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Insights on CO_2 Utilization through Reverse Water Gas Shift Reaction in Membrane Reactors: A Multi-scale Mathematical Modeling Approach

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ABSTRACT

The rising levels of carbon dioxide (CO_2) in the atmosphere significantly contribute to climate change, highlighting the need for effective CO_2 mitigation strategies. While capturing and storing CO_2 is important, converting it into useful products offers additional environmental and economic benefits. One promising method is the reverse water gas shift (RWGS) reaction, which transforms CO_2 into carbon monoxide (CO). Membrane reactors (MR), which integrate selective membranes with equilibrium limited chemical reactions, have the potential to intensify processes based on the RWGS reaction. In such reactors, by-products like water are removed in-situ from the reaction zone, effectively shifting the reaction equilibrium to favor higher CO_2 conversion. This study develops a comprehensive multi-scale mathematical model for RWGS membrane reactors. We integrate the microscale permeance model (for LTA-4A membrane) with the RWGS MR unit scale and the system's scale models. The effectiveness of applying sweep gas has been suggested, and the optimal H_2 perm-selectivity is found in the range from 30 to 50. A detailed membrane permeance model for LTA-4A membranes is integrated in the MR model to assess how species permeance changes with varying reactor conditions. We propose a sweep recycle configuration and compare it with the conventional sweeping configuration commonly assumed in most literature. A thermal efficiency analysis is conducted to evaluate the proposed recycling configuration, providing insights into the practical feasibility of membrane reactors for CO_2 utilization.

Keywords: Multiscale Modelling, Carbon Dioxide, Modelling and Simulations, Membranes, Process Intensification

INTRODUCTION

Current environmental challenges necessitate the mitigation of CO_2 emissions. However, CO_2 emissions from certain industries are expected to remain significant in the foreseeable future. CO_2 utilization presents an innovative approach to reducing atmospheric CO_2 by using it as a feedstock to produce valuable products [1].

Process intensification through steam separation is a promising concept that enables the development of novel CO_2 utilization pathways [2], since most CO_2 utilization processes produce H_2O as a side product. Water-permeable membranes enable in-situ selective water transfer to shift the reaction forward, according to the Le Chatelier's principle. Membrane reactors (MRs) combine the selective permeable membranes with traditional catalytic processes, enhancing production, separation, and energy efficiency [3].

The core principle of water-permeable membrane reactors lies in their selective permeability, allowing water molecules to pass while retaining other reactants and products. This permeability is typically achieved through the use of hydrophilic membrane [4], made from materials like polymers, ceramics, and composite materials, which exhibit hydrothermal stability, good permeance and perm-selectivity [5]. Among the various types of membranes, LTA zeolite membranes have garnered significant attention [6]. LTA-4A is well-reported for its high hydrophilicity, small pore size (0.42 nm) comparing to other zeolites (0.735 nm for FAU, 0.65 nm for MOR, 0.51 nm for ZSM-5) [7]. The excellent performance of LTA membranes can be attributed to their unique structural properties, excellent thermal and chemical stability at high temperature and pressure, and high affinity for water. The modeling of gas species permeation in the presence of water through LTA membrane has been investigated [8].

The application of membrane reactors technology to conduct various reactions utilizing CO_2 as a reactant have been recently reviewed [7,10,11]. Some key reactions of interest are the conversion of CO_2 to CO, methane, methanol and dimethyl ether. Among the various CO_2 utilization pathways, the reverse water gas shift (RWGS) reaction, eq. (1), has gained significant attention due to its ability to produce syngas, a mixture of H_2 and CO [11]. Syngas serves as a fundamental feedstock for synthesizing a wide array of chemicals and fuels, including methanol, higher alcohols, and hydrocarbons via the Fischer–Tropsch synthesis. Despite its importance, the RWGS reaction has been rarely investigated within MR modeling [12].

$$\mathrm{CO_2 + H_2 \rightleftharpoons CO + H_2O} \tag{1}$$

Although a few RWGS MR models exist, they tend to oversimplify membrane characteristics and overlook practical aspects. For example, a N_2 stream has frequently been considered as the sweep gas by default [13,14,15], which is not practical in industrial application. The sweep stream will contain H_2, which is difficult to recover from N_2. The evaluation of sweeping conditions still requires more attention. Additionally, although numerous simulations have been conducted to assess the performance of MRs under the assumption of constant species permeance, the lack of detailed models that accurately represent membrane characteristics has limited the predictive capabilities of these systems. The H_2O/H_2 permselectivity has been suggested the value greater than 100, though this remains a topic of debate.

