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Design of an integrated membrane system for a high level hydrogen purification

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Abstract

Aim of this work is the theoretical analysis of the potential of integrated membrane systems to recover hydrogen at a very high purity level (with CO content lower than 10 ppm), suitable for fuel cell applications. Both polymeric and palladium (Pd) separators as well as a Pd-based membrane reactor have been investigated in order to identify the appropriate operation conditions for each unit taking advantage of the synergic effects of their combination in the design of the whole integrated system. A feed stream containing hydrogen, carbon monoxide and carbon dioxide has been considered. By means of a screening of different materials it has been possible to identify a membrane able to achieve high hydrogen purity and recovery. In order to improve the single membrane stage performance, a two stage system has been analysed taking into account both compression and membrane surface requirements. At fixed stage cut values, higher purity levels are reached in a two membrane stage arrangement with an increase of membrane surface and compression requirements. High hydrogen purities can also be achieved by operating at high feed pressure values. The presence of a membrane reactor to further enhance the hydrogen amount by converting the carbon monoxide has also been investigated. As a low driving force is available (e.g. 5 atm), the combination that seems to be the most convenient assumes that the syngas mixture is first fed to the two-stage polymeric membrane unit, then the permeate stream is further treated in a palladium separator (Pd-Sep) while the retentate streams are processed in two palladium membrane reactors (Pd-MRs). On the contrary, at 10 atm a single polymeric stage followed by a Pd-Sep and a Pd-MR represents the most adequate solution because a comparable membrane surface is combined to lower compression power and H_2 losses.

Keywords: Integrated membrane systems; Hydrogen purification; Membrane reactor; Membrane separator

1. Introduction

The rapid development in industrial and transport sectors and improvements in living standards have grown the global energy consumption. Today, energy systems are largely based on combustion of petroleum, natural gas and coal. These are all non-renewable sources of primary energy, which use has caused, in the time, a rise in global concentration of greenhouse gases (e.g. CO_2) in the atmosphere, leading to a generalized earth warming. Traditional energy systems (power plants or vehicles) are characterised by a low efficiency since over the 60% of the input energy is wasted or lost in the process. Therefore, both new energy sources and more efficient systems should be explored in order to approach a more environmental friendly and rational energetic utilization for a sustainable development [1].

In the last years, an alternative to the fossil sources seems to be the use of the hydrogen directly as clean fuel or as feed for producing other fuels and commodities. Today, about half of the produced hydrogen is used in ammonia synthesis while one third in refineries; the rest in metallurgical, chemical, and space applications. For what concerns the refineries, they both produce (e.g. production of aromatics) and consume hydrogen (e.g. hydro-treating processes). In the last years, a more severe aromatics emission control, more strict environmental legislations, combined with a low quality feedstock use, have increased the requirement of hydrogen in the refineries that absorb a large part of the worldwide production. Therefore, plants for hydrogen production have been built close to the refineries to meet their needs [2].

Furthermore, the hydrogen demand is expected to increase in next future when it will begin to be used in fuel cell appli-

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Abbreviations: C, compressor; Pol-Sep, polymeric membrane separator; Pd-Sep, palladium-based membrane separator; Pd-MR$_{1\,\text{atm}}$, palladium-based membrane reactor at 1 atm; Pd-MR, palladium-based membrane reactor; R_1, R_2, R_3, R_4, R_5, retentate streams; P_1, P_2, P_3, P_4, P_5, permeate streams

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Nomenclature

A^{m}	membrane area (m^2)
c_i	concentration of the species i ($kmol\,m^{-3}$)
$c_{i,0}$	feed concentration of the species i ($kmol\,m^{-3}$)
C_p	hydrogen heat capacity ($kJ\,kg^{-1}\,K^{-1}$)
$C_{p_{mix}}$	specific heat of the mixture on lumen side ($kJ\,kg^{-1}\,K^{-1}$)
D	membrane reactor diameter (m)
$D_{i,r}$	radial effective diffusivity ($m^2\,s^{-1}$)
hp	power of compression (hp)
h_W	wall-heat transfer coefficient ($kJ\,m^{-2}\,s^{-1}\,K^{-1}$)
ΔH	reaction enthalpy ($kJ\,kmol^{-1}$)
J_i	permeation flux of the species i ($kg\,m^{-2}\,s^{-1}$)
J_{H_2}	hydrogen flow rate ($kg\,m^{-2}\,s^{-1}$)
k	ratio of specific heat of gas at constant pressure to specific heat of gas at constant volume
l	membrane thickness
n	exponential coefficient
N_s	number of stages of compression
$p_{H_2,lumen}$	hydrogen partial pressure (kPa)
$p_{H_2,shell}$	hydrogen partial pressure (kPa)
p_{ih}	upstream i-partial pressure (kPa)
p_{il}	downstream i-partial pressure (kPa)
p_1	compressor intake pressure (lbf/ft^2)
p_2	compressor final delivery pressure (lbf/ft^2)
P_{H_2}	Hydrogen permeance
q_f	gas flow rate at intake conditions (ft^3/min)
r	radial coordinate (m)
R	H_2O/CO feed molar ratio
$\Re_i$	reaction rate ($kmol\,m^{-3}\,s^{-1}$)
T	temperature in membrane reactor (K)
T_0	feed temperature (K)
u_s	superficial velocity referred to whole section of lumen side ($m\,s^{-1}$)
V^{f}	permeator volume (m^3)
$v_z = u_s/\varepsilon$	interstitial fluid velocity in the axial direction ($m\,s^{-1}$)
z	axial coordinate (m)

