

Feasibility Study of Employing a Catalytic Membrane Reactor for a Pressurized CO₂ and Purified H₂ Production in a Water Gas Shift Reaction

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요 약

이 논문은 촉매막반응기(catalytic membrane reactor)에서의 중요한 두 요소인 수소선택도와 수소투과량 및 Ar sweep 유량과 압력이 수성가스전이반응의 성능에 미치는 영향에 대하여 1차원 반응기모델과 반응속도식에 근거한 연구결과를 나타내고 있다. 연소전 이산화탄소 포집의 한 방법으로서, 촉매막반응기를 사용하여 원통부분에서는 고압/고농도의 이산화탄소를 관부분에서는 고순도의 수소를 동시에 얻을 수 있는지에 대한 가능성을 검토하였다. 또한, 고농도의 이산화탄소와 고순도의 수소를 동시에 얻기 위해 필요한 수소투과량, 수소선택도, Ar sweep 유량 및 압력에 대한 지침을 나타내었다. 그 결과 $1 \times 10^{-8} \text{ molm}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ 의 수소투과량과 10000의 수소선택도를 가진 막을 장착한 촉매막반응기에서는 8 atm의 압력과 $6.7 \times 10^{-4} \text{ mols}^{-1}$ 의 Ar sweep 유량의 조건하에서 약 90%의 농도를 가진 이산화탄소와 100%의 순도를 가진 수소가 동시에 얻어짐이 밝혀졌다.

주제어 : 촉매막반응기, 수성가스전이반응, 연소전 이산화탄소 포집, 수소선택도, 수소투과량

Abstract : The effect of two important parameters of a catalytic membrane reactor (CMR), hydrogen selectivity and hydrogen permeance, coupled with an Ar sweep flow and an operating pressure on the performance of a water gas shift reaction in a CMR has been extensively studied using a one-dimensional reactor model and reaction kinetics. As an alternative pre-combustion CO₂ capture method, the feasibility of capturing a pressurized and concentrated CO₂ in a retentate (a shell side of a CMR) and separating a purified H₂ in a permeate (a tube side of a CMR) simultaneously in a CMR was examined and a guideline for a hydrogen permeance, a hydrogen selectivity, an Ar sweep flow rate, and an operating pressure to achieve a simultaneous capture of a concentrate CO₂ in a retentate and production of a purified H₂ in a permeate is presented. For example, with an operating pressure of 8 atm and Ar sweep gas for rate of $6.7 \times 10^{-4} \text{ mols}^{-1}$, a concentrated CO₂ in a retentate (~90%) and a purified H₂ in a permeate (~100%) was simultaneously obtained in a CMR fitted with a membrane with hydrogen permeance of $1 \times 10^{-8} \text{ mol m}^{-2}\text{s}^{-1}\text{Pa}^{-1}$ and a hydrogen selectivity of 10000.

Keywords : Catalytic membrane reactor, Water gas shift reaction, Pre-combustion CO₂ capture, Hydrogen selectivity, Hydrogen permeance

1. Introduction

Recent issues like environmental pollutions and CO₂ emissions have led to a strong demand for a clean energy such as solar energy, hydrogen, and fuel cells. However, it is very unlikely for these technologies to realize in a near future from an economical point of view and it will be inevitable to depend on current fossil fuel based energy. Therefore, many efforts have been made to reduce or capture CO₂, which is considered as a green house gas causing a global warming, released from the use of current fossil fuels and three different types of CO₂ capture methods,

post-combustion, oxy-fuel, and pre-combustion have been extensively studied so far[1-5]. A post-combustion CO₂ capture is to capture CO₂ from a flue gas released from burning fossil fuels and a commercially available amine absorption technology can be used for this method, but it is very expensive and energy-intensive process. In addition, an additional compression step is required for a subsequent CO₂ sequestration because the pressure of a captured CO₂ is relatively low. Oxy-fuel is a new concept of using pure O₂ instead of air so that a flue gas after gasification contains only CO₂ and steam. In oxy-fuel, a concentrated CO₂ can be obtained in a flue gas by removing steam in

