function, but with different amplitude, with a phase shift and the mean value which is equal to the steady-state one.

On the other hand, frequency response of a nonlinear system is a complex periodic function. For a weakly nonlinear system (Weiner and Spina, 1980), if the input x is modulated in a cosine-wave form, with amplitude A and frequency ω , around a steady-state value x_s :

$$x(t) = x_s + A \cos(\omega t) \quad (1)$$

after long enough (theoretically infinite) time, the output of the system would contain the basic harmonic (y) which has the same frequency as the input modulation, a non-periodic (the so-

called DC) component (y_{DC}) and an infinite number of higher harmonics (y_{II}, y_{III}, \dots) (Douglas, 1972; Weiner and Spina, 1980):

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

where $y(t)$ represents the output, y_s its steady-state value, while B_i and φ_i are the amplitude and the phase shift of the i -th harmonic of the output, respectively.

One convenient approach of analysing the frequency response of weakly nonlinear systems is the concept of higher order frequency response functions (FRFs). This approach is based on Volterra series and the generalized Fourier transform (Nikolić, 2016; Petkovska and Seidel-Morgenstern, 2013; Petkovska et al., 2018; Weiner and Spina, 1980). Using this approach, the nonlinear model of a weakly nonlinear system can be replaced with a series of FRFs of different orders: $G_{y,x}^{(1)}(\omega_1)$, $G_{y,x,x}^{(2)}(\omega_1, \omega_2), \dots, G_{y,x,\dots,x}^{(n)}(\omega_1, \dots, \omega_n), \dots$. These FRFs are directly related with the DC component and different harmonics of the frequency response (Nikolić, 2016; Petkovska and Seidel-Morgenstern, 2013; Petkovska et al., 2018).

This method can be applied on weakly nonlinear, stable systems, without multiple steady-states, which can be represented with convergent Volterra series (Nikolić, 2016; Petkovska and Seidel-Morgenstern, 2013; Živković et al., 2020a).

In order to evaluate a forced periodic operation around a steady-state point, only the time-average value of the periodic steady-state response is of interest. Using equation (2) it is easily concluded that the DC (non-periodic) component of the frequency response equals the difference between the time-average and the steady-state value of the output. Using the concept of higher order FRFs, the DC component can be written as the following infinite series (Weiner and Spina, 1980):

$$y_{DC} = 2\left(\frac{A}{2}\right)^2 G_{y,x,x}^{(2)}(\omega, -\omega) + 6\left(\frac{A}{2}\right)^4 G_{y,x,x,x,x}^{(4)}(\omega, \omega, -\omega, -\omega) + \dots \quad (3)$$

In equation (3) $G_{y,x,x}^{(2)}(\omega, -\omega)$ is the asymmetrical second order FRF, $G_{y,x,x,x,x}^{(4)}(\omega, \omega, -\omega, -\omega)$ the asymmetrical fourth order FRF, etc.

For weakly nonlinear systems, the significance of different terms in equation (3) decreases with the increase of the corresponding FRF order. As a consequence, the DC component can be approximated with its dominant term, which is proportional to the asymmetrical second order function and the square of the input amplitude (Marković et al., 2008):

$$y_{DC} \approx 2\left(\frac{A}{2}\right)^2 G_{y,x,x}^{(2)}(\omega, -\omega) \quad (4)$$

Equation (4) is the foundation of the NFR method for evaluating periodic operations with one modulated input. The sign of $G_{y,x,x}^{(2)}(\omega, -\omega)$ determines whether the periodic operation would be superior to the corresponding steady-state one, while its magnitude determines the possible improvement.

The FRFs of interest are derived starting from a nonlinear dynamic model of the investigated system. The derivation procedure of the FRFs is standard and it can be found in our previous publications (Marković *et al.*, 2008; Nikolić-Paunić and Petkovska, 2013; Nikolić *et al.*, 2014a, 2014b, 2015; Nikolić, 2016; Nikolić and Petkovska, 2016; Nikolić *et al.*, 2016a, 2016b, 2020; Petkovska *et al.*, 2010; Petkovska and Seidel-Morgenstern, 2013; Petkovska *et al.*, 2018).

3 Methanol synthesis reaction.

In this paper the focus is on the production of methanol from syngas (a mixture of CO, CO₂ and H₂) using a commercial Cu/ZnO/Al₂O₃ catalyst. The overall reaction mechanism assumes the reactions of CO and CO₂ hydrogenation:



and the reverse water-gas shift reaction (RWGS):



(see e.g. Graaf *et al.* (1988)).

Kinetic model

The NFR analysis presented in this work is based on a mathematical model of the reactor incorporating a reaction kinetic model of methanol synthesis presented in Seidel *et al.* (2018, 2020), which showed reasonable agreement with steady state and dynamic experimental data from the Ph.D. Thesis of Vollbrecht (2007). The model is based on a Langmuir-Hinshelwood mechanism which implies three main steps: adsorption of the reactants on the catalyst surface, reaction of the adsorbed species and desorption of the reaction products. Adsorption and desorption are assumed to be in equilibrium. Further, the model assumes three different active centres on the catalytic surface, i.e.

- oxidized surface centres (⊙)
- reduced surface centres (*)
- active surface centres for heterolytic decomposition of hydrogen (⊗).

The fraction of the reduced surface centres was denoted by ϕ . Following Ovesen et al. (1997), changes in the catalyst morphology due to the oxidizing influence of CO_2 and H_2O and the reducing influence of CO and H_2 were also taken into account and modelled with the following dynamic equation:

$$\frac{d\phi}{dt} = k_1^+ \left(y_{\text{CO}}(\phi_{\text{max}} - \phi) - \frac{1}{K_1} y_{\text{CO}_2} \phi \right) + k_2^+ \left(y_{\text{H}_2}(\phi_{\text{max}} - \phi) - \frac{1}{K_2} y_{\text{H}_2\text{O}} \phi \right) \quad (8)$$

In equation (8) it is assumed that the maximal value of the fraction of the reduced centres is limited to ϕ_{max} . In the current study the maximal value $\phi_{\text{max}} = 0.9$ was used (Seidel et al. 2020).

The equilibrium constants

$$K_1 = \frac{k_1^+}{k_1^-} = \left(\frac{-\Delta G_1}{RT} \right) \quad (9)$$

$$K_2 = \frac{k_2^+}{k_2^-} = \left(\frac{-\Delta G_2}{RT} \right) \quad (10)$$

were fitted separately to the steady state data (Seidel et al. 2018), whereas the dynamic rate constants k_1^+ , k_2^+ were fitted to dynamic data (Seidel et al. 2018).

Finally, also an ideal gas phase was assumed. Catalyst deactivation, and further side reactions were neglected. With all of these assumptions the following lumped reaction rate expression were obtained (Seidel et al. 2018, 2020):

- For the reaction of CO hydrogenation (Eq. (5))

$$r_1 = (1 - \phi) k_1 \left(p_{\text{CO}} p_{\text{H}_2}^2 - \frac{1}{K_{P1}} p_{\text{CH}_3\text{OH}} \right) \theta^{\ominus} \theta^{\otimes 4} \quad (11)$$

- For the reaction of CO_2 hydrogenation (Eq. (6))

$$r_2 = \phi^2 k_2 \left(p_{\text{CO}_2} p_{\text{H}_2}^2 - \frac{1}{K_{P2}} \frac{p_{\text{CH}_3\text{OH}} p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \right) \theta^{*2} \theta^{\otimes 4} \quad (12)$$

- For the reverse water-gas shift reaction (RWGS) (Eq. (7))

$$r_3 = \phi(1 - \phi)^{-1} k_3 \left(p_{\text{CO}_2} - \frac{1}{K_{P3}} \frac{p_{\text{CO}} p_{\text{H}_2\text{O}}}{p_{\text{H}_2}} \right) \theta^{*} \theta^{\ominus} \quad (13)$$

The corresponding relative amounts of free active surface centres are given with the following expressions (Seidel et al., 2018):

$$\theta^{\ominus} = \left(1 + K_{\text{CH}_3\text{OH}}^{\ominus} p_{\text{CH}_3\text{OH}} + K_{\text{CO}_2}^{\ominus} p_{\text{CO}_2} + K_{\text{CO}}^{\ominus} p_{\text{CO}} \right)^{-1} \quad (14)$$

$$\theta^{\otimes} = \left(1 + \sqrt{K_{\text{H}_2} p_{\text{H}_2}} \right)^{-1} \quad (15)$$

$$\theta^{*} = \left(1 + K_{\text{CH}_3\text{OH}}^{*} p_{\text{CH}_3\text{OH}} + K_{\text{CO}_2}^{*} p_{\text{CO}_2} + K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}} + \frac{K_{\text{O}} K_{\text{H}_2\text{O}} p_{\text{H}_2\text{O}}}{K_{\text{H}_2} p_{\text{H}_2}} \right)^{-1} \quad (16)$$

The reaction rate constants k_j were determined based on the modified Arrhenius equation:

$$k_j = A_{k,j} \exp\left(-B_j\left(\frac{T_{ref}}{T} - 1\right)\right), j = 1, 2, 3 \quad (17)$$

with the reference temperature $T_{ref}=523.15$ K (Seidel *et al.*, 2018; Vollbrecht, 2007) and $j=1,2,3$ corresponding to CO hydrogenation, CO₂ hydrogenation and reversed water-gas shift reaction, respectively.

The equilibrium constants of the chemical reactions defined by equations (5-7), as functions of temperature (Vollbrecht, 2007), are given in Appendix A.

The values of the kinetic parameters used in this paper are given in Table 1. These values are somewhat different than the ones reported in our previous publications (Seidel *et al.* 2018, 2020), as they have been refitted to the experimental data of Vollbrecht (2007), by using $\phi \leq 0.9$ in the constraint set of the nonlinear least squares problem. In Table 1, the specific amount of surface centres q_{sat} is also given.

The zero values of some parameters which are given in Table 1 (i.e. $K_{CH_3OH}^*$, K_{H_2O} , K_O , $K_{CH_3OH}^\ominus$, $K_{CO_2}^\ominus$) are an outcome of parameter identification for the specific experimental data considered. These parameters have a physical meaning in the original mechanism assumed and the general form of the kinetic model is provided by presenting also the terms in which these parameters appear.

For more details of the kinetic model the reader is referred to Seidel *et al.* (2018).

Table 1. Parameters and constant used in kinetic model

Parameter	Unit	Value
ϕ_{max}	-	0.9
$A_{k,CO}$	mol /kg _{cat} /s /bar ³	0.00673
B_{CO}	-	26.4549
A_{k,CO_2}	mol /kg _{cat} /s /bar ³	0.0430
B_{CO_2}	-	1.5308
$A_{k,RWGS}$	mol/kg _{cat} /s /bar	0.0117
B_{RWGS}	-	15.6154
$\sqrt{K_{H_2}}$	bar ^{-1/2}	1.1064
$K_{CH_3OH}^*$	bar ⁻¹	0
K_{H_2O}	bar ⁻¹	0
K_O	-	0
K_{CO}	bar ⁻¹	0.1497
$K_{CH_3OH}^\ominus$	bar ⁻¹	0
$K_{CO_2}^*$	bar ⁻¹	0.0629
$K_{CO_2}^\ominus$	bar ⁻¹	0
ΔG_1	kJ/mol	0.336
ΔG_2	kJ/mol	21.841
k_1^+	s ⁻¹	79.174 10 ⁻⁴
k_2^+	s ⁻¹	1.88 10 ⁻⁵
q_{sat}	mol/kg _{cat}	0.98

4. Application of the NFR method to evaluate the potential of single input forced periodic operation of methanol synthesis reactor

In this Section, the NFR method is applied for the analysis and evaluation of possible improvement of methanol production, for forced periodic operations with single input modulations. The analysis is performed for a laboratory-scale uniformly mixed reactor such as the Micro-Berty reactor, which was used for kinetic measurements (*Vollbrecht, 2007*) on which the kinetic model used in this study is based. The Micro-Berty reactor, often used for kinetic measurements for heterogeneously catalysed reactions, was designed in such a way to achieve very good mixing and assure gradientless or uniform conditions in the whole reactor volume (*Berty 1974; Warnecke et al., 2020*). The residence time distribution was evaluated by *Vollbrecht (PhD Thesis, 2007)* and indeed found to be very close to exponential. Therefore, the usage of the simple CSTR reactor model, which assumes perfect mixing, is justified. The theoretical results present below will also serve as a basis for a planned later experimental validation using this same reactor type.

4.1. Mathematical model

The mathematical model of the catalytic reactor for methanol synthesis is based on the following assumptions (the assumptions listed here are consistent with the assumptions used for the kinetic model presented above):

- The reaction 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 with the maximal adsorption capacity q_{sat} (Table 1),
- The catalyst deactivation can be neglected,
- The reaction mechanism is defined with equations (5-7) and all other reactions can be neglected.

The Micro-Berty reactor can be modelled as a continuous stirred tank reactor (CSTR). As stated above, the reactor system in which methanol synthesis occurs is established for the case when total pressure (p_{tot}) is constant

$$p_{tot} = \sum_{i=1}^6 p_i = const \quad (18)$$

Considering that during methanol synthesis the total number of moles is decreasing and that the total pressure is held constant, the volumetric outlet flow-rate is also changing.

The mathematical model of the analysed system can be described with the following equations:

- material balances for each component i

$$V_G \frac{dp_i}{dt} + m_{cat} q_{sat} RT \sum_{l=1}^6 \frac{\partial \theta_l dp_l}{\partial p_i dt} = \dot{V}_0 p_{i,0} - \dot{V} p_i + m_{cat} RT \sum_{j=1}^3 v_{ij} r_j, \quad i = 1, \dots, 6 \quad (19)$$

- total material balance for the case when total pressure is held constant

$$m_{cat} q_{sat} RT \sum_{i=1}^6 \sum_{l=1}^6 \frac{\partial \theta_l dp_l}{\partial p_i dt} = \dot{V}_0 p_{tot} - \dot{V} p_{tot} + m_{cat} RT \sum_{i=1}^6 \sum_{j=1}^3 v_{ij} r_j \quad (20)$$

- the equation describing the catalyst dynamics

$$\frac{d\phi}{dt} = k_1^+ \left(\frac{p_3}{p_{tot}} (\phi_{max} - \phi) - \frac{1}{K_1 p_{tot}} p_2 \phi \right) + k_2^+ \left(\frac{p_4}{p_{tot}} (\phi_{max} - \phi) - \frac{1}{K_2 p_{tot}} p_5 \phi \right) \quad (21)$$

The outlet volumetric flow-rate (\dot{V}) is evaluated based on the total material balance (Eq. (20))

which can be reformulated as follows:

$$\dot{V} = \dot{V}_0 + m_{cat} \frac{RT}{p_{tot}} \sum_{i=1}^6 \sum_{j=1}^3 v_{ij} r_j - m_{cat} q_{sat} \frac{RT}{p_{tot}} \sum_{i=1}^6 \sum_{l=1}^6 \frac{\partial \theta_l dp_l}{\partial p_i dt} \quad (20a)$$

In equations (18-20) p_i represents the partial pressure of component i ($i=1$ for CH₃OH, $i=2$ for CO₂, $i=3$ for CO, $i=4$ for H₂, $i=5$ for H₂O and $i=6$ for N₂).

The adsorption equilibrium is described with the competitive adsorption Langmuir isotherm. The elements of the Jacobian matrix, $\left(\frac{\partial \theta_i}{\partial p_l} \right)$ which are used in the mathematical model (Eqs. (19-20)), are given in Appendix B. In order to evaluate the total concentration of each component on the catalyst surface, it is necessary to determine the concentration of each component on each active surface centre of catalyst.

For analysis in the frequency domain, it is convenient to introduce dimensionless variables (defined in Tab. 2) and to use dimensionless mathematical model. The dimensionless input and output variables are defined as relative deviations from their steady-state values, as shown in Tab.2.

Table 2 The definitions of dimensionless variables

Dimensionless variables	Definitions
Partial pressure of component i	$P_i = \frac{p_i - p_{i,s}}{p_{i,s}}, i = 1, \dots, 6$
Partial pressure of component i in the inlet stream	$P_{i,0} = \frac{p_{i,0} - p_{i0,s}}{p_{i0,s}}, i = 1, \dots, 6$
Time	$\tau = \frac{t}{\tau_{0,s}} = \frac{t}{V_G / \dot{V}_{0,s}}$
Fraction of reduced centres on the catalyst surface	$\Phi = \frac{\phi - \phi_s}{\phi_s}$

Volumetric flow-rate of the inlet stream	$u_0 = \frac{V_0 - V_{0,s}}{\dot{V}_{0,s}}$
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) (Tab.2) is defined based on the steady-state residence time ($\tau_{0,s}$) calculated using the steady-state inlet volumetric flow-rate ($\dot{V}_{0,s}$) and volume of the reactor (V_G), as follows:

$$\tau_{0,s} = \frac{V_G}{\dot{V}_{0,s}} \quad (22)$$

For applying the NFR analysis, all nonlinear terms in the mathematical model need to be given in the polynomial form or expanded in Taylor series around a previously established steady-state point (*Petkovska and Seidel-Morgenstern, 2013; Nikolić, 2016; Petkovska et al., 2018*). Therefore, the nonlinear terms (reaction rate expressions (Eqs. (11-13)) from the mathematical model (Eqs. (19-20)) are replaced by their Taylor series expansions, which are given in Appendix C.

