An Intensified Membrane Reactor Concept for Mild Haber-Bosch Synthesis

Damla Sivaci, Ahmet K. Avci*

Department of Chemical Engineering Bogazici University, Bebek 34342, Istanbul, Türkiye
**avciahme@bogazici.edu.tr*

Highlights

- The reactor comprises catalytic reaction, heat exchange and membrane separation functions.
- The effect of membrane separation on N_2 conversion is drastic.
- The possibility of Fe-based NH_3 synthesis at 50 bar is demonstrated.

1. Introduction

The increasing usage of fossil fuels has resulted in significant climate change. In this regard, efforts for replacing fossil fuel-based energy with renewables are gaining increasing interest. Intermittency of renewable energy systems, an important drawback for their commercial use, calls for the need of their storage. A promising option is to use solar and/or wind-based electricity to electrolyze water for making green H_2 and storing it in the form of molecules such as NH_3. With a high gravimetric H_2 proportion, a high volumetric H_2 energy density, and the ease of liquefaction for handling, storage, and transportation, NH_3 is being considered as a H_2 carrier (ref). Moreover, NH_3 is needed to make fertilizers and is considered as a clean fuel [2]. NH_3 is conventionally synthesized *via* an exothermic equilibrium reaction demanding harsh conditions (>~200 bar, ~673-773 K) that can deliver effluent NH_3 fraction of ~25% [3]. The extreme operating conditions prevents the conventional Haber-Bosch process (having capacities >~10^3 t_{NH3}/d) to be feasibly downscaled to the capacities of green (renewable energy integrated) NH_3 synthesis (~3-50 t_{NH3}/d). We hereby aim to intensify NH_3 synthesis in a novel reactor that includes cascades of Fe-based catalyst packed reactors and NH_3-selective membrane-decorated microchannel heat exchangers. The novel concept offers modularity and can operate at milder conditions (50 bar) without being constrained by the strong thermodynamic limits.

2. Methods

The cascade of packed–bed reactors (PBRs) and microchannel membrane heat exchangers (micro–HEXs) is modeled using ANSYS and MATLAB under 2D, non-isothermal, steady-state conditions. Permeate and reaction channels, hosting sweep gas and the PBR effluent, respectively, are physically segregated by layers of zirconia-supported $ZnCl_2$-immobilized molten salt (IMS) membrane that is selective for NH_3 transport [4]. Each Fe-based catalyst packed adiabatic PBR effluent, composed of H_2-N_2-NH_3 mixture, is supplied into the reaction channels while N_2 is supplied in the permeate channels as the sweep gas that also regulates the temperature of the PBR effluent. Modeling of this system considers the conservation of mass, momentum, and energy in the PBR and the microchannel membrane heat exchangers. Membrane separation, i.e. selective transport of NH_3 from reaction to permeate channel is modeled by Fick's' law. Upon membrane separation and cooling in the micro–HEX unit, exit of the reaction channel is dosed to the next PBR where Fe-catalyzed NH_3 synthesis takes place. Due to the laminar flow conditions in the micro-HEX units, heat transfer and separation is solved simultaneously in ANSYS (v. 19.2) for both co- and counter-current flow of the sweep and PBR effluent flows. The solutions are compared with a lower-cost model developed in MATLAB, which is also used in simulating adiabatic catalytic reaction in the PBRs by a one-dimensional pseudohomogeneus model. Upon validating the similarity of ANSYS and MATLAB models, the latter is used as the platform for integrating PBR and the micro-HEX models.

3. Results and discussion

Figure 1. shows the temperature and cumulative conversion graphs of the system consisting of 5 PBRs and 4 micro-HEXs in counter-current flow. The maximum temperature of 623K, thermal stability limit of the $ZnCl_2$-IMS membrane [4], is exceeded by ~15 K and the cumulative N_2 conversion is 31%. It is observed that when working in co-current mode (not presented here), temperatures deviate significantly and eventually reach to 740 K, which is not suitable for the membrane. Cumulative N_2 conversion continues to increase and reaches to 37.8%. When the membraneless case is examined, the temperature

values are quite low (~585 K, Figure 2). Likewise, the cumulative N_2 conversion is ~11%. In the co-current mode the temperature drops to 460 K and the cumulative conversion is ~9%.

