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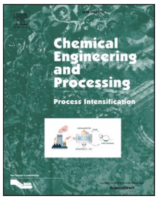

Membrane reactors for sustainable hydrogen production through steam reforming of hydrocarbons: A review

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ABSTRACT

Membrane reactors - as promising technology for pursuing the Process Intensification Strategy in various chemical processes - were reviewed in the field of steam reforming of methane and liquid hydrocarbons for sustainable hydrogen production. A summary of the advantages and disadvantages of each considered process was presented. Drawbacks and current issues of the traditional reactors in fuel processing processes, which can be overcome using membrane reactors, were also described.

In particular, steam reforming processes are the major hydrogen production methods; therefore, in this review the effects of different operating parameters, such as reaction temperature, pressure, feed composition, reactor configuration, feed and sweep gas flow rates were analyzed and discussed in terms of methane conversion, hydrogen recovery, hydrogen yield and CO selectivity. A deep discussion was proposed about the effects of the hydrogen removal from reaction zone (the so called "shift effect") toward the permeation zone in the membrane reactors, highlighting the benefits of their adoption over the traditional reactors.

1. Introduction

The general description of a membrane reactor (MR) deals with the definition of a device in which the reaction and separation of one or more products occur simultaneously [1]. The separation function is given by a selective membrane that is allocated in a reactor module to constitute an integrated reaction/separation system. MRs move under the principles of the Process Intensification Strategy, making possible to achieve the same performance of the catalytic traditional reactors (TRs), but operating at milder conditions, meanwhile requiring a reduced number of devices for achieving a pure product stream of interest [2,3]. Due to the integration of the reaction and separation stages in a single unit, a MR results to be a compact device showing economic advantages in terms of capital and operational costs over the TRs [4–8]. Currently, different MR configurations may be noticed such as tube in tube, multi-tubes in shell, planar, multi-hollow fibers etc. [1,5,8–13]. Fig. 1 shows a MR configuration dealing with two concentric tubes as a tube in tube solution. In the proposed scheme, the inner tube is filled by catalyst pellets in the lumen side and the separative membrane layer may be coated on the internal surface of the inner tube, which plays also the role of membrane support. Otherwise, the coating of the selective layer is realized on the outer surface of the inner tube and the catalyst is packed in the annulus of the MR and the permeated stream is collected in the lumen side [1,5].

On the other hand, the inner tube may consist of the membrane itself in the case it is a self-supported dense walled typology.

For instance, in the configuration of Fig. 1, one or more products of a specific reaction process may permeate through the membrane and are collected in the annular section of the MR module. In some case, a sweep gas may be used to enhance the permeation driving force and the product removal. A sweep gas may be supplied in co-current or counter-current modality with respect to the MR feed stream. Therefore, in case of a membrane possessing full perm-selectivity toward a product, it is possible to recover the former with a high purity, reducing the downstream separation load [1,5–8].

Abbreviations: CVD, chemical vapor deposition; ELP, electroless plating; ESR, ethanol steam reforming; GHSV, gas hourly space velocity; GSR, glycerol steam reforming; HT, high temperature; LT, low temperature; MR, membrane reactor; MSR, methanol steam reforming; NG, natural gas; PEMFC, polymer electrolyte membrane fuel cell; PP-ELP, pore plating electroless plating; PROX, preferential oxidation; PSS, porous stainless steel; SF, sweep factor; SRM, steam reforming of methane; TR, traditional reactor; WGS, water gas shift; YSZ, yttria stabilized zirconia.

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Nomenclature

B^0_{H2}	Pre-exponential factor
J_{H2}	Hydrogen permeating flux
$p_{H_2,\,perm}$	Hydrogen partial pressure in the permeate side
$p_{H_2,\,ret}$	Hydrogen partial pressure in the retentate side
ΔH	Enthalpy changes
d_P	Pore diameter
E_a	Apparent activation energy
J^{HP}_{H2}	Hydrogen permeating flux contribute due to Hagen-Pouiselle equations
J^{K}_{H2}	Hydrogen permeating flux contribute due to Knudsen flow equations
J^{SD}_{H2}	Hydrogen permeating flux contribute due to solution/diffusion mechanism
J^{TOT}_{H2}	Total hydrogen permeating flux
K	Equilibrium constant
N	Dependence factor on the hydrogen partial pressure
R	Universal gas constant
$r_{A,\ forward}$	Consumption rate of reactant A through the forward reaction
$r_{A,reverse}$	Production rate of the reactant A through the reverse reaction
r_A	Net reaction rate of reactant A
T	Temperature
η	Viscosity
Δp_{H2}	Transmembrane hydrogen partial pressure
ε	Membrane porosity
τ	Tortuosity
δ	Membrane thickness

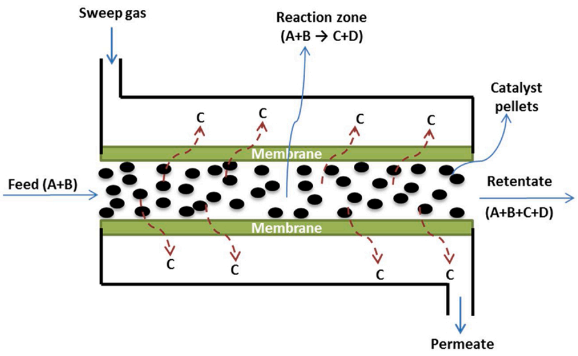

Fig. 1. Scheme of a tube in tube membrane reactor configuration.

The main application of a product removal from the reaction zone for permeation through a membrane refers to limited equilibrium reactions [1,6]. The removal of a reaction product leads to an enhancement of the reaction conversion or to the same conversion of an equivalent TR, but achieved at milder reaction conditions. Furthermore, the adoption of MRs allows to avoiding that undesiderable secondary reactions may take place [6].

In case of a reversible reaction carried out in conventional reformers (closed system):

$$aA + bB \leftrightarrow cC + dD \tag{1}$$

the equilibrium constant is considered as:

$$K = \frac{[C]^c[D]^d}{[A]^a[B]^b} \tag{2}$$

For a specific reaction condition, K has a specific value that can obtained from Van't Hoff equation:

$$\frac{dlnK}{dT} = \frac{\Delta H}{RT^2} \tag{3}$$

At the beginning of the reaction, the concentration of the products is zero. During the reaction development, the concentration of the reactants decreases and that of the products increases. Therefore, the value of the concentration ratio in the Eq. (2) will be increased until the final value of the equilibrium constant is reached. Further conversion of the reactants will be stopped and a specific conversion value is obtained for a given temperature, pressure and feed composition. In a MR, removing one or more products from the reaction zone, the numerator of the concentration ratio in Eq. (2) is maintained at a low value, preventing that the equilibrium composition may be reached. Therefore, the direct reaction can proceed further and the conversion can exceed the correspondent value of the closed system at the same reaction conditions. This is the well-known mechanism that in a MR is called "shift effect" [1,5,9–13]. From the reaction kinetic point of view, the overall consumption rate of the product A (Eq. (1)) is given by:

$$r_A = r_{A,\ forward} - r_{A,reverse} \tag{4}$$

Forward and reverse reaction rates directly depend on the reactants and products concentration, respectively. In a MR, removing the product from the reaction zone reduces the reverse reaction rate, consequently improving the overall conversion rate of reactants [1].

Nowadays, one of the most studied fields in which MR technology is applied refers to hydrogen generation [1,4,6,9,10]. The former is considered as an environmentally friendly, clean and highly efficient energy carrier. Many efforts are currently done to develop technologies useful for producing cost-effective and sustainable hydrogen, especially for fuel cell applications [10].

Several reviews from literature dealt with deep discussions on MRs technology, their fundamentals and adoption to generate hydrogen, but - to our best knowledge - there are not reviews strictly dedicated to the sustainable hydrogen generation via MRs technology combined to the exploitation of light hydrocarbons.

Hence, in this work, the application of MRs to produce hydrogen via steam reforming of liquid hydrocarbons such as methanol, ethanol and glycerol is reviewed, discussing on the related MRs performance compared to those of MRs used to carry out the steam reforming of methane as a fossil-fuel based process. Furthermore, the latest advancements and the future perspectives of a decarbonized society based on the sustainable hydrogen generation coming from the exploitation of light hydrocarbons and alternative technologies such as the MRs are analyzed and discussed.

