

MASS TRANSFER COEFFICIENT IN MULTI-STAGE REFORMER/MEMBRANE MODULES FOR HYDROGEN PRODUCTION

Diego Barba^a, Mauro Capocelli^{a,*}, Marcello De Falco^a, Giovanni Franchi^a, Vincenzo Piemonte^b

^aUnit of Process Engineering, Department of Engineering, Università Campus Bio-Medico di Roma, via Álvaro del Portillo 21, 00128 Rome, Italy.

^bUnit of Chemical-physics Fundamentals in Chemical Engineering, Department of Engineering, Università Campus Bio-Medico di Roma, via Álvaro del Portillo 21, 00128 Rome, Italy.

*Corresponding author: m.capocelli@unicampus.it;

Abstract

Hydrogen is a promising energy carrier, exploitable to extract energy from fossil fuels, biomasses as well as intermittent renewable energy sources and its generation from fossil fuels with CO₂ separation at the source is one of the most promising pathway for fossil fuels utilization.

This work is focused on a particular configuration, called Reformer and Membrane Module (RMM), which alternates stages of Steam Reforming (SR) reaction with H₂ separation stages to overcome the thermodynamic limits of the conventional SR. The configuration has numerous advantages with respect to the more studied and tested membrane reactors and has been tested on a pilot scale during a pilot-scale research project.

Although the numerous modelling works appeared in the literature, the design features of the material exchanger (in the so-called RMM architecture) of different geometrical configurations have not been developed and the mass transfer correlations, capable of providing design tools useful for such membrane modules, are not available.

The purpose of this work is therefore to apply a physical-mathematical model of the mass transfer, in three different geometries, considering both concentration polarization and membrane permeation, in order to: i) simulate the cited experimental results, ii) estimate the scaling-up correlations for the “material exchange modules”; iii) identify the mass transfer limiting regime in relation to the gas mass flow rate.

1. Introduction

Hydrogen is a promising energy carrier, exploitable to extract energy from fossil fuels, biomasses as well as intermittent renewable energy sources [1-3]. Generating hydrogen from fossil fuels is among the most promising alternative in the framework of carbonaceous fuels utilization with simultaneous CO₂ sequestration [1,2]. The adoption of H₂ as an energy vector would represent a radical change in the energy sector impacting the production, distribution and consumption since it can be converted into both electrical power and heat using fuel cells or combustion engines without generating CO₂ emissions locally [4-6].

The current world hydrogen consumption is more than 50 Mton/year [1] and is consistently devoted to the chemical and petrochemical sectors, e.g. for ammonia and methanol synthesis, hydrogenation, hydrocracking and hydrodesulphurization processes with a very small fraction currently used for energy purposes [1-4].

Nowadays, the most reliable and cheapest way to produce H₂ is the steam reforming (SR) of light hydrocarbons (natural gas, gasoline) [2,3] that cost in the range of 2-4 \$/kg_{H₂} [1]. The technology for SMR is well developed and is applicable to a wide range of scales, from 1 t/h H₂ (small decentralized units) to about 100 t/h (large ammonia manufacturing plants) and renewable energy sources would hardly replace these sources in the next future. At present, the global warming potential (GWP) of hydrogen production via the SMR process is around 10 kg CO₂/kg of H₂ produced [4,6-9].

Even including the costs of CO₂ recovery and sequestration, the cost of hydrogen production from fossil fuels is expected to be much lower than alternative production routes (e.g. electrolysis) in large-scale markets [8-10]. Looking at the projected trends (150 million tonnes by 2040) it may replace more than 18 million barrels/day of petroleum assumed that the hydrogen fuel cell vehicles have been made 2.5 times more efficient than gasoline cars by that time [11,12].

The Membrane Reactors (MR) are manufactured including selective membranes directly inside the reaction environment (e.g. in the catalytic tubes) so that the hydrogen produced by the reactions is immediately removed [13]. The MR configuration has been extensively tested and discussed as the solution to overcome the thermodynamic limit of SR thanks to the continuous separation of the produced H₂ [4,5,13-15]. Pd-based supported membranes are the most promising type thanks to the very high selectivity and the good permeation flux resulting into H₂ purities > 99%. Beside the costs of precious metals, the major challenges for their complete affirmation are the mechanical stability of thin membranes as well as the chemical stability (e.g. poisoning by CO and H₂S) [5]. Some

interesting results appeared also in the context of dense ceramic and microporous membranes, although there is not a clear winner from the commercial point of view [5].

An alternative approach is to arrange separation modules downstream to reaction units creating a multi stage reactor-membrane modules (RMM configuration), object of this study. An innovative 20 Nm³/h prototypal RMM plant has been developed, designed, built and tested during the Research Project (founded by MIUR, Italy) entitled “Pure hydrogen from natural gas reforming up to total conversion obtained by integrating chemical reaction and membrane separation” [16]. The pilot plant is represented in Figure 1 and comprises two-step reformers and membrane modules working at 550–650°C. It was built and tested by Tecnimont-KT Kinetics Technologies in Chieti (Italy) and represents the unique example of this technology at Technology Readiness Level higher than 6 [17,18]. More than 1500 hours of experiments on three types of commercial membranes addressed the potential of selective membrane application in industrial high-temperature chemical processes. The RMM, based on 2 stages of reaction and separation, allows to exceed equilibrium conversion of about 20%. The higher the removal of hydrogen carried out with membrane, the higher the increase of global feed conversion. By increasing hydrogen recovery up to 50% and 70% through sweeping steam, the 2-stage RMM configuration may allow to exceed equilibrium conversion up to 30 and 40% respectively. RMM architecture working at 600°C and 650°C may reach a conversion up to 72% and 90% respectively with 4 stages [16-20]. More recently, Reinertsen and SINTEF are working on a similar project with the aim of realizing a package unit of a pilot 40 ft - container producing 25-100 Nm³/h hydrogen [21].



Figure 1 - Overall View of the Pilot Plan

The first experimental data collected at the Chieti Pilot plant during the testing phase as well as the average H_2 permeability at the operating conditions can be found in our previous works [16-19]. The authors have also assessed and compared the benefits and drawbacks of the MMR configuration in relation to the MR [17-20,22]. Globally, the Research Project proved that the RMM presents a production cost 10% lower than those of the conventional H_2 scheme, allows to implement a direct CO_2 sequestration unit [22] and shows the following main advantages with respect to the MR arrangement:

- the MR is mechanically complex and presents a large and unpractical heat transfer surface: in the MR, the concentric tube geometry yields an imbalance between the surfaces required for heat transfer (outer tube) and the available surface for mass transfer (of the inner membrane tube);
- RMM enables the de-coupling of separation and reaction operating temperature, increasing the stability and the durability of the membranes; and equivalently enabling the independent optimization of the reforming temperature;
- RMM simplifies the mechanical design of membrane tubes compared with the one embedded in a catalyst tube; a simple shell and tube geometry can be selected for the tubular separation module;

- RMM simplifies maintenance of the Pd/Ag membrane modules and catalyst replacement.

With these premises, we analyzed multiple data related to the pilot plant experiments and, through the mathematical modeling dedicated to the membrane modules, we estimated the mass transfer coefficients. By selecting several data at different flow-rate, gas composition, temperatures and different geometrical configurations, in this work we calculated semi-empirical correlation useful to scale-up the RMM. The aforementioned mathematical model has been carefully validated through experimental data in order to extrapolate the values of the transport coefficients and the correlations necessary to scale-up the “material exchangers”, which represents the core of the RMM architecture.