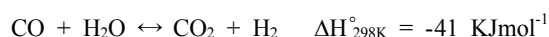
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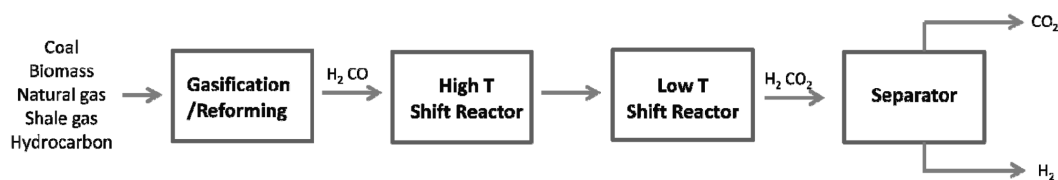
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a cooler, but this process requires an additional air separation unit (ASU) to separate O₂ from air to provide a pure O₂ to a gasification/reforming process. A pre-combustion CO₂ capture is to separate CO₂ from a stream containing mainly H₂ and CO₂ in order to only combust H₂, a clean fuel, and the captured CO₂ can be further sequestered. Figure 1(a) shows a gasification/reforming process to produce a synthesis gas coupled with a pre-combustion CO₂ capture process. Initially, different feed streams such as coal, biomass, natural gas (NG), shale gas, and hydrocarbon are fed to a gasifier or reformer to produce a synthesis gas, a H₂-CO rich stream, and then undergo high temperature and low temperature shift reactors to produce H₂-CO₂ rich stream by a water-gas shift reaction described in reaction 1.

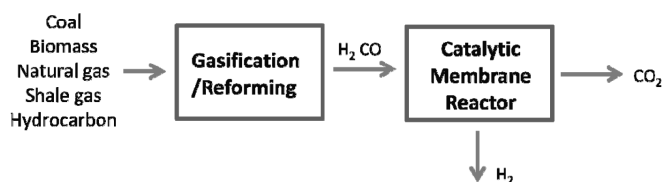


This stream is then separated into H₂ and CO₂ by a separator and H₂-rich stream is combusted and CO₂-rich stream is transported and further sequestered. This process is called a two-step process because a shift reactor and a separator are needed independently and separators using solvents, physical/chemical adsorbents, or membranes can be used [1]. Figure 1(b) presents a new concept of a one-step process employing a catalytic membrane reactor (CMR) combining a reactor for a water gas shift reaction and a separator for H₂-CO₂ separation and this process is very simple and cost-efficient because two independent units are merged onto a single unit. Moreover, a simultaneous production of a pressurized and concentrated CO₂ in a retentate (a shell side of a CMR) and purified H₂ in a permeate (a tube side of a CMR) can be achieved in a CMR with the use of a hydrogen separation membrane and an enhanced H₂ production is expected from an equilibrium shift by continuously removing H₂ during reaction (*Le Chatelier's principle*) [6].

A CMR consists of a reactor with a catalyst for reaction and a separator with a membrane for separation and has been extensively used for H₂ producing processes like various reforming reactions [7-12]. For a membrane separation, there are two key factors to determine the quality of a membrane of interest, hydrogen permeance and hydrogen selectivity [13]. A hydrogen permeance (Q_{H_2}) is defined as a hydrogen molar flux divided by pressure and can be obtained by the formula, $Q_{H_2} = \frac{F_{H_2}}{A \Delta p}$, where Q_{H_2} is a hydrogen permeance (mol m⁻² s⁻¹ Pa⁻¹), F_{H_2} is the molar flow rate of hydrogen (mol s⁻¹), A is the membrane area (m²), and Δp is the pressure difference between a retentate and a permeate in a CMR (Pa). A hydrogen selectivity is defined as the ratio of a hydrogen permeance and other gas molecule's permeance with a higher hydrogen selectivity meaning a higher hydrogen permeance than other gas molecule. Many researchers have shown the benefit of a CMR both theoretically and experimentally and have reported an enhanced reactant conversion and H₂ production because of an equilibrium shift driven by continuously removing H₂ during reaction in various reforming reactions. Similarly, there are some research results reporting the application of a CMR for a water gas shift reaction close to a concept of a one-step process introduced in Figure 1(b). Tosti et al. [14] reported a CO conversion close to 100% far exceeding the equilibrium conversion of about 80% for a water gas shift reaction in a CMR equipped with a low temperature shift catalyst and a Pd-Ag membrane with infinite hydrogen selectivity. Basile et al. [15] studied a water gas shift reaction in a CMR with a low temperature shift catalyst and Pd or Pd-Ag membranes with infinite hydrogen selectivity by varying a feed molar flow and N₂ sweep molar flow. They found that a Co conversion of close to 100% was obtained and simulation data fitted very well



(a) Two-step process: reactor and separator



(b) One-step process: catalytic membrane reactor

Figure 1. A pre-combustion CO₂ capture for a gasification/reforming process (a) two-step process: reactor and separator (b) one-step process: catalytic membrane reactor.

with experimental data. Although previous results showed the benefits of employing a CMR for a water gas shift reaction, little work has been done in their studies to investigate the effect of a wider range of hydrogen permeance and hydrogen selectivity, two important factors of a membrane, on the performance of a CMR. Therefore, the effect of hydrogen selectivity and hydrogen permeance coupled with an operating pressure and Ar flow rate on the performance of a CMR is extensively examined and the feasibility studies of a simultaneous production of a concentrated CO₂ in a retentate and a purified H₂ in a permeate are performed in this paper.

