

# Membrane reformers heated by molten salts: a simulation study

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The increasing demand of hydrogen is stimulating the development of new technologies for producing large amounts of it at low cost. A promising process is based on the integration of selective membranes in steam reforming reactors; by this way, continuous hydrogen removal from reaction environment prevents equilibrium conditions to be achieved: quite high methane conversions can thus be obtained at relatively low temperatures and very pure hydrogen is collected in the permeation zone. The lower thermal level required in membrane reactors allows the furnace used in traditional reformers to be replaced by heat exchangers with an heating fluid.

Unfortunately, not much is known about the optimal design and operating conditions of membrane reactors. The aim of this work is to explore the behaviour of suitable membrane reactor geometries and the effect of the thermal flux profile along the axial coordinate by a two-dimensional mathematical model. A molten salt entering at 823 K is used as heating fluid. The constraint on membrane temperature  $T \leq 820$  K, that is the current technological threshold for the Pd-Ag membranes, is taken into account in simulation assessment.

## 1. Introduction

Hydrogen is widely used in chemical industry for the manufacture of important products, as ammonia and methanol, and in refinery for hydroprocessing. Moreover, in the next future, the application of fuel cell (PEM, SOFC, MCFC) technology in many stationary and mobile fields will probably increase the requirement of pure hydrogen.

The natural gas (methane) steam reforming is the main process for the production of hydrogen: because of the high endothermicity of the process, the large amount of heat needed is supplied in a furnace where part of the natural gas feed is burned (about 20-30%). The typical operating temperatures are within the range 850-950°C.

Integrating a selective membrane in the reaction environment allows a reaction product ( $H_2$ ) to be removed, avoiding equilibrium conditions to be achieved and consequently enabling to obtain higher methane conversions at lower temperatures. The lower thermal level allows different heat sources to be used as an heating fluid: in this work the possibility to use a molten salt at 823 K, obtained by Archimede solar plant, patented by ENEA, is studied.

Therefore, using membrane reformers gives the following benefits:

- the furnace is avoided and all the methane is used as reaction feed, with  $CO_2$  emission reduction and natural gas saving;

- the reactor is very compact, since both steam reforming reaction and the separation step are performed in a single equipment. Compactness should allow a larger spreading of small plants to produce hydrogen, everywhere an heating fluid at about 800-850 K is available;
- the hydrogen produced is very pure thanks to the infinite selectivity of Pd-Ag membranes. Therefore the reformer can be matched easily with a fuel cell.

The aim of the present work is the assessment of membrane reformer performance using a molten salt as heating fluid: the simple configuration shown in Fig.1 (a triple tube) is assumed and a mathematical model is used to simulate the process .

## 2. Mathematical model

The main reactions taken into account in modelling steam reforming reactors are:



Secondary reactions as carbon formation are not considered.

The model is based on mass, energy and momentum balances. The two-dimensional nature of the model allows axial and radial concentrations and temperature profiles to be evaluated.

### 2.1 Mass balances

Mass balances for all the gas mixture components are :

$$\frac{\partial(u_z \cdot c_i)}{\partial \tilde{z}} = \frac{d_p \cdot L}{Pe_{mr} \cdot r_{i,o}^2} \left( \frac{\partial^2(u_z \cdot c_i)}{\partial \tilde{r}^2} + \frac{1}{\tilde{r}} \frac{\partial(u_z \cdot c_i)}{\partial \tilde{r}} \right) - \rho_b \cdot L \cdot \sum_{j=1}^3 \eta_j \cdot R_j \quad (4)$$

where  $u_z$  is the gas mixture velocity,  $c_i$  is the mole concentration of component  $i$  ( $i = \text{CH}_4, \text{H}_2\text{O}, \text{H}_2, \text{CO}, \text{CO}_2$ ),  $\tilde{z}$  and  $\tilde{r}$  are dimensionless axial and radial coordinates,  $d_p$  is the particle diameter,  $L$  and  $r_{i,o}$  are the reactor length and the intermediate catalytic bed tube radius, respectively,  $\rho_b$  is the packed bed density,  $\eta_j$  and  $R_j$  are the effectiveness factor and the intrinsic rate of reaction  $j$  [Xu et al., 1989] and  $Pe_{mr}$  is the mass effective radial Peclet number, given by Kulkarni et al. (1980) for Reynolds number greater than 1000.

