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On the energy efficiency of hydrogen production processes via steam reforming using membrane reactors

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ABSTRACT

The novel paradigm of distributed energy production foresees the production of hydrogen from methane and biomasses in small plants, which may take advantage from membrane-based processes. By means of a modeling approach, this paper compares the energy efficiency of two membrane-based processes to produce H_2 from methane steam reforming. The two-step process (TS) envisages a high temperature classical reactor and a following WGS stage in a membrane reactor, while the alternative process uses a simple packed-bed membrane reactor (MR). Both processes show a general increase of H_2 production and energy efficiency with the pressure and a maximum energy efficiency for S/C of 4, while the increase of the space velocity reduces the performances of the MR. The results show that the TS process performs better than the studied MR and that the maximum energy efficiency of both processes is between 30 and 40%. A comparison with the literature shows that the TS process may achieve similar performances respect to an intensified MR.

Introduction

Following the Paris Agreement (2015), the EU energy policy for next decades till 2050 is focused on security, efficiency and diversification of energy sources in order to cut down the CO_2 emissions. Such strategy encourages the use of renewable or low-emission energy sources and also implies the distributed generation of energy [1]. To obtain such targets, the wide use of H_2 as an energy vector for different kind of civil final energy uses is foreseen [2,3]. However, so far, such strategy is hindered by the lack of a proper distribution infrastructure [3,4] therefore a solution may be to produce H_2 in distributed facilities. Hydrogen can be produced from diverse renewable sources: generally, from renewable energy via water electrolysis, which allows using H_2 as energy storage mean [4–8], but also from methane or ethanol via steam reforming; such last processes may be CO_2-neutral if the fuels come from biomasses (e.g. bio-methane, bio-ethanol) [9–12]. The purity of H_2 generated by steam reforming reactions depends on both the technology used and on the considered feed stocks, therefore a separation step could be required to recover

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hydrogen from a gas mixture containing also CO_2, CO, N_2 or water vapor with the desired purity [6,13]. In this context, among the available new technologies to enhance the H_2 production in small distributed facilities, membrane reactors (MRs) are attracting great interest due to their higher efficiency with respect to classical configurations [14–20], especially when using Pd-based membranes to selectively separate H_2 from the other reaction products. A reaction and a selective separation take simultaneously place in a membrane reactor: according to the Le Châtelier's principle, it is possible to obtain values of reaction conversion higher than those achieved under the thermodynamic equilibrium thanks to the continuous removal of one of the products ("shift effect" of the membrane) [14,15]. These membranes are generally in form of tubes and can be dense self-supported (generally 50–150 μm of wall thickness) or composite, in which few μm thin Pd-layers are deposited over porous supports (both metal and ceramic) [19–24].

In their basic and most studied configuration, membrane reactors are conceived as packed bed tubular reactors, where catalyst may be inside or outside (annular-like packed bed) the membrane tube, although they may also be realized in the fluidized bed configuration [14]. In the first case, both dense and composite membranes may be used, while the fluidized bed reactors use thin film supported membranes.

At the moment, the main issue limiting the wide application of Pd-based membranes is the high cost of the Pd. However, research on membrane-based processes still receives great interest as in the next future they may be used in small distributed facilities to produce H_2 for energy uses. In this case, a key factor for the application of such processes in the distributed generation scheme is their optimization in terms of energy efficiency [11,12,21]. Another important parameter to be considered in the process is the Hydrogen Yield (HY) of the reactions, which is the amount of H_2 obtained respect to the fuel introduced in the reactor [12]. Generally, the energy efficiency of the process and the HY may not be maximized for the same operative conditions, so the process optimization depends on the target to be achieved (i.e. maximum H_2 production or maximum energy efficiency). In the following, some example of researches from literature whose aim was to identify optimal operative conditions and configurations for membrane reactors and membrane-based processes will be presented.

Regarding the operative conditions, temperature in MR is generally lower than 500 °C in case of the use of dense self-supported membranes, while for supported membranes it may reach 600 °C. Pressure, instead, reaches values of at least some bar up to 20, which improves the shift effect ad increases the H_2 production. For example, Hedayati et al. studied the ethanol steam reforming process catalytic MR performing an exergetic analysis based on experimental data. Operative conditions such as temperature (600–650 °C) and pressure (4–12 bar) were varied, while the feed flow rate S/C was 1.6. Higher pressure values led to highest exergy efficiency due to the increase of H_2 permeation. Exergy efficiency depends on the feed flow rate: it increases for high flow rates although the average value is maintained around 20% [21]. Di Marcoberardino and Manzolini performed experimental tests for methane steam reforming in a fixed-bed membrane reactor. They operated with pressure in the range of 4–6 bar and temperature between 550 and 600 °C, the obtained methane conversion rate between 23% and 47%. They also evidenced the negative influence of the space velocity (SV, mol h^{-1} g_{CAT}^{-1}) on the methane conversion rate: at 400 kPa and 600 °C, when the SV passes from 0.010 to 0.020, the methane conversion rate passes from 0.25 to 0.185 [25].

Saidi and Jahangiri studied via simulations the ethanol steam reforming over Co/Al_2O_3 catalyst in a catalytic membrane reactor. They validated a 2-D model based on experimental test performed in a single tube MR. Their results confirmed that in such reactors the production of hydrogen is favored by high pressures, temperatures and with high H_2O/ethanol molar ratio. Particularly, values of HY higher than 80% are achieved for pressures higher than 12 bar, T higher than 500 °C and for a H_2O/ethanol molar ratio higher than 6 [18]. Patrascu and Sheintuch, instead, studied a single tube packed-bed membrane reactor in annular configuration. Temperature was kept between 440 and 525 °C and pressure varied from 1 to 20 bar, with S/C of 3. They obtained a 90% CH_4 conversion and 80% HY at 10 bar [26]. Kim et al. tested methane SR in a MR packed with commercial Ru-based catalyst. By operating at 500 °C and with a pressure difference of around 5 bar between feed and permeate side, they showed a CH_4 conversion of 80%. Their membrane could not achieve an infinite selectivity, obtaining H_2 purity at the permeate side of 98.7% [27]. Lower temperatures and pressures (225–250 °C, 3 and 5 bar) were studied by Israni and Harold in the case of methanol steam reforming, which focused on the effects of impurities on the H_2 permeance in a packed bed reactor with supported membrane, finding that an increase in CO concentration hinders H_2 permeance [28].