After incorporating the dimensionless variables (Tab. 2) in the mathematical model equations (19-21) and expanding all nonlinear terms into Taylor series form, the following set of dimensionless model equations is obtained:

$$\begin{aligned} \frac{dP_i}{d\tau} + m_{cat} q_{sat} \frac{RT}{V_G} \left[\sum_{l=1}^6 p_{l,s} \partial \theta_i dP_l \right] + \frac{\dot{V}_s}{\dot{V}_{0,s}} (P_i + v + vP_i) - \frac{RT}{\dot{V}_{0,s} p_{i,s}} m_{cat} \left(\sum_{l=1}^6 (v_{i,1} q_l + v_{i,2} \vartheta_l + v_{i,3} S_l \right. \\ \left.) P_l + (v_{i,1} q_7 + v_{i,2} \vartheta_7 + v_{i,3} S_7) \Phi \right) \\ = \frac{p_{i0,s}}{p_{i,s}} (P_{i,0} + v_0 + v_0 P_{i,0}) + \frac{RT}{\dot{V}_{0,s} p_{i,s}} m_{cat} \left(\sum_{l=1}^6 \sum_{k=l}^6 (v_{i,1} Q_{lk} + v_{i,2} U_{lk} + v_{i,3} S_{lk}) P_l P_k \right. \\ \left. + (v_{i,1} Q_{77} + v_{i,2} U_{77} + v_{i,3} S_{77}) \Phi^2 + \Phi \sum_{l=1}^6 (v_{i,1} Q_{l7} + v_{i,2} U_{l7} + v_{i,3} S_{l7}) P_l \right) + \dots \end{aligned} \quad (23)$$

$i = 1, \dots, 6$

$$\begin{aligned}
m_{cat}q_{sat}\frac{V_{0,s}}{V_G}\sum_{i=1}^6\sum_{l=1}^6p_{l,s}\frac{\partial\theta_i dP_l}{\partial p_l d\tau} + \frac{V_s p_{tot}}{RT}v - m_{cat}\sum_{i=1}^6\left(\sum_{l=1}^6(v_{i,1}q_l + v_{i,2}\vartheta_l + v_{i,3}s_l)P_l + (v_{i,1}q_7 + v_{i,2}\vartheta_7 + v_{i,3}s_7)\Phi\right) = \frac{\dot{V}_{0,s}p_{tot}}{RT}v_o + m_{cat}\sum_{i=1}^6\left(\sum_{l=1}^6\sum_{k=l}^6(v_{i,1}Q_{lk} + v_{i,2}U_{lk} + v_{i,3}S_{lk})P_l P_k + (v_{i,1}Q_{77} + v_{i,2}U_{77} + v_{i,3}S_{77})\Phi^2 + \Phi\sum_{l=1}^6(v_{i,1}Q_{l7} + v_{i,2}U_{l7} + v_{i,3}S_{l7})P_l\right) + \dots
\end{aligned} \tag{24}$$

$$\begin{aligned}
\frac{d\Phi}{d\tau} + [E_2]P_2 + \left[-\frac{(\phi_{max} - \phi_s)}{\phi_s}E_1\right]_3 P_3 + \left[-\frac{(\phi_{max} - \phi_s)}{\phi_s}E_3\right]_4 P_4 + [E_4]P_5 \\
+ [E_1 + E_2 + E_3 + E_4]\Phi \\
= [-E_2]P_3\Phi + [-E_1]P_2\Phi + [-E_3]P_4\Phi + [-E_4]P_5\Phi
\end{aligned} \tag{25}$$

The auxiliary coefficients q , Q , ϑ , U , s , S as well as the auxiliary parameters E_1 - E_4 used in this dimensionless mathematical model (Eqs. (23-25)) are given Appendices C and D.

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

The inputs which can be modulated for the analysed system are:

- partial pressure of CO₂ in the feed stream,
- partial pressure of CO in the feed stream,
- partial pressure of H₂ in the feed stream and
- total volumetric flow-rate of the feed stream.

The outputs of the analysed system are the following variables:

- the partial pressures of all components in the outlet stream,
- the fraction of reduced active surface centres of the catalyst in the reactor (which in fact represents the state of the catalyst in the reactor) and
- the volumetric flow-rate of the outlet stream.

The vectors of inputs \mathbf{X} and outputs \mathbf{Y} in the dimensionless form are defined, as follows:

$$\mathbf{X} = \begin{bmatrix} P_{CO_2,0} \\ P_{CO,0} \\ P_{H_2,0} \\ v_0 \end{bmatrix} \quad \mathbf{Y} = \begin{bmatrix} CH_3OH \\ P_{CO_2} \\ P_{CO} \\ P_{H_2} \\ P_{H_2O} \\ \Phi \\ v \end{bmatrix} \quad (26)$$

The FRFs which correlate an output y ($y=1,\dots,7$) with a modulated input x ($x=1,\dots,4$) will be denoted as G -functions. For implementation of the NFR method for evaluating the potential forced periodic operations, it was necessary to derive:

- the first order frequency response functions marked as $G_{y,x}^{(1)}(\omega)$,
- the asymmetrical second order frequency response functions marked as $G_{y,x,x}^{(2)}(\omega, -\omega)$.

The \mathbf{G} -FRFs were derived by implementing a standard derivation procedure which was given in our previous publications (*Petkovska and Seidel-Morgenstern, 2013; Nikolić, 2016; Petkovska et al., 2018*).

4. 3. Derivation of the FRFs

The periodic modulation of input X_x , defined as a dimensionless inlet partial pressure of CO_2 , CO or H_2 (for $x=1, 2$ or 3) or dimensionless flow-rate ($x=4$), with a forcing frequency ω and forcing amplitude A_x , in the shape of a co-sinusoidal function of frequency, is defined as follows:

$$X_x(\tau) = A_x \cos(\omega\tau) = \left(\frac{A_x}{2}\right)e^{j\omega\tau} + \left(\frac{A_x}{2}\right)e^{-j\omega\tau} \quad (27)$$

In the cases when the partial pressure of one of the reactants is the modulated input, the partial pressure of the inert (N_2) is adjusted in order to assure isobaric conditions (constant total pressure) in the reactor.

For the general case, when input X_x is periodically modulated, the output Y_y , based on the Volterra series (*Volterra, 1959*) can be written in the following way:

$$Y_y = \left(\frac{A_x}{2}\right)e^{j\omega\tau} G_{y,x}^{(1)}(\omega) + \left(\frac{A_x}{2}\right)e^{-j\omega\tau} G_{y,x}^{(1)}(-\omega) + \dots + 2\left(\frac{A_x}{2}\right)^2 e^0 G_{y,x,x}^{(2)}(\omega, -\omega) + \dots \quad (28)$$

After substituting the definitions of the dimensionless input (Eq.(27)) and outputs (Eq.(28)) in the dimensionless mathematical model (Eq.(23-25)) and after collecting the terms with $A_x e^{j\omega}$, a set of linear algebraic equations, defining the first order \mathbf{G} -FRFs is obtained. This set of equations can be written in the matrix form given with Eq. (29):

$$\begin{bmatrix} \alpha_{11} & \cdots & \alpha_{17} \\ \vdots & \ddots & \vdots \\ \alpha_{71} & \cdots & \alpha_{77} \end{bmatrix} \times \begin{bmatrix} G_{1,1}^{(1)}(\omega) & \cdots & G_{1,4}^{(1)}(\omega) \\ \vdots & \ddots & \vdots \\ G_{7,1}^{(1)}(\omega) & \cdots & G_{7,4}^{(1)}(\omega) \end{bmatrix} = \begin{bmatrix} \frac{p_{CO_2,0,s}}{p_{CO_2,s}} & 0 & 0 & \frac{p_{CO_2,0,s}}{p_{CO_2,s}} \\ 0 & \frac{p_{CO,0,s}}{p_{CO,s}} & 0 & \frac{p_{CO,0,s}}{p_{CO,s}} \\ 0 & 0 & \frac{p_{H_2,0,s}}{p_{H_2,s}} & \frac{p_{H_2,0,s}}{p_{H_2,s}} \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{\dot{V}_{0,s} p_{tot}}{RT} \end{bmatrix} \quad (29)$$

The solution of this matrix equation gives the matrix of all first order FRFs for all combinations of outputs and inputs:

$$\begin{bmatrix} G_{1,1}^{(1)}(\omega) & \cdots & G_{1,4}^{(1)}(\omega) \\ \vdots & \ddots & \vdots \\ G_{7,1}^{(1)}(\omega) & \cdots & G_{7,4}^{(1)}(\omega) \end{bmatrix} = \begin{bmatrix} \alpha_{11} & \cdots & \alpha_{17} \\ \vdots & \ddots & \vdots \\ \alpha_{71} & \cdots & \alpha_{77} \end{bmatrix}^{-1} \times \begin{bmatrix} 0 & 0 & 0 & 0 \\ \frac{p_{CO_2,0,s}}{p_{CO_2,s}} & 0 & 0 & \frac{p_{CO_2,0,s}}{p_{CO_2,s}} \\ 0 & \frac{p_{CO,0,s}}{p_{CO,s}} & 0 & \frac{p_{CO,0,s}}{p_{CO,s}} \\ 0 & 0 & \frac{p_{H_2,0,s}}{p_{H_2,s}} & \frac{p_{H_2,0,s}}{p_{H_2,s}} \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{\dot{V}_{0,s} p_{tot}}{RT} \end{bmatrix} \quad (30)$$

By collecting the non-periodic terms with $\left(\left(\frac{A_x}{2}\right)^2 e^0\right)$, a set of linear algebraic equations defining the asymmetrical second order \mathbf{G} -FRFs is obtained, which are again written in the matrix form and given with Eq. (31):

$$2 \times \begin{bmatrix} \gamma_{11} & \cdots & \gamma_{17} \\ \vdots & \ddots & \vdots \\ \gamma_{71} & \cdots & \gamma_{77} \end{bmatrix} \times \begin{bmatrix} G_{1,1,1}^{(2)}(\omega, -\omega) & \cdots & G_{1,4,4}^{(2)}(\omega, -\omega) \\ \vdots & \ddots & \vdots \\ G_{7,1,1}^{(2)}(\omega, -\omega) & \cdots & G_{7,4,4}^{(2)}(\omega, -\omega) \end{bmatrix} = \begin{bmatrix} \Gamma_{11} & \cdots & \Gamma_{14} \\ \vdots & \ddots & \vdots \\ \Gamma_{71} & \cdots & \Gamma_{74} \end{bmatrix} \quad (31)$$

The solution of this matrix equation results with a matrix of the ASO G -FRFs for all combinations of the inputs and outputs:

$$\begin{bmatrix} G_{1,1,1}^{(2)}(\omega, -\omega) & \cdots & G_{1,4,4}^{(2)}(\omega, -\omega) \\ \vdots & \ddots & \vdots \\ G_{7,1,1}^{(2)}(\omega, -\omega) & \cdots & G_{7,4,4}^{(2)}(\omega, -\omega) \end{bmatrix} = 2 \times \begin{bmatrix} \gamma_{11} & \cdots & \gamma_{17} \\ \vdots & \ddots & \vdots \\ \gamma_{71} & \cdots & \gamma_{77} \end{bmatrix}^{-1} \times \begin{bmatrix} \Gamma_{11} & \cdots & \Gamma_{14} \\ \vdots & \ddots & \vdots \\ \Gamma_{71} & \cdots & \Gamma_{74} \end{bmatrix}$$

The definitions of the coefficients α_{ij} used in equations (29) and (30) are given in Appendix E. The definitions of the coefficients γ_{ij} used in equation (31) and (32) are given in Appendix F.

4.4. Identification and evaluation of regions of possible improvement

The main goal of implementing forced periodic operations is to improve the reactor performance, e.g. through increase of methanol production, conversion or yield. All these performance criteria can be evaluated based on the time-average outlet molar flow-rate of methanol, which has been chosen as the main indicator of possible improvement that should be maximized.

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

$$\dot{n}_{CH_3OH} = \frac{p_{CH_3OH}\dot{V}}{RT} \quad (33)$$

It is convenient to use the dimensionless molar flow-rate of methanol, which is defined as a relative deviation from its steady-state value, in an analogous way as the dimensionless partial pressures (Table 2):

$$\dot{N}_{CH_3OH} = \frac{\dot{n}_{CH_3OH} - \dot{n}_{CH_3OH,s}}{\dot{n}_{CH_3OH,s}} = \frac{p_{CH_3OH}\dot{V} - p_{CH_3OH,s}\dot{V}_s}{p_{CH_3OH,s}\dot{V}_s} = P_{CH_3OH} + u + P_{CH_3OH}u \quad (34)$$

The non-periodic (DC) component of the outlet molar flow-rate of methanol, which is the measure of improvement of methanol production, can be evaluated in the following way:

$$\dot{N}_{CH_3OH,DC} = P_{CH_3OH,DC} + u_{DC} + (P_{CH_3OH}u)_{DC} \quad (35)$$

The outlet molar flow-rate of methanol is an additional output which is of interest, which can be associated to additional sets of FRFs, which will be denoted as H -functions. If one of the inputs X_x is modulated in a co-sinusoidal way, the DC component of outlet molar flow-rate of methanol can be approximately evaluated using the corresponding H ASO FRF:

$$\dot{N}_{CH_3OH,DC} \approx 2\left(\frac{A_x}{2}\right)^2 H_{1,x,x}^{(2)}(\omega, -\omega) \quad (36)$$

Based on equations (35 and 36) it is relatively easy to derive a relation between the H ASO FRFs and the previously derived G -FRFs, corresponding to the methanol partial pressure and the outlet flow-rate. The asymmetrical second order H -FRF is:

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

$x = 1, 2, 3$ or 4 (37)

Based on the NFK method, the mean (time-average) value of the outlet molar flow rate of methanol for co-sinusoidal modulation of input X_x , can be approximately calculated using the following expression:

$$(\dot{n}_{CH_3OH})_{mean} \approx \dot{n}_{CH_3OH,s} \left(1 + 2 \left(\frac{A_x}{2} \right)^2 H_{1,x,x}^{(2)}(\omega, -\omega) \right) \quad (38)$$

where

$$\dot{n}_{CH_3OH,s} = \frac{p_{CH_3OH,s} \dot{V}_s}{RT} \quad (39)$$

is the outlet molar flow-rate of methanol in steady state, while $(\dot{n}_{CH_3OH})_{mean}$ is the time average value of the outlet molar flows-rate over an integer number of periods P :

$$(\dot{n}_{CH_3OH})_{mean} = \frac{1}{P} \int_{kP}^{(k+1)P} \dot{n}_{CH_3OH}(t) dt = \frac{1}{P} \int_{kP}^{(k+1)P} p_{CH_3OH}(t) \dot{V}(t) dt \quad (40)$$

Based on the mean value of the methanol outlet molar flow rate, several performance indicators were defined. One of them is the normalized methanol production rate per unit mass of catalyst for the periodic operation (PO):

$$\left(\dot{n}_{CH_3OH}^{norm} \right)_{PO} = \frac{(\dot{n}_{CH_3OH})_{mean}}{m_{cat}} \quad (41)$$

Other two performance indicators analysed are yield of methanol based of total carbon:

$$\left(Y_{CH_3OH}^{totC} \right)_{PO} = \frac{(\dot{n}_{CH_3OH})_{mean}}{(\dot{n}_{CO_2} + \dot{n}_{CO})_{0,mean}} \quad (42)$$

and yield of methanol based on hydrogen:

$$\left(Y_{CH_3OH}^{H_2} \right)_{PO} = 2 \frac{(\dot{n}_{CH_3OH})_{mean}}{(\dot{n}_{H_2,0})_{mean}} \quad (43)$$

It should be noticed that for single input modulations, the mean values of the molar flow-rates of the reactants in the feed stream are identical to their steady-state values. Using this fact and equation (38), the yields defined in equations (42) and (43) can be evaluated based on their steady-state values and function $H_{1,x,x}^{(2)}(\omega, -\omega)$:

$$\left(Y_{CH_3OH}^{totC} \right)_{PO} \approx \left(Y_{CH_3OH}^{totC} \right)_{SS} \left(1 + 2 \left(\frac{A_x}{2} \right)^2 H_{1,x,x}^{(2)}(\omega, -\omega) \right) \quad (44)$$

and

$$\left(Y_{CH_3OH}^{H_2} \right)_{PO} \approx \left(Y_{CH_3OH}^{H_2} \right)_{SS} \left(1 + 2 \left(\frac{A_x}{2} \right)^2 H_{1,x,x}^{(2)}(\omega, -\omega) \right) \quad (45)$$

where

$$\left(Y_{CH_3OH}^{totC}\right)_{SS} = \frac{\dot{n}_{CH_3OH,s}}{(\dot{n}_{CO_2} + \dot{n}_{CO})_{0,s}} \quad (46)$$

and

$$\left(Y_{CH_3OH}^{H_2}\right)_{SS} = 2 \frac{(\dot{n}_{CH_3OH})_s}{\dot{n}_{H_2,0,s}} \quad (47)$$

are the yields of methanol based on total carbon and based on hydrogen, respectively, corresponding to the chosen steady-state point.

Based on the sign of ASO H -FRF $H_{1,x,x}^{(2)}(\omega, -\omega)$, it is possible to predict whether the improvement owing to periodic modulation of the input X_x is possible at all, or not (*Petkovska and Seidel-Morgenstern, 2013; Nikolić, 2016; Petkovska et al., 2018*). The improvement can be achieved only if $H_{1,x,x}^{(2)}(\omega, -\omega)$ is positive.

5. Simulation results and discussion

In this Section, the simulation results based on the NFR analysis, for periodically operated isothermal, isobaric, lab-scale Micro-Berty reactor are given, for cases of single input modulations of the reactant partial pressures in the feed stream, or its volumetric flow-rate. The analysis was performed for a lab-scale reactor of the volume of the reaction mixture (i.e. gas phase) $V_G=10.3 \text{ ml}$ and with a mass of catalyst $m_{cat} = 0.00395 \text{ kg}$.

5.1. Choosing the optimal steady-state for analysis

The first step in the analysis of forced periodic operation is to determine the optimal steady state, around which the system inputs should be modulated.

The optimal steady-state was chosen based on multi-objective optimization with two objective functions: normalized outlet molar flow-rate of methanol ($\text{mmol}/(\text{min kg}_{cat})$) and yield of methanol based on total carbon, which both need to be maximized. The multi-objective optimization problem was solved using ϵ -Constraint method (Haimes *et al.*, 1971). The variables optimized were the mole fractions of all reactants (CO_2 , CO and H_2) in feed stream and the reactor temperature. The values of reactor pressure, the flow-rate of the feed stream and the mole fraction of the inert (N_2) were fixed. The optimization was performed in the range of validity of the kinetic model (Vollbrecht, 2007, Seidel *et al.*, 2018) (mole fractions of CO_2 and CO between 0 and 1, mole fraction of H_2 between 0.5 and 1 and temperature between 473 and 533 K). In the multi-objective optimization, both objective functions were defined with the same weight and the result of the optimization is obtained in the form of a Pareto front. By choosing the appropriate points from the Pareto front, one can give different weights to different objective functions that correspond e.g. to high conversion and low methanol production or vice versa. More details about multi-objective optimization can be found e.g. in (Ehrgott, 2005).

The resulting Pareto front with the marked selected optimal steady-state point is given in Appendix G (Figure G.1). An overview of the optimization results for that selected steady-state point is given in Table 3.