Greek symbols

ε	bed voidage fraction
η	isentropic efficiency for reciprocating compressors
θ	stage cut
λ_{er}	effective radial thermal conductivity ($kJ\,m^{-1}\,s^{-1}\,K^{-1}$)
ρ_g	mixture density lumen side ($kg\,m^{-3}$)
Ψ	hydrogen loss (%)

Subscripts

h	high
i	compound
l	low
mix	mixture
r	radial direction
w	wall
0	at reactor inlet
1–5	membrane units in the sequence

cations. This technology seem to be a valid alternative to the conventional ones, since the chemical energy stored in the fuel is converted directly into electricity with a higher efficiency. At present, the fuel cells operative costs per kWh are still too high in comparison with both conventional power plant and internal combustion engines. Hydrogen can be produced at a high purity level on site (for industrial needs) or on board (for vehicles) by reforming reactions; however, at low temperature, for example in a proton exchange membrane, the presence of CO over 10 ppm poisons the catalyst electrode. In order to achieve this goal, the water gas shift reaction (WGSR) has been utilised to convert CO into hydrogen before a selective CO removal [1,3–5].

In recent times, membrane-based gas separation is becoming more popular due to its inherent advantages over the conventional separation methods. Membranes offer easy operability, economic viability for small unit operations, compactness and lower energy costs [6,7]. The use of polymeric membranes has generated a huge interest by virtue of a rising development in polymer science and in the membrane module engineering with significant improvements in productivity and selectivity of these units, and reliability in the time with reduced manufacture costs. In particular, since the first large industrial application (1980), membrane-based gas separation has grown into a US$ 150 million/year business in 2000, with a growth rate expected for the next 20 years close to 10% per year [8].

Inorganic (ceramic, metallic, zeolite, and carbon) membranes can be favourably used in the field of gas separations at high temperature and pressure values [9–12]. A specific example is represented by the Pd-based membranes that offer higher selectivity values for hydrogen in comparison with other membrane materials and good mechanical and thermal stability [13,14].

Membrane reactors (MRs) are devices capable to combine the separation and reaction steps in a single unit. A specific application of the MRs is the selective removal of a product from the reaction ambient in order to enhance the conversion value shifting continuously the equilibrium [2,15]. Pd-based membranes are particularly indicated in those reactive systems in which hydrogen is a product of the reaction [16–18].

The development of integrated processes, in which membrane units have an important role, can offer significant improvements in chemical processing since it reduces equipment size, energy consumption, product losses in the respect of environmental security [19]. This principle has been successfully applied in those circumstances where reaction and separation steps are strongly related and the sequence of units is a fundamental aspect. Referring to processes in which H_2 recovery and/or purification is involved, different approaches have been followed depending on the primary sources and final use of the product.

A simply and compact system patented by Nissan Motor Company utilises a membrane unit on downstream of a steam reformer, fed by a liquid fuel, to supply hydrogen to a small scale mobile fuel cell. The rate of hydrogen permeation through the membrane is maintained at a fixed value by controlling the hydrogen partial pressure on permeate side by recycling the portion in excess of the stream supplied to the anode chamber as a sweep gas [20]. In order to maximize the H_2 production, a conventional WGS reactor has been coupled to a CH_4 partial oxidation membrane reactor. The last one is based on a mixed conducting ceramic membrane capable to be preferentially permeated by oxygen at high temperature ($T > 800\,°C$). Maximum CO conversion occurred with a H_2O/CO ratio of 2, beyond which the enhancement in hydrogen production is small [21]. In order to increase the hydrogen recovery from the steam-methane-reformer off gas, a selective surface flow carbon membrane has been used to extract hydrogen from the low pressure waste gases of a pressure swing adsorption unit. The optimal configuration allowed a net recovery of seven points moving from a hydrogen recovery value of 77–78% by the base PSA process to 84–85% in the integrated scheme [22]. A wide prospect of integrated H_2 membrane separations has been analysed with reference to power plants, demonstrating how technical solutions are not fully explored [23]. The concept of heat integration in a membrane reactor for the electric power generation is applied in a recent patent. Catalytic or steam reforming and WGSR occur on one side of the membrane while hydrogen combustion on the other side. A portion of the heat of combusted hydrogen is transmitted to the endothermic reformer process by an inorganic supported asymmetric membrane that favours in the meantime the permeation of the hydrogen, produced by reaction, toward the hydrocarbon combustion embodiment [24].

