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Equilibrium modelling of catalytic steam reforming of methane in membrane reactors with oxygen addition

John R. Grace*, Xuantian Li, C. Jim Lim

Department of Chemical and Biological Engineering, University of British Columbia, 2216 Main Mall, Vancouver, BC, Canada V6T 1Z4

Abstract

It has previously been demonstrated that permselective membranes can increase the yields of hydrogen, improve the product quality and minimize or even eliminate the adverse effect of system pressure in catalytic steam methane reforming. At the same time, oxygen addition can lead to autothermal operation by providing some or all of the required endothermic heat of the reforming reaction. Previous comparison of reactor model predictions with experimental results has demonstrated, at least for the fluidized bed membrane reactors (FBMRs) investigated so far, that the product distribution in the non-permeate stream approaches very closely to the shifted chemical equilibrium after allowance is made for the removal of hydrogen. In this paper, we adapt an equilibrium model devised for gasification to predict the influence of various process parameters. It is shown that it should be possible to operate autothermally and free of coke formation over a considerable range of temperature, pressure and steam-to-methane ratio. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogen; Methane; Reforming; Membranes; Equilibrium modelling

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1. Introduction

Hydrogen is an important industrial gas in hydrocarbon processing and synthesis, ammonia production, iron ore reduction and several clean energy applications, e.g. fuel cells and rocket fuels. Mostly, hydrogen is produced commercially on a large scale by steam methane reforming (SMR) in externally heated fixed bed reactors, and on a small scale by electrolysis of water. SMR is a reversible process usually conducted at temperatures of about 700–800°C catalysed by nickel oxide supported on α-alumina [1]. Conventional SMR suffers from a number of significant disadvantages — low catalyst effectiveness factors, large temperature gradients, low yields, and catalyst coking. Various configurations have been proposed over several decades for improving the process performance [2]. One promising concept is to use permselective membranes, e.g. made of palladium or palladium alloy, to selectively remove hydrogen in situ, thereby causing a forward shift in the chemical equilibrium, leading in turn to improved overall hydrogen yields [3,4]. This means that the process can be carried out at lower temperatures than in conventional SMR. In addition, the permeate hydrogen is very pure, so that there is no need for additional purification, as in the conventional process where pressure swing adsorption (PSA) is widely used. A further advantage of the in situ withdrawal of hydrogen is that it reduces, and can even virtually eliminate, the adverse effect of elevated system pressures on the equilibrium conversion caused by the increase in the number of moles in the

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* Corresponding author. Tel.: +1-604-822-3238; fax: +1-604-822-6003.
E-mail address: jgrace@chml.ubc.ca (J.R. Grace).

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principal reactions:

$$CH_4 + H_2O \Leftrightarrow CO + 3H_2 \quad (1)$$

$$CO + H_2O \Leftrightarrow CO_2 + H_2 \quad (2)$$

$$CH_4 + 2H_2O \Leftrightarrow CO_2 + 4H_2 \quad (3)$$

Adris [5] and Adris et al. [6] demonstrated that an experimental pilot scale fluidized bed membrane reactor (FBMR) provided with immersed vertical palladium membrane tubes could significantly improve hydrogen yields over those which could be achieved without the permeable surfaces. Roy [7] improved on the performance of this reactor by using niobium–tantalum tubes coated with very thin layers of palladium alloy on both inside and outside [8], resulting in an increase in hydrogen permeation by about an order of magnitude relative to the pure palladium tubes which had been employed previously.

The addition of limited quantities of oxygen over $Ni/\alpha\text{-}Al_2O_3$ catalysts can also be used to produce hydrogen by partial oxidation of methane

$$CH_4 + 0.5O_2 \Leftrightarrow CO + 2H_2 \quad (4)$$

This reaction can again be promoted by hydrogen withdrawal through permeable membranes [9–11]. Clearly addition of oxygen can also lead to full oxidation

$$CH_4 + 2O_2 \Leftrightarrow CO_2 + 2H_2O \quad (5)$$

Reactions (4) and (5) are both exothermic, whereas reforming equations (1) and (3) are strongly endothermic. Roy [7] demonstrated that the required endothermic heat of the steam methane reforming reactions could be provided by adding oxygen to partially oxidize the methane, without any serious penalty in the hydrogen production rate.

