

Staged-separation membrane reactor for steam methane reforming

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Received 5 April 2007; received in revised form 25 June 2007; accepted 25 June 2007

Abstract

A novel concept of the staged-separation membrane reactor is introduced in this paper. This new reactor design retains the advantage of regular membrane reactors for achieving super-equilibrium conversion while reaction and membrane separation are carried out in two separate units. This obviates the restriction of the regular membrane reactor where membrane separation and reaction occur in the same unit, and so must be operated under the same conditions. With the membranes outside the reactor for the staged-separation membrane reactor, it becomes possible to operate under more favorable conditions for both reaction and membrane separation to achieve better overall performance. Steam methane reforming for hydrogen production was used as the example to elucidate the concept of the staged-separation membrane reactor. The performance of the staged-separation membrane reactor was compared with that of a regular membrane reactor and a traditional reformer together with an ex situ membrane purifier for hydrogen production via steam methane reforming. The staged-separation membrane reactor performed much better. The allocation of membrane area to the two membrane modules was optimized. The effects of temperature, steam-to-carbon ratio and pressure for reformer modules and membrane area for membrane modules were simulated for various cases.

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Keywords: Hydrogen; Membrane; Palladium; Steam methane reforming; Staged-separation; Reactor design

1. Introduction

Hydrogen is a major industrial commodity used as a feedstock or intermediate in a wide range of chemical, petrochemical and metallurgical processes, including hydrogenation of fuels, synthesis gas generation, reduction of mineral ores, and production of ammonia and other chemical products such as aniline. Due to rapid advancements in fuel cells in recent years, hydrogen is achieving increasing importance as a clean energy alternative. Steam methane reforming (SMR) is the most common and cost-effective method for hydrogen production.

SMR is carried out commercially in externally heated fixed-bed reactors on a very large scale. It is a reversible process usually conducted at temperatures of about 700–900 °C, catalyzed by nickel oxide supported on α -alumina [1]. Due to mass and heat transfer issues, the fixed-bed SMR suffers from significant disadvantages—low catalyst effectiveness factors and large

temperature gradients [2]. In addition, in order to obtain hydrogen of a purity required in most cases, the reactor-off gas (ROG) must go through a series of steps, such as high and low shift reactions, and pressure swing adsorption. Continuous efforts have been made over the past six decades to improve the process performance. Fluidized-beds have been employed to improve mass transfer and heat transfer in SMR [3,4]. Compared with fixed-beds, the temperature distributions is much more uniform in fluidized-bed of SMR and the catalyst effectiveness factor is increased many times. For SMR in the tubular fixed-bed reactors, the catalyst rings have a diameter of ~ 17 mm with lengths of 6–17 mm. Due to the limitation of diffusion, the internal surfaces of the catalysts are hardly accessible by the reactants and hence the catalyst effectiveness factors are only in the order of ~ 0.01 . In contrast, the mean particle size of the catalyst in fluidized-bed for SMR is only about 100 μm , much smaller than that of fixed-bed catalyst and so most of the catalyst surfaces are accessible by reactants. In addition, the fluidization of fluidized-bed increases the mass transfer between gas phase and catalyst surface. Therefore, the catalyst effectiveness factor approaches 1.0 in the fluidized-bed reactor for SMR. Membrane separation has also been employed to improve the performance of conventional fixed-bed SMR process [5,6]. Due to the selective and contin-

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uous removal of hydrogen in situ from the reaction zone, SMR reactions shift towards the product side. Hence, compared with the traditional reactors, membrane reactors (MR) can achieve higher conversions at the same temperature or the same conversion at lower temperatures. Moreover, if membranes with perfect selectivity to hydrogen, such as dense Pd-based membranes, are employed, very pure hydrogen is obtained so that there is no need for additional purification as in the conventional process where pressure swing adsorption is widely used. Further improvements of SMR performance by combining fluidization technologies and membrane separation have been explored by Adris et al [3,4,7].

The operating temperature of membrane SMR reactions is chosen to be a compromise among several factors. Both membrane permeance and the thermodynamics of SMR reaction are favorable at higher temperatures but membrane stability is favorable at lower temperatures. Hence, a compromised temperature of $\sim 550^\circ\text{C}$ was usually chosen for SMR in the membrane reactors [8]. However, even 550°C is tough for most commonly used thin Pd-based membranes. If Pd-based membranes are operated at lower temperatures, e.g. 450°C , Pd-based membranes are still able to remain similar stability with a reduced thickness. Since hydrogen permeance of a Pd-based membrane is nearly inversely proportional to its thickness, the reduced thickness means higher hydrogen permeance, and consequently, the membrane surface area is reduced as well for achieving the same hydrogen separation capacity. As it is well known, palladium is very expensive. The reduction in both area and thickness of the Pd-based membrane as a result of the reduced operating temperature considerably decreases the membrane cost in a membrane reactor.

Another issue in membrane reactor-SMR process is the compactness of the reactor. The typical SMR catalyst, Ni-based catalyst supported on alumina, is very active and efficient [1]. Consequently, SMR is usually carried out at high space velocities resulting in compact industrial reactors. However, a membrane SMR reactor has to be greatly enlarged to accommodate sufficient membrane area and simultaneously to keep the gas and membrane properly distributed so that good fluidization can be attained in the fluidized-bed. This causes extra cost as well.

