



Modelling and Simulation of Porous Catalyst Pellets for Unsteady-State Methanation of CO/CO₂ Mixtures: Behavior of Non-Isothermal Pellets

Jannik Schumacher^{1*}, Dominik Meyer¹, Jens Friedland¹, Robert Güttel¹

¹ Institute of Chemical Engineering, Ulm University, Ulm, Germany

**Corresponding author E-Mail: jannik.schumacher@uni-ulm.de*

1. Introduction

The methanation process is a promising part of a sustainable energy supply and infrastructure via the power-to-gas (PtG) process. However, since the availability of renewable energy and carbon sources is fluctuating, the methanation has to be operated probably under unsteady-state conditions as well, depending on the upstream storage capacities [1]. One of the main challenges arising from this situation is the dynamic behavior of the porous catalyst pellets used for methanation, where heat and mass transfer as well as the chemical reaction occur simultaneously. Though dynamically changing spatial profiles of temperature and concentrations develop, which are coupled non-linearly. Since the measurement of those profiles, especially under operando-conditions is very challenging [2], modelling and simulation provides a powerful tool for analyzing the occurring dynamic processes. Among methanation of pure CO₂ and CO, a mixture of both carbon oxides is of interest, especially when considering process gases as a carbon source, for example blast furnace gas. However, when switching from CO₂ to CO-methanation or between various mixtures of both, the dynamic profiles change in an unpredictable way. This originates from the different reaction mechanism for CO and CO₂ hydrogenation. Thus, the present contribution analyses the dynamic behavior at particle scale based on modelling and simulation.

2. Methods

This work puts emphasis on the interaction of mass and heat transfer under unsteady-state methanation conditions and focusses on the intraparticle processes. The model equations for heat and mass balance arising from the unsteady-state reaction-diffusion problem are implemented in Aspen Custom Modeler for simulation. The binary friction diffusion models are used in accordance to Kerkhof [3], while the reaction kinetics are taken from Zhang [4]. For simulation typical methanation conditions are chosen with respect to temperature, pressure and reactant composition. Since the external heat transfer resistance is expected to predominate the internal, the external resistances are calculated as well. Effects on the reactor scale are neglected by assuming an ideally mixed gas bulk in order to isolate the effects on the particle scale. Based on the dynamic profiles developing upon switching between CO₂- and CO-rich periods the core temperature and the surface methane flux are used as indicators for the pellet performance. These indicators are used to study the influence of structural parameters, such as diffusion length or pore size, on the dynamic behaviour.

3. Results and discussion

Figure 1 (left) exemplarily shows the simulated spatial profiles of the involved components under isothermal conditions and negligible external mass transfer resistances for the methanation of a mixture of CO and CO₂. It becomes obvious that CO₂ diffuses deeper into the particle, since it is less reactive than CO. The inflection point in the CO₂ profile also indicates that it is converted to CH₄ once CO is already converted to a high extent. Although H₂ is provided at the surface below the stoichiometric required fraction, it is not consumed completely along the radial direction because of its high diffusion coefficient.

Figure 1 (right) shows the surface flux densities of the components during the periodic exchange of CO and CO₂ at the surface. Note that the molar fraction of H₂ and N₂ at the pellet surface are identical to Figure 1 (left). The overshoot of the H₂ flux density, induced by the switch from the CO to the CO₂-containing feed, shows that different time constants are inflicted in the behaviour of the components. Since the penetration depth of CO₂ is higher than that of CO, the switch from CO to CO₂ leads to a fast decrease of the CO molar fraction in the porous pellet, while CO₂ needs much longer to achieve a steady-state profile. Thus, in the transient phase a situation with less C-containing reactants exists in the pellet, which leads to a temporary minimum in the flux density of the co-reactant H₂. As well as the reaction rate passes through a minimum. In addition, the higher CO reactivity can be seen in the increased methane flux density during the CO rich feed. Note that the sign of the flux density indicates the transport direction and the minimum is discussed considering its absolute amount. Even though heat transport is decoupled from mass transport in first approximation, the temperature and concentration profiles are non-linearly coupled via the reaction kinetics. Thus, an additional time constant is added to the process by extension to a non-isothermal model, which increases the complexity of the problem further.

