ELSEVIER

Catalysis Today 46 (1998) 193–201

CATALYSIS TODAY

Membrane reforming for hydrogen

Kim Aasberg-Petersen*, Charlotte Stub Nielsen, Susanne Lægsgaard Jørgensen

Haldor Topsøe A/S, Nymøllevej 55, DK-2800, Lyngby, Denmark

Abstract

Steam reforming of hydrocarbon feedstocks is by far the most dominating process technology for production of hydrogen. This process requires high temperatures to reach satisfactory conversions so alternative process routes are being sought. One such alternative is a process based on membrane reforming in which hydrogen is continuously removed from the reaction zone pushing the chemical equilibrium and enabling operation at moderate temperatures.

This paper presents the results of an analysis of the membrane reforming process. The influence of various process parameters on the reactor performance is elucidated by detailed reactor calculations. It is shown that in general it is not possible to obtain satisfactory conversions of methane at temperatures below 600–650°C.

A comparison of the process economics with state-of-the-art hydrogen plants shows that membrane reforming only becomes attractive if the cost of electricity is very low and if the membranes are 100% selective to hydrogen. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Membrane reforming; Hydrogen; Economic; Pressure

1. Introduction

Steam reforming is the established process for conversion of natural gas or other hydrocarbons into synthesis gas. In a typical hydrogen plant the hydrocarbons are converted into hydrogen in a tubular steam reformer according to the following reaction (for methane):

$$CH_4 + H_2O = CO + 3H_2 \quad \Delta H^0_{298} = 206\,\mathrm{kJ/mol} \tag{1}$$

The steam reforming is accompanied by the shift reaction:

$$CO + H_2O = H_2 + CO_2 \quad \Delta H^0_{298} = -41\,\mathrm{kJ/mol} \tag{2}$$

High temperatures are needed to obtain satisfactory conversions of methane, as illustrated in Fig. 1. Usually, the exit temperature from the tubular steam reformer is 850–950°C. In a typical hydrogen plant the effluent from the steam reformer is cooled and additional hydrogen is produced in a downstream shift reactor. Final product purification is carried out by a Pressure Swing Adsorption (PSA) unit. A block diagram of a typical hydrogen plant is shown in Fig. 2.

The energy efficiency of a hydrogen plant is high [1], but hydrogen manufacture is costly [1]. Therefore, many attempts are made to find alternative process routes for hydrogen production. One such alternative is a process based on steam reforming in a hydrogen permeable palladium membrane reactor.

Palladium membranes are unique in the sense that they are able to separate hydrogen from a gas mixture of other components with a selectivity of 100%. The

---

*Corresponding author.

PII: S0920-5861(98)00341-1

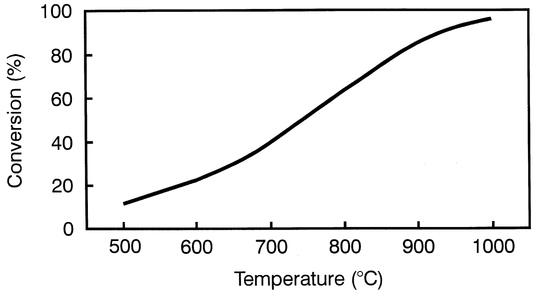

Fig. 1. Methane conversion at equilibrium. P=25 bar abs; steam to carbon ratio is 2.5.

permeation of hydrogen through palladium membranes is described by the following relation that is valid as long as the diffusion of hydrogen through the metal is considered the rate determining step:

$$F = \frac{D \cdot A}{l}\left(\sqrt{P_{\mathrm{H}_2}r} - \sqrt{P_{\mathrm{H}_2},p}\right) \; [\mathrm{Nm}^3/\mathrm{h}] \qquad (3)$$

D is the apparent diffusion coefficient $(\mathrm{m}^2/hr\sqrt{\mathrm{bar}})$ which is dependent on the temperature and the nature of the palladium alloy present. A is the area of the membrane (m^2), P_{H_2}, r and P_{H_2}, p is the pressure of hydrogen (bar) on respectively the retentate and permeate sweep side of the membrane [2], l is the membrane thickness (m).