2. Membrane reactors

The MR concept was formulated since 1950 although a special interest about this new technology was registered only when new inorganic membrane materials were adopted and the MR applications involved high-temperature industrial processes. In the last three decades, a large literature was addressed about the MR technology, dealing with different approaches in specific areas. Furthermore, different kind of MRs were developed, depending on the typology of membranes adopted. They may be subdivided in: inorganic MRs [6–10], zeolite MRs [11,12], polymeric MRs [13,14], photo-catalytic MRs [15,16], membrane bio-reactors [17,18], electrochemical MRs (including electrolytic cells fuel cells etc.) [19]. In all the aforementioned classes, the combination of a MR operation with a chemical and/or biochemical reaction is directed to intensify the whole process. Therefore, the membrane plays the most significative role, determining if a MR is used to remove or add a chemical species, working under “extractor” of “distributor” modality [20]. A further configuration is possible, called “contactor” modality, in which the membrane favors the contact between catalyst and reactants to better develop the reaction process without operating any separation process [20,21]. In a MR operated under “extractor” modality, the membrane removes selectively a desired species from the reaction mixture for permeation. MRs operated under extractor configuration, adopted in thermodynamically restricted reactions, allow the enhancement of the selectivity towards a particular intermediate species in a cascade reaction, due to its selective removal from the reaction medium [20]. This mechanism represents the aforementioned “shift effect”, which is responsible also for the reduction of sequential reactions [1,6,10]. This MR modality is particularly adopted in dehydrogenations or hydrogen generation reactions such as steam reforming or water gas shift (WGS), carried out using hydrogen selective membranes [4,10,21].

MRs operated under “distributor” modality allow to add a limiting reactant along the reactor uniformly in order to prevent hot spots and side reactions. It is particularly adopted in partial oxidation reactions, in which the membrane selectively adds the target oxygen to achieve both high conversions and product selectivities. Furthermore, being not reactants and oxygen premixed, flammable mixtures are avoided and flame back firing into the feed is prevented as well [20].

MRs used under “contactor” modality allow that the two-sided geometry of the membranes may bring reactants into contact each other easier [20].

3. Palladium membranes for MR applications

Most of the MR applications deals with the utilization of inorganic membranes due to their resistance at medium-high temperature operations. The choice of the inorganic material to be used for membrane preparation and successive utilization in a MR depends on the specific reaction process, on the final desired product and related purity, and on the operation conditions [1,10]. Ceramic, metallic, zeolite, carbon and composite membranes are generally adopted in MRs to carry out reaction processes [22,23]. Furthermore, in applications of MRs for hydrogen generation a general categorization subdivides them into packed-bed and fluidized-bed MRs [1,24].

Packed-bed MRs are largely addressed in the scientific literature, with many applications of them dealing with planar and tubular configurations, in which the catalyst is loaded as a packed bed directly in contact with an inorganic membrane [1,5,6,10]. On the other hand, the fluidized bed MRs are generally constituted of a bundle of membranes immersed in a catalytic bed, which is operated under bubbling or turbulent regime due to the need (which represents also the main limitation) of maintaining suspended the catalytic bed. In the applications of MR technology for hydrogen generation, metallic membranes represent the most adopted typology because a number of metals possesses high hydrogen perm-selectivity with respect to all the other gases [25,26]. In particular, palladium and its alloys dominate over the other inorganic membrane materials due to their characteristics of full hydrogen perm-selectivity [27–29]. The performance of every kind of inorganic membrane material is currently evaluated in terms of hydrogen permeability, perm-selectivity and thermal stability. As shown in Fig. 2, V, Nb and Ta show the highest hydrogen permeabilities but they possess conversely the lowest mechanical resistance, due to the effects of a severe hydrogen embrittlement phenomenon [27], which is responsible for the membrane failure in case of prolonged hydrogen exposure.

Pd possesses the highest hydrogen permeability a part from the aforementioned materials (V, Nb and Ta), but it is not subjected to a drastic embrittlement phenomenon if alloyed with other metals such as Ag, Ni, Au, Ru, Cu etc. [30].

Hydrogen permeation through Pd walls is developed under a solution-diffusion mechanism, which involves a number of activated stages: a) molecular hydrogen dissociation at the membrane surface; b) atomic hydrogen adsorption on the membrane surface; c) atomic hydrogem dissolution into the palladium bulk; d) atomic hydrogen diffusion through the membrane; e) re-combination from the atomic molecular hydrogen at the gas/metal interface; f) molecular hydrogen desorption [27–29,31]. Ideally, the equation expressing the hydrogen flux permeating through a Pd-based membrane is reported below:

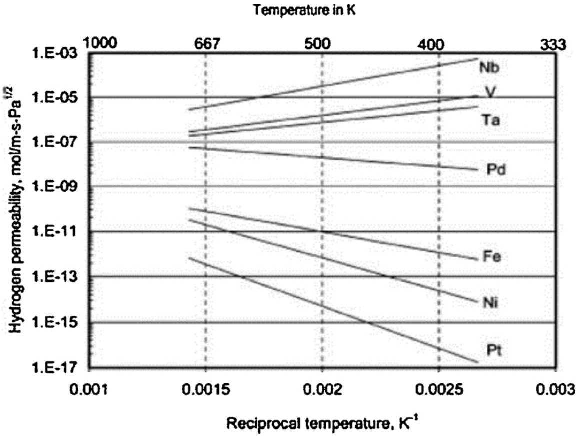

Fig. 2. H_2 permeability vs 1/T for such metals as Nb, V, Ta, Pd, Fe, Ni, Pt. With permission of reprint of Taylor & Francis from Conde et al. [27].

$$J_{H_2}^{Permeating} = \frac{B_{H_2}}{\delta}\left(p^{n}_{H_2,\,retentate} - p^{n}_{H_2,permeate}\right) \tag{5}$$

where $J_{H2}^{Permeating}$ represents the hydrogen permeating flux, B_{H2} the hydrogen permeability, δ the membrane thickness, $p_{H2,retentate}$ and $p_{H2,\,permeate}$ the hydrogen partial pressures in the retentate and permeate sides, respectively, and “n” the hydrogen partial pressure exponent, which ranges between 0.5 and 1 [29,31]. The latter variable may depend on the rate limiting step of the hydrogen diffusion through the palladium wall.

Hydrogen membrane permeability (B_{H2}) depends on temperature as an Arrhenius like equation:

$$B_{H_2} = B_H 2^0.\exp\left(-\frac{E_a}{R.T}\right) \tag{6}$$

B_{H2}° is a pre-exponential factor, E_a the apparent activation energy, R the universal gas constant and T the temperature. In case of hydrogen bulk diffusion controlling the permeation process as the rate limiting step, Eq. (5) becomes the Sieverts-Fick law and the pre-exponential factor “n” is equal to 0.5.

$$J_{H_2}^{Permeating} = \frac{B_{H_2}}{\delta}\left(p^{0.5}_{H_2,\,retentate} - p^{0.5}_{H_2,permeate}\right) \tag{7}$$

When the n-value is higher than 0.5, the surface effects play a relevant role and the hydrogen transport through the membrane is regulated by other mechanisms such as Knudsen diffusion, etc. In case of n = 1, the surface-reaction controls the hydrogen permeation instead of diffusion [31].

In case of fully hydrogen perm-selective Pd-based membranes, the driving force regulating the hydrogen permeation through the membrane is represented by the hydrogen partial pressure square root difference between reaction and permeate sides.

In recent years, much attention was paid to supported Pd-Pd/alloys membranes, constituted of a dense Pd/Pd-alloy film as top layer deposited on a porous support among Vycor glass, Al_2O_3, SiO_2 and B_2O_3 or porous stainless steel (PSS) [29,31]. This kind of supported Pd-based membranes combines reduced membrane cost, due to low Pd content, and enhanced mechanical characteristics, due to the presence of the porous support.

The dense Pd/Pd-alloys layer greatly affects the whole membrane

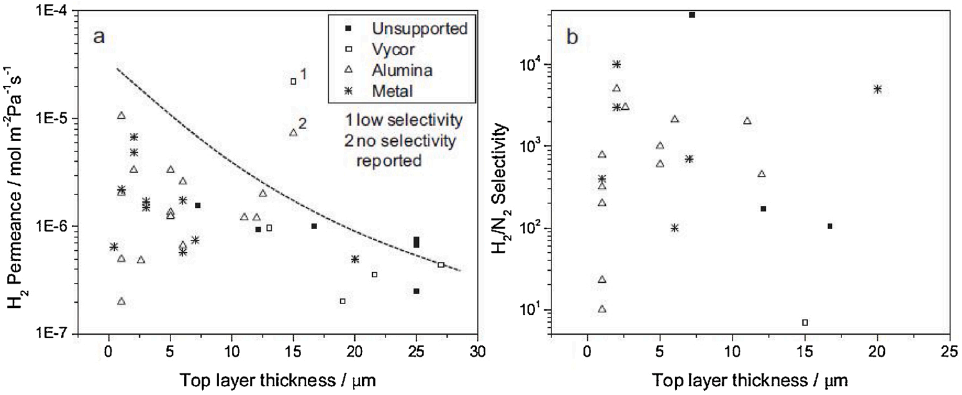

Fig. 3. Supported and self-standing Pd-based membranes: a) H_2 permeance vs thickness of the Pd-layer; b) ideal H_2/N_2 selectivity vs thickness thickness of the Pd-layer. With permission of reprint of Elsevier from You & Oyama [31].

performance, which may be expressed by the reference perm-selectivity ($\alpha_{H2/N2}$), represented by the ratio between the ideal H_2 and N_2 permeances. Fig. 3 shows a graph in which H_2 permeance is plotted against H_2/N_2 selectivity as a function of the thickness of the Pd layer for both self-standing and supported membranes.