It is the combination of an FBMR with oxygen addition for reforming of natural gas which is the subject of this paper. However, the approach could be applied to other types of reactors, and could be readily extended to reforming or dehydrogenation of other hydrocarbons, where hydrogen is withdrawn in situ and oxygen is introduced to help provide the energy requirements of the main reactions.

2. Justification for the modelling approach

Modelling of membrane reactors presents interesting challenges because of the coupling of selective diffusion through the permeable surface with chemical reactions and mass transfer on the reactor side. Adris et al. [12] proposed a comprehensive reactor model which treated the fluidized bed as a two-phase bubbling bed in parallel with permeable tubes, where inert sweep gas and hydrogen which has permeated through the tube surfaces flow along the inside of tubes, while hydrogen diffuses through the tube walls. The model was shown to give excellent agreement with the experimental data. This model was later extended by Islam [13] and Roy [7] to include oxidation of methane by oxygen, as well as to account for the significantly enhanced permeation of the hydrogen through the coated (and more permeable) membrane tubes. Again predictions were in good agreement with experimental results [7].

In each of these modelling studies, the overall composition of the various reactants and products at any height in the reactor for the molar feed flow rates investigated was found to be mainly controlled by two factors: (a) the quantity of hydrogen which had permeated through the surfaces, which in turn depends on the partial pressures of hydrogen on the inside and outside, as well as on the total surface area of all the immersed tubes and the tube permeability; (b) chemical equilibrium at the given temperature and overall pressure on the reactor side. For the conditions studied so far, chosen to be as close as possible to those likely to prevail in any commercial FBMR SMR process, there is sufficient catalyst activity that the local composition on the reactor side approaches closely to that which would be achieved there at equilibrium, given the proportions of carbon, hydrogen and oxygen. It is therefore justifiable to consider chemical equilibrium as an excellent approximation for modelling the overall composition of the product stream for a given permeate flow rate. In fact, this approach has been applied (e.g. [14]) at even lower temperatures than those investigated in this paper.

In practice, this approach leads to a limiting case, likely to be approached closely in practice. Hence, if one wishes to predict the influence of key process variables (temperature, pressure, steam-to-methane ratio, membrane tube capacity) on conversion and product composition for a given total hydrogen permeation flow, equilibrium considerations provide an excellent basis. Clearly reactor models, with allowance for the rate of permeation through permselective tubes, may still be required, however, to calculate such features as the membrane surface area to achieve the required hydrogen permeate flow and the heat release pattern within the bed, as well as for examining the effect of varying the tube permeability, sweep gas flow rate and inside-tube pressure. Models of this kind are available [7,12], but they require much more computational effort and many more assumptions than the approach followed in this paper.

3. Modelling approach

In order to predict the product distribution, we have adapted the approach followed by Li et al. [15] in predicting the composition of the products of gasification of carbonaceous materials. In this earlier work carbon, hydrogen, oxygen, nitrogen and sulphur were all included. Nitrogen is absent in the steam reformer, and considerable pains are taken to eliminate sulphur from the feed stream to avoid catalyst poisoning. With these two elements omitted for the case of the steam reformer with oxygen addition, the model considers 20 chemical species in the gas phase in these three elements, as well as the possibility of solid carbon forming as an additional species. It would clearly be possible to add nitrogen if, e.g. air were to be fed instead of pure oxygen for ammonia production (where nitrogen is needed), but the greatest potential of the FBMR process is for production of pure hydrogen, so this case has not been treated here.

The model is solved using the RAND algorithm and standard methods [16–18]. The initial element abundance is calculated from the feed rate of the reactants, with the hydrogen abundance adjusted to account for the pre-specified withdrawal rate of hydrogen through the permselective membrane tubes. The range of hydrogen withdrawal explored should be achievable in practice with thin palladium coatings on porous surfaces of high surface area. An overall enthalpy balance is also applied, with the overall heats of formation and enthalpies of the various components obtained from standard thermodynamic sources (e.g. [19,20]). The method was validated by comparing with data

Table 1
Comparison between equilibrium model predictions and experimental data of Roy [7][a]