The principle of membrane reforming with hydrogen selective palladium membranes is illustrated in Fig. 3. The membrane continuously removes hydrogen produced in the catalytic reaction zone thus pushing the chemical equilibrium and allowing higher methane conversions at lower temperature. The hydrogen permeating the membrane is 100% pure but produced at low pressure because the permeation flux is proportional to the difference between the square root of the hydrogen partial pressure on the two sides of the membrane. A drawback in the use of palladium membranes in large-scale reforming plants is the availability and the price of palladium metal. Furthermore the hydrogen permeability of conventional palladium (alloy) membranes is low compared to the very high catalytic reaction rates and the high industrial space velocities. The development of membrane reactors with high permeation rates is, therefore, very desirable. The only way to drastically increase the permeation rate is to decrease the membrane thickness. Research in preparation of ultrathin supported palladium membranes is therefore carried out [3–5].

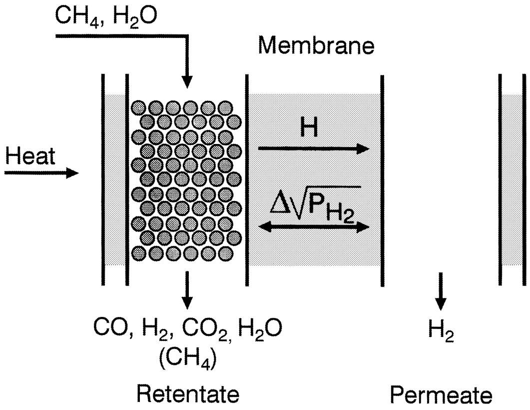

Fig. 3. Principle of membrane reforming. Hydrogen is continuously removed from the reaction zone by the membranes. The hydrogen flux through the membrane is proportional to the difference between the square root of the partial pressures of hydrogen at the two sides of the membrane.

Many investigators [6–9] have experimentally demonstrated that performing the steam reforming reaction in a membrane reactor results in high conversions of methane at low to moderate temperatures,

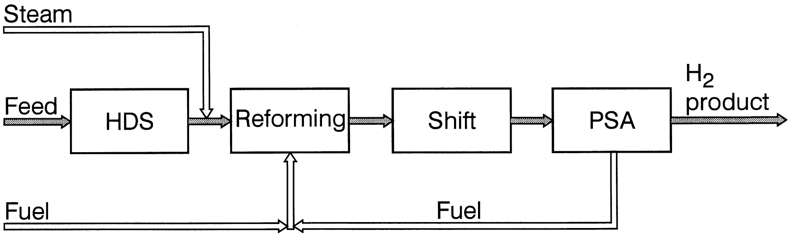

Fig. 2. Block diagram for a typical hydrogen plant. The process gas leaving the reformer is cooled and more hydrogen is produced in a shift reactor. Final purification is done in a pressure swing adsorption (PSA) unit. HDS: Hydro Desulphurization.

