Haber-Bosch 2.0 - Exploring Load-Flexible Ammonia Synthesis via Polytropic Fixed-Bed Reactors

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Highlights

- The polytropic reactor is notably less sensitive to disturbances compared to adiabatic operation.
- Loads as low as 10 % with N_2 conversions of at least 20 % are achievable.
- Significant load changes, such as 10 to 150 % in 10 min, can be handled safely and smoothly.

1. Introduction

The Power-to-Ammonia concept is a promising solution for global, chemical-based storage and transportation of renewable energies[1]. However, using electrolytically produced hydrogen as a reactant for ammonia synthesis introduces new challenges. The intermittent nature of renewable energy supply results in changing hydrogen flows induced by the electrolyzer unit. To reduce costly intermediate hydrogen storage, it is essential to develop an ammonia synthesis reactor system capable of operating safely and efficiently across a wide load-range as well as under dynamic conditions.

The conventional heat integrated, adiabatic, quench-cooled multi-bed reactor system (i.e., autothermal reactor concept) is known to be prone to oscillatory behavior under variable loads[2]. While advanced control strategies can improve process stability, handling changing loads, especially ramping the reactor from low to high loads, is still challenging and time consuming[3]. Thus, this study focuses on numerical simulation studies to identify alternative reactor and operation concepts for enabling load-flexible ammonia synthesis. One promising approach is using a polytropic fixed-bed reactor, which offers both a compact design and significant faster responses to load changes compared to an autothermal reactor[4].

2. Methods

For the mathematical description of the polytropic fixed-bed reactor, a two-dimensional dynamic pseudo-homogeneous reactor model, considering heat and mass dispersion, is developed. Gas densities are determined via the Peng-Robinson equation of state. Activity-based kinetic models are chosen to describe the reaction rate on a commercially used magnetite-based iron catalyst[5] as well as on a more active Ru-based catalyst[6]. Furthermore, a catalyst effectiveness factor is included to account for temperature-dependent intraparticle mass transport limitations. The pressure loss is described by the Ergun equation and changes in fluid velocity are calculated via mass conservation. To solve the reactor model, the PDE system is discretized in both spatial domains by applying the finite volume method. The resulting DAE system is solved in MATLAB using the IDAS integrator from the SUNDIALS suite. The influence of key operational parameters (e.g., feed load, temperature, pressure, cooling) on the operating range and on the transient behavior (including stability) of the reactor is investigated by detailed numerical simulation studies.

3. Results and discussion

The simulation results prove that the polytropic fixed-bed reactor is significantly less sensitive to disturbances compared to the conventional reactor concept. Following a pressure drop of 20 bar, exit temperature oscillations with amplitudes of up to 50 °C were observed for the adiabatic multi-bed reactor (Fig. 1, left). In contrast, the exit temperature is only marginally affected under polytropic operation (Fig. 1, right). Transitions between states are remarkably faster for the polytropic reactor due

