Forced Periodic Operation of Methanol Synthesis: Experimental Determination of Reactor Outlets

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Highlights

- Evaluation of the potential of forced periodic reactor operation
- Analysis for methanol synthesis using a $Cu/ZnO/Al_2O_3$ catalyst
- Simultaneous modulation of feed concentrations and volumetric flowrate
- Flexible experimental set-up with a reactor of the Berty-type

1 Introduction

Continuous chemical processes are preferably operated keeping inlet conditions constant and exploiting steady states. Imposing forced periodic reactor regimes has the potential to increase achievable product amounts [1]. Desired effects can be enhanced by modulating simultaneously two inputs, for example the feed concentration of a reactant *i*, x_i^{in}, and the total volumetric inlet flowrate, $\dot{V}_{tot}^{in}$. Besides the shapes of the modulations, the frequencies, ω, and amplitudes, A, an additional degree of freedom is the phase shift between the two inputs, φ (Fig. 1). In [2] the dynamic operation concept was studied theoretically and approaches were suggested to identify case specific optimal forcing parameters. Experimentally determined mean acetic acid fluxes produced in periodically operated hydrolysis of acetic anhydride were significantly larger than fluxes achievable using steady state operation [3].

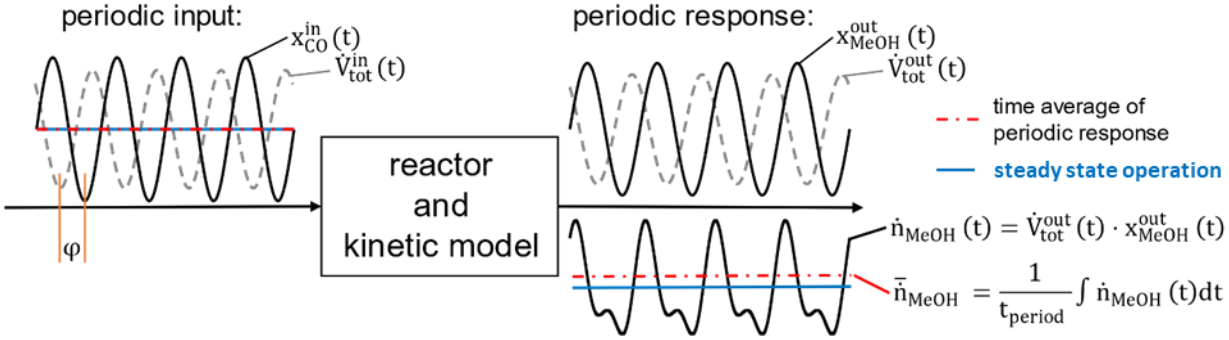

Figure 1: Illustration of forced periodic operation exploiting a simultaneous modulation of two inputs.

2. Methods

Based on preliminary results [4,5], forced periodic operation is currently investigated for the methanol synthesis on a commercially available catalyst ($Cu/ZnO/Al_2O_3$, BASF). A gradientless isothermal Berty-reactor is the heart of a set-up which enables the implementation of complex gas supply strategies. The reactor has a gas phase volume of 280 mL. It was filled with 4.3 g catalyst. Isobaric conditions could be maintained with a back-pressure regulator. Experiments were carried out for temperatures up to 260°C and for pressures up to 60 bar. The fluctuating outlet compositions were quantified with a benchtop mass spectrometer and a micro-GC. After storing the reactor effluent during an integer number of periods in a collection vessel, mean outlet concentrations can be determined rapidly and accurately. The stoichiometry of the CO and CO_2 hydrogenation reactions triggers dynamic volume contractions. These were quantified using recorded transient outlet concentrations of N_2, which was added as marker to the feed. The data acquisition system (Siemens Simatic/PCS7/WinCC) and in-house evaluation scripts (MATLAB®) enable automatic operation and support efficient processing of the output information.