In Fig. 3a, the upper bound between hydrogen permeance and top layer thickness is plotted to indicate as higher is the Pd thickness as lower is the H_2 permeance due to the hydrogen diffusion through a thicker bulk. Concerning the self-standing Pd/Pd-alloys membranes, wall thickness equal to 20 μm represents the limit for this Pd-membranes class owing to the low resistance to mechanical stress [31]. For supported Pd/Pd-alloys membranes, the best performance in terms of hydrogen permeance are observed in the region of very thin Pd layers. Nevertheless, the presence of defects in the thin Pd layers may limit the H_2/N_2 selectivities with respect to the self-standing class, Fig. 3b. Consequently, the H_2 perm-selectivity of supported Pd-based membranes may vary depending on the effectiveness of the dense Pd/Pd-alloys layer deposition. Beside the presence of defects in the top layer, the contamination due to harmful compounds, the presence and typology of the substrate and the intermediate layer play a further role, considerably responsible for the membrane performance. Table 1 summarizes the performance in terms of hydrogen perm-selectivity and permeance, reporting also the operating conditions and thickness of the top layer of a number of supported Pd membranes. For some of them, the hydrogen perm-selectivity is full and indicated as "∞". In this case, the correspondent hydrogen partial pressure exponent ('n') assumes the value of 0.5, indicating that the Sieverts-Fick law regulates the hydrogen permeation through the membrane.

In case of supported Pd-based membranes presenting finite values of hydrogen perm-selectivity, *n*-value is equal to 1, which indicates that the hydrogen permeation is taking place very fast due to a thin Pd layer (< 5 μm). For thicker Pd layer (> 5 μm), deviations from Sieverts law (*n*-value > 0.5) are mainly caused by high hydrogen pressure, surface reaction rate decrease due to contaminants absorption, concentration polarization effect and pin-holes formation. In the former case, a fraction of hydrogen may permeate into the defects via Knudsen or viscous flow beside the hydrogen diffusion through the palladium bulk [31] (Eq. 8).

$$J_{H_2}^{Total} = \frac{1}{\frac{1}{J_{H_2}^{SD}} + \frac{1}{J_{H_2}^{K}} + \frac{1}{J_{H_2}^{HP}}} \tag{8}$$

J_{H2}^{Total} represents the total hydrogen permeating through the membrane, J_{H2}^{SD} the hydrogen permeating via solution/diffusion mechanism, J_{H2}^{K} the hydrogen permeated via Knudsen mechanism (Eq. 9) and J_{H2}^{HP} that permeating via viscous flow/Hagen-Pouiselle mechanism (Eq. 10).

Table 1

Performance of supported Pd/Pd-alloys membranes from literature.

Membrane typology	Preparation technique	Separative layer (μm)	T (°C)	Δp (bar)	H_2 permeance (mol/m^2·sPa)	Ideal Selectivity ($\alpha_{H2/N2}$)	Ref.
Pd/Al_2O_3	ELP	5	400	1	$4.3\cdot10^{-4}$	∞	[32]
Pd/PSS	PP-ELP	20	450	–	–	∞	[33]
$Ru/Pd/Al_2O_3/PHA$	ELP	6.8	500	1	–	∞[a]	[34]
Pd/PSS	ELP	10	400	2	$8.7\cdot10^{-7}$	~ 11,800	[35]
Pd/Al_2O_3	ELP	0.9	450	~ 1	$4.0\cdot10^{-6}$	9200	[36]
Pd/YSZ/PSS	ELP	25–30	500	–	$3.1\cdot10^{-4}$[c]	400[b]	[37]
Pd/Al_2O_3	ELP	2–4	400	–	–	500	[38]
$Pd\text{-}Ag/ZrO_2$	PVD	1.0	400	1	$8.0\cdot10^{-6}$	500	[39]
Pd-Ag/PSS	PVD	2.8	400	–	$1.5\cdot10^{-5}$	2900	[40]
$Pd\text{-}Cu/Al_2O_3$	MVS	20	400	0.5	$1.8\cdot10^{-6}$	~1800	[41]
Pd-Cu/PSS	ELP	~7	400	4	$1.9\cdot10^{-6}$[b]	~890	[42]
Pd-Cu/MPSS	SIEP	~17	550	~7	–	~90	[43]
Pd-Cu-Pd	ELP + GD	19	450	–	$2.8\cdot10^{-6}$[b]	2100	[44]
$Pd\text{-}Cu/Al_2O_3\text{-}PNS$	MS	7	~540	2	$5.3\cdot10^{-7}$[b]	∞	[45]
$Pd\text{-}Cu/CeO_2/PNS$	MS		500	4	$7.0\cdot10^{-7}$[b]	> 50,000	[46]
$Pd\text{-}Au/\alpha\text{-}Al_2O_3$	ELP	8	400	0.5	$2.7\cdot10^{-6}$	~500	[47]
Pd-Au/YSZ	ELP	5	500	6	–	4300	[48]
Pd-Au/PSS	ELP	~15	450	1	5.5[d]	> 2700[a]	[49]
Pd-Au/PSS	ELP	7	420	0.5	5.6[d]	220[a]	[50]
Pd-Au/PSS	ELP	~15	350	1	11.2[d]	900[a]	[51]

[a] H_2/He.

[b] Separation factor using $H_2\text{-}N_2$ mixture.

[c] [mol/m^2·s·Pa$^{0.5}$].

[d] Nm^3 m^{-2} h^{-1} bar$^{-0.5}$.

$$J^{K}_{H_2} = \frac{\varepsilon d_P}{\tau L}\left(\frac{8}{9\pi MRT}\right)^{1/2}\Delta p_{H_2} \tag{9}$$

$$J^{HP}_{H_2} = \frac{r^2}{8\eta L P_0} P_{AVE}\Delta p_{H_2} \tag{10}$$

where ε is the membrane porosity, d_P the pore diameter, τ the tortuosity, L the thickness, M the molecular weight of diffusing gas, Δp_{H2} the transmembrane hydrogen partial pressure, η the viscosity, P_{AVE} the average pressure, P_0 the outlet pressure, r the radius.

On the other hand, a critical issue affecting the H_2 permeation performance of Pd-based membranes is represented by the effects of contaminants such as H_2S, CO, unsaturated hydrocarbons, coke etc. [52]. In particular, the poisoning effects of H_2S containing H_2 rich-gas mixtures on the surface of Pd-coated membranes deal with a progressive loss of the membrane performance (lower H_2 permeability and perm-selectivity) up to achieve the membrane failure due to the deterioration of the selective layer. This is caused by the formation of the palladium sulphide, whose lattice constant is twice than of pure Pd, determining structural stress with the formation of cracks [52,53]. Some Pd-alloys seem to be more H_2S resistant such as those based Pd alloyed with Au and Cu.

The permeation H_2 rich-gas mixtures containing CO through Pd-based membranes may be affected by the negative influence of CO, causing the decrease of the H_2 permeation performance. This is due to the adsorbed CO that blocks available dissociation sites for the H_2 adsorption. This effect depends on the operating temperature (particularly below 150 °C) and the CO concentration. Also in this case, alloys of palladium with other metals such as Cu, Ni, Fe, Pt, and Ag improve the resistance to the aforementioned CO effects [52,53].

The coke deposition on Pd-based membranes may be responsible for a loss of the H_2 permeation performance, particularly at high temperature. C-atoms penetrate into the palladium lattice, determining its expansion and the consequent membrane failure.

The presence of light-hydrocarbons in H_2 rich-gas mixtures may affect the Pd-based membranes performance. Indeed, light-hydrocarbons may be decomposed at high temperatures over the palladium surface, forming Pd-C species, coke deposition and the consequent depletion of the H_2 permeation characteristics of the membrane. In this case, since high temperatures are responsible for the light hydrocarbon decomposition, favoring the membrane fouling by coke deposition, operating temperature equal to or above 600 °C are not recommended to avoid severe membrane performance depletion [52].

