

# Progress on Modeling and Design of Membrane Reactors for Hydrogen Production

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This paper presents an overview of recent research carried out by the authors on the development and analysis of mathematical models describing hydrogen production in membrane reactors. The case considered is that of methane steam reforming (SR) in a reactor with the typical double pipe configuration, in which a hydrogen-permeable membrane is present on the outer wall of the innermost tube. The model developed accounts for the rate of reaction, convective and dispersive transport in the axial and radial directions, and hydrogen permeation across the membrane. Density variations with pressure and gas composition have been accounted for, leading to a full coupling of mass and momentum transport. Different geometric aspect ratios have also been studied to assess the influence of catalyst volume on the overall performance of the system. The presence of two distinct transport regimes, in which hydrogen permeation is limited either by transport within the packed bed or permeation across the membrane, has been identified, along with the operating conditions that determine their range of existence. This has allowed the development of a simplified model, valid under the hypothesis that the reaction is fast compared to transport. In the permeation-controlled regime, the permeate flow rate and recovery may be found by solving a set of two PDEs, whereas an analytical solution is available for the transport-controlled regime. The main steps and observations that have brought to the development of the simplified model are presented, along with a guide to its implementation.

## 1. Introduction

The study of integrated membrane reactors, in which one of the products is selectively removed from the reacting volume as it is being produced, has been attracting much interest. In particular, the use of membrane reactors for the production of  $H_2$  allows to shift the equilibrium of the reaction to high values of feed conversion while maintaining a fairly low operating temperature even when endothermic reactions are carried out. In order to adequately design a membrane reactor, several different phenomena must be taken into account, namely the reaction itself, mass transport within the reactor packed bed, and hydrogen permeation across the membrane. These mechanisms depend on temperature, pressure, feed flow rate and composition, reactor dimensions, membrane permeance, catalyst activity, and mass dispersion. The high number of operating parameters and the wide range of values that they can assume, give an indication of the complexity of the problem and of the difficulty in designing the system. Previous work carried out by the authors of the present article has shown that it is possible to describe the system in terms of four dimensionless parameters (Murmura et al. 2015, 2016a, 2017a) and that integral quantities, such as the  $H_2$  permeate flow rate and yield, can be obtained through a simplified model, valid when the characteristic time of the reaction is low compared to that of mass transport (Murmura et al. 2016b). In the present work a procedure for a "first approximation" design of membrane reactors using a simplified model is described. The results of this work are valid when the temperature of the reactor may be considered to be uniform and when the characteristic time of the reaction is low compared to the characteristic time of mass transport.

## 2. Problem description and main equations

The system considered consists of a membrane reactor formed by two co-axial cylinder. The feed enters the annular volume between the two cylinders, in which the catalyst bed is packed.  $H_2$  produced inside the reactor

permeates across the selective membrane, placed on the outer wall of the innermost tube, and is collected in the inner cylindrical volume. The feed composition has been evaluated by considering the equilibrium conditions of methane SR at a fixed temperature and steam to carbon ratio. In other terms, the presence of pre-reforming unit before the membrane reactor has been considered. The system has been described through momentum and mass balance equations. The former has been expressed through Darcy's law for flow in porous media, accounting for both radial and axial components of velocity. Mass balance equations have instead been written by considering both axial and radial convection and dispersion, and the rate of the SR reaction. This has been expressed through the relation proposed by Wei and Iglesia (2004). Density variations with pressure and gas composition have been considered, leading to full coupling between mass and momentum transport. With regards to H<sub>2</sub> permeation, Sieverts' law has been applied, according to which the permeating flux is proportional to the difference between the square roots of the partial pressure of H<sub>2</sub> at the membrane surface in the retentate and permeate sides, respectively (Ward and Dao, 1999). The model has been developed under the assumptions of uniform temperature, negligible H<sub>2</sub> partial pressure in the permeate side, and infinite selectivity of the membrane towards H<sub>2</sub>. The justification of the hypotheses and a thorough explanation of the equations used are reported in previous papers (Murmura et al., 2017); here, the dimensionless formulation is reported. The parameters used to develop the dimensionless form of the problem are the inner reactor radius,  $R_1$ , as reference length; the inlet gas velocity,  $U$ , as characteristic velocity; the atmospheric pressure,  $P_{atm}$ , as reference pressure, the molecular weight of hydrogen,  $W_h$ , as reference mass; the molecular diffusivity,  $D_m$ , as reference diffusion constant. The continuity and mass balance equations thus become