From the permeation modelling point of view, a first benchmark in the theoretical modelling of H₂ permeation through a Pd self-supported membrane has been developed by Ward et al. [23]. The model was utilized to individuate the rate-limiting processes among the fundamental kinetic steps: i) external mass transfer (binary mixtures); ii) surface adsorption and desorption; iii) transitions to and from the bulk metal; iv) diffusion within the metal. On this basis, Caravella et al. modelled the transport in Pd-alloy membranes considering both the non-ideal hydrogen transport in membrane (influences of support, inhibition by CO by the Sievert-Langmuir equation and the effect of membrane polarization) and external mass transfer resistance on the hydrogen permeation [24-26]. Their results are reported as an “adjusted” pressure exponent of the Sieverts-type empirical law and it is function of several factors such as temperature, total pressure, membrane thickness and non-ideal behaviours. The theoretical meaning of the adjusted-Sieverts exponent can be explained by dividing the overall hydrogen permeation into several elementary steps (adsorption, desorption, diffusion in the Pd-based layer, and the two transitions surface-to-bulk and bulk-to surface) [26,27]. Sarti et al. tested a Pd₈₀-Ag₂₀ (NGK) in a shell & tube configuration with different mixtures and operating conditions. The experimental tests were performed used mixture of H₂/N₂/CH₄. At the same time a theoretical model, based on the previous model of Ward et al., was developed to analyse the competitive adsorption of hydrogen and carbon monoxide molecules. The experimental tests show the existence of a concentration polarization phenomena due to non-permeable species [28-31]. In the first experimental setup [28], Sherwood number follow a boundary layer type of correlation whereas in the second [30], it was found a linear correlation between Sherwood and Péclet numbers. Globally, the concentration polarization has been extensively discussed in the literature and has been included in several models and at different conditions, mainly by modifying the exponent for the pressure dependence in the Sievert law equation [26-32].

Other authors discussed the transport-reaction-permeation regimes also addressing the competitive adsorption limiting the overall H₂ permeation [14,15]. Barbieri et al. [33] interpreted the observed decrease in hydrogen flux through a palladium-silver membrane over the time with a CO inhibition (by up to 2 bar) in terms of a Sieverts-Langmuir model, assuming a linear correlation between the decrease in hydrogen permeance and the surface coverage by carbon monoxide. Consequently, they accounted for the membrane surface fraction not available for hydrogen permeation using a Langmuir affinity constant for carbon monoxide and a temperature dependent 'permeance reduction factor' [33].

At the best of our knowledge, although the numerous modelling works appeared in the literature, the design features of the material exchanger (in the so-called RMM architecture) of different geometrical configurations have not been developed and the mass transfer correlations, capable of providing design tools useful for such membrane modules, are not available.

The purpose of this work is therefore to apply a physical-mathematical model of the mass transfer, in three different geometries and considering both concentration polarization and membrane permeation, to simulate the cited experimental results, thereby estimating the scaling-up correlations for the "material exchange modules".

2. Materials & Methods

The Pilot Plant, realized by Tecnimont-KT Kinetics Technologies in Chieti (Italy), includes two reaction zones (R1, R2) and two separation zones as depicted in the block diagram of Fig. 2. The reaction zone is 15 meters high and consists of a radiant area (with burners and catalytic tubes) and a convective zone where superheated steam is produced. The separation zone consists of two membrane separators; the first presenting two membranes (M-01 and M-02) working in parallel, the second including a single module (M-03). The natural gas (NG) is provided by the NG network at 12 barg and is desulfurized in the HDS unit. Steam is added to the feed and the mixture is preheated in the convective zone. The stream enters the first reformer where the reactions take place at 550-680°C [16-19]. The effluent (syngas) is cooled in an air cooler to 450 °C and enters in the first stage of separation. The syngas is depleted of H₂ (30-35 %) and enters in the second reaction zone and successively separated in the second membrane stage. Permeates of both membranes are mixed and sent to the flare or to the cooling system in case of sweeping (water vapor condensation with

cooling water in closed cycle). The retentate stream is sent to the flare. The tests have been realized for 4 months to investigate the long term stability of the structured catalyst and membrane modules, to carry out a comparison between structured catalyst and traditional Ni-based pellets, to test effectiveness of RMM architecture integrated with CPO reactor and to prove the improvement obtained by the RMM enhancement. Further details on the pilot plant can be found in the cited literature [16-19].

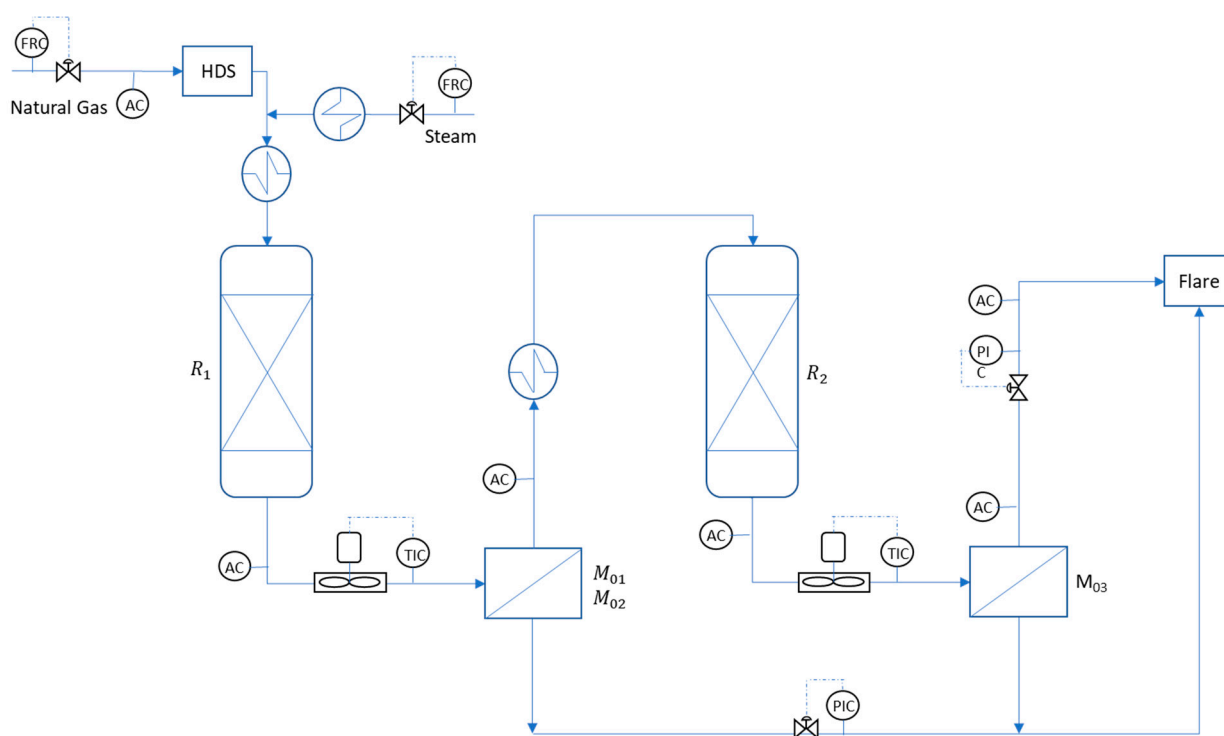


Figure 2. Simplified process scheme of the Pilot Plant including two reactors and two membrane modules.

More than 70 tests, each running for around 10 hours, have been performed varying the main operating conditions: temperature and pressure as well as steam to carbon ration in the reforming section and flowrate in the membrane modules. At the beginning of the test runs the heating is realized by steam and nitrogen to reach a temperature above 300°C (heating rate under 2.5-3°C/min). Due to the endothermicity of the reaction, a slight temperature drop is observed after the feed introduction. This paper focused on the results related to the permeation zone, highlighted in Fig. 2 and presented in the Section 4. The main independent variable considered for the scaling-up correlations is the syngas flowrate (out of the reforming) resulting in different mass transfer coefficients.

The main geometrical characteristics of the separation units are summarized in the Table 1. The first membrane module M-01 contains 13 tubular membrane of palladium supported on alumina (Fig. 2a). The M-02 module (Figure 3-b) consists of five plate membranes with each side consisting of a dense Pd–Ag layer deposited on the external surface of a α -alumina support (each side is formed by two Pd–Ag panels welded in series). Both membranes can be used with sweeping gas. The last membrane module M-03 used in the present work is similar to the M-01 but includes three tubular membranes (Fig 3-c).