4. Steam reforming of natural gas

Steam reforming of natural gas (NG) represents the main process adopted for industrial hydrogen production [4]. The reaction process is performed in TRs at hard and harsh conditions, with an outlet reformed stream rich in CO and H_2 (synthesis gas). The former is then used for large scale ammonia and methanol production. NG is mostly constituted of methane, therefore NG steam reforming may be well represented by the steam reforming of methane (SRM), which involves the reaction process scheme reported below. R1 represents the SRM, R2 the WGS reaction, and R3 the overall SRM process.

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \left(\Delta H = 206.2\ \text{kJ mol}^{-1}\right) \tag{R1}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \left(\Delta H = -41.2\ \text{kJ mol}^{-1}\right) \tag{R2}$$

$$CH_4 + 2H_2O \leftrightarrow CO_2 + 4H_2 \quad \left(\Delta H = 165.0\ \text{kJ mol}^{-1}\right) \tag{R3}$$

SRM is a highly endothermic and a reversible process, in which methane conversion is limited by the thermodynamic equilibrium value [1,4,54–61]. In other words, the thermodynamic limitation is the main issue in the progress of the reaction, the kinetic and catalyst activity are not highly determining and the heat transfer to catalytic bed is the rate controlling step. Conventionally, SRM is carried out at temperatures higher than 1100 K and, to facilitate the heat transfer, the reaction is developed in fixed bed small diameter tubes suspended within a furnace with different firing configuration [54]. Nevertheless, the high temperatures required for converting as much as possible methane into hydrogen during SRM in TRs determine the need of expensive reformer construction materials adoption such as high alloy nickel chromium steel to withstand the thermal stresses. Irreversible coke formation, considerable energy consumption, creation of temperature profile inside the catalyst bed due to heat transfer limitation and higher possibility of NO_x formation in the furnace are other critical drawbacks [55]. Therefore, to overcome these problems it is desirable to lower the reaction temperature, meanwhile keeping the conversion of methane at high levels. MRs equipped with hydrogen selective membranes are an attractive option to reach this purpose [1,9,27,56–58]. Hence, removing hydrogen from the reaction side by membrane permeation shifts an equilibrium limited reaction towards the reaction products and, thereby, methane conversion is enhanced due to Le Chatelier's principle.

The "shift effect" present in hydrogen perm-selective MRs (which operate as non-closed systems) makes possible to achieve higher conversions of an equivalent TR operated at the same conditions or, otherwise, the same conversion but operating at milder conditions.

Fig. 4 illustrates schematically how a MR may overcome the restrictions of the thermodynamic equilibrium limited reactions carried out in a TR (which operates as a closed system).

Data from literature confirm this ability and Figs. 5 and 6 show a parametric comparison between MRs and TRs performance in terms of methane conversion and hydrogen yield during SMR reaction, respectively [58-69]. In Figs. 5 and 6, each methane conversion and H_2 yield obtained in a MR from a published study was plotted against those obtained in a TR from the same study. For instance, if in a specific publication, among those reported in the aforementioned figures, methane conversion in the MR was 70 % and in the TR 60 %, these data represented a coordinate (6070) in Fig. 5. Hence, the dashed line represents the theoretical equivalence between MR and TR methane conversions, but since methane conversions and H_2 yields in the reported MRs of Figs. 5 and 6 were higher than those of the correspondent TR, thus all points were above the dashed line.

In particular, the enhancement of the hydrogen yield in a MR is due to the improved conversion, which is driven by the shift effect induced by the membrane permeation. Indeed, a higher methane conversion determines a larger hydrogen production and, consequently, a higher hydrogen yield.

Furthermore, depending on the hydrogen perm-selectivity

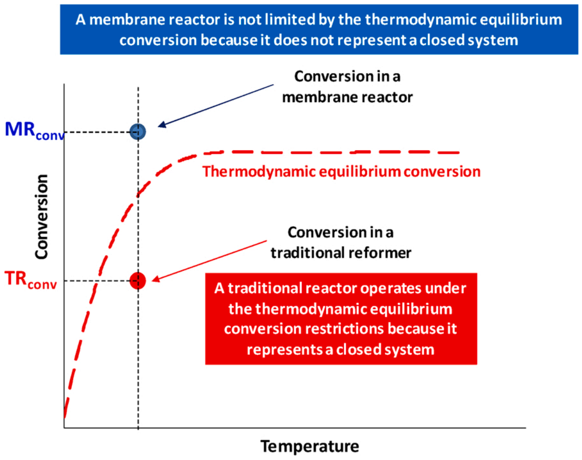

Fig. 4. Schematic representation of the MRs and TRs behaviors under thermodynamic equilibrium limited reactions (conversion vs temperature).

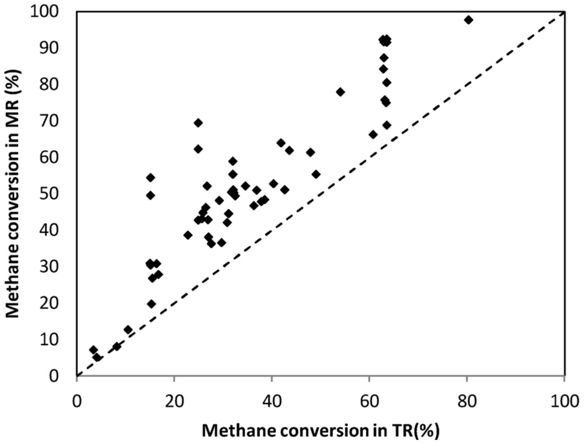

Fig. 5. Methane conversion in MRs and TRs during SRM process. Data extracted from [58–68].

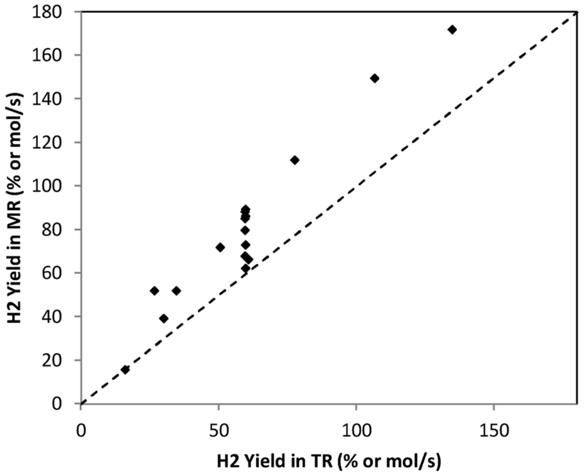

Fig. 6. Hydrogen yield in MRs and TRs during SRM process. Data extracted from [57,59,60].

characteristics of the adopted membrane in the MR and the required standards of the hydrogen purity requested by the final user, high grade or pure hydrogen may be attained in the MR permeate stream. This represents a great benefit for the MRs because they do not require any further hydrogen separation stages.

Most of the industrial plants used to generate hydrogen from SRM reaction deals with the presence of a conventional reformer, followed by two WGS reactors, which are responsible for the transformation of CO, present in the outlet streams of the TR, into further hydrogen and CO_2 [5,6,10]. SRM is an endothermic reaction, whereas WGS is exothermic. The desirable operating temperatures in TRs are commonly higher than 973 K, while in both the WGS reactors (high temperature and low temperature reactors in series each other) the temperatures are lower than 723 K. Consequently, it is not possible to intensify the whole process, carrying out both the reactions simultaneously. Cooling down the outlet stream coming from the TR to enter the WGS reactors involves a large energy penalty. Using a MR, the hydrogen removal determines both the shift of the equilibrium of both the WGS and SRM reactions towards the products, enhancing both the reactions conversions and the hydrogen production. Hence, both reactions may proceed simultaneously in the MR as a single unit, with an intensification of the process system itself, reducing the energy penalties and the costs as well.

For instance, Fig. 7 shows a comparison between conventional and membrane-based integrated systems for generating hydrogen from NG steam reforming. As illustrated in Fig. 7b, in an intensified membrane-based process, the retentate stream coming out from the second MR results to be concentrated and compressed in CO_2 (>80 %), and hence easy to recover. This involves over a conventional integrated process (Fig. 7a) reduced energy consumption, lower footprint, and the reduction of number of devices for reaction–separation–purification.

5. Steam reforming of liquid hydrocarbons

Hydrogen fuel cells represent promising candidates for energy production and a suitable replacement for internal combustion engines [59]. Hydrogen is a carbon-free energy carrier that, combined to proton exchange membrane fuel cells (PEMFCs), involves a clean process for energy production, generating water as unique byproduct [70]. In comparison with internal combustion engines, PEMFCs do not possess a maximum theoretical efficiency, which may be restricted to 40 % by Carnot’s rule. Their theoretical efficiency may be also 100 %. Furthermore, they do not have any moving components, not losing any useful energy due to the friction.