$$\nabla \cdot (-\tilde{f}\tilde{P}\tilde{\nabla}\tilde{P}) = 0 \quad ; \quad \nabla \cdot \left( -\beta\omega_i\tilde{f}\tilde{P}\tilde{\nabla}\tilde{P} - \frac{1}{Pe}\tilde{f}\tilde{P}\tilde{\mathbb{D}} \cdot \tilde{\nabla}\omega_i \right) = v_i \frac{W_i}{W_m} Da\tilde{f}\tilde{P}\omega_m(1-\eta) \quad (1)$$

where  $\tilde{P} = P/P_{atm}$ ,  $\tilde{f} = f/W_h$ , and  $\tilde{\nabla} = R_1\nabla$  and  $f$  is the average molecular weight of the mixture. The other variables appearing in Eq. (2) are  $\omega_i$ ,  $W_i$  and  $v_i$  which represent the mass fraction, molecular weight, and stoichiometric coefficient, respectively, of the  $i$ -th component. The dimensionless groups introduced are

$$Pe = \frac{UR_1}{D}, \quad Da = \frac{\mathcal{R}TkR_1}{U}, \quad \beta = \frac{kP_{atm}}{\mu R_1 U} \quad (2)$$

$$1 - \eta = 1 - \frac{W_w^2 W_m \tilde{P}^2 \tilde{f}^2 \omega_h^4 \omega_c}{W_h^2 W_c \tilde{K}_{eq} \omega_m \omega_w^1} \quad (3)$$

The parameter  $(1 - \eta)$  accounts for the distance of the system from equilibrium conditions;  $\beta$  measures pressure drops in packed bed, which, in common reactor configurations, are found to be always negligible (Murmura et al., 2016a) and whose influence has therefore not been studied extensively. The boundary conditions are those of fixed inlet gas velocity and composition and fixed outlet pressure (Eqs. (4) and (5)), zero flux in correspondence of the outer reactor wall (Eq. (6)) and hydrogen permeation in correspondence of the membrane (Eq. (7))

$$\text{in } \tilde{z} = 0: \quad \omega_i = \omega_i^0 \quad ; \quad \tilde{v}_z = v_z/U = 1 \quad (4)$$

$$\text{in } \tilde{z} = L/R_1: \quad \tilde{P} = P_L/P_{atm} = \alpha \quad ; \quad \frac{\partial \omega_i}{\partial \tilde{z}} = 0 \quad (5)$$

$$\text{in } \tilde{r} = \sigma \quad \tilde{\nabla}\tilde{P} \cdot \mathbf{n} = 0 \quad ; \quad \tilde{\nabla}\omega_i \cdot \mathbf{n} = 0 \quad (6)$$

$$\text{in } \tilde{r} = 1 \quad \left( \omega_h \beta \tilde{\nabla}\tilde{P} + \frac{1}{Pe} \tilde{\mathbb{D}} \cdot \tilde{\nabla}\omega_h \right) \cdot \mathbf{n} = -\gamma \sqrt{\frac{\omega_h}{\tilde{f}\tilde{P}}} \quad ; \quad -\tilde{\mathbf{v}} \cdot \mathbf{n} = -\gamma \sqrt{\frac{\omega_h}{\tilde{f}\tilde{P}}} \quad (7)$$

where  $\sigma$  is the ratio between the outer and inner radii,  $\mathbf{n}$  is the unit vector directed towards the reactor's axis,  $\alpha$  is the dimensionless operating pressure, and  $\gamma$  is a parameter accounting for membrane permeability

$$\gamma = \mathbb{P}_m \frac{\mathcal{R}TP_{atm}^{-1/2}}{W_h} \frac{1}{U} \quad (8)$$

For a given reactor geometry, the system may therefore be studied through the parameters  $Pe$ ,  $Da$ ,  $\gamma$ , and  $\alpha$ . The performance of the system has been studied in terms of

1. overall permeate flow rate of H<sub>2</sub> ( $\Pi_h$ )
2. separator-based yield (from here on "yield"): the ratio between the permeate and inlet flow rate of H<sub>2</sub> ( $\Psi_s$ )
3. reactor-based recovery (from here on "recovery"): the ratio between the permeate flow rate of H<sub>2</sub> and the sum of the inlet flow rate and production rate of H<sub>2</sub> ( $\Psi_r$ ).

