Efficient deactivation and thermal heat management modelling of an industrial methanation reactor validated by real-plant data.

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Highlights

- A state-of-the-art biogas methanation reactor is modeled and validated with real-plant data.
- The model allows optimization of the heat management.
- Time-dependent deactivation is modeled with a quasi-steady-state approach.
- Valuable insights to the long-time behavior of industrial-scale reactors are presented.

1. Introduction

Due to its capability to be used in chemical storage of surplus renewable energy in power-to-X plants, the CO_2 methanation reaction is of increasing interest. Induced by the strong exothermicity of the heterogeneously catalyzed CO_2 hydrogenation and related local hot spots in industrial-scale reactors, catalyst deactivation is a major concern. In order to achieve sufficiently long stable operation periods, the loss in catalytic activity needs to be considered in reactor design. For a robust prediction of the reactor behavior and lifetime, mathematical models describing the loss of catalytic activity over time are therefore required.

Despite a variety of deactivation mechanisms [1], such as poising, fouling and sintering, all causes of deactivation are lumped together in one single, purely empirical expression in most studies [2]. For methanation only few attempts were made to include physical knowledge into the deactivation models. For instance, Champon et al. [3] correlated the catalytic activity with the active surface area which decreases with time due to particle sintering depending on local temperature and partial pressures.

From application perspective, the feed gas to the methanation reactor typically consists of a complex mixture of CO, CO_2, H_2 and water, while inert gases and further components might also be present. Interestingly, the presence of CO in H_2/CO_2 mixtures can increase the methanation rate compared to pure CO_2 hydrogenation conditions under intrinsic conditions [4]. However, addition of CO favors deactivation by coking which needs to be considered for industrial application.

In this study, we consequently model the long-time behavior of an industrial-scale methanation reactor with the aim at finding optimal operation windows while mitigating catalyst deactivation. Therefore, emphasis is on analyzing the impact of operating conditions on the temperature profile formation.

2. Methods

A comprehensive 1D reactor model is set up considering the HZI plate type heat exchanger reactor geometry for a 240 kW biogas methanation plant, already introduced by Moioli et al. [5]. This geometry offers an excellent performance due to an efficient cooling by boiling water. The model presented here assumes a pseudo-homogeneous reaction phase, while mass transport limitations are considered via the Thiele approach. Appropriate heat transfer correlation are chosen for both reactive side and cooling side. For description of the time-dependent deactivation, a quasi-steady-state approach is chosen considering the loss of the catalytic activity over time at each axial position in the reactor. The loss of catalytic activity is described based on various models from literature with increasing complexity.

3. Results and discussion

The simulation results are validated with experimental data of the plate type reactor, as illustrated in figure 1. We can moreover show that the model predicts the steady-state experimental data presented by Moioli et al. [5] also at different loads.

Steady-state simulations are performed to identify operating conditions with ideal temperature and conversion profiles and a optimal usage of the high cooling potential. Further, the addition of CO to the feed gas is evaluated with respect to its impact on temperature profile and product gas composition.
Regarding the deactivation modelling, we reduced both the implementation complexity and the computational effort compared to fully time-dependent distributed models by using a quasi-steady-state approach. Herein, a steady-state model is solved at each time-step, while otherwise an expensive partial differential equation system needed to be solved. The assumption of a quasi-steady-state behavior is valid due to the strongly deviating characteristic times of the deactivation and the residence time in the reactor. Applying the time-dependent model, we explore the applicability of different deactivation models, starting from purely empirical activity functions to models considering physical knowledge about the mechanisms of catalyst deactivation.

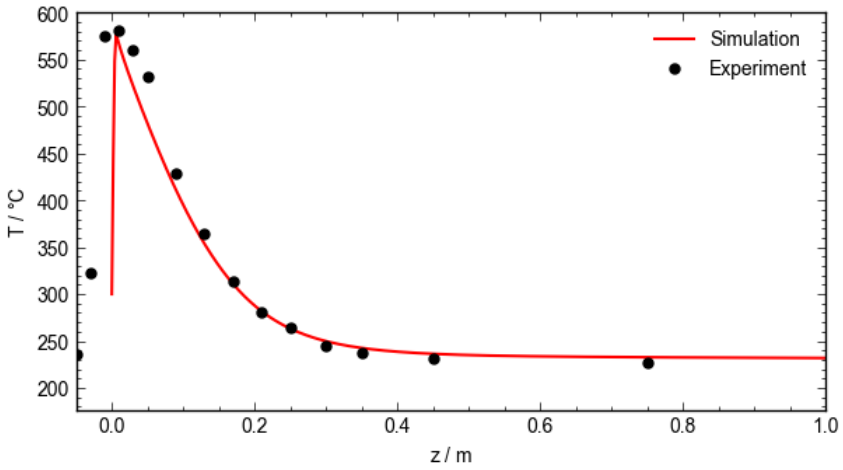

Figure 1. Validation of the steady-state model with experimental data from Moioli et al. [5]; Experimental and simulation conditions: 22 $Nm^3\ h^{-1}$ purified biogas (CO_2:CH_4 = 1:1) with hydrogen (H_2:CO_2 = 4:1) as inlet, cooling temperature 230 °C, 8 bar.

4. Conclusions

The industrial-scale HZI plate type methanation reactor is modeled. Applying optimization strategies, favorable operation windows are determined maximizing the potential of the reactor geometry. With our quasi-steady-state deactivation model, we present an efficient way to predict the long-term behavior of catalytic reactors at industrial scale. We guide the way of transforming lab-scale kinetic deactivation experiments to the application in industrial relevant models. In the context of highly exothermic reactions like the CO_2 hydrogenation our results are extremely valuable for the model-driven design of reactors with long-term robust operation.

References

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Keywords
Deactivation modelling, industrial biogas methanation, quasi-steady-state model approach, heat management.