This work provides insights into the use of RWGS MRs for CO_2 utilization. We develop a dimensionless MR model and, under the assumption of constant membrane permeance, evaluate reactor performance across various sweeping conditions and species permeance-selectivity. Additionally, we integrate a detailed membrane permeance model for an LTA-4A zeolite membrane to assess how species permeance changes with varying reactor conditions, an area currently under explored in the literature. Furthermore, we propose a recycling configuration and compare it with the conventional sweeping configuration that is commonly assumed in most literature. A thermal efficiency analysis is conducted to examine the proposed recycling configuration.

MODELING

In this section, the RWGS process is modeled at three different scales: The microscale permeance in LTA-4A membrane and its dependence on local conditions, the RWGS MR unit scale, and the system's scale including recycling.

Permeance model of the membrane

The LTA-4A membrane is selected to model the species permenace for its good performance in selective permeation of water. Zito et al. propose a validated permeance model for light gases in the presence of water for the 4A zeolite [8]. The trans-membrane flux is given as the sum of surface and gas translation diffusion flux [15] :

$$J_i = \rho C_{\mu s_i} D_{SD} \Gamma \frac{d\theta_i}{dl} + \frac{\epsilon\left(C_{\mu s_i}\right)}{\tau\left(C_{\mu s_i}\right)} \frac{1}{\zeta} \frac{\lambda}{RT} \sqrt{\frac{8RT}{\pi M}}\, e^{-\frac{E_{GT}}{RT}} \frac{dP_i}{dl} \tag{2}$$

The permeance is described as the ratio between the transmembrane flux and the driving force:

$$Q_i = \frac{J_i}{\left(P^R y_i^R - P^P y_i^P\right)} \tag{3}$$

$$Q_i = \rho C_{\mu s} D_{\mathrm{SD},i} \Gamma_i \frac{\theta_i^R - \theta_i^P}{\left(P^R y_i^R - P^P y_i^P\right) \cdot \delta_{\mathrm{membrane}}} + \frac{\varepsilon(C_{\mu s})}{\tau(C_{\mu s})} \frac{\lambda}{\zeta \mathrm{RT}} \sqrt{\frac{8\mathrm{RT}}{\pi M_i}} \frac{e^{-\frac{E_{\mathrm{GT}}}{\mathrm{RT}}}}{\delta_{\mathrm{membrane}}} \tag{4}$$

The permeance is then integrated into the MR model proposed in the following section, including the impact on membrane selectivity, $S_i = \frac{Q_{\mathrm{H2O}}}{Q_i}$.

Membrane reactor model

A packed-bed tubular and concentric membrane reactor is illustrated in Figure 1. In this configuration, the catalyst particles bed is placed in the annular chamber, through which the reactant stream is introduced, serving as the retentate side. Inside the membrane (the tubular chamber) sweeping stream can be introduced in co-current direction with respect to the feed stream. The model obeys the following assumptions: One-dimensional flow, isothermal operation, assuming heat supplied continuously from the furnace, no pressure drops in both retentate and permeate side, assuming pressure regulator implemented to maintain constant pressure,, and absence of internal and external mass transfer resistance. The RWGS reaction kinetic rate expression is taken after Gine et al. 's work for CuO/Al_2O_3,[16], the dimensionless component balance equations are given as follows:

$$\frac{d\,\widetilde{F_i^R}}{d\,Pe_m} = \alpha_i B\left(y_{CO_2} y_{H_2} - \frac{y_{CO} y_{H_2O}}{Keq_1}\right) - \frac{1}{S_i}\left(y_i^R - P_r^{-1} y_i^P\right) \tag{5}$$

$$\frac{d\,\widetilde{F_i^P}}{d\,Pe_m} = \frac{1}{S_i}\left(y_i^R - P_r^{-1} y_i^P\right) \tag{6}$$