Regarding the best performances and the optimal design of packed bed MRs, interesting studies were made by Murmura et al. [29–31]. The authors developed an analytical model based on transport phenomena and dimensionless variables. The model was validated with experimental data and can be applied to a class of reactors that share geometrical characteristics. They characterized the behavior of such reactors by identifying different operative regimes (transport-limited or membrane-limited) and identifying a critical operative pressure which differentiates between such two regimes. Moreover, by applying such models, the authors found optimal operative conditions and design methods for such type of reactors applied to the steam reforming of hydrocarbons to produce hydrogen. Namely, the authors focused on S/C of 3 and found the optimal pressures to maximize the HY: it is the above mentioned critical pressure. They also state that the gas mixture should be pre-reformed before entering the membrane reactor and complete the SR reaction: this would allow exploiting the permeation surface of the membrane optimally. In terms of the reactor design, the focus of [31] was on the effects of the annulus size and of the reactor length. Results tell that reactions occur in a boundary layer and that the size of the catalyst annulus should be that of the boundary layer in order to maximize the H_2 production. Besides, when a given length is reached, no more reaction occur because the complete CH_4 conversion as been achieved.

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Regarding the performances of complex membrane-based processes producing H_2 to feed a fuel cell, many studies have been performed on the steam reforming of methane and ethanol, including independent membrane separators or intensified membrane reactors. For example, Tosti and Manzolini studied via computer simulation three different configurations for a H_2 processor to feed a 4 kW FC via bio-ethanol conversion: i) simple reformer followed by two classical H_2 purification units, ii) a reformer followed by a membrane separator and iii) a multi-tube packed bed membrane reformer. The systems show a net energy efficiency ranging from 32.4% to 41.2%: the processes including membranes have better efficiency in energy conversion efficiency respect to the classic reforming process. They also showed that an increase in the steam to carbon ratio (S/C) reduces the energy efficiency in all cases, due to the growing energy demand for the water evaporation [11].

Mendes et al. instead compared two different schemes: i) a conventional reformer followed by a two steps (high and low temperature reactors) water gas shift reaction (WGS and a final H_2 purifier to obtain the required purity levels to feed a PEM Fuel Cell (PEMFC); and ii) a classic reformer followed by a membrane packed bed WGS reactor. They stated that an increase of the water-to-ethanol molar ratio leads to a greater HY. In both processes the majority of H_2 is expected to be produced in the reformer, while the WGS reactors would account, respectively, for a share of the produced H_2 of the 28% in the first configuration and for the 22% in the second one. Moreover, in the second process scheme, an optimal membrane reformer temperature of 360 °C has to be chosen in order to achieve a trade-off between the CO conversion in the WGS reactions and the membrane permeability, leading to a maximum H_2 recovery [12].

Not only packed bed, but also fluidized bed are under study and they show interesting results as they generally allow to obtain the same amount of H_2 with less permeation surface area. Campanari et al. modeled and analyzed a process including a fluidized bed membrane reformer aimed at feeding H_2 to a fuel cell cogeneration system (MREF) under both thermodynamic and techno-economic standpoints. They state that the MREF achieves significant reduction in CO_2 emissions and doubles the economic savings of auto-thermal SR or classical SR cogenerators. Electric efficiency of the whole process varies in the range 35–40% [32]. Roses and Gallucci presented a simulation analysis of two different micro-cogeneration system based on a 2 kW PEMFC, one of whom fed by a fluidized membrane reactor. They demonstrated that the use of membrane reactors leads to 43% electric efficiency, while a traditional process cannot overcome 34%. In this study temperature was set to 600–650 °C and pressure varied between 6 and 14 bar. Moreover, they compared fluidized bed and fixed bed membrane reactors and indicated that a fluidized bed reactor can improve the hydrogen production, leading to a 25% lower surface area for a particular amount of H_2. However, they also studied the case of a packed bed membrane reactor preceded by a classical pre-reforming section: they demonstrated that such a configuration increases the H_2 recovery respect to a simple packed bed MR and that may reach performances similar to a fluidized bed MR, also showing uniformity of temperature inside the reactor [33]. Di Marcoberardino and Manzolini studied via simulations a micro-cogeneration system based on a FC fed by an auto-thermal membrane reformer. This configuration aims at obtaining a 40% electric efficiency and 90% total energy efficiency by using a 0.3 m^2 membrane surface area with sweep gas operation at P = 8 bar, T = 600 °C and S/C = 2.5. The use of a vacuum pump for recovering the hydrogen reduces the required membrane area up to 0.15 m^2 with a similar electric efficiency of around 38% [34].

Among all these membrane reactor configurations, in this work we want to focus on a particular solution the so-called two-step process (TS): it consists of a classic reformer followed by a membrane reactor. The TS process was also studied via experimental tests [35,36].

Borgognoni et al. tested a TS plant with a traditional reformer followed by a multi-tube permeator made up of 19 Pd-Ag self-supported tubes of 150 μm wall thickness. They demonstrated the positive effect of rising both operative pressure (from 1 to 4.9 bar) and reformer temperature (from 570 to 720 °C) on the HY. Particularly, HY rises from 0.13 to 0.40 or from 0.16 to 0.72 in case of increasing pressure or temperature, respectively. They also stated that an increase of S/C improves the hydrogen production, while the rise of the space velocity leads to a reduction of the produced hydrogen [35]. In addition, the same experimental setup, was used to perform combined methane and ethanol steam reforming reactions. The operative pressure was varied from 1 to 5 bar, maintaining the reformer and permeator temperatures at 760 and 350 °C, respectively. In these experiments, the hydrogen yield decreased as the methane/ethanol molar ratio was increased. A hydrogen yield up to 35% was achieved at 5 bar in presence of a high water excess (feed water/ethanol/methane molar ratio of 26/1/4) [36].

The aim of this paper is to further investigate the performances of the Two Step process for the case of methane SR. This particular configuration is not widely investigated in literature especially for the case of methane SR, while similar process schemes have been proposed by introducing a pre-reforming stage as in the above-mentioned work of Gallucci and Roses [33]. Also, as previously mentioned, Murmura et al. showed that a packed bed MR fed by a pre-reformed gas stream shows higher reaction efficiencies [29,30]. For such reason this work aims at exploring a wide range of operative conditions for a TS process and compare its performances to that of a packed bed MR and to other results coming from the mentioned literature.