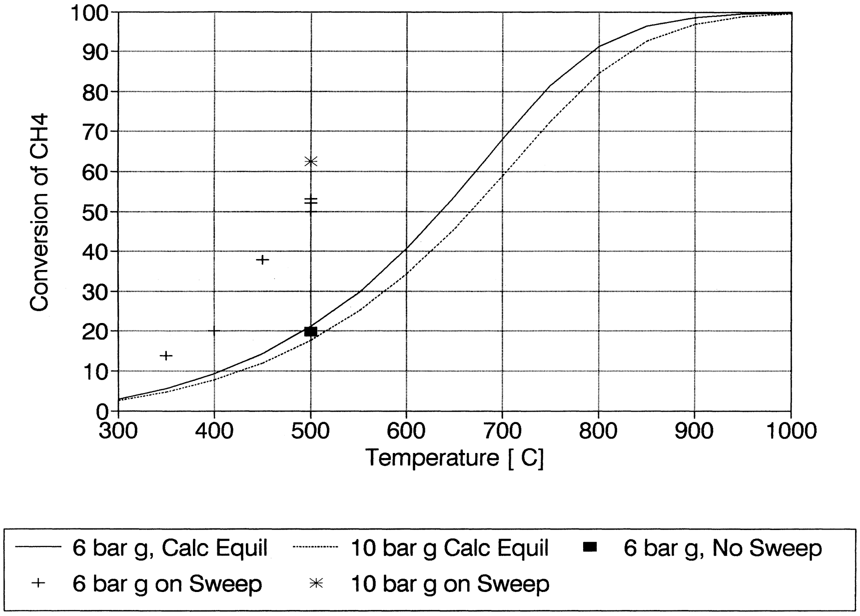

Fig. 4. Methane conversions in laboratory membrane steam reforming reactor [6]. Nitrogen used as sweep gas on permeate side. The conversions are higher than the calculated equilibrium conversions with no membrane.

as shown in Fig. 4. Bredesen et al. [10] have concluded that large-scale hydrogen production using membrane steam reforming has lower operating costs and needs lower plant investment than traditional hydrogen production. However, few authors have analyzed the sensitivity of the performance of the membrane reactor towards typical operating parameters such as temperature and pressure.

In this paper the performance of the membrane reactor is analyzed by means of detailed reactor calculations. Optimized process schemes are selected and a comparison with state-of-the-art hydrogen plants is made with respect to investment and yearly operating costs.

2. The membrane steam reforming process

A block diagram of the membrane steam reforming (MR) process is shown in Fig. 5. The main difference from the process diagram shown in Fig. 2 is that no purification of the hydrogen stream leaving the MR reactor is needed as it is assumed that only hydrogen permeates through the membrane. On the other hand, the hydrogen must be compressed to reach the desired delivery pressure.

The optimization of the MR reactor is complex and depends on a number of factors including feed properties, desired pressure of the permeate hydrogen and the membrane permeation rate. A number of process

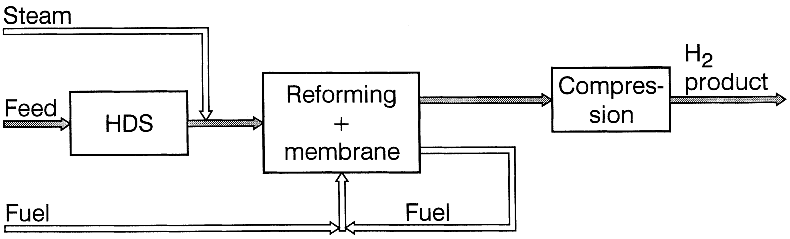

Fig. 5. Block diagram for membrane reforming process. The pure hydrogen at the reformer exit is cooled and compressed to the desired pressure.

Table 1
Input parameters used in the MR process and reactor simulations

MRR[a] feed temperature (°C)	635
MRR exit pressure (bar abs.)	25–45
Steam-to-carbon ratio[b] (mol/mol)	2.5–3.0
Hydrogen pressure in MRR (bar abs.)	1.5–3.5
Exit temperature (retentate stream, °C)	600–825
ΔP_{H_2}, MRR exit (bar)	0.5–2.0
Permeation rate ($Nm^3/h/m^2/bar^{0.5}$)	250

[a] MR Reactor.
[b] Inlet steam to carbon in natural gas.

simulations and reactor design calculations have been performed to highlight the influence of various operating parameters upon the reactor performance. In Table 1 the input parameters to the simulations are given. The natural gas feed has in all cases been adjusted to give a hydrogen production of 67 000 Nm^3/h.

The calculations were performed in two steps. First, the total process was simulated with a selected set of the parameters given in Table 1. In this manner, the required MR reactor duty and the amount of natural gas feed were determined. In the second step, detailed reactor calculations were made to determine the required membrane area. It has been assumed that no sweep gas is used at the permeate side. The reactor was simulated as a number of catalyst filled tubes each containing one or more membrane tubes. Heat is supplied to the external surface of the catalyst filled tubes (see Fig. 3).