Table 3. Overview of the chosen optimal steady-state point for analysis.

<i>Fixed parameters</i>			
p_{tot} (bar)	$\dot{V}_{0,s}$ (ml/min)		$y_{N_2,s}$
60	6.93		0.15
<i>Optimization parameters</i>			
$y_{CO_2,s}$	$y_{CO,s}$	$y_{H_2,s}$	T_s [K]
0.021	0.185	0.644	473

Outputs

$y_{CH_3OH,s}$	$y_{CO_2,s}$	$y_{CO,s}$	$y_{H_2,s}$	$y_{H_2O,s}$	$y_{N_2,s}$	$\dot{V}_{out,s}$ ml/min
0.168	0.026	0.081	0.522	0.002	0.200	5.186
Performance indicators						
$(\dot{n}_{CH_3OH}^{norm})_{SS}$ [mmol/min/kg _{cat}]		$(Y_{CH_3OH}^{totC})_{SS}$ (%)		$(Y_{CH_3OH}^{H_2})_{SS}$ (%)		
336.91		61.05		39.09		

5.2. Results for single input modulations around their optimal steady-state values

The simulation results of NFR analysis for single input modulations around optimal steady-state are presented here. The asymmetrical second order H -FRFs which correlate the outlet molar flow-rate of methanol to the 4 inputs related to the feed reactor steam (partial pressures of CO_2 , CO , H_2 and the volumetric flow-rate), are given in Figure 1, as a function of dimensionless forcing frequency. The analysis of H ASO FRFs was done for the dimensionless forcing frequencies in a wide range between 0.001 and 100, which, for the case of the laboratory-scale reactor analysed in this work, correspond to the range of periods of the input modulations between 560000 seconds (9333 minutes or 155 hours) and 5.6 seconds.

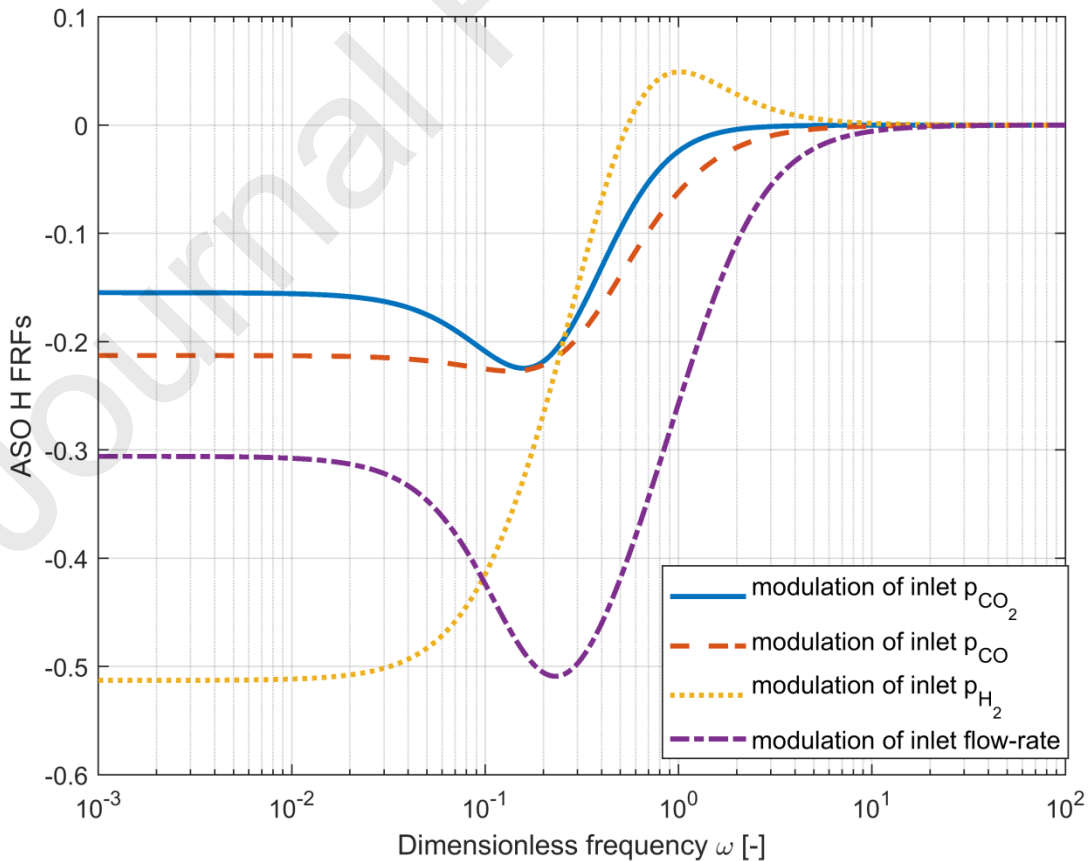


Figure 1. The asymmetrical second order **H** FRFs for single input modulations of partial pressures of CO₂, CO and H₂ or volumetric flow-rate around their optimal steady-state values, vs. dimensionless frequency.

As stated above, for the frequency range in which those **H**-ASO FRFs ($H_{1,x,x}^{(2)}(\omega, -\omega)$, $x = 1, \dots, 4$) are negative or equal to zero the improvement with single input modulations cannot be achieved, meaning that the steady-state operation is superior to periodic processes with any of the single input modulations. On the other hand, if **H**-ASO FRFs are positive, the improvement could be obtained by periodic operations.

Based on results presented in Fig.1, it can be concluded that:

- In all analysed cases of single input modulations around the optimal steady-state, the **H** ASO FRFs tend to zero for high forcing frequencies, meaning that the high frequency input modulations have no influence on the process performances. On the other hand, for low forcing frequencies, all **H** ASO FRFs have asymptotic values which are negative, meaning that the improvement is not possible. For the forcing frequencies between the highest and the lowest, some of the **H** ASO FRFs reach extremes (minimum for modulation of the inlet partial pressure of CO₂ or inlet volumetric flow-rate and maximum for modulation of partial pressure of H₂). For the forcing frequencies which correspond to the extremes, the highest deterioration (for modulation of partial pressures of CO₂ or inlet volumetric flow-rate) or highest improvement (for periodic modulation of partial pressure of H₂) of process performances is achieved.
- For single input modulations of CO₂, CO and inlet volumetric flow-rate around the optimal steady-state, the **H**-ASO FRFs which correlate the outlet molar flow-rate of methanol to modulated inputs ($H^{(2)}_{1,1,1}(\omega, -\omega)$, $H^{(2)}_{1,2,2}(\omega, -\omega)$, $H^{(2)}_{1,4,4}(\omega, -\omega)$), are negative and tend to zero for high forcing frequencies. Consequently, periodic modulations of these inputs cannot improve the process of methanol synthesis.
- For single input modulation of H₂ partial pressure around its optimal steady-state value, the corresponding **H**-ASO FRF which correlates the outlet molar flow-rate of methanol to the modulated input ($H^{(2)}_{1,3,3}(\omega, -\omega)$) is positive for forcing frequencies higher than 0.55 and also tends to zero for high forcing frequencies. The maximal value of this ASO FRF of 0.049 is obtained for dimensionless forcing frequency $\omega \approx 1$. The maximal possible increase of the normalized outlet molar flow rate of methanol corresponding to this is 0.13% (when the highest possible forcing amplitude is used), which is practically insignificant.

5.5. Analysis of maximal possible improvement for single input modulations

The results of the previous section show that, under the defined conditions, it is not possible to improve the reactor performance by periodic modulation of partial pressures of CO and CO₂ or the volumetric flow-rate around the chosen optimal steady-state point, as corresponding ASO *H*-FRFs are negative in the whole frequency range. Some insignificant improvement (maximal increase or the normalized outlet molar flow-rate of methanol is 0.13%) is possible for periodic modulation of partial pressure of hydrogen, considering that the corresponding ASO *H*-FRF is positive for some forcing frequencies (Figure 1).

Nevertheless, generally it would be possible that single input modulations around some other steady-state points would result with process improvement. In this section we explore these possibilities.

Considering the fact that, for periodic operations with single input modulations, the possible improvement is directly proportional to the corresponding ASO *H*-FRF, four optimizations were performed, in which the conditions that maximize the ASO *H*-FRFs for the four analysed inputs ($H_{1,x,x}^{(2)}(\omega, -\omega)$, $x = 1, \dots, 4$) were determined. The optimization variables were the steady-state mole fractions of CO₂, CO and H₂ in the feed stream, the steady-state temperature and the forcing frequency.

The details about these steady-state points, for which maximal ASO *H*-FRFs are obtained, can be found in the Supplementary material. The values of the input and output variables, corresponding to the steady state points used for single input modulations of partial pressures of CO₂, CO, H₂ and inlet volumetric flow-rate, are given in Tables S1-S4, respectively.

The corresponding, maximized ASO *H*-FRFs, for all four investigated inputs, are shown in Fig. 2, as functions of dimensionless forcing frequency.

A short overview of these cases is given in Table 4. In this table, the maximal possible values of the normalized methanol flow-rate, yield of methanol based on total carbon and yield of methanol based on hydrogen, corresponding to the periodic operations defined in such a way that the ASO *H*-FRFs are maximized, are compared with their corresponding steady-state values. The performance criteria for the periodic operations were calculated for the frequencies corresponding to the maxima of the *H*-FRFs shown in Fig. 2, and for the maximal possible values of the amplitudes. The percentage of the maximal possible improvement (which is the same for all three performance indicators) is also given in the last column of Table 4.

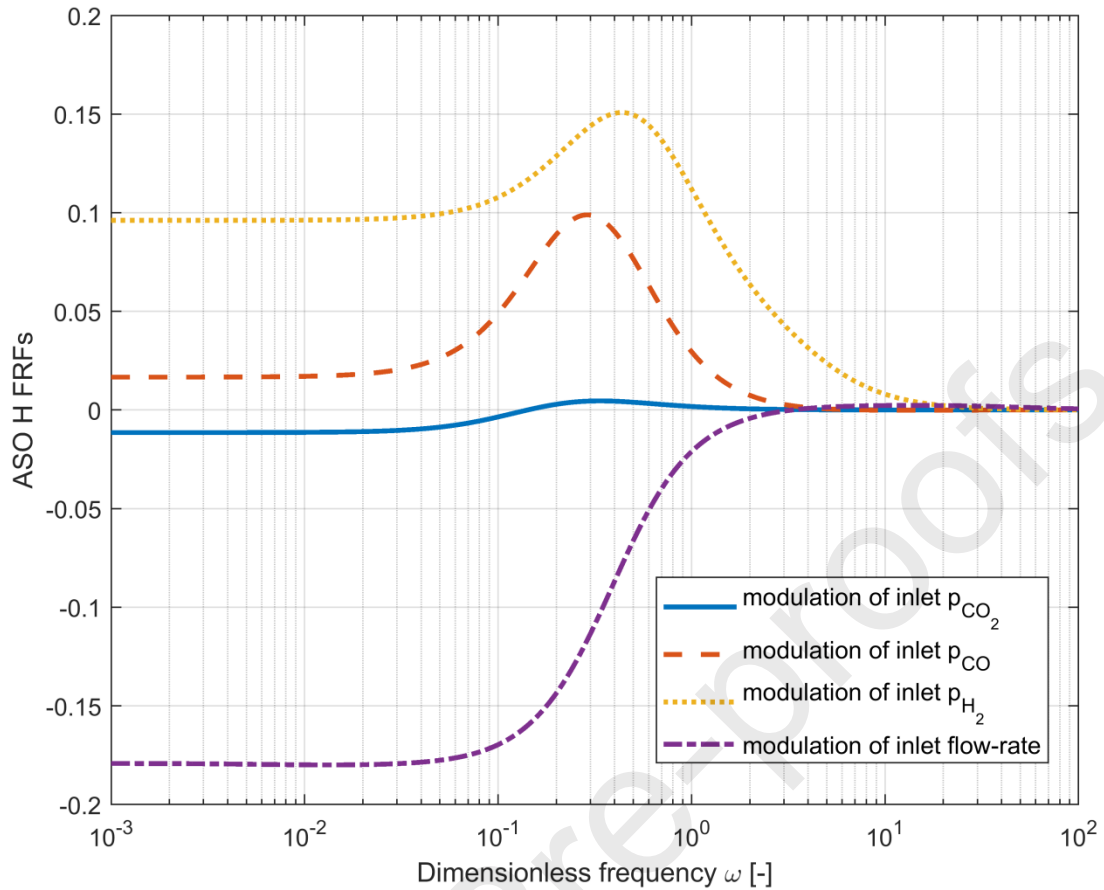


Figure 2. The maximal possible values of the asymmetrical second order H -FRFs for single input modulations of the partial pressures of CO_2 , CO and H_2 and volumetric flow-rate of the feed steam vs. dimensionless frequency.

Table 4. The normalized outlet molar flow-rate and yields of methanol based on total carbon and on hydrogen for the cases corresponding to the maximal ASO H -FRFs, for steady-state and periodic operations.

Modulated input	$(\dot{n}_{\text{CH}_3\text{OH}}^{\text{norm}})_{\text{SS}}$ [mmol/min/ kg _{cat}]	$(Y_{\text{CH}_3\text{OH}}^{\text{totC}})_{\text{SS}}$ %	$(Y_{\text{CH}_3\text{OH}}^{\text{H}_2})_{\text{SS}}$ %	$(\dot{n}_{\text{CH}_3\text{OH}}^{\text{norm}})_{\text{PO}}$ [mmol/min/ kg _{cat}]	$(Y_{\text{CH}_3\text{OH}}^{\text{totC}})_{\text{PO}}$ %	$(Y_{\text{CH}_3\text{OH}}^{\text{H}_2})_{\text{PO}}$ %	Max impr. [%]
P_{CO_2}	59.95	11.19	6.89	60.09	11.21	6.91	0.23
P_{CO}	102.82	29.64	10.66	107.90	31.10	11.19	4.95
P_{H_2}	261.72	27.93	39.11	263.50	28.12	39.37	0.68
v_0	7.69	28.89	0.68	7.70	28.92	0.69	0.12

The shapes of the H ASO FRFs for single input modulations around the new steady states which correspond to the maximal H ASO FRFs (defined in Tables S1 to S4), shown in Fig 2, are different from the shapes of the functions calculated for the optimal steady-state shown in Fig. 1. This is a result of the fact that the functions correspond to very different steady-states.

Based on the results presented in Fig. 2 it can be concluded that for single input modulations of inlet partial pressures of CO_2 , CO , H_2 or inlet volumetric flow-rate around the new steady-states determined in order to maximize the ASO H -FRFs improvement is possible for all cases, in certain ranges of forcing frequencies. On the other hand, the results presented in Table 4 show that the possible improvement is very small (the highest improvement is obtained for partial pressure of CO in the feed stream as the modulated input, and it is possible in the whole frequency range).

Nevertheless, despite the fact that some improvement is possible in comparison to the corresponding steady-states around which the four inputs should be modulated, all performance criteria corresponding to the periodic operations with modulation of the inlet partial pressures of CO_2 , CO , H_2 or the volumetric flow-rate of the feed stream, presented in Table 3, are by far worse than the performance criteria corresponding to the optimal steady-state defined in Section 5.1 (Table 3). So, the conclusion of this analysis is that none of these four periodic operations with single input modulations is acceptable.

6. Conclusions

The goal of this two-part manuscript is to present the results of a comprehensive study of the potential of using forced periodic operations in order to improve the performance of a chemical reactor for isothermal and isobaric methanol synthesis from syngas. Four potential forced periodic inputs are considered: partial pressures of all reactants (CO_2 , CO and H_2) in the feed stream and its total volumetric flow-rate. Because of the quantity of the obtained results, the manuscript needed to be split into two parts.

In this first part of the manuscript, only the results for single input modulations are shown. Here are the most important results of this analysis:

- Periodic modulations of the partial pressures of CO_2 , CO and volumetric flow-rate of the feed stream, around the optimal steady state, always result with performance deterioration, instead of performance improvement, in the whole frequency range. Therefore, such periodic operations are unacceptable.

- Periodic modulation of the partial pressure of H_2 around the optimal steady state could lead to improvement of the reactor performances for some forcing frequencies with the maximal possible improvement of 0.13% which is practically insignificant.
- It is possible to find some cases for which some limited improvement can be achieved with periodic modulations of the analysed inputs, if the inputs would be modulated around some other steady-state points. Nevertheless, all these cases correspond to reactor performances that are much worse than for the optimal steady-state process. Accordingly, these periodic operations are also unacceptable.
- Analysis of periodic operations with simultaneous modulation of two inputs is the next logical step, as it is a well-known fact that such operations have high potential for improvement (*Petkovska and Seidel-Morgenstern, 2013; Felischak et al., 2021*), owing to the cross-effect between the two modulated inputs, which can be easily adjusted by adjusting the phase difference between the two inputs. This analysis will be presented in the second part of our manuscript.

It is important to point out that frequency response functions for the four inputs, derived and presented here, are necessary for the analysis of the periodic operations with simultaneous modulation of two inputs, i.e. the analysis and results presented in Part II would not be possible without the results presented in Part I.

In both parts of our manuscript, the analysis was performed by using the nonlinear frequency response analysis. Even for a complex case, such as the reactor for methanol synthesis, with four potential modulated inputs and a large number of outputs, the NFR method was proven as a very useful and efficient tool for evaluating whether the reactor performance could be improved by using forced periodic operations, or not.