Experimental methodology and modeling approach

General process configuration

In this work, the energy analysis of two different membrane processes for producing ultra-pure hydrogen via methane steam reforming has been modeled. A basic scheme of each process is shown in Fig. 1. In the first case, a two-step process (TS) based on a high temperature steam reformer coupled with a membrane reactor for the WGS, has been studied (Fig. 1a) while the second one consists of a single multi-tube

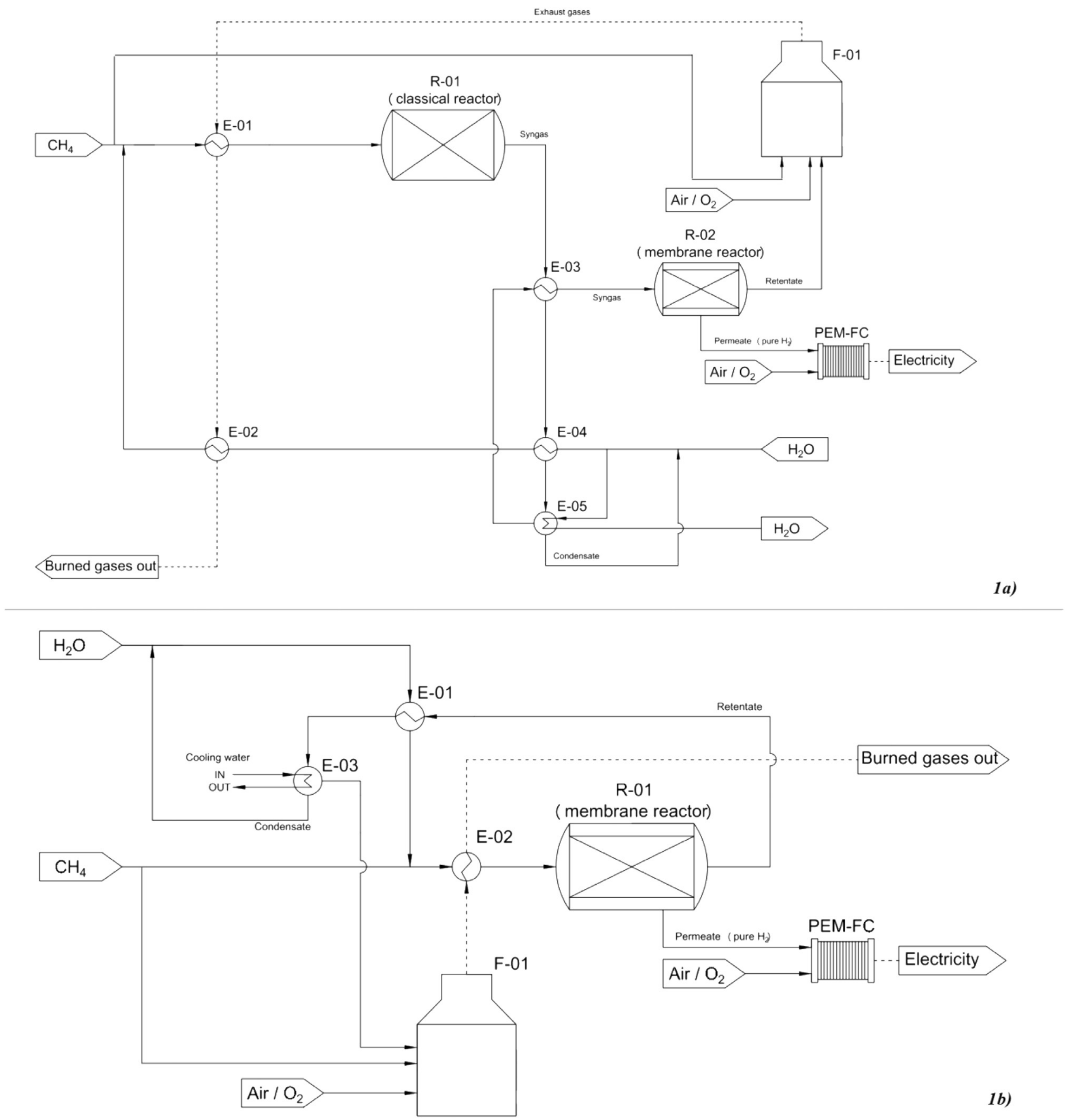

Fig. 1 — Scheme of the two studied processes: a) illustrates the TS process and b) the MR process.

membrane packed bed steam reformer (MR) producing directly an ultra-pure hydrogen flux by permeation through the selective membrane (Fig. 1b).

In both processes, the main reactants (methane and water) are mixed and heated up before being sent to the first reactor. In the TS process, the temperature of the first conventional reactor is kept in the range between 650 and 900 °C to generate a syngas via steam reforming. To adjust the ratio H_2O/CO, part of the water is removed from the syngas which is sent to a WGS membrane reactor. In this second reactor, the water-gas shift reaction occurs simultaneously to the selective permeation of hydrogen through the membrane. The retentate, containing typically syngas and H_2O, is burnt and used for the energy optimization of the plant, while the permeate, consisting on ultra-pure H_2, feeds a PEMFC to produce electric power. Pressure in the classical reactor and in the feed side of the membrane reactor is the same and higher than 3 bar, while in the permeated side of the membrane reactor is set to 1 bar.

In the MR process, the production and separation of H_2 occur simultaneously in a single device. The temperature ofthe membrane reactor is maintained at 500 °C and, similarly to the previous case, the ultra-pure H_2 is sent to a FC for generation of electric power, while the retentate is burnt to provide internal heat. In all cases, the heat transfer between diverse streams is carried out with an efficiency of 80%. After the optimization, further heat is provided to the feed stream by feeding additional CH_4 in the burner. Pressure in the feed side is generally higher than 5 bar while in the permeated side is 1 bar. Both plants are sized to provide 1 kW electric power in the FC.

Main chemical reactions

The main chemical reaction for both proposed configurations is the methane steam reforming (1), which is an endothermic chemical process favored by high temperatures and low pressures, accordingly to the thermodynamics.

$$CH_4 + H_2O = CO + 3H_2 \ \Delta H_{298K} = 206 \text{ kJ mol}^{-1} \quad (1)$$

Additionally to this main chemical reaction, the water-gas shift (2), is also taken into account, being favored at temperatures in the range 200–400 °C due to the contrary effect of thermodynamic and kinetic.

$$CO + H_2O = CO_2 + H_2 \ \Delta H_{298K} = -41 \text{ kJ mol}^{-1} \quad (2)$$

Thus, the overall reaction can be defined as follows:

$$CH_4 + 2H_2O = CO_2 + 4H_2 \ \Delta H_{298K} = 165 \text{ kJ mol}^{-1} \quad (3)$$

Other possible reactions are the CO conversion to methane, i.e. the reverse reaction (1) and the Boudouard reaction (4), which describes an equilibrium between CO, C and CO_2:

$$2CO = CO_2 + C \ \Delta H = -41 \text{ kcal mol}^{-1} \quad (4)$$

However, in this work, only reactions (1–3) were considered. In fact, the used equilibrium constants come from experimental works and implicitly include the effects of possible side reactions (see paragraph 2.4).