The permeability value, that accounts for the diffusion and solubility of hydrogen in palladium and palladium-silver alloys, is calculated for the different materials on the basis of the theoretical and experimental works of Holleck [34] and Sarti et al [28] according to the following general expression by recalling that diffusion is an energetically activated process and that Sieverts' constant represents the equilibrium reaction constant for hydrogen dissociation:

$$P_{H_2} = \frac{1}{2} D_{0,H} \exp\left(\frac{\Delta S_R^0}{R}\right) \exp\left(-\frac{E_D + \Delta H_R^0}{RT}\right) = P_{H_2}^0 \exp\left(-\frac{E_a}{RT}\right) \quad (1)$$

Where $P_{H_2}^0$ is the permeability pre-exponential factor and E_a is the activation energy for hydrogen permeability, that contains contributions from the activation energy for the diffusion of hydrogen atoms, the standard enthalpy of the surface dissociation reaction as well as the entropy change of the dissociation reaction.

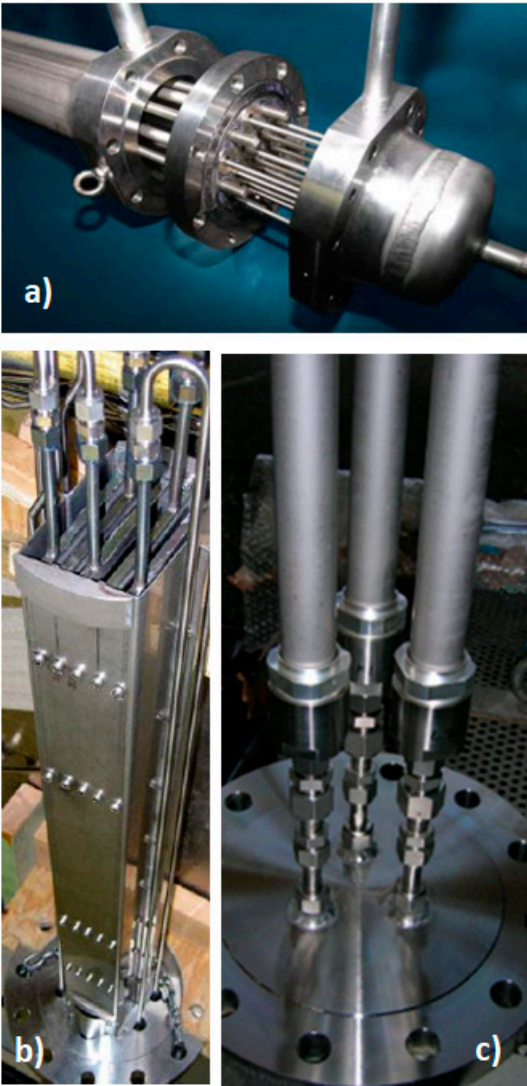


Figure 3. Photography of the membrane modules a) tubular M-01; b) Flat Plates M-02; c) tubular module M-03

Geometrical Features	Membrane Modules		
	M-01	M-02	M-03
ID _{shell} , in	5	6	6
N _m	13	5	3
OD _{tube} mm	14	-	30
δ μm	2.5	25	2.5
L cm	69	0.39 x 2	45
A _{TOT} m ²	0,4	0.6	0.13
T, °C	408-438	402-424	397-455
P ^R , bar	11-11.5	11.5	11
P ^P , bar	1,4-1.6	1.4	1.3
W, kg/h	29-46.4	29-46.4	29-46.4
F, kmol/h	1.9-3.1	1.9-3.1	1.9-3.1

Table 1 - Characteristics of the experimental apparatus and operative conditions

3. Mathematical Modelling

The present section describes the differential equations used to model the permeation phenomena and the procedure to estimate the mass transfer coefficient from the experimental data.

The main variables of the mathematical model are represented in Fig. 4, that shows the longitudinal flux of the syngas (in the external tube) flowing in counter-current to the permeated flux of hydrogen and sweep gas (in the inner tube). The schematic representation is based on the experiments related to the shell & tube configuration (M-01 and M-03) with the H₂ flux occurring from the outside to the inside of the tubes, where OD_t is the external diameter of the inner tube and ID_s is the diameter of the shell. The same configuration can be used for plate membranes (M-02) where the permeation channel is realized between two interspaces.

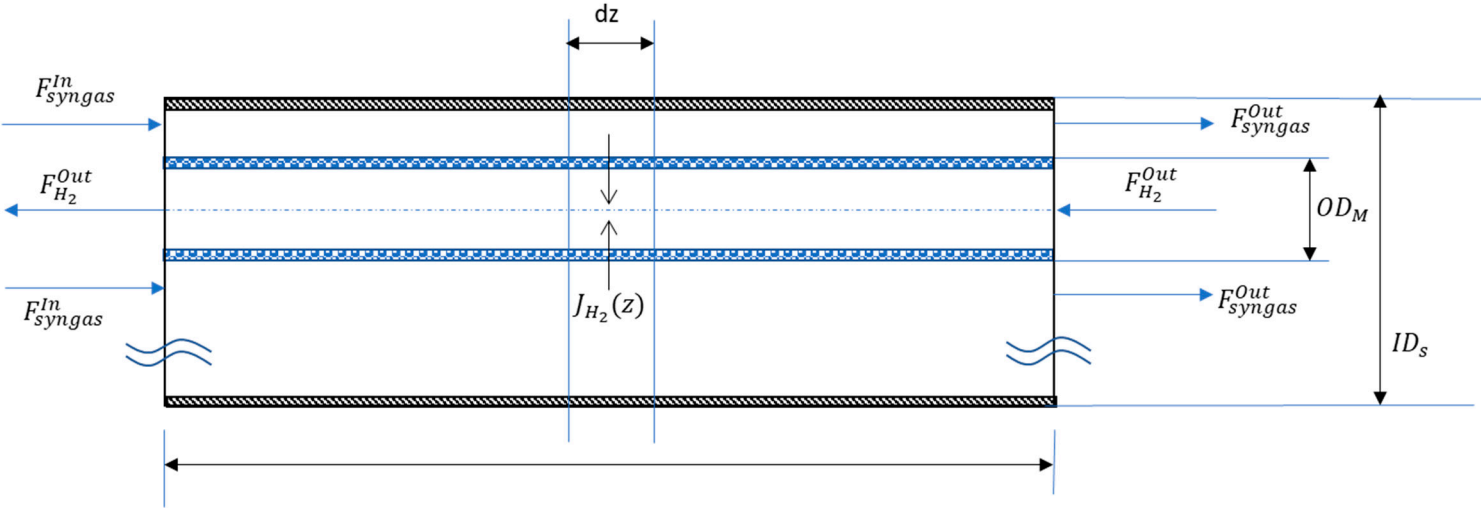


Figure 4. Reference scheme of the Material Exchanger for the mathematical model

The membrane is simulated as an isotherm and isobar material exchanger (considering both permeance and molar fraction in the retentate side as constants) enabling the selective hydrogen permeation. Referring to the membrane infinitesimal volume of a length dz , the variation of the mass flow F_j can be written as in equations 2 and 3, respectively for the permeate and the retentate side (with the minus sign if the flow is counter-current).

$$\frac{d}{dz} F_j^R = -J_j * 2\pi(r + \delta) \quad (2)$$

$$\frac{d}{dz} F_j^P = \pm J_j * 2\pi(r + \delta) \quad (3)$$

The Hydrogen flux J_{H_2} through the membrane is calculated by adopting the schematization of the film theory represented in Fig. 5. The mass transfer resistances considered in the diffusive process are concentrated from the bulk to the membrane wall on both the side of the membrane (retentate/permeate side) as well as through the palladium membrane (internal diffusion according to the Sievert-Fick law). In the absence of sweeping gas the resistance in the permeate side is null and $p_{H_2}^{RI} = p_{H_2}^P$. The fluxes $J_{H_2}^R$, $J_{H_2}^M$, $J_{H_2}^P$, respectively related to the driving force in the three abovementioned zones, are expressed by the Equations 4-6. For the experimental tests performed in absence of vapour sweeping, the resistance in the permeate side is neglected and the analysis is focuses on the mass transport coefficient on the retentate side, explicated by Eq.7 that takes into account the concentration polarization phenomena with the mass transfer coefficient F_G^{R*} depending on the concentration at the interface [38].