Nomenclature

A_x	amplitude of input x (partial pressure of CO ₂ , CO or H ₂ or the volumetric flow rate)
E	auxiliary parameters for catalyst dynamic equation in dimensionless form
$G_{y,x}^{(n)}(\omega, \dots, \omega)$	n^{th} order FRF which correlate the output y to modulated input x
ΔG [J/mol]	Gibbs free energy
$H_{i,x,x}^{(2)}(\omega, \dots, \omega)$	H ASO FRF which correlate the outlet molar flow-rate of component i to modulated input x
J	Jacobian matrix
k_j	reaction rate constant ($j = 1$ for CO ₂ hydrogenation, $j = 2$ for CO hydrogenation, $j = 3$ for RWGS)
k_1^+, k_2^+ [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_{Pi} [bar ⁻²]	reaction rate constant for ($i=1$) CO or ($i=2$) CO ₂ hydrogenation
K_{P3} [–]	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_{tot} [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 centers
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 CO ₂ hydrogenation, $j = 3$ for RWGS)
t [s]	time
T [K]	temperature

V_G [m ³ , ml]	volume of the gas phase in the reactor
\dot{V} [m ³ /s]	volumetric flow rate
x, z	input (general symbol)
\mathbf{X}	vector of dimensionless inputs
y	output (general symbol)
\mathbf{Y}	vector of dimensionless outputs
y_i	molar fraction of component i ($i = 1, \dots, 6$ or $i = \text{CH}_3\text{OH}, \text{CO}_2, \text{CO}, \text{H}_2, \text{H}_2\text{O}, \text{N}_2$)
$Y_{\text{CH}_3\text{OH}}^{\text{totC}}$	yield of methanol based on total carbon
$Y_{\text{CH}_3\text{OH}}^{\text{H}_2}$	yield of methanol based on hydrogen
<i>Greek letters</i>	
α	first order FRF matrix coefficients
γ, Γ	ASO FRF matrix coefficients
θ	relative amount of free active surface centre
τ	dimensionless time
$\tau_{0,s}$ [s]	residence time based on 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 centres on catalyst surface
Φ	dimensionless fraction of reduced centres on catalyst surface
ω	dimensionless frequency
<i>Subscripts</i>	
DC	non-periodic component (<i>direct current</i>)
i	component ($i=1$ for CH ₃ OH, $i=2$ for CO ₂ , $i=3$ for CO, $i=4$ for H ₂ , $i=5$ for H ₂ O, $i=6$ for N ₂)
f	volumetric flow rate modulation
j	reaction ($j = 1$ for CO ₂ hydrogenation, $j = 2$ for CO hydrogenation, $j = 3$ for RWGS)
PO	periodic operation
SS	steady-state operation
0	feed stream

mean mean value of periodic operation

ref referent value

s steady-state

tot C total carbon

Superscripts

H_2 based on hydrogen

max maximal value

totC based on total carbon

*

⊙ oxidized surface centre

⊗ surface centre for hydrogen

Abbreviations

AC Active centres on catalyst surface

ASO Asymmetrical Second Order

FRF Frequency Response Function

NFR Nonlinear Frequency Response

RWGS Reverse water-gas shift

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Appendix

Appendix A - Temperature dependence of equilibrium constants of chemical reactions

[Vollbrecht, 2007]

$$\log(K_{P1}) = 13.814 + \frac{3784.7}{T} - 9.2833 \log(T) + 3.1475 \cdot 10^{-3}T - 4.2613 (10)^{-7}T^2$$

$$[\log(\text{bar}^{-2})] \quad (\text{A.1})$$

$$\log(K_{P2}) = 15.0921 + \frac{1581.7}{T} - 8.7639 \log(T) + 2.1105 \cdot 10^{-3}T - 1.9303 (10)^{-7}T^2$$

$$[\log(\text{bar}^{-2})] \quad (\text{A.2})$$

$$\log(K_{P3}) = 1.2777 - \frac{2167}{T} + 0.5194 \log(T) - 1.037 \cdot 10^{-3}T + 2.331 \cdot 10^{-7}T^2 \quad [-]$$

$$(\text{A.3})$$

Appendix B Jacobian matrix

In Appendix B, the Jacobian matrix is given, which elements $\left(\frac{\partial \theta_i}{\partial p_i}\right)$ are used in mathematical model (Eqs. 19-20), with the following definition

$$J_{i,l} = \frac{\partial \theta_i}{\partial p_i} \quad (\text{B.1})$$

In order to evaluate the total concentration of each component on the catalyst surface, it is necessary to determine the concentration of each component on each active surface centre of catalyst.

The corresponding adsorption isotherms are given as follows

$$\theta_i^{\odot} = K_i^{\odot} p_i \theta^{\odot}, \text{ for } i = \text{CH}_3\text{OH}, \text{CO}_2, \text{CO} \quad (\text{B.2})$$

$$\theta_i^* = K_i^* p_i \theta^*, \text{ for } i = \text{CH}_3\text{OH}, \text{CO}_2, \text{H}_2\text{O} \quad (\text{B.3})$$

$$\theta_H^* = \sqrt{K_H p_{H_2} \theta^*} \quad (\text{B.4})$$

$$\theta_H^{\otimes} = \sqrt{K_H p_{H_2} \theta^{\otimes}} \quad (\text{B.5})$$

The three active surface centres on catalyst are defined, and on each type of active centre the components which can be adsorbed are:

- on oxidized AC (\odot), CH_3OH , CO_2 and CO can be adsorbed,
- on reduced AC ($*$), CH_3OH , CO_2 , H_2 and H_2O can be adsorbed,
- on AC for RWGS reaction (\otimes), H_2 can be adsorbed (In the model it is assumed that in the solid phase hydrogen occurs only in elementary form. Thus, one H_2 is adsorbed and occupies two places in the solid phase, corresponding to the square roots in Eqs. (B.4) and (B.5)).

$$J = \begin{pmatrix} \frac{\partial p_{CH_3OH}}{\partial \theta_{CO_2}} & \frac{\partial p_{CO_2}}{\partial \theta_{CO_2}} & \frac{\partial p_{CO}}{\partial \theta_{CO_2}} & \frac{\partial p_{H_2}}{\partial \theta_{CO_2}} & \frac{\partial p_{H_2O}}{\partial \theta_{CO_2}} & \frac{\partial p_{N_2}}{\partial \theta_{CO_2}} \\ \frac{\partial p_{CH_3OH}}{\partial \theta_{CO}} & \frac{\partial p_{CO_2}}{\partial \theta_{CO}} & \frac{\partial p_{CO}}{\partial \theta_{CO}} & \frac{\partial p_{H_2}}{\partial \theta_{CO}} & \frac{\partial p_{H_2O}}{\partial \theta_{CO}} & \frac{\partial p_{N_2}}{\partial \theta_{CO}} \\ \frac{\partial p_{CH_3OH}}{\partial \theta_H} & \frac{\partial p_{CO_2}}{\partial \theta_H} & \frac{\partial p_{CO}}{\partial \theta_H} & \frac{\partial p_{H_2}}{\partial \theta_H} & \frac{\partial p_{H_2O}}{\partial \theta_H} & \frac{\partial p_{N_2}}{\partial \theta_H} \\ \frac{\partial p_{CH_3OH}}{\partial \theta_{H_2O}} & \frac{\partial p_{CO_2}}{\partial \theta_{H_2O}} & \frac{\partial p_{CO}}{\partial \theta_{H_2O}} & \frac{\partial p_{H_2}}{\partial \theta_{H_2O}} & \frac{\partial p_{H_2O}}{\partial \theta_{H_2O}} & \frac{\partial p_{N_2}}{\partial \theta_{H_2O}} \\ \frac{\partial p_{CH_3OH}}{\partial \theta_{N_2}} & \frac{\partial p_{CO_2}}{\partial \theta_{N_2}} & \frac{\partial p_{CO}}{\partial \theta_{N_2}} & \frac{\partial p_{H_2}}{\partial \theta_{N_2}} & \frac{\partial p_{H_2O}}{\partial \theta_{N_2}} & \frac{\partial p_{N_2}}{\partial \theta_{N_2}} \\ \frac{\partial p_{CH_3OH}}{\partial p_{CO_2}} & \frac{\partial p_{CO_2}}{\partial p_{CO_2}} & \frac{\partial p_{CO}}{\partial p_{CO_2}} & \frac{\partial p_{H_2}}{\partial p_{CO_2}} & \frac{\partial p_{H_2O}}{\partial p_{CO_2}} & \frac{\partial p_{N_2}}{\partial p_{CO_2}} \end{pmatrix} \quad (B.6)$$

$$J = J^\odot + J^\otimes + J^* \quad (B.7)$$

$$J^\odot = \begin{pmatrix} \frac{\partial \theta_{CH_3OH}^\odot}{\partial p_{CH_3OH}} & \frac{\partial \theta_{CH_3OH}^\odot}{\partial p_{CO_2}} & \frac{\partial \theta_{CH_3OH}^\odot}{\partial p_{CO}} & 0 & 0 & 0 \\ \frac{\partial \theta_{CO_2}^\odot}{\partial p_{CH_3OH}} & \frac{\partial \theta_{CO_2}^\odot}{\partial p_{CO_2}} & \frac{\partial \theta_{CO_2}^\odot}{\partial p_{CO}} & 0 & 0 & 0 \\ \frac{\partial \theta_{CO}^\odot}{\partial p_{CH_3OH}} & \frac{\partial \theta_{CO}^\odot}{\partial p_{CO_2}} & \frac{\partial \theta_{CO}^\odot}{\partial p_{CO}} & 0 & 0 & 0 \\ \frac{\partial \theta_{CH_3OH}^\odot}{\partial p_{CH_3OH}} & \frac{\partial \theta_{CH_3OH}^\odot}{\partial p_{CO_2}} & \frac{\partial \theta_{CH_3OH}^\odot}{\partial p_{CO}} & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (B.8)$$

$$J^\odot(1,1) = \frac{\partial \theta_{CH_3OH}^\odot}{\partial p_{CH_3OH}} = K_{CH_3OH}^\odot \theta^\odot - K_{CH_3OH}^\odot{}^2 p_{CH_3OH} \theta^{\odot 2} \quad (B.9)$$

$$J^\odot(1,2) = \frac{\partial \theta_{CH_3OH}^\odot}{\partial p_{CO_2}} = -K_{CH_3OH}^\odot K_{CO_2}^\odot p_{CH_3OH} \theta^{\odot 2} \quad (B.10)$$

$$J^\odot(1,3) = \frac{\partial \theta_{CH_3OH}^\odot}{\partial p_{CO}} = -K_{CH_3OH}^\odot K_{CO}^\odot p_{CH_3OH} \theta^{\odot 2} \quad (B.11)$$

$$J^\odot(2,1) = \frac{\partial \theta_{CO_2}^\odot}{\partial p_{CH_3OH}} = -K_{CO_2}^\odot K_{CH_3OH}^\odot p_{CO_2} \theta^{\odot 2} \quad (B.12)$$

$$J^\odot(2,2) = \frac{\partial \theta_{CO_2}^\odot}{\partial p_{CO_2}} = K_{CO_2}^\odot \theta^\odot - K_{CO_2}^\odot{}^2 p_{CO_2} \theta^{\odot 2} \quad (B.13)$$

$$J^{\odot}(2,3) = \frac{\partial^2 \theta_{CO_2}}{\partial p_{CO_2}} = -K_{CO_2}^{\odot} K_{CO_2}^{\odot} p_{CO_2} \theta^{\odot 2} \quad (B.14)$$

$$J^{\odot}(3,1) = \frac{\partial \theta_{CO_2}}{\partial p_{CH_3OH}} = -K_{CO_2}^{\odot} K_{CH_3OH}^{\odot} p_{CO_2} \theta^{\odot 2} \quad (B.15)$$

$$J^{\odot}(3,2) = \frac{\partial \theta_{CO_2}}{\partial p_{CO_2}} = -K_{CO_2}^{\odot} K_{CO_2}^{\odot} p_{CO_2} \theta^{\odot 2} \quad (B.16)$$

$$J^{\odot}(3,3) = \frac{\partial \theta_{CO_2}}{\partial p_{CO_2}} = K_{CO_2}^{\odot} \theta^{\odot} - K_{CO_2}^{\odot 2} p_{CO_2} \theta^{\odot 2} \quad (B.17)$$

$$J^{\otimes} = \begin{pmatrix} 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & \frac{\partial \theta_H^{\otimes}}{\partial p_{H_2}} & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (B.18)$$

$$J^{\otimes}(4,4) = \frac{\partial \theta_H^{\otimes}}{\partial p_{H_2}} = \frac{1}{2\sqrt{K_{H_2} p_{H_2}}}^{-1/2} \theta^{\otimes} - \frac{1}{2} K_{H_2} \theta^{\otimes 2} \quad (B.19)$$

$$J^* = \begin{pmatrix} \frac{\partial \theta_{CH_3OH}^*}{\partial p_{CH_3OH}} & \frac{\partial \theta_{CH_3OH}^*}{\partial p_{CO_2}} & 0 & \frac{\partial \theta_{CH_3OH}^*}{\partial p_{H_2}} & \frac{\partial \theta_{CH_3OH}^*}{\partial p_{H_2O}} & 0 \\ \frac{\partial \theta_{CO_2}^*}{\partial p_{CH_3OH}} & \frac{\partial \theta_{CO_2}^*}{\partial p_{CO_2}} & 0 & \frac{\partial \theta_{CO_2}^*}{\partial p_{H_2}} & \frac{\partial \theta_{CO_2}^*}{\partial p_{H_2O}} & 0 \\ \frac{\partial \theta_{CH_3OH}^*}{\partial p_{CH_3OH}} & \frac{\partial \theta_{CH_3OH}^*}{\partial p_{CO_2}} & 0 & \frac{\partial \theta_{CH_3OH}^*}{\partial p_{H_2}} & \frac{\partial \theta_{CH_3OH}^*}{\partial p_{H_2O}} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \\ \frac{\partial \theta_H^*}{\partial p_{CH_3OH}} & \frac{\partial \theta_H^*}{\partial p_{CO_2}} & 0 & \frac{\partial \theta_H^*}{\partial p_{H_2}} & \frac{\partial \theta_H^*}{\partial p_{H_2O}} & 0 \\ \frac{\partial \theta_{CH_3OH}^*}{\partial p_{CH_3OH}} & \frac{\partial \theta_{CH_3OH}^*}{\partial p_{CO_2}} & 0 & \frac{\partial \theta_{CH_3OH}^*}{\partial p_{H_2}} & \frac{\partial \theta_{CH_3OH}^*}{\partial p_{H_2O}} & 0 \\ \frac{\partial \theta_{H_2O}^*}{\partial p_{CH_3OH}} & \frac{\partial \theta_{H_2O}^*}{\partial p_{CO_2}} & 0 & \frac{\partial \theta_{H_2O}^*}{\partial p_{H_2}} & \frac{\partial \theta_{H_2O}^*}{\partial p_{H_2O}} & 0 \\ \frac{\partial \theta_{CH_3OH}^*}{\partial p_{CH_3OH}} & \frac{\partial \theta_{CH_3OH}^*}{\partial p_{CO_2}} & 0 & \frac{\partial \theta_{CH_3OH}^*}{\partial p_{H_2}} & \frac{\partial \theta_{CH_3OH}^*}{\partial p_{H_2O}} & 0 \\ 0 & 0 & 0 & 0 & 0 & 0 \end{pmatrix} \quad (B.20)$$

$$J^*(1,1) = \frac{\partial \theta_{CH_3OH}^*}{\partial p_{CH_3OH}} = K_{CH_3OH}^* \theta^* - K_{CH_3OH}^{*2} p_{CH_3OH} \theta^{*2} \quad (B.21)$$

$$J^*(1,2) = \frac{\partial \theta_{CH_3OH}^*}{\partial p_{CO_2}} = -K_{CH_3OH}^* K_{CO_2}^* p_{CH_3OH} \theta^{*2} \quad (B.22)$$

$$J^*(1,4) = \frac{\partial \theta_{CH_3OH}^*}{\partial p_{H_2}} = K_{CH_3OH}^* p_{CH_3OH} \frac{K_{H_2O} K_0 p_{H_2O}}{K_{H_2} p_{H_2}^2} \theta^{*2} \quad (B.23)$$

$$J^*(1,5) = \frac{\partial \theta_{CH_3OH}^*}{\partial p_{H_2O}} = -K_{CH_3OH}^* p_{CH_3OH} K_{H_2O} \left(1 + \frac{K_0}{K_{H_2} p_{H_2}}\right) \theta^{*2} \quad (B.24)$$

$$J^*(2,1) = \frac{\partial \theta_{CO_2}^*}{\partial p_{CH_3OH}} = -K_{CO_2}^* K_{CH_3OH}^* p_{CO_2} \theta^{*2} \quad (B.25)$$

$$J^*(2,2) = \frac{\partial \theta_{CO_2}^*}{\partial p_{CO_2}} = K_{CO_2}^* \theta^* - K_{CO_2}^{*2} p_{CO_2} \theta^{*2} \quad (B.26)$$

$$J^*(2,4) = \frac{\partial \theta_{CO_2}}{\partial p_{H_2}} = K_{CO_2}^* p_{CO_2} \frac{K_{H_2 O} K_{OH} p_{H_2 O}}{K_{H_2} p_{H_2}^2} \theta^{*2} \quad (B.27)$$

$$J^*(2,5) = \frac{\partial \theta_{CO_2}^*}{\partial p_{H_2 O}} = -K_{CO_2}^* p_{CO_2} K_{H_2 O} \left(1 + \frac{K_O}{K_{H_2} p_{H_2}}\right) \theta^{*2} \quad (B.28)$$

$$J^*(4,1) = \frac{\partial \theta_H^*}{\partial p_{CH_3 OH}} = -\sqrt{K_{H_2} K_{CH_3 OH}^*} \sqrt{p_{H_2} \theta^{*2}} \quad (B.29)$$

$$J^*(4,2) = \frac{\partial \theta_H^*}{\partial p_{CO_2}} = -\sqrt{K_{H_2} K_{CO_2}^*} \sqrt{p_{H_2} \theta^{*2}} \quad (B.30)$$

$$J^*(4,4) = \frac{\partial \theta_H^*}{\partial p_{H_2}} = \frac{1}{2} \sqrt{K_{H_2} p_{H_2}^{-1/2}} \theta^* + \sqrt{K_{H_2} p_{H_2} \frac{K_{H_2 O} K_{OH} p_{H_2 O}}{K_{H_2} p_{H_2}^2}} \theta^{*2} \quad (B.31)$$

$$J^*(4,5) = \frac{\partial \theta_H^*}{\partial p_{H_2 O}} = -\sqrt{K_{H_2} K_{H_2 O}} \left(1 + \frac{K_O}{K_{H_2} p_{H_2}}\right) p_{H_2}^{1/2} \theta^{*2} \quad (B.32)$$

$$J^*(5,1) = \frac{\partial \theta_{H_2 O}^*}{\partial p_{CH_3 OH}} = -K_{H_2 O} K_{CH_3 OH}^* p_{H_2 O} \theta^{*2} \quad (B.33)$$

$$J^*(5,2) = \frac{\partial \theta_{H_2 O}^*}{\partial p_{CO_2}} = -K_{H_2 O} K_{CO_2}^* p_{H_2 O} \theta^{*2} \quad (B.34)$$

$$J^*(5,4) = \frac{\partial \theta_{H_2 O}^*}{\partial p_{H_2}} = K_{H_2 O} p_{H_2 O} \frac{K_{H_2 O} K_{OH} p_{H_2 O}}{K_{H_2} p_{H_2}^2} \theta^{*2} \quad (B.35)$$

$$J^*(5,5) = \frac{\partial \theta_{H_2 O}^*}{\partial p_{H_2 O}} = K_{H_2 O} \theta^* - K_{H_2 O}^2 p_{H_2 O} \left(1 + \frac{K_O}{K_{H_2} p_{H_2}}\right) \theta^{*2} \quad (B.36)$$

Appendix C Taylor series expansion of nonlinear terms (reaction rates expressions)

For the multi-variables function $f(x,y,..z)$, the Taylor expansion is defined as:

$$\begin{aligned} f(x,y,..z), \\ &= f(x_s, y_s, ..z_s) + \left(\frac{\partial f}{\partial x}\right)_{x_s, y_s, ..z_s} (x - x_s) + \left(\frac{\partial f}{\partial y}\right)_{x_s, y_s, ..z_s} (y - y_s) + \dots + \left(\frac{\partial f}{\partial z}\right)_{x_s, y_s, ..z_s} (z - z_s) \\ &+ \left(\frac{\partial^2 f}{\partial x^2}\right)_{x_s, y_s, ..z_s} \frac{(x - x_s)^2}{2!} + \left(\frac{\partial^2 f}{\partial y^2}\right)_{x_s, y_s, ..z_s} \frac{(y - y_s)^2}{2!} + \dots + \left(\frac{\partial^2 f}{\partial z^2}\right)_{x_s, y_s, ..z_s} \frac{(z - z_s)^2}{2!} \\ &+ \left(\frac{\partial^2 f}{\partial x \partial y}\right)_{x_s, y_s, ..z_s} (x - x_s)(y - y_s) + \dots + \left(\frac{\partial^2 f}{\partial x \partial z}\right)_{x_s, y_s, ..z_s} (x - x_s)(z - z_s) \\ &+ \dots + \left(\frac{\partial^2 f}{\partial y \partial z}\right)_{x_s, y_s, ..z_s} (y - y_s)(z - z_s) + \dots \end{aligned} \quad (C.1)$$

The nonlinear terms (reaction rate expressions) are expanded in Taylor series up to second order (which are necessary for derivation of second order FRFs) around the steady state values and given in Appendix C.1-C.3.