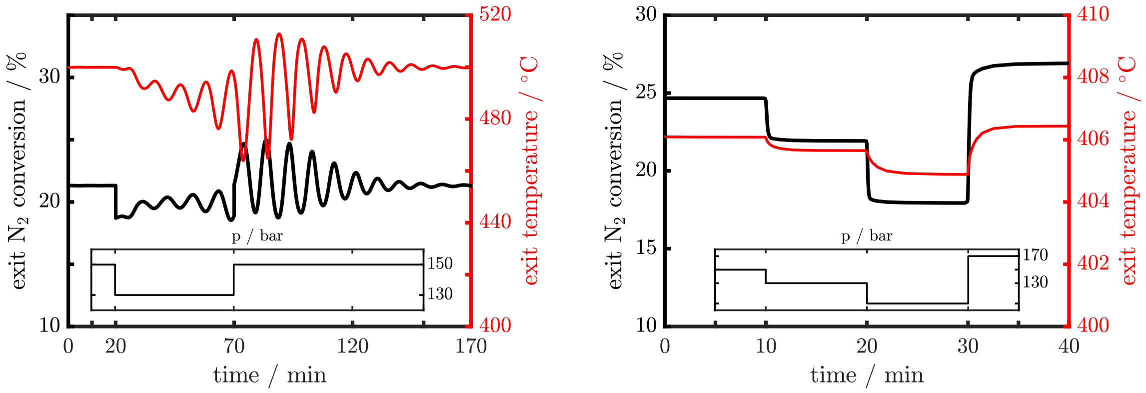

Figure 1. Dynamic simulations of an autothermal three-bed reactor (left) and a polytropic fixed-bed reactor (right) subjected to changing pressures. Feed temperature is set to 200 °C, GHSV is 7500 h^{-1} and Fe-based catalyst are utilized. Reactor dimensions of the autothermal three-bed reactor were taken from literature[2] and were scaled to match the reference GHSV. Both concepts feature a feed-effluent heat exchanger for heat integration.

to external heat supply via the cooling jacket. In adiabatic operation, the thermal intertia of the reactor system has a major impact on the energy balance, as heat is only supplied by convection and reaction, resulting in large time constants. Fig. 1 also shows that the polytropic concept achieves higher conversions under identical conditions ($t < 10$ min), as lower temperatures are thermodynamically favorable for ammonia synthesis. In further simulations, it was found that the polytropic reactor can be operated safely over a wide load-range, even at loads of only 10 %, while maintaining adequate nitrogen conversions of at least 20 %. For drastic load changes, such as ramping the polytropic reactor from 10 to 150 % load in less than ten minutes, fast, smooth, and stable transitions among different steady-states were observed. Utilizing more active Ru-based catalysts leads to increased hot spot and exit temperatures. However, these temperatures can still be controlled through cooling.

4. Conclusions

The feasibility of load-flexible ammonia synthesis via polytropic fixed-bed reactors was demonstrated by detailed numerical simulation studies. The proposed reactor concept can be operated over a remarkably wide load-range and fast transient transitions are viable. Due to reduced reactor temperatures increased N_2 conversions are achievable. In general, this study shows that an efficient cooling concept can prevent instabilities and highlights further opportunities to optimize the reactor and its operation.

References

[1] O. Elishav, B. M. Lis, E. M. Miller, D. J. Arent, A. Valera-Medina, A. G. Dana, G. E. Shter, G. S. Grader, 2020. Progress and Prospective of Nitrogen-Based Alternative Fuels. Chemical Reviews 120, 5352-5436.

[2] J. C. Morud, S. Skogestad, 1998. Analysis of Instability in an Industrial Ammonia Reactor. AIChE Journal 44 (4), 888-895.

[3] J. W. Rosbo, T. K. S. Ritschel, S. Hørsholt, J. K. Huusom, J. B. Jørgensen, 2023. Flexible Operation, Optimisation and Stabilising Control of a Quench Cooled Ammonia Reactor for Power-to-Ammonia. Computers & Chemical Engineering 176, 108316.

[4] J. Bremer, K. H. G. Rätze, K. Sundmacher, 2017. CO2 Methanation: Optimal Start-Up Control of a Fixed-Bed Reactor for Power-to-Gas Applications. AIChE Journal 63 (1), 23-31.

[5] D. C. Dyson, J.M. Simon 1968. Kineitc Expression with Diffusion Correction for Ammonia Synthesis on Industrial Catalyst. Industrial & Engineering Chemistry Researrch 7 (4), 605-610.

[6] I. Rossetti, N. Pernicone, F. Ferrero, L. Forni, 2006. Kinetic Study of Ammonia Synthesis on a Promoted Ru/C Catalyst. Industrial & Engineering Chemistry Research 45 (12), 4150-4155.

Keywords

Ammonia; Polytropic Fixed-Bed Reactor; Load-Flexible Reactor Operation; Dynamic Reactor Simulation.