A hybrid system has been proposed to use waste organic matter as source for electrical power generation. This integrated system comprises a gasifier fed with biomass, a biological shift reactor which enzimatically reforms CO and water to hydrogen, and a low temperature fuel cell. The biological unit replaces a thermal water gas shift reactor and a partial oxidation module [25]. The possibility of integration of gas separating membrane systems with aerobic or anaerobic bioreactors has been considered to obtain technically pure combustible gases (H_2 and CH_4) by a complete utilization of microbial biomass produced in solar bioreactors. Polymeric active membranes, containing liquid carriers, have been used as membrane contactors to favours the CO_2/H_2 separation [26].

This work, differently from those above cited where a single membrane unit was properly integrated in a production cycle, intends to combine multiple membrane units taking advantage of their inherent characteristics to recover hydrogen at a high purity level, lowering the CO content of the gas stream. In more detail, a recovery of 90%, according to the commercial membrane performance on industrial gas stream [27–29], of high purity hydrogen (99.9995%) from a syngas stream, by means of a proper integration of membrane separators and reactors, is discussed. At first, the performance of single membrane units has been evaluated in order to verify the possibility to meet the target of the separation. The difficulty to reach the objective suggests the use of integrated membrane systems capable to keep low the request of membrane surface and compression power, reducing the hydrogen loss. The quantitative determination of the main parameters (membrane surface, compression power) allows a conscious choice of the most appropriate configuration. The approach proposed in this work could allow a further development of the membrane technology in integrated separation processes. However, the ultimate choice of the most adequate global integrated system requires an economic evaluation that overcomes the purpose of this work.

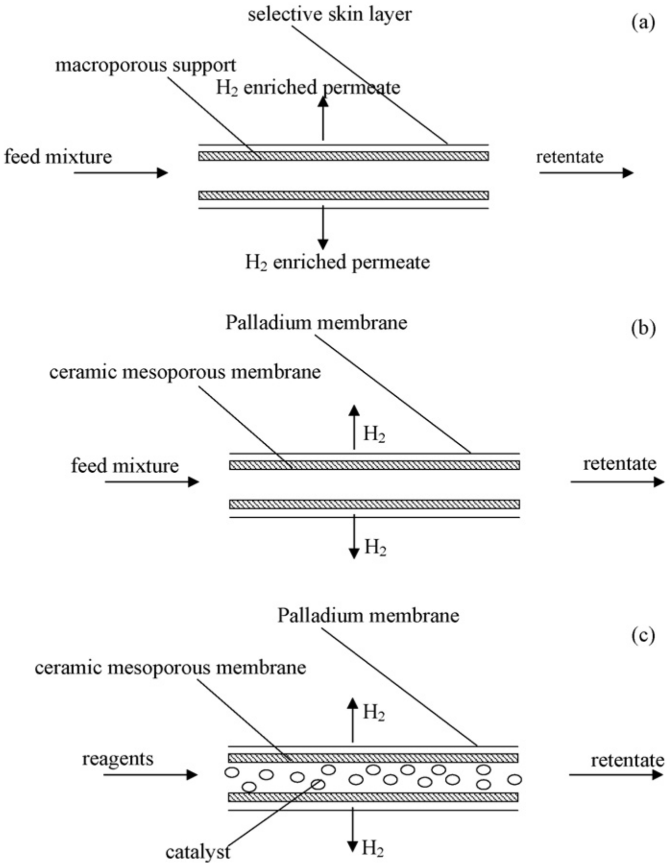

Fig. 1. Scheme of membrane units: (a) polymeric separator (Pol-Sep); (b) Pd-Sep; (c) Pd-MR.

2. Mathematical modelling

2.1. Permeation systems

A one-dimensional mathematical model to simulate the performance in steady state of both polymeric and palladium membrane modules has been developed. The polymeric and palladium separators are outlined in Fig. 1a and b.

Differential mass balance equations based on co-current flow mode have been formulated and solved using a Runge–Kutta 4th order method. Concerning the polymeric unit analysis, the simulation code uses as input data the gas permeances through commercial polyimide hollow fibers whose order is $H_2 > CO_2 > CO$ [30] (see Table 1) whereas, for the palladium-based units, the hydrogen permeance is the following:

$$P_{H_2}(\mathrm{mol\,m^{-2}\,s^{-1}\,Pa^{-0.5}}) = 3.2 \times 10^{-3} \exp\left(-\frac{1276}{T}\right) \quad (1)$$

Table 1
Permeation rate and selectivity values considered in the polymeric unit

Transport property	Type A	Type B–H
H_2 permeance ($\mathrm{mol\,m^{-2}\,s^{-1}\,Pa^{-1}}$)	3.35×10^{-8}	1.67×10^{-7}
H_2/CO_2 selectivity	10	5
H_2/CO selectivity	100	55

This expression has been obtained by using literature experimental data at different temperatures on Pd-coated composite tubular membranes (length 20 cm and diameter 1 cm) [31]. The permeate pressure has been assumed equal to 1.1 atm, without using sweep gas to extract the permeate stream; due to the different nature of the materials, the operating temperatures for the polymeric and the palladium units have been fixed at 300 K and 600 K, respectively. The possibility to compress the feed stream has been also taken into account. The composition (mol%) of the reference feed stream is the following: H_2 45%, CO_2 6%, CO 49%.

