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Evaluation of possible improvements of forced periodically operated reactor in which methanol synthesis takes place – based on the Nonlinear Frequency Response analysis

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ABSTRACT

The continuous industrial chemical processes are typically designed through steady-state conditions. Nevertheless, there is evidence that processes can be intensified by applying optimized forced periodic operation. Possible improvements in reactor performances caused by the implementation of forced periodic operation (FPO) can be successfully evaluated by applying a nonlinear frequency response (NFR) analysis, before experimental investigation. In this study, we will present the results of two case studies based on heterogeneously catalyzed methanol synthesis in a continuous stirred tank reactor (CSTR). The first is an isothermal case, and the second is a more complicated and more realistic, non-isothermal case.

Keywords: methanol synthesis, process intensification, nonlinear frequency response method, forced periodic operation, continuous stirred tank reactor

1. INTRODUCTION

Methanol is produced in large quantities worldwide commonly from synthesis gas using heterogeneous catalysts [1]. This type of alcohol is more and more interesting, particularly in the context of power exploitation and energy storage [1]. There is already an awareness that renewable energies in combination with chemical energy conversion will play a crucial role in future energy scenarios [2]. Methanol, with the role of chemical storage of energy, can be obtained in (electro-) catalytic processes from waste CO and CO2 released from industry and renewable electricity. All these processes are dynamic and nonlinear in nature so FPO could be beneficial [2]. The NFR method is a reliable analytical tool for the analysis of forced periodically operated processes and for evaluating possible improvements and finding the best forcing parameters [3]. The application of this method to the periodic operation of chemical reactors is recent. However, it has already been proven on several process systems, CSTR [4–8], plug flow and dispersed flow tubular reactor [6], Sabatier reaction [9], and experimentally confirmed for hydrolysis of acetic anhydride [7].

This study presents the results of the application of the NFR method for the evaluation of improvement of the production of methanol obtained from renewable sources in isothermal and non-isothermal CSTR.

2. THEORY

2.1 Kinetic model

Methanol synthesis from CO, CO_2, and H_2 in the presence of a heterogeneous catalyst (commercial $Cu/ZnO/Al_2O_3$) considered in this paper takes place through three chemical reactions represented schematically in Fig. 1 [8].

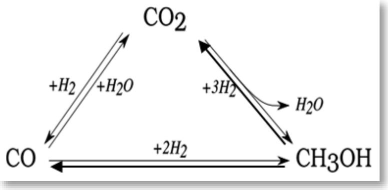

Fig. 1. Schematic representation of the methanol synthesis

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The simplified lumped reaction kinetics presented elsewhere was used for the computations [10]. It assumes a Langmuir–Hinshelwood mechanism with three different active surface centers. The resulting expressions for the three reaction rates are the following:

$$r_{CO} = (1-\phi)k_1\left(p_{CO}{p_{H_2}}^2 - \frac{1}{K_{P1}}p_{CH_3OH}\right)\theta^{\odot}{\theta^{\otimes}}^4$$

$$r_{CO2} = \phi^2 k_2\left(p_{CO_2}{p_{H_2}}^2 - \frac{1}{K_{P2}}\frac{p_{CH_3OH}p_{H_2O}}{p_{H_2}}\right){\theta^{*}}^2{\theta^{\otimes}}^4$$

$$r_{rwgs} = \phi(1-\phi)^{-1}k_3\left(p_{CO_2} - \frac{1}{K_{P3}}\frac{p_{CO}p_{H_2O}}{p_{H_2}}\right)\theta^{*}\theta^{\odot}$$

Where: $\theta^{\odot}, \theta^{\otimes}$ and θ^{*} are the catalyst surface coverages of: oxidized, reduced and heterolytic decomposition of H_2 surface centres, respectively.

Dynamic changes of the catalyst under reaction conditions are as follows:

$$\frac{d\phi}{dt} = k_1^{+}\left(y_{CO}\left(\phi_{max}-\phi\right) - \frac{1}{K_1}y_{CO_2}\phi\right) + k_2^{+}\left(y_{H_2}\left(\phi_{max}-\phi\right) - \frac{1}{K_2}y_{H_2O}\phi\right)$$

2.2 Forced Periodic Operation

The FPO of processes represents a group of innovative principles in process design that can lead to remarkable process improvement [11]. Consequently, the FPO is one of the inventive ways of process intensification. The basic principles of FPO are when one or more inputs of a system are periodically modulated around their corresponding previously established steady-state (SS), as is represented in Fig. 2 [3].