2. Materials and Methods

A one-dimensional reactor model with reaction kinetics was used to model a CMR[16] using equations 1-7 with F_i representing a molar flow rate of species i in a retentate and F_i^{tube} representing a molar flow rate of species i in a permeate. It is assumed that r_i^{tube} is proportional to pressure difference of species i between a retentate and a permeate.

$$\frac{dF_i}{dW} = -r_i - r_i^{tube} \quad (1)$$

$$\frac{dF_i^{tube}}{dW} = r_i^{tube} \quad (2)$$

$$P_i = \frac{F_i}{\sum F_i} P_{total} \quad (3)$$

$$P_i^{tube} = \frac{F_i^{tube}}{\sum F_i^{tube}} P_{total} \quad (4)$$

$$r_{H_2}^{tube} = K_{H_2}^{tube} (P_{H_2} - P_{H_2}^{tube}) \quad (5)$$

$$K_{H_2}^{tube} = \frac{Q_{H_2} A_c}{W} \quad (6)$$

$$r_i^{tube} = \frac{K_{H_2}^{tube}}{\alpha_i} (P_i - P_i^{tube}) \quad (7)$$

From previously reported reaction kinetics for a water gas shift reaction[17], an empirical rate equation (Equation 8 and 9) obtained from kinetic data at 473 K by Phatak et al.[18] was chosen for this study because the kinetic data were obtained using a Pt/CeO₂ catalyst showing high stability in air and at high temperatures as well as sulfur tolerance. The composition of a flue gas obtained from different gasifiers such as GE Energy Radiant,

Table 1. Reaction conditions and membrane properties used in a catalytic membrane reactor

Reactant	CO _{in} (mol s ⁻¹)	10 ⁻⁶
	CO : H ₂ O : H ₂ : CO ₂	1 : 0.9 : 0.8 : 0.3
Reactor	T (K)	473
	P (atm)	1-8
	Catalyst used (g)	2
Tubular membrane	Length (cm)	4
	Tube diameter (cm)	1
	H ₂ permeance (mol m ⁻² s ⁻¹ Pa ⁻¹)	1×10 ⁻⁸ - 1×10 ⁻⁷
	H ₂ selectivity	10 - 10000
	Ar sweep flow (mol s ⁻¹)	6.7×10 ⁻¹⁰ - 6.7×10 ⁻⁴

Conoco-Phillips E-Gas, KBR, and Shell was used for a feed stream to a CMR and reaction conditions and membrane properties are shown in Table 1.

$$r_{co} \left(\frac{mol}{s} \right) = 5.9 \times 10^{-7} (P_{CO})^{-0.33} (P_{H_2O})^{0.44} (P_{CO_2})^{-0.09} (P_{H_2})^{-0.38} \left(1 - \frac{P_{CO_2} P_{H_2}}{K_{eq} P_{CO} P_{H_2O}} \right) \quad (8)$$

$$K_{eq} = \exp(4577.8/T - 4.33) \quad (9)$$

3. Results and Discussion

3.1. Effect of an operating pressure and a hydrogen selectivity on the performance of a CMR

CMR studies were carried out at an operating pressure of 1-8 atm and a reaction temperature of 473 K using various membranes with a hydrogen selectivity ranging from 10 to 10000. The broad range of a hydrogen selectivity was chosen to extensively investigate the effect of a hydrogen selectivity on the performance of a CMR and the hydrogen selectivity of 10 represents a microporous membrane with a Knudsen diffusion mechanism, in which a permeance of a gas molecule is inversely proportional to the square root of its molecular weight while the hydrogen selectivity of 10000 represents a hydrogen perm-selective membrane like a palladium membrane[19,20]. Figure 2 shows the effect of an operating pressure and a hydrogen selectivity on a CO conversion at 473 K in a CMR fitted with a membrane with a hydrogen permeance of 1 × 10⁻⁸ mol m⁻²s⁻¹Pa⁻¹. An equilibrium CO conversion of 0.846 at the reaction condition (dashed line) was obtained from UniSim[®] Design Suite using a Gibbs reactor model and Peng-Robinson equation of state. For a membrane with a hydrogen selectivity of 10, a CO conversion slightly increased with pressure initially because of an increased driving force between a retentate and a permeate caused by increased pressure,