The main assumptions of the model are the following ones:

- isothermal conditions inside the permeator;
- ideal gas behaviour;
- plug flow on both permeate and feed sides;
- co-current flow mode;
- negligible pressure drops along the membrane unit;
- permeation rate of the gas species not affected by the mixture composition and feed pressure;
- Pd-based membranes permeable only to the hydrogen (infinite selectivity).

The mass balance equations are reported below.

$$u_s \frac{dc_i}{dz} = -\frac{A^m}{V^f} J_i \quad \text{(feed-retentate side)} \tag{2}$$

B.C. $z = 0,\ c_i = c_{i,0}$

$$u_s \frac{dc_i}{dz} = \frac{A^m}{V^f} J_i \quad \text{(permeate side)} \tag{3}$$

B.C. $z = 0,\ c_i = 0$

For both organic and metallic dense membranes the permeation process occurs according to the solution–diffusion mechanism. The permeation flux of the species i through a dense (non-porous) membrane (J_i) is expressed as the product between the permeance (P_i/l) and the applied driving force ($p_{ih}^n - p_{il}^n$) by the equation

$$J_i = \left(\frac{P_i}{l}\right)(p_{ih}^n - p_{il}^n) \tag{4}$$

with n equal to 1 for the passage of all gases through a polymeric membrane and n, usually, equal to 0.5 for the permeation of the hydrogen through the Pd films (Sievert's law) [32].

2.2. Membrane reactors

The reaction system has been represented by a continuous single-phase model (pseudo-homogeneous). Thus, the two-dimensional differential equations written in steady state for the lumen side with the appropriate boundary conditions are the following:

$$v_z \rho_g C_{p_{\mathrm{mix}}} \frac{\partial T}{\partial z} = \frac{1}{r}\frac{\partial}{\partial r}\left(r\lambda_{\mathrm{er}}\frac{\partial T}{\partial r}\right) + \Re_i(-\Delta H(T)) \quad \text{(energy balance)} \tag{5}$$

$$v_z \frac{\partial c_i}{\partial z} = \frac{1}{r}\frac{\partial}{\partial r}\left(r D_{i,r}\frac{\partial c_i}{\partial r}\right) + \Re_i \quad \text{(mass balance)} \tag{6}$$

B.C.1 : $\forall z,\ r = 0: \quad \frac{\partial c_i}{\partial r} = 0; \quad \frac{\partial T}{\partial r} = 0$

B.C.2 : $\forall z,\ r = D/2:$

$$-D_{i,r}\frac{\partial c_i}{\partial r} = P_{H_2}\left(\sqrt{p_{H_2,\mathrm{lumen}}} - \sqrt{p_{H_2,\mathrm{shell}}}\right)$$

$$-\lambda_{\mathrm{er}}\frac{\partial T}{\partial r} = h_w(T - T_w) + J_{H_2}C_p(T - T_w)$$

B.C.3 : $\forall r,\ z = 0: \quad c_i = c_{i,0},\ T = T_0$

These non-linear equations have been discretised by an orthogonal collocation procedure in finite elements giving a set of ordinary differential equations. Heat and mass one-dimensional differential equations have been also written for the shell side. All equations have been solved by a 4th order Runge–Kutta procedure. Only water gas shift reaction occurs in the membrane reactor (absence of competitive reactions). As reaction rate the expression devised by Temkin has been used [33]. A scheme of the Pd-MR is reported in Fig. 1c. For the membrane reactor working in non-isothermal conditions a sweep gas stream with a flow rate 10 times higher than the dry feed syngas stream has been considered to limit the temperature hot spots and increase further the driving force for the H_2 permeation [34]. The use of a sweep gas determines a dilution of hydrogen recovered in the permeate side of the Pd-MR with respect to the Pd-Sep. However, as sweep gas, superheat steam has been assumed in all simulation tests; this choice is justified by the easiness of the following H_2–H_2O separation and humidification needs for hydrogen stream to the fuel cell. Thus, in the following, the performance of both Pd-based units will be considered independently on the hydrogen dilution.