Bed *P* (MPa)	Bed *T* (K)	H_2O	O_2	H_2 permeated	CH_4 conversion		Total H_2 generated	
					Experimental	Predicted	Experimental	Predicted
0.68	923	4.1	0.44	0.55	0.76	0.76	1.95	2.06
0.68	923	4.1	0.45	0.55	0.77	0.76	1.93	2.05
0.68	923	4.1	0.50	0.55	0.79	0.78	1.93	2.03
0.68	923	4.1	0.56	0.52	0.81	0.80	1.91	1.98
0.68	923	4.1	0.62	0.51	0.82	0.82	1.88	1.94
0.68	923	4.1	0.35	0.57	0.74	0.73	1.98	2.11
0.68	923	3.1	0.35	0.46	0.66	0.65	1.67	1.80
0.68	923	2.4	0.35	0.37	0.59	0.59	1.40	1.54
0.99	873	3.1	0.40	0.42	0.52	0.53	1.26	1.27
0.99	898	3.1	0.40	0.47	0.56	0.58	1.41	1.45
0.99	923	3.1	0.40	0.52	0.60	0.63	1.55	1.64
0.68	849	4.1	0.45	0.43	0.62	0.59	1.49	1.44
0.68	873	4.1	0.45	0.47	0.67	0.65	1.60	1.64
0.68	898	4.1	0.45	0.52	0.73	0.71	1.82	1.85
0.68	922	4.1	0.45	0.55	0.77	0.76	1.93	2.05
0.68	873	4.1	0.45	0.44	0.68	0.64	1.58	1.62
0.78	873	4.1	0.45	0.47	0.67	0.63	1.59	1.58
0.88	873	4.1	0.58	0.48	0.63	0.62	1.54	1.54
0.99	873	4.1	0.45	0.50	0.62	0.61	1.49	1.51

[a] All substance amounts are in moles per mole of methane fed. Simulation temperature has been taken as 50°C below the bed temperature to allow for drop in temperature in the freeboard region.

Table 2
Values of variables taken in equilibrium modelling[a]

	Cases								
	1	*2*	3	4	5	6	7	8	9
Temperature (°C)	580	*580*	580	580	650	580	580	580	580
Pressure (MPa)	2.9	*2.9*	2.9	2.9	2.9	4.0	2.9	2.9	2.9
H_2O fed (mol)	2.5	*3.0*	3.5	4.0	3.0	3.0	3.0	3.0	3.0
O_2 fed (mol)	0.3	*0.3*	0.3	0.3	0.3	0.3	0.15	0	0

[a] Case 2 is the base case. Basis of 1 mol methane in all cases.

provided by Hougen et al. [21], Massey [22] and Probstein and Hicks [23]. Details of the equations, methodology and validation are given by Li et al. [15].

4. Results and discussion

Table 1 gives results of the free energy minimization model in comparison with experimental results of Roy [7] obtained in a 100 mm diameter pilot plant with 11 high flux membrane tubes, where oxygen was fed to provide the heat. With allowance for a 50°C drop in the freeboard region, a realistic value, it is seen that the equilibrium model does an excellent job of predicting the methane conversion and a good fit for the total hydrogen production, both expressed per mole of methane fed to the reactor.

To show the effect of the key variables, nine cases have been considered, with conditions given in Table 2, based on 1 mol of pure methane. Case 2 is the base case, corresponding approximately to autothermal conditions and to realistic operating conditions. Changes are made one variable at a time from the base conditions to show the influence of individual parameters. The corresponding element (C, H and O) abundances for the nine cases appear in Table 3. In the figures that follow, all variables assume their case 2 values, except where specified otherwise.

The molar fractions of the various gases in the main (i.e. non-permeate) stream are plotted in Fig. 1 as a function of the total hydrogen which has permeated for four different values of the steam-to-methane ratio. All compounds except those for which curves are plotted are predicted to be present only in extremely small quantities. As hydrogen permeation increases, the mole fraction of the hydrogen-containing species (water, methane and hydrogen itself) decrease

Table 3
Initial elemental abundance for the nine cases covered in Table 2

Case	Feed streams			Element abundance			Fractions		
	CH_4	H_2O	O_2	C	H	O	C/total	H/total	O/total
1	1	2.5	0.3	1	9	3.1	0.076	0.69	0.24
2	1	3	0.3	1	10	3.6	0.069	0.68	0.25
3	1	3.5	0.3	1	11	4.1	0.062	0.68	0.25
4	1	4	0.3	1	12	4.6	0.057	0.68	0.26
5	1	3	0.3	1	10	3.6	0.069	0.68	0.25
6	1	3	0.3	1	10	3.6	0.069	0.68	0.25
7	1	3	0.15	1	10	3.3	0.070	0.70	0.23
8	1	3	0	1	10	3	0.071	0.71	0.21
9	1	3	0	1	10	3	0.071	0.71	0.21