2.1. Effect of feed pressure and steam-to-carbon ratio

The results of the calculations to determine the effect of feed pressure and the steam-to-carbon (*S*/*C*) ratio are given in Table 2.

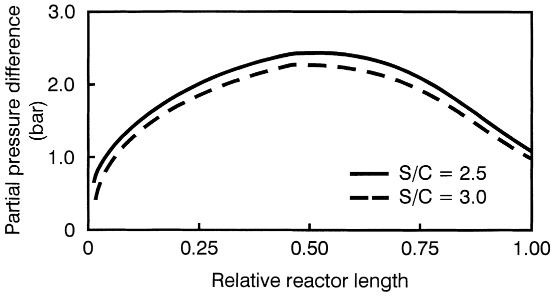

Fig. 6. Hydrogen partial pressure differences in membrane reactor. The largest driving force is obtained with the lower steam-to-carbon ratio (*S*/*C*).

It has earlier been reported [6] that a steam-to-carbon ratio of 2.5 is sufficient to avoid the formation of carbon. Increasing the *S*/*C*-ratio beyond 2.5 increases the rate of hydrogen production but also dilutes the hydrogen in the retentate stream due to the higher steam content. The latter effect is dominant and the driving force for hydrogen permeation through the membrane is lower in the complete length of the reactor as illustrated in Fig. 6. Hence, a larger membrane area is needed if the *S*/*C*-ratio is increased.

The following calculations have all been made with an *S*/*C*-ratio equal to 2.5.

Increasing the reaction pressure seems to be advantageous as regards the reactor, as shown in Table 2. However, if the feed gas is not available at the relatively high pressures required natural gas compressors must be installed. Such compressors are expensive and consume a lot of energy. Furthermore, the total plant must be designed to allow operation at the high pressures. If high pressure feed gas is available this aspect must be considered before the operation pressure is fixed.

Table 2
MR reactor duty, required membrane area, and feed consumption as a function of steam-to-carbon ratio and exit pressure. ΔP_{H_2} (reactor exit)=1 bar; P_{H_2}=3.5 bar abs.; T_{EXIT}=750°C.

Steam-to-carbon ratio (mol/mol)	Exit pressure (bar abs.)	Feed consumption $\left(\frac{GJ}{1000\,(Nm^3H_2}\right)$	MR duty (GJ/hr)	Membrane area ($m^2/1000\ Nm^3H_2/h$)
2.5	25	11.84	192.0	8.8
3.0	25	11.84	195.0	9.5
2.5	35	10.67	177.0	6.7
2.5	45	10.17	170.7	5.8

Table 3
The effect of exit temperature and hydrogen pressure upon the MR reactor performance $\Delta P_{H_2,EXIT}$=1.0 bar

P_{H_2} (bar abs.)	Exit temperature (°C)	Duty (GJ/h)	Feed consumption (GJ/1000 Nm^3 H_2)	Membrane area (m^2/1000 Nm^3H_2/h)
3.5	775	197.5	11.51	8.11
3.5	750	192.0	11.84	8.81
3.5	700	183.3	13.56	10.70
1.5	700	159.0	10.13	5.50
1.5	650	148.5	10.75	6.52
1.5	625	143.1	11.59	6.79

2.2. *Effect of hydrogen pressure and temperature at reactor exit*

Calculations have been made to highlight the influence of the hydrogen pressure and the reactor exit temperature on feed consumption and membrane area. The calculations have been made for a fixed value of the hydrogen pressure difference at the reactor outlet. The results are shown in Table 3.

A low hydrogen pressure in the permeate stream increases the driving force for permeation through the membrane thus reducing the required membrane area at a given temperature. Furthermore, a lower hydrogen pressure on the permeate side of the membrane signifies that the partial pressure of hydrogen on the retentate side is also lower at the reactor exit. Since chemical equilibrium is attained in the catalyst bed, the methane leakage will also be lower, (see Fig. 7). Hence, a low hydrogen pressure results in a high methane conversion and in low feed consumption.