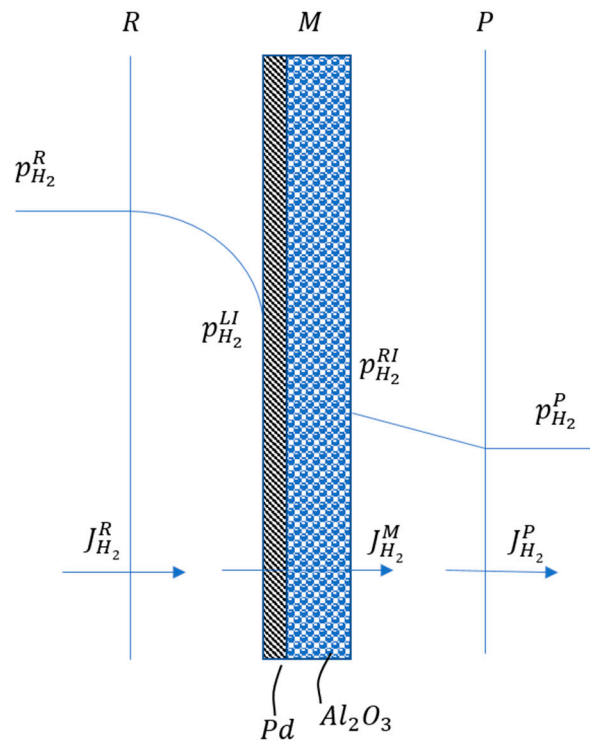


Figure 5. Schematic of the Film Theory considered for the flux characterization

$$J_{H_2}^R = F_G^{R*} (p_{H_2}^R - p_{H_2}^{LI}) \quad (4)$$

$$J_{H_2}^M = \frac{P_{H_2}}{\delta} \left(\sqrt{p_{H_2}^{LI}} - \sqrt{p_{H_2}^{RI}} \right) \quad (5)$$

$$J_{H_2}^P = F_G^{P*} (p_{H_2}^{RI} - p_{H_2}^P) \quad (6)$$

$$F_G^{R*} = \frac{F_G^R}{(p - p_{H_2})_{ML}} = F_G^R \ln \left(\frac{1 - y_{H_2}^{LI}}{1 - y_{H_2}^R} \right) \quad (7)$$

A mathematical algorithm is implemented to estimate the mass transfer coefficients in the retentate side (F_G^R) by knowing the observed experimental compositions, with the partial pressure as the unknown variable alongside the membrane. On the other hand, the membrane permeance is fixed on the basis of Eq. 1 (calculated in agreement with the literature results [28,29,34]) by dividing the permeability P_{H_2} by the membrane thickness δ and thus does not represent a dependent variable of the mathematical model. The calculation procedure starts by assuming an initial value of F_G . At each step, the algorithm calculates the molar fraction of hydrogen on retentate side ($y_{H_2}^{LI}$) by solving the nonlinear Eq. 7 (by means of Levenberg-Marquardt algorithm).

The Eqs. 8 and 9 show the linearization of the driving force of the Sieverts Law here implemented to calculate the overall mass transfer coefficient F_{OG} in the

$$J_{H_2}^R = J_{H_2}^M \quad (7)$$

$$J_{H_2}^M = \frac{P_{H_2}}{\delta} \frac{p_{H_2}^{IS} - p_{H_2}^{ID}}{\sqrt{p_{H_2}^{IS}} + \sqrt{p_{H_2}^{ID}}} \quad (8)$$

$$\frac{1}{F_{OG}} = \frac{(P - P_{H_2})_{ML}}{F_G} + \frac{\sqrt{P_{H_2}^{IS}} + \sqrt{P_{H_2}^{ID}}}{P_{H_2}/\delta} = \frac{1}{F_G^*} + \frac{1}{P_{H_2}^*} \quad (9)$$

The numerical integration is performed in Matlab by dividing the domain in 100 elements. The algorithm stops when the difference between flow of hydrogen on permeate side (at the inlet of membrane) simulated by the mathematical model and the experimental value is minimized. In particular an error of 1% between calculated and experimental values has been accepted.

Eventually, the estimated mass transfer coefficient F_G^R can be correlated with the geometrical and operating conditions, keeping in mind that the experiments are realized with different membranes, at different temperature and flow rates by means of the non-dimensional numbers Re , Sc and Sh , also depending on the physical properties of the mixture on retentate side. The analysis of the competitive adsorption, well characterized in the abovementioned papers [13-15], is kept outside of the model due to the low concentration of CO. The operation and geometrical parameters assumed to calculate these numbers are reported in the Table 2, respectively for the tubular (M-01 and M-02) and the plate (M-03) modules.

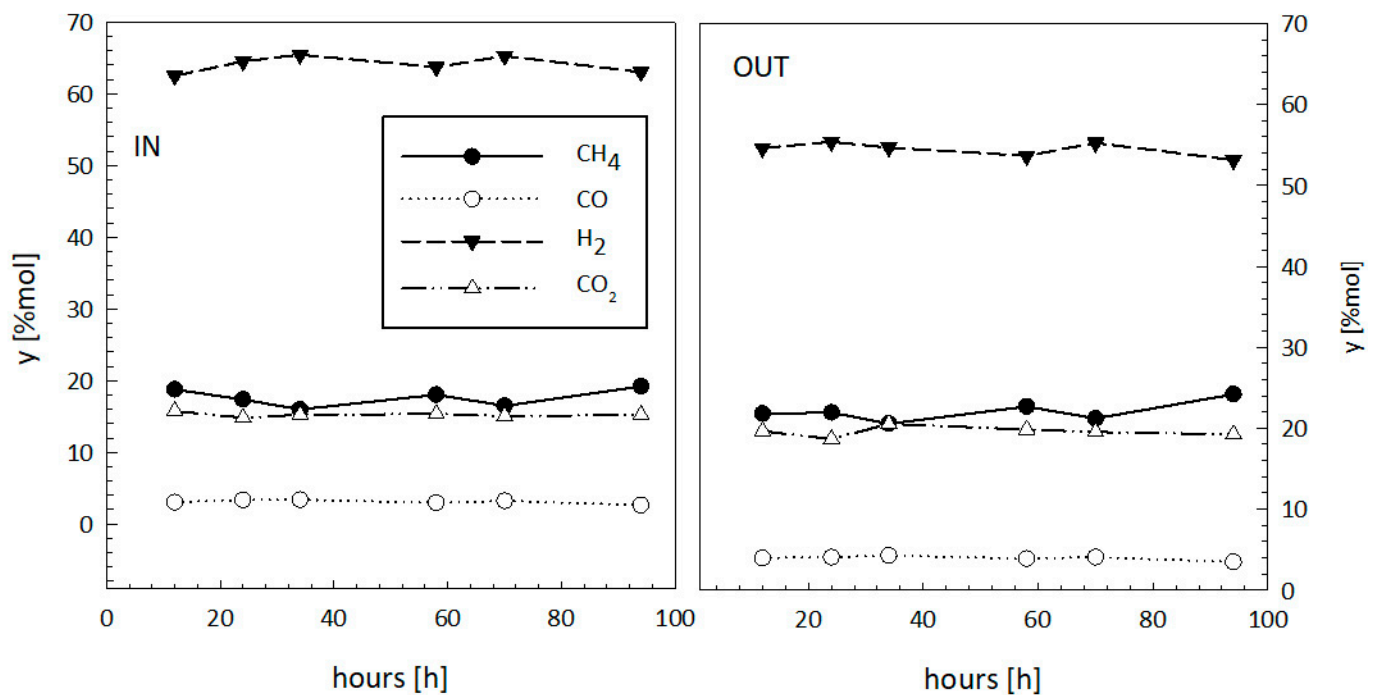
Table 2 - Parameters and dimensionless numbers in relation to the module characteristics

Variables	Tubular membrane (M-01, M-02)	Flat plat module (M-03)
$v, \text{m/s}$	$\frac{F}{3600 \rho_m^R a_s}$	$\frac{F}{3600 \rho_m^R a_s}$
a_{shell}, m^2	$\frac{\pi(ID_{shell}^2 - OD_t^2 N_m)}{4}$	$6 dw$
D_{eq}, m	$4 \frac{(P_t^2 - \pi OD_t^2 / 4)}{\pi OD_t}$	$2 \frac{dw}{d + w}$
Re	$\frac{\rho v D_{eq}}{\mu}$	$\frac{\rho v D_{eq}}{\mu}$
Sc	$\frac{\mu}{\rho D_{H_2, m}}$	$\frac{\mu}{\rho D_{H_2, m}}$
Sh	$\frac{F_G^R D_{eq}}{c_{tot} D_{H_2, mix}}$	$\frac{F_G^R D_{eq}}{c_{tot} D_{H_2, mix}}$

4. Results & Discussion

As described in Section 2, 70 test runs have been selected for the purpose of this work. The experimental data obtained from a singular test (as a clarifying example) are reported in Fig. 6. The inlet and outlet flowrates and temperatures were available as experimental data for the coefficient estimation.