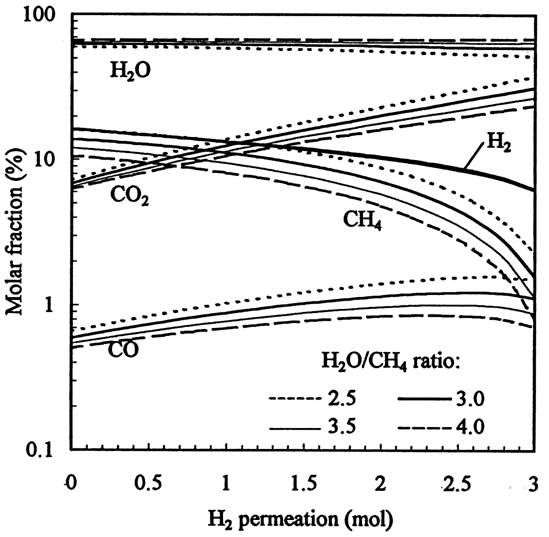

Fig. 1. Effect of hydrogen removal by permeation and steam-to-methane ratio on the composition of the main reactor product stream. Case 2 (Table 2) conditions except where specified.

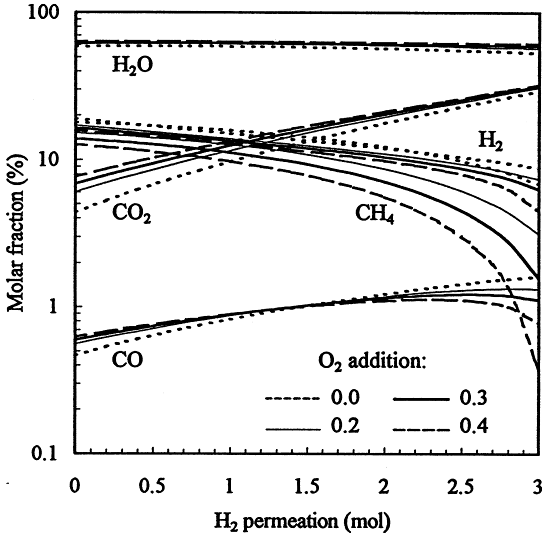

Fig. 2. Effect of oxygen addition and hydrogen removal by permeation on the composition of the main reactor product stream.

in the main stream, so that the concentrations of CO_2 and CO tend to increase. The influence of the steam-to-methane ratio becomes more significant at high permeation rates, with the concentrations of the reducing species dropping sharply when the hydrogen permeation reaches about 3 mol/mol CH_4.

Fig. 2 shows similar plots with the oxygen addition as the parameter. As expected, increasing the oxygen flow (with the reactor temperature held constant) leads to higher CO_2 and H_2O concentrations in the main stream, while the concentrations of methane and hydrogen decrease. CO shows more complex behaviour, with its concentration increasing as more oxygen is added at low hydrogen permeation rates and decreasing at high permeation rates.

As shown in Fig. 3, addition of more oxygen causes an increase in the conversion of methane and a decrease in the conversion of steam. Negative steam conversions can arise at high oxygen feed rates because H_2O is a product of the combustion of methane. The steam conversion curves terminate in an "impossible region" in the lower right-hand corner of the graph because oxidation of the methane ends up taking precedence, and all the uncombusted hydrogen which can be produced by reforming has already been withdrawn through the permeable membrane tubes.

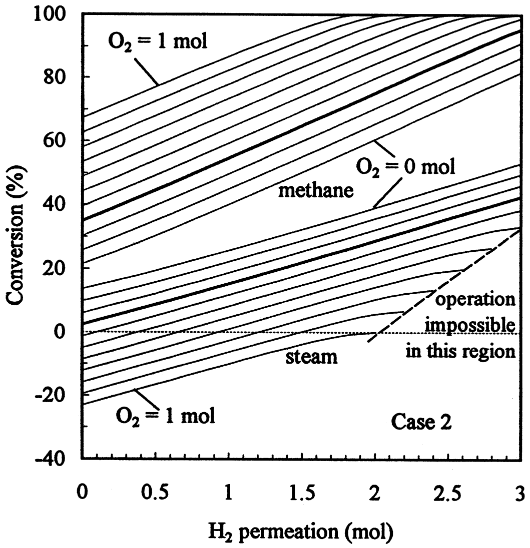

Fig. 3. Effect of oxygen addition and hydrogen removal by permeation on the conversion of methane and steam. Bold lines are for an O_2/CH_4 molar ratio of 0.3.