We present here a novel staged-separation membrane reactor concept to address these issues by splitting the membrane reactor into two distinct units, a reaction unit and a membrane unit. This allows the staged reactor to operate under different but favorable conditions for both reaction and membrane separation to achieve better overall performance. At the same time, super-equilibrium conversion is still achievable by subjecting the retentate of the first membrane module to further reaction. This novel concept is described in detail in the following section.

2. Staged-separation membrane reactor (SSMR)

Fig. 1 schematically shows the concept of a staged-separation membrane reactor for SMR. A two-stage reaction/separation and reaction/separation sequence is proposed, with a reformer unit followed by a membrane unit, each unit consisting of two mod-

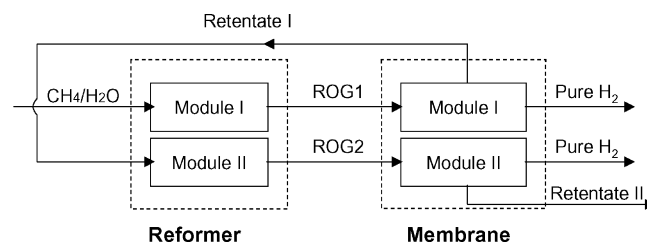


Fig. 1. Schematic diagram of staged-separation membrane reactor.

ules. The two units are isolated and can therefore be operated under different conditions. For example, the reformer modules can be operated at higher temperatures, e.g. $750\text{--}850^\circ\text{C}$ and so a higher methane conversion is achievable due to a more favorable thermodynamic condition. The membrane modules can be operated at a mild temperature, say 450°C , at which membrane degradation is alleviated and consequently membrane lifetime is extended.

Major advantages of the staged-separation membrane reactor are summarized as below:

- (1) Favorable conditions for both reaction and separation—for a membrane reactor, the membrane modules are located inside the reaction bed so the operating conditions for membrane separation and reaction must be identical. Hence, the membrane reactor is operated under conditions where neither the reaction nor the separation is close to its optimum conditions, causing the overall performance of the membrane reactor to be compromised. For the staged-separation membrane reactor, membrane modules and reaction modules are physically separated. The operating conditions can then differ and be more favorable for both separation and reaction.
- (2) Lower cost—for staged-separation membrane reactor, the membrane module is able to operate at a milder temperature. Hence, thinner Pd-based membranes can be employed to attain the same stability as thicker membranes at higher temperature. For example, hydrogen permeability of Pd–25%Ag membrane only decreases by 20% from 550°C to 450°C . Hence, hydrogen permeance of $15\ \mu\text{m}$ Pd–25%Ag alloy membrane at 450°C is approximately 40% higher than that of $25\ \mu\text{m}$ Pd–25%Ag alloy membrane at 550°C . Moreover, the metal content of a $15\ \mu\text{m}$ membrane is only 60% of a $25\ \mu\text{m}$ membrane of the same area. Thus the membrane module cost of the staged-separation membrane reactor can be considerably reduced while maintaining the same hydrogen separation capacity and lifetime with thinner membranes.
- (3) System compactness—typical catalysts for SMR are quite efficient. Hence, comparably large membrane area is required to extract a large amount of hydrogen. The membrane reactor for SMR has to be enlarged to accommodate sufficient membrane area, while simultaneously keeping them properly distributed in the bed so that good fluidization can be achieved in a fluidized-bed or good mass and heat transfer can be achieved in a fixed-bed. Therefore, the membrane reactor becomes much bigger than the traditional

reactor for SMR. SSMR has no such issue. Therefore, SSMR can be more compact, and consequently the overall cost could be lower.

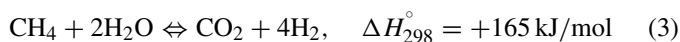
- (4) Avoiding contamination or oxidation of the membrane—unlike the traditional membrane reactor, the membrane in the staged-separation membrane reactor has no direct physical contact with catalyst particles. Therefore, it is easier to avoid deposition of the components of the catalyst on the surface of the membrane, causing potential degradation of membrane performance.

These advantages of this novel staged-separation membrane reactor over the regular membrane reactor enable it to be scaled up, operated, controlled and maintained easier. Hydrogen by SSMR-SMR could be cheaper, with the same purity as obtained from the regular membrane reactor. Therefore, the potential for industrial application is significant.

3. Modeling

3.1. Steam methane reforming

SMR involves reversible reactions: the reforming reactions (1) and (3), and the water–gas shift (WGS) reaction (2):



Reactions (1) and (3) are endothermic whereas reaction (2) is mildly exothermic. The heat needed for (1) will be provided by combusting the ROG. The conversion of methane is limited by thermodynamic equilibrium and is favored at high temperature and low pressure.

