

# Optimization of a Membrane Reactor for Low Temperature Methane Steam Reforming

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The main aim of this study is the optimization of a membrane reactor (MR) for H<sub>2</sub> production via CH<sub>4</sub> steam reforming (MSR). Reactions take place over a Ni-Pt/CeZnLa foam supported catalyst at operating temperature of 500 °C and pressure of 10 bar. A permeable membrane with Pd-Ru deposited on a ceramic dense support is used to selectively remove the produced H<sub>2</sub> from the reaction zone. In this way, chemical equilibrium is shifted towards H<sub>2</sub> production, thus enabling the achievement of a high CH<sub>4</sub> conversion at relatively low temperature levels. A model-based optimization framework has been developed in order to calculate the optimal operating conditions for the highly interactive reactor system. A nonlinear, two-dimensional, and pseudo-homogeneous mathematical model of the membrane fixed-bed reactor validated using results from an experimental MR installed at the Process Systems Design and Implementation Laboratory (PSDI) of CPERI/CERTH is utilized in the optimization framework. The mathematical model consists of mass, energy and momentum balances considering both axial and radial gradients of temperature and concentration. The optimal steam to carbon ratio and sweep gas flow rate that minimize the overall CH<sub>4</sub> utilization (i.e. reformed CH<sub>4</sub> and equivalent CH<sub>4</sub> for heating purposes) have been calculated for a range of H<sub>2</sub> production rates. The optimal reactor design is also calculated for a given pure H<sub>2</sub> production rate.

## 1. Introduction

In recent years, H<sub>2</sub> has attracted much attention as it is considered the ideal energy carrier (Urbaniec et al., 2010). Due to the extensive resources of natural gas, MSR is one of the most promising and viable solutions for H<sub>2</sub> and synthesis gas (syngas) production. MSR is an endothermic reaction that usually takes place over a Ni-based catalyst and at temperatures greater than 800 °C in order to achieve sufficiently high CH<sub>4</sub> conversion and thus greater H<sub>2</sub> production (Kyriakides et al., 2014). This implies that high amounts of heat are required along with expensive reactor construction materials. In order to reduce the reaction temperature and eventually the cost of H<sub>2</sub> production, several alternative technologies have been proposed. In Pd-based MR produced H<sub>2</sub> is directly separated from the reactive mixture allowing for H<sub>2</sub> to be produced at much lower temperatures (500 °C) but with similar CH<sub>4</sub> conversion values to that achieved at elevated temperatures (Bientinesi and Petarca, 2010). The driving force for H<sub>2</sub> separation through the Pd-based membrane is the difference of the square roots of partial pressure at the two sides of the membrane. The separation driving force can be maximized if a sweep gas stream, usually consisted of H<sub>2</sub>O, N<sub>2</sub>, or He, is used to lower the partial pressure of H<sub>2</sub> in the permeation zone. Steam is more appealing industrially as it can be easily separated afterwards by condensation. The H<sub>2</sub> stream is free of CO and CO<sub>2</sub>, hence making it suitable for fuel cell devices that are sensitive to impurities. The lower

reaction temperature also favours the water gas shift reaction (WGS) resulting in significantly lower CO concentration at the reactor exit stream (De Falco et al., 2011).

MSR (Gallucci et al., 2004) and biogas steam reforming (Saebea et al., 2014) studies in MR during the past decades have attempted to systematically address the enhancement of the MSR performance. One-dimensional and two-dimensional (Marin et al., 2012) mathematical models have been used to study the reactor behaviour. Different reactor designs aiming to control large axial temperature peaks and limit the concentration polarization effect have been explored (Tiemersma et al., 2006). Simakov and Sheintuch (2011) calculated the optimal operating reactor conditions, De Falco et al (2014) the reactive inlet stream conditions that achieved the maximum CH<sub>4</sub> conversion and H<sub>2</sub> yield, whereas Silva et al (2010) tested different models and methodologies in order to reach high CH<sub>4</sub> conversions and H<sub>2</sub> recoveries.

