# Evaluation of the relevant mass and heat transfer phenomena in a packed bed membrane reactor for the direct conversion of CO2 to dimethyl ether

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***Highlights***

- Intraparticle mass transfer limitations and concentration polarization affect the direct conversion of CO2 to dimethyl ether (DME)
- Developed easy-to-use correlations from rigorous 2D heterogeneous models.

## 1. Introduction

The direct conversion of $CO_2$ to dimethyl ether (DME) is an attractive $CO_2$ recycling solution [1]. Besides, this technology presents advantages over the traditional DME synthesis (i.e., conversion of syngas to methanol and subsequent dehydration in two steps) by reducing the processing steps and increasing the overall yields. The one-step DME synthesis requires a bifunctional catalyst combining a hydrogenation metal and an acid catalysts (e.g., physical mixtures of Cu/ZnO/Al2O3 and HZSM-5 catalysts) and optimized operation conditions (ca. 200-300 $^{0}$C and ca. 30-50 bar) to balance the kinetics and thermodynamic requirements. Both the methanol and DME production are exothermic and thermodynamically limited reactions, thus favored by higher pressures and low temperatures. Besides, all the reactions lead to significant water formation, which poses even stronger thermodynamic limitations and contributes to catalyst deactivation during long-term operation [2]. Thus, effective thermal management strategies as well as in situ removal of water are key to achieve high DME yields and catalyst stability [4]. In our recent works, we propose the use of a packed bed membrane reactor to combine reaction and separation (i.e. in this case product removal) to overcome the thermodynamic limitations (Le Chatelier principle) and meet cooling requirements [6,7]. In this work, we dive into the heat and mass transfer effects at different reactor scales via the implementation of 2D heterogeneous particle and reactor models in Matlab. These limitations are often neglected given the complexity of this reaction system. Thus, in this work, once a particular transport phenomenon is identified as significant using the rigorous modeling approach, these results are used to develop simplified easy-to-use correlations that can be used by a wider audience (e.g., for process design in industry).

## 2. Methods

First, a particle model is developed by solving mass and heat balances in the two catalyst particles (i.e., Cu/ZnO/Al2O3 HZSM-5) to assess the extent of intra-particle mass and heat transfer limitations under relevant reaction conditions, as well as their impact on the performance of the packed bed reactor, with and without the membrane (i.e., PBR and PBMR, respectively). Then, using a rigorous modeling approach, we propose and develop a Thiele modulus-efficiency correlation for the calculation of the effective reaction rate via a short-cut method, which does not require to couple reactor and particle model. Thereafter, we investigate the particle-fluid interphase to assess the relevance of external mass or heat transfer limitation, and we further analyze deviations from the ideal plug flow behavior via the implementation of the axial dispersion model, using the axial dispersion coefficient approach. Finally, the introduction of the membrane in the packed bed reactor adds more complexity to the transport phenomena as concentration gradients can develop in the radial direction giving rise to a phenomenon of concentration polarization (CP). Further, we develop a 2D packed bed membrane reactor model to evaluate the relevance of the radial concentration gradients generated by the presence of the membrane. From the simulations results of the 2D model, we developed a Sherwood-type correlation to account for the CP phenomena via a simplified approach.

## 3. Results and discussion

Intra-particle diffusion limitations were found relevant for particle larger than 1 mm and temperature above 220 ºC, such that the catalyst efficiency drops down to 50% and 5% for the Cu/ZnO/Al2O3 and the HZSM-5, respectively, in the most critical conditions (i.e., 270 ºC and Dp of 10 mm). A component-specific Thiele modulus-efficiency correlation was developed based on the results of the rigorous particle model to account for pore-diffusion limitations without having to solve a complex heterogeneous reactor model. This correlation shows the typical behavior reported in literature for power law kinetics and accurately predicts the reaction performance with deviation of less than 5% for values of the Thiele modulus lower than 2. In the packed bed membrane reactor (PBMR), the concentration polarization (CP) also showed to affect the reactor performance. The concentration of water at the surface of the membrane selective layer was found to be up to 64% lower than the concentration in the bulk phase, hindering the effectiveness of the membrane separation. To account for this phenomenon via a simplified approach, a Sherwood-type correlation was developed to determine a CP mass transfer coefficient, based on the results obtained via the rigorous 2D PBMR model. Such correlation showed to predict with high accuracy (i.e., errors lower than 5%) the effect of the CP on the PBMR performance. Differently from the pore diffusion and CP phenomena, the intra-particle heat transfer, the particle-fluid mass and heat transfer as well as the axial dispersion were found to have a negligible effect on the reactor behavior. Finally, given the relevant mass/heat transfer phenomena, this study proposes some examples on further reactor optimization strategies, such as the reduction of the zeolite loading in the bifunctional catalyst bed of by ca. 90% with respect to what is reported in literature.

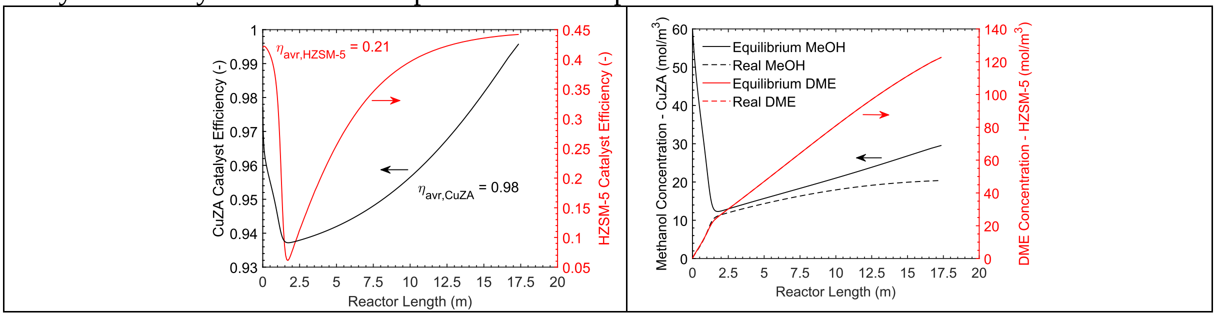


**Figure 1.** Catalyst efficiency (a) and methanol real (i.e., in the reactor) and equilibrium concentration (b) for both the CuZA (left axis) and HZSM-5 (right axis) as a function of the reactor length.

## 4. Conclusions

This study demonstrates that intra-particle diffusion and concentration polarization are both phenomena that affect the packed bed (membrane) reactor performance for the CO2 hydrogenation to DME, especially at conditions which are relevant to large scale operation. Thanks to the findings of this work, the PBMR and PBR could be further optimized, in view of the relevant mass/heat transfer phenomena. As an example, due to the fast methanol dehydration reaction, a considerably large fraction (i.e., up to 90%) of the zeolite in the catalytic bed could be removed with no effect on the final DME yield. Finally, to reduce the effects of the CP phenomenon, the geometry of the membrane can be optimized.

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***Keywords***

"Membrane reactor modeling"; "Intra-particle diffusion limitations"; "Concentration polarization"; "$CO_2$ hydrogenation, DME synthesis".

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