Typical catalysts, e.g. Ni/Al₂O₃, are very active for SMR reaction and excess catalyst is generally charged in industrial reformer [1]. All the above reactions therefore achieve thermodynamic equilibrium at the bed exit temperature. Therefore, reaction equilibrium is assumed for SMR for all conditions studied. In the regular membrane reactor, the reaction kinetics may locally affect hydrogen partial pressure and hence the membrane permeation. In contrast, in the staged-separation membrane reactor, the membrane separation and reaction are in different units and so the reaction kinetics has no impact on membrane separation as long as the reaction attains its equilibrium at bed exit temperature. Therefore, an equilibrium model is used for SSMR. Since reaction (3) is obtained by adding reactions (1) and (2), only reactions (1) and (2) are taken into account in our modeling. The composition of product mixture of SMR is determined by equilibria of reactions (1) and (2). The equilibrium constants for both reactions (1) and (2) at all temperatures were obtained from the literature [1]. When the off-gas of reformer I flows through the membrane module I, part of its hydrogen is extracted while the retentate passes through to reformer II for further conversion. New equilibria are attained based on the remaining composition.

3.2. Membrane separation

It is well known that hydrogen permeation through Pd-based membrane involves seven sequential steps: (1) adsorption of hydrogen molecules; (2) dissociation of hydrogen molecules into atoms; (3) diffusion of atoms through the upstream surface layer; (4) diffusion of atoms through the bulk membrane; (5) diffusion of atoms through the downstream surface layer; (6) recombination of hydrogen atoms to form molecules; and (7) desorption of hydrogen molecules. Step 4 is usually rate-determining. Hydrogen flow rate through the membrane is given by

$$Q_{\text{H}} = K \frac{A}{\delta} e^{-\Delta E/RT} [P_{\text{th}}^{0.5} - P_{\text{p}}^{0.5}] \quad (4)$$

where Q_{H} is the hydrogen permeation rate through the membrane (mol/min), K the pre-exponential factor (mol m/(m² min bar^{0.5})), A the membrane area (m²), δ the membrane thickness (m), ΔE the apparent activation energy for hydrogen permeation (kJ/mol), R the universal gas constant 8.314 J/mol/K, T the membrane temperature (K), P_{th} the hydrogen partial pressure on feed side (bar), and P_{p} is the hydrogen pressure on permeate side (bar).

We studied hydrogen permeation performance of Pd–25%Ag alloy membranes with thickness of 15–50 μm for the temperature range of 400–650 °C using pure hydrogen. It was found that the pre-exponential factor is 2.07×10^{-3} mol m/(m² min bar^{0.5}), and the apparent activation energy is 9.18 kJ/mol for hydrogen permeating through Pd–25%Ag alloy membrane. These values are in good agreement with the results of Ali et al. [9].

The product mixture from SMR contains H₂, CO, CO₂, CH₄ and steam. It was found that the presence of steam decreased the permeability of thin Pd membranes by electroless plating at 380 °C due to competitive adsorption of steam, whereas the impact of CO on the membrane was negligible under that condition [10]. We found that CO₂ and CH₄ had no impact on the permeability of Pd–25%Ag alloy membrane, whereas impact of steam was insignificant at temperatures of 450 °C or higher for Pd–25%Ag alloy membranes 15 μm or thicker. Therefore, the influences of all impurities in the SMR off gas on membrane permeation are omitted in our modeling. In addition, the following assumptions are made for our modeling for hydrogen separation from SMR off gas by Pd–25%Ag alloy membrane:

- (1) Permeation operation is isothermal.
- (2) Plug flow prevails on the retentate side, and concentration gradients normal to membrane surface are neglected.
- (3) Hydrogen diffusion in the membrane is the rate-determining step for the hydrogen permeation from the feed side to the permeate side.
- (4) The selectivity of Pd–25%Ag alloy membrane is perfect for hydrogen. In other words, the gases other than hydrogen do not permeate through the membrane.
- (5) The product mixture from reformers does not undergo further reaction on the membrane surface or in the gas phase.

As the gas mixture passes along the membrane, hydrogen is extracted, and so the driving force (difference in the square root of the hydrogen partial pressures across the membrane) decreases. The hydrogen passing through a given area of membrane can be determined by integrating the local permeation flux along the membrane.

4. Results and discussion

The worldwide depletion of oil reserves and global warming make it imperative to develop and commercialize fuel cell technologies. Over the next several decades, hydrogen fuel cell vehicles (FCV's) are expected to increasingly replace fossil-fuel-powered internal combustion engine vehicles. A critical factor in the successful transition from the conventional car to fuel cell car is the reality and perception of hydrogen availability. Any successful transition pathway must achieve a cost effective route for the supply of hydrogen fuel to FCV's during a transition period. SMR is a well-developed technology offering an efficient, economic, and widely used process for hydrogen production. The efficiency of SMR in large industrial scale is about 65–75%, somewhat lower for smaller scale units. It is projected by Duane et al. [11] that the initial hydrogen generation will be based on SMR, with a hydrogen production capacity of 50–100 N m³/h with a methane efficiency (hydrogen to methane yield) of about 2 in the initial transition period from current gas stations based on gasoline to stations based on hydrogen for fuel cell vehicles. Hence, in this paper all modeling is based on methane feed rate of 50 N m³/h, resulting in a hydrogen capacity of 100 N m³/h. Various process parameters, such as SMR reaction temperature, pressure and steam/carbon ratio etc. will be optimized for SSMR-SMR.