Appendix C.1. Taylor series expansion of the expression for the reaction rate of CO hydrogenation (Eq.11)

Taylor series expansion of the expression for the reaction rate of CO hydrogenation is given here.

$$r_1 = (1 - \phi)k_1\left(p_3p_4^2 - \frac{1}{K_{p1}}p_1\right)\theta^\ominus \theta^\otimes^4 \quad (\text{C.1.1})$$

$$f_{1,s} = (1 - \phi_s)k_1\left(p_{3,s}p_{4,s}^2 - \frac{1}{K_{p1}}p_{1,s}\right) \quad (\text{C.1.2})$$

$$\begin{aligned} r_1 &\approx r_{1,s} + q_1P_{CH_3OH} + q_2P_{CO_2} + q_3P_{CO} + q_4P_{H_2} + q_5P_{H_2O} + q_6P_{N_2} + q_7\Phi + Q_{11}P_{CH_3OH}^2 + Q_{22} \\ &P_{CO_2}^2 + Q_{33}P_{CO}^2 + Q_{44}P_{H_2}^2 + Q_{55}P_{H_2O}^2 + Q_{66}P_{N_2}^2 + Q_{77}\Phi^2 + Q_{12}P_{CH_3OH}P_{CO_2} + Q_{13}P_{CH_3OH}P_{CO} \\ &+ Q_{14}P_{CH_3OH}P_{H_2} + Q_{15}P_{CH_3OH}P_{H_2O} + Q_{16}P_{CH_3OH}P_{N_2} + Q_{23}P_{CO_2}P_{CO} \\ &+ Q_{24}P_{CO_2}P_{H_2} + Q_{25}P_{CO_2}P_{H_2O} + Q_{26}P_{CO_2}P_{N_2} + Q_{34}P_{CO}P_{H_2} + Q_{35}P_{CO}P_{H_2O} + Q_{36}P_{CO}P_{N_2} \\ &+ Q_{45}P_{H_2}P_{H_2O} + Q_{46}P_{H_2}P_{N_2} + Q_{56}P_{H_2O}P_{N_2} + Q_{17}P_{CH_3OH}\Phi + Q_{27}P_{CO_2}\Phi \\ &+ Q_{37}P_{CO}\Phi + Q_{47}P_{H_2}\Phi + Q_{57}P_{H_2O}\Phi + Q_{67}P_{N_2}\Phi = r_{1,s} + \sum_{i=1}^6 q_iP_i + q_7\Phi \\ &+ \sum_{i=1}^6 \sum_{l=1}^6 Q_{il}P_iP_l + \sum_{i=1}^6 Q_{i7}P_i\Phi + Q_{77}\Phi^2 \end{aligned} \quad (\text{C.1.3})$$

$$q_1 = -f_{1,s}\theta_s^\ominus{}^2\theta_s^\otimes{}^4K_{CH_3OH}^\ominus p_{1,s} - (1 - \phi_s)\frac{k_1}{K_{p1}}p_{1,s}\theta_s^\ominus\theta_s^\otimes{}^4 \quad (\text{C.1.4})$$

$$q_2 = -f_{1,s}\theta_s^\ominus{}^2\theta_s^\otimes{}^4K_{CO_2}^\ominus p_{2,s} \quad (\text{C.1.5})$$

$$q_3 = -f_{1,s}\theta_s^\ominus{}^2\theta_s^\otimes{}^4K_{CO}^\ominus p_{3,s} + (1 - \phi_s)k_1p_{3,s}p_{4,s}^2\theta_s^\ominus\theta_s^\otimes{}^4 \quad (\text{C.1.6})$$

$$q_4 = -2f_{1,s}\theta_s^\ominus\theta_s^\otimes{}^5K_{H_2}^{1/2}p_{4,s}^{1/2} + 2(1 - \phi_s)k_1p_{3,s}p_{4,s}^2\theta_s^\ominus\theta_s^\otimes{}^4 \quad (\text{C.1.7})$$

$$q_7 = -\phi_s k_1\left(p_{3,s}p_{4,s}^2 - \frac{1}{K_{p1}}p_{1,s}\right)\theta_s^\ominus\theta_s^\otimes{}^4 \quad (\text{C.1.8})$$

$$Q_{11} = f_{1,s}\theta_s^\ominus{}^3\theta_s^\otimes{}^4K_{CH_3OH}^\ominus{}^2 p_{1,s}^2 + (1 - \phi_s)\frac{k_1}{K_{p1}}p_{1,s}^2K_{CH_3OH}^\ominus\theta_s^\ominus{}^2\theta_s^\otimes{}^4 \quad (\text{C.1.9})$$

$$Q_{22} = f_{1,s}\theta_s^\ominus{}^3\theta_s^\otimes{}^4K_{CO_2}^\ominus{}^2 p_{2,s}^2 \quad (\text{C.1.10})$$

$$Q_{33} = f_{1,s}\theta_s^\ominus{}^3\theta_s^\otimes{}^4K_{CO}^\ominus{}^2 p_{3,s}^2 - (1 - \phi_s)k_1p_{3,s}^2p_{4,s}^2K_{CO}^\ominus\theta_s^\ominus{}^2\theta_s^\otimes{}^4 \quad (\text{C.1.11})$$

$$\begin{aligned} Q_{44} &= (1 - \phi_s)k_1p_{3,s}p_{4,s}^2\theta_s^\ominus\theta_s^\otimes{}^4 + \frac{1}{2}f_{1,s}\theta_s^\ominus\theta_s^\otimes{}^5K_{H_2}^{1/2}p_{4,s}^{1/2} + \frac{5}{2}f_{1,s}\theta_s^\ominus\theta_s^\otimes{}^6K_{H_2}p_{4,s} + 4 \\ &(1 - \phi_s)k_1p_{3,s}p_{4,s}^{5/2}K_{H_2}^{1/2}\theta_s^\ominus\theta_s^\otimes{}^5 \end{aligned} \quad (\text{C.1.12})$$

$$Q_{12} = 2f_{1,s}\theta_s^{\ominus 3}\theta_s^{\otimes 4}K_{CH_3OH}^{\ominus}K_{CO_2}^{\ominus}p_{1,s}p_{2,s} + (1 - \phi_s)\frac{1}{K_{P1}}p_{1,s}K_{CO_2}^{\ominus}p_{2,s}\theta_s^{\ominus 4}\theta_s^{\otimes 4} \quad (C.1.13)$$

$$Q_{13} = 2f_{1,s}\theta_s^{\ominus 3}\theta_s^{\otimes 4}K_{CH_3OH}^{\ominus}K_{CO}^{\ominus}p_{1,s}p_{3,s} + (1 - \phi_s)\frac{k_1}{K_{P1}}p_{1,s}K_{CO}^{\ominus}p_{3,s}\theta_s^{\ominus 2}\theta_s^{\otimes 4} - (1 - \phi_s)k_1p_{3,s}p_{4,s}^2K_{CH_3OH}^{\ominus}p_{1,s}\theta_s^{\ominus 2}\theta_s^{\otimes 4} \quad (C.1.14)$$

$$Q_{14} = -2(1 - \phi_s)k_1p_{3,s}p_{4,s}^2K_{CH_3OH}^{\ominus}p_{1,s}\theta_s^{\ominus 2}\theta_s^{\otimes 4} + 2f_{1,s}\theta_s^{\ominus 2}\theta_s^{\otimes 5}K_{CH_3OH}^{\ominus}p_{1,s}K_{H_2}^{1/2}p_{4,s}^{1/2} + 2(1 - \phi_s)\frac{k_1}{K_{P1}}p_{1,s}K_{H_2}^{1/2}p_{4,s}^{1/2}\theta_s^{\ominus}\theta_s^{\otimes 5} \quad (C.1.15)$$

$$Q_{23} = 2f_{1,s}\theta_s^{\ominus 3}\theta_s^{\otimes 4}K_{CO_2}^{\ominus}K_{CO}^{\ominus}p_{2,s}p_{3,s} - (1 - \phi_s)k_1p_{3,s}p_{4,s}^2K_{CO_2}^{\ominus}p_{4,s}\theta_s^{\ominus 2}\theta_s^{\otimes 4} \quad (C.1.16)$$

$$Q_{24} = -2(1 - \phi_s)k_1p_{3,s}p_{4,s}^2K_{CO_2}^{\ominus}p_{2,s}\theta_s^{\ominus 2}\theta_s^{\otimes 4} + 2f_{1,s}\theta_s^{\ominus 2}\theta_s^{\otimes 5}K_{CO_2}^{\ominus}p_{2,s}K_{H_2}^{1/2}p_{4,s}^{1/2} \quad (C.1.17)$$

$$Q_{34} = -2(1 - \phi_s)k_1p_{3,s}^2p_{4,s}^2K_{CO}^{\ominus}\theta_s^{\ominus 2}\theta_s^{\otimes 4} + 2(1 - \phi_s)k_1p_{3,s}p_{4,s}^2\theta_s^{\ominus}\theta_s^{\otimes 4} + 2f_{1,s}\theta_s^{\ominus 2}\theta_s^{\otimes 5}K_{CO}^{\ominus}p_{3,s}K_{H_2}^{1/2}p_{4,s}^{1/2} - 2(1 - \phi_s)k_1p_{3,s}p_{4,s}^{5/2}K_{H_2}^{1/2}\theta_s^{\ominus}\theta_s^{\otimes 5} \quad (C.1.18)$$

$$Q_{17} = \phi_s k_1 \left(p_{3,s}p_{4,s}^2 - \frac{1}{K_{P1}}p_{1,s} \right) K_{CH_3OH}^{\ominus} p_{1,s} \theta_s^{\ominus 2} \theta_s^{\otimes 4} + \phi_s \frac{k_1}{K_{P1}} p_{1,s} \theta_s^{\ominus} \theta_s^{\otimes 4} \quad (C.1.19)$$

$$Q_{27} = \phi_s k_1 \left(p_{3,s}p_{4,s}^2 - \frac{1}{K_{P1}}p_{1,s} \right) K_{CO_2}^{\ominus} p_{2,s} \theta_s^{\ominus 2} \theta_s^{\otimes 4} \quad (C.1.20)$$

$$Q_{37} = \phi_s k_1 \left(p_{3,s}p_{4,s}^2 - \frac{1}{K_{P1}}p_{1,s} \right) K_{CO}^{\ominus} p_{3,s} \theta_s^{\ominus 2} \theta_s^{\otimes 4} - \phi_s k_1 p_{3,s} p_{4,s}^2 \theta_s^{\ominus} \theta_s^{\otimes 4} \quad (C.1.21)$$

$$Q_{47} = 2\phi_s k_1 \left(p_{3,s}p_{4,s}^2 - \frac{1}{K_{P1}}p_{1,s} \right) K_{H_2}^{1/2} p_{4,s}^{1/2} \theta_s^{\ominus} \theta_s^{\otimes 5} - 2\phi_s k_1 p_{3,s} p_{4,s}^2 \theta_s^{\ominus} \theta_s^{\otimes 4} \quad (C.1.22)$$

The following coefficients are equal to zero:

$$q_5, q_6, Q_{15}, Q_{16}, Q_{25}, Q_{26}, Q_{55}, Q_{66}, Q_{77}, Q_{35}, Q_{36}, Q_{45}, Q_{46}, Q_{56}, Q_{57}, Q_{67}$$

Appendix C.2. Taylor series expansion of reaction rate of CO₂ hydrogenations (Eq.12)

The Taylor series expansion of the expression for the reaction rate of CO₂ hydrogenation is given here.

$$r_2 = \phi^2 k_2 \left(p_2 p_4^2 - \frac{1}{K_{P2}} \frac{p_1 p_5}{p_4} \right) \theta^*{}^2 \theta^{\otimes 4} \quad (C.2.1)$$

$$f_{2,s} = \phi_s^2 k_2 \left(p_{2,s} p_{4,s}^2 - \frac{1}{K_{P2}} \frac{p_{1,s} p_{5,s}}{p_{4,s}} \right) \quad (C.2.2)$$

$$\begin{aligned}
r_2 \approx & r_{2,s} + \vartheta_1 P_{CH_3OH} + \vartheta_2 P_{CO_2} + \vartheta_3 P_{CO} + \vartheta_4 P_{H_2} + \vartheta_5 P_{H_2O} + \vartheta_6 P_{N_2} + \vartheta_7 \Phi + U_{11} P_{CH_3OH}^- \\
& + U_{22} P_{CO_2}^2 + U_{33} P_{CO}^2 + U_{44} P_{H_2}^2 + U_{55} P_{H_2O}^2 + U_{66} P_{N_2}^2 + U_{77} \Phi^2 + U_{12} P_{CH_3OH} P_{CO_2} \\
& + U_{13} P_{CH_3OH} P_{CO} + U_{14} P_{CH_3OH} P_{H_2} + U_{15} P_{CH_3OH} P_{H_2O} + U_{16} P_{CH_3OH} P_{N_2} + U_{23} P_{CO_2} P_{CO} \\
& + U_{24} P_{CO_2} P_{H_2} + U_{25} P_{CO_2} P_{H_2O} + U_{26} P_{CO_2} P_{N_2} + U_{34} P_{CO} P_{H_2} + U_{35} P_{CO} P_{H_2O} \\
& + U_{36} P_{CO} P_{N_2} + U_{45} P_{H_2} P_{H_2O} + U_{46} P_{H_2} P_{N_2} + U_{56} P_{H_2O} P_{N_2} + U_{17} P_{CH_3OH} \Phi + U_{27} P_{CO_2} \Phi \\
& + U_{37} P_{CO} \Phi + U_{47} P_{H_2} \Phi + U_{57} P_{H_2O} \Phi + U_{67} P_{N_2} \Phi = r_{2,s} + \sum_{i=1}^6 \vartheta_i P_i + \vartheta_7 \Phi \\
& + \sum_{i=1}^6 \sum_{l=i}^6 U_{il} P_i P_l + \sum_{i=1}^6 U_{i7} P_i \Phi + U_{77} \Phi^2
\end{aligned} \tag{C.2.3}$$

$$\varepsilon = \frac{K_0 K_{H_2O} p_{5,s}}{K_{H_2} p_{4,s}} \tag{C.2.4}$$

$$\epsilon = \frac{1 p_{1,s} p_{5,s}}{K_{P_2} p_{4,s}} \tag{C.2.5}$$

$$\vartheta_1 = -2f_{2,s} \theta_s^*{}^3 \theta_s^{\otimes 4} K_{CH_3OH}^* p_{1,s} - \phi_s^2 k_2 \beta \theta_s^*{}^2 \theta_s^{\otimes 4} \tag{C.2.6}$$

$$\vartheta_2 = -2f_{2,s} \theta_s^*{}^3 \theta_s^{\otimes 4} K_{CO_2}^* p_{2,s} + \phi_s^2 k_2 p_{2,s} p_{4,s}^2 \theta_s^*{}^2 \theta_s^{\otimes 4} \tag{C.2.7}$$

$$\vartheta_4 = 2f_{2,s} \theta_s^*{}^3 \theta_s^{\otimes 4} \varepsilon - 2f_{2,s} \theta_s^*{}^2 \theta_s^{\otimes 5} K_{H_2}^{1/2} p_{4,s}^{1/2} + \phi_s^2 k_2 (2p_{2,s} p_{4,s}^2 + \epsilon) \theta_s^*{}^2 \theta_s^{\otimes 4} \tag{C.2.8}$$

$$\vartheta_5 = -2f_{2,s} \theta_s^*{}^3 \theta_s^{\otimes 4} (K_{H_2O} p_{5,s} + \varepsilon) - \phi_s^2 k_2 \epsilon \theta_s^*{}^2 \theta_s^{\otimes 4} \tag{C.2.9}$$

$$\vartheta_7 = 2f_{2,s} \theta_s^*{}^2 \theta_s^{\otimes 4} \tag{C.2.10}$$

$$U_{11} = 3f_{2,s} \theta_s^*{}^4 \theta_s^{\otimes 4} K_{CH_3OH}^*{}^2 p_{1,s}^2 + 2K_{CH_3OH}^* p_{1,s} \phi_s^2 k_2 \epsilon \theta_s^*{}^3 \theta_s^{\otimes 4} \tag{C.2.11}$$