Fig. 4 shows that the influence of temperature is relatively weak, especially as the hydrogen permeation rate is increased. Note, however, that the permeability of palladium to hydrogen increases with increasing temperature, and this effect is not taken into account

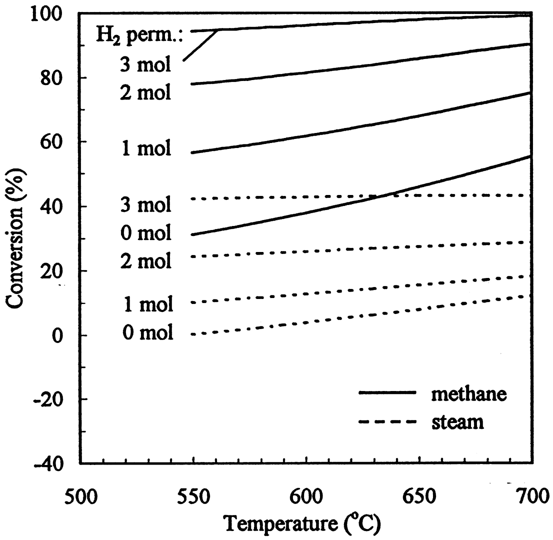

Fig. 4. Effect of reactor temperature on methane and steam conversions for different quantities of hydrogen withdrawn by permeation at an O_2/CH_4 molar ratio of 0.3.

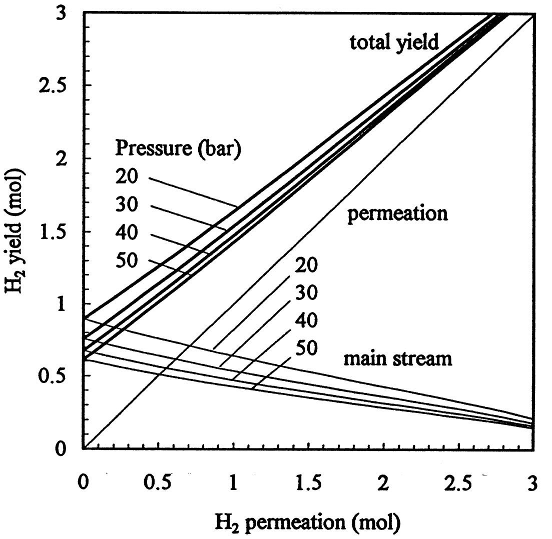

Fig. 5. Effect of overall system pressure on main stream hydrogen yield and overall yield for different amounts of hydrogen removal by permeation.

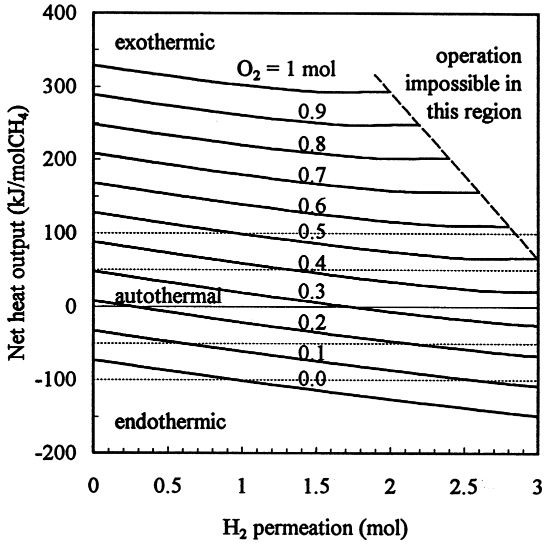

Fig. 6. Net heat output predicted from energy balance with different oxygen feed and hydrogen permeation per mole of methane fed. All reactants are fed at 400°C.

by the equilibrium model. Fig. 5 shows how the system pressure in the range 20–50 bar affects the hydrogen yield in the mainstream and the overall yield (i.e. sum of that in the main stream and that withdrawn through the membrane tubes). The effect of increased reactor-side pressure on increasing the hydrogen permeation rate through the membrane tubes (for constant tube internal pressure) is not taken into account. For the range of conditions covered, increasing reactor pressure leads to significantly lower hydrogen yields, but the effect is diminished as the hydrogen permeation rate increases, as predicted from Le Chatelier's principle.