Permeation area assessment

The plant sizing and, particularly, the membrane design were performed on the basis of the amount of required H_2 to power a 1 kW_{el} PEMFC. Considering a typical PEMFC efficiency of around 50%, the estimated H_2 flow rate required by the PEMFC is around 29.8 mol h^{-1}.

In order to compare the results achieved for both proposed configurations, the permeation area was sized based on the procedure described in a previous paper [37].

Table 1 collects the main parameters considered in the present study, including both mechanical characteristics and operative conditions of the H_2 selective membranes. The membranes have 10 mm diameter and 0.15 mm wall thickness. Such geometrical characteristics are the same adopted in multi-tube devices already in use at ENEA laboratories [35,36].

In this work, a membrane unit consisting of 50 tubes has been considered for both processes (TS and MR). Such number of tubes is obtained as a trade-off between the need to obtain acceptable hydrogen recovery values (higher than 50%) at low pressure operation and the need to keep the membrane module as small as possible.

Table 1 – Geometrical characteristics and operative conditions of H_2 selective membranes made of $Pd_{77}Ag_{23}$.

Geometrical characteristics	L [m]	5 E−01
	D [m]	1 E−02
	s [m]	1.5 E−04
Operative conditions	T [°C]	3.5 E02
	Pe_0 [mol m^{-1} s^{-1} $Pa^{-0.5}$]	5.22 E−08
	Ea [J mol^{-1}]	7.89 E03
	Pe(623 K) [mol s^{-1} m^{-1} $Pa^{-0.5}$]	1.137 E−08

Model analysis

The proposed model operates in two different phases: i) reactor simulator (RS) and ii) energy analysis (EA). The RS uses a finite elements code to simulate both the traditional and the tubular membrane reactor. By assuming isothermal conditions, the mass balances are carried out on the basis of chemical reaction and permeation kinetics. In particular, when simulating the traditional reactor, the permeation kinetics is disabled, while a permeator can be simulated by disabling the reaction kinetics. In a second phase, an energy analysis of the processes (from here, denoted as EA) is executed to evaluate their performances in terms of energy efficiency (η) and hydrogen yield (HY). The simulation procedure is repeated until the required energy power is achieved. Thus, starting from a given feed flow rate, the enthalpy balances are resolved for each process. If an output energy of 1 kW power is achieved, the energy optimization is then assessed and both η and HY parameters are evaluated. Otherwise, the feed flow rate is modified and the analysis is performed again until the desired output electric power is reached. The flow chart for this iterative logic model is depicted in Fig. 2.

Reactor simulator

The kinetic code simulates a tubular reactor by using a 1-D finite elements method, assessing the methane reforming and the water gas shift in both a traditional and a membrane reactor. While the traditional reactor is a tubular packed bed one, the membrane reactor considered in the simulation tool is made of a Pd membrane tube filled with catalyst and of an external cylindrical shell in which the permeated hydrogen is collected (see Fig. 3).

The kinetic code simulates the tubular reactor by using a 1-D finite model. Main assumptions of the code are: i) plug flow fluid reactor, ii) perfect mixing (negligible radial dispersion), iii) ideal gas behavior, iv) isothermal conditions, v) negligible pressure losses through the catalyst bed. The code postulates the kinetic model of Xu and Froment for the methane reforming [38], while the water gas shift has been considered under thermodynamic equilibrium conditions (equilibrium constant for literature [39,40]). In fact, the kinetics of the water gas shift can be considered very high, in particular when compared to the permeation kinetics. By neglecting the contribution of side reactions (see Section 2.2), the mass

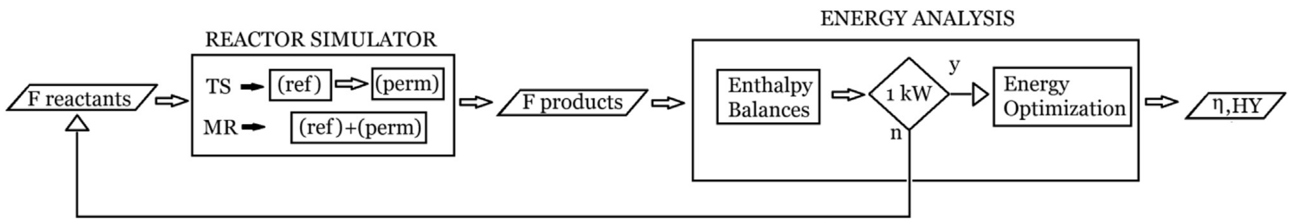

Fig. 2 – Logic scheme for the proposed resolution model.

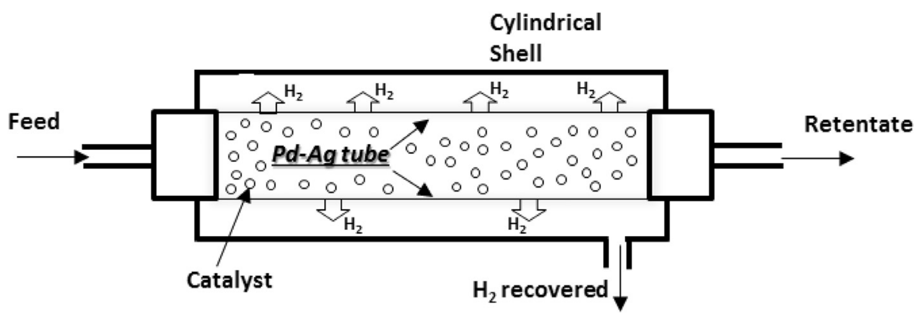

Fig. 3 – Schematic view of a packed-bed membrane reactor.

balance of the different species inside the reaction zone along the z-axis can be written as [41]:

$$\frac{dF_i}{dz} = K_i \cdot \pi \cdot r_m^2 - J_i \cdot 2 \cdot \pi \cdot r_m \tag{5}$$

Where F_i is the molar flux of the i-th specie, K_i is the volumetric rate of production of the i-th specie, J_i is the permeation flux of the i-th specie in the element r_m is the radius of the membrane tube. According with the Sieverts' law, the hydrogen across the Pd-based membrane wall can be written as:

$$J_{H2,perm} = \frac{Pe}{t}\left(p^{0.5}_{H2,lumen} - p^{0.5}_{H2,shell}\right) \tag{6}$$

The permeability coefficient varies with temperature according to an Arrhenius-type dependence:

$$Pe = Pe_0 \cdot e^{\frac{-E_a}{R \cdot T}} \tag{7}$$

where E_a is the activation energy of the permeation process (J mol^{-1}), R is the ideal gas constant (8.314 J mol^{-1} K^{-1}) and Pe_0 is the pre-exponential factor (mol s^{-1} m^{-1} $Pa^{-0.5}$).