The dimensionless variables are defined as follows:

$$\widetilde{F_i^R} = \frac{F_i^R}{F_{\mathrm{CO2},0}^R}, \quad \widetilde{F_i^P} = \frac{F_i^P}{F_{\mathrm{CO2},0}^R}, \quad \widetilde{F_{\mathrm{N2}}^P} = \frac{F_{\mathrm{N2}}^P}{F_{\mathrm{CO2},0}^R}, \quad P_r = \frac{P^R}{P^P},$$

$$S_i = \frac{Q_{\mathrm{H2O}}}{Q_i}, Pe_m = \frac{(2\pi R_{\mathrm{in}} Q_{\mathrm{H2O}} P^R) z}{F_{\mathrm{CO2},0}^R}, B = \frac{A^R \rho_s (1-\varepsilon) k_1 C_{FP}}{2\pi R_{\mathrm{in}} Q_{\mathrm{H2O}} P^R}$$

The $F_{\mathrm{CO2},0}^R$ represents the CO_2 inlet flow rate. It is assumed that only CO_2 and H_2 are fed into the reactor, with n is defined as the feed molar ratio between H_2 and CO_2. Q_i refers to the permeance of species i. P^R and P^P are the pressures on the retentate and permeate sides, respectively. A^R is the cross-section area of the retentate side and R_{in} is the radius of inner tube, k_1 is the rate constant for the RWGS reaction, Keq_1 is the RWGS reaction equilibrium constant, ρ_s is the catalyst solid density, ε is the void fraction of the catalyst bed, Q_i is the permeance of species i, C_{FP} is the reaction correction factor. The conversion of CO_2 is expressed as follows:

$$X = \frac{F_{CO_2,0} - F_{CO_2}}{F_{CO_2,0}} = 1 - \frac{F_{CO_2}}{F_{CO_2,0}} = 1 - \widetilde{F_{CO_2}^R} - \widetilde{F_{CO_2}^P} \tag{7}$$

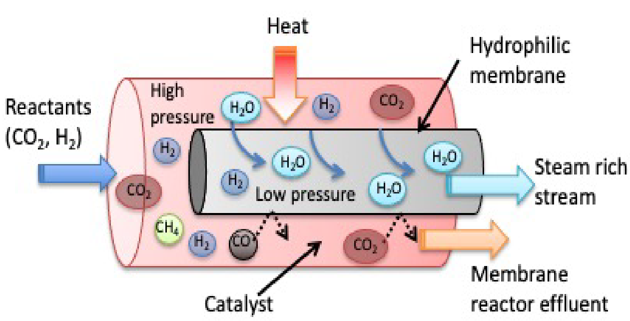

Figure 1. Schematic of a membrane reactor utilizing a hydrophilic membrane.

Reactor system flowsheet

A simple reactor system flowsheet including the upstream and downstream operations is proposed to further evaluate the MR performance. In the conventional design as shown in Figure 2, two streams are fed into the reactor, the compressed feed stream serves as the retentate side while a low pressure pure H_2 stream serves as the sweep gas in the permeate side. In Figure 3 we propose a recycle configuration, where instead of using an extra stream for sweeping, the retentate effluent is recycled to the permeate side serving as the sweep gas, after pressure reduction. In both designs, the heat integration is considered, and the product streams are all cooled down and fed to a flash unit for water separation. The feed, sweep and product streams in both configurations are all set to standard conditions for thermal efficiency comparisons. The reactor system is simulated in Aspen Plus, where the detailed MR model developed in MATLAB is embeded.

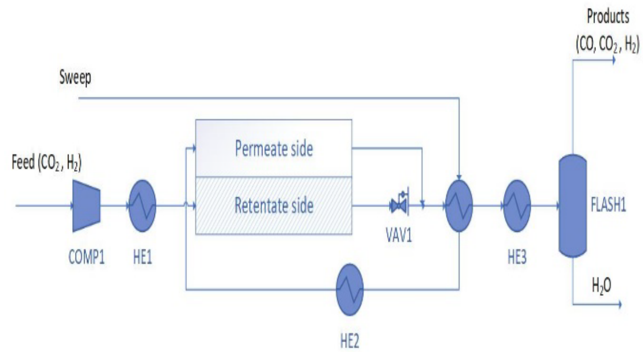

Figure 2. The conventional design for MR model with heat integration, H_2 stream serves as the sweep gas.