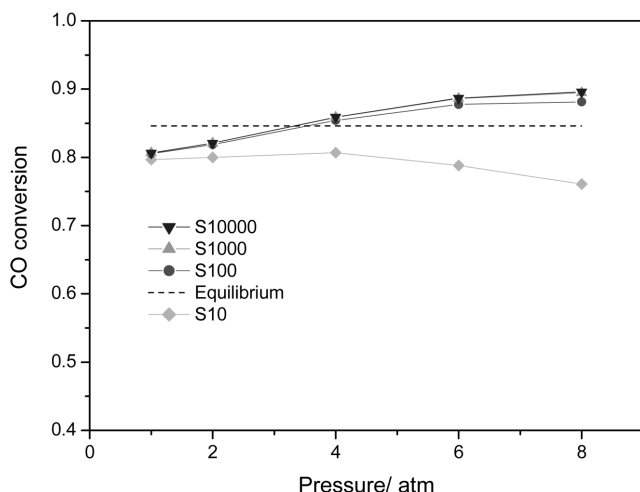
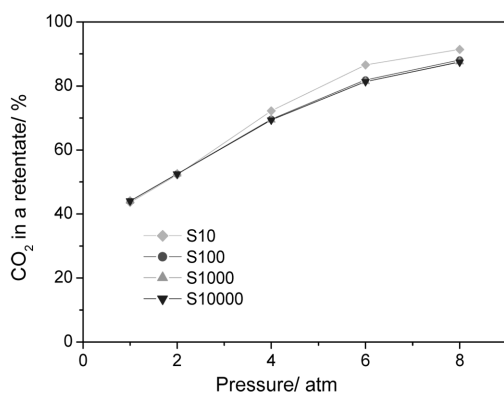


Figure 2. Effect of an operating pressure and a hydrogen selectivity on a CO conversion in a catalytic membrane reactor (S: hydrogen selectivity, dashed line: equilibrium conversion, H_2 permeance = $1 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, $T = 473 \text{ K}$).

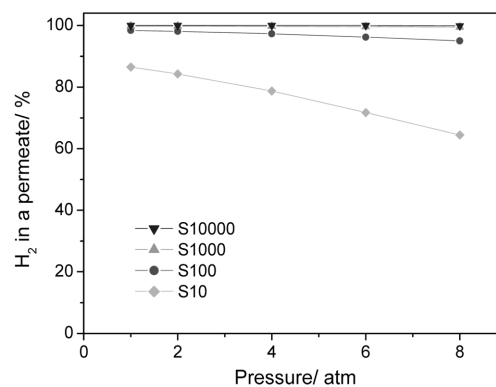
but then declined with pressure. In addition, for all pressures studied a CO conversion was less than an equilibrium conversion of 84.6 indicating no benefit of using a CMR and it is surmised that a low hydrogen selectivity of 10 led to a permeation of a reactant, CO, through a membrane and less CO to react remained in a shell side of a CMR (retentate) resulting in a low CO conversion. However, as a hydrogen selectivity increased, a CO conversion higher than the equilibrium was obtained at a certain pressure range. For example, for a hydrogen selectivity of 100 a CO conversion increased with pressure considerably because of an increased driving force between a retentate and a permeate and then exceeded an equilibrium at a pressure of about 3.5 atm confirming the benefit of a CMR that an enhanced reactant conversion can be obtained by a shift of equilibrium by continuously removing hydrogen during reaction. Moreover, for a hydrogen selectivity of 1000 and 10000 a similar trend of in-

creasing CO conversion with pressure was observed and a CO conversion surpassed an equilibrium one at a pressure of about 3.25 atm also confirming the benefit of a membrane reactor. One interesting thing to note is that a CO conversion increased noticeably at low pressure and then increased only slightly at high pressure and it is conjectured that an additional pressure effect of driving more hydrogen through a membrane decreased under a current hydrogen permeance of $1 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$. In other words, it can be said that a membrane with a higher hydrogen permeance is required to fully utilize the benefit of a CMR at high pressure.