The net heat output of the process is plotted as a function of the hydrogen permeation and oxygen feed in Fig. 6. Here all three reactants (methane, steam and oxygen) are assumed to be fed at a temperature of 400°C. A positive heat output signifies that heat must be removed from the reactor to maintain the temperature at the specified (case 2) level of 580°C, whereas heat must be added for negative outputs. For negligible heat losses from the system, autothermal operation is reached at a net heat output of 0. From the figure it is clear that more oxygen is needed to maintain autothermal conditions as more hydrogen is extracted from the permeable tubes. This occurs because increased hydrogen removal causes greater conversion, and hence more energy is required to supply the endothermic heat of the reforming reactions. Operation is impossible in the upper right-hand corner for the same reason as the curves terminate in the lower right-hand corner of Fig. 3, i.e. all hydrogen which can be produced after all the oxygen has reacted has already been withdrawn through the membrane surface.

As shown in Fig. 7, it becomes more difficult to achieve autothermal operation as the steam-to-methane ratio increases. Fig. 8 demonstrates that the feed temperature also plays a significant role. Clearly less oxygen is required to maintain autothermal conditions and higher hydrogen yields are possible at a given oxygen-to-methane molar feed ratio if the feed gases are pre-heated prior to entering the reactor, thereby reducing the sensible heat load. For example, with negligible heat losses, the figure shows that 0.33 mol O_2 are required to maintain a reactor temperature of 580°C if 2.2 mol H_2 are withdrawn by permeation for a feed temperature of 400°C, whereas only 0.23 mol are required if the gas is fed at 600°C.

Fig. 9 provides a ternary diagram on C, H, O coordinates. Points are shown corresponding to the various reactants (CH_4, H_2O and O_2) and products (H_2, CO, and CO_2). Coke formation is a serious operational

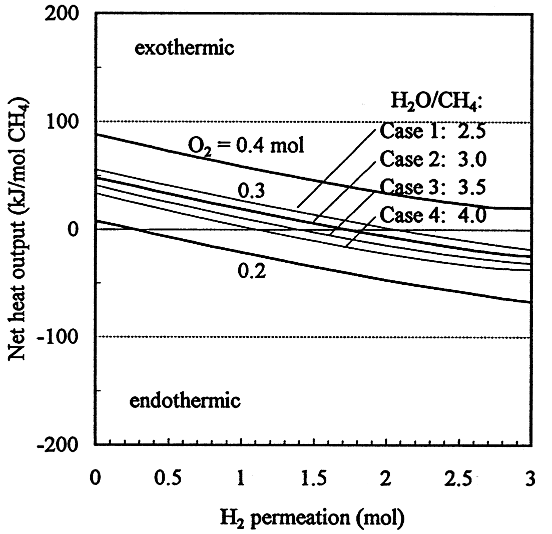

Fig. 7. Influence of steam-to-methane ratio, oxygen feed and hydrogen permeation on net heat release. All reactants are fed at 400°C.

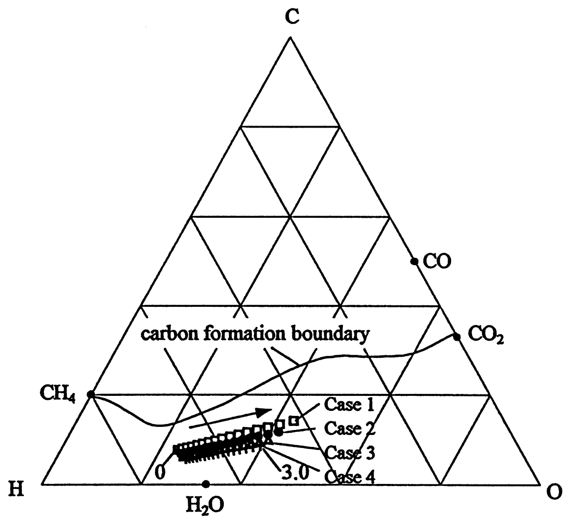

Fig. 9. Ternary diagram showing migration of operating composition as hydrogen is removed by permeation in relation to an empirical carbon-formation boundary.

