On the Numerical Simulation of Packed Bed Membrane Reactors for Methanol Synthesis from CO_2 and H_2: Suitable Alternatives to Packed Bed Reactor Technology

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Abstract

Methanol is considered to be a potential energy carrier. Currently, its synthesis from CO_2 is performed in conventional reactors, although its yield can be improved if a packed bed membrane reactor (PBMR) is used instead. The objective of this work is to select potential PBMRs as an alternative to the conventional ones.

Introduction

The economic development of our society strongly depends on fossil fuels. Methanol has been proposed as an economic and environmental alternative to them (Olah 2005). Methanol can be synthesized from H_2 and CO_2 in conventional packed bed reactors (PBRs). However, these devices are thermodynamically limited. In this context, the application of process intensification methodologies has allowed to enhance the methanol synthesis through the use of PBMRs (Menéndez et al. 2003). These reactors not only increase the conversion of CO_2 and selectivity to methanol but also allow to reduce the severity of the operation conditions (i.e., pressure and temperature). The aim of this work is to select potential PBMRs to replace the conventional PBRs in a determined range of operation conditions in the methanol synthesis process.

Experimental

A one dimensional model for a PBMR was developed following the next hypothesis: steady state, isothermal operation and plug flow. The membrane was considered to be inert. A pseudo homogeneous model was assumed for the packed bed (retentate side). For the permeate side two flow configurations of the sweep gas were analyzed: co-current and counter-current. In order to validate the model experimental data were collected from Gallucci et. al. (Gallucci et al. 2004). The set of ordinary differential equations was solved using a Runge-Kutta-Fehlberg numerical method in Python 3.0. For the counter-current mode, the shooting method was used (boundary value problem). In the simulations, the kinetics from Bussche et al. was used (Bussche and Froment 1996). For realistic results, experimental permeances of hydrogen, methanol and water were collected from a Linde Type A zeolite tested in the Aragon Institute of Engineering Research. A good agreement between the simulation results and literature data was found.

Once validated, a PBR of 0.50 m in length was simulated by allowing the permenances to be zero. Its results of conversion, selectivity and yield were setted as the target to be overcome by the PBMR potential candidates. In order to screen them, simulations of the PBMR model were performed exploring the entire experimental region: pressures (5-50bar) and temperatures (200-250°C). These simulations were executed every 0.10m until reaching the 0.50m reactor length. The results were analyzed statistically and then plotted on heat maps by means of algorithms implemented in R.

Results and Discussion

The simulated conversion and yield with the 0.50 m length PBR were 23.9% and 14.8%, respectively. These values were closed to the equilibrium ones. In comparison to the PBR, PBMRs showed a better performance from 20cm length and in a range of pressures and temperatures from 30-50bar and 230-250°C, respectively. The heat maps revealed a total of 17 potential candidates in the co-current operation mode, whereas 15 were found for the counter-current mode. The more suitable operation conditions for methanol synthesis were 250°C, 50bar and 0.50m reactor length in both configurations (Figure 1). The PBMR in co-current mode attained 60.8% more yield than the PBR, whereas in counter-current the yield increase was 36.5%. The most promising candidates are showed in Table 1.

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Conclusions

The applied methodology has allowed to find suitable PBMRs which demonstrate better performance than the conventional PBR. These candidates offer the possibility of performing the methanol synthesis not only with less reactor length but also with less severe operation conditios, with finally could impact the economy of the process.

Table 1. PBMRs suitable to replace the conventional PBR.

Reactor configuration	Rector Length [m]	Yield increase [%]
Co-current	0.30	34.5
	0.40	50.0
	0.50	60.8
Counter-current	0.30	12.2
	0.40	33.8
	0.50	36.5

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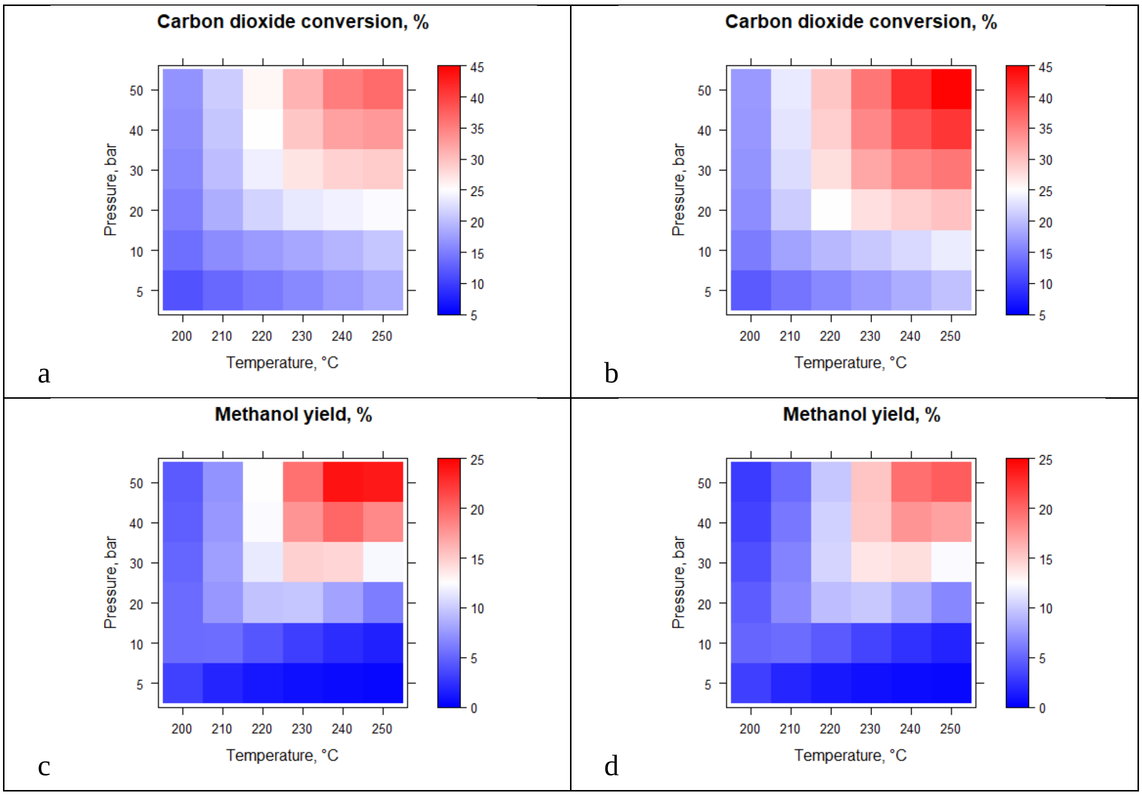

Figure 1. CO_2 conversion and yield to methanol for the analyzed range of pressures and temperatures. Feed flow rate=800mL$_{STP}$/min, sweep gas flow rate=1600mL$_{STP}$/min. H_2/CO_2 feed molar ratio=3. Reactor length= 0.5m. Pressure was maintained equal at both permeate and retentate sides. Graphics a,c were obtained in co-current operation mode. Graphics b,d were obtained for counter-current operation mode.