The disadvantage of a low permeate hydrogen pressure is a higher energy consumption for compression of hydrogen. This is further discussed in Section 3.

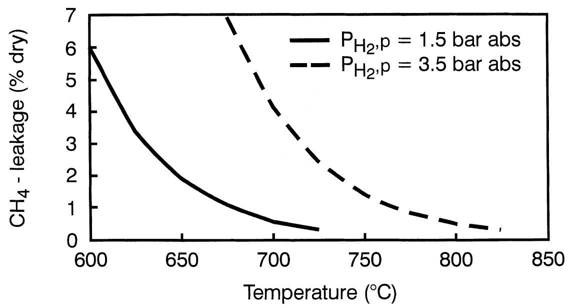

Fig. 7. Methane leakage at membrane reactor exit relative to the combined dry flow of the retentate and permeate streams. $\Delta P_{H_2} = 1$ bar. The highest methane conversions are obtained at low hydrogen permeate pressures ($P_{H_2,p}$).

Reducing the temperature at a given hydrogen pressure reduces the required heat input to the reactor mainly because less heat is needed for raising the temperature of the reaction mixture. However, reducing the temperature also reduces the methane conversion due to equilibrium limitations. Hence, the feed consumption increases with lower temperatures.

It is also clear from Fig. 7 that to reduce the temperature it is necessary to reduce the hydrogen pressure on the permeate side to maintain a satisfactory methane conversion. The selected pressure at 650°C is 1.5 bar abs. Reducing the temperature below 600–650°C is, therefore, not feasible even with a membrane.

2.3. *Effect of hydrogen partial pressure difference at reactor exit*

The effect of the hydrogen partial pressure difference at the reactor exit of the membrane area and the feed consumption is shown in Fig. 8. The calculations have been made using a fixed value of the hydrogen pressure at the permeate side of the membrane. A low value of the pressure difference indicates that the mean driving force for hydrogen permeation is low and a higher membrane area is needed. On the other hand, the feed consumption decreases with decreasing pressure difference because higher methane conversions are obtained when the partial pressure of hydrogen in the retentate stream is low, as pointed out in Section 2.2.

A calculation made with the (theoretical) partial pressure difference of zero at the reactor outlet shows that the methane leakage is above 2% at temperatures lower than 585°C and a hydrogen pressure of 1.5 bar -

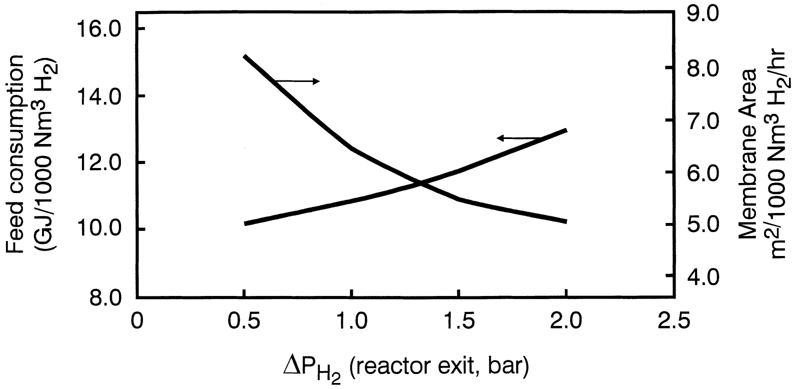

Fig. 8. The effect of the hydrogen partial pressure difference at the reactor exit. T=650°C. High partial pressure differences increase the feed consumption and decrease the required membrane area.

abs. This confirms that satisfactory methane conversion cannot be achieved at temperatures below ca. 600–650°C with realistic operating conditions.

