Intensification of a chemical reactor for methanol synthesis through forced periodic operations - Evaluation based on Nonlinear Frequency Response Analysis

Daliborka Nikolic [a] (daliborkan@ihtm.bg.ac.rs), Carsten Seidel [b] (carsten.seidel@ovgu.de), Achim Kienle [b, c] (kienle@mpi-magdeburg.mpg.de), Andreas Seidel-Morgenstern [b ,c] (anseidel@ovgu.de), Menka Petkovska [d] (menka@tmf.bg.ac.rs)

[a] Institute of Chemistry, Technology and Metallurgy, University of Belgrade, Njegoseva 12, 11000 Belgrade, Serbia
[b] Otto-von-Guericke-University, Universitatplatz 2, D-39103 Magdeburg, Germany
[c] Max-Planck-Institute for Dynamics of Complex Technical Systems, Sandtorstrasse 1, D-39106 Magdeburg, Germany
[d] Faculty of Technology and Metallurgy, University of Belgrade, Karnegijeva 4, 11000 Belgrade, Serbia

Forced periodic operations, as a potential way of process intensification, have been known and investigated for decades. Most investigations in this area are dealing with forced periodic operations of chemical reactors [1].

In our previous research, we have developed a new, nonlinear frequency response (NFR) method, as a fast and easy analytical method for evaluating the performances of forced periodically operated chemical reactors. The NFR method is mathematically based on Volterra series, generalized Fourier transform and the concept of higher-order frequency response functions (FRFs). The NFR method gives an answer whether and in which cases it would be possible to achieve process improvement by periodic modulation of one of more inputs, and also gives an estimate of the magnitude of that improvement. In order to apply the NFR method it is necessary to derive the asymmetrical second order (ASO) frequency response functions (FRFs), which correlate the DC component (non-periodic term) of the output of interest to the modulated input(s). The NFR method also enables determining the optimal forcing parameters which should be used in order to achieve the highest possible improvement by periodic modulation of one or more input(s) (the shape of the periodic input modulation(s), the forcing frequency, the forcing amplitude(s) and, for simultaneous modulations of two inputs, the phase difference between them)[2].

The starting point for deriving the asymmetrical second order FRFs and applying the NFR method is a nonlinear dynamic model of the reactor. In that sense, it is essential that the mathematical model and its parameters are reliable, with special emphasis on a good kinetic model and its parameters.

In this work, the NFR method is implemented for evaluation of possible improvement for the reaction of methanol synthesis by hydrogenation of CO and CO_2, using a standard $Cu/ZnO/Al_2O_3$ catalyst. For start, a forced periodically operated isothermal continuous-stirred tank reactor (CSTR) is considered. A simplified (lumped) kinetic model of methanol synthesis with 14 parameters [3] which were estimated from the results of an extensive experimental investigation [4], is used.

The NFR method is performed for evaluation of possible increase of methanol production by modulating the mole fractions of CO and CO_2 in the feed stream, as well as their simultaneous modulation. The necessary asymmetrical second order frequency response functions correlating the methanol production with the modulated inputs are derived and the forcing parameters leading to improvement of the reactor performance are determined. The results of the NFR analysis will further be used for rigorous optimisation of the forced periodic operations and planning the best experimental scenarios. The final step will be experimental investigation and confirmation on a laboratory scale reactor.

References

[1] R.R. Silveston and R.R. Hudgins, ed*., Periodic Operation of Reactors*, Amsterdam: Elsevier, **2012.**
[2] M. Petkovska, D. Nikolić, A. Seidel-Morgenstern, Nonlinear Frequency Response Method for Evaluating Forced Periodic Operations of Chemical Reactors - Review, *Israel J. Chem*. 58, **2018**, 663-61
[3] C. Seidel, A. Jorke, B. Vollbrecht, A. Seidel-Morgenstern, A. Kienle, Kinetic modeling of methanol synthesis from renewable resources*, Chem. Eng,. Sci.* 175, **2018**, 130-138
[4] Vollbrecht, B., **2007**. Zur Kinetik der Methanolsynthese an einem technischen Cu/ZnO/Al2O3-Katalysator. PhD thesis, Otto-von-Guericke-Universität, Magdeburg.