One of the main obstacles to widespread use of hydrogen as energy source in portable applications is represented by the hydrogen transport, distribution and saving due to safety, mechanical and economic issues. To overcome these issues, onboard and distributed hydrogen production at the consumption place, using liquid fuels such as methanol, ethanol etc., was proposed instead of a stationary (central) production of hydrogen necessarily involving its transportation and storage in automobiles [71,72].

In details, the benefits due to the utilization of methanol, ethanol and glycerol as feedstocks to generate hydrogen include [67,73–79]:

- Numerous and available sources such as oil, natural gas, coal and biomass may be used to methanol and ethanol production.
- Their production technologies in large scales are well established.
- At room temperature, they are liquid and their transportation and storage are easy and safe.
- Methanol has high hydrogen to carbon ratio and gives the highest hydrogen ratio in product.
- Required reforming conditions are mild: temperature range is relatively low and pressure is generally atmospheric.
- Using methanol, there are not C—C bonds; consequently, this reduces the possibility of coke formation.
- Sulfur and nitrogen compounds (SO_x and NO_x) are not formed.
- Ethanol, glycerol and methanol can be produced from biomass and renewable resources; therefore, their production do not increase the net amount of CO_2, presenting a low impact on the environment.
- Glycerol is a byproduct of biodiesel production and, theoretically, 100 g of glycerol are producible per 1 kg of biodiesel produced.
- The utilization of crude glycerol in common industrial application is limited and its conversion to hydrogen is an attractive idea to disposal of surplus glycerol.
- Without high investments, exiting gasoline refueling stations could be converted to methanol and ethanol distribution.

Regarding to methanol utilization in reforming reactions to produce hydrogen, CO is the unique byproduct produced during methanol steam reforming (MSR) reaction [76]. The whole reaction mechanism for the MSR reaction takes into account also the WGS and methanol decomposition reactions:

$$\text{Methanol Steam Reforming: } CH_3OH + H_2O \leftrightarrow CO_2 + 3H_2 \qquad (11)$$

$$\text{Water Gas Shift Reaction: } CO + H_2O \leftrightarrow CO_2 + H_2 \qquad (12)$$

$$\text{Methanol Decomposition: } CH_3OH \leftrightarrow CO + 2H_2 \ (13)$$

Concerning the ethanol exploitation for producing hydrogen via ethanol steam reforming (ESR) reaction, the reaction mechanism results to be more complex than that of the MSR reaction. Indeed, it depends

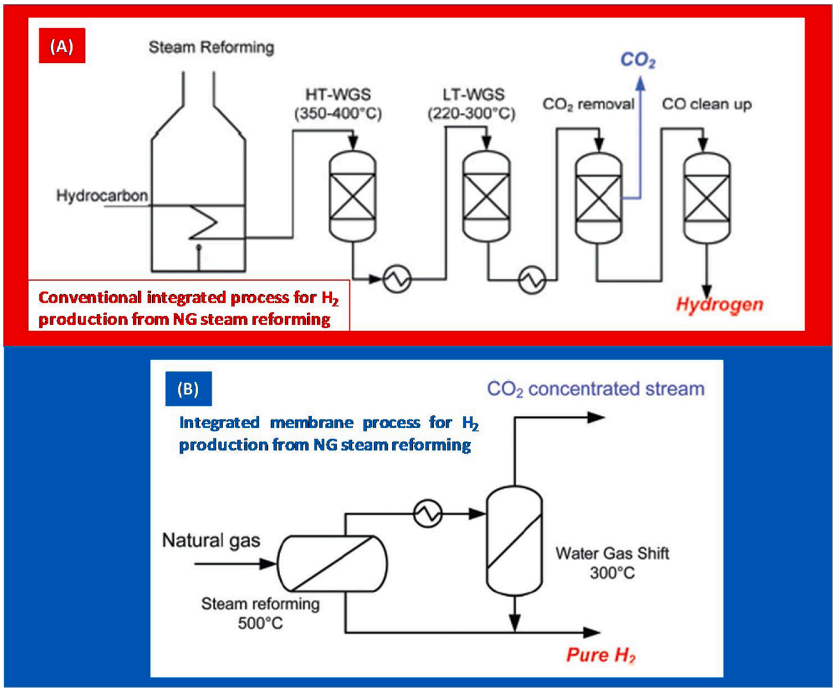

Fig. 7. Hydrogen production from NG steam reforming reaction: scheme of an integrated conventional system (A); scheme of an integrated membrane system (B). Adapted from Drioli et al. [3].

strictly on the type of catalyst used [79]. Hence, the reaction mechanism of the ESR reaction developed on noble metal-based catalysts involves: 1) the ethanol decomposition reaction that produces hydrogen, CO and CH_4, 2) WGS and SRM reactions:

$$C_2H_5OH \leftrightarrow CO + CH_4 + H_2 \tag{14}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{15}$$

$$CH_4 + 2H_2O \leftrightarrow 4H_2 + CO_2 \tag{16}$$

$$C_2H_5OH + 3H_2O \leftrightarrow 6H_2 + 2CO_2 \tag{17}$$

At lower operating temperatures, other reactions such as dehydrogenation of ethanol to acetaldehyde, decomposition of the acetaldehyde to CO and CH_4, and acetaldehyde steam reforming are also involved in the ESR reaction scheme:

$$C_2H_5OH \leftrightarrow CH_3CHO + H_2 \tag{18}$$

$$CH_3CHO + 3H_2O \leftrightarrow 5H_2 + 2CO_2 \tag{19}$$

$$CH_3CHO \leftrightarrow CH_4 + CO \tag{20}$$

The reaction scheme for glycerol steam reforming reaction includes glycerol decomposition and WGS reactions:

$$3H_8O_3 \rightarrow 3CO + 4H_2 \tag{21}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{22}$$

$$3H_8O_3 + 3H_2O \rightarrow 3CO_2 + 7H_2 \tag{23}$$

Nevertheless, further secondary reactions are possible and, according to the literature [74], they are reported in the following:

$$C_3H_8O_3 + H_2 \rightarrow 3CH_4 + 3CO + 3H_2O \tag{24}$$

$$C_3H_8O_3 + 2H_2 \rightarrow 2CH_4 + CO + 2H_2O \tag{25}$$

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{26}$$

$$CO_2 + 4H_2 \rightarrow CH_4 + 2H_2O \tag{27}$$

$$CO_2 + CH_4 \rightarrow 2CO + 2H_2 \tag{28}$$

$$CH_4 + H_2O \rightarrow CO + 3H_2 \tag{29}$$

A crucial issue during whatever catalytic reaction is the formation of coke. In fact, it may be responsible for the depletion of the catalytic activity and for the covering or poisoning effect on the membrane in MR utilization. Generally, coke formation in the steam reforming of hydrocarbons can take place according to the reactions reported below:

$$2CO \rightarrow CO_2 + C \tag{30}$$

$$CH_4 \rightarrow 2H_2 + C \tag{31}$$

$$CO + H_2 \rightarrow H_2O + C \tag{32}$$

$$CO_2 + 2H_2 \rightarrow 2H_2O + C \tag{33}$$

Furthermore, steam reforming of hydrocarbons carried out TRs generates reformed streams rich in CO, CO_2 and CH_4, beside hydrogen. It is well-known that hydrogen rich-streams with CO concentration higher than 10 ppm may be responsible for the PEMFC anode catalyst poisoning [30]. Consequently, reformed streams need to be purified before feeding a PEMFC, by means of some additional processes such as the aforementioned high temperature and low temperature WGS reactors, in which the CO content is reduced because CO is transformed into CO_2 and further hydrogen (CO content is reduced up to 0.5 %); preferential oxidation (PROX) reactors, in which the residual CO is converted into CO_2 (CO content is lowered to less than 10 ppm), and pressure swing adsorption (PSA) to separate hydrogen from CO_2. In conventional operations, a fraction of produced hydrogen needs to be consumed as well as for these additional reactions O_2 supplying is also required. Furthermore, heat supply equipment and complex energy integration between different process units (conventional reformer, WGS reactors and PROX reactor) constitute other needs. These operations increase the complexity and the costs of the overall process, leading to an uneconomical downscaling. Some of the requirements for reforming processes in mobile applications are the reduction of reformer size, the process intensification and the enhancement of the process efficiency [3,21].

MRs are attractive hydrogen generators from reforming processes, which may combine in the meantime the hydrogen separation/purification in a single device without needing any further purification stage, intensifying the whole process, reducing the cost of downstream processing, and improving the process efficiency.