3. Economic analysis of hydrogen production using membrane integrated steam reformer processes

3.1. Selected process schemes

Based on the discussions in the previous sections, process schemes according to Figs. 9 and 10 are selected for economic analysis. Main process parameters are listed in Table 4.

Case 1 represents state-of-the-art hydrogen production based on steam reforming, medium temperature shift conversion and hydrogen purification by pressure swing absorption (PSA). The off-gas from the PSA is used as fuel for the reformer. Upstream the steam reformer, an adiabatic prereformer converts higher hydrocarbons into a mixture of methane, hydrogen and carbon oxides.

The schemes in Cases 2 and 3 are based on integrated steam reforming and membrane purification. The pure hydrogen is compressed to 20 bar g before being exported as product. The retentate exit the membrane/reforming reactor is expanded and used as fuel for the reactor.

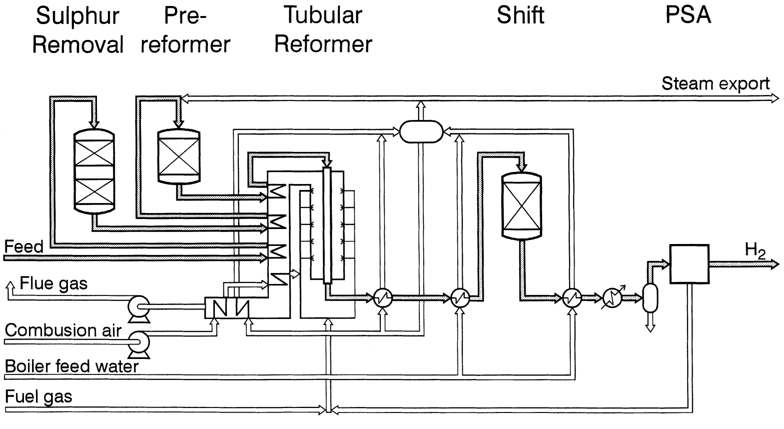

Fig. 9. Typical process layout for a Topsøe hydrogen plant based on advanced tubular steam reforming technology. The hydrogen is purified by shift conversion followed by pressure swing adsorption (PSA) to delivery pressure.

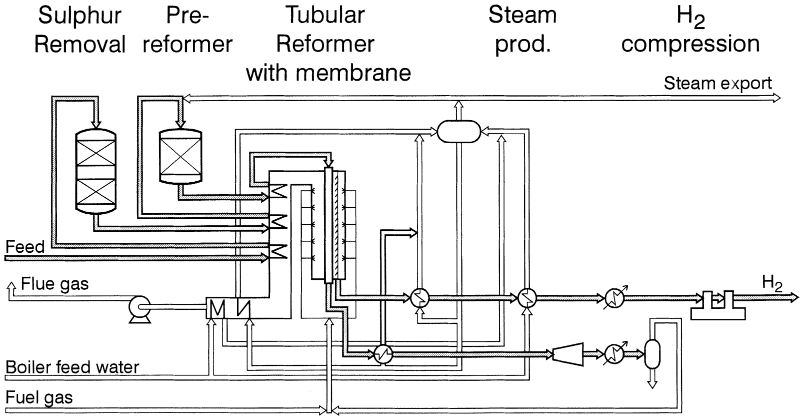

Fig. 10. Assumed process layout for a hydrogen plant based on membrane integrated steam reforming technology. The low pressure hydrogen from the membrane reformer is compressed to the desired level.

Table 4
Main process parameters for evaluated schemes

Case	1	2	3
H_2 production (Nm^3/h)	67 000	67 000	67 000
Feed	Natural gas	Natural gas	Natural gas
Reformer	Ordinary	Membrane integrated	Membrane integrated
Reformer, exit temp. (°C)	930	750	650
S/C[b] (mol/mol)	2.5	2.5	2.5
Shift	MT[c]	–	–
PSA, eff. (%)	89	–	–
ΔP_{H_2} membrane (bar)	–	1.0	1.0
P_{H_2} exit reformer (bar g)	23.5[a]	2.5	0.5
H2 product pressure (bar g)	20	20	20

[a] Total gas pressure.
[b] Steam to carbon ratio.
[c] Medium temperature shift reactor.