### 3. Overview of main results

The model presented above has been studied over a wide range of operating conditions. It was found that density variations, often neglected, are significant and cause non-negligible convective fluxes in the radial direction. This phenomenon is at the basis of the concentration-polarization often observed when operating membrane reactors. The shape of the concentration profiles of  $H_2$ , and consequently of methane and the other components, switches between two regimes: one in which  $H_2$  permeation is limited by transport across the packed bed, and one in which it is limited by the membrane itself. When working with a fixed inlet gas velocity, the following observations can be made:

1. At low  $P$ , permeation is limited by transport within the packed bed. As pressure increases above a threshold value permeation becomes limited by the membrane.
2. The pressure value in correspondence of which the switch occurs, referred to as “critical pressure”, depends on  $Pe$  and membrane permeability, defined through the parameter  $\gamma$ . In particular, the critical pressure increases with increasing values of  $\gamma$  and  $Pe$  (Murmura et al., 2017a).
3. When all other parameters are fixed, the critical pressure represents the value in correspondence of which it is convenient to operate, since further increases in pressure bring only a negligible increase in hydrogen recovery and a decrease in the yield (Murmura et al., 2017a).
4. In the transport-controlled regime (low  $P$ ) the  $H_2$  concentration at the membrane reaches values close to zero and a strong concentration gradient is observable in proximity of the membrane. When the characteristic time of the reaction is low,  $CH_4$  is almost immediately converted to compensate  $H_2$  permeation and its concentration also approaches zero (Murmura et al., 2016b).
5. In the membrane-controlled regime (high  $P$ ) the radial concentration profiles remain almost uniform, and the behavior of the reactor approaches that of a plug flow reactor (Murmura et al., 2016b).
6. If the curves depicting the yield as a function of pressure are normalized with respect to the critical pressure and the maximum yield, they all collapse on the same master curve, regardless of the operating parameters or reactor dimension (Murmura et al., 2017b).

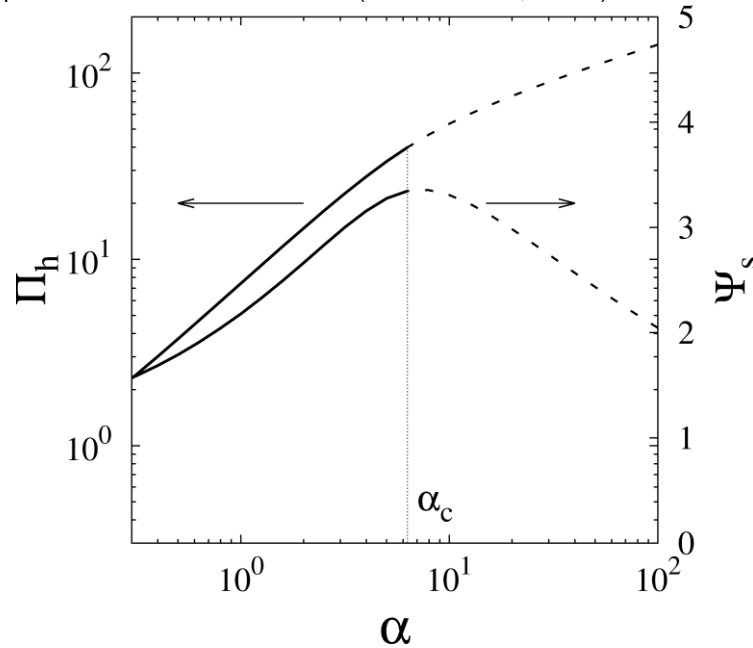


Figure 1: Permeate flow rate and hydrogen yield at  $Pe=10$ ,  $Da=10$ , and  $\gamma=1$ . The continuous and dashed lines indicate the transport-controlled and membrane-controlled regimes, respectively. The critical pressure,  $\alpha_c$  has been indicated.