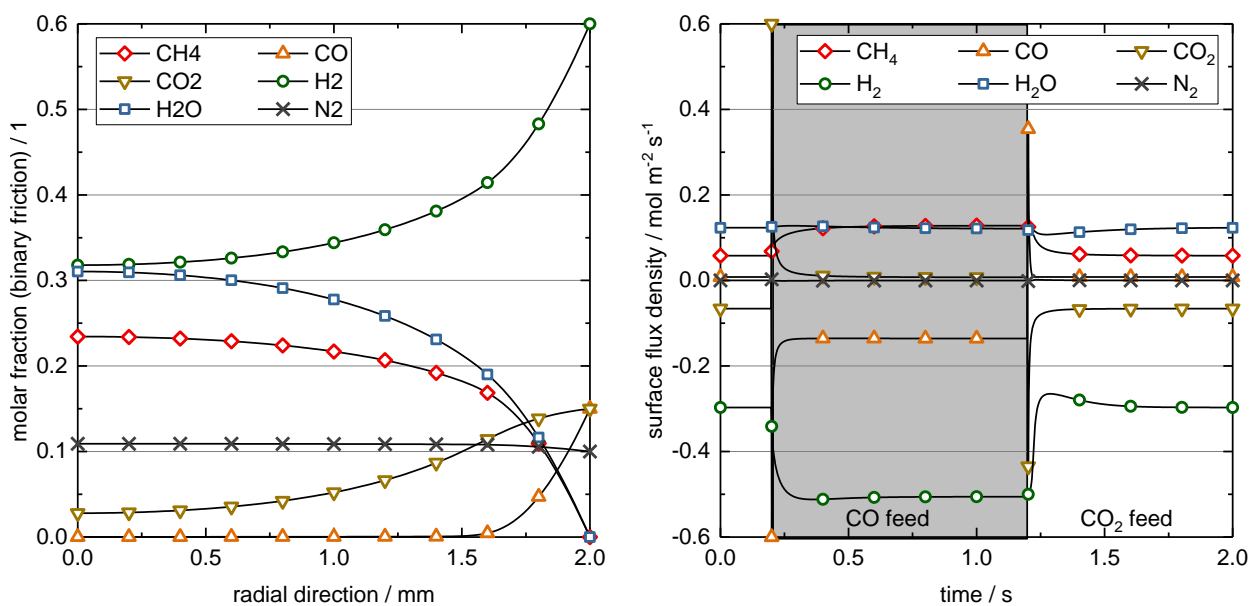


Figure 1. Steady-state mole fraction profiles (left) and unsteady-state flux densities (right) for CO/CO₂-methanation

4. Conclusions

Even though the methanation of CO/CO₂-mixtures is a rather simple heterogeneously catalyzed gas phase reaction, the concentration profiles in the pellet show a rather complex behavior for the steady-state case. This is mainly due to the volume contraction during reaction, which adds viscous flow to the pure diffusive transport mechanism. Considering the dynamic behavior, highly non-linear features are observed, such as the overshoot in H₂. This is caused by the reaction-diffusion problem only, since we considered the reaction to be in steady-state at any time. Therefore, this underlines the importance of the presented study for the interpretation of experiments on dynamic reactor operation, where similar observations are often explained by sorption effects. Moreover, the results show that as expected the time constants of the mass transport and chemical reaction govern the dynamic behavior of the porous system.

References

- [1] J. Lefebvre, M. Götz, S. Bajohr, R. Reimert, T. Kolb, *Fuel Process. Technol.* 132 (2015) 83–90.
- [2] T. Titze, C. Chmelik, J. Kullmann, L. Prager, E. Miersemann, R. Gläser, D. Enke, J. Weitkamp, J. Kärger, *Angew. Chem.* 127 (2015) 5148–5153.
- [3] P. Kerkhof, *The Chemical Engineering Journal* 64 (1996) 319-343.
- [4] J. Zhang, N. Fatah, S. Capela, Y. Kara, O. Guerrini, A. Khodakov, *Fuel* 111 (2013) 845-854