The model can be discretized by dividing the reactor into the finite elemental volumes along the z-axis (see Fig. 4b). The mass balance for each finite element, denoted in general with the subscript k, has been calculated by Equation (5) (Fig. 4b). In this expression, F^i_{k+1} (mol s^{-1}) represents the flow rate leaving the k-th finite element, F^i_k (mol s^{-1}) is the flow rate entering the k-th finite element, J^i_k (mol s^{-1} m^{-2}) is the permeated flux, A_k (m^2) is the membrane permeation area of the finite element and R^i_k (mol s^{-1}) is the rate of production of the i-th specie in the k-th finite element by the chemical reactions. In equation (5) the value of J^i is maintained always equal to zero except for H_2 that, in each k-th element of the reactor, depends on equation (6). Finally, the equilibrium constants for the considered chemical reactions are taken from literature [38,42].

$$F^i_{k+1} = F^i_k - J^i_k A_k + R^i_k \tag{8}$$

ii) *Energy process analysis*

Once the enthalpy balances have verified the production of the required amount of H_2, the energy optimization analysis is undertaken. The optimization includes the assessment of the

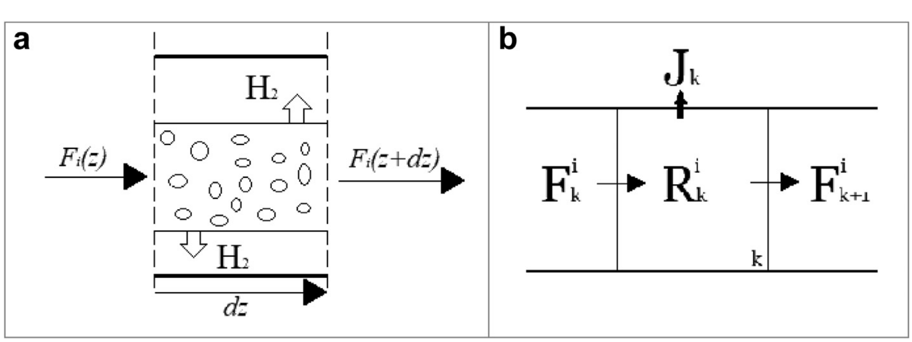

Fig. 4 – View of a) an elemental volume of the tubular reactor and b) its discrete representation.

heat that can be recovered by the heat exchangers and it allows analyzing the energy efficiency of the plant. Thus, the heat recovery optimization has been evaluated by means of a pinch analysis, from which it has been possible to evaluate the amount of additional heat required to heat up the fuel mix. As main assumption, it has been considered that only the 80% of energy contained in the warm fluxes could be exploited. The analysis allowed identifying the additional heat needed to balance the global energy requirements of the plant. This additional heat would be supplied by a burner fed with methane with a combustion efficiency of 98%. Fig. 5 shows the result of the pinch analysis considering S/C = 3 and P = 10 bar for the TS plant configuration, where the hot curve includes the heat recovery curve and the cold curve includes the heat requirements of the system. The pinch distance between the two curves in all analyses undertaken was 10 °C.

This pinch analysis shows that the waste heat power accounts for around 0.8 kW, which is near the amount of recoverable waste heat coming from FC. This heat power, whose temperature is lower than 90 °C, cannot be exploited to warm up the feed stream and was not recovered in the present work, which considers that a plant scaled-up from this study would serve industrial applications without considering possible cogeneration of heat and electricity. On the contrary, the recovery of low temperature heat can be an option in case the plant would serve domestic applications.

Results and discussion

The calculation of the energy efficiency (η) for each plant configuration is performed according to the next expression:

$$\eta = \frac{E_{FC}}{E_{CH4}} \tag{9}$$

Where E_{FC} is the FC power (kW) and E_{CH4} is the amount of power, calculated from the low heating value (kW), coming from the methane used as feedstock for the plants. Another important parameter for result discussion is HY, calculated as the moles of produced H_2 respect to the amount of hydrogen introduced in the reactor, considering the stoichiometry of methane SR reaction of formula (3) [36].

$$HY = \frac{Q_{H2,perm}}{4 \cdot Q_{CH4,reac}} \tag{10}$$

Where $Q_{H2,perm}$ is the molar flow rate of H_2 permeated from the membrane module and going to the FC, while $Q_{CH4,reac}$ is the molar flow rate of CH_4 fed to the reactor.

These parameters have been calculated and evaluated for both TS and MR processes. The TS process operates at temperatures in the range 650–900 °C in the reformer and at 350 °C in the next WGS membrane reactor, while the MR system operates at the maximum temperature of 500 °C. Table 2 includes particular conditions for each case study performed in this work. Marked differences in the operative conditions for the diverse sets of simulations can be observed. In the TS process, the considered pressure variation is from 3 to 15 bar: 3 bar is considered a low pressure condition, where the H_2 permeated flux is enough for the TS process, while 15 bar is considered an upper limit for the membranes to guarantee mechanical resistance. For the MR process, the minimum pressure considered is 5 bar because there is no possibility to recover the necessary H_2 permeate flow rate in case of lower reaction pressure. Regarding the reforming temperature, while in the first two sets of simulations of the TS process, the reforming temperature is 800 °C, in the third set the T is changed between 650 °C and 900 °C. For the MR process, instead, no variation was imposed because temperatures lower than 500 °C would not favor the steam reforming reaction adequately, while higher temperatures would compromise the mechanical stability of the membranes [37].

The S/C variation was studied for both processes, by varying the value of the parameter between 3 and 12. The increase of S/C allows improving the production of H_2 due to the increase of one of the two reactants (H_2O), but may affect the energy efficiency of both processes. The minimum value of 3 is chosen due to the stoichiometry of the reaction, while

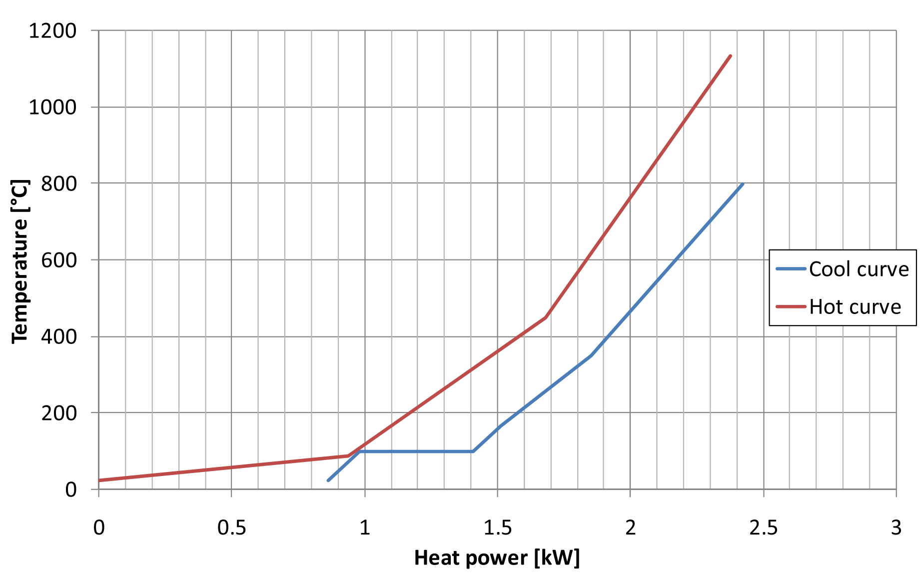

Fig. 5 – Pinch analysis curves for the case S/C = 3, P = 10 bar.