In the inner tube a sweeping gas (water vapour) flows to carry permeated hydrogen out of the membrane module. Hydrogen mass balance gives:

$$\frac{dY_{H_2}}{d\tilde{z}} = \pm \frac{N_{H_2}^m \cdot 2\pi \cdot r_{o,i}}{F_{CH_4}^0} \quad (5)$$

where  $Y_{H_2}$  is the ratio between permeated hydrogen and inlet methane flow rate ( $F_{CH_4}^0$ ),  $r_{o,i}$  is the inner tube radius and  $N_{H_2}^m$  is the hydrogen flux permeating through the membrane: it is calculated by the well-known Sievert law:

$$N_{H_2}^m = \frac{B_H}{\delta} \cdot (p_{H_2,react}^{0.5} - p_{H_2,perm}^{0.5}) \quad (6)$$

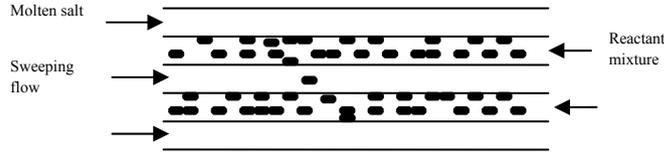


Figure 1- Triple tube configuration

In eq.6 ,  $B_H$  is the hydrogen permeability, calculated according Shu et al. (1994) for Pd-Ag membranes,  $\delta$  is the membrane thickness,  $p_{H_2,react}$  and  $p_{H_2,perm}$  are the hydrogen partial pressures in reaction and permeation zone, respectively.

The sign + or – in eq.5 has to be used in co-current and counter-current sweeping gas configuration, respectively.

## 2.2 Energy balances

The energy balance in the reaction environment is:

$$\frac{\partial T^R}{\partial \tilde{z}} = \frac{\lambda_{er} \cdot L}{(u_z \cdot c_{tot}) \cdot c_{p,m} \cdot r_{i,o}^2} * \left( \frac{\partial^2 T^R}{\partial \tilde{r}^2} + \frac{1}{\tilde{r}} * \frac{\partial T^R}{\partial \tilde{r}} \right) + \frac{\rho_b \cdot L \cdot \sum_{i=1}^3 \eta_j \cdot (-\Delta H_j) \cdot R_j}{(u_z \cdot c_{tot}) \cdot c_{p,m}} \quad (7)$$

where  $\lambda_{er}$  is the effective radial thermal conductivity of packed bed and gas mixture, considered as a pseudo-homogeneous phase;  $\lambda_{er}$  is calculated according Elnashaie et al. (1993).

Energy balances in the molten salt tube (eq.8) and in permeation zone (eq.9) are:

$$\frac{dT_{MS}}{d\tilde{z}} = \pm \frac{U \cdot L}{w_{MS} \cdot c_{p,MS}} * (T_{MS} - T^R) * 2\pi r_{i,o} \quad (8)$$

$$\frac{dT_P}{d\tilde{z}} = \frac{L}{F_{P,tot} \cdot c_{p,perm}} \cdot \left[ U_1 \cdot 2\pi \cdot r_{i,i} \cdot (T^R - T^P) + N_{H_2}^m \cdot \pi \cdot r_{o,i} \cdot (h_{R,H_2} - h_{P,H_2}) \right] \quad (9)$$

where  $w_{MS}$  is the mass flow rate of the molten salt,  $U$  and  $U_1$  are the overall heat transfer coefficients between heating fluid and packed bed and between packed bed and permeation zone, respectively. In eq.8 the sign + or – is used dependently on molten salt co-current or counter-current configuration.

### 2.3 Momentum balance

The momentum balance is considered only in the reaction zone:

$$\frac{dP}{dz} = \frac{f \cdot G \cdot \mu_g \cdot L}{\rho_g \cdot d_p^2} \cdot \frac{(1 - \epsilon)^2}{\epsilon^3} \quad (10)$$

The friction factor  $f$  is evaluated by the well-known Ergun equation.

In the heating fluid and sweeping gas section the pressure drop is neglected.

### 3. Results and discussion

A comparison between co-current and counter-current configurations is reported in Figure 2 where methane conversion and  $Y_{H_2}$  are reported for different residence times. We can observe that counter-current configuration has to be preferred at long residence times due to better conversion obtained; on the contrary, co-current configuration is probably more advantageous at short residence times since, even if methane conversion is slightly worse than in the counter-current case, the pure hydrogen permeated and collected is greater. Really, the co-current configuration gives a strong hydrogen mass transfer rate through the membrane because of quick increase of  $H_2$  partial pressure in the first part of the reformer (short residence time) where the large temperature difference between heating fluid and reaction environment allows good methane conversions to be achieved.