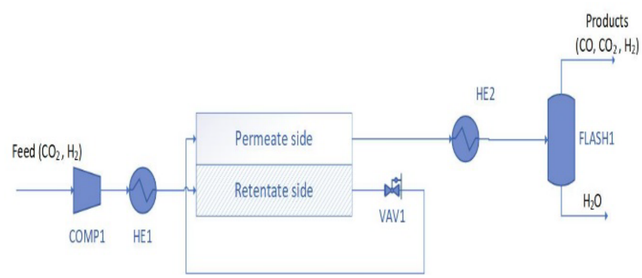

Figure 3. The recycle configuration for MR model with heat integration. The outlet of the retentate side serves as the sweep gas.

The thermal efficiency is defined as the ratio between the heating value of the produced syngas to the total used hydrogen and the external heat and power demands for the system, which is defined as:

$$\eta_{en} = \frac{\dot{n}_{\mathrm{CO}} \cdot \mathrm{LHV_{CO}} + \dot{n}_{\mathrm{H2,out}} \cdot \mathrm{LHV_{H2}}}{\dot{n}_{\mathrm{H2,in}} \cdot \mathrm{LHV_{H2}} + E_{MR} + E_{vav1} + E_2 + P_{\mathrm{COMP}}} \tag{8}$$

where LHV is the lower heating value, n is the molar flow rate, E_i represents the required heat for block i, P_{COMP} represents the power input for the compressor.

RESULT AND DISCUSSION

Membrane reactor performance analysis

The effect of different sweeping scenarios on CO_2 conversion, as a function of H_2 perm-selectivity and Pe_m, is shown in Figure 4. The membrane permeance is assumed constant along the reactor.

In the no-sweep gas scenario (Figure. 4a), increasing S_{H_2O/H_2} initially enhances CO_2 conversion, as the removal of reaction product H_2O is more significant than the leaking of reactant H_2, which shift the equilibrium toward higher CO_2 conversion, according to Le Chatelier's

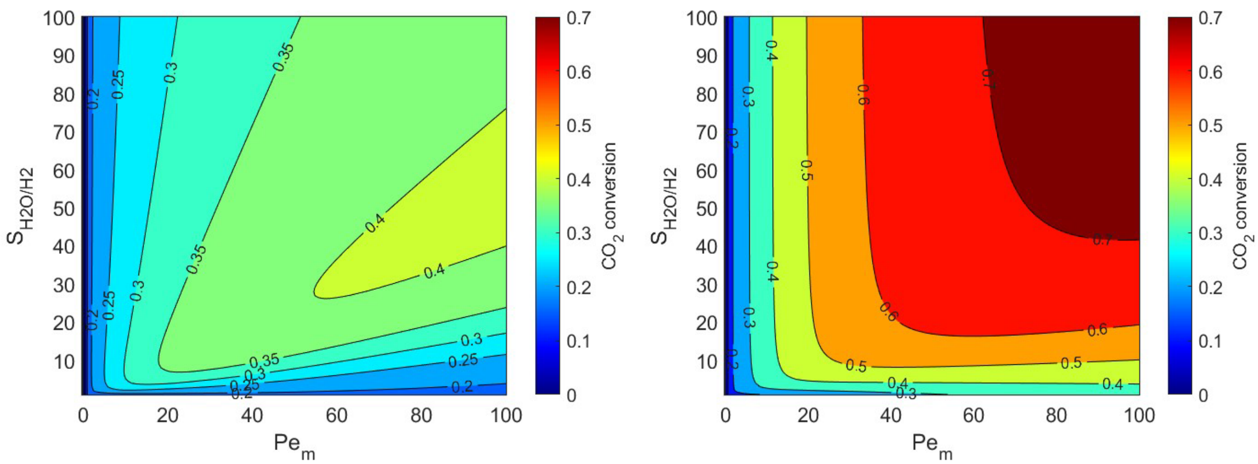

Figure 4: Comparison of CO_2 conversion varying with Pe_m under different S_{H_2O/H_2}. T = 300°C, H_2/CO_2 ratio= 3, pressure ratio Pr = 20, dimensionless number B = 1. The membrane is impermeable to CO and CO_2. Co-current configuration. (a) No sweep gas applied in the peremeate side. (b) H_2 sweep gas ratio of 10.

principle. However, once the perm-selectivity exceeds a certain threshold, increasing S_{H_2O/H_2} leads to a CO_2 conversion decline. This is due to reduced H_2 leakage to the permeate side, which increases the partial pressure of water in the permeate side. The increased water partial pressure decreases the driving force for the forward reaction, thus limiting the CO_2 conversion potential. This effect is more pronounced at low membrane permeances.