3. Results

Fig. 2 illustrates results of a typical run. Sinusoidal perturbations of the molar fraction of CO and the total volumetric flowrate were applied at the inlet (frequency $\omega = 0.381\ h^{-1}$, t_{period}~23 min, normalized amplitudes $A_{CO} = 0.63$ and $A_f = 0.41$). N_2 was used to compensate the CO modulation. The two inputs were shifted by a phase angle $\varphi = 161°$. The time averaged molar inlet fractions of CO, CO_2, H_2 and N_2 were $x_{i,av}^{in} = 0.12,\ 0.04, 0.45, 0.39$, and the averaged inlet flowrate was 3.2 NL/min. The dynamics of the volume contraction is connected with the extents of the reactions and could be well specified using the recorded fluctuations of the N_2 concentrations. For the conditions of this run, the time resolution of the GC (~1.5 min) enabled simple direct integration of the concentration profiles, which provided the mean molar outlet flux of methanol marked in the figure.

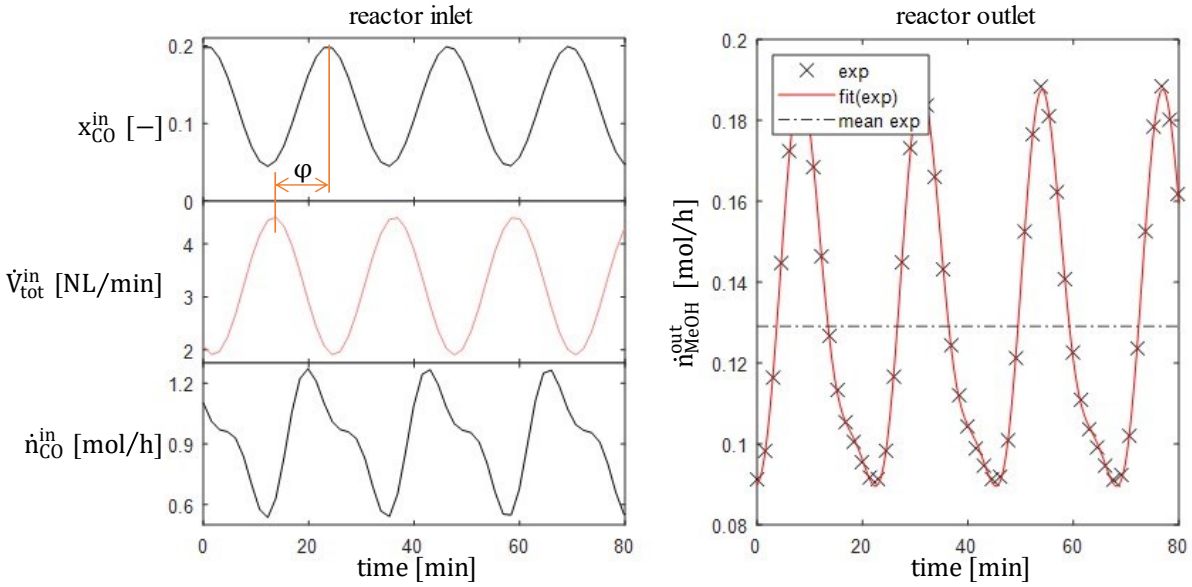

Figure 2: Experimental illustration of periodically operated methanol synthesis at T = 250°C and p = 50 bar. Harmonically modulated were the inlet molar fraction of CO (combined with a symmetrical N_2 modulation) and the total volumetric inlet flowrate using the marked phase shift φ.

4. Conclusion and outlook

A flexible experimental set-up has been installed and was tested successfully. This equipment allows studying the synthesis of methanol for a broad range of forcing scenarios applied in periodic operating regimes. Experimental results for different strategies and a comparison with theoretical predictions will be presented at the poster.

References

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Keywords

Process intensification, forced periodic operation, methanol synthesis, experimental demonstration

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