In all cases heat integration is maximized to produce steam at 40 bar for process use and export.

3.2. Economic basis

Operating costs include consumption of feed, fuel and electricity. Credit is given to export steam. Operating costs are calculated for two examples (A and B) based on the unit prices and calorific conversions listed in Table 5. Feed is given twice the calorific value of import fuel, which is often seen at refineries. Steam is usually of less interest and is valued as fuel. As power consumption is a significant factor in the membrane-based schemes due to product compres-

Table 5
Assumed unit prices and conversion factors for economic evaluation

Type	Example A	Example B
Feed US$/GJ	4.8	4.8
Fuel US$/GJ	2.4	2.4
Steam US$/GJ	2.4	2.4
El US$/GJ	4.8	2.4

Feed: Natural gas, LHV (Lower Heating Value) 36660 kJ/Nm^3.
Fuel: Natural gas, LHV 36660 kJ/Nm^3.
Steam: P,T=40 bar g, 400°C.
Net. calorific conversion: 2720 kJ/kg.
Electric power: 11623 kJ/kW.

Table 6
Example A: Operating costs and investment

Case	1	2	3
Feed US\$/h	3798.4	3793.8	3456.8
Fuel US\$/h	476.6	483.2	543.4
Stea, US\$/h	−297.7	−250.3	−176.2
El US\$/h	39.6	229.8	452.0
Total			
US\$/h	4016.9	4256.5	4276.0
MM US\$/year[a]	32.14	34.05	34.21
ΔMM US\$/year	Base	1.91	2.07
Investment			
ΔMM US\$	Base	−1.00	−2.64
Payback of Δ investment			
years		0.5[b]	1.3[b]

[a] 1 year=8000 h.

[b] Time it will take for the saving in investment to be spent during operation due to higher operating costs compared to 'Base'.

sion, two cost scenarios are studied. Example A represents a normal scenario where the power has the same calorific value as the feed. Power is given low cost (as fuel) in example B.

The investments are estimated using estimating procedures (Q-estimate) and long-term experience from designing gas production plants. In the investment calculations it is assumed that the membranes are ceramic tubes covered with a 2 μm thick layer of a Pd/Ag-alloy with a hydrogen flux of 250 $Nm^3/m^2/bar^{1/2}h$ [11] and 100% selectivity towards hydrogen.

3.3. Evaluation

Annual operating costs and investments for the three cases are listed in Table 6 (example A) and Table 7 (example B).

The figures in Table 6 indicate that at normal electric power cost the operating costs for the membrane based schemes are very high, in the order of 2 MM US\$/year or about 6% more than that of the standard steam reformer-based layout (Case 1). The estimated investment prices for the two membrane-based cases are lower than for the state-of-the-art steam reformer scheme.

However, due to the high operating costs simple payback time for the extra investment is only 0.5 and 1.3 years for selecting Case 1 instead of Cases 2 and 3. Normal payback time for a hydrogen plant is in the range of 4–15 years.

Table 7
Example B: Operating costs and investment

Case	1	2	3
Total			
US\$/h	3997.1	4141.6	4050.0
MM US\$/year[a]	31.98	33.13	32.40
MM US\$/year	Base	1.15	0.42
Investment			
MM US\$	Base	−1.00	−2.64
Payback time of years Δ investment			
years	0	0.9[b]	6.3[b]

[a] 1 year=8000 h.

[b] Time it will take for the saving in investment to be spent during operation due to higher operating costs compared to 'Base'.

The differences in operating costs are smaller in example B (Table 7, low cost of electricity) although noteworthy. Selecting the ordinary state-of-the-art steam reformer layout gives savings of about 0.5 MM US\$/year (1.2%) in operating costs. Investments are unchanged. With these lower operating costs, simple payback times for the extra investment in Case 1 have increased to 0.9 and 6.3 years, respectively, compared with Cases 2 and 3.