The compression power has been evaluated by means of following equation developed for a multistage compressor, assuming an isentropic process with an equal division of work between cylinders and intercooling of gas to original intake temperature [35]:

$$\mathrm{hp} = \frac{3.03 \times 10^{-5} k N_s}{k-1} p_1 q_f \left[\frac{(p_2/p_1)^{((k-1)/kN_s)} - 1}{\eta}\right] \tag{7}$$

The amount of hydrogen contained in the retentate streams referred to the feed hydrogen quantity will be considered in the following as the hydrogen loss for the system ($\Psi(\%) = (H_2,\ \text{retentate}/H_2,\ \text{reference feed})$). In a next study the eventuality to treat the retentate streams improving the global recovery of the hydrogen will be analysed.

3. Results and discussion

The effect of feed pressure on the performance of different membrane configurations in terms of membrane surface to achieve a fixed hydrogen purity (99.9995%) and global recovery (90% of the total feed value) has been investigated and discussed in the following. The contribution of the theoretical power of gas compressors and hydrogen loss has been also taken into account.

3.1. Polymeric membrane units

At a fixed global recovery, the effect of the driving force on the purity of both permeate and retentate streams exiting from the polymeric module has been investigated with particular attention for H_2 (the most permeable species which has to be purified) and CO (which content has to be reduced under 10 ppm). These components separate in opposite way in the permeate and retentate streams, as a consequence of their permeation rate according to the data showed in Table 1. In fact, the permeate stream enriches in the more permeable species (available at low pressure value) while the CO becomes more concentrate in the retentate one (at the feed pressure value). The purity level achievable is a strong function of the recovery, usually expressed by the stage cut variable (θ = permeate flow rate/feed flow rate). Thus, as the stage cut increases, a decrease of the hydrogen purity combined to an increase of carbon monoxide concentration in the permeate stream is observed for both membrane types. Hydrogen concentration in both streams is, however, strongly influenced by the driving force of the process as shown in Figs. 2 (permeate side) and 3 (retentate side). Furthermore, higher global recoveries (θ) are associated to higher membrane surface areas, see Fig. 2a (polymeric membrane type A) and b (polymeric membrane type B–H).

At a fixed stage cut value, a higher feed pressure, corresponding to an enhanced driving force, allows to reach a higher hydrogen purity. However, the difference in H_2 concentration is more evident at high stage cut values. In addition, the effect of the pressure is more significant moving from 5 atm to 10 atm, while it reduces moving towards 25 atm. At the same operating conditions, membrane type A allows to achieve slightly higher H_2 purity levels than membrane type B–H, but it requires a membrane surface one order of magnitude higher.

As to the CO concentration in the permeate stream, it decreases with the pressure applied in the whole range of investigated stage cuts (0.1–0.45). This behaviour is more significant at high stage cuts ($\theta > 0.3$) while for $\theta < 0.25$ the influence of the feed pressure in the range 10–25 atm is less marked. Some CO concentration values in the permeate stream for both membrane types are reported in Table 2.

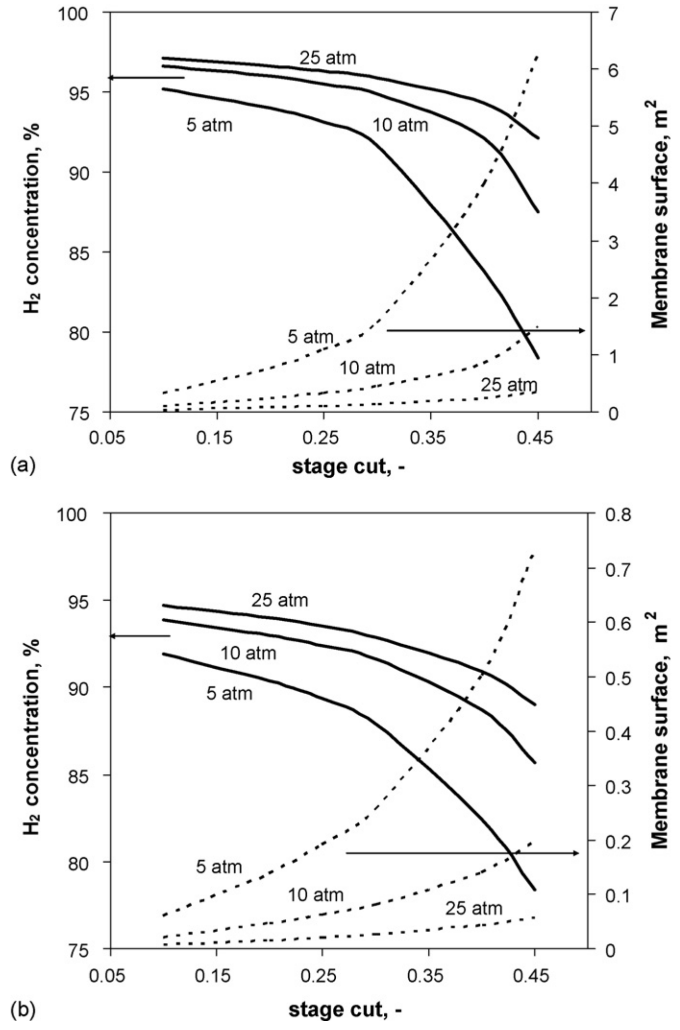

Fig. 2. H_2 permeate concentration (solid lines) and membrane surface (dotted lines) vs. stage cut at different feed pressure values: (a) membrane type A; (b) membrane type B–H.