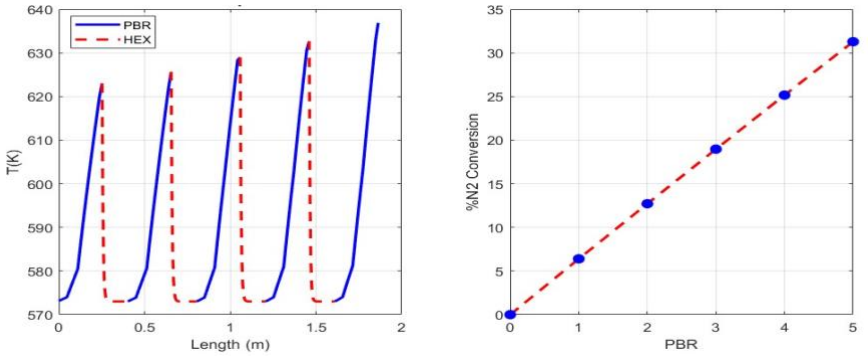

Figure 1. Temperature profile and cumulative N_2 conversion in counter-current model with membrane (573K, 50 bar, and 1.5×10^{-3} m^3kgcat^{-1} s^{-1}).

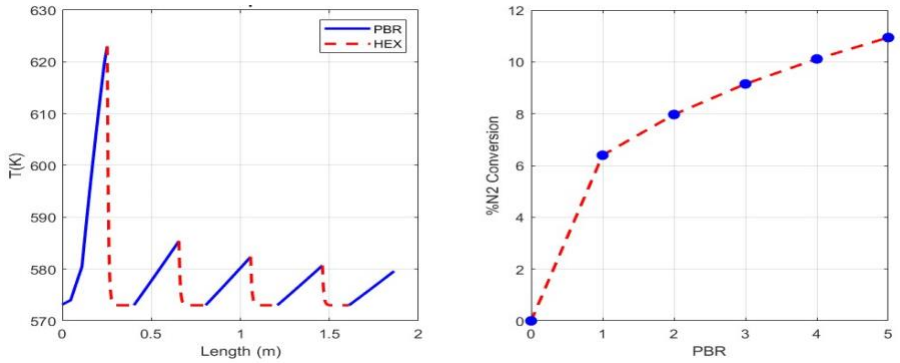

Figure 2. Temperature profile and cumulative N_2 conversion in counter-current model without membrane (573K, 50 bar, and 1.5×10^{-3} m^3kgcat^{-1} s^{-1}).

4. Conclusions

The preliminary results show that the temperature control is provided better in the counter-current operation of the micro-HEX units. The presence of the membrane makes significant difference in both modes and can increase N_2 conversion by three times at 50 bar, which is much less than involved in the conventional Haber-Bosch process. Studies regarding sizing and optimization of the proposed intensified reactor concept are on-going.

References

[1] Olabi, A. G., Abdelkareem, M. A., Al-Murisi, M., Shehata, N., Alami, A. H., Radwan, A., Wilberforce, T., Chae, K.-J., & Sayed, E. T. (2023). Recent progress in green ammonia: Production, applications, assessment; barriers, and its role in achieving the Sustainable Development Goals. *Energy Conversion and Management*, *277*, 116594. https://doi.org/10.1016/j.enconman.2022.116594

[2] Shen, H., Choi, C., Masa, J., Li, X., Qiu, J., Jung, Y., & Sun, Z. (2021). Electrochemical ammonia synthesis: Mechanistic understanding and catalyst design. *Chem*, *7*(7), 1708–1754. https://doi.org/10.1016/j.chempr.2021.01.009

[3] Humphreys, J., Lan, R., & Tao, S. (2020). Development and recent progress on ammonia synthesis catalysts for Haber–Bosch process. *Advanced Energy and Sustainability Research*, *2*(1), 2000043. https://doi.org/10.1002/aesr.202000043

[4] Laciak, D.V., Pez, G.P., & Burban, P.M. (1992). Molten salt facilitated transport membranes Part 2. Separation of ammonia from nitrogen and hydrogen at high temperatures. *J. Membr. Sci*. *65*, 31-38.

Keywords

Ammonia, Membrane separation, Mild Haber-Bosch synthesis, Process intensification