Figure 3 presents the effect of an operating pressure and a hydrogen selectivity on a CO_2 concentration in a retentate (a shell side of a CMR) and H_2 concentration (H_2 purity) in a permeate (a tube side of a CMR) with a fixed hydrogen permeance of $1 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and this is to test the feasibility of employing a CMR, a simple and less expensive process, for a water gas shift reaction after a gasification/reforming process as a pre-combustion CO_2 capture method as described in Figure 1(b). For a CO_2 concentration in a retentate, it is apparent that pressure had a positive effect for all CMRs studied and a CO_2 concentration close to 90% was obtained at 8 atm in a retentate side for all membranes while a CO_2 concentration of about 40% was attained at 1 atm for all membranes as shown in Figure 3(a). It is believed that pressure was a strong driving force for a H_2 penetration through a membrane resulting in less H_2 and more CO_2 in a retentate. Interestingly, the highest CO_2 concentration in a retentate was achieved in a membrane with a hydrogen selectivity of 10 and it is conjectured that reactants such as CO and H_2O as well as H_2 could easily pass through a membrane with pressure due to a low hydrogen selectivity and this resulted in a relatively increased CO_2 concentration in a retentate. On the other hand, the effect of an operating pressure and a hydrogen selectivity on a H_2 concentration in a permeate is shown in Figure



(a) CO_2 concentration in a retentate



(b) H_2 concentration in a permeate

Figure 3. Effect of an operating pressure and a hydrogen selectivity on the performance of a catalytic membrane reactor (S: hydrogen selectivity, H_2 permeance = $1 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, $T = 473 \text{ K}$).

3(b). For a membrane with a hydrogen selectivity of 10 a H₂ concentration obviously decreased dramatically with pressure from 87% at 1 atm to 64% at 8 atm because pressure made other species such as CO, H₂O, CO₂ pass through a membrane leading to a less H₂ concentration in a permeate. There was a slight decrease of a H₂ concentration in a permeate with pressure for a membrane with a hydrogen selectivity of 100 (98% at 1 atm and 95% at 8 atm) and little decrease for a hydrogen selectivity of 1000 and 10000 with pressure (close to 100%). From combined results presented in Figure 3(a) and 3(b), it can be concluded that a membrane with a hydrogen selectivity close to 100 is required to obtain a pressurized and concentrated CO₂ close to 90% in a retentate and a purified H₂ close to 95% in a permeate at the same time. In addition, these results suggest that a membrane should be very carefully chosen depending on its application and there can be no big advantages of using expensive Pd-based membranes with infinite selectivity compared to other inexpensive membranes with a hydrogen selectivity of about 100 for a pre-combustion CO₂ capture in a CMR.

3.2. Effect of a hydrogen permeance and an operating pressure on the performance of a CMR

Figure 4 presents the effect of a hydrogen permeance and pressure on a H₂ yield at 473 K in a CMR with a fixed hydrogen selectivity of 10000 representing Pd-based membranes. The range of a hydrogen permeance studied was $1 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ to $1 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and an equilibrium H₂ yield of $1.65 \times 10^{-6} \text{ mol s}^{-1}$ at the reaction condition (dashed line) was obtained from UniSim[®] Design Suite using a Gibbs reactor model and Peng-Robinson equation of state. For an operating pressure of 1 atm, a H₂ yield increased with an increasing H₂ permeance

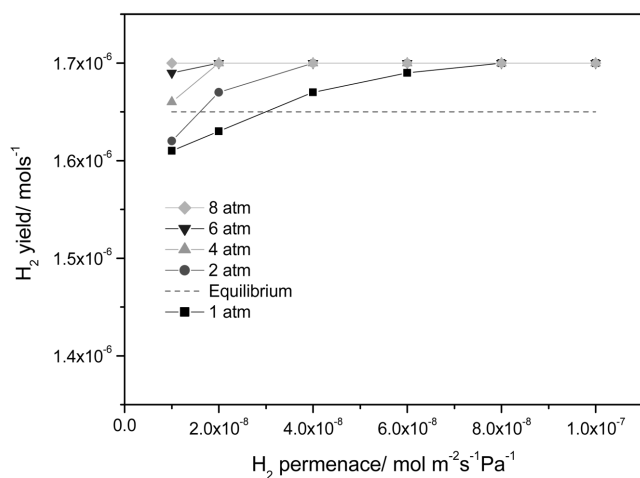


Figure 4. Effect of a H₂ permeance and an operating pressure on a H₂ yield in a catalytic membrane reactor (H₂ selectivity = 10000, dashed line: equilibrium yield, T = 473 K).