The main problems which currently limit the use of the MR technology are related to the membranes costs. It is clear that, as for all the technologies developed at the laboratory scale level, this problem can be overcome when the request for this new technology increases, and therefore it is necessary to proceed to a scale up. In this case, in fact, a widespread diffusion of the technology implies the lowering of the costs connected to the production [21].

6. Operating parameters effects

In several reviews about MR technology present in literature, many aspects were analysed and discussed, often dealing with the status and the advancements of the inorganic membrane materials selective to hydrogen separation, MRs modeling and scalability from laboratory to pilot/industrial scale. Rarely, it was reviewed in deep the impact of the operating conditions on the performance of MRs in which the steam reforming of various renewable fuels such as methanol, ethanol, glycerol and, for comparison, methane is taking place. Hence, in the following sub-paragraphs, the main variables (pressure, temperature, feed flow rate, MR modality, feed concentration, sweep-gas flow rate) affecting the MRs performance under steam reforming of the aforementioned feedstocks are considered and discussed in detail.

6.1. Effect of pressure

A pressure increase in a MR shows two competitive effects on the reactants conversion. The first is negative and related to thermodynamics issues of steam reforming reaction. In the stoichiometric equations related to the steam reforming of methanol, ethanol, glycerol and methane, the reactions proceed with an increase of the moles number towards the reaction products. Therefore, the conversion of the reactants is unfavored by a pressure increase. On the contrary, the second effect, the aforementioned shift effect, related to hydrogen permeation through the membranes, plays a positive role.

By increasing the reaction pressure, the hydrogen permeation driving force (which is represented ideally by the hydrogen partial pressure square root difference between retentate and permeate side) is enhanced. According to Richardson’s equation, as high the pressure as high the hydrogen removed from the reaction side for permeation through the membrane, shifting the reactions towards further reaction products formation, with a consequent improvement of the conversions. The two distinct effects compete each other and, in most of cases, the “shift effect” results to be prevalent on the “thermodynamics effect”, globally determining improved performance in terms of conversion and hydrogen yield and recovery [80–103].

On the other hand, as a consequence of general better performance at higher operating pressures, another positive effect is related to the CO concentration, which generally decreases by increasing pressure. This is generally due to its positive effect on WGS reaction, present in all the reaction schemes of the aforementioned steam reforming reactions, determining a larger consumption of CO. The effect of pressure on the CH_4 selectivity in steam reforming of liquid hydrocarbons is generally not significant. Also in this case, there are two competitive effects. By considering the stoichiometry of the methanation reaction, an increase of pressure favors the reaction between hydrogen with CO_x to produce CH_4. On the other hand, the removal of hydrogen in a MR from the reaction side shifts the reaction to lower CH_4 formation. Nevertheless, the positive effect of pressure on CH_4 formation is generally slightly prevalent and the CH_4 content in the products increases with the pressure [85,87,94,95,98]. Table 2 illustrates some of the most significative reaction performance in MRs as a function of reaction pressure. As shown, an increase of pressure globally determines an enhancement of the reaction conversion as well as hydrogen recovery and yield. Although not included in Table 2, another important parameter to be taken into account in MRs is the hydrogen purity. This may vary depending on the hydrogen perm-selectivities of the inorganic membranes adopted inside the MRs. In general, no influence is noticed about hydrogen purity as a consequence of a pressure variation in case of thick walled Pd-based membranes, because they are dense and fully hydrogen

Table 2

Effect of the pressure on the different performance parameters in steam reforming of different hydrocarbons.

Hydrocarbon	Catalyst	Membrane	p [bar]	Conversion [%]	H_2 recovery [%]	H_2 yield [%]	CO selectivity [%]	Reference
Methane	$NiO/CaAl_2O_4$	Pd-Ag	2→5	55.6→47.1	–	–	–	[56]
Methane	Ru/Al_2O_3	Pd on PSS	1→5	50.6→64	–	–	10.6→4	[61]
Methane	Ni/Al_2O_3	Pd-Ag	1→3	22.7→31.8	25.7→57	–	0.5→0.2	[81]
Methane	Ni catalyst	Pd	1→9	67.8→90	–	–	–	[89]
Methane	Ni-doped SiO_2 top layer supported on Al_2O_3		1→4	59→79	–	1.3→3.2	–	[90]
Methane	Ru/Al_2O_3	Pd-based	2→9	50.7→82.7	–	–	–	[91]
Methane	alumina-supported nickel catalyst	Pd on PSS	1→3	75.5→97	–	–	4.2→0.6	[92]
Methane	Ru/Al_2O_3	Pd on PSS	5→ 6	72.9 → 79.5	97.9→98.7	–	–	[93]
Ethanol	$Co_3[Si_2O_5]2(OH)_2$ supported over cordierite	Pd-Ag	7.3→11.3	–	27→54	–	5.3→4.2	[73]
Ethanol	Ni/ZrO_2	Pd on PSS	8→12	80→93	32→84	–	3.2→1.2	[85]
Ethanol	Co/Al_2O_3	Pd on PSS	3→8	86→99	6.8→53		4.5→2.8	[87]
Ethanol	$Pd–Rh/CeO_2$	Pd	1→11	–	–	4.3→66	–	[94]
Ethanol		Pd–Ag	1→8	73→95.5	43.9→96.3	–	–	[95]
Methanol	$Cu/ZnO/Al_2O_3$	Silica	1.5→10	85 → 94		82 → 93	0.3 → 0.06	[75]
Methanol	$Cu/ZnO/Al_2O_3$	Pd-Ag	2→16	38→69	64→97	–		[78]
Methanol	$CuO/ZnO/Al_2O_3$	Pd	1.5→2.5	71.7→84 55.9→58.7	23.4→41.7 19→35	73.4→82 57.8→58.7	1.07→1.21 0.62→0.4	[84]
Methanol	$Cu/ZnO/Al_2O_3$	Pd-Ag	1.5→2.5	98→100 57→62	–	22.5→31.5 4.9→6.7	4.1→3.96	[96]
Methanol	Cu/Zn/Mg	Pd-Ag	1.5→3.5	–	64.1→91.7 30.7→70.8	63.5→65.3	–	[97]
Methanol	$Cu/ZnO/Al_2O_3$	Pd-Ag	2→10	79→87	51→90	–	–	[98]
Methanol	$Cu/ZnO/Al_2O_3$	Silica	1.5→10	79 → 88	–	77 → 85	0.52 → 0.26	[99]
Glycerol	$Ni/CeO2/Al_2O_3$	Pd-Ag	1→5	17.4→27.4	0→3.9	15.2→13.3	–	[100]
Glycerol	Ru/Al_2O_3	Pd–Ag	1→5	11.3→15.1	9.6→16.9	5.3→7.4	–	[101]
Glycerol	$Co-Ni/Al_2O_3$	Pd–Ag	1→ 10	46 → 81	17 → 56	–	6.6 → 0.9	[102]
Glycerol	$Co-Al_2O_3$	Pd–Ag	1→4	43.6→91.8		33.8→62.8		[103]

perm-selective. Hence, a change of purity would be determined by the membrane failure [58]. In case of supported Pd-based membranes (not fully hydrogen perm-selective), in which a thin dense layer of Pd/Pd-alloy is deposited on a porous substrate, higher pressures could allow to gaseous products beside hydrogen to pass through the defects of the dense thin layer with a different mechanism with respect to the solution-diffusion (Knudsen, Hagen-Pouseille) [63]. Nevertheless, most of hydrogen passes through the dense layer of Pd/Pd-alloy for solution diffusion (Eq. (7)).

Furthermore, in some steam reforming reactions, an increase of pressure may determine an increase of coke formation, which is responsible for the catalyst deactivation, resulting in higher CH_4 and CO_2 formation, which – at higher pressure conditions – may pass as larger flow rates across the defects of the thin, dense, selective layer.

6.2. *Effect of feed flow rate (space velocity)*

A decrease of the feed flow rate grows up the residence time of reactants in the catalytic bed favoring a higher contact time within reactants and catalyst [104–111]. This favors the conversion and the hydrogen yield [10,56,112–117]. As a consequence, at lower feed flow rates a larger amount of hydrogen is produced, determining higher hydrogen concentration in the reaction side and, hence, higher hydrogen partial pressures. This globally favors the hydrogen permeation driving force and a larger shift effect on the reaction system. Taking into account the aforementioned benefits of the shift effect present in the MRs during steam reforming reactions of hydrocarbons, Table 3 illustrates the performance of a number of reaction systems from literature showing the effects of the feed flow rate (space velocity) variation on the reaction performance. As expected, higher values of the space velocity induce a general decrease of the reaction performance in terms of conversion, hydrogen yield and recovery, independently of which kind of steam reforming reaction is carried out in the MR.