In the applied sweep gas scenario (Figure 4b), a high sweep flow rate significantly improves the CO_2 conversion for the entire range of Pe_m and S_{H_2O/H_2} values compared to the case represented in Figure 4a. The sweep gas facilitates the continuous removal of H_2O, maintaining a favorable partial pressure gradient and preventing water accumulation in the reactor. Nevertheless, there is a threshold value for S_{H_2O/H_2}, beyond which further increases do not significantly improve in CO_2 conversion. These simulations suggest that high S_{H_2O/H_2} and Pe_m are not always desirable in any cases, applying sweep gas can significantly improve the MR performance.

Permeance analysis

The detailed permeance model reveals that the permeance of species is also influenced by the differences in their partial pressures, which vary continuously within the reactor. We integrated this permeance model into the MR model to examine how membrane properties change along the reactor as species' partial pressures change.

Figure 5 shows the permeance of different gas species through the LTA-4A membrane as Pe_m increases. The H_2O permeance is the highest and remains nearly constant as Pe_m increases, primarily due to the membrane's strong affinity for water and its hydrophilic nature. CO_2 permeance is the lowest and decreases as Pe_m increases. The H_2 and CO permeance also declines as Pe_m increases. Additionally, the H_2 and CO permeance are similar in value compared to CO_2 and H_2O. And for Pe_m values smaller than 20, H_2 permeance is higher, while the CO permeance becomes higher as Pe_m exceeds 20. This is due to the fact that H_2 permeance experiences a larger decline compared to CO permeance as Pe_m increases.

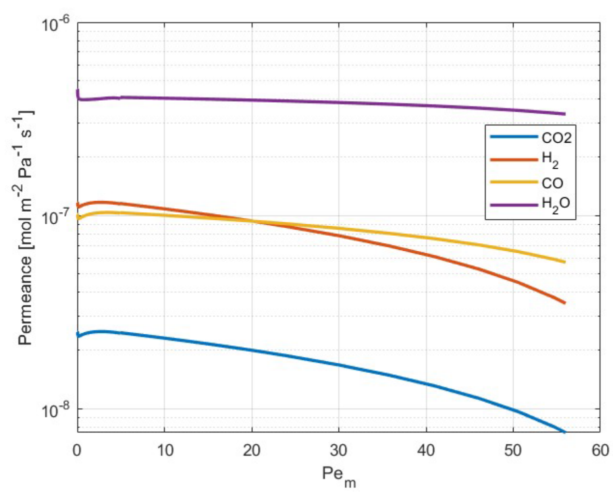

Figure 5. The gas species permeance of LTA-4A membrane along the reactor for different gas species. T = 300°C. H_2/CO_2 feed ratio = 3, reaction pressure is 10 bar, permeate pressure is 1 bar. Co-current configuration.

The varying permeance of these species plays a critical role in the MR performance. Figure 6 shows that perm-selectivity for all gas species increases as Pe_m increases. CO_2 perm-selectivity ranges from 15 to 45 along the whole MR. The large boundary highlights the importance of integrating the permeance model into the MR model for process simulation. Additionally, CO perm-selectivity shows similar value to H_2 perm-selectivity. Since most literature only considers H_2 perm-selectivity in simulations, the competing CO perm-selectivity values raise the question of whether it is appropriate to assume only H_2 permeation in the MR model.

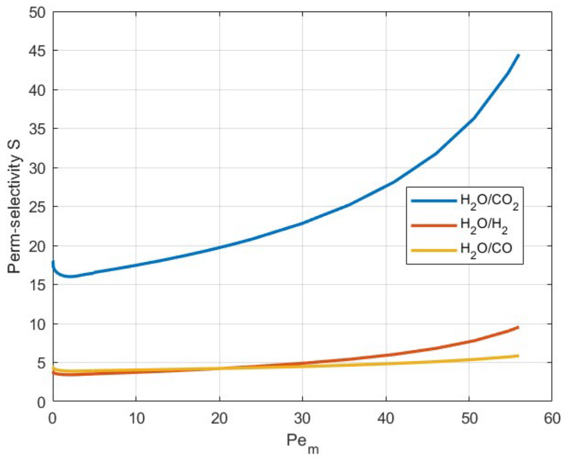

Figure 6. The species perm-selectivity of LTA-4A membrane along the reactor for different gas species. T = 300°C. H_2/CO_2 ratio=3, reaction pressure is 10 bar, permeate pressure is 1 bar. Co-current configuration.

