Optimal operation policies for load changes of fixed bed methanation reactors

Moritz R. Langer, Hannsjörg Freund

Institute of Reaction Engineering and Catalysis,
TU Dortmund University, Dortmund, Germany

Hydrogen is a key component within the transition of the energy sector towards green and renewable resources. However, the storage, distribution and reuse of hydrogen is still subject of research to achieve an efficient integration into the energy system. Power-to-X (PtX) technologies, such as the methanation, are widely discussed for further processing of green hydrogen. In case of CO_2 methanation, hydrogen is converted to methane using CO_2 from abundant sources such as industrial exhaust gases or air capture. The produced methane can be stored, distributed and used as natural gas substitute by exploiting the existing natural gas infrastructure. The main concept is to build decentralized small- to medium-sized plants directly at sites where renewable energy is produced and CO_2 sources are available. Hydrogen is received from water splitting in electrolysers, which can follow the fluctuations of renewable energy supply comparatively easily. However, for the further processing in PtX plants dealing with these fluctuations is more challenging. To operate such plants economically, expensive storage facilities for hydrogen or CO_2 should be avoided. This implies that fluctuations in the reactant supply will propagate to the plant and thus also to the catalytic reactors. However, particularly the exothermic nature of the hydrogenation reaction poses challenges for the design of such load-flexible reactors. These challenges are addressed in recent numerical studies by developing concepts for temperature control by catalyst particle design [1] and by optimization methods targeting the packing and reactor scale [2,3]. While these methods can be used to design load flexible reactors that are safe in operation, the product quality can suffer from load changes, and therefore fail to meet the requirements for injection into the natural gas grid.

In this contribution, we provide a methodology to generate optimal operation policies for load changes of chemical reactors in order to avoid off-spec products that do not fulfill the target requirements. The approach is based on a reactor design optimized

according to the multi-steady-state method developed in our group [3]. Herein, an optimization problem is formulated to optimize the reactor design simultaneously for multiple steady state operating points within a desired load range. An important constraint is that the outlet composition at steady-state operation meets the target requirements. Afterwards, a subsequent optimization problem is formulated for the optimized reactor, in which the dosage trajectories of reactants at desired load changes are optimized with respect to a high overall methane yield. In order to correctly describe the dynamic reactor behavior, a kinetic model is used in combination with a heterogeneous reactor model, which explicitly takes the storage capacity and dynamics of the catalyst into account (Fig. 1). The operation trajectories resulting from the optimization task ultimately lead to operation policies that enable a load flexible, safe and efficient dynamic reactor operation.

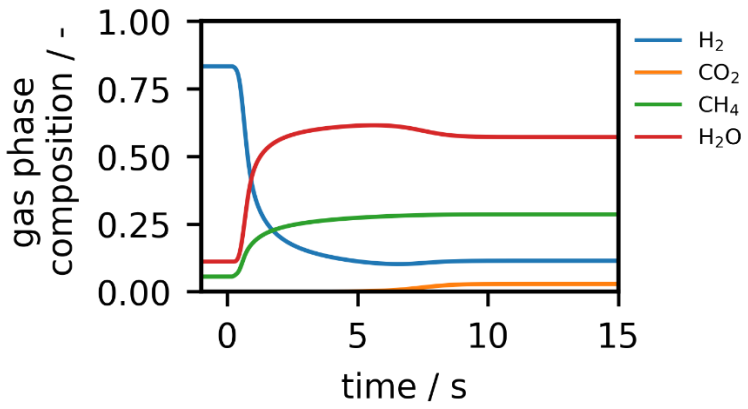

Figure 1: Simulated outlet composition of an isothermal PFR after an instantaneous change of the inlet composition. At time t = 0 s, a change of inlet composition was simulated from hydrogen excess (H2/CO2 = 19/1 mol/mol) to stoichiometric feed composition. Reaction conditions: T = 300°C, p = 10 bar, flowrate = 0.5 ml_{STP} min^{-1} mg_{cat}^{-1}. The underlying kinetic model is able to describe the dynamics of the catalyst.

References

[1] Zimmermann, R., Bremer, J., Sundmacher, K., Optimal Catalyst Particle Design for Flexible Fixed-Bed CO_2 Methanation Reactors, *Chem. Eng. J.* (2020)

[2] Fischer, K. L., Freund, H., On the optimal design of load flexible fixed bed reactors: Integration of dynamics into the design problem, *Chem. Eng. J.* (2020)

[3] Fischer, K. L., Freund, H., Intensification of Load Flexible Fixed Bed Reactors by Optimal Design of Staged Reactor Setups, *Chem. Eng. Process.* (2021)