In Fig. 3a and b for membrane types A and B–H respectively, due to the almost equimolar concentration of the H_2 and CO in the feed stream, for stage cut values lower than 0.20 no effect of the feed pressure on the retentate composition for both polymeric membrane types has been observed. As expected, at the lowest stage cut investigated (corresponding to the highest H_2

Table 2

CO concentrations in the permeate stream as a function of stage cut at three different feed pressure values

Stage cut (θ)	Membrane type A, p_{feed} (atm)			Membrane type B–H, p_{feed} (atm)		
	5	10	25	5	10	25
	CO concentration (mol%)					
0.1	2.3	1.6	1.3	3.8	2.7	2.3
0.2	2.9	1.9	1.5	4.6	3.2	2.6
0.25	3.4	2.1	1.7	5.2	3.5	2.9
0.3	4.2	2.4	1.9	6.1	3.9	3.2
0.4	9.1	3.9	2.7	9.9	5.6	4.3
0.45	13.3	6.6	3.9	13.5	7.4	5.4

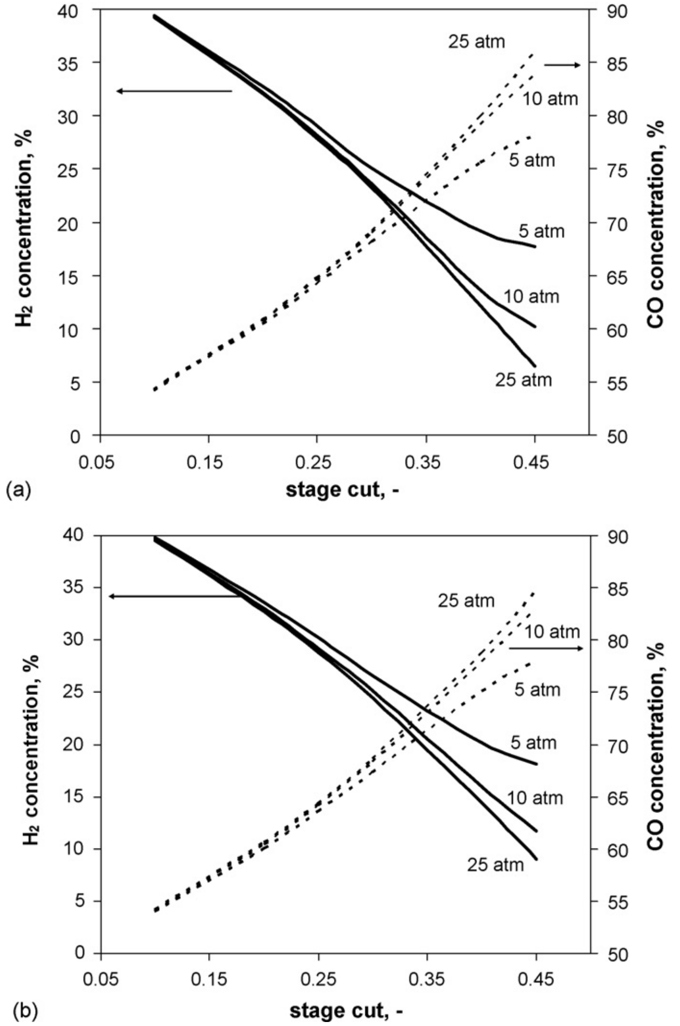

Fig. 3. H_2 (solid lines) and CO (dotted lines) retentate concentration vs. stage cut at different feed pressure values: (a) membrane type A; (b) membrane type B–H.

concentration in the permeate side) the retentate composition does not significantly change with respect to the feed one.

Therefore, the obtained results by comparing the performance of these two commercial membrane types in a single polymeric stage up to 25 atm do not meet the goal of the separation. The use of multistage systems further improves the H_2 purity at the permeate side, decreasing the CO content in the same stream. In fact, at a fixed stage cut, a single membrane stage is characterised by the lowest membrane surface requirement, but also the lowest concentration of the more permeable component in the permeate stream. The purity level can be enhanced by an appropriate distribution of the separation load between the stages without increasing significantly the membrane surface [36]. Therefore, in analogy with the single stage configuration, a global stage cut value equal to 0.1 has been chosen for the two-stage system in order to enrich the permeate stream in H_2.