6.3. *Effect of reactor configuration*

Various studies present in literature proposed different MR configurations [73,77]. On one hand, a MR configuration may consist of a reactor geometry in which the reaction and selective separation of hydrogen do not occur simultaneously (staged MR modality). In this case, the reaction takes place in the reaction zone, which is confined in a part of the MR, not in direct contact with the hydrogen selective membrane. Hence, the hydrogen produced during the steam reforming reaction permeates through the membrane and is collected in the permeate side, Fig. 8a. On the other hand, another MR configuration may consist of a reactor geometry in which both reaction and hydrogen separation take place simultaneously (catalytic MR modality). In this case, the catalytic bed is in direct contact with the hydrogen selective membrane, Fig. 8b. Sharma et al. [57] demonstrated that, comparing a staged with a catalytic Pd-based MR, the hydrogen permeating flux and related permeate purity were found comparable. Furthermore, at optimized conditions, the catalytic MR performance in terms of conversion and hydrogen yield were equivalent to the staged MR. Dominguez et al. [73] also compared a staged with a catalytic MR during ESR reaction. Fig. 9 shows that ethanol conversion and hydrogen yield increase with

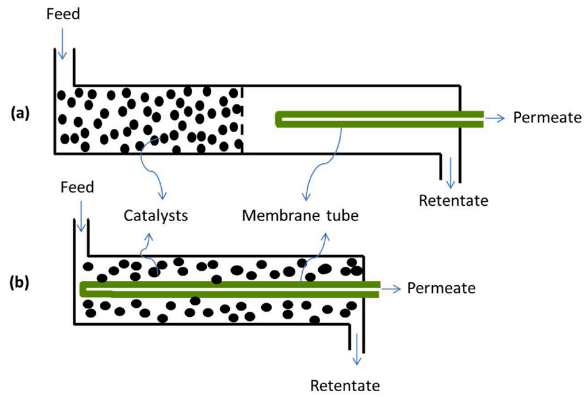

Fig. 8. Two different membrane reactor configurations: (a) staged membrane reactor and (b): catalytic membrane reactor.

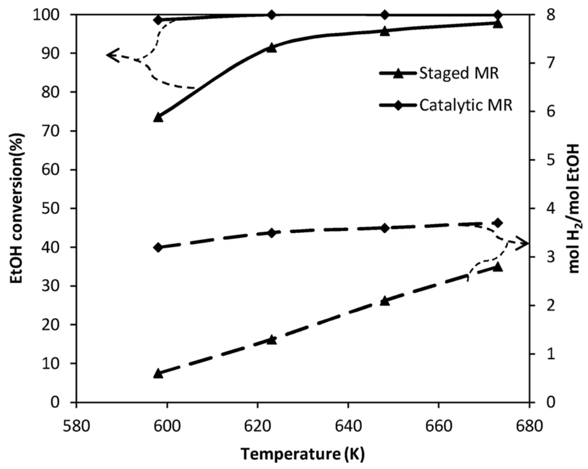

Fig. 9. Performance of the staged MR and catalytic MR in ethanol steam reforming process.

Table 3
Effect of the feed flow rate on the different performance parameters in steam reforming of different hydrocarbons.

Hydrocarbon	Catalyst	Membrane	GHSV [h^{-1}]	Conversion [%]	H_2 recovery [%]	H_2 yield [%]	CO selectivity [%]	Reference
Methane	Ni-based	Pd	4400→6900	51→31	90→82	–	–	[104]
Methane	Ni (ICI 41−6)	Pd-Ru	18→68[a]	84→64	–	–	–	[116]
Methane	Ni/Al_2O_3	Pd-Ag	32→172[a]	72.7→21	–	–	–	[117]
Ethanol	Ni/ZrO_2	Pd	800→1200	94.3→79.2	38.4→12.8	39.5→34.5	–	[85]
Ethanol	$Pd–Rh/CeO_2$	Pd	1200→4500	–	15.6→14.2	65.7→43.5	–	[94]
Ethanol	$Rh/La–Al_2O_3$	Pd–Ag	8500→22,500	–	–	4.3→2.8	7→6.7	[105]
Methanol	$Cu/ZnO/Al_2O_3$	Pd–Ag	800→25,000 2000→25,000	100→25 100→65	–	–	12→0 10→4	[67]
Methanol	$Cu/ZnO/Al_2O_3$	Pd-Ag	9000→42,000	100→25.5	–	–	36→22	[78]
Methanol	$Cu/ZnO/Al_2O_3$	Pd-Ag	1800→10,250	98.7→37	–	22.5→1.5*	–	[96]
Methanol	$Cu/ZnO/Al_2O_3$	Silica	2000 → 10,000	92 → 73	–	90 → 72	0.12 →0.83	[99]
Methanol	$Cu/ZnO/Al_2O_3$	Pd–Ag	4000→14,000	97→78	95→50.5	–	–	[106]
Glycerol	Ru/Al_2O_3	Pd–Ag	0.1→1[b]	57→11.5	55→17	–	–	[101]
Glycerol	$Co-Ni/Al_2O_3$	Pd–Ag	1 → 10[b]	46 → 17	17 → 8	–	6.6 → 4.8	[102]

[a] Feed flow rate (sccm).
[b] WHSV (h^{-1}).

temperature during ESR reaction for both MR modalities. Nevertheless, the catalytic MR modality seems to better perform than the staged MR. Probably, in the catalytic membrane configuration the continuous removal of hydrogen from the reaction zone as it is produced in the catalytic bed enhances both conversion and hydrogen yield, favoring the consumption of some intermediate species such as CO, CH_4 and acetaldehyde. In the staged MR modality, the development of the ESR reaction without a continuous and immediate removal of hydrogen favors the formation of byproducts and intermediates, which determine a lower hydrogen concentration in the reaction side (consequently, a lower hydrogen partial pressure), involving lower hydrogen permeation driving force and, globally, decreased performance.

6.4. *Effect of temperature*

The steam reforming reactions considered in this review (ethanol, methanol, glycerol and methane) are all endothermic. From a thermodynamic point of view, they are favored at higher temperatures. Table 4 illustrates the performance of several MRs used for producing hydrogen from steam reforming of various hydrocarbons. It appears evident that higher temperatures improve the catalytic activity, resulting in higher conversions and hydrogen yields. Moreover, as described by the Richardson eq. (8), the temperature dependence of the hydrogen permeation through Pd-based membranes follows an Arrhenius-like equation. Consequently, the hydrogen permeating flux is increased by raising the temperatures, making more effective the shift effect on the steam reforming reactions considered [107–111]. Nevertheless, CO selectivity raises by increasing the temperature. Indeed, two main sources of CO production are the decomposition reaction of liquid fuels such as methanol and ethanol and the reverse of WGS reaction. Decomposition reaction is endothermic and WGS exothermic, so that both reactions move toward further CO formation as temperature increases.

6.5. *Effect of the feed molar ratio*

Another important parameter useful to influence the steam reforming reactions of hydrocarbons is the feed molar ratio. The presence of steam in the reaction environment has the desired effect on the steam reforming catalyst activity and selectivity [74,77,84,88,94,95,99,102,103,112,113]. Using the sub-stoichiometric feed molar ratio in the inlet stream leads to poor conversion and increases the possibility of by-products and coke formation. Generally, increasing the feed molar ratio up to 2–3 times the stoichiometric value enhances the conversion, Table 5. Nevertheless, above certain feed molar ratios, the conversion remains almost constant. Feed dilution at a constant total inlet flow rate means a low space velocity, increases the contact time between reactants and catalytic bed and, consequently, improves the conversion. Higher feed molar ratios involve a larger water content in the feed, which contributes to shift ESR, MSR, WGS, GSR and SRM reactions toward the reaction products, favoring a higher hydrogen production and, consequently, the hydrogen yield (mole of produced H_2/mole of feed inlet). In the meanwhile, a higher feed molar ratio lowers CO formation due to the enhanced WGS reaction up to achieve negligible CO values.

However, using very high feed molar ratios, the consequent excess of water in the reaction environment dilutes the produced hydrogen, resulting in a lower hydrogen partial pressure in the retentate side. This lowers the hydrogen permeation driving force, inducing a lower hydrogen permeating flux through the membrane and the recovery. Therefore, to select an optimal feed molar ratio, it is necessary to balance the different effects, which may conflict within each other.