Thermal efficiency comparative analysis

Figure 7 shows the thermal efficiency of the RWGS process with varying CO_2 conversion in the product stream, achieved by changing the reactor length. The recycling configuration has higher thermal efficiency compared to the conventional one across the entire range of CO_2 conversion. Additionally, the efficiency of the recycling configuration remains almost constant as CO_2 conversion increases, while that of the conventional design drops. The sweep gas used in conventional design requires a significant amount of heat to maintain the temperature of the sweep gas. This additional heating leads to a decrease in thermal efficiency. As operating pressure increases from 10 bar to 20 bar, thermal efficiency declines for both configurations. This is because higher pressures increase the enthalpy of the flows, requiring more energy to maintain the system's operational temperature. However, the decrease in thermal efficiency for the conventional design is more significantly affected by the increase in operating pressure, showing a reduction of around 15%, while the recycling configuration experiences only about a 5% decrease in thermal efficiency. This suggests that the recycling configuration remains preferable when the system operates at high pressure.

CONCLUSIONS

This study presents a multi-scale modeling approach to evaluate RWGS performance in MR for CO2 utilization. Through the development of a dimensionless model, integration of a detailed membrane permeance model for LTA-4A zeolite, and the simulation of a simple process system, we provided insights into the performance of membrane reactors under various conditions.

Our findings highlight the importance of optimal sweeping conditions and membrane properties in enhancing CO_2 conversion. Specifically, sweep gas improves conversion significantly compared to the no-sweep configuration. The analysis reveals that one can locate the optimal H_2 perm-selectivity, beyond which the performance gains diminish. It could be in the range around 30 to 50 for Pe_m smaller than 70. Additionally, the species variable permeance was found to be a critical factor that should be considered in modeling the MR, with

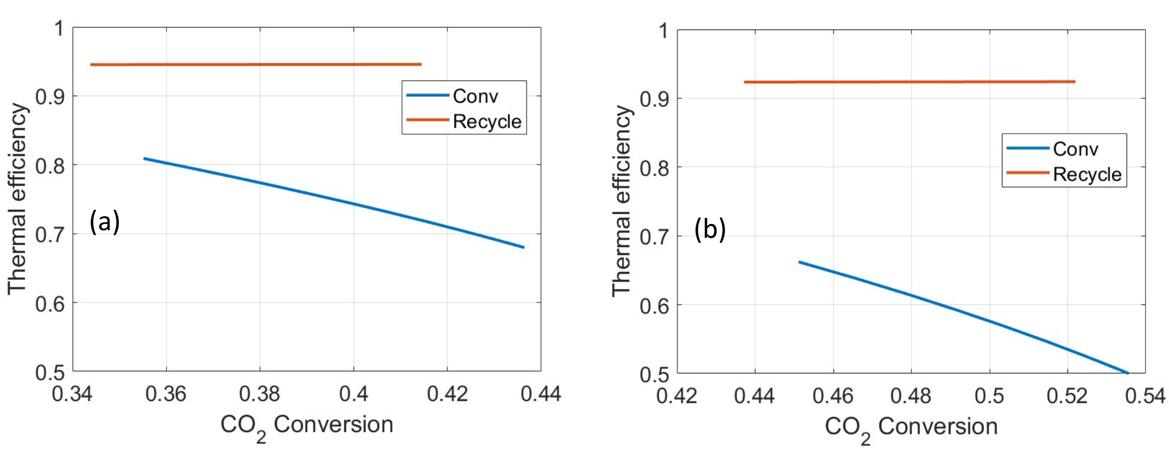

Figure 7: Thermal efficiency for different configurations as a function of CO_2 conversion. H_2/CO_2 feed ratio= 3. T = 300°C. (a) Reaction pressure of 10 bar. (b) Reaction pressure of 20 bar.

H_2O showing the highest permeance, which remained almost constant across the reactor, while CO, CO_2 and H_2 permeance decreased with increasing reactor length.

Thermal efficiency analysis shows that the recycling configuration outperforms the conventional configuration for all CO_2 conversion values, maintaining a more stable thermal efficiency as CO_2 conversion increases. This suggests that the recycling design is more energy-efficient, particularly under high-pressure conditions, and offering significant advantages in practical applications.

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