$$U_{22} = 3f_{2,s} \theta_s^*{}^4 \theta_s^{\otimes 4} K_{CO_2}^*{}^2 p_{2,s}^2 - 2K_{CO_2}^* \phi_s^2 k_2 p_{2,s}^2 p_{4,s}^2 \theta_s^*{}^3 \theta_s^{\otimes 4} \tag{C.2.12}$$

$$\begin{aligned}
U_{44} = & 3f_{2,s} \theta_s^*{}^4 \theta_s^{\otimes 4} \varepsilon^2 - 2f_{2,s} \theta_s^*{}^3 \theta_s^{\otimes 4} \varepsilon - 4f_{2,s} \theta_s^*{}^3 \theta_s^{\otimes 5} K_{H_2}^{1/2} p_{4,s}^{1/2} \alpha + \frac{5}{2} f_{2,s} \theta_s^*{}^2 \theta_s^{\otimes 6} K_{H_2} p_{4,s} \\
& + \frac{1}{2} f_{2,s} \theta_s^*{}^2 \theta_s^{\otimes 5} K_{H_2}^{1/2} p_{4,s}^{1/2} + 2\varepsilon \phi_s^2 k_2 (2p_{2,s} p_{4,s}^2 + \epsilon) \theta_s^*{}^3 \theta_s^{\otimes 4} - 2K_{H_2}^{1/2} p_{4,s}^{1/2} \phi_s^2 k_2 \\
& (2p_{2,s} p_{4,s}^2 + \epsilon) \theta_s^*{}^2 \theta_s^{\otimes 5} + f_{2,s} \theta_s^*{}^2 \theta_s^{\otimes 4}
\end{aligned} \tag{C.2.13}$$

$$U_{55} = 3f_{2,s} \theta_s^*{}^4 \theta_s^{\otimes 4} (K_{H_2O} p_{5,s} + \varepsilon)^2 + 2(K_{H_2O} p_{5,s} + \varepsilon) \phi_s^2 k_2 \beta \theta_s^*{}^3 \theta_s^{\otimes 4} \tag{C.2.14}$$

$$U_{77} = f_{2,s} \theta_s^*{}^2 \theta_s^{\otimes 4} \tag{C.2.15}$$

$$U_{12} = 6f_{2,s} \theta_s^*{}^4 \theta_s^{\otimes 4} K_{CH_3OH}^* K_{CO_2}^* p_{1,s} p_{2,s} - 2K_{CH_3OH}^* p_{1,s} \phi_s^2 k_2 p_{2,s} p_{4,s}^2 \theta_s^*{}^3 \theta_s^{\otimes 4} + 2K_{CO_2}^* p_{2,s} \phi_s^2 k_2 \beta \theta_s^*{}^3 \theta_s^{\otimes 4} \tag{C.2.16}$$

$$\begin{aligned}
U_{14} = & -6f_{2,s} \theta_s^*{}^4 \theta_s^{\otimes 4} K_{CH_3OH}^* p_{1,s} \varepsilon + 4f_{2,s} \theta_s^*{}^3 \theta_s^{\otimes 5} K_{CH_3OH}^* p_{1,s} K_{H_2}^{1/2} p_{4,s}^{1/2} - 2K_{CH_3OH}^* p_{1,s} \phi_s^2 k_2 \\
& (2p_{2,s} p_{4,s}^2 + \epsilon) \theta_s^*{}^3 \theta_s^{\otimes 4} - 2\varepsilon \phi_s^2 k_2 \beta \theta_s^*{}^3 \theta_s^{\otimes 4} + 2K_{H_2}^{1/2} p_{4,s}^{1/2} \phi_s^2 k_2 \epsilon \theta_s^*{}^2 \theta_s^{\otimes 5} + \phi_s^2 k_2 \epsilon \theta_s^*{}^2 \\
& \theta_s^{\otimes 4}
\end{aligned} \tag{C.2.17}$$

$$U_{15} = 6f_{2,s} \theta_s^*{}^4 \theta_s^{\otimes 4} K_{CH_3OH}^* p_{1,s} (K_{H_2O} p_{5,s} + \varepsilon) + 2(K_{H_2O} p_{5,s} + \varepsilon) \phi_s^2 k_2 \epsilon \theta_s^*{}^3 \theta_s^{\otimes 4} + 2K_{CH_3OH}^* p_{1,s} \phi_s^2 k_2 \epsilon \theta_s^*{}^3 \theta_s^{\otimes 4} - \phi_s^2 k_2 \epsilon \theta_s^*{}^2 \theta_s^{\otimes 4} \tag{C.2.18}$$

$$U_{24} = -6f_{2,s}\theta_s^* \theta_s^{\otimes 4} K_{CO_2}^* p_{2,s} \varepsilon + 4f_{2,s}\theta_s^* \theta_s^{\otimes 4} K_{CO_2}^* p_{2,s} K_{H_2}^{1/2} p_{4,s}^{1/2} + 2\varepsilon \phi_s^2 k_2 p_{2,s} p_{4,s}^2 \theta_s^* \theta_s^{\otimes 4} - 2K_{H_2}^{1/2} \phi_s^2 k_2 p_{2,s} p_{4,s}^{5/2} \theta_s^* \theta_s^{\otimes 5} - 2K_{CO_2}^* p_{2,s} \phi_s^2 k_2 (2p_{2,s} p_{4,s}^2 + \varepsilon) \theta_s^* \theta_s^{\otimes 4} + 2\phi_s^2 k_2 p_{2,s} p_{4,s}^2 \theta_s^* \theta_s^{\otimes 4} \quad (C.2.19)$$

$$U_{25} = 6f_{2,s}\theta_s^* \theta_s^{\otimes 4} K_{CO_2}^* p_{2,s} (K_{H_2} p_{5,s} + \varepsilon) - 2\phi_s^2 k_2 p_{2,s} p_{4,s}^2 (K_{H_2} p_{5,s} + \varepsilon) \theta_s^* \theta_s^{\otimes 4} + 2K_{CO_2}^* p_{2,s} \phi_s^2 k_2 \varepsilon \theta_s^* \theta_s^{\otimes 4} \quad (C.2.20)$$

$$U_{45} = -6f_{2,s}\theta_s^* \theta_s^{\otimes 4} (K_{H_2} p_{5,s} + \varepsilon) \varepsilon + 2f_{2,s}\theta_s^* \theta_s^{\otimes 4} \varepsilon + 4f_{2,s}\theta_s^* \theta_s^{\otimes 5} K_{H_2}^{1/2} p_{4,s}^{1/2} (K_{H_2} p_{5,s} + \varepsilon) - 2\phi_s^2 k_2 (2p_{2,s} p_{4,s}^2 + \varepsilon) (K_{H_2} p_{5,s} + \varepsilon) \theta_s^* \theta_s^{\otimes 4} - 2\varepsilon \phi_s^2 k_2 \varepsilon \theta_s^* \theta_s^{\otimes 4} + 2K_{H_2}^{1/2} p_{4,s}^{1/2} \phi_s^2 k_2 \varepsilon \theta_s^* \theta_s^{\otimes 5} + \phi_s^2 k_2 \varepsilon \theta_s^* \theta_s^{\otimes 4} \quad (C.2.21)$$

$$U_{17} = -4f_{2,s}\theta_s^* \theta_s^{\otimes 4} K_{CH_3OH}^* p_{1,s} - 2\phi_s^2 k_2 \varepsilon \theta_s^* \theta_s^{\otimes 4} \quad (C.2.22)$$

$$U_{27} = -4f_{2,s}\theta_s^* \theta_s^{\otimes 4} K_{CO_2}^* p_{2,s} + 2\phi_s^2 k_2 p_{2,s} p_{4,s}^2 \theta_s^* \theta_s^{\otimes 4} \quad (C.2.23)$$

$$U_{47} = 4f_{2,s}\theta_s^* \theta_s^{\otimes 4} \varepsilon - 4f_{2,s}\theta_s^* \theta_s^{\otimes 5} K_{H_2}^{1/2} p_{4,s}^{1/2} + 2\phi_s^2 k_2 (2p_{2,s} p_{4,s}^2 + \varepsilon) \theta_s^* \theta_s^{\otimes 4} \quad (C.2.24)$$

$$U_{57} = -4f_{2,s}\theta_s^* \theta_s^{\otimes 4} (K_{H_2} p_{5,s} + \varepsilon) - 2\phi_s^2 k_2 \varepsilon \theta_s^* \theta_s^{\otimes 4} \quad (C.2.25)$$

The following coefficients are equal to zero:

$$\vartheta_3, \vartheta_6, U_{33}, U_{66}, U_{13}, U_{16}, U_{23}, U_{26}, U_{34}, U_{35}, U_{36}, U_{46}, U_{56}, U_{37}, U_{67}$$

Appendix C.3. Taylor series expansion of reaction rate of RWGS reactions (Eq.13)

Taylor series expansion of the expression for the reaction rate of reverse water-gas shift reaction (Eq. 13) is given below.

$$r_3 = \phi(1 - \phi)^{-1} k_3 \left(p_2 - \frac{1}{K_{P_3}} \frac{p_3 p_5}{p_4} \right) \theta^* \theta \quad (C.3.1)$$

$$f_s = \phi_s(1 - \phi_s)^{-1} k_3 \left(p_{2,s} - \frac{1}{K_{P_3}} \frac{p_{3,s} p_{5,s}}{p_{4,s}} \right) \quad (C.3.2)$$

r_3

$$\begin{aligned} &\approx r_{3,s} + s_1 P_{CH_3OH} + s_2 P_{CO_2} + s_3 P_{CO} + s_4 P_{H_2} + s_5 P_{H_2O} + s_6 P_{N_2} + s_7 \Phi + S_{11} P_{CH_3OH}^2 + S_{22} \\ &P_{CO_2}^2 + S_{33} P_{CO}^2 + S_{44} P_{H_2}^2 + S_{55} P_{H_2O}^2 + S_{66} P_{N_2}^2 + S_{77} \Phi^2 + S_{12} P_{CH_3OH} P_{CO_2} + S_{13} \\ &P_{CH_3OH} P_{CO} + S_{14} P_{CH_3OH} P_{H_2} + S_{15} P_{CH_3OH} P_{H_2O} + S_{16} P_{CH_3OH} P_{N_2} + S_{23} P_{CO_2} P_{CO} + S_{24} P_{CO_2} P_{H_2} \\ &+ S_{25} P_{CO_2} P_{H_2O} + S_{26} P_{CO_2} P_{N_2} + S_{34} P_{CO} P_{H_2} + S_{35} P_{CO} P_{H_2O} + S_{36} P_{CO} P_{N_2} \\ &+ S_{45} P_{H_2} P_{H_2O} + S_{46} P_{H_2} P_{N_2} + S_{56} P_{H_2O} P_{N_2} + S_{17} P_{CH_3OH} \Phi + S_{27} P_{CO_2} \Phi + S_{37} P_{CO} \Phi \\ &+ S_{47} P_{H_2} \Phi + S_{57} P_{H_2O} \Phi + S_{67} P_{N_2} \Phi = r_{3,s} + \sum_{i=1}^6 s_i P_i + s_7 \Phi + \sum_{i=1}^6 \sum_{l=1}^6 S_{il} P_i P_l \\ &+ \sum_{i=1}^6 S_{i7} P_i \Phi + S_{77} \Phi^2 \end{aligned} \quad (C.3.3)$$

$$\zeta = \frac{1}{K_{P_3}} \frac{p_{3,s} p_{5,s}}{p_{4,s}} \quad (C.3.4)$$

$$s_1 = -f_{3,s}\theta_s^* \theta_s^\ominus K_{CH_3OH}^* p_{1,s} - f_{3,s}\theta_s^* \theta_s^\ominus K_{CH_3OH}^\ominus p_{1,s} \quad (C.3.5)$$

$$s_2 = -f_{3,s}\theta_s^* \theta_s^\ominus K_{CO_2}^* p_{2,s} - f_{3,s}\theta_s^* \theta_s^\ominus K_{CO_2}^\ominus p_{2,s} + \phi_s(1 - \phi_s)^{-1} k_3 p_{2,s} \theta_s^* \theta_s^\ominus \quad (C.3.6)$$

$$s_3 = -f_{3,s}\theta_s^* \theta_s^\ominus K_{CO}^\ominus p_{3,s} - \phi_s(1 - \phi_s)^{-1} k_3 \zeta \theta_s^* \theta_s^\ominus \quad (C.3.7)$$

$$s_4 = f_{3,s}\theta_s^* \theta_s^\ominus \varepsilon + \phi_s(1 - \phi_s)^{-1} k_3 \zeta \theta_s^* \theta_s^\ominus \quad (C.3.8)$$

$$s_5 = -f_{3,s}\theta_s^* \theta_s^\ominus (K_{H_2O} p_{5,s} + \varepsilon) - \phi_s(1 - \phi_s)^{-1} k_3 \zeta \theta_s^* \theta_s^\ominus \quad (C.3.9)$$

$$s_7 = \phi_s(1 - \phi_s)^{-2} k_3 (p_{2,s} - \zeta) \theta_s^* \theta_s^\ominus \quad (C.3.10)$$

$$S_{11} = f_{3,s}\theta_s^* \theta_s^\ominus p_{1,s}^2 (\theta_s^* K_{CH_3OH}^* + \theta_s^\ominus K_{CH_3OH}^\ominus + \theta_s^* \theta_s^\ominus K_{CH_3OH}^* K_{CH_3OH}^\ominus) \quad (C.3.11)$$

$$S_{22} = f_{3,s}\theta_s^* \theta_s^\ominus p_{2,s}^2 (\theta_s^* K_{CO_2}^* + \theta_s^\ominus K_{CO_2}^\ominus + \theta_s^* \theta_s^\ominus K_{CO_2}^* K_{CO_2}^\ominus) - \phi_s(1 - \phi_s)^{-1} k_3 p_{2,s}^2 \theta_s^* \theta_s^\ominus (K_{CO_2}^* \theta_s^* + K_{CO_2}^\ominus \theta_s^\ominus) \quad (C.3.12)$$

$$S_{33} = f_{3,s}\theta_s^* \theta_s^\ominus K_{CO}^\ominus p_{3,s}^2 + K_{CO}^\ominus p_{3,s} \phi_s(1 - \phi_s)^{-1} k_3 \zeta \theta_s^* \theta_s^\ominus^2 \quad (C.3.13)$$

$$S_{44} = f_{3,s}\theta_s^* \theta_s^\ominus \varepsilon (\varepsilon \theta_s^* - 1) + \varepsilon \phi_s(1 - \phi_s)^{-1} k_3 \zeta \theta_s^* \theta_s^\ominus - \phi_s(1 - \phi_s)^{-1} k_3 \zeta \theta_s^* \theta_s^\ominus \quad (C.3.14)$$

$$S_{55} = f_{3,s}\theta_s^* \theta_s^\ominus (K_{H_2O} p_{5,s} + \varepsilon)^2 + (K_{H_2O} p_{5,s} + \varepsilon) \phi_s(1 - \phi_s)^{-1} k_3 \zeta \theta_s^* \theta_s^\ominus \quad (C.3.15)$$

$$S_{77} = \phi_s^2 (1 - \phi_s)^{-3} k_3 (p_{2,s} - \zeta) \theta_s^* \theta_s^\ominus \quad (C.3.16)$$

$$S_{12} = f_{3,s}\theta_s^* \theta_s^\ominus p_{1,s} p_{2,s} (2\theta_s^* K_{CH_3OH}^* K_{CO_2}^* + 2\theta_s^\ominus K_{CH_3OH}^\ominus K_{CO_2}^\ominus + \theta_s^* \theta_s^\ominus K_{CH_3OH}^* K_{CO_2}^\ominus + \theta_s^* \theta_s^\ominus K_{CH_3OH}^\ominus K_{CO_2}^*) - p_{1,s} \theta_s^* \theta_s^\ominus \phi_s(1 - \phi_s)^{-1} k_3 p_{2,s} (K_{CH_3OH}^* \theta_s^* + K_{CH_3OH}^\ominus \theta_s^\ominus) \quad (C.3.17)$$

$$S_{13} = f_{3,s}\theta_s^* \theta_s^\ominus p_{1,s} p_{3,s} (\theta_s^* \theta_s^\ominus K_{CH_3OH}^* K_{CO}^\ominus + 2\theta_s^\ominus K_{CH_3OH}^\ominus K_{CO}^\ominus) + p_{1,s} \theta_s^* \theta_s^\ominus \phi_s(1 - \phi_s)^{-1} k_3 \zeta (K_{CH_3OH}^* \theta_s^* + K_{CH_3OH}^\ominus \theta_s^\ominus) \quad (C.3.18)$$

$$S_{14} = -f_{3,s}\theta_s^* \theta_s^\ominus p_{1,s} \varepsilon (2\theta_s^* K_{CH_3OH}^* + \theta_s^\ominus K_{CH_3OH}^\ominus) - p_{1,s} \theta_s^* \theta_s^\ominus \phi_s(1 - \phi_s)^{-1} k_3 \zeta (K_1^* \theta_s^* + K_{CH_3OH}^\ominus \theta_s^\ominus) \quad (C.3.19)$$

$$S_{15} = f_{3,s}\theta_s^* \theta_s^\ominus p_{1,s} (K_{H_2O} p_{5,s} + \varepsilon) (2\theta_s^* K_{CH_3OH}^* + \theta_s^\ominus K_{CH_3OH}^\ominus) + p_{1,s} \theta_s^* \theta_s^\ominus \phi_s(1 - \phi_s)^{-1} k_3 \zeta (K_{CH_3OH}^* \theta_s^* + K_{CH_3OH}^\ominus \theta_s^\ominus) \quad (C.3.20)$$

$$S_{23} = f_{3,s}\theta_s^* \theta_s^\ominus p_{2,s} p_{3,s} (\theta_s^* \theta_s^\ominus K_{CO_2}^* K_{CO}^\ominus + 2\theta_s^\ominus K_{CO_2}^\ominus K_{CO}^\ominus) + p_{2,s} \theta_s^* \theta_s^\ominus \phi_s(1 - \phi_s)^{-1} k_3 \zeta (\theta_s^* K_{CO_2}^* + \theta_s^\ominus K_{CO_2}^\ominus) - K_{CO}^\ominus p_{CO,s} \phi_s(1 - \phi_s)^{-1} k_3 p_{2,s} \theta_s^* \theta_s^\ominus^2 \quad (C.3.21)$$