Extensive research on steam methane reforming in Pd-based membrane reactors has been carried out in recent decades to achieve higher methane conversions and to obtain pure hydrogen in a single step [2,6,12]. While some researchers have conducted MR-SMR in fixed-bed or fluidized-bed at 600 °C or higher [12,13], the stability of Pd-based membranes is reduced when membrane temperature is higher or the membrane is thinner. We found that hydrogen selectivity for a 10 μm Pd membrane obtained by electroless plating considerably decreased over 10–20 h period at 550 °C, whereas it remained stable for more than 1000 h if it is operated at 450 °C or lower. The actual temperature needs to be constrained for practical MR-SMR pro-

cesses even though SMR is thermodynamically favored by high temperature. It is more feasible to operate MR-SMR at about 550 °C or lower with Pd-based membrane thickness of 25 μm or thicker in order to achieve appropriate membrane lifetime [5,14]. Table 1 compares the performance of a regular membrane reactor (MR) with the staged-separation membrane reactor for hydrogen production. The base case condition for the reformer is a steam-to-carbon ratio of 3.0 at 25 bar and 750 °C. Because the membrane modules are isolated from the reformer modules for SSMR-SMR as shown in Fig. 1, the reformer modules can be operated at higher temperature, e.g. 750 °C, and membrane modules can be operated at a lower temperature, e.g. 450 °C. Consequently, thinner Pd–25Ag alloy membranes are possible due to this lower temperature of membrane modules. In addition, higher conversions of methane are achievable for SMR at higher temperatures, increasing the hydrogen partial pressure in the off-gas and accordingly increasing the driving force for hydrogen permeation through the membrane. As a result of these two factors, the amount of Pd used in the SSMR-SMR is considerably reduced. As listed in Table 1, 1.255 kg of Pd (25 μm Pd–25%Ag) is required to extract 100 m³/h hydrogen for MR-SMR while only 0.207 kg of Pd (15 μm Pd–25%Ag) is required to obtain the same amount hydrogen for SSMR-SMR. The Pd cost of SSMR-SMR is only 16.5% of that for MR-SMR. Further increasing in SMR temperature can lead to further reduction in Pd cost. Moreover, it is of significance that membrane area is reduced from 5.57 m² for MR-SMR to 1.53 m² for SSMR, a reduction of more than 70%. Hence, the number of membrane panels is greatly reduced. As described above, the commercial catalyst of SMR is very efficient and so the traditional reformer is compact. However, the size of the regular membrane reactor has to be enlarged to accommodate sufficient membrane modules. The reduced number of membrane panels in SSMR-SMR reduces the reactor size and hence the overall cost.

Pure hydrogen can also be obtained by separating hydrogen from ROG with an ex situ membrane purifier downstream of a traditional SMR reactor. The case was simulated for the same conditions as for the SSMR-SMR, where the SMR temperature was 750 °C and the separation temperature was 450 °C, with a 15 μm Pd–25Ag alloy membrane. Pure hydrogen yield, which is defined as the mol number of hydrogen recovered by the membrane per mol methane fed to the reformer, is shown in Fig. 2 where H₂ partial pressure at feed exit is referred to as H₂ partial pressure at exit of the retentate side of membrane module II.

Table 1

Comparison of staged-membrane membrane reaction with a regular membrane reactor at a methane feed rate of 50 m³/h, steam-to-carbon ratio of 3.0 and pressure of 25 bar

Variable	Unit	MR-SMR	SSMR-SMR					
Reaction T	C	550	670	700	750	750	780	780
Membrane T	C	550	450	450	450	450	450	450
Membrane thickness	μm	25	15	15	15	15	15	15
Membrane area required	m ²	5.57	2.90	2.05	1.53	2.10	1.38	1.86
Pure H ₂ yield (H ₂ /CH ₄ ratio)	–	2.0	2.0	2.0	2.0	2.4	2.0	2.4
Pure H ₂ produced	m ³ /h	100	100	100	100	120	100	120
Pd mass (Pd–25%Ag)	kg	1.255	0.392	0.277	0.207	0.284	0.187	0.252
Pd mass ratio to MR-SMR	–	1.00	0.313	0.221	0.165	0.226	0.149	0.200

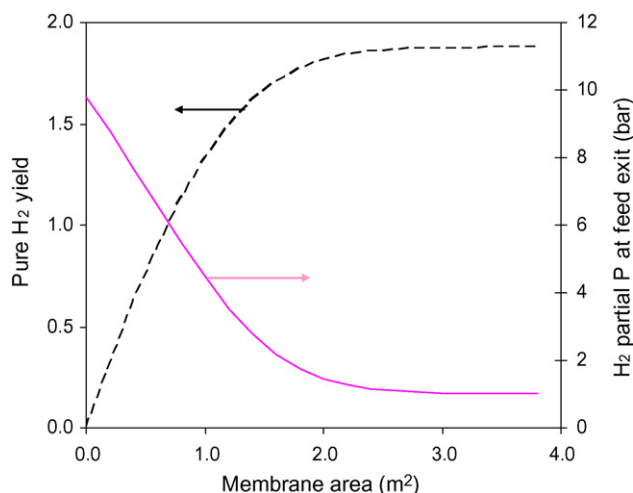


Fig. 2. Pure H₂ yield as a function of membrane area for a traditional reformer with a membrane purifier downstream at reaction temperature of 750 °C, steam-to-carbon ratio of 3.0, pressure of 25 bar and membrane temperature of 450 °C.