The figure shows the gas concentrations both at the outlet of the first reactor (entrance to the membrane) and at the outlet of the membrane. The example is related to the first installed membrane module (M-01). The operating conditions are also reported, referring to the process diagram of Fig. 2. The Table also reports the characterization of the natural gas supplied to the overall RMM process.



Natural Gas from Snam Gas Network

PCI kJ/Nm ³	ρ kg/Nm ³	CH ₄ %mol	C ₂ + %mol	CO ₂ %mol	N ₂ %mol
33873	0.684	99.392	0.078	0.053	0.477

Operating Parameters

Variable	NG	Steam	R01	ECN ^R	ECN ^P
F, kg/h	5	24	-	-	-
T, °C	-	-	550	408	-
P, barg	-	-	10.3	11.3	1.47

Figure 6. Complete report of a single test run in the M-01

At this point, to perform the mass transfer coefficient estimation, the experimental data have been grouped in different levels of flowrate to find a possible correlation between F_{OG} and the Reynold number, relative to the three tested membrane: 5 values for M-01, 3 values for M-02 and 3 values for M-03. These average experimental data (eg. composition, hydrogen recovery, flow-rate and permeability) are summarized in Tables 3-5.

Table 3 - Experimental tests: mean composition and operative conditions of the M-01

Parameter	Unit	1		2		3		4		5	
		IN	OUT	IN	OUT	IN	OUT	IN	OUT	IN	OUT
F	kmolh ⁻¹	1.94	1.74	2.10	1.91	2.30	2.12	2.57	2.34	3.06	2.78
H ₂ O	mol %	56	60	54	58	57	61	57	62	57	62
CO	mol %	1	2	1	1	1	1	1	1	1	1
CO ₂	mol %	6	7	6	7	6	7	6	7	6	7
CH ₄	mol %	8	9	11	13	8	9	9	10	9	10
H ₂	mol %	29	22	28	21	28	22	27	20	27	20
HRF	%	32		32		28		32		33	
\bar{J}	kmolh ⁻¹ m ⁻²	0.471		0.480		0.491		0.513		0.712	
$\overline{K_{H_2}}$	kmolh ⁻¹ m ⁻² bar ^{0.5}	1.92		2.13		2.01		2.10		2.16	

Table 4 - Experimental tests: mean composition and operative conditions of M-02.

Parameter	Unit	1		2		3	
		IN	OUT	IN	OUT	IN	OUT
F	kmolh ⁻¹	1.94	1.81	2.31	2.15	3.06	2.89
H ₂ O	mol %	56	58	56	60	57	60
CO	mol %	1	2	1	1	1	1
CO ₂	mol %	6	7	6	7	6	6
CH ₄	mol %	8	9	9	9	9	10
H ₂	mol %	29	24	28	23	27	23
HRF	%	23		24		20	
\bar{J}	kmolh ⁻¹ m ⁻²	0.209		0.218		0.239	
$\overline{K_{H_2}}$	kmolh ⁻¹ m ⁻² bar ^{0.5}	0.21		0.22		0.24	

Table 5 - Experimental tests: mean composition and operative conditions of M-03.

Parameter	Unit	1		2		3	
		IN	OUT	IN	OUT	IN	OUT
F	kmolh ⁻¹	1.82	1.80	2.23	2.20	2.84	2.80
H ₂ O	mol %	54	55	55	56	56	57
CO	mol %	2	2	2	2	1	1
CO ₂	mol %	8	8	8	8	8	8
CH ₄	mol %	7	7	7	7	7	7
H ₂	mol %	29	28	28	27	28	27
HRF	%	3		4		5	
\bar{J}	kmolh ⁻¹ m ⁻²	0.175		0.230		0.326	
$\overline{K_{H_2}}$	kmolh ⁻¹ m ⁻² bar ^{0.5}	4.97		4.93		5.47	

By implementing the described procedure with the independent variables fixed at the values in Table 3-5, the mass transfer coefficient F_G has been estimated. Figure 7 reports the F_G estimation results versus the Reynolds number characterizing each experiments. Each point represents the average value at each Reynolds number with error bars confined in the range $\pm 15\%$. The values globally follow a good linear correlation with the Reynolds number in the semi-log diagram, qualitatively confirming the observations made by Catalano et al. [28].