Figure 1 shows the behavior of the permeate flow rate and  $H_2$  yield. The transition between the two regimes has been evidenced by the use of continuous lines for the transport-controlled regime and dashed lines for the membrane controlled-regime. Although the analysis carried out at fixed velocity has been useful to identify and understand the two transport regimes, in most cases of practical interest the inlet flow rate is a fixed parameter. In these conditions, when pressure is increased the density of the gaseous mixture increases and, for continuity, the velocity must decrease. The membrane-controlled regime thus appears at low  $P$  whereas the transport controlled regime appears at higher  $P$ . The transition is less evident when studying the behavior

of the permeate flow rate, but is very noticeable when looking at the recovery. In addition, when the flow rate is constant, the identification of the critical pressure as the optimal operating pressure becomes very visible, as increases of this parameter beyond  $\alpha_c$  bring no benefit to the H<sub>2</sub> recovery. Figure 2 shows hydrogen concentration profiles for three axial coordinates ( $z = 2, 5,$  and  $8$ ) evaluated in same conditions reported in Figure 1 for  $\alpha$  values of 1 (left) and 20 (right).

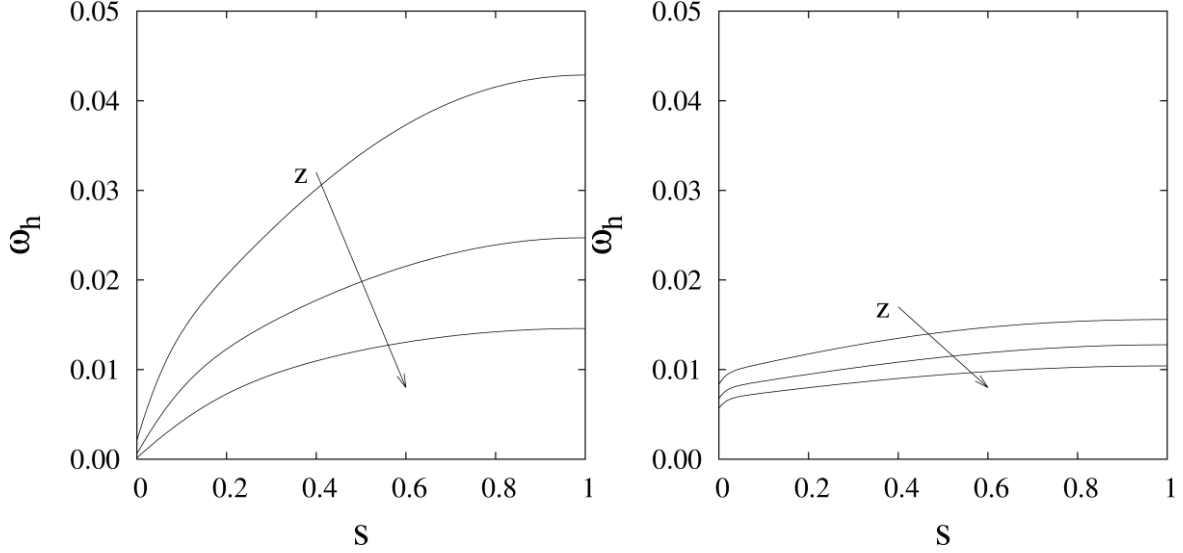


Figure 2: Hydrogen mass fraction along the reactor's cross-section and for three axial coordinates in the transport-controlled (left) and membrane-controlled (right) regimes.

#### 4. Simplified model: development and use

From this starting point, two distinct sets of equations have been developed to evaluate the overall permeate flow rate in the transport and membrane controlled regimes (Murmura et al., 2016b). In the following paragraphs, all variables are intended in their dimensionless forms. The main assumptions made in the development of the simplified model are:

1. Axial dispersion is negligible with respect to axial convection;
2. Radial convection is negligible with respect to radial dispersion;
3. Average molecular mass is constant in the entire domain;
4. Pressure drops are negligible.