6.6. *Effect of sweep gas flow rate*

The use of a sweep gas inside the permeate stream of a MR involves a decrease of the hydrogen partial pressure at this side for dilution, meanwhile increasing the hydrogen permeation driving force, favoring higher conversion, hydrogen yield and recovery to be reached. Nevertheless, the use of a sweep gas involves also a drawback related to the need of its separation from hydrogen to guarantee the hydrogen purity of the stream collected in the permeate side. At laboratory scale, several times inert gases such as N_2, He or Ar are used [103–115]. Realistically, at larger scale only steam could be used as a sweep gas because easy to separate from hydrogen for condensation. Table 6 illustrates a number of studies dealing with the effect of the sweep gas on various steam reforming reactions. In this table, the effect of the sweep gas flow rate is considered introducing the sweep factor, which presents the ratio between the sweep gas and feed molar flow rates as: Eq. (34):

$$SF = \frac{Sweep\ gas\ molar\ flow\ rate}{Feed\ molar\ flow\ rate} \tag{34}$$

It should be noted that, in Table 5, the increase of conversion depends on the sweep factor growth. Nevertheless, it is not recommended to increase the sweep factor above certain values because it could not have any advantageous effect on the MR performance.

7. Conclusion and future trends

MRs offer many advantages over the TRs in terms of both economic and environmental features. Using the MRs the number of operational units, the complexity and production cost, energy consumption and equipment sizes are reduced. The adoption of the MR technology in the

Table 4
Effect of temperature on the different performance parameters in steam reforming of different hydrocarbons.

Hydrocarbon	Catalyst	Membrane	[h]T [K]	Conversion [%]	H_2 recovery [%]	H_2 yield [%]	CO selectivity [%]	Reference
Methane	Ni-Al_2O_3	Pd-Ag	400→500	13.2→30.5	–	–	0.1→1.1	[81]
Methane	NieAl_2O_3	Pd-Ag	550→600	23→41	8.5→23	–	–	[107]
Ethanol	$Co_3[Si_2O_5]2(OH)_2$ supported over cordierite	Pd-Ag	325→400	98.6→100	–	3.2→3.7	3→5.3	[73]
Ethanol	Pd–Rh/CeO_2	Pd	550→650	98.2→98.8	–	14→54.7[a]	–	[94]
Ethanol	Co/Al_2O_3	Pd-Ag	573→973	35→100	63→99	29→83	–	[108]
Methanol	Cu/ZnO/Al_2O_3	Silica	493 → 573	70 → 95	–	74→ 88	0.18 →1.29	[75]
Methanol	Pd-Ag with catalytic property		350→450	79.7→97.9	31.2→38.2	–	32→40	[77]
Methanol	Cu/ZnO/Al_2O_3	Pd-Ag	200→350	15→100	38→77	–	–	[78]
Methanol	CuO/ZnO/Al_2O_3	Pd/Al_2O_3	280→330	58→84	35→42	59→82	0.4→1.2	[84]
Methanol	Cu/ZnO/Al_2O_3	Silica	493 → 573	66 → 90	–	67 → 86	0.3 → 1.6	[89]
Methanol	CuO/ZnO/Al_2O_3	Pd-Ag	200→250	34.6→50.8	–	–	0.05→0.47	[109]
Glycerol	Ni/CeO_2/Al_2O_3	Pd-Ag	400→450	10.4→22.3	–	1.4→2.3	–	[100, 110]
Glycerol	Co-Ni/Al_2O_3	Pd-Ag	623 →773	41 → 56	12 → 36	–	6.9 → 5.1	[102]
Glycerol	Pd-Ni		300→500	12.5→99.5	61.5→73.5	–	–	[111]

[a] Volumetric yield.

Table 5
Effect of feed concentration on the different performance parameters in steam reforming of different hydrocarbons.

Hydrocarbon	Catalyst	Membrane	] S/F ratio [a]	Conversion [%]	H_2 recovery [%]	H_2 yield [%]	CO selectivity [%]	Reference
Methane	Ni-based	Ceramic	2→9	65→100	2.4→4	–	–	[103]
Ethanol	Pd–Rh/CeO_2	Pd	0.5→4	–	–	1.3→2.3	–	[94]
Ethanol	Co based	Pd–Ag	1→10	32→93	70→61	–	–	[95]
Ethanol	Co/Al_2O_3	Pd–Ag	2→10	33→100	–	28→88	–	[108]
Ethanol	Ir/CeO_2	Pd	0.5 → 4	–	55 → 90	57 → 87	–	[112]
Methanol	Pd-Ag self –supported membrane with proprietary catalyst (ME_100®)		1.12→18	80→81	32→38	–	18→2	[77]
Methanol	Cu/ZnO/Al_2O_3	Silica	1→3	88→92	48→44	–	3→1.2	[88]
Methanol	Cu/ZnO/Al_2O_3	Pd-Ag	1→4	94→100	–	93.7→100	–	[97]
Methanol	Cu/ZnO/Al_2O_3	Silica	1→ 3	83→ 89	–	83→87	3.3 →1.6	[99]

a: S/F ratio (feed molar ratio) = molar ratio of steam to inlet hydrocarbon.

Table 6
Effect of sweep gas flow on the different performance parameters in steam reforming of different hydrocarbons.

Hydrocarbon	Catalyst	Membrane	Sweep factor [a]	Conversion [%]	H_2 recovery [%]	H_2 yield [%]	CO selectivity [%]	Reference
Methane	Ru/Al_2O_3	Pd-Ag	93→485[b]	69→85	62→90	–	6.2→4.5	[61]
Methane	Ni-Al_2O_3	Pd-Ag	0.6→1.6	23→44	20→37	–	–	[81]
Methane	Ni based	Pd	367→562[b]	57→77	–	–	–	[89]
Methane	Ni/Al_2O_3	Pd-Ag	0→5	40→97	–	–	–	[115]
Ethanol	–	Pd–Ag	1 →20	79.4→98	–	–	–	[95]
Ethanol	Co/Al_2O_3	Pd–Ag	1→10	61→89	82→99	49→83	–	[108]
Methanol	Cu/ZnO/Al_2O_3	Pd–Ag	2.5→8.9	98.4→100	–	22→29	–	[96]
Methanol	Cu/Zn/Mg	Pd–Ag	1.1→9.7		31→74	62.5→65.4	–	[78]
Methanol	Cu/ZnO/Al_2O_3	Silica	0→60	92→95.5	4→39	–	–	[114]
Glycerol	Co-Al_2O_3	Pd–Ag	2.5→22.5	46→50	3.4→4.5	–	–	[103]

a: Sweep factor = sweep gas molar flow rate/ inlet hydrocarbon molar flow rate.
b: Sweep gas flow rate as standard cubic centimeters per minutes.

field of hydrogen production makes possible to overcome the intrinsic limitations connected to the conventional processes such as the thermodynamic constrains. Pd and Pd-alloys result the dominant materials among others in the preparation of inorganic membranes to be installed in MRs for generating hydrogen from catalytic processes. However, the application of Pd-based MRs at industrial scale seems to be still far to be realized owing to the high cost of Pd and to the membrane limitations in terms of resistance under harsh environments in long-time operations. Currently, most of the industrial companies involved in the field of hydrogen production using pilot-scale MRs are highlighting the importance of the experimentation at larger scale because useful to fully understand that a catalytic MR well operating at industrial level closely depends on 1) the right selection of the most adequate catalysts for a specific chemical process, 2) the hydrogen selective membranes adopted and 3) the protocols for the process management under operations.

A widespread commercial application of MRs in various processes will be possible only if MR operation and membrane properties will be optimized passing through the simplification of the membrane production stage. It is worth of noting that MRs are limited in applications at larger scale, and this cannot be dependent only on the relatively low membrane/MR performance (low membrane permeability and selectivity, thermal and chemical resistance, etc.), but more probably to not optimized MR module design and, sometimes, to engineering analyses. Many efforts are currently made about the research on new inorganic membrane materials or on the combination of the existent ones in order to prepare new membranes and MR solutions able to meet the industrial needs.

The perspectives of MR technology in industry (fuel processing, chemical and petrochemical industries etc.) are hence linked to the possible development of the Integrated Membrane Operations in the same industrial cycle, with consequent and realistic advantages in terms of plant compactness, low environmental impact, high process efficiency, energy saving and reduced costs. However, the MRs implementation in industry will be concretely realized once a few issues, such as the membrane/MR fabrication costs reduction, the enhancement of membrane performance in terms of stability under harsh environment, poisoning, and aging phenomena, and the current lack of industry-produced MR commercial-scale units, will be solved.

In the meantime, the prospect of generating hydrogen from steam reforming of light hydrocarbons is strongly linked to the research advances on the enhancement of productivity through the catalytic engineering and the progress of chemical reactors (among them, the MRs), a part from the general and economical attention towards the exploitation of alternative sources instead of the fossil fuels, the social appreciation, and the widely accepted utilization of the hydrogen energy in our society.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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