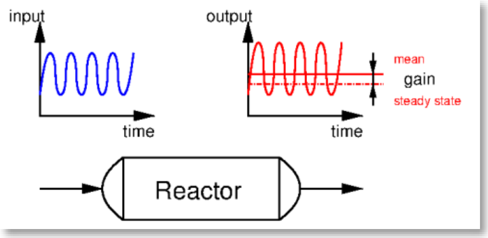


Fig. 2. Schematic representation of the FPO principle

In chemical engineering, the standard way to design and operate continuous processes is based on the optimal SS design. Nevertheless, it is shown that perturbing the system periodically can sometimes result in better performance than the optimal SS operation [1, 3–5, 7, 9, 10]. Although it has not yet been physically clarified, the process improvement owing to FPO is certainly a consequence of process nonlinearity [3]. Also, it is important to note that in comparison to the SS performance, the resulting performances of using FPO could be improved, deteriorated or unchanged [4].

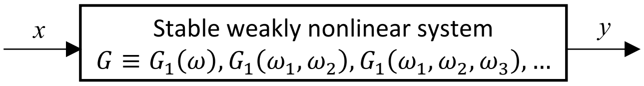
2.3 Nonlinear Fraquency Response method

The NFR method has proved to be a reliable mathematical tool for evaluating possible improvements and finding the best forcing parameters of chemical reactor systems caused by FPO [12]. The reliability of the NFR method is confirmed experimentally for the case of hydrolysis of acetic anhydride. [7]

The limitation of NFR method is that it can be applied to stable weakly nonlinear systems without multiple SSs [12]. Another requirement for this method to be applied successfully is the existence of a representative nonlinear mathematical model of the analysed system.

2.3.1 Single input modulation

Practically, the NFR method is based on the Volterra series, the generalized Fourier transform and the concept of higher-order frequency response functions (FRFs) [12]. Using this approach the nonlinear model can be replaced with a series of FRFs of different orders (*G_1, G_2, G_3, …*):



Frequency response is the quasi-stationary response of a stable system to a periodic input modulation around its SS value. If the input *x* is modulated in a cosine waveform, for a weakly nonlinear system, with amplitude *A* and frequency *ω*, around SS value *x* the output of the system would contain the basic harmonic ($B_I\cos(\omega t+\varphi_I)$), a non-periodic DC component ($\boldsymbol{y_{DC}}$) and an infinite number of higher harmonics:

$$x = x_s + A\cos(\omega t) \xrightarrow[t\to\infty]{}$$

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

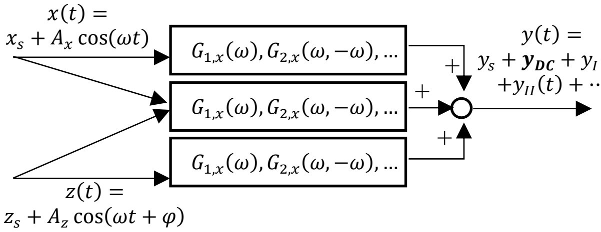
$$\boldsymbol{y_{DC}} = 2\left(\frac{A}{2}\right)^2 G_2(\omega,-\omega) - 6\left(\frac{A}{2}\right)^4 G_4(\omega,\omega,-\omega,-\omega) + \cdots$$

Where $G_2(\omega,-\omega)$ is asymmetrical second-order (ASO) FRF.

The derived FRFs are directly related to the DC component and different harmonics of the frequency response [5, 6]. The determination of $G_2(\omega,-\omega)$ function defines whether the periodic operation would be superior to the corresponding steady state and its magnitude determines the possible improvements

2.3.2 Simultaneous modulation of two inputs

Like in the previous case, If one or more inputs (x_s, z_s, ...) of a weakly nonlinear system is/are periodically modulated around a SS, the frequency response of the system output is obtained as a sum of the output SS value (y_s), the basis harmonic (y_I), an infinite number of higher harmonics (y_{II}, y_{III},...) and a non-periodic (DC) term (y_{DC}):



To evaluate the potential of an FPO of a system, it is only necessary to predict the DC component of the output, as it determines the time-average performance of the analysed system.

$$y_{DC} = gain$$

The DC component of an output *y* is a sum of the contributions of the DC component of the single inputs (*x* and *z*) separately and the DC component originating from the cross-effect of both inputs:

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

While the cross-effect contribution can be approximately evaluated as follows:

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

Cross ASO term ($G^*_{2,xz}(\omega,\varphi)$) is a function of both frequency and phase difference between the two modulated inputs, and is evaluated in the following way:

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

3. RESULTS

In this Section, the simulation results based on the NFR analysis, for periodically operated isothermal and non-isothermal, isobaric, lab-scale Micro-Berty reactor (CSTR) are given.