problem in conventional steam reforming. An empirical carbon formation boundary is plotted in Fig. 9 based on equilibrium predictions from the literature compiled by Li et al. [15], with 99% conversion of solid carbon into gaseous species taken as the boundary between the carbon-forming region and conditions where only gaseous species are encountered. In reality, this line depends somewhat on the temperature, pressure and form of the solid carbon (usually considered to be graphite). However, variations due to these factors are relatively minor, and a single boundary has been plotted in the figure for purposes of illustration. Note that for normal steam-to-methane molar ratios (2.5 or more) employed in steam reforming, the starting composition, with or without small quantities of oxygen, is predicted to lie in the non-carbon-forming region, well below the carbon formation boundary, providing that the reactants are well distributed in the reactor. Addition of oxygen clearly moves the system further from the boundary, i.e. oxygen addition helps to prevent coke formation, as is well known for various catalytic processes. Extraction of hydrogen leads to migration of the reactor side operating point along a line directed away from the H vertex as shown. Because of the shape of the carbon formation boundary, it is seen that hydrogen withdrawal by permeation is not predicted to lead to any greater likelihood of carbon formation, and it may actually take one further from the boundary. This is an important finding with practical implications, and it differs from previous analyses [14,24,25] which suggest that hydrogen removal, like reducing the proportion of water vapour, necessarily

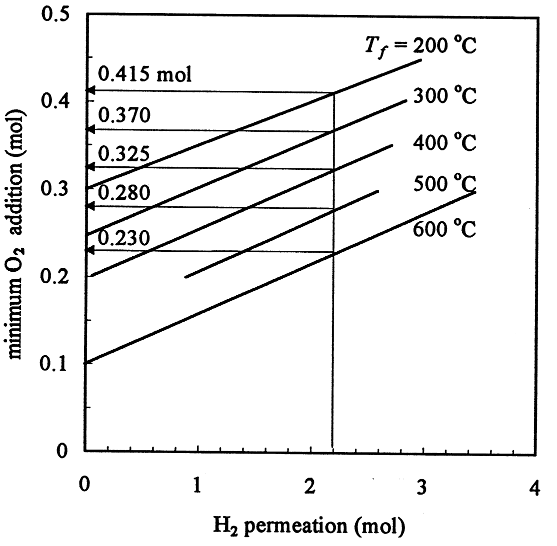

Fig. 8. Required oxygen addition per mole of methane to maintain autothermal conditions assuming negligible heat losses as a function of the feed temperature of the reactants and the hydrogen removal by permeation.

increases the tendency for carbon deposition to occur. It is notable that experimental tests [5,7] have not revealed any signs of coke formation in the FBMR reactor, although clearly there is a need to confirm this for longer times of operation than the approximately 300 h logged so far.

5. Conclusion

Equilibrium modelling of the steam methane reforming process with oxygen addition and in situ hydrogen withdrawal shows that there are complex interactions between a number of factors. The complexity is partly caused by the fact that water is both a product of the oxidation reactions required to provide autothermal conditions and a reactant required for the reforming reactions. In addition, hydrogen enters with both principal reactants (methane and steam), and the extent to which it can be removed by permeation is limited in practice by the number of tubes that can be accommodated in a given volume of reactor. Nevertheless, the equilibrium predictions presented above serve to provide guidance with respect to the thermodynamic limits of what can be achieved, and our previous experimental work suggests that these limits are likely to be closely approached in practice. Equilibrium modelling is clearly simpler than reactor modelling, and it is a useful tool for investigating different scenarios, as well as for making first estimates of optimum operating conditions for particular hydrogen applications.

The results indicate that autothermal operation can be realized with approximately 0.3 mol of oxygen per mole of methane feed, the oxygen requirement becoming larger as more hydrogen is extracted through the membrane tubes and as the temperature of the feed streams decrease. Methane conversions increase with increase in temperature, oxygen-to-methane feed ratio, and steam-to-methane ratio. The extent of the backwards shift in the chemical equilibrium due to increasing pressure is also decreased by the in situ withdrawal of hydrogen. Sufficient hydrogen extraction can virtually eliminate this influence on the equilibrium. Since increased reactor pressure increases the driving force for permeation through the tubes, the overall influence of elevated pressures can be essentially neutralized for large permeation capacities.