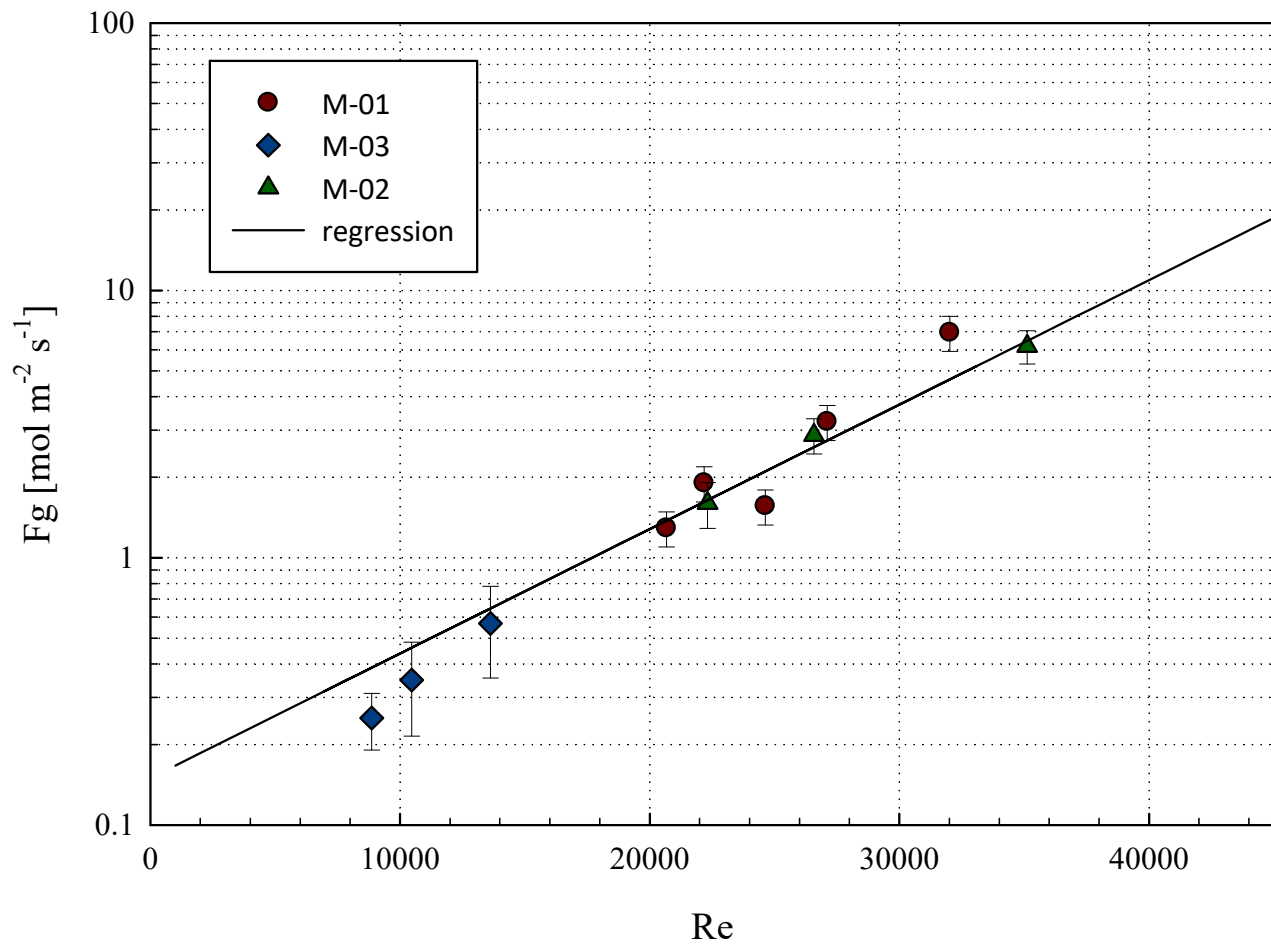


Figure 7. Mass transfer function of Reynolds number.

By adopting the approach of non-dimensional analysis the mass transfer dimensionless group j_D (Eq. 10) [35] is correlated with the Reynolds number in Figure 8.

$$j_D = Sh \cdot Sc^{-1/3} \quad (10)$$

This representation allowed to produce a correlation equation (Eq. 11) valid in the range of tested conditions for the different geometries.

$$j_D = 9.298 \cdot \exp(Re \cdot 10^{-4}) \quad (11)$$

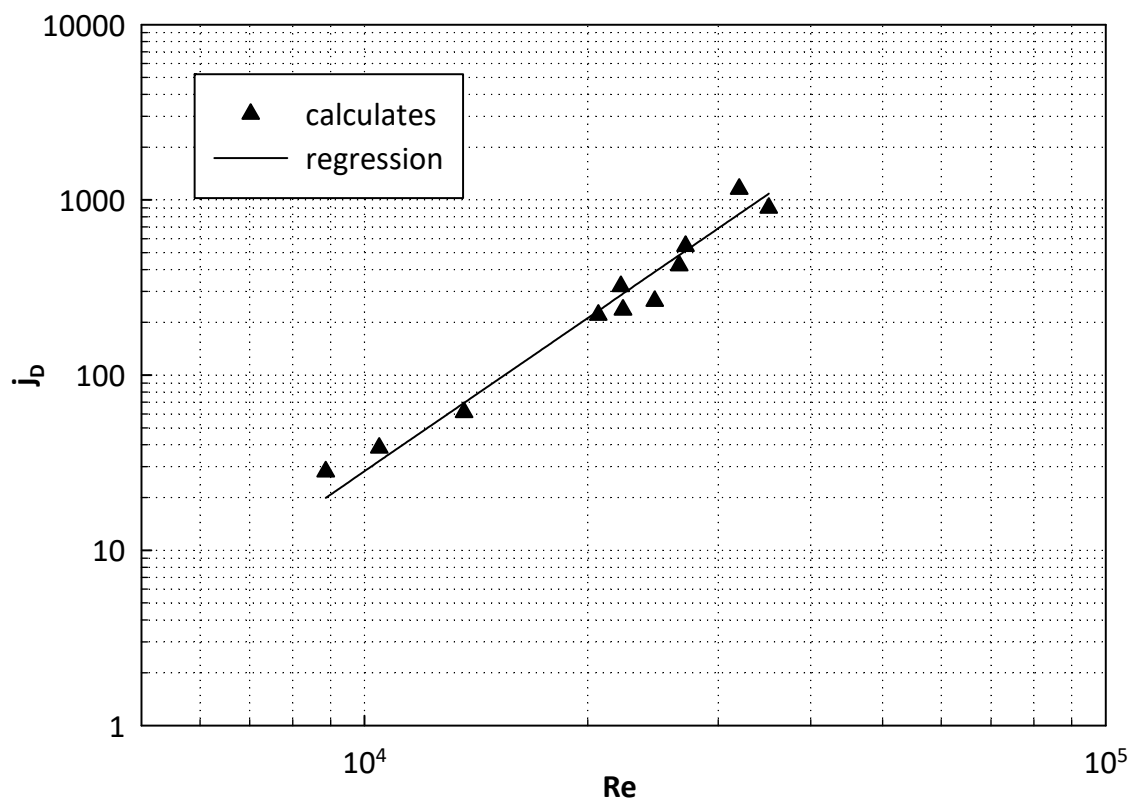


Figure 8. J_D vs. Re

Furthermore, to test again the reliability of the procedure, the obtained correlation (Eq. 11) has been tested by reproducing the experimental results by implementing our model with a feedforward approach where, in this case both the permeability and the F_G are known parameters and this latter is calculated though Eq. 11. The modelling results, presented again in comparison with the observed ones, are in the form of calculated compositions at the exit of the membrane modules. These results are compared against the experimental values in the Parity diagram of Figure 9, finding an acceptable agreement. This last validation result confirms the goodness of the correlation obtained for the gas-side coefficient.

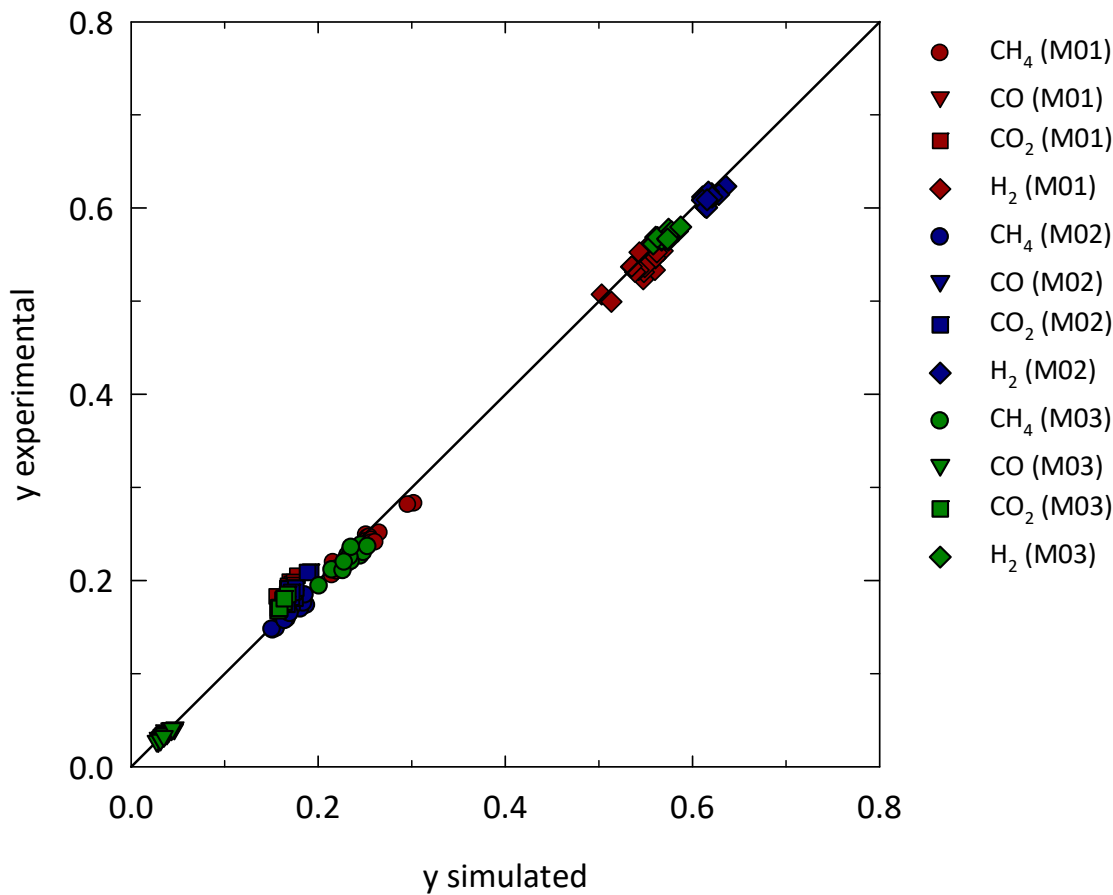


Figure 9. Parity plot of gas composition (molar fraction) for the whole experimental campaign.