3.1 Single input modulation of isothermal CSTR

Four potential forced periodic inputs are considered, partial pressures of all reactants (CO_2, CO and H_2) in the feed stream and its feed volumetric flow rate. The optimal SS was chosen based maximalization criterion of multi-objective optimization with two objective functions: normalized outlet molar flow rate of methanol and yield of methanol based on total carbon. The multi-objective optimization problem was solved using the ε-Constraint method [6]. Fig. 3 presented the simulation results of NFR analysis for single input modulation around chosen optimal SS (temperature of 473 K, feed volumetric flow-rate of 0.93 ml min^{-1}, feed composition: 2.1% CO_2, 18.5%, 64.4% H_2 and 15% N_2*)* [5]. For the selected optimal SS, the calculated normalized outlet molar flow rate of methanol is 336.91 *mmol* min^{-1} kg_{cat}^{-1}), the yield of methanol based on total carbon is 61.05% and the yield of methanol based on hydrogen is 39.09%. Single input modulations of CO_2, CO and inlet volumetric flow rate, the *H*-ASO FRFs which correlate the outlet molar flow rate of methanol to modulated inputs are negative which means that periodic modulations of these inputs cannot improve the process of methanol synthesis. Periodic modulation of the partial pressure of H_2 could lead to improvement of the reactor performances for some forcing frequencies (ω>0.55) with the maximal possible improvement of 0.13% which is practically negligible.

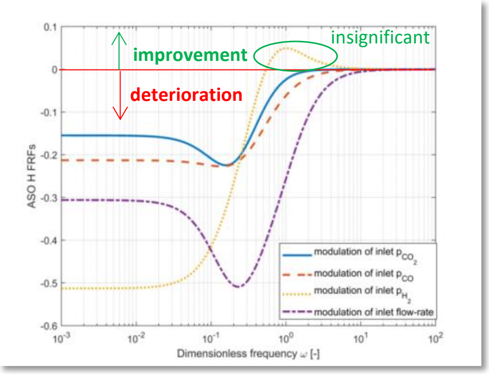


Fig. 3. Isothermal CSTR single input modulations ASO FRFs around corresponding steady-state [5]

3.2 Simultaneous modulation of two inputs of isothermal CSTR

The same SS for analysis as in the previous case is chosen. Six different cases of simultaneous modulations of two inputs are considered: partial pressures of all reactants in the feed stream and its total volumetric flow rate (CO_2 & CO, CO_2 & H_2, CO & H_2, CO_2 & total flow rate, CO & total flow rate and H_2 & total flow-rate).

For all cases with simultaneous modulation of partial pressures of two reactants, the potential improvements are possible, although insignificant. For the cases with simultaneous modulation of partial pressure of one reactant and the inlet volumetric flow rate, some measurable improvements can be achieved. The best case, as can be seen in Table 1, was the simultaneous modulation of the inlet partial pressure of CO and inlet volumetric flow rate, with a maximal predicted increase of the normalized outlet molar flow rate of methanol of 33.51% [5].

An advantage of simultaneous modulation of two inputs vs single input modulation is presented in Fig. 4 [5]. Dashed lines, which are for frequencies lower than zero, represent single input modulations of the feed CO partial pressure and feed volumetric flow rate, while solid line, which for all frequencies show the improvement of the reactor system, represents its cross ASO term.

A multi-objective numerical optimization was conducted using Julia software and the resulting Pareto front is presented in Fig. 5 [8]. Excellent agreement between rigorous numerical simulation and NFR method results is also visible in Fig. 5. The Displayed Pareto front clearly shows the advantage of forced periodic operated reactor system versus steady-state operated process.

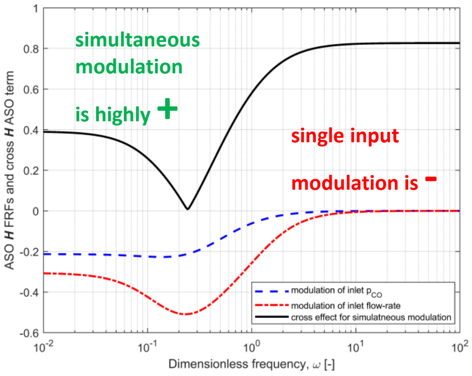


Fig. 4. Isothermal CSTR simultaneous input modulation (inlet partial pressure of CO and inlet volumetric flow-rate) cross ASO term [5]