$$S_{24} = -f_{3,s}\theta_s^* \theta_s^\ominus \varepsilon p_{2,s} (2\theta_s^* K_{CO_2}^* + \theta_s^\ominus K_{CO_2}^\ominus) - p_{2,s} \theta_s^* \theta_s^\ominus \phi_s(1 - \phi_s)^{-1} k_3 \zeta (\theta_s^* K_{CO_2}^* + \theta_s^\ominus K_{CO_2}^\ominus) + \varepsilon \phi_s(1 - \phi_s)^{-1} k_3 p_{2,s} \theta_s^* \theta_s^\ominus^2 \quad (C.3.22)$$

$$S_{25} = f_{3,s}\theta_s^* \theta_s^\ominus (K_{H_2O} p_{5,s} + \varepsilon) p_{2,s} (2\theta_s^* K_{CO_2}^* + \theta_s^\ominus K_{CO_2}^\ominus) + p_{2,s} \theta_s^* \theta_s^\ominus \phi_s(1 - \phi_s)^{-1} k_3 \zeta (\theta_s^* K_{CO_2}^* + \theta_s^\ominus K_{CO_2}^\ominus) - (K_{H_2O} p_{5,s} + \varepsilon) \phi_s(1 - \phi_s)^{-1} k_3 p_{2,s} \theta_s^* \theta_s^\ominus^2 \quad (C.3.23)$$

$$S_{34} = -f_{3,s}\theta_s^*{}^2\theta_s^{\odot 2}K_{CO}^{\odot}p_{3,s}\varepsilon - \theta_s^*\theta_s^{\odot}\phi_s(1-\phi_s)^{-1}k_3\zeta(\theta_s^*\varepsilon + \theta_s^{\odot}K_{CO}^{\odot}p_{3,s}) + \phi_s(1-\phi_s)^{-1}k_3\zeta\theta_s^*\theta_s^{\odot} \quad (C.3.24)$$

$$S_{35} = f_{3,s}\theta_s^*{}^2\theta_s^{\odot 2}K_{CO}^{\odot}p_{3,s}(K_{H_2O}p_{5,s} + \varepsilon) + \theta_s^*\theta_s^{\odot}\phi_s(1-\phi_s)^{-1}k_3\zeta[\theta_s^*(K_{H_2O}p_{5,s} + \varepsilon) + \theta_s^{\odot}K_{CO}^{\odot}p_{3,s}] - \phi_s(1-\phi_s)^{-1}k_3\zeta\theta_s^*\theta_s^{\odot} \quad (C.3.25)$$

$$S_{45} = f_{3,s}\theta_s^*{}^2\theta_s^{\odot}\varepsilon[1 - 2\theta_s^*(K_{H_2O}p_{5,s} + \varepsilon)] - \theta_s^*{}^2\theta_s^{\odot}\phi_s(1-\phi_s)^{-1}k_3\zeta(2\varepsilon + K_{H_2O}p_{5,s}) + \phi_s(1-\phi_s)^{-1}k_3\zeta\theta_s^*\theta_s^{\odot} \quad (C.3.26)$$

$$S_{17} = -(1-\phi_s)^{-1}f_{3,s}\theta_s^*\theta_s^{\odot}p_{1,s}(K_{CH_3OH}^*\theta_s^* + K_{CH_3OH}^{\odot}\theta_s^{\odot}) \quad (C.3.27)$$

$$S_{27} = -(1-\phi_s)^{-1}f_{3,s}\theta_s^*\theta_s^{\odot}p_{2,s}(\theta_s^*K_{CO_2}^* + \theta_s^{\odot}K_{CO_2}^{\odot}) + \phi_s(1-\phi_s)^{-2}k_3p_{2,s}\theta_s^*\theta_s^{\odot} \quad (C.3.28)$$

$$S_{37} = -(1-\phi_s)^{-1}f_{3,s}\theta_s^*\theta_s^{\odot 2}K_{CO}^{\odot}p_{3,s} - \phi_s(1-\phi_s)^{-2}k_3\zeta\theta_s^*\theta_s^{\odot} \quad (C.3.29)$$

$$S_{47} = (1-\phi_s)^{-1}f_{3,s}\theta_s^*{}^2\theta_s^{\odot}\varepsilon + \phi_s(1-\phi_s)^{-2}k_3\zeta\theta_s^*\theta_s^{\odot} \quad (C.3.30)$$

$$S_{57} = -(1-\phi_s)^{-1}f_{3,s}\theta_s^*{}^2\theta_s^{\odot}(K_{H_2O}p_{5,s} + \varepsilon) - \phi_s(1-\phi_s)^{-2}k_3\zeta\theta_s^*\theta_s^{\odot} \quad (C.3.31)$$

The following coefficients are equal to zero:

$$s_6, S_{16}, S_{26}, S_{36}, S_{46}, S_{56}, S_{66}, S_{76}$$

Appendix D. The auxiliary parameters in Eq. (25) of dimensionless mathematical model

The auxiliary parameters used in Eq. (25) of dimensionless mathematical model, which describes the catalyst dynamic, are defined as follows:

$$E_1 = k_1^+ \frac{p_{3,s} V_G}{p_{tot} \dot{V}_{0,s}} \quad (D.1)$$

$$E_2 = \frac{k_1^+ p_{2,s} V_G}{K_1 p_{tot} \dot{V}_{0,s}} \quad (D.2)$$

$$E_3 = k_2^+ \frac{p_{4,s} V_G}{p_{tot} \dot{V}_{0,s}} \quad (D.3)$$

$$E_4 = \frac{k_2^+ p_{5,s} V_G}{K_2 p_{tot} \dot{V}_{0,s}} \quad (D.4)$$

Appendix E – Coefficients used in matrix equation for derivation of first order G FRFs

The coefficients α_{il} are defined in the following way:

$$\alpha_{il} = m_{cat} q_{sat} \frac{RT p_{i,s}}{V_G p_{i,s}} \left(\frac{\partial \theta_i}{\partial p_i} \right) j\omega - \frac{RT}{p_{i,s} \dot{V}_{0,s}} m_{cat} (v_{i,1} q_l + v_{i,2} \vartheta_l + v_{i,3} S_l), \quad i \neq l, i, l = 1, \dots, 5 \quad (E.1)$$

$$\alpha_{ii} = \left(1 + m_{cat} q_{sat} \frac{RT}{V_G} \left(\frac{\partial \theta_i}{\partial p_i} \right) \right) j\omega + \frac{\dot{V}_s}{\dot{V}_{0,s}} - \frac{RT}{p_{i,s} \dot{V}_{0,s}} m_{cat} (v_{i,1} q_i + v_{i,2} \vartheta_i + v_{i,3} S_i), \quad i = 1, \dots, 5$$

$$\alpha_{i6} = -\frac{RT}{p_{i,s}\dot{V}_{0,s}}m_{cat}(v_{i,1}q_l + v_{i,2}\vartheta_l + v_{i,3}s_l), \quad i = 1, \dots, 5 \quad (E.3)$$

$$\alpha_{i7} = \frac{\dot{V}_s}{\dot{V}_{0,s}}, i = 1, \dots, 5 \quad (E.4)$$

$$\alpha_{62} = E_2 \quad (E.5)$$

$$\alpha_{63} = -\frac{(\phi_{max} - \phi_s)}{\phi_s}E_1 \quad (E.6)$$

$$\alpha_{64} = -\frac{(\phi_{max} - \phi_s)}{\phi_s}E_3 \quad (E.7)$$

$$\alpha_{65} = E_4 \quad (E.8)$$

$$\alpha_{66} = j\omega + E_1 + E_2 + E_3 + E_4 \quad (E.9)$$

The coefficients α_{61}, α_{67} are equal to zero ($\alpha_{61} = \alpha_{67} = 0$).

$$\alpha_{7i} = m_{cat}q_{sat}\frac{\dot{V}_{0,s}}{V_G}p_{i,s}\sum_{l=1}^5\frac{\partial\theta_l}{\partial p_l}j\omega - m_{cat}(-2q_i - 2\vartheta_i), \quad i = 1, \dots, 5 \quad (E.10)$$

$$\alpha_{76} = -m_{cat}(-2q_7 - 2\vartheta_7) \quad (E.11)$$

$$\alpha_{77} = \frac{\dot{V}_s p_{tot}}{RT} \quad (E.12)$$

Appendix F– Coefficients used in matrix equation for derivation of the G ASO FRFs

The coefficients γ_{il} are in correlation with coefficients α_{il} , as follows

$$\gamma_{il} = Re(\alpha_{il}) \text{ for } i, l = 1, \dots, 5, \quad (F.1)$$

$$\gamma_{7i} = Re(\alpha_{7i}) \text{ for } i = 1, \dots, 5, \quad (F.2)$$

$$\gamma_{66} = Re(\alpha_{66}) \quad (F.3)$$

$$\gamma_{6i} = \alpha_{6i} \text{ for } i = 1, \dots, 7 \neq 6 \quad (F.4)$$

$$\gamma_{i6} = \alpha_{i6} \text{ for } i = 1, \dots, 7 \neq 6 \quad (F.5)$$

$$\gamma_{i7} = \alpha_{i7} \text{ for } i = 1, \dots, 5 \quad (F.6)$$

The auxiliary functions are defined as follows:

Γ_{ix}

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

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

$$= 1, \dots, 5; x = 1, \dots, 4$$

(F. 7)

 Γ_{6x}

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

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

$$G_{6,x}^{(1)}(\omega)) + [-E_4](G_{5,x}^{(1)}(\omega)G_{6,x}^{(1)}(-\omega) + G_{5,x}^{(1)}(-\omega)G_{6,x}^{(1)}(\omega)), x = 1, \dots, 4$$

(F. 8)

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

$$= 1, \dots, 4$$

(F. 9)

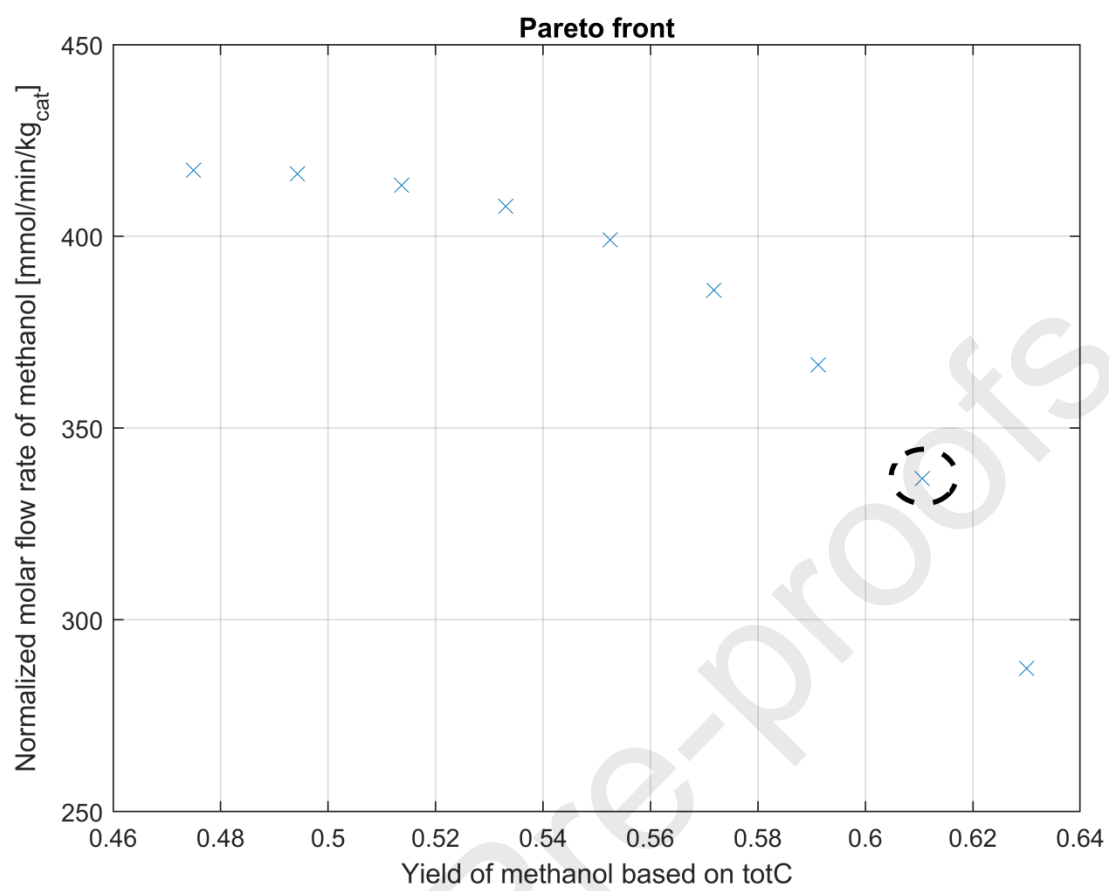


Figure G.1. Pareto front for optimal steady-state with respect of two objective functions (normalized outlet molar flow-rate of methanol ($mmol/min/kg_{cat}$) and yield of methanol based on total carbon (%))

References

- Armstrong C. D., Teixeira, A.R., (2020). Advances in dynamically controlled catalytic reaction engineering, *Reaction, Chemistry & Engineering*, DOI: 10.1039/d0re00330a
- Bailey, J.E. (1973). Periodic operation of chemical reactors: A review. *Chemical Engineering Communications*, 1, pp. 111-124.
- Berty. J.M., 1974: Reactor for Vapor-Phase Catalytic Studies. *Chem. Eng. Prog.* 70, 5, 78-84.
- Chanchlani, K.G., Hudgins, R.R., Silveston, P.L., (1992) Activation of Cu/ZnO methanol catalysts by periodic compositions switching, *Progress in Catalysis*, pp. 331-333
- Chanchlani, K.G., Hugins, R.R., Silveston, P.L., (1994) Methanol Synthesis Under periodic Operation: An Experimental Investigation, *The Canadian Journal of Chemical Engineering*, 72, pp. 657-671
- Chen, C.C., Hwang, C. and Yang R.Y. (1994). Optimal periodic forcing of nonlinear chemical processes for performance improvements. *The Canadian Journal of Chemical Engineering*, 71, pp. 672-682.
- Currie, R., Nikolić, D., Petkovska, M., Simakov, D., (2018), CO₂ Conversion Enhancement in a Periodically Operated Sabatier Reactor: Nonlinear Frequency Response Analysis and Simulation-based Study, *Israel Journal of Chemistry*, 58(6), pp. 762-775
- Douglas, J.M. and Rippin, D.W.T. (1966). Unsteady state process operation. *Chemical Engineering Science*, 21, pp. 305-315.
- Douglas, J.M. (1967). Periodic reactor operation. *Industrial and Engineering Chemistry Process Design and Development*, 6, pp. 43-48.
- Douglas, J.M. (1972). *Process Dynamics and Control*. New Jersey: Prentice-Hall, Englewood Cliffs.
- Ehrgott, M. *Multicriteria optimization: Second edition*; Springer Science & Media, 2005; pp. 1–323. doi:10.1007/3-540-27659-9.
- Felischak, M., Kaps, L., Hamel, C., Nikolic, D., Petkovska, M., Seidel-Morgenstern, A. (2021). Analysis and experimental demonstration of forced periodic operation of an adiabatic stirred tank reactor: Simultaneous modulation of inlet concentration and total flow-rate, *Chemical Engineering Journal*, 410, 128197, <https://doi.org/10.1016/j.cej.2020.128197>.
-

Fencsak, M. (2020), Enhanced reactor performance by dynamic operation: Application of inherent and forced periodic behaviour, PhD Thesis, Faculty of Process and Systems Engineering, Otto-von-Guericke University.

Fiedler, E., Grossmann, G., Kersebohm, D.B., Weiss, G., Witte, C., (2000). Methanol. Wiley-VCH Verlag GmbH & Co, KGaA.

Graaf, G.H., Stamhuis, E.J., Beenackers, A.A.C.M., (1988). Kinetics of low-pressure methanol synthesis, *Chemical Engineering Science*, 43,12,p.3185-3195.

Haimes Y.V., Lasdon L.S., Wismer D.A., (1971). On a bicriterion formation of the problems of integrated system identification and system optimization. *IEEE Transactions on Systems, Man and Cybernetics*. <https://doi.org/10.1109/TSMC.1971.4308298>.

Larsen H. H., Sonderberg Petersen, L., (2013). DTU International Energy Report 2013: Energy Storage Options for Future Sustainable Energy Systems. Technical University Denmark.

Marković, A., Seidel-Morgenstern, A. and Petkovska, M. (2008). Evaluation of the potential of periodically operated reactors based on the second order frequency response functions. *Chemical Engineering Research and Design*, 86, pp. 682-691.

Martin, M., (2016) Methodology for solar and wind energy chemical storage facilities design under uncertainty: methanol production from CO₂ and hydrogen. *Comput. Chem. Eng.* 92, 43-54.

Nikolić-Paunić, D. and Petkovska, M. (2013). Evaluation of periodic processes with two modulated inputs based on nonlinear frequency response analysis. Case study: CSTR with modulation of the inlet concentration and flow-rate. *Chemical Engineering Science*, 104, pp. 208-219.

Nikolić, D., Seidel-Morgenstern, A. and Petkovska, M. (2014a). Nonlinear frequency response analysis of forced periodic operations of non-isothermal CSTR with single input modulations. Part I: Modulation of inlet concentration or flow-rate. *Chemical Engineering Science*, 117, pp. 71-84.

Nikolić, D., Seidel-Morgenstern, A. and Petkovska, M. (2014b). Nonlinear frequency response analysis of forced periodic operations of non-isothermal CSTR with single input modulations. Part II: Modulation of inlet temperature or temperature of the heating/cooling fluid. *Chemical Engineering Science*, 117, pp. 31-44.

Nikolić, D., Seidel-Morgenstern, A. and Petkovska, M. (2015). Nonlinear frequency response analysis of forced periodic operation of non-isothermal CSTR with simultaneous modulation of inlet concentration and inlet temperature. *Chemical Engineering Science*, 137, pp. 40-58.