The main aim of this study is the optimization of a MR for H<sub>2</sub> production via MSR using an experimentally validated process model for a novel catalyst and reactor configuration. To this end, a model-based optimization framework has been developed in order to calculate the optimal reactor configuration and operating conditions. The mathematical framework is formulated in such way that it allows adjustments in the reactor configuration, which enables the efficient study of different configurations of this highly interacting process system. A two-dimensional, nonlinear, and pseudo-homogeneous mathematical model of the membrane fixed-bed reactor has been developed and validated using experimental results from the MR installed at the PSDI/CPERI/CERTH. The mathematical model consists of mass, energy and momentum balances where both axial and radial gradients of temperature and mass are fully considered. More specifically, the process model takes into consideration the complex reaction mechanism of the reforming reactions, convective and molecular diffusion of the reacting mixture species, diffusion of H<sub>2</sub> through the membrane, and thermal effects due to reaction and heat exchange with an external heat source. The main challenge is the optimal balance of the species and heat transport that subsequently control the extent of the reactions along the reactor length. For each case, the optimal inlet stream conditions (i.e. inlet flow rate, steam to carbon ratio (S/C) and sweep gas flow rate) are calculated in order to satisfy the imposed H<sub>2</sub> stream specifications for given reactor dimensions. Similarly, different reactor configurations are assessed based on the requirements in overall CH<sub>4</sub> utilization. For each reactor configuration N<sub>2</sub> or H<sub>2</sub>O sweep gas streams are used. Additionally, the optimal geometrical characteristics of the reactor are calculated for a given pure H<sub>2</sub> production.

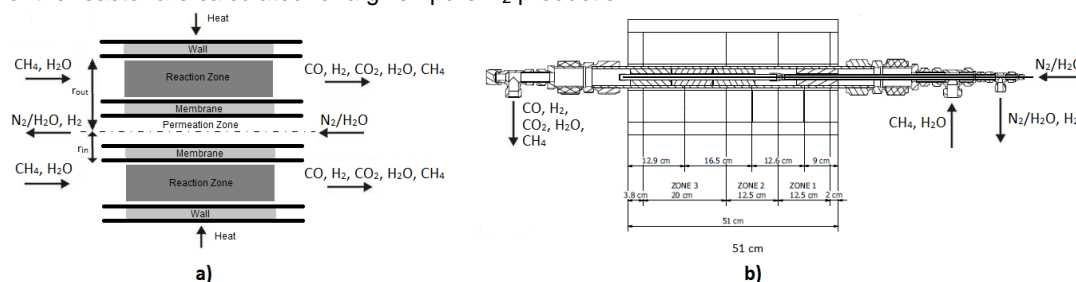


Figure 1: (a) Schematic of a membrane reactor for low temperature steam reforming, and (b) membrane reactor configuration at CPERI/CERTH.

## 2. Process description, reaction scheme and kinetic model

The experimental MR consists of two coaxial tubes as shown in Figure 1(a). The area between the two tubes forms the reaction zone, whereas the area inside the inner tube that is consisted of a Pd-Ru layer deposited on a ceramic dense support forms the permeation zone. A binary mixture of CH<sub>4</sub> and steam is fed into the reaction zone that surrounds the membrane at a defined molar steam to carbon ratio. MSR and WGS reactions take place over a Ni-Pt/CeZnLa foam supported catalyst at a temperature range of 450 - 550 °C and at reaction pressure of 10 bar (Angeli et al., 2013). The difference between the square roots of H<sub>2</sub> partial pressure in the reaction and in permeation zone is the driving force for H<sub>2</sub> removal through the permeable and selective Pd-Ru membrane. Finally, sweep gas (e.g., N<sub>2</sub> or H<sub>2</sub>O) flowing through the permeation zone carries the permeated H<sub>2</sub> to storage. Figure 1(b) shows the pilot reactor configuration, where experiments were conducted and is installed at PSDI/CPERI/CERTH. Detailed description referring to liquid and gas delivery module, reactor, product stream module and unit automation can be found at Kyriakides et al. (2014). The length of the reaction zone is 0.5 m, whereas the length of the membrane surface is 0.4 m attached on a draft tube that is used for support. Four cylindrical parts of foam-supported catalyst are placed inside the reaction zone, 0.1 m length each. One is placed at the area

over a tube before the membrane (at the entrance of the reactor) and the other three are placed at the area around the membrane.