Pure hydrogen yield is found to increase with membrane area initially and then to level off because the hydrogen concentration on the reactor side decreases along the flow direction until the hydrogen partial pressure is very close to the pressure on the permeate side, as shown in Fig. 2. Fig. 3 shows that the remaining hydrogen concentration in the reactor side was very low, with the membrane purifier already having recovered most of hydrogen from the ROG. It is clear that the maximum hydrogen achievable is about 1.88 mol hydrogen per mol methane for a traditional reformer with a membrane purifier at 750 °C. As shown in Table 1, pure hydrogen yield of 2.4 is achievable for the SSMR-SMR under the same conditions. Therefore, SSMR-SMR not only possesses better performance than MR-SMR but it can also achieve higher yield than the traditional SMR reactors with ex situ membrane purifiers downstream.

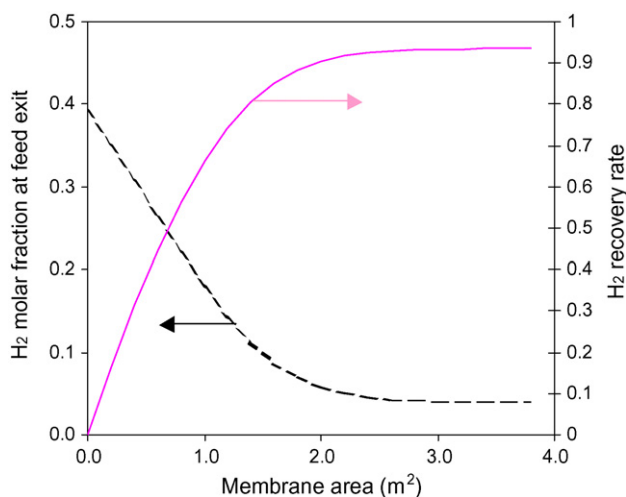


Fig. 3. H₂ molar fraction and H₂ recovery rate as functions of membrane area for a traditional reformer with a membrane purifier downstream at reaction temperature of 750 °C, steam-to-carbon ratio of 3.0, pressure of 25 bar and membrane temperature of 450 °C.

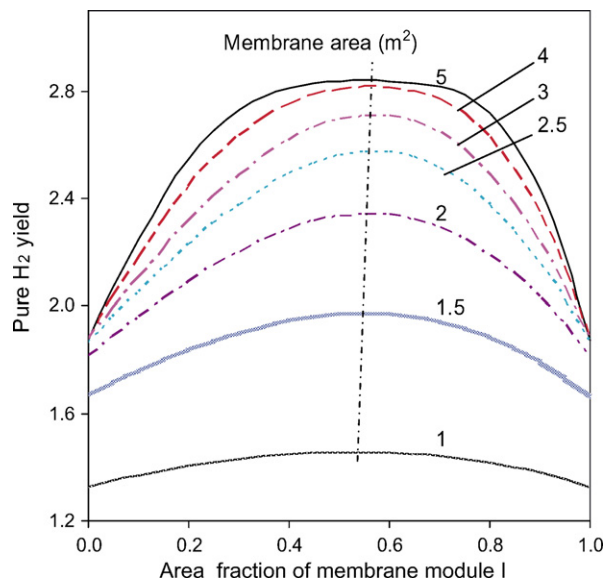


Fig. 4. Pure H₂ yield as function of area fraction of membrane module I for a staged-separation membrane reactor at reaction temperature of 750 °C, steam-to-carbon ratio of 3.0, pressure of 25 bar and membrane temperature of 450 °C.

As shown in Fig. 1, two relatively independent membrane modules were present in this novel SSMR-SMR system. With the total membrane area fixed, the allocation of membrane area in each module was optimized for the conditions of the base case, where the reformers operated at 750 °C at a methane feed rate of 50 N m³/h, steam-to-carbon ratio of 3.0 and the pressure of 25 bar, and membrane modules operated at 450 °C and 25 bar using a 15 μm Pd–25%Ag alloy membrane. These conditions remain same for subsequent cases unless otherwise stated. Fig. 4 gives the pure hydrogen yield as a function of the area fraction of membrane module I for different total membrane areas. The best hydrogen yield was achieved when ~55% of the membrane area was allocated to membrane module I. This percentage rose a little when the total membrane area increased. Note that the hydrogen yield changed little near the maximum peak position. This gives us more flexibility in practical applications since the optimum point may change due to the alteration of conditions. For simplicity, it can be assumed that the optimum hydrogen yield can be achieved for most cases with 55% of the membrane area in the first membrane module. It should be pointed out that when the area of the first module is 0% or 100% of the total area, SSMR becomes a traditional reformer with an ex situ membrane purifier. Therefore, it is clearly seen from Fig. 4 that the SSMR-SMR always gives better yields than a traditional reformer with an ex situ membrane purifier downstream for all circumstances.