Table 3
Composition (mol%) of the permeate stream exiting from the second membrane stage and total membrane surface request for $\theta = 0.1$

Component	Membrane type A, p_{feed} (atm)		Membrane type B–H, p_{feed} (atm)	
	5	10	5	10
	Composition (mol%)			
H_2	99.3	99.6	98.0	98.7
CO	0.1	0.05	0.2	0.1
	Total membrane surface (m^2)			
	1.21	0.38	0.213	0.072

The membrane unit produces a significant enhancement of the H_2 concentration in the permeate stream, but the CO content remains still significantly higher than 10 ppm also operating at low stage cuts (see Table 3); consequently this configuration can be proposed only as first stage for the hydrogen separation in an integrated system. By considering that the achievable purity level depends mainly on the pressure ratio and membrane selectivity for the component involved in the separation, an increase of four orders of magnitude in the selectivity at the pressure investigated in this study is necessary to meet the hydrogen purity target in a single stage unit. Less stringent selectivity requirements for multistage polymeric systems occur.

3.2. Palladium-based membrane units

As an alternative, the feed stream can also be treated by a palladium-based membrane. In this case the permeate stream will contain pure hydrogen and the separation target will be reached. However, the technical feasibility often conflicts with the process economics, due to the palladium cost. In fact high hydrogen recoveries, that can be achieved by properly choosing the operating conditions, are linked to high membrane surfaces. Furthermore, high amounts of palladium are required to produce films (>50 μm) in order to guarantee the permeation of the only hydrogen (ideal selectivity) for long time runs [37]. In Fig. 4 the effect of the feed pressure on the membrane surface and hydrogen loss at different stage cut values is represented. An exponential increase of the membrane area is observed at low pressure values as stage cut rises. The increase of the driving force (a higher feed pressure) allows to obtain the same recovery

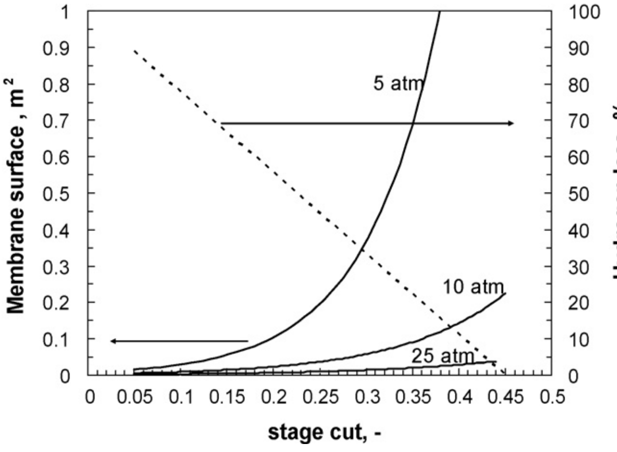

Fig. 4. Membrane surface (solid lines) and hydrogen loss (dotted line) of a Pd-Sep vs. stage cut at three different feed pressures.

with lower membrane surfaces. Thus, for a stage cut equal to 0.1, by increasing the feed pressure from 5 atm to 10 atm a saving of membrane surface of 67% is obtained while, when the feed pressure increases up to 25 atm, the saving of membrane surface is equal to 90%. At $\theta = 0.4$, moving from 5 atm to 10 atm, the membrane surface is reduced of 6.5 times, whereas if the feed pressure is raised up to 25 atm (five times higher) the membrane area reduction is close to 45 times. In consideration of this fact, high H_2 recoveries in a single membrane stage need high feed pressure values to keep low the membrane surfaces. A linear decrease of the hydrogen loss is observed as θ increases for all feed pressure values.

By coupling the separation and the reaction steps in a Pd-MR, it is possible to enhance the hydrogen driving force across the membrane, since an additional hydrogen amount is produced by CO conversion according to the WGSR. In membrane reactors, typically, the CO conversion is favoured by a high residence time of the reagents (low feed flow rates), a high feed pressure (high hydrogen partial pressure), and a high H_2O/CO feed molar ratio (R). For this specific syngas stream, containing almost 50% of hydrogen, high pressures favour the H_2 permeation along the membrane reactor.

As showed in Fig. 5a and b, as the feed pressure rises, at fixed membrane surface, both hydrogen fractional recovery (permeate H_2 flow rate/feed H_2 flow rate) and CO conversion increase as well. This trend remains valid for both feed H_2O/CO molar ratios investigated ($R = 1$ and 2). For the lowest membrane surface values the difference among the curves is significant while, as the membrane surface increases, this difference becomes less important. At fixed R, low membrane surfaces require high feed pressures to achieve a significant H_2 fractional recovery because a high driving force is necessary to promote the H_2 permeation. On the other hand, a higher H_2 permeation rate allows to shift continuously the chemical equilibrium towards the products (CO_2, H_2) with an evident decrease of the CO content in the stream. As a further consequence, the hydrogen flow rate in the permeate increases. By increasing the feed H_2O/CO molar ratio at a fixed feed pressure, the CO conversion increases due to the higher H_2O amount supplied to the Pd-MR that forces the forward reaction. This situation overcomes the negative effect of a residence time decrease for the reagents (Fig. 5b). However, $R > 2$ is not justified because it lowers further the residence times reducing the hydrogen removal [21,38]. Therefore, the separation target can be obtained by combining high feed pressures with low membrane surfaces or *vice versa*. Nevertheless, a Pd-MR, in which a syngas stream at 1 atm is processed, is not capable to achieve the separation target independently on its size.