The reaction scheme is consisted of one endothermic reaction (MSR) and one exothermic reaction (WGS), both reversible, and is shown in Table 1. The overall products are CO, CO<sub>2</sub> and H<sub>2</sub>. The reaction rate expressions are based on the Langmuir-Hinselwood mechanism given by Xu and Froment (1989).

Table 1: Reaction scheme of the membrane steam reforming

Reaction		Reaction Enthalpy
Methane steam reforming	$\text{CH}_4 + \text{H}_2\text{O} \leftrightarrow \text{CO} + 3\text{H}_2$	$\Delta H_{298}^o = 206,000 \text{ J/mol}$
Water-Gas swift	$\text{CO} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + \text{H}_2$	$\Delta H_{298}^o = 165,000 \text{ J/mol}$
Overall Methane steam reforming	$\text{CH}_4 + 2\text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 4\text{H}_2$	$\Delta H_{298}^o = -41,000 \text{ J/mol}$

### 3. Process model

The mathematical model is based on two-dimensional mass, energy, and momentum balances, considering radial gradients of concentration and temperature. The nonlinear and pseudo-homogeneous model consists of: a) the mass balances for every component both in the reaction Eq(1) and permeation zone Eq(2), b) the energy balance in the reaction zone Eq(3), and c) the momentum balance in the reaction zone Eq(4). The H<sub>2</sub> flux through the membrane is calculated by Sieverts law Eq(5).

$$u \frac{\partial C_i}{\partial z} = \varepsilon D_{er} \left( \frac{1}{r} \frac{\partial C_i}{\partial r} + \frac{\partial^2 C_i}{\partial r^2} \right) + \rho_b \sum_{j=1}^3 R_j v_{i,j}, \quad i = \text{CH}_4, \text{H}_2\text{O}, \text{H}_2, \text{CO}, \text{CO}_2 \quad (1)$$

$$u_p \frac{\partial C_{i,p}}{\partial z} = \frac{2}{r_i} N_m, \quad i = \text{H}_2, \quad u_p \frac{\partial C_{i,p}}{\partial z} = 0, \quad i = \text{N}_2 \quad (2)$$

$$u \rho C_p \frac{\partial T}{\partial z} = k_r \left( \frac{1}{r} \frac{\partial T}{\partial r} - \frac{\partial^2 T}{\partial r^2} \right) + \rho_b \sum_{j=1}^3 \Delta H r_j R_j \quad (3)$$

$$\frac{\partial P}{\partial z} = \frac{f G \mu (1 - \varepsilon)^2}{\rho d_p^2 \varepsilon^3}, \quad f = 150 + 1.75 \frac{\text{Re}_p}{1 - \varepsilon}, \quad \text{Re}_p = \frac{G d_p}{\mu} \quad (4)$$

$$N_m = \frac{Q \exp(-E/R_g T_m)}{d_m} (p_{\text{H}_2,r}^{0.5} - p_{\text{H}_2,p}^{0.5}) \quad (5)$$

The main model assumptions are as follows: a) steady-state operation, b) plug-flow conditions, c) ideal-gas behaviour, d) constant density of reactive mixture, e) 100% selectivity of the membrane towards H<sub>2</sub> permeation of other components is negligible, f) pseudo-homogeneous model, g) radial gradient in permeation zone is negligible, h) back-mixing in axial direction in both zones is negligible, i) constant temperature and pressure in permeation zone at their inlet values is maintained, j) heat exchange between permeation and reaction zones is negligible, k) constant wall temperature in the reactor heating jacket is considered and l) constant velocity in reaction and permeation zone (based on the inlet flow rates).

The boundary conditions in the reaction zone for the wall and membrane side, as well as at the reactor inlet are given below:

$$z = 0, \quad \forall r \in [r_i, r_o]: (u C_i) = (u C_i)_{in}, \quad T = T_{in}, \quad P = P_{in} \quad (6)$$

$$r = r_o, \quad \forall z \in [0, L]: \frac{\partial C_i}{\partial r} = 0, \quad k_r \frac{\partial T}{\partial r} = h_w (T_w - T) \quad (7)$$