On this basis, referring to the film theory schematized in Fig. 5, it is possible to calculate the relative weight of the mass transfer resistance R of the elementary steps (in-series), reported in Eq. 12 and 13, respectively for the gas-phase in the retentate zone R^{cp} (including the concentration polarization) and the one related to the permeation through the membrane R^m .

$$R^{cp} = \frac{(P - P_{H_2})_{ML}}{F_G} \quad (12)$$

$$R^m = \frac{\sqrt{P_{H_2}^{IS}} + \sqrt{P_{H_2}^{ID}}}{K_{H_2}} \quad (13)$$

Figure 10 shows the calculated resistance for the experimental conditions versus the Reynolds number. The resistance relative to the permeation step through the membrane is confined in a band (red) between the calculated values for the tubular (M-01,02) and plane (M-03) modules, having

different thicknesses and different Pd-Ag ratios. The concentration polarization resistance R^{cp} is an order of magnitude higher than the resistance R^m due to the permeation in the membrane layer (according to the mechanisms postulated by Sieverts). It is worth of noticing that these data were obtained for membranes of different materials and different configurations. Therefore, in this work we enabled the calculation of the mass transfer coefficients in these peculiar “material exchangers” highlighting the two regimes of Fig. 10, practically extending the work of Catalano et al. [27,28], being realized at very low numbers of Reynolds.

In the left side of the graph, the gas-side transport appears the limiting step; in the second, for Reynolds numbers greater than 25000, the two resistances are comparable. As the number of Reynolds increases, the controlling step becomes the transport across the membrane, characterized by the Sievert's law.

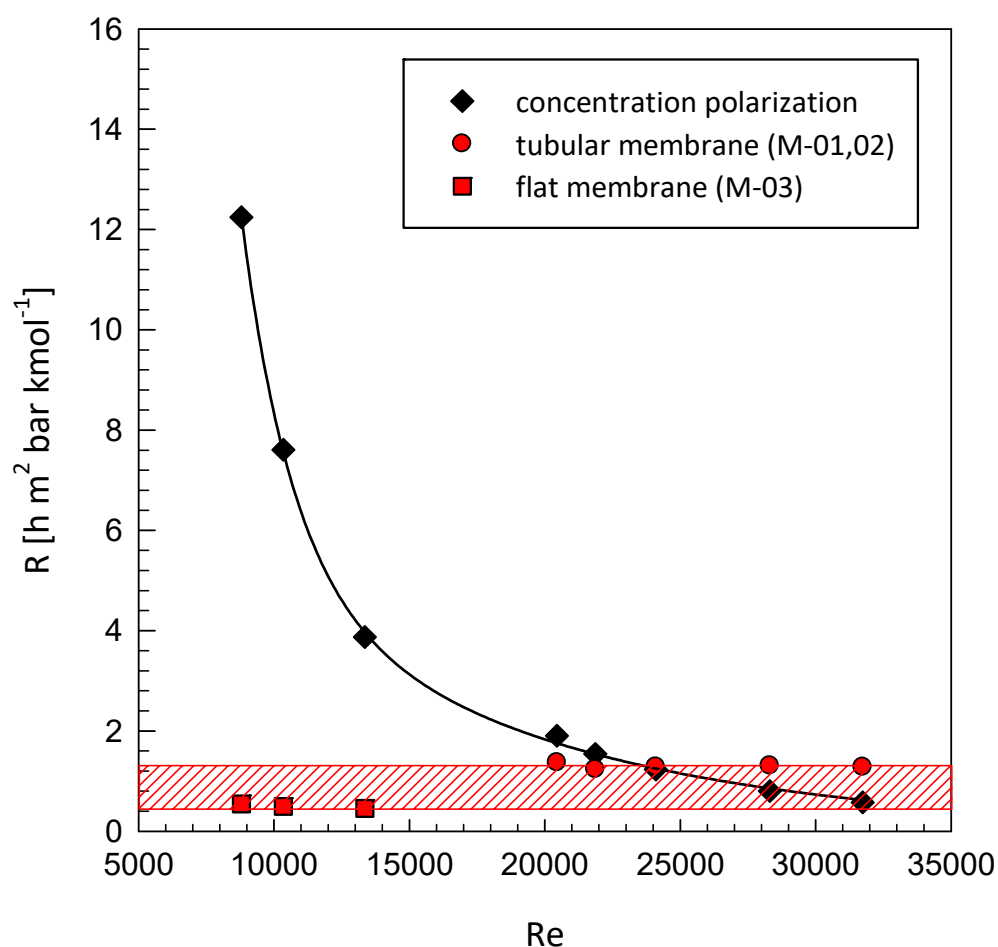


Figure 10. Effect of the Reynolds number on the mass transfer resistance in the gas phase and through the membrane.

5. Conclusions

The extensive use of hydrogen as a carrier would be a solution to the current conflict between economic expansion and pollution. It is also the only way to decarbonize the conversion processes of fossil fuels, waste and biomass. In this paper we give new strength to the research on multistage reactors with intermediate hydrogen separation (so called RMM architecture), focusing in particular on the “material exchanger” design, basically on the scale-up of these arrangement of metal membrane devices. The correlations now available in the literature focused on the estimation of the permeation direct from the Sievert Law (with or without changes of the exponent relating to partial pressures) resulting into a partial or inaccurate approximation of the phenomenology. Our approach, although still affected by simplifications, allows a more correct estimation of the transport coefficients in the membrane material exchangers for H₂ separation, tested for different membrane layers, composition as well as different operating conditions straddling two zone characterized by two different rate-limiting steps.

In this work, we report the experimental tests obtained at the pilot plant designed during the R&D Project entitled “Pure hydrogen from natural gas reforming up to total conversion obtained by integrating chemical reaction and membrane separation” and constructed by Tecnimont-KT Kinetics Technologies in Chieti (Italy). Many test runs have been collected and organized in relation to the flow rates and the membrane-type.

A good correlation between our model and the experimental results validate the estimation of mass transfer coefficient. Furthermore, it was possible to find reliable scaling-up correlations including the whole set of data from different membrane configuration and operation conditions. The proposed correlation also allowed us to show that in the operating conditions, the mass transfer resistance due to concentration polarization can limit the hydrogen flux.

Nomenclature

- a = shell area of membranes [m^2];
- $D_{H_2,m}$ = diffusivity of hydrogen in the mixture retentate side [m^2s^{-1}];
- D_{eq} = equivalent diameter of membranes [m];
- d = channel depth [m];
- E_a = activation energy for hydrogen permeation through metallic membranes [J];
- F = molar flow rate [kmolh^{-1}];
- F_G = mass transfer coefficient [$\text{kmolh}^{-1}\text{m}^{-2}$];
- F = matrix of molar flow rate [kmolh^{-1}];
- ID_{shell} = internal shell diameter [m];
- J_{H_2} = hydrogen flux [$\text{kmolh}^{-1}\text{m}^{-2}$];
- K_{H_2} = hydrogen permeance [$\text{kmolh}^{-1}\text{m}^{-2} \text{bar}^{-0.5}$];
- L = membrane length.
- N_m = number of membranes;
- OD_t = outside tube diameter [m];
- P_{H_2} = hydrogen permeability [$\text{kmolh}^{-1}\text{m}^{-1} \text{bar}^{-0.5}$];
- $P_{H_2}^0$ = pre-exponential factor of hydrogen permeability.
- P_t = tube pitch [m];
- p_{H_2} = hydrogen partial pressure on the right/left interface [bar];
- r = membrane internal radius;
- Re = average Reynolds number
- v_m^R = average velocity of the mixture, retentate side [m s^{-1}];
- Sc = average Schmidt number.
- w = channel width [m];
- y_{H_2} = hydrogen molar fraction on the retentate/left interface of i -esimo step;

apices and subscripts

- j = H_2O , CO , CO_2 , CH_4 ;
- l = relative to the left-interface in the film theory
- mix = relative to the mixture
- P = relative to the permeate;