Fig. 5 shows the pure hydrogen yield achievable for SSMR-SMR as a function of total membrane area for optimized membrane area allocation in membrane module under base case conditions. For example, the yield is 2.7 for a membrane area of 3.0 m², with 135 N m³/h of pure hydrogen produced under this condition.

Fig. 6 shows the composition of the retentate stream for membrane module II as a function of total membrane area with the optimized area allocation of the two modules. Due to extrac-

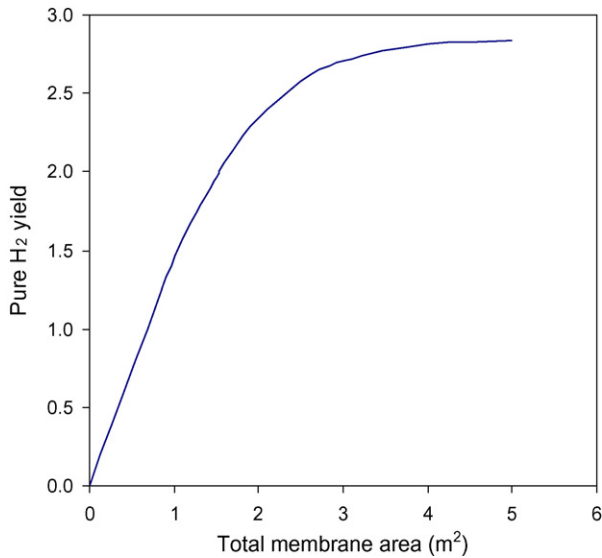


Fig. 5. Maximum pure H₂ yield achievable for staged-separation membrane reactor as a function of membrane area at reaction temperature of 750 °C, steam-to-carbon ratio of 3.0, pressure of 25 bar and membrane temperature of 450 °C.

tion of hydrogen by the membrane, H₂ molar fraction increased whereas the CO, CO₂ and H₂O molar fractions increased with area. The molar fractions of H₂, CO, CO₂ and H₂O in the final exhaust gas changed quickly initially, and then more slowly with increasing membrane area, before reaching a final plateau. In contrast, CH₄ molar fraction appeared to decrease slightly with increasing membrane area. Fig. 7 shows the final conversion of methane and the amount of the remained hydrogen in the retentate, the separated hydrogen and the total hydrogen produced against the total membrane area with optimized allocation of two modules. It is seen that overall methane conversion increased with membrane area. Methane conversion increased to over 80% from 56.1%, the equilibrium conversion for a traditional reformer without membrane. Therefore, SSMR maintained the

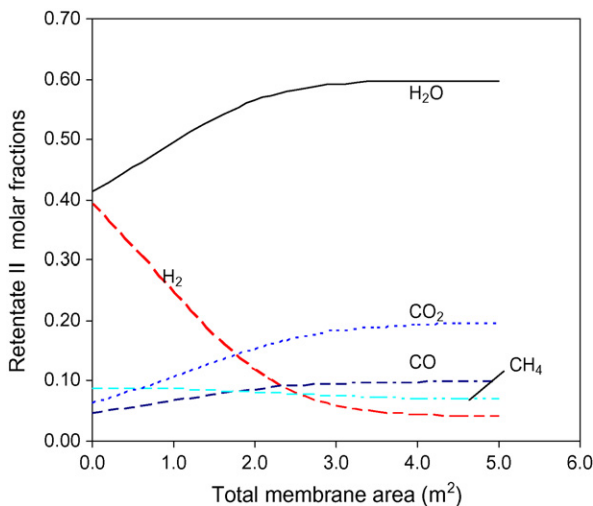


Fig. 6. Compositions of gases in retentate of membrane module II for staged-separation membrane reactor as function of membrane area at reaction temperature of 750 °C, steam-to-carbon ratio of 3.0, pressure of 25 bar and membrane temperature of 450 °C.

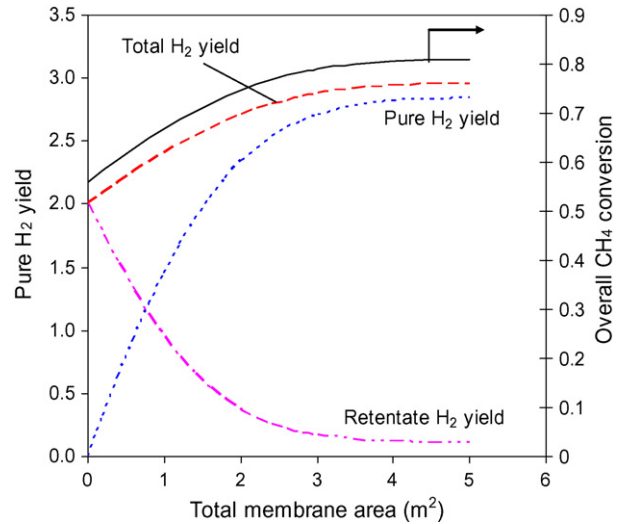


Fig. 7. Final conversion of methane and amount of hydrogen remaining in retentate, separated hydrogen and total hydrogen produced vs. total membrane area with optimum allocation for two modules at reaction temperature of 750 °C, steam-to-carbon ratio of 3.0, pressure of 25 bar and membrane temperature of 450 °C.

advantage of the regular membrane reactor for achieving conversions beyond equilibrium. The remaining hydrogen in the retentate decreased, while the separated hydrogen increased with increasing membrane area. The total hydrogen produced via SMR increased with membrane area as well.