$$r = r_i, \quad \forall z \in [0, L]: \frac{\partial C_i}{\partial r} = 0, \quad i = \text{CH}_4, \text{H}_2\text{O}, \text{CO}, \text{CO}_2, \varepsilon \cdot D_{er} \frac{\partial C_j}{\partial r} = N_m, \quad j = \text{H}_2, \quad \frac{\partial T}{\partial r} = 0 \quad (8)$$

$$z = L: (u_p C_{j,p}) = (u_p C_{j,p})_m, \quad j = N_2, H_2 \quad (9)$$

#### 4. Model validation

Modelling Eq(1) to Eq(5) have been discretized using a backward finite differencing scheme in the axial and radial direction. The number of selected grid points in the axial direction is 30 and in the radial direction ten. Grid points both in radial and axial directions are equally spaced. The overall number of equations and variables in the model are 2,167 and 2,183. The remaining variables are fixed and correspond to the inlet stream conditions (concentration, temperature, and pressure), reactor dimensions, wall temperature and Sieverts law parameters. The solution of the nonlinear set of modelling equation is performed by MINOS 5.5 (Murtagh and Saunders, 1983) that employs an augmented project Lagrangian algorithm.

Experiments have been performed at the MR installed at PSDI/CPERI/CERTH in order to accurately calculate the effective membrane permeability that can be achieved during the operation of this reactor. Moreover, experiments have been performed in order to test the performance of the MSR in the MR. The different conditions tested correspond to temperature, reaction zone pressure, permeation zone pressure, S/C ratio and total inlet flow rate changes. The simulated results were fitted to the experimental results by adjusting the values of five parameters. The estimated parameters of the reactor model are effective radial diffusivity, effective radial conductivity, thermal transmittance of the wall and the Sieverts law parameter that were estimated to be equal to  $3 \cdot 10^{-6} \text{ m}^2/\text{s}$ ,  $10^3 \text{ W/m}\cdot\text{K}$ ,  $100 \text{ W/m}^2\cdot\text{K}$ ,  $6 \cdot 10^{-6} \text{ mol}/(\text{bar}^{0.5}\cdot\text{m}\cdot\text{s})$  and  $15,700 \text{ J/mol}$ . Sieverts parameter values were calculated assuming an effective permeability of  $10 \text{ Nm}^3/(\text{m}^2\cdot\text{h}\cdot\text{bar}^{0.5})$ , which corresponds to  $\text{H}_2$  molar fraction close to the conditions that are expected to prevail within the membrane  $\text{CH}_4$  steam reforming reactor. The predicted value of ideal permeability was approximately  $40 \text{ Nm}^3/(\text{m}^2\cdot\text{h}\cdot\text{bar}^{0.5})$ . Such a value is quite close to values reported in the literature (van Delft et al., 2009) for a similar type of membrane.

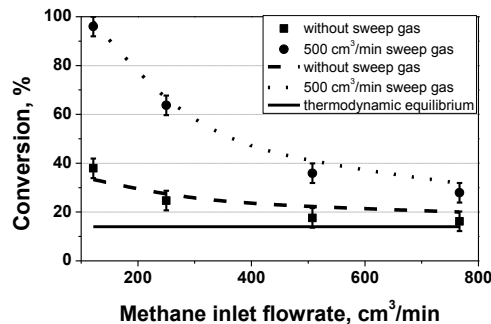


Figure 2:  $\text{CH}_4$  conversion versus  $\text{CH}_4$  inlet flow rate, experimental (symbol) vs simulation (curve).

The simulation results for the  $\text{CH}_4$  conversion at different  $\text{CH}_4$  inlet flow rates exhibit sufficient agreement with the experimental conversion values used for the estimation of the model parameters (Figure 2). The mathematical process model with the regressed model parameters has been tested on experimental data at reaction zone pressure of 10 bar, permeation zone pressure of 1 bar for a range of  $\text{CH}_4$  inlet flow rates and temperature. The largest differences appear in the reactor test without the use of the sweep gas. Such discrepancy may be attributed to the difficulty in simulating the molecular diffusion of  $\text{H}_2$  in the membrane side, especially for high conversion rates. The calculated  $\text{CH}_4$  conversion values are within the experimental error for the reactor tests with a sweep gas for the entire range of  $\text{CH}_4$  inlet flow rates. Overall, the mathematical model shows good predictive power of the  $\text{CH}_4$  conversion in the MR.

