Application of a kinetic model for direct DME synthesis on Cu/ZnO/ZrO$_2$ and H-FER-20 for industrially relevant conditions

Gabriela Rodrigues Niquini[*], Karla Herrera Delgado, Stephan Pitter, Jörg Sauer

Institute of Catalysis Research and Technology (IKFT), Karlsruhe Institute of Technology (KIT), Hermann-von Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen, Germany

*Corresponding author: gabriela.niquini@kit.edu

Highlights
- Simulations using a recently developed kinetic model.
- Studies on effect of pressure, temperature and gas composition in DME yield.
- Insights about implementation of direct DME synthesis in industrial scale.

1. Introduction

Dimethyl ether (DME) is an energy carrier that can be used as a diesel substituent or be further converted to intermediates/precursors in the synthesis of liquid organic compounds of high demand in the chemical industry. It is traditionally produced in a two-step process: in the first step, syngas (CO/CO$_2$/H$_2$) is converted to methanol via the following overall reactions: $CO + 2\,H_2 \rightleftarrows CH_3OH$; $CO_2 + 3\,H_2 \rightleftarrows CH_3OH + H_2O$, and the reverse water-gas shift reaction can take place in parallel: $CO_2 + H_2 \rightleftarrows CO + H_2O$. In the second step, methanol is dehydrated to DME: $2\,CH_3OH \rightleftarrows CH_3OCH_3 + H_2O$. A single-step approach enables overcoming thermodynamic equilibrium in the methanol synthesis by its *in situ* consumption and may also lead to lower investment costs. This process has been already implemented in pilot scale [1].

For the traditional CO-rich process, the catalysts Cu/ZnO/Al$_2$O$_3$ (CZA) and γ-Al$_2$O$_3$ are used respectively for methanol synthesis and methanol dehydration. However, it has been shown that Cu/ZnO/ZrO$_2$ (CZZ) combined with H-FER-20 (FER) have a higher productivity for CO$_2$-rich syngas, as well as more tolerance to water, which is the major cause of loss of catalyst activity [2].

Kinetic models are fundamental for reactor dimensioning, techno-economic analyses and assessing the more suitable operating conditions, giving inputs to the implementation of the process in industrial scale. The objective of this work is to simulate the direct DME synthesis on CZZ/FER for industrially relevant conditions, obtaining insights about the influence of each process variable.

2. Methods

For the simulations in industrial conditions, our recently published kinetic model for direct DME synthesis. [3] was implemented in Matlab R2021b. Simulations were performed at the following conditions: 30–70 bar, 200–250 °C, gas hourly space velocity (GHSV) between 0.05 and 4 s^{-1} and CO$_2$/CO$_X$ ratio between 0.2 and 0.8. Equilibrium calculations for the corresponding values of pressure, temperature and gas composition were carried out in Aspen Plus V12.

3. Results and discussion

Here, two exemplary cases are presented: one with CO$_2$/CO$_X$ = 0.3 and GHSV = 0.2 s^{-1} (Figures 1a and 1b) and one with CO$_2$/CO$_X$ = 0.6 and GHSV = 0.15 s^{-1} (Figures 1c and 1d). The contour plots (Figures 1a and 1c) show the DME outlet concentration as a function of pressure and temperature. In both cases, for a fixed pressure, the production of DME reaches a maximum with respect to temperature and then decreases, showing the effect of thermodynamic limitation. Additionally, we present, for both cases, the DME concentration as a function of the reactor length for a chosen pressure of 50 bar and the equilibrium values. It is observable that, for T = 250 °C, the production of DME is limited by equilibrium, and, for 220 °C, the reaction is still in the kinetic regime. Such plots provide information about the mass of catalyst required to achieve thermodynamic equilibrium in a given condition and are fundamental in reactor design.