Table 2 – Range of variation of the operative conditions in the sensitivity analysis.

Set of simulations	TS	MR
1	P = 3–15 bar; S/C = 3; T_{ref} = 800 °C; T_{WGS} = 350 °C	P = 5–15 bar; S/C = 3; T_{ref} = 500 °C
2	P = 10 bar; S/C = 3–12; T_{ref} = 800 °C; T_{WGS} = 350 °C	P = 10 bar; S/C = 3–12; T_{ref} = 500 °C
3	P = 10 bar; S/C = 3; T_{ref} = 650–900 °C; T_{WGS} = 350 °C	–
4	–	P = 10 bar; S/C = 3–12; T_{ref} = 500 °C; SV = 0.043–0.200 mol $h^{-1}g_{CAT}^{-1}$

12 is more than the double respect to [10], where the maximum considered was 5.

The influence of the SV was studied only for the MR process by exploring its variation between 0.043 and 0.200 mol h^{-1} g_{CAT}^{-1} with a constant reactants flow rate: this would lead to a variation of the output. In the TS process, instead, with the experimental kinetics adopted, the methane conversion showed no significant variation with the SV.

Results obtained

Fig. 6 shows the variation of both η and HY vs pressure, with S/C = 3: the TS configuration operates better than MR for the entire range of pressures. The MR only reaches the performance of TS plant when operative pressure is increased up to 10 bar. Thereon, an increase of operative pressure allows MR overcoming the performance of TS system. The increase of operative pressure improves the permeation efficiency in the TS process, as it grows from around 73%–92%. These high values are possible due to the separation of most excess of water in the condenser placed at the reformer outlet. A similar behavior takes place in the MR when operating at relatively low pressures since H_2 recovery from the membrane reactor is penalized by dilution effect of water excess (lower H_2 partial pressure in the feed stream and, hence, lower permeation). The slight reduction in the energy efficiency for P = 15 bar when TS process is considered despite the high HY is mainly due to the amount of methane required in the burner. The HY increases for both configurations due to the increased H_2 permeated flux for given amount of methane fed, thanks to the shift effect. However, for high pressure values, the HY reaches a plateau for both configurations.

Such results are in accordance with literature [9,11,22] and also show that to increase the pressure in the plant above 10–12 bar is not convenient: in fact, it does not significantly improve the process, while at the same time it rises the risk of mechanical damage to the membranes.

Additionally, the influence of the S/C ratio has been explored in a second set of simulations, where it was varied from 3 to 12 maintaining a constant pressure of 10 bar (Fig. 7). In general, higher values of S/C have a negative influence on the energy efficiency for both systems, due to the increase of the energy demand for the evaporation of additional water. Particularly, a maximum efficiency is reached in case of considering S/C = 4, in spite of the stoichiometric value for the methane SR is S/C = 2. This fact confirms that certain excess of reactants shifts the equilibrium right-wards. However, a significant increase of energy consumption is required when exceeding that value, reducing the energy efficiency of both processes. This behavior is in accordance to previous results found in the literature [11]. HY values reflect a noteworthy behavior for the MR process. It increases until S/C = 6 thanks to the higher amount of H_2 produced, but hereafter it decreases due to the excess of water in the membrane lumen, which provokes a reduction of the H_2 partial pressure and hence the driving force of the permeation process. The HY in the TS process, instead, is not influenced by the excess of water thanks to its removal via the condenser.

A reduction of the energy efficiency of the two processes is reported by Mendes and al [12]. Too, while Tosti and Borgognoni also found an increase of the HY with the S/C [35].

Next, the influence of the reforming temperature in the TS process has been also evaluated in a third set of simulations performed in the range of 650–900 °C, at constant P = 10 bar

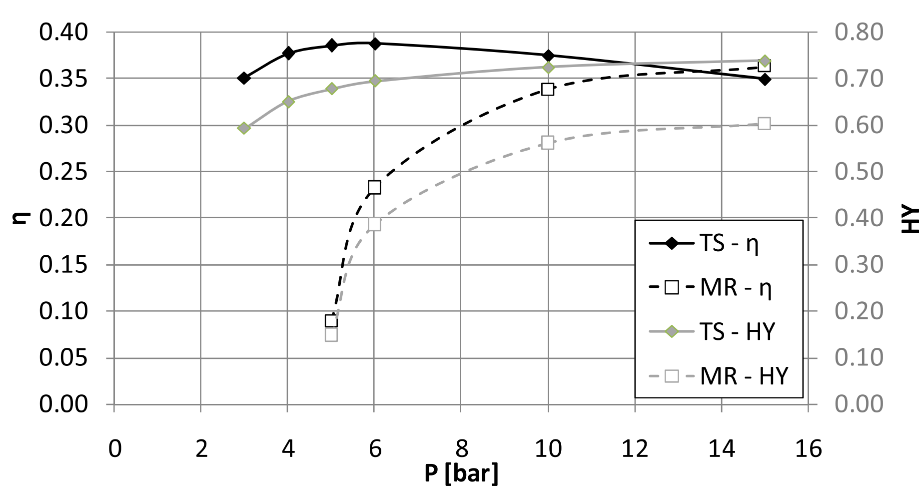

Fig. 6 – Pressure effect on energy efficiency and hydrogen yield.