#### 5. Optimization

The optimal steam to carbon ratio and sweep gas flow rate that minimize the overall  $\text{CH}_4$  utilization have been calculated for a range of  $\text{H}_2$  production rates (Figure 3, 4(a)). The results apply to four different cases. Without utilization (burning) of reaction zone outlet stream unreacted  $\text{CH}_4$  by using  $\text{N}_2$  (Case1) or  $\text{H}_2\text{O}$  (Case2) as sweep gas and with utilization of the reaction zone outlet stream by using  $\text{N}_2$  (Case3) or  $\text{H}_2\text{O}$  (Case4) as sweep gas. In each case, a pure  $\text{H}_2$  produced flow rate (the amount of  $\text{H}_2$  that is produced and recovered through the membrane) is specified and the total amount of required  $\text{CH}_4$  is calculated. The variables to be optimized (decision variables) are  $\text{CH}_4$ ,  $\text{H}_2\text{O}$  and sweep gas inlet flow rates. The total

amount of required  $\text{CH}_4$  for the achievement of a given  $\text{H}_2$  production is the amount of  $\text{CH}_4$  needed to heat up the inlet streams ( $\text{CH}_4$ ,  $\text{H}_2\text{O}$  and sweep gas,  $F_{\text{CH}_4\text{MH}}$ ,  $F_{\text{CH}_4\text{SH}}$ ,  $F_{\text{CH}_4\text{SGH}}$ , the amount of  $\text{CH}_4$  needed to heat up the reactor ( $F_{\text{CH}_4\text{RH}}$ ) and the  $\text{CH}_4$  needed for the reaction ( $F_{\text{CH}_4\text{inlet}}$ ). The objective function, which is minimized, is shown at Eq(10).

$$F = (F_{\text{CH}_4\text{MH}} + F_{\text{CH}_4\text{SH}} + F_{\text{CH}_4\text{SGH}} + F_{\text{CH}_4\text{RH}} + F_{\text{CH}_4\text{inlet}}) \quad (10)$$

The overall optimal  $\text{CH}_4$  utilization is calculated for several pure  $\text{H}_2$  produced flow rates and is shown in Figure 3a. By comparing Case 1 to 3, where  $\text{N}_2$  is used as sweep gas, it is clear that the utilization of the reactor outlet stream does not improve significantly the overall  $\text{CH}_4$  needs. However, by comparing Cases 2 and 4, where  $\text{H}_2\text{O}$  is used as sweep gas, the utilization of the reactor outlet stream improves the overall  $\text{CH}_4$  needs mainly attributed to the higher specific heat of water. The optimum flow rate of sweep gas for a range of  $\text{H}_2$  production rates is shown in Figure 3(b). The optimum flow rate of sweep gas is not related to pure  $\text{H}_2$  produced linearly. Higher  $\text{H}_2$  production necessitates the higher sweep gas stream flow rate. Eventually, at optimal operating conditions the flow rate of sweep gas grows exponentially. The optimum S/C ratio for a range of  $\text{H}_2$  production rates is shown in Figure 4a. The optimum S/C ratio remains invariant in each case, which is attributed to the effect steam has on the reaction kinetic rates and  $\text{H}_2$  separation rate. The effect on the reaction rates is positive, however,  $\text{H}_2$  separation rate deteriorates at a greater pace because of  $\text{H}_2$ 's partial pressure decrease.

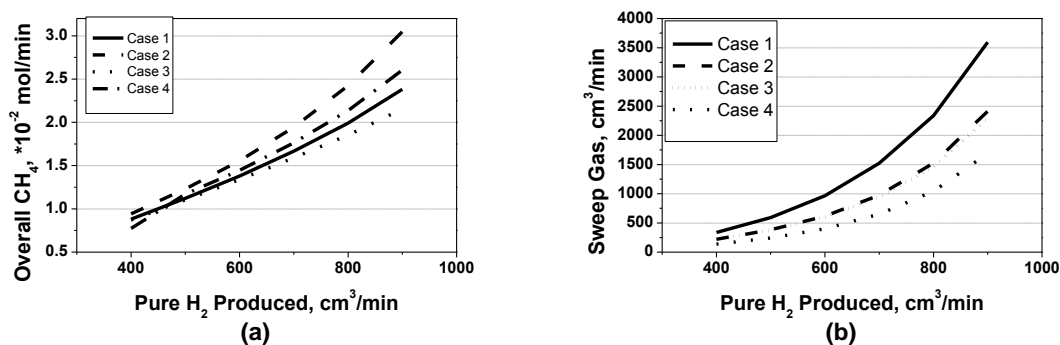


Figure 3: (a) Overall  $\text{CH}_4$  utilization versus pure  $\text{H}_2$  production, and (b) optimal sweep gas flow rate versus pure  $\text{H}_2$  production.