- R = relative to the retentate-side;
- RI =relative to the right-interface in the film theory
- s = relative to the shell-side
- t = tube-side

Greekletter

- δ = membrane thickness, [m].
- μ_{mix} = viscosity of mixture, retentate side [Pa s];
- ρ_{mix} = density of mixture, retentate side [kg/m³];

References

- [1] https://www.hydrogen.energy.gov/pdfs/hpep_report_2013.pdf
- [2] US Department of Energy. <http://hydrogen.pnl.gov/hydrogen-data/hydrogen-production>
- [3] S. Sharma, S. K. Ghoshal. Hydrogen the future transportation fuel: From production to applications. *Renewable and Sustainable Energy Reviews* 43 (2015) 1151–1158
- [4] De Falco M., Piemonte V., Solar enriched methane production by steam reforming process: reactor design, *International Journal of Hydrogen Energy*, 36, (2011) 7759–7762. (doi:10.1016/j.ijhydene.2011.01.044)
- [5] M.Voldsund, K.Jordal, R.Anantharaman, Hydrogen production with CO₂capture, *international journal of hydrogen energy* 41 (2016) 4969e4992
- [6] T. Abbasi, S.A. Abbas, Decarbonization of fossil fuels as a strategy to control global warming, *Renewable and Sustainable Energy Reviews* 15 (2011) 1828–1834
- [7] Capocelli, M. and De Falco, M. (2016) Enriched methane: A ready solution for the transition towards the hydrogen economy. In *Enriched Methane: The First Step Towards the Hydrogen Economy* (Editors: M. de Falco and A. Basile). Springer International Publishing, Switzerland, 1–21
- [8] Erickson W, Tang PA, Vernon Reformation of hydrocarbon fuels. In: *Handbook of hydrogen energy*. CRC Press, Taylor & Francis Group, Boca Rato.
- [9] McDowall W, Eames M (2006) Forecasts, scenarios, visions, backcasts and roadmaps to the hydrogen economy: a review of the hydrogen futures literature. *Energy Policy* 34(11):1236–1250
- [10] Züttel A. *Hydrogen storage methods*. Springer-Verlag; 2004.
- [11] <https://www.economist.com/science-and-technology/2017/09/25/electric-vehicles-powered-by-fuel-cells-get-a-second-look>
- [12] Tushar K. Ghosh, Mark A. Prelas. *Energy Resources and Systems: Volume 2: Renewable Resources* Springer Science & Business Media, 2011
- [13] M.A. Murmura, S. Cerbelli, M.C. Annesini. An equilibrium theory for catalytic steam reforming in membrane reactors. *Chemical Engineering Science* 160 (2017) 291–303.
- [14] M.A. Murmura, S. Cerbelli, M.C. Annesini Transport-reaction-permeation regimes in catalytic membrane reactors for hydrogen production. The steam reforming of methane as a case study. *Chemical Engineering Science* 162 (2017) 88–103
- [15] H.Abir, M.Sheintuch. Modeling H₂ transport through a Pd or Pd/Ag membrane, and its inhibition by co-adsorbates, from first principles. *Journal of Membrane Science* 466 (2014) 58–69
- [16] D. Barba, F. Giacobbe, A. De Cesaris, A. Farace, G. Iaquaniello, A. Pipino. Membrane reforming in converting natural gas to hydrogen (part one). *International Journal of Hydrogen Energy* 33 (2008) 3700 – 3709.
- [17] G. Iaquaniello, F. Giacobbe, B. Morico, S. Cosenza, A. Farace. Membrane reforming in converting natural gas to hydrogen: Production costs, Part II. *International Journal of hydrogen energy* 33 (2008) 6595 – 6601.
- [18] M. De Falco, D. Barba, S. Cosenza, G. Iaquaniello, A. Farace, G. Giacobbe. Reformer and membrane modules plant to optimize natural gas conversion to hydrogen. *Asia-Pac. J. Chem. Eng.* 2009; 4: 259–269.

[19]	De Falco, Salladini A, Iaquaniello G. Reformer and membrane modules for methane conversion: experimental assessment and perspectives of an innovative architecture. <i>ChemSus Chem</i> . 2011 22;4(8).
[20]	G.Iaquaniello, A. Salladini, E. Palo, G. Centi. Catalytic partial oxidation coupled with membrane purification to improve resource and energy efficiency in syngas production. <i>ChemSusChem</i> 8 (2015) 717
[21]	ENERGY ANALYSIS AND MODELING OF MEMBRANE REACTORS Promeca 2017
[22]	M. De Falco, A. Salladini, E. Palo, G. Iaquaniello. Pd-Alloy Membrane Reactor for Natural Gas Steam Reforming: an Innovative Process Design for the Capture of CO ₂ . <i>Ind. Eng. Chem. Res.</i> , 2015, 54 (27), 6950–6958
[23]	T. L. Ward, T. Dao. Model of hydrogen permeation behavior in palladium membranes <i>Journal of Membrane Science</i> 153 (1999) 211–231.
[24]	Caravella, A., Barbieri, G., Drioli, E. Concentration polarization analysis in self-supported Pd-based membranes. <i>Sep. Purif. Technol.</i> 66, 613–624 (2009).
[25]	Caravella, A., Scura, F., Barbieri, G., Drioli, E. Sieverts law empirical exponent for Pd-based membranes: Critical analysis in pure H ₂ permeation. <i>J. Phys. Chem. B</i> 114, 6033–6047 (2010).
[26]	Caravella, A., Scura, F., Barbieri, G., Drioli, E. Inhibition by CO and polarization in Pd-based membranes: A novel permeation reduction coefficient. <i>J. Phys. Chem. B</i> 114, 12264–12276 (2010).
[27]	Caravella, A., Hara, S., Drioli, E., Barbieri, G. Sieverts law pressure exponent for hydrogen permeation through Pd-based membranes: Coupled influence of non-ideal diffusion and multicomponent external mass transfer <i>Int. J. Hydrogen Energy</i> 38, 16229–16244 (2013).
[28]	Catalano, J., Giacinti Baschetti, M., Sarti, G. C. Influence of the gas phase resistance on hydrogen flux through thin palladium-silver membranes. <i>J. Memb. Sci.</i> 339, 57–67 (2009).
[29]	Catalano, J., Giacinti Baschetti, M., Sarti, G. C. Hydrogen permeation in palladium-based membranes in the presence of carbon monoxide. <i>J. Memb. Sci.</i> 362, 221–233 (2010).
[30]	Catalano, J., Giacinti Baschetti, M., Sarti, G. C. Influence of water vapor on hydrogen permeation through 2.5 μm Pd-Ag membranes. <i>Int. J. Hydrogen Energy</i> 36, 8658–8673 (2011).
[31]	Pizzi, D., Worth, R., Giacinti Baschetti, M., Sarti, G. C. & Noda, K. ichi. Hydrogen permeability of 2.5 μm palladium-silver membranes deposited on ceramic supports. <i>J. Memb. Sci.</i> 325, 446–453 (2008).
[32]	Flanagan, T. B.; Wang, D. Exponents for the pressure dependence of hydrogen permeation through Pd and Pd-Ag alloy membranes. <i>J. Phys. Chem. C</i> 114, 14482–14488 (2010).
[33]	Barbieri, G., Scura, F., Lentini, F., De Luca, G., Drioli, E. A novel model equation for the permeation of hydrogen in mixture with carbon monoxide through Pd-Ag membranes. <i>Sep. Purif. Technol.</i> 61, 217–224 (2008).
[34]	Holleck. Diffusion and Solubility of Hydrogen in Palladium and Palladium-Silver Alloys <i>The Journal of Physical Chemistry</i> 74? umber 3 February 6, 970
[35]	Treybal. Mass Transfer Operations Third Edition. McGraw-Hill Chemical Engineering Series New York