In Figure 3, the effect of molten salt flow rate on methane conversion is reported: a larger amount of heat is supplied to the reaction mixture and better performance is achieved in the reformer at increasing molten salt flow rate. Moreover, a 773.2 K maximum membrane temperature is reached at a 3 kg/s molten salt flow rate so that the membrane temperature is always below the technological threshold assumed equal to 820 K. This remarkable advantage depends on the fact that, in a membrane reactor, increasing heat flow supplied gives higher conversions and thus larger amounts of heat absorbed by the reaction, therefore preventing the temperature to reach too high values. However, increasing molten salt flow rate has some drawbacks concerning cost (a greater molten salt heating plant is required) and pressure drop in the molten salt section.

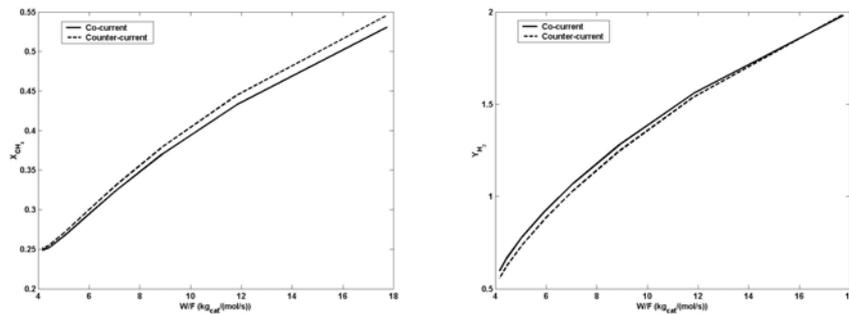


Figure 2 – Methane conversion and hydrogen recover per mole of methane in co-current and counter-current molten salt configuration ( $w_{MS} = 1$  kg/s).

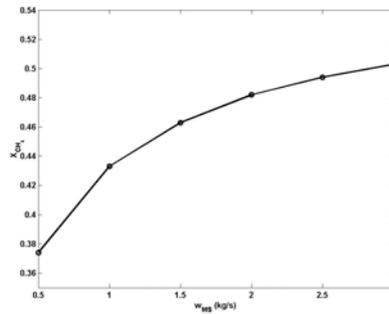


Figure 3 – Methane conversion vs. molten salt flow ( $W/F = 11.8 \text{ kg}_{cat}/(\text{mol/s})$ )

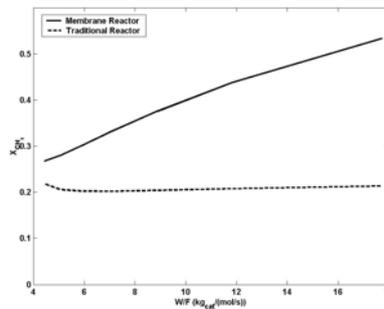


Figure 4 – Membrane reactor and traditional reactor conversion with  $w_{MS} = 2 \text{ kg/s}$

A further comparison between co-current and counter-current configuration is performed as regards sweeping gas flow. The counter-current configuration seems to offer better separation properties since the more uniform driving force (hydrogen partial pressure difference between reaction and sweeping gas zone) along the reactor allows all the membrane surface to be well exploited.

Finally, a comparison between the performance of the membrane reactor and of the traditional reformer is made in order to assess the benefits in integrating membrane in the reaction environment. Remarkable improvements in terms of methane conversion can be observed, mainly at long residence times (Fig.4). Methane conversion cannot go over equilibrium value which is quickly reached in the traditional reformer at relatively low residence times while, in the membrane reactor, there is no equilibrium and more time the gas mixture stays in contact with the catalyst and with the selective membrane more hydrogen is produced and collected through the membrane. Therefore, the advantages in integrating membrane in the reforming reactor are more evident at long residence time; if the residence time is short, the performance of membrane reactor is similar to that one of a traditional reformer.

#### **4. Conclusion**

Integrating the ultra-selective palladium membrane in a methane steam reformer environment avoids equilibrium conditions to be achieved and consequently allows the reaction to be carried out at lower thermal level, thus permitting to use heat exchangers in place of a furnace to supply heat required by reactions.

The behaviour of the system obtained by matching the reformer with a molten salt heating source is analyzed through a two-dimensional model based on mass, energy and momentum balances.

Simulations show that the molten salt heating fluid is able to satisfy reaction heat requirements and that the membrane temperature is always below the technological threshold required from Pd-based membranes, even at high heating fluid flow rates.

Co-current and counter-current configurations, concerning both heating fluid and sweeping vapour flows, have been compared and useful suggestions have been deduced about advantageous operation.

To conclude, the membrane reformer heated by molten salts seems to allow remarkable benefits in comparison with the traditional technology: the advantage in terms of methane conversion is stronger when residence time in the catalytic packed bed is longer.

#### **5. References**

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