Simulation results referring to overall  $\text{CH}_4$  utilization for a number of different reactor lengths for 900  $\text{cm}^3/\text{min}$  and 800  $\text{cm}^3/\text{min}$  of pure  $\text{H}_2$  production flow rate are shown in Figure 4(b). When the length of the reactor is small, for given membrane and reactor diameters, the overall  $\text{CH}_4$  utilization is high. As the length increases the overall  $\text{CH}_4$  utilization decreases asymptotically.

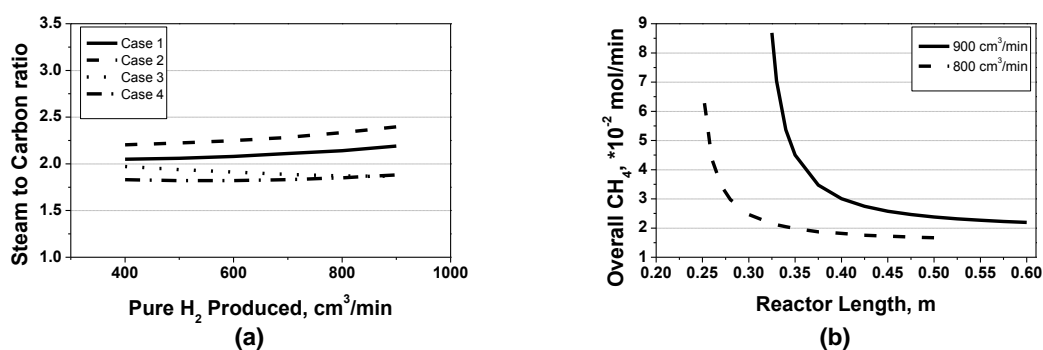


Figure 4: (a) Optimal steam to carbon ratio versus pure  $\text{H}_2$  production, and (b) overall  $\text{CH}_4$  utilization versus reactor length.

Indicative results referring to the optimal length of the reactor for a range of pure  $\text{H}_2$  flow rates are shown in Table 2. The length along with  $\text{CH}_4$ ,  $\text{H}_2\text{O}$ , and sweep gas inlet flow rates are the variables to be optimized. The overall  $\text{CH}_4$  utilization, sweep gas used and membrane surface is also shown.

Table 2: Optimal CH<sub>4</sub>, H<sub>2</sub>O and Sweep Gas inlet flow rates for a range of pure H<sub>2</sub> flow rate.

H <sub>2</sub> produced, cm <sup>3</sup> /min	Length, m	Overall CH <sub>4</sub> , mol/min	Sweep gas, cm <sup>3</sup> /min	Membrane surface, m <sup>2</sup>
500	0.241	0.0145	2,875	0.0106
600	0.291	0.0174	3,474	0.0128
700	0.342	0.0204	4,090	0.0150
800	0.392	0.0233	4,706	0.0172
900	0.443	0.0262	5,329	0.0195

## 6. Conclusions

The optimal steam to carbon ratio and sweep gas flow rate that minimize the overall CH<sub>4</sub> utilization (i.e. reformed CH<sub>4</sub> and equivalent CH<sub>4</sub> for heating purposes) have been calculated for a range of H<sub>2</sub> production rates for a MR using an experimentally validated process model for a novel catalyst and reactor configuration. The former factor seems to remain independent of the production level due to the role of steam in reaction kinetics and H<sub>2</sub> removal. The latter factor exhibits a nonlinear dependency on H<sub>2</sub> production level. Additionally, the optimal reactor length and subsequently the catalyst amount and membrane surface area for a given H<sub>2</sub> production rate are calculated.

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