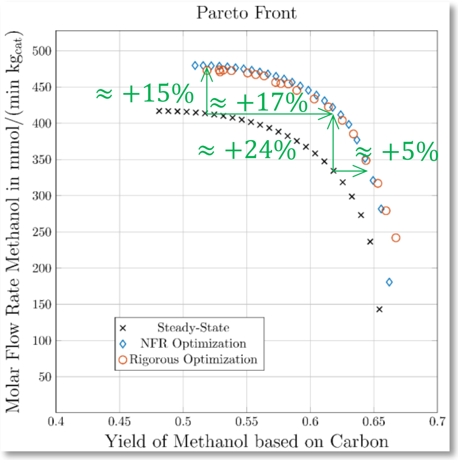


Fig. 5. Multi-objective optimization pareto front of yield of nethanol and normalized methanol production (steady state - crosses, rigorous numerical – circles and NFR – lozenge) [8]

3.3 *Single input modulation of non-isothermal CSTR*

In the case of non-isothermal CSTR five potential forced periodic inputs can be considered, partial pressures of all reactants in the feed stream, feed volumetric flow rate and inlet temperature. Of them, two cases have been analysed so far, total inlet flow rate and inlet temperature. Deterioration of performance in the entire frequency range for the analysed steady-state with a forcing amplitude of 0.5 for periodic modulation of volumetric flow-rate is observed (Fig. 6a). While in the case of periodic modulation of inlet temperature, some improvement is possible, although a modest, for the analysed steady state with a forcing amplitude of 0.05 (Fig. 6b).

In this case, also, excellent agreement was obtained between the results obtained by the NFR method and the numerical simulation. The results in support of this are shown in Table 2 for one chosen period of modulation and for forcing amplitudes of 0.5 and 0.05, for modulation of inlet flow rate and inlet temperature, respectively.

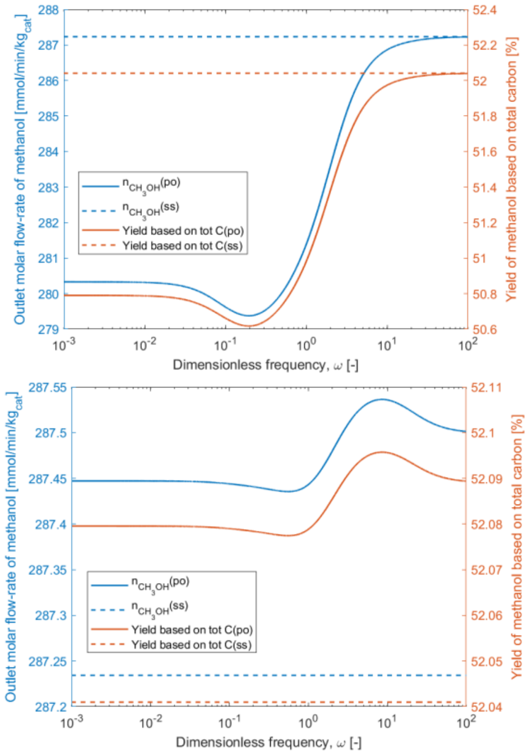


Fig. 6. Non-isothermal CSTR single input modulation of a) total inlet flow and b) inlet temperature

Table 1 The best result which can be obtained by simultaneous modulations of two inputs [5]

Modulated inputs	**Maximal increase of $\dot{n}^{norm}_{CH_3OH}$ [%]**	**Change of $Y^{totC}_{CH_3OH}$ [%]**	**Change of $Y^{H_2}_{CH_3OH}$ [%]**	**Optimal forcing parameters**			
				A_x [-]	A_z [-]	ω [-]	φ [rad]
Inlet partial pressure of CO and total inlet volumetric flow-rate	33.51	-2.12	+33.51	0.81	1	>30	0.006

Table 2 Comparison of the results of the NFR method and numerical simulation

		Performance indicators	
		$\left(\dot{n}^{norm}_{CH_3OH}\right)_{SS}$ **[mmol min^{-1} kg$_{cat}$$^{-1}$]**	$\left(Y^{totC}_{CH_3OH}\right)_{SS}$ **[%]**
Period of modulation [s]			*Single input modulation of flow rate*
89.3	NFR	286.47	51.63
	Numerical	286.04 (0.15%)*	51.41 (0.42%)*
			Single input modulation of temperature
89.3	NFR	287.53	52.09
	Numerical	287.52 (0.006%)*	52.02 (0.14%)*

*Error between NFR and numerical prediction

4. CONCLUSIONS

The NFR method was confirmed to be a useful and powerful theoretical tool for the analysis, design, and optimization of forced periodically operated chemical reactor systems, before experimental investigation. In the case of isothermal CSTR, all six combinations of input modulation and simultaneous modulation of two inputs can provide an improvement, even though the separate single input modulation would lead to deterioration of process performances. In the case of non-isothermal CSTR, in contrast to isothermal, single input modulations (inlet temperature) can give some improvement.

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DECLARATION OF INTEREST STATEMENT

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. All authors read and approved the final manuscript.

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