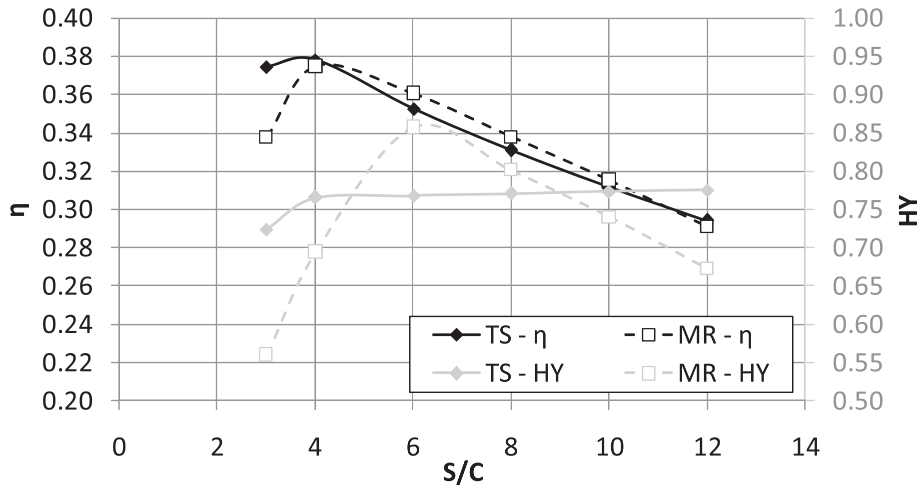

Fig. 7 – Energy efficiency and hydrogen yield of the two plants vs. S/C ratio.

and S/C = 3. Table 3 shows the values of η and HY respect to T_{ref}. The energy efficiency does not change significantly with temperature, its value is around 37%, while the HY is between 79% and 74%.

The slight reduction of the HY with temperature is due to the shift of the WGS reaction towards the formation of CO and H_2O. For such reasons, the optimal temperature in terms of HY is 720 °C.

Finally, for the MR plant, the influence of the SV has been enquired by considering a reduction of the mass of catalyst for a fixed value of the feed mass flow rate. This choice allows evaluating the reduction in the output power of the fuel cell, which corresponds to a reduction in the energy efficiency, at constant operative conditions (T_{ref} = 500 °C and P = 10 bar) and with the same amount of fuel introduced. Fig. 8 shows the influence of the SV on the plant output power: the maximum power of 1 kW is obtained at an efficiency of 33.8%. An increase of SV up to 0.2 leads to a reduction of the FC power of about 12.5%, which corresponds to an efficiency of 29.5%. The reason is the reduction of the methane conversion and of the HY in the MR, which leads to a lower amount of H_2 produced.

The following Table 4 shows the ratio between the hydrogen molar flow rate and the membrane area. This ratio is quite constant around the value of 76 mol h^{-1} m^{-2} for all of the simulations performed. However, when the SV increase, it decreases proportionally to the decrease of the FC power showed in Fig. 8.

Tables 5 and 6 show the obtained results. In the tables, $Q_{CH4,reac}$ (mol h^{-1}) is the molar flow rate of CH_4 fed into the reactor, which does not include the additional CH_4 flow rate fed into the plant, while P_{CH4} is the heat power of the total amount of methane feeding the plant.

Table 3 – Energy efficiency and HY of the TS plant vs. T_{ref} [°C].

T_{ref} [°C]	650	720	800	900
HY	78.8%	78.3%	76.9%	74.6%
η	37.4%	37.7%	37.8%	37.6%

Comparison with literature

The obtained results are in accordance with the studied literature concerning the steam reforming of hydrocarbons in membrane processes. A comparison between this work and the literature has been done considering both the results of previous simulations and experimental tests.

Tosti and Manzolini studied two membrane processes [11]: the first one is analogous to the TS adopted in this work, with a first reforming stage followed by a WGS membrane reactor, reforming temperature of 780 °C, an operative pressure of 6 bar, a S/C of 3 and WGS temperature of 350 °C. The authors obtained a net energy efficiency of around 39.5%, a result which is comparable to the one showed in this work (38.7%). The second membrane process is a MR, operating at 600 °C, with inlet pressure of 8 bar, permeate pressure of 1.22 bar and S/C ratio of 3, shows a net energy efficiency of 41.2%, higher than what obtained by the MR in this work. The difference is in the higher operative temperature and in the different configuration of the membranes (self supported in this work, supported in Ref. [11]). The two different results show that a packed bed MR obtains comparable results respect to a TS process if it operates at high pressures and temperatures.

The membrane-based plant studied by Mendes et al. for the case of ethanol reforming [12] corresponds to the TS system studied in this work. Many similarities can be found in the obtained results. First, it achieves the best energy efficiency values for low values of water-to-ethanol molar ratio. Particularly, the maximum energy efficiency is achieved at a molar ratio of 3. Moreover, they find that the HY is constant and the energy efficiency is favored by the pressure increase, although such improvement does not appear to be significant above 10 bar. Such result is comparable to what obtained in this work.

The work of Di Berardino and Manzolini [25] in a membrane reactor, analogous to the MR studied in this work, confirms that an increase in the space velocity reduces the methane conversion and the hydrogen yield.

The values of energy efficiency of the membrane reformer in a cogeneration plant shown by Refs. [32,33] are consistent with those obtained by this paper. Particularly, in Ref. [32] values between 35% and 40% for a MR operating at 600 °C

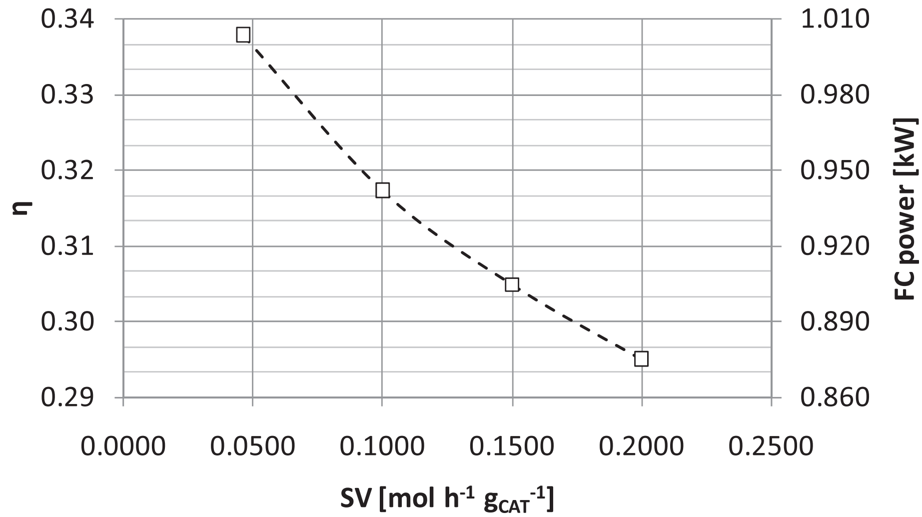

Fig. 8 – Energy efficiency and FC power in the MR plant vs. SV [mol h^{-1} g_{CAT}^{-1}].

and at 8 bar pressure are reported, while in Ref. [33] Roses and Gallucci showed that a membrane reformer operating at the same conditions exhibits up to 43% electrical energy efficiency, a value higher than that obtained in this paper. In the same work, the authors demonstrated that a pre-reforming stage can improve the performances of a packed bed membrane reformer. Such result confirms the better achievements obtained in this work by the TS respect to the MR configuration, especially for low pressure operations.