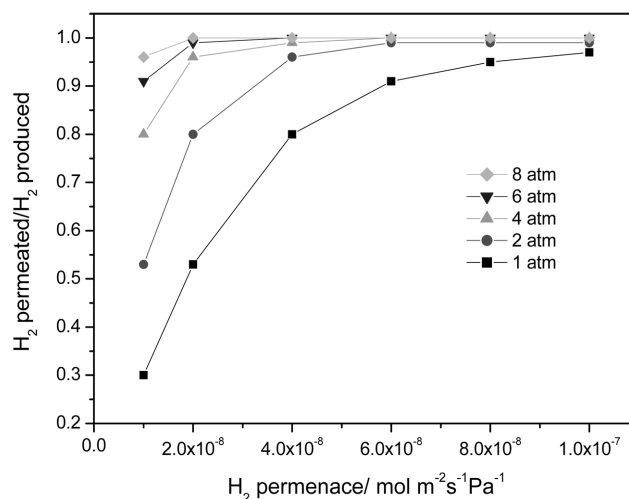


Figure 5. Effect of a hydrogen permeance and an operating pressure on the ratio of a hydrogen permeated and hydrogen produced (H₂ selectivity = 10000, T = 473 K).

and a H₂ yield higher than an equilibrium one was attained at a hydrogen permeance higher than $3 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ due to a continuous removal of hydrogen through a membrane confirming the benefit of a CMR. A similar trend was obtained for an operating pressure of 2 atm and a H₂ yield higher than an equilibrium one was attained at a hydrogen permeance higher than $1.5 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$, which is less than the one obtained for 1 atm. In addition, a H₂ yield higher than an equilibrium one was obtained for an operating pressure of 4, 6, and 8 atm irrespective of a hydrogen permeance. Apparently, a hydrogen permeance was favorable for a H₂ yield and an increased pressure lowered minimum hydrogen permeance required to achieve a H₂ yield higher than an equilibrium one. It is also noteworthy that a H₂ yield reached a saturated yield of $1.7 \times 10^{-6} \text{ mol s}^{-1}$ for all hydrogen permeance studied in this paper possibly because most of hydrogen produced was removed from a retentate during reaction resulting in no further driving force for H₂ transport through a membrane at a high hydrogen permeance. A ratio of a hydrogen permeated through a membrane and a hydrogen produced during reaction is shown in Figure 5 and obviously there was a significant difference in the ratio for 1 atm leading to a big change in a H₂ yield with a hydrogen permeance while there was less difference in the ratio with higher pressure resulting in a slight change in a H₂ yield. In addition, the ratio was close to 1.0 for all pressure at a hydrogen permeance of $1 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ and these results can explain why a saturated H₂ yield was obtained at a hydrogen permeance of $1 \times 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$.

The effect of a hydrogen permeance and an operating pressure on a CO₂ concentration in a retentate and a H₂ concentration (H₂ purity) in a permeate is shown in Figure 6(a) and 6(b), respectively. A H₂ concentration in a permeate close to 100% was

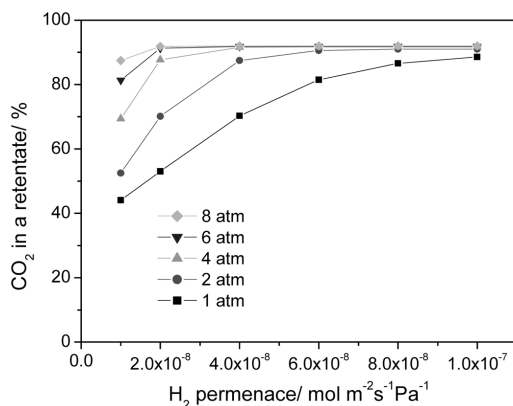
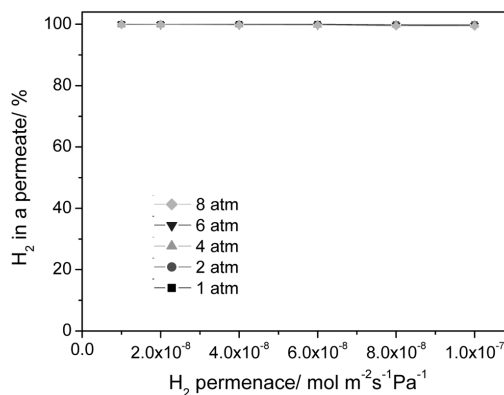
(a) CO₂ concentration in a retentate(b) H₂ concentration in a permeate

Figure 6. Effect of a hydrogen permeance and an operating pressure on the performance of a catalytic membrane reactor (H_2 selectivity = 10000, $T = 473$ K).

obtained for all hydrogen permeance studied because a membrane with a hydrogen selectivity of 10000 was used. For a CO₂ concentration in a retentate, a general trend of a higher CO₂ concentration with pressure was attained mainly because pressure was favorable for hydrogen permeation through a membrane. For a hydrogen permeance of 1×10^{-8} to 1×10^{-7} mol m⁻²s⁻¹Pa⁻¹, a significant increase of a CO₂ concentration from 44 to 89% was observed for a pressure of 1atm with a slight increase of a CO₂ concentration from 88 to 92 for a pressure of 8 atm. In other words, for a high operating pressure a CO₂ concentration close to 90% was attained even at a hydrogen permeance of 1×10^{-8} mol m⁻²s⁻¹Pa⁻¹ because higher pressure led to a higher driving force for a H₂ transport through a membrane.