Nikolić, D., (2016) Forced Periodically Operated Chemical Reactors- Evaluation and Analysis by the Nonlinear Frequency Response Method, PhD Thesis, Faculty of Technology and Metallurgy, University of Belgrade.

Nikolić, D., Seidel-Morgenstern, A., Petkovska, M. (2016a). Periodic operation with modulation of inlet concentration and flow-rate Part I Non-isothermal continuous stirred-tank reactor, *Chemical Engineering and Technology*, Volume 39, Issue 11, p. 2020-2028

Nikolić, D., Felischak, M., Seidel-Morgenstern, A., Petkovska, M. (2016b), Periodic operation with modulation of inlet concentration and flow-rate Part II Adiabatic continuous stirred-tank reactor, *Chemical Engineering and Technology*, Volume 39, Issue 11, p. 2126-2134

Nikolić, D., Petkovska, M. (2016), Evaluation of Performance of Periodically Operated Reactors for Single Input Modulations of General Waveforms, *Chemie Ingenieur Technik*, Volume 88, Issue 11, p. 1715-1722

Nikolić, D., Seidel-Morgenstern, A., Petkovska, M., (2020), Nonlinear frequency response analysis of forced periodic operations with simultaneous modulation of two general waveform inputs with application on adiabatic CSTR with square-wave modulations, *Chemical Engineering Science*, 226

Olah, G.A., (2004). After oil and gas: methanol economy. *Catal. Lett.* 93 (1), 1-2.

Olah, G.A., (2005). Beyond oil and gas: methanol economy. *Angew. Chem. Int. Ed.* 44 (18), 2636-2639.

Ovesen, C.V., Clausen, B.S., Schiotz, J., Stoltze, P., Topsoe, H., Norskov, J. K., (1997). Kinetic Implications of Dynamical Changes in Catalyst Morphology during Methanol Synthesis over Cu/ZnO Catalysts, *Journal of Catalysis*, 168, 2, p. 133-142.

Parulekar, S. J. (2003). Systematic performance analysis of continuous processes subject to multiple input cycling. *Chemical Engineering Science* 58, pp. 5173-5194

Petkovska, M., Nikolić, D., Marković, A. and Seidel-Morgenstern, A. (2010). Fast evaluation of periodic operation of a heterogeneous reactor based on nonlinear frequency response analysis. *Chemical Engineering Science*, 65, pp. 3632-3637.

Petkovska, M. and Seidel-Morgenstern, A. (2015). Evaluation of periodic processes. in: Silveston, R.R. and Hudgins, R.R., ed., *Periodic Operation of Reactors*, Amsterdam: Elsevier, pp. 387-413.

Petkovska, M., Nikolić, D., Seidel-Morgenstern, A., (2018), Nonlinear Frequency Response Method for Evaluating Forced Periodic Operations of Chemical Reactors, *Israel Journal of Chemistry* 58(6), pp. 1-20.

Raeuchle, K., Plass, L., Wernicke, H. J., Bertau, M., (2016). Methanol for renewable energy storage and utilization. *Energy Technol.* 4(1), 193-200.

Renken, A. (1972). The use of periodic operation to improve the performance of continuous stirred tank reactors. *Chemical Engineering Science*, 27, pp. 1925-1932.

Schadlich, K., Hoffmann, U. and Hofmann, H. (1983). Periodical operation of chemical processes and evaluation of conversion improvements. *Chemical Engineering Science*, 38, pp. 1375-1384.

Seidel, C., Jorke, A., Vollbrecht, B., Seidel-Morgenstern, A., Kienle, A., (2018). Kinetic modeling of methanol synthesis from renewable resources, *Chemical Engineering Science*, 175, 130-138

Seidel, C., Jorke, A., Vollbrecht, B., Seidel-Morgenstern, A., Kienle, A., (2020), Corrigendum to Kinetic Modelling of Methanol Synthesis from Renewable Resources, (*Chem. Eng. Sci.* 175 (2018), 130-138), *Chemical Engineering Science* 223, 115724.

Silveston, P.L. (1987). Periodic operation of chemical reactors-a review of the experimental literature. *Sadhana*, 10, pp. 217-246.

Silveston, P., Hudgins, R. and Renken, A. (1995). Periodic operation of catalytic reactors – introduction and overview, *Catalysis Today*, 25 pp. 91-112.

Silveston, P.L. (1998). *Composition Modulation of Catalytic Reactors*. Amsterdam: Gordon and Breach Science Publishers.

Silveston, P.L. and Hudgins, R.R. (editors) (2013). *Periodic Operation of Reactors*, Amsterdam: Elsevier

Slatboom Y., Bos M.J., Pieper J., Vrieswijk V., Likožar B., Kersten S.R.A., Brilman D.W.F., (2020). Critical assessment of steady-state kinetic models for the synthesis of methanol over an industrial Cu/ZnO/Al₂O₃ catalyst, *Chemical Engineering Journal* 389, 124181.

Sterman L.E. and Ydstie B.E. (1990a). Unsteady-state multivariable analysis of periodically perturbed systems. *Chemical Engineering Science*, 45, pp.737-749.

Sterman, L. E. and Ydstie B. E. (1990b). The steady-state process with periodic perturbations. *Chemical Engineering Science* 45, pp.721-736.

Sterman L. E. and Ydstie B.E (1991). Periodic forcing of the CSTR: an Application of the Generalized II-Criterion, *AIChE Journal* 37, pp. 986-996.

Van Gerven, T. and Stankiewicz A., (2009). Structure, Energy, Synergy, Time - The Fundamentals of Process Intensification, *Ind Eng Chem Res*, 48, 5, pp.2465-2474.

Vollbrecht B., 2007. Zur Kinetic der Methanolsynthese an einem technischen Cu/ZnO/Al₂O₃-Katalysator. PhD thesis, Otto-von-Guericke-Universitat Magdeburg.

Volterra, V. (1959). *Theory of Functionals and Integral and Integrodifferential Equations*. New York: Dover.

Warnecke F., Lin L., Haag S., Freund H. (2020): Identification of Reaction Pathways and Kinetic Modeling of Olefin Interconversion over an H-ZSM-5, Catalyst, *Industrial & Engineering Chemistry Research*, 59,28, 12696-12709, DOI: 10.1021/acs.iecr.0c01747.

Weiner, D.D. and Spina, J.F. (1980). *Sinusoidal Analysis and Modeling of Weakly Nonlinear Circuits*. New York: Van Nostrand Reinhold Company

Živković L., Vidaković-Koch T., Petkovska M., (2020a). Computer-Aided Nonlinear Frequency Response Method for Investigating the Dynamics of Chemical Engineering Systems, *Processes*, 8, 1354, doi:10.3390/pr8111354

Živković L., Milić V., Vidaković-Koch T., Petkovska M., (2020b). Rapid Multi-Objective Optimization of Periodically Operated Processes Based on the Computer-Aided Nonlinear Frequency Response Method, *Processes*, 8, 1357, doi:10.3390/pr8111357.

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:

Daliborka Nikolić: Theoretical Investigation, Formal analysis, Software, Writing and Paper Preparation

Carsten Seidel: Theoretical Investigation, Formal analysis, Software, Reviewing Paper

Matthias Felischak: Experimental Investigation, Formal analysis, Software, Reviewing Paper

Tamara Miličić: Theoretical Investigation, Formal analysis, Software

Achim Kienle: Theoretical Investigation, Supervision, Reviewing, Validation, Reviewing Paper

Andreas Seidel-Morgenstern: Experimental Investigation, Supervision, Reviewing, Validation, Reviewing Paper

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

Highlights

- Quantifying forced periodic operation of chemical reactor
- Analysis by the Nonlinear Frequency Response method
- Methanol synthesis in isothermal and isobaric lab-scale CSTR
- Single input modulations (partial pressures of all reactants and volumetric flow-rate)
- No significant improvement could be obtained with single input modulations

Figure captions

Figure 1. The asymmetrical second order H FRFs for single input modulations of partial pressures of CO₂, CO and H₂ or volumetric flow-rate around their optimal steady-state values, vs. dimensionless frequency.

Figure 2. The maximal possible values of the asymmetrical second order H -FRFS for single input modulations of the partial pressures of CO_2 , CO and H_2 and volumetric flow-rate of the feed steam vs. dimensionless frequency.

Figure G.1. Pareto front for optimal steady-state with respect of two objective functions (normalized outlet molar flow-rate of methanol ($\text{mmol}/\text{min}/\text{kg}_{\text{cat}}$) and yield of methanol based on total carbon (%))

Tables

Table 1. Parameters and constant used in kinetic model

Parameter	Unit	Value
ϕ_{max}	-	0.9
$A_{k,CO}$	$\text{mol}/\text{kg}_{\text{cat}}/\text{s}/\text{bar}^3$	0.00673
B_{CO}	-	26.4549
A_{k,CO_2}	$\text{mol}/\text{kg}_{\text{cat}}/\text{s}/\text{bar}^3$	0.0430
B_{CO_2}	-	1.5308
$A_{k,RWGS}$	$\text{mol}/\text{kg}_{\text{cat}}/\text{s}/\text{bar}$	0.0117
B_{RWGS}	-	15.6154
$\sqrt{K_{H_2}}$	$\text{bar}^{-1/2}$	1.1064
$K_{CH_3OH}^*$	bar^{-1}	0
K_{H_2O}	bar^{-1}	0
K_O	-	0
K_{CO}	bar^{-1}	0.1497
$K_{CH_3OH}^\ominus$	bar^{-1}	0
$K_{CO_2}^*$	bar^{-1}	0.0629
$K_{CO_2}^\ominus$	bar^{-1}	0

ΔG_1	kJ/mol	0.336
ΔG_2	kJ/mol	21.841
k_1^+	s^{-1}	$79.174 \cdot 10^{-4}$
k_2^+	s^{-1}	$1.88 \cdot 10^{-5}$
q_{sat}	mol/kg_{cat}	0.98

Table 2 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 centres 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 3. Overview of the chosen optimal steady-state point for analysis.

Fixed parameters						
p_{tot} (bar)		$\dot{V}_{0,s}$ (ml/min)			$y_{N_2,s}$	
60		6.93			0.15	
Optimization parameters						
$y_{CO_2,s}$		$y_{CO,s}$	$y_{H_2,s}$		T_s [K]	
0.021		0.185	0.644		473	
Outputs						
$y_{CH_3OH,s}$	$y_{CO_2,s}$	$y_{CO,s}$	$y_{H_2,s}$	$y_{H_2O,s}$	$y_{N_2,s}$	$\dot{V}_{out,s}$ ml/min
0.168	0.026	0.081	0.522	0.002	0.200	5.186
Performance indicators						
$(\dot{n}_{CH_3OH}^{norm})_{SS}$ [mmol/min/kg _{cat}]		$(Y_{CH_3OH}^{totC})_{SS}$ (%)		$(Y_{CH_3OH}^{H_2})_{SS}$ (%)		
336.91		61.05		39.09		

Table 4. The normalized outlet molar flow-rate and yields of methanol based on total carbon and on hydrogen for the cases corresponding to the maximal ASO H -FRFs, for steady-state and periodic operations.

Modulated input	$(\dot{n}_{CH_3OH}^{norm})_{SS}$ [mmol/min/kg _{cat}]	$(Y_{CH_3OH}^{totC})_{SS}$ %	$(Y_{CH_3OH}^{H_2})_{SS}$ %	$(\dot{n}_{CH_3OH}^{norm})_{PO}$ [mmol/min/kg _{cat}]	$(Y_{CH_3OH}^{totC})_{PO}$ %	$(Y_{CH_3OH}^{H_2})_{PO}$ %	Max impr. [%]
P_{CO_2}	59.95	11.19	6.89	60.09	11.21	6.91	0.23
P_{CO}	102.82	29.64	10.66	107.90	31.10	11.19	4.95
P_{H_2}	261.72	27.93	39.11	263.50	28.12	39.37	0.68
v_0	7.69	28.89	0.68	7.70	28.92	0.69	0.12

Table S1 The values of input and output variables for steady-state ($p_{tot}=60$ bar) with respect to maximal value of H ASO FRF $H^{(2)}_{1,1,1}(\omega,-\omega)$

Inputs (steady-state)						
Molar fraction of component, [-]					Temperature [K]	
$y_{0,s}$ (CO ₂)	$y_{0,s}$ (CO)	$y_{0,s}$ (H ₂)			T [K]	
0.0014	0.1988	0.6498			473	
Forcing parameters for maximal improvement						
Forcing frequency, dimesionless [-]					0.3364	
Forcing amplitude of CO ₂					1	
Ouputs (steady-state)						
\dot{V}_{out} , ml/min		6.6204				
y_s (CH ₃ OH)	y_s (CO ₂)	y_s (CO)	y_s (H ₂)	y_s (H ₂ O)	y_s (N ₂)	$y_{tot,s}$
0.0234	0.0014	0.1847	0.6333	$5.89 \cdot 10^{-5}$	0.1570	1
$\dot{n}_{CH_3OH,s}^{norm}$ [mmol/min/ kg _{cat}]		55.95				
Yield of methanol based on total C, %		11.19				
Yield of methanol based on H ₂ , %		6.89				
Ouputs for periodic modulation with maximal improvement						
$H^{(2)}_{1,1,1}(\omega,-\omega)^{max}$		0.0046				
$(\dot{n}_{CH_3OH})_{mean}^{norm}$ [mmol/min/kg _{cat}]		60.09				
Yield of methanol based on total C, %		11.21				
Yield of methanol based on H ₂ , %		6.91				
Maximal increase of outlet molar flow-rate of methanol, yield of methanol based on tot C or based on H ₂ , %		0.23				

Table S2 The values of input and output variables for steady-state ($p_{tot}=60$ bar) with respect to maximal value of H ASO FRF $H^{(2)}_{1,2,2}(\omega,-\omega)$

Inputs (steady-state)						
$y_{0,s}$ (CO ₂)	$y_{0,s}$ (CO)	$y_{0,s}$ (H ₂)			T [K]	
0.0814	0.0482	0.7204			473	
Forcing parameters for maximal improvement						
Forcing frequency, dimensionless [-]					0.2889	
Forcing amplitude of CO					1	
Outputs (steady-state)						
\dot{V}_{out} , ml/min		6.3696				
y_s (CH ₃ OH)	y_s (CO ₂)	y_s (CO)	y_s (H ₂)	y_s (H ₂ O)	y_s (N ₂)	$y_{tot,s}$
0.0416	0.0734	0.0253	0.6824	0.0147	0.1625	1
$\dot{n}_{CH_3OH,s}^{norm}$ [mmol/min/ kg _{cat}]		102.82				
Yield of methanol based on tot C, %		29.64				
Yield of methanol based on H ₂ , %		10.66				
Outputs for periodic modulation with maximal improvement						
$H^{(2)}_{1,2,2}(\omega,-\omega)^{max}$		0.0989				
$(\dot{n}_{CH_3OH}^{norm})_{mean}$ [mmol/min/ kg _{cat}]		107.90				
Yield of methanol based on tot C, %		31.10				
Yield of methanol based on H ₂ , %		11.19				
Maximal increase of outlet molar flow-rate of methanol, yield of methanol based on total C or based on H ₂ , %		4.95				

Table S3 The values of input and output variables for steady-state ($p_{tot} = 60$ bar) with respect to maximal value of H ASO FRF $H^{(2)}_{1,3,3}(\omega, -\omega)$

Inputs (steady-state)						
$y_{0,s}$ (CO ₂)	$y_{0,s}$ (CO)	$y_{0,s}$ (H ₂)			T [K]	
0.0250	0.3250	0.5000			533	
Forcing parameters for maximal improvement						
Forcing frequency, dimensionless [-]					0.4354	
Forcing amplitude of H ₂					0.3000	
Outputs (steady-state)						
\dot{V}_{out} , ml/min		6.2826				
y_s (CH ₃ OH)	y_s (CO ₂)	y_s (CO)	y_s (H ₂)	y_s (H ₂ O)	y_s (N ₂)	$y_{tot,s}$
0.1215	0.0304	0.2831	0.3778	$6.56 \cdot 10^{-4}$	0.1865	1
$\dot{n}_{CH_3OH,s}^{norm}$ [mmol/min/ kg _{cat}]		261.72				
Yield of methanol based on total C, %		27.93				
Yield of methanol based on H ₂ , %		39.11				
Outputs for periodic modulation with maximal improvement						
$H^{(2)}_{1,3,3}(\omega, -\omega)^{max}$		0.1508				
$(\dot{n}_{CH_3OH}^{norm})_{mean}$ [mmol/min/ kg _{cat}]		263.50				
Yield of methanol based on total C, %		28.12				
Yield of methanol based on H ₂ , %		39.37				
Maximal increase of outlet molar flow-rate of methanol, yield of methanol based on total C or based on H ₂ , %		0.68				

Table S4 The values of input and output variables for steady-state ($p_{tot} = 60$ bar) with respect to maximal value of H ASO FRF $H^{(2)}_{1,4,4}(\omega, -\omega)$

Inputs (steady-state)						
$y_{0,s}$ (CO ₂)	$y_{0,s}$ (CO)	$y_{0,s}$ (H ₂)			T [K]	
3.5166 10 ⁻⁴	0.0096	0.8400			473	
Forcing parameters for maximal improvement						
Forcing frequency, dimensionless [-]					13.6903	
Forcing amplitude of inlet volumetric flow-rate					1	
Outputs (steady-state)						
\dot{V}_{out} , ml/min		8.844				
y_s (CH ₃ OH)	y_s (CO ₂)	y_s (CO)	y_s (H ₂)	y_s (H ₂ O)	y_s (N ₂)	$y_{tot,s}$
0.0029	1.7707 10 ⁻⁴	0.0069	0.8389	1.7663*10 ⁻⁴	0.1509	1
$\dot{n}_{CH_3OH,s}^{norm}$ [mmol/min/ kg _{cat}]		7.69				
Yield of methanol based on total C, %		28.89				
Yield of methanol based on H ₂ , %		0.68				
Outputs for periodic modulation with maximal improvement						
$H^{(2)}_{1,4,4}(\omega, -\omega)^{max}$		0.0023				
$(\dot{n}_{CH_3OH}^{norm})_{mean}$ [mmol/min/ kg _{cat}]		7.70				
Yield of methanol based on total C, %		28.92				
Yield of methanol based on H ₂ , %		0.69				
Maximal increase of outlet molar flow-rate of methanol, yield of methanol based on total C or based on H ₂ , %		0.12				