The effects of reaction temperature, steam-to-carbon ratio and pressure of reformers were also studied under the same conditions as the base case, except for the parameter varied. Fig. 8 demonstrates that pure hydrogen yield increased with increasing reformer temperature. Hence, the membrane area can be reduced to achieve same yield by increasing reformer temperature. Also note that the pure hydrogen yield showed almost no further increase when the membrane area increased from 4 m² to 5 m², indicating the maximum hydrogen yields achievable at

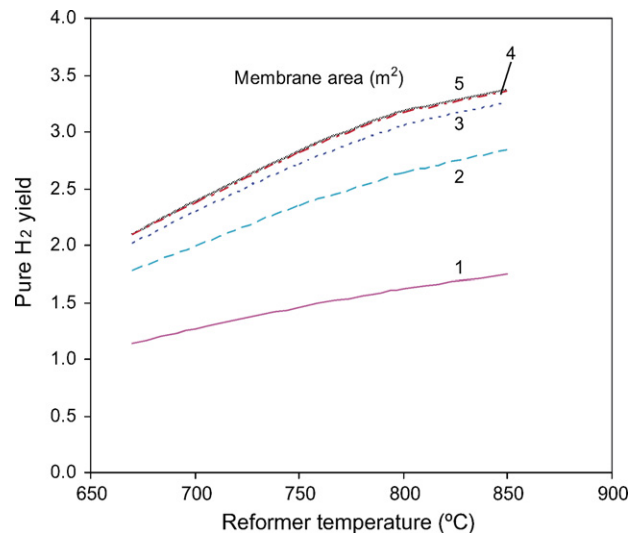


Fig. 8. Effect of reformer temperature on pure H₂ yield for staged-separation membrane reactor at steam-to-carbon ratio of 3.0, pressure of 25 bar and membrane temperature of 450 °C.

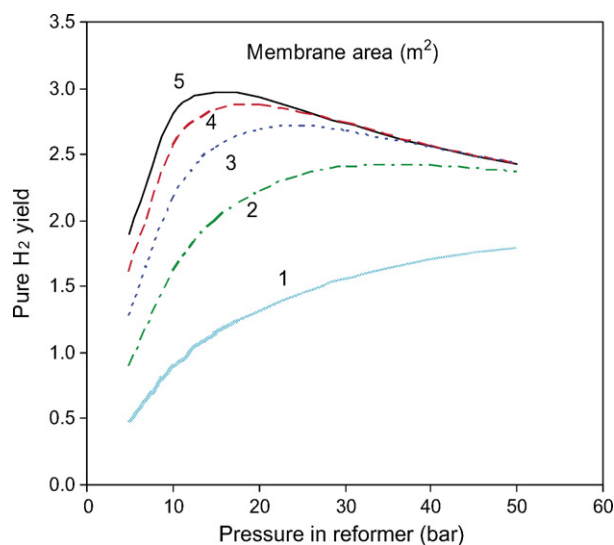


Fig. 9. Effect of reformer pressure on pure H₂ yield for staged-separation membrane reactor at reaction temperature of 750 °C, steam-to-carbon ratio of 3.0 and membrane temperature of 450 °C.

the corresponding temperatures are approached for the SSMR-SMR. For example, the maximum achievable pure H₂ yield is 2.84 at 750 °C and 3.19 at 800 °C.

The effect of reformer pressure on pure H₂ yield for SSMR-SMR is plotted in Fig. 9. In the pressure range of 5–50 bar, pure H₂ yield increased with pressure for smaller membrane areas whereas it increased first and then decreased with increasing pressure for larger membrane areas. The optimized pressure for achieving maximum pure H₂ yield was a function of the membrane area of the SSMR-SMR.

The effect of steam-to-carbon ratio on pure H₂ yield is shown in Fig. 10. Zero carbon formation was assumed in gas phase or on the surface of the catalyst in reactor bed. The effect of

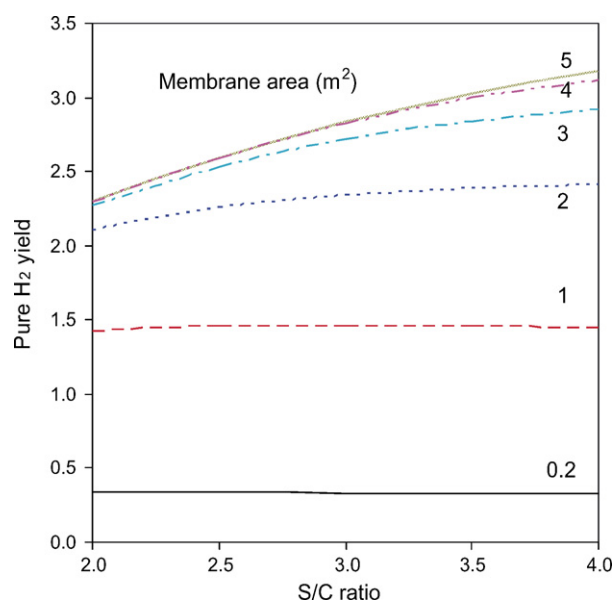


Fig. 10. Effect of steam-to-carbon ratio on pure H₂ yield for staged-separation membrane reactor at reaction temperature of 750 °C, pressure of 25 bar and membrane temperature of 450 °C.