Table 4 – Ratio between hydrogen flow rate and membrane area vs. SV.

SV [mol h^{-1} g_{CAT}^{-1}]	Q_{H2}/A_{memb}[mol h^{-1} m^{-2}]
0,0463	75,9
0,1000	71,3
0,1500	68,5
0,2000	66,4

Table 5 – Results of the simulations related to the TS plant.

Set	$Q_{CH4.reac}$ [mol h^{-1}]	SV [mol h^{-1} g_{CAT}^{-1}]	HY	P_{CH4} [kW]	η
1	12.60	0.200	59%	2.86	35.06%
	11.50	0.183	65%	2.66	37.68%
	11.00	0.175	68%	2.60	38.53%
	10.75	0.171	69%	2.59	38.74%
	9.69	0.154	77%	2.68	37.43%
	9.55	0.152	78%	2.87	34.89%
2	9.69	0.163	72%	2.68	37.43%
	9.72	0.193	77%	2.65	37.80%
	9.70	0.269	77%	2.84	35.26%
	9.66	0.345	77%	3.03	33.09%
	9.63	0.420	77%	321	31.15%
	9.61	0.496	78%	3.41	29.42%
	9.58	0.570	78%	3.59	27.82%
3	9.45	0.150	83%	2.68	38.04%
	9.51	0.151	88%	2.65	39.49%
	9.69	0.154	86%	2.65	38.98%
	10.00	0.159	83%	2.66	38.10%

Table 7 compares the values of the energy efficiency of the TS and MR processes studied in this work and the values of η reported in some of the referenced papers, in order to focus on the magnitude of such parameter and its variability.

From Table 7 it can be seen that the range of variation of η is between 30% and 43%, depending on operative conditions and type of reactors. However, the TS process, despite requiring the classical reformer to operate at higher temperature, may achieve similar values of plants based on a MR.

For what concerns the HY, results obtained in this paper should be compared principally to the experimental tests performed by Borgognoni et al. at ENEA laboratories [35,36]. In absolute terms, in the pure methane SR performed in the TS process, they achieved a maximum HY around 70%, for 750 °C T at 3.5 bar [35]; higher pressure and temperature values were not explored, so that this work may be seen as the ideal prosecution of the experimental one. The positive influence of pressure and temperature obtained in that work is confirmed, as expected, in the results presented.

In the end, the plateau-like behavior exposed in Fig. 6 in this work is confirmed by Murmura et al. [30] which, by means

Table 6 – Results of the simulations related to the MR plant.

Set	$Q_{CH4.reac}$ [mol h^{-1}]	SV [mol h^{-1} g_{CAT}^{-1}]	HY	P_{CH4} [kW]	η
1	50.00	0.1739	15%	11.15	8.92%
	19.30	0.0671	39%	4.30	23.26%
	13.30	0.0463	56%	2.97	33.78%
	12.40	0.0431	60%	2.77	36.27%
2	13.30	0.0463	56%	2.97	33.78%
	10.73	0.0467	69%	2.67	37.48%
	8.70	0.0530	86%	2.78	36.07%
	9.30	0.0728	80%	2.96	33.79%
	10.10	0.0966	74%	3.18	31.52%
	11.10	0.1255	67%	3.44	29.09%
4	13.30	0.0463	56%	2.97	33.78%
	13.30	0.1000	53%	2.97	31.73%
	13.30	0.1500	51%	2.97	30.48%
	13.30	0.2000	49%	2.97	29.50%

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Table 7 – Comparison between references and this work.

Ref.	TS process	MR process	Notes
[11]	$\eta = 39.5\%$	$\eta = 41.2\%$	MR in Ref. [11] works at T = 600 °C.
[12]	$\eta = 30.0\%$	–	Higher efficiencies in this work may be due to better heat exploitation. Best efficiency with low S/C. Pressure favours η only till 10 bar.
[25]	–	Not indicated	Negative effects of the SV on the methane conversion.
[32]	–	$\eta = 35–40\%$	T = 600 °C.
[33]	–	$\eta = 43\%$	Fluidized membrane reactor, T = 600 °C.
[34]	–	$\eta = 38–40\%$	Auto-thermal reforming in fluidized membrane reactor, T = 600 C.
[35]	Not indicated	–	P, T_{ref} increase HY. S/C increases production of H_2.
This work	$\eta = 38.7\%$	$\eta = 33.6\%$	

of a simplified model, described the variation of the HY vs. pressure from 1 to 10 bar in an annular-like membrane packed bed reactor. They exhibit very similar curves, also showing that an increase in the methane flow rate (i.e. of the SV) leads to a decrease of the HY.

Conclusions

This work explored the potential of methane steam reforming in two different membrane systems and compared their performances to other literature works in terms of the efficiency of energy conversion and of the Hydrogen Yield. In particular, the work explored the potential of the Two Step (TS) process fed with methane under several operative conditions which were not treated in previous experimental works and compared them to the performances of a packed bed Membrane Reactor (MR). Both systems were designed to produce the amount of ultra-pure hydrogen required in a FC of 1 kW_{el} while the energy consumption was optimized through a pinch analysis for heat recovery. Results obtained are the following.

The TS plant exhibits energy efficiency values in the range of 35–40% for pressure between 3 and 10 bar, respectively. The optimum reforming temperature is around 720 °C, while a steam-to-carbon ratio of 4 allows obtaining the maximum energy efficiency. The hydrogen yield is favored by increasing both pressure and S/C, but is not significantly affected by the reforming temperature. The energy efficiency for the MR plant is greatly favored by the pressure increase, achieving at least similar values to the TS plant only if pressure overcomes 10 bar. In this mean, a maximum of the energy efficiency is attained with S/C = 4, as occurring for the previous TS plant study, and with a space velocity of 0.0463 mol h^{-1} g_{CAT}^{-1}. For this configuration, the hydrogen yield is always favored by the pressure, while it reaches a maximum for S/C = 6.

These results are generally in accordance with literature and they indicate that a packed bed MR plant does not achieve comparable performances respect to a TS plant unless operating at high pressure values. The energy efficiency for both plant configurations at their best performances are extremely similar and it is estimated to be around 40%. Moreover, the hydrogen yield has been evaluated to reach quite high values, typically ranged between 60 and 80%.

Due to the growing interest in the biomass exploitation for producing hydrogen, future work would investigate the ethanol steam reforming for the two process configurations.

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