The mass balance equations therefore become

$$-\frac{\partial \rho_i}{\partial z} + \frac{D_{rr}}{Pe} \rho_{tot} \left( \frac{1}{r} \frac{\partial \omega_i}{\partial r} + \frac{\partial^2 \omega_i}{\partial r^2} \right) + v_i Da \rho_m (1 - \eta) = 0 \quad (9)$$

where  $v_i$  is the stoichiometric coefficients of the  $i$ -th component, corrected to account for the fact that balance equations are expressed in terms of mass.

Additional assumptions have been tailored to the limiting regime. In conditions in which the membrane limits hydrogen permeation, the radial concentration gradients may be neglected and the system may be described through a plug-flow reactor model. The mass balance equations for hydrogen and methane thus become

$$-\frac{\partial \rho_m}{\partial z} + v_m Da^* \rho_m (1 - \eta) = 0 \quad ; \quad -\frac{\partial \rho_h}{\partial z} + v_h Da^* \rho_h (1 - \eta) = \sqrt{\rho_h} \quad (10)$$

where  $Da^* = \frac{Da}{2\gamma} (\sigma^2 - 1)$ .

The CO<sub>2</sub> and H<sub>2</sub>O densities can be expressed in terms of CH<sub>4</sub> density, taking into account the stoichiometry of the reaction

$$\rho_c = \rho_c^0 - \frac{v_c}{v_m} (\rho_m^0 - \rho_m) \quad ; \quad \rho_w = \rho_w^0 - \frac{v_w}{v_m} (\rho_m^0 - \rho_m) \quad (11)$$

and the total amount of H<sub>2</sub> permeating across the membrane may be determined by an overall mass balance

$$\Pi_h = \pi(\sigma^2 - 1) \left[ \rho_h^0 - \rho_h^{out} - \frac{v_h}{v_m} (\rho_m^0 - \rho_m^{out}) \right] \quad (12)$$

On the other hand, when hydrogen permeation is limited by transport within the packed bed a simplified model has been developed for the condition, often verified, in which the characteristic time of reaction is significantly lower than the characteristic time of transport. In this case, the problem can be reduced to a pure-transport problem, in which the mass fractions of all components are tied by the reaction equilibrium conditions. It should be noted that the imposition of this constraint, along with the obvious consideration that the sum of the mass fractions must be equal to 1, results in a problem that can be fully described by determining the behavior of the mass fractions of only two of the four components present in the system.

When the membrane resistance is negligible, the hydrogen concentration in correspondence of the membrane can be assumed to be equal to zero. Given the additional constraint of equilibrium conditions, the methane concentration must also be equal to zero. In these conditions the problem may be studied in terms of an auxiliary variable, resulting from the linear combination of the hydrogen and methane densities

$$\Omega = -v_m \rho_h + v_h \rho_m \quad (13)$$

$$-\frac{\partial \Omega}{\partial z} + \varepsilon \left( \frac{1}{r} \frac{\partial \Omega}{\partial r} + \frac{\partial^2 \Omega}{\partial r^2} \right) = 0 \quad (14)$$

where  $\varepsilon = \frac{D_{rr}}{Pe}$  and the boundary conditions are the same as those reported in Eqs. (4)-(6) for the inlet, outlet, and outer wall. In correspondence of the membrane wall, on the other hand, one can set

$$\Omega = 0 \quad (15)$$

The solution to this problem may be expressed through Bessel's function as

$$\Omega = \Omega^0 \sum_{n=1}^{\infty} \frac{1}{N(\lambda_n)} \exp(-\varepsilon \lambda_n^2 z) R_0(\lambda_n, r) \int_{r=1}^{\sigma} r R_0(\lambda_n, r) dr \quad (16)$$

where

$$\frac{1}{N(\lambda_n)} = \frac{\pi^2}{2} \frac{\lambda_n^2 J_0^2(\lambda_n)}{J_0^2(\lambda_n) - J_1^2(\lambda_n \sigma)} \quad (17)$$

$$R_0(\lambda_n, r) = J_0(\lambda_n r) Y'_0(\lambda_n \sigma) - J'_0(\lambda_n \sigma) Y_0(\lambda_n r) \quad (18)$$

and  $\lambda_n$  are the roots of

$$J_0(\lambda_n) Y'_0(\lambda_n \sigma) - J'_0(\lambda_n \sigma) Y_0(\lambda_n) \quad (19)$$

These expressions are valid when studying an annular domain and when the boundary conditions are of zero concentration on the inner wall and zero flux on the outer wall.