S/C ratio is not evident for small membrane areas. As membrane area increased, the effect of steam-to-carbon ratio became increasingly evident, with the pure hydrogen yield increasing with increasing steam-to-carbon ratio. This occurs because the addition of steam increases the conversion of methane, thereby increasing the partial pressure of H₂ in the ROG.

5. Conclusion

A novel concept of staged-separation membrane reactor was proposed and simulated for the steam methane reforming process for hydrogen production. This staged-separation membrane reactor was found to retain the advantage of a regular membrane reactor for achieving super-equilibrium conversion with the reaction and membrane separation carried out under different conditions so that better overall performance can be achieved for both reaction and membrane separation. For hydrogen production via SSMR-SMR, the SMR reaction can be carried out at 750 °C or even higher for more favorable thermodynamics, while in the meantime membrane separation for pure hydrogen production can be carried out at 450 °C or lower to obtain better membrane stability. In contrast, for SMR in the regular membrane reactor, due to having to use identical conditions for reaction and membrane separation, compromising is required and consequently neither reaction nor membrane separation approaches its optimum conditions. Compared with the conventional membrane reactor, the metal cost of palladium-based membranes decreases by 86.5% and the membrane area decreases by >70% to achieve equal hydrogen production capacity. The volume of reformer decreases accordingly. Hence, the costs of both the reactor and membrane module are reduced.

Under the same conditions for SMR, SSMR can achieve better hydrogen yield than the traditional reformer with an ex situ membrane purifier downstream. For example, at a reformer temperature of 750 °C, the maximum hydrogen yield is about 1.88 for the traditional reformer with an ex situ membrane purifier, while it is 2.8 for SSMR.

The effects of temperature, steam-to-carbon ratio and pressure of the reformer and membrane area for membrane modules were simulated under various conditions. The allocation of membrane area to the two membrane modules was optimized as well.

References

- [1] J. Rostrup-Nielsen, *Catalytic Steam Reforming*, Catalysis-Science and Technology, 5, Springer-Verlag, 1984, p. 3.
- [2] J.R. Grace, X. Li, C.J. Lim, Equilibrium modelling of catalytic steam reforming of methane in membrane reactors with oxygen addition, *Catal. Today* 64 (2001) 141.
- [3] A.M. Adris, S. Elnashaie, R. Hughes, A fluidized-bed membrane reactor for the steam reforming of methane, *Can. J. Chem. Eng.* 69 (1991) 1061.
- [4] A.M. Adris, B.B. Pruden, C.J. Lim, J.R. Grace, On the reported attempts to radically improve the performance of the steam methane reforming reactor, *Can. J. Chem. Eng.* 74 (1996) 177.
- [5] S. Uemiyama, N. Sato, H. Ando, T. Matsuda, E. Kikuchi, Steam reforming of methane in a hydrogen-permeable membrane reactor, *Appl. Catal.* 67 (1991) 223.

- [6] J. Shu, B.P.A. Grandjean, S. Kaliaguine, Methane steam reforming in asymmetric Pd–Ag and Pd–Ag/porous Ss membrane reactors, *Appl. Catal. A: Gen.* 119 (1994) 305.
- [7] A.M. Adris, J.R. Grace, Characteristics of fluidized-bed membrane reactors: scale-up and practical issues, *Ind. Eng. Chem. Res.* 36 (1997) 4549.
- [8] J.R. Grace, S. Elnashaie, C.J. Lim, Hydrogen production in fluidized beds with in situ membranes, *Int. J. Chem. React. Eng.* 3 (2005).
- [9] J.K. Ali, E.J. Newson, D.W.T. Rippin, Deactivation and regeneration of Pd–Ag membranes for dehydrogenation reactions, *J. Membr. Sci.* 89 (1994) 171.
- [10] A. Li, W. Liang, R. Hughes, The effect of carbon monoxide and steam on the hydrogen permeability of a Pd/stainless steel membrane, *J. Membr. Sci.* 165 (2000) 135.
- [11] G.D.A. Duane, B. Myers, Brian D. James, John S. Lettow, C.E. Sandy Thomas, Reed C. Kuhn, Cost and Performance Comparison Of Stationary Hydrogen Fueling Appliances, DOE report, Directed Technologies Inc., 2002.
- [12] K. Jarosch, H.I. de Lasa, Permeability, selectivity, and testing of hydrogen diffusion membranes suitable for use in steam reforming, *Ind. Eng. Chem. Res.* 40 (2001) 5391.
- [13] A.M. Adris, C.J. Lim, J.R. Grace, The fluidized-bed membrane reactor for steam methane reforming: model verification and parametric study, *Chem. Eng. Sci.* 52 (1997) 1609.
- [14] J. Shu, B.P.A. Grandjean, S. Kaliaguine, Asymmetric Pd–Ag stainless-steel catalytic membranes for methane steam reforming, *Catal. Today* 25 (1995) 327.