These results are in conflict with findings by Bredesen et al. [10]. They claim that hydrogen production using palladium membranes in the reformer can reduce investments by 10–20% and consumption by 5–10%. The plant investment figure (91.8 MM US\$ for 95 000 Nm^3/h H_2) for conventional H_2 production, however, appears to be very high. It is not possible to establish the reason for the difference as no basis for the investment and operating costs are given in the paper by Bredesen et al. [10].

In short, these cost examples indicate that the membrane integrated reforming process of today is not competitive to the traditional steam reforming process. Only very exceptional unit cost scenarios with low cost power and membranes through which only hydrogen permeates can make the membrane integrated reforming process an interesting alternative.

4. Conclusions

This paper presents the results of a membrane reactor analysis and an economic evaluation of a membrane reforming process as compared to state-of-the-art technology for hydrogen production.

The process economics of the membrane reforming process has been evaluated at 650°C and 750°C. The results show that the membrane process is economically favoured by operation at the lower temperature. This indicates that the temperature should be reduced more to further lower the cost of hydrogen production by membrane reforming. However, the reactor analysis shows that further temperature reduction is not feasible because the methane leakage and, thereby, the feed consumption becomes too high. To overcome this, the natural gas feed pressure must be increased beyond the normal values encountered in the industry. This possibility will require additional investments in the membrane reforming process.

In the comparative economic evaluation it has been assumed that the membranes are only permeable to hydrogen with a flux of 250 $Nm^3/m^2\ bar^{0.5}\ h$. The membranes are assumed to be made by ceramic tubes covered with a 2 μm thin layer of a Pd-alloy. Under these conditions the membrane reforming process only appears to be fairly economically attractive at very low prices of electric power. It can thus be concluded that membrane reforming will probably only gain wide acceptance if the membrane fluxes are improved significantly as compared with the assumptions used in this work while maintaining a 100% selectivity to hydrogen production.

References

[1] J. Rostrup-Nielsen, Catal. Today 21 (1994) 257–267.
[2] G. Saracco, V. Specchia, Catal. Rev. Sci. Eng. 36(2) (1994) 305–384.
[3] S. Lægsgaard Jørgensen, G. Mogensen, P. Lehrmann, J. Hyldtoft, P.E. Højlund Nielsen, ESF Network on Catalytic Membrane Reactors, Fourth workshop, May 30–31 1997, Oslo, Norway, 51.
[4] V.M. Gryaznov, O.S. Serebryannikova, Y.M. Serov, N.N. Ermilova, A.N Karavanov, A.P Mischenko, N.V Oreknova, Appl. Catal. A: General 96 (1993) 15–23.
[5] J. Shu, B.P.A. Grandjean, E. Ghali, S. Kaliaguirre, J. Membr. Sci. 77 (1993) 181–195.
[6] S. Lægsgaard Jørgensen, P.E. Højlund Nielsen, P. Lehrmann, Catal. Today 25 (1995) 303–307.
[7] S. Uemiya, T. Martsuda, E. Kikuchi, J. Membr. Sci. 56 (1991) 315–325.
[8] G. Barbieri, V. Violante, F.P. Di Maio, A. Criscudi, E. Drioli, Ind. Eng. Chem. Res. 36 (1997) 3369–3374.
[9] J. Shu, B.P.A. Grandjean, S. Kaliaguine, Catal. Today 25 (1998) 327–332.
[10] R. Bredesen., J. Sogge, UN Seminar on the Ecological Applications of Innovative Membrane Technology in the Chemical Industry, Cetraro, Calabria, Italy, May 1–4, 1996.
[11] S. Lægsgaard Jørgensen, G. Mogensen, P. Lehrmann, J. Hyldtoft, P.E. Højlund Nielsen, 2nd IEA Advanced Fuel Cell Workshop on Fuel Processing for Modular (<=100 kW) Fuel Cell Power Packages, September 19–October 1, 1997, Wislikoten Switzerland, 353–371.