3.3. Effect of an Ar sweep flow and an operating pressure on the performance of a CMR

There are two methods to increase a hydrogen permeation through a membrane in order to fully utilize the benefits of a CMR. One is to pressurize a retentate so that more hydrogen can pass through a membrane and the other is to use an inert sweep gas in a permeate so that a hydrogen concentration difference between a retentate and a permeate increases by continuously sweeping a permeated hydrogen. Figure 7 shows the effect of two factors, an Ar sweep flow rate and an operating pressure, on a CO conversion at 473 K in a CMR with a fixed hydrogen permeance of 1×10^{-8} mol m⁻²s⁻¹Pa⁻¹ and hydrogen selectivity of 10000. The general trend of higher CO conversion with an Ar sweep flow rate was obtained reflecting the benefit of using a sweep flow in a CMR for an improved driving force for a hydrogen permeation. For an operating pressure of 1 and 2 atm, a CO conversion never exceeded an equilibrium one irrespective of an Ar sweep flow rate, but a CO conversion surpassing an equilibrium one appeared for a pressure of 4,6, and 8 atm. Res-

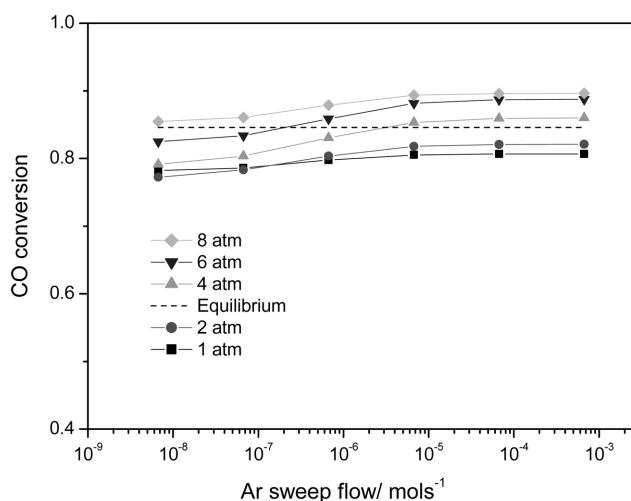


Figure 7. Effect of an Ar sweep flow and an operating pressure on a CO conversion in a catalytic membrane reactor (H_2 permeance = 1×10^{-8} mol m⁻²s⁻¹Pa⁻¹, H_2 selectivity = 10000, dashed line: equilibrium conversion, $T = 473$ K).

pective Ar sweep flow rates of 3.5×10^{-6} and 2.0×10^{-7} mol s⁻¹ were required to achieve a CO conversion higher than an equilibrium one for respective operating pressures of 4 and 6 atm while a CO conversion higher than an equilibrium was attained at 8 atm irrespective of an Ar sweep flow rate. The effect of an Ar sweep flow and an operating pressure on a CO₂ concentration in a retentate and a H₂ concentration in a permeate is shown in Figure 8(a) and 8(b). A clear trend of an increasing CO₂ concentration with both an Ar sweep flow and an operating pressure was obtained, but a CO₂ concentration close to 90% was obtained only with an Ar sweep flow rate of 6.7×10^{-4} mols⁻¹ and an operating pressure of 8 atm because a membrane with a low hydrogen permeance of 1×10^{-8} mol m⁻²s⁻¹Pa⁻¹ was used in a CMR and these results confirm the need to develop a hydrogen separation membrane with a high hydrogen permeance.