Comparing the two cases, the formation of DME is significantly lower for $CO_2/CO_X = 0.6$ even for a lower GHSV. This highlights the challenges of producing DME from CO_2-rich syngas and the necessity of the research in more active catalysts, in order for the process to be competitive.
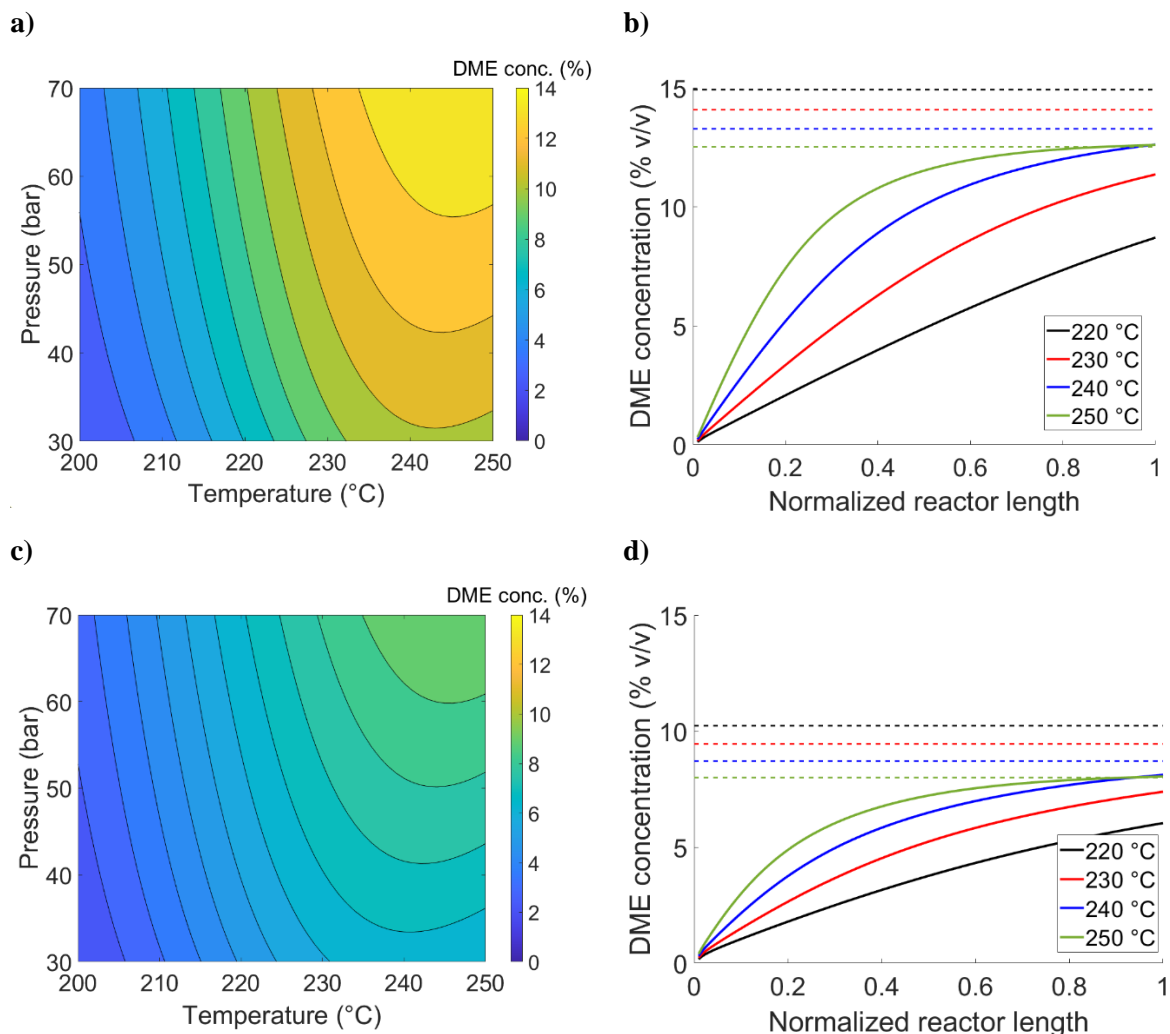
Figure 1. Simulations of direct DME synthesis on CZZ/FER in the following conditions: (a,b) $CO_2/CO_X = 0.3$ and GHSV = 0.2 s^{-1}; (c,d) $CO_2/CO_X = 0.6$ and GHSV = 0.15 s^{-1}. In (c,d), p = 50 bar; continuous lines correspond to the simulations, and dashed lines, to equilibrium.

4. Conclusions

The kinetic model enables the prediction of the product distribution for single-step DME synthesis in industrial conditions, correctly showing the expected trend with variations in pressure, temperature and GHSV. It presents potential to be used in techno-economic analyses and dimensioning of reactor units for direct DME synthesis. In future work, the model will be validated in a large-scale profile reactor.

References

[1] V. Dieterich, A. Buttler, A. Hanel, H. Spliethoff, S. Fendt, Energy Environ. Sci 13 (2020) 3207–3252
[2] S. Wild, S. Polierer, T. A. Zevaco, D. Guse, M. Kind, S. Pitter, K. Herrera Delgado, J. Sauer, RSC Adv. 11 (2021) 2556–2564
[3] G. Rodrigues Niquini, B. Lacerda de Oliveira Campos, K. Herrera Delgado, S. Pitter, J. Sauer, Chem. Eng. J. 480 (2024) 147968

Keywords

Direct dimethyl ether synthesis; kinetic modeling; process simulation