CAMURE-11 11th International Symposium on Catalysis in Multiphase Reactors
ISMR-10 10th International Symposium on Multifunctional Reactors
MILANO, ITALY - 21-24 March, 2021

Effect of membrane properties on the direct conversion of CO_2 to dimethyl ether in a fixed bed membrane reactor

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1. Introduction

Nowadays, the need to reduce anthropogenic CO_2 emissions is well accepted [1]. Thus, capturing and either storing or converting CO_2 as a replacement for fossil fuels is of utmost importance [2]. In this scenario, the direct conversion of CO_2 into dimethyl ether (DME) plays a key role. Nowadays, DME is produced from a fossil based syngas via a two steps approach: hydrogenation of CO to methanol followed by dehydration to DME. Besides utilizing a fossil resource, this route suffer from important thermodynamic limitations. In pursuit of sustainability, replacing the carbon source by CO_2 is an attractive alternative which, nevertheless, poses even greater thermodynamic limitations and limits the DME yields. Coupling the two reaction steps in a single reactor has the potential to increase CO_2 conversion beyond the thermodynamic equilibrium, while the DME yield remains limited. Therefore, the in situ removal of H_2O, a major reaction product, is key to increase the final DME yield [3]. One of the most promising technologies for water removal is the use of a membrane reactor. The main feature of such reactor is that the reaction and separation of a target product occur at the same time, enhancing the reactions beyond thermodynamic equilibrium (*Le Chatelier* principle). In this work, the effect of using a membrane reactor for the direct conversion of CO_2 to DME is analysed through first-principle modelling.

2. Methods

A thermodynamic study is performed with Aspen Plus in order to identify the optimal range of operating conditions and to establish the limiting values of CO_2 conversion and DME yield. NRTL model is used to describe the liquid phase, as suggested by Song et al. [4], and Peng & Robinson for the gas phase, as suggested by De Falco et al. [5]. Further, a comprehensive 1D plug flow reactor model is implemented in MATLAB® R2019 and used to study the effect of the membrane properties on the process, using the kinetics derived by Lu et al. for a Cu-ZnO-Al_2O_3/HZSM-5 bifunctional catalyst [6]. The model assumes isothermal conditions, no pressure drop, and kinetic control regime (i.e., absence of transport limitations). Through a parametric study, the optimal values of water permeance and H_2O/H_2 selectivity are estimated to gain insight into the desired membrane properties. In addition, the effect of the parameters regulating the trans-membrane driving force (i.e. sweep gas flow rate and pressure difference across the membrane) is studied. Finally, the potential of this technology is shown by comparing its performance with that of a traditional packed bed reactor.

3. Results and discussion

The thermodynamic analysis shows that the desired reactions are enhanced at low temperature and high pressure. Even at these conditions, however, CO_2 conversion and DME yield are lower than 50%. The effect of the membrane properties on the reactor performance is shown in Figure 1. Regardless of the H_2O/H_2 selectivity, both CO_2 conversion and DME yield show a maximum at values of water permeance of around $5 \cdot 10^{-3}$ $mol \cdot s^{-1} \cdot m^{-2} \cdot Pa^{-1}$. In a similar fashion, greater H_2O/H_2 selectivity results in higher conversions and yields, but increasing the selectivity beyond values of 20 does not result in significant effects.

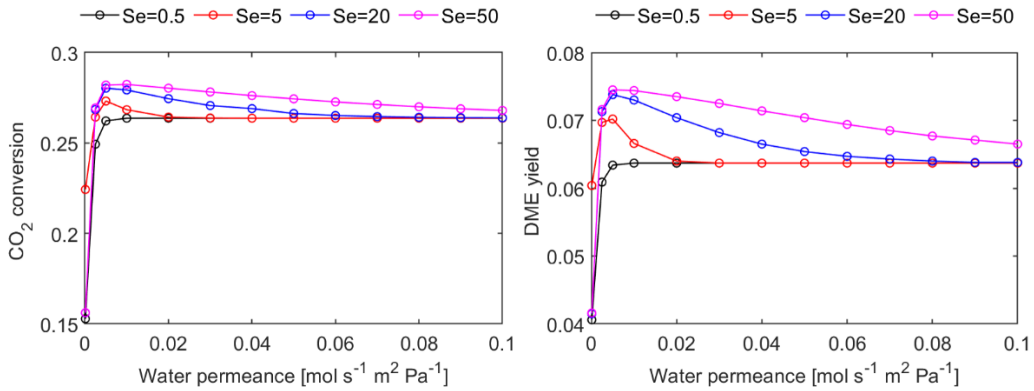

Figure 1. CO_2 conversion and DME yield as a function of water permeance at different values oh H_2O/H_2 selectivity

The sweep gas flow rate has to be 5 times higher than the feed one; while no transmembrane pressure difference is required to achieve the desired effect on the products yield. Finally, Figure 2 shows the comparison between a membrane reactor and the conventional packed bed reactor under the same operating conditions (40 bar, 220 °C and residence time of 40 $g_{cat}h\ mol^{-1}_{CO_2}$), and reveals a great potential of the membrane reactor technology for the CO_2 to DME conversion.

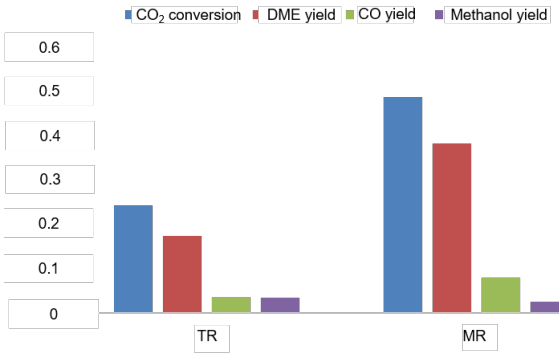

Figure 2. Comparison between a conventional (TR) and a membrane reactor (MR) working in the same operating conditions

4. Conclusions

The application of a membrane reactor for the selective water removal in the CO_2 direct conversion to DME has been modelled with both ASPEN and a 1D model. The optimal membrane properties have been estimated. The optimal parameters regulating the trans-membrane driving force have been determined. In the end, the potential of the membrane reactor has been shown by a comparison with the traditional reactor, working in the same operating conditions. In particular, a membrane reactor can achieve the equilibrium conversion and product yield.

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