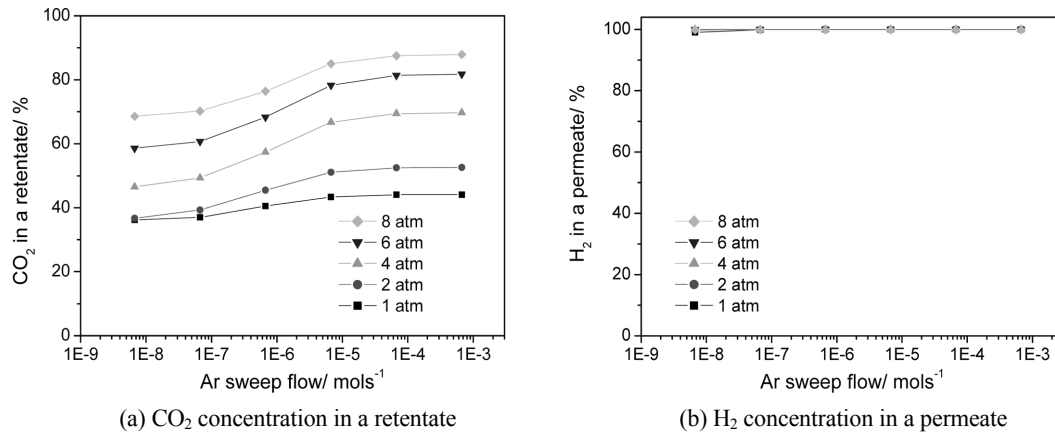


Figure 8. Effect of an Ar sweep flow and an operating pressure on the performance of a catalytic membrane reactor (H_2 permeance = 1×10^{-8} mol m⁻²s⁻¹Pa⁻¹, H_2 selectivity = 10000, $T = 473$ K).

4. Conclusions

A numerical simulation using a one-dimensional reactor model and reaction kinetics has been carried out for a water gas shift reaction in a catalytic membrane reactor (CMR) with a feed stream obtained from real coal gasifiers and feasibility studies of a simultaneous production of a pressurized and concentrated CO₂ and a purified H₂ in a CMR have been performed.

It was found that a CO conversion never surpassed the equilibrium one for all pressure studied for a membrane with a hydrogen selectivity of 10 and a CO conversion higher than the equilibrium one was obtained only for a membrane with a hydrogen selectivity of 100, 1000, 10000, reflecting the benefit of employing a CMR.

A hydrogen permeance of a membrane had a positive effect on a H₂ yield in a CMR and a H₂ yield higher than an equilibrium one was obtained for all pressure studied. A further analysis using a ratio of hydrogen permeated and hydrogen produced revealed that a significant H₂ yield increase was observed at a low pressure because of a dramatic change of the ratio while a slight H₂ yield was obtained at a high pressure due to a little change of the ratio.

A CO conversion never exceeded an equilibrium one for an operating pressure of 1 and 2 atm irrespective of Ar sweep flow rate while a minimum Ar sweep flow rate to obtain a CO conversion higher than an equilibrium one existed for an operating pressure of 4 and 6 atm. Interestingly, a CO conversion surpassing an equilibrium one was observed for all Ar sweep flow rates studied at an operating pressure of 8 atm. For a hydrogen permeance of 1×10^{-8} mol m⁻²s⁻¹Pa⁻¹ and a hydrogen selectivity of 10000, a concentrated CO₂ in a retentate (~90%) and a purified H₂ in a permeate (~100%) was attained simultaneously only at an Ar flow rate of 6.7×10^{-4} mols⁻¹ and an operating pressure of 8 atm.

In conclusion, these studies provide a very useful guideline for a hydrogen permeance and a hydrogen selectivity coupled with an operating pressure and an Ar sweep flow to achieve a simultaneous production of a concentrated CO₂ in a retentate and a purified H₂ in a permeate and show the feasibility of employing a CMR as a pre-combustion CO₂ capture method.

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Nomenclature

F_i	Molar flow rate of species i on a shell side of a CMR (retentate) (mol s ⁻¹)
F_i^{tube}	Molar flow rate of species i on a tube side of a CMR (permeate) (mol s ⁻¹)
W	Catalyst weight (g)
r_i	Reaction rate equation of reaction i (mol s ⁻¹ g ⁻¹)
r_i^{tube}	Permeation rate equation of species i through a membrane (mol s ⁻¹ g ⁻¹)
P_i	Partial pressure of species i on a shell side of a CMR (retentate) (atm)
P_i^{tube}	Partial pressure of species i on a tube side of a CMR (permeate) (atm)
P_{total}	Total pressure on a shell side of a CMR (retentate) (atm)
P_{total}^{tube}	Total pressure on a tube side of a CMR (permeate) (atm)
$K_{H_2}^{tube}$	Proportional constant of $r_{H_2}^{tube}$ (mol s ⁻¹ g ⁻¹ atm ⁻¹)
Q_{H_2}	Hydrogen permeance (mol m ⁻² s ⁻¹ Pa ⁻¹)
A_c	Cross-sectional area of a membrane (m ²)

α_i	Hydrogen selectivity of species i
T	Temperature (K)
K_{eq}	Equilibrium Constant

Abbreviations

CMR Catalytic Membrane Reactor

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