Plotting the results on a ternary diagram on which an empirical carbon-formation boundary is also included suggests that hydrogen permeation, as well as oxygen addition, may in fact decrease the probability of coke formation on the catalyst and on the permeable membrane tubes. In any case, oxygen certainly reduces coke formation. Overall, there are indications that the additions of permeable membranes and oxygen to SMR reactors facilitate operation at lower temperatures, lower steam-to-methane ratios and higher reactor pressures than in conventional steam reformers while producing a purer product stream, requiring less reactor volume and operating with reduced inventories of catalyst.

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References

[1] J.R. Rostrop-Nielsen, Catalysis Science and Technology, Springer, Berlin, 1984.
[2] A.M. Adris, B.B. Pruden, C.J. Lim, J.R. Grace, Can. J. Chem. Eng. 74 (1996) 177.
[3] A.M. Adris, S.S.E.H. Elnashaie, R. Hughes, Can. J. Chem. Eng. 69 (1991) 1061.
[4] S. Uemiya, N. Sato, H. Ando, T. Matsuda, E. Kikuchi, Appl. Catal. 67 (1991) 223.
[5] A.M. Adris, A fluidized bed membrane reactor for steam methane reforming: experimental verification and model validation, Ph.D. Dissertation, University of British Columbia, Vancouver, BC, 1994.
[6] A.M. Adris, C.J. Lim, J.R. Grace, Chem. Eng. Sci. 49 (1994) 5833.
[7] S. Roy, Fluidized bed steam reforming with high-flux membranes and oxygen input, Ph.D. Thesis, University of Calgary, Alta., 1998.
[8] R.E. Buxbaum, A.B. Kinney, Ind. Eng. Chem. Res. 35 (1996) 530.
[9] L. Mleczko, T. Ostrowski, T. Wurzel, Chem. Eng. Sci. 51 (1996) 3187.
[10] T. Ostrowski, A. Giroir-Fendler, C. Mirodatos, L. Mleczko, Catal. Today 40 (1998) 181.

[11] T. Ostrowski, L. Mleczko, Can. J. Chem. Eng. 77 (1999) 363.

[12] A.M. Adris, C.J. Lim, J.R. Grace, Chem. Eng. Sci. 52 (1997) 1609.

[13] M.T. Islam, Mathematical modeling of a fluidized bed reformer with oxygen input, M.Sc. Dissertation, University of Calgary, Alta., 1997.

[14] S. Laegsgaard Jorgensen, P.E. Hojlund Nielsen, P. Lehrmann, 25 (1995) 303.

[15] X. Li, J.R. Grace, A.P. Watkinson, C.J. Lim, A. Ergüdenler, Fuel, in press.

[16] F. van Zegeren, S.H. Storey, The Computation of Chemical Equilibrium, Cambridge University Press, Cambridge, 1970.

[17] R. Holub, P. Vonka, The Chemical Equilibrium of Gaseous Species, Reidel, Dordrecht, 1976.

[18] W.R. Smith, R.W. Missen, Chemical Reaction Equilibrium Analysis: Theory and Algorithms, Wiley, New York, 1982.

[19] L.B. Prankatz, Thermodynamic properties of elements and oxides, US Bur. Mines Bulletin 672, 1982.

[20] M.W. Chase, C.A. Davies, D.J. Downey, D.J. Frurip, R.A. McDonald, A.D. Syverud, JANAF Thermodynamic Tables, 3rd Edition, J. Phys. Chem. Ref. Data 14, Suppl. 1, 1985.

[21] O.A. Hougen, K. Watson, R.A. Ragatz, Chemical Process Principles: II. Thermodynamics, 2nd Edition, Wiley, New York, 1964.

[22] L.G. Massey, in: C.Y. Wen, E.S. Lee (Eds.), Coal Conversion Technology, Addison-Wesley, Reading, MA, 1979.

[23] R.F. Probstein, R.W. Hicks, Synthetic Fuels, McGraw-Hill, New York, 1982.

[24] S. Paloumbis, E.E. Petersen, ACS Symp. Ser. 38 (1982) 489.

[25] K. Hou, M. Fowles, R. Hughes, Chem. Eng. Sci. 54 (1999) 3873.