The local permeating hydrogen flux can be determined through

$$\pi_h(z) = \varepsilon \left. \frac{\partial \rho_h}{\partial r} \right|_{r=1,z} = \varepsilon \Omega^0 \sum_{n=1}^{\infty} \frac{1}{N(\lambda_n)} \exp(-\varepsilon \lambda_n^2 z) R'_0(\lambda_n, r) \int_{r=1}^{\sigma} r R_0(\lambda_n, r) dr \quad (20)$$

Given that the inner radius of the reactor is equal to 1, in dimensionless terms, the total mass flow rate of permeating hydrogen is given by

$$\Pi_h = 2\pi \Omega^0 \sum_{n=1}^{\infty} \frac{1}{N(\lambda_n)} \frac{1}{\lambda_n^2} [1 - \exp(-\varepsilon \lambda_n^2 z)] R'_0(\lambda_n, r) \int_{r=1}^{\sigma} r R_0(\lambda_n, r) dr = 2\pi \Omega^0 g(Pe) \quad (21)$$

where  $g(Pe)$  is a function that accounts for the dispersive contribution to mass transport and depends exclusively on the Peclet number and the geometric dimensions of the reactor. Once the Bessel function to use has been identified, it may be used to find the solution to a given problem, with a good degree of approximation. The remaining difficulties lie in the identification of the first root of the Bessel function of Eq. (23),  $\lambda_1$ , and in solving the integral introduced in Eq. (20). With regards to the roots, their value depends on the  $\sigma$  and has been reported in Table 1 for  $\sigma \in [1, 2]$ . It should be emphasized that the correct identification of the first root is of paramount importance for the correct evaluation of the permeate.

Table 1: First roots of the Bessel function reported in Eq. (19) for  $\sigma \in [1.1, 2]$

$\sigma$	$\lambda_1$
1.1	15.378
1.2	7.5220
1.3	6.5000
1.4	4.0500
1.5	2.9000
1.6	2.3755
1.7	2.0118
1.8	1.7388
1.9	1.5420
2.0	1.3068

The integral in Eq. (20) is given by

$$\int_{r=1}^{\sigma} r R_0(\lambda_n, r) dr = -\frac{1}{\lambda_n} (Y_1(\lambda_n) J_1(\lambda_n \sigma) - Y_1(\lambda_n \sigma) J_1(\lambda_n)) \quad (22)$$

In order to verify that the problem has been solved correctly, Eq. (23) shown below should be verified.

$$\sum_{n=1}^{\infty} \frac{1}{N(\lambda_n)} R_0(\lambda_n, r) \int_{r=1}^{\sigma} r R_0(\lambda_n, r) dr = 1 \quad (23)$$

which corresponds to the condition  $\Omega = \Omega^0$  in  $z = 0$ , from Eq. (16). It has been observed that an error lower than 2% must be achieved to guarantee the correctness of the solution. Equations (12) and (21) yield the permeate flow rate obtained in conditions in which hydrogen permeation is limited by the membrane and by transport, respectively. In order to determine, for a given operating condition, the actual permeate flow rate, the smallest of the two values should be taken. In correspondence of the critical pressure, the two expressions will result in the same value.

## 5. Conclusions

This work presents an overview of studies carried out on modeling and design of membrane reactors for hydrogen production. In particular, the evolution from a fully coupled model to a simplified, pure transport, model is explained and justified through observations made on the permeate flow rate, hydrogen yield and recovery, and concentration profiles. In addition, the detailed procedure for the use of the simplified model has been reported.

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