In Table 4, a summary of membrane surface needs for a Pd-Sep and a Pd-MR with $R = 2$ is reported. It is possible to observe that high feed pressures favour the performance of the Pd-Sep more markedly than Pd-MR. However, for a feed pressure up to 10 atm, a Pd-MR requires a lower membrane surface than a Pd-Sep. In fact, at 10 atm the difference between the surfaces for the membrane units is two times while it increases at one order of magnitude at a feed pressure of 5 atm. On the contrary, at 25 atm a Pd-Sep needs a surface 2.5 times lower than a Pd-MR since the reverse reaction occurs prevalently for the last unit, with a consume of H_2. Therefore, the use of a high feed pressure value (e.g. 25 atm) is not justified in a Pd-MR for the WGSR.

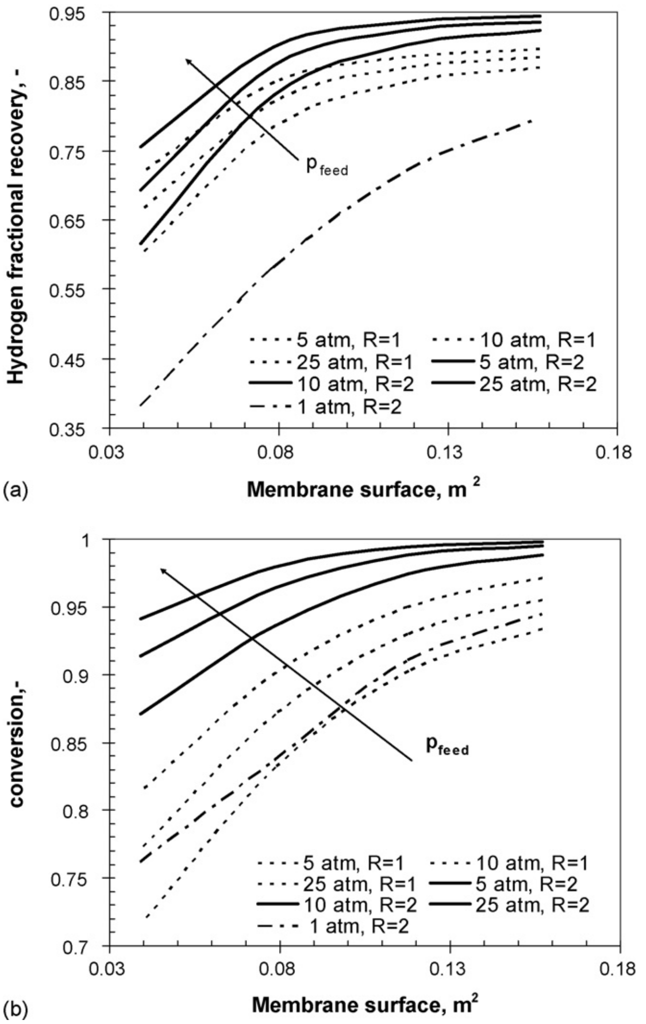

Fig. 5. (a) Hydrogen fractional recovery and (b) CO conversion vs. membrane surface of a Pd-MR. Effect of the feed pressure (p_{feed}) and reagents feed molar ratio ($R = H_2O/CO$). Solid lines for $R = 2$, dotted lines for $R = 1$, dotted-dashed lines for $R = 2$ and 1 atm.

For the single Pd-MR, moving from 5 atm to 25 atm, Ψ changes from 12.0% to 18.0%, while the H_2/CO ratio in the retentate streams varies from 4.3 to 8.2.

On the basis of the achieved results, the possibility to integrate membrane units in order to reduce the membrane surface and compression power has been investigated. Main results are reported in the next section.

Table 4
Compression power and membrane surface to recover the 90% of H_2 at 99.9995% purity level as a function of the feed pressure

p_{feed} (atm)	Compression power (hp)	Membrane surfaces (m^2)	
		Pd-MR	Pd-Sep
5	0.079	0.118	1.3
10	0.108	0.09	0.19
25	0.151	0.078	0.029

3.3. Integrated membrane systems

The identification of the most favourable integrated sequence in terms of membrane surface, that lead to the recovery of a hydrogen flow rate (1 N m^3/h) required by a polymeric fuel cell of power 0.90 kWh, has been performed taking advantage of the analysis of the performance of the single stage membrane units. A feed H_2O/CO molar ratio equal to 2 has been assumed for the Pd-MRs in all the sequences, according to what discussed in the single stage Pd-MR investigation. In the following the Pd-MR, the Pd-Sep and the Pol-Sep will be indicated by means of a dark grey, grey and white box, respectively.

The fundamental strategy, on which is based the arrangement of the membrane units in order to reduce the membrane surface requirement, considers the H_2 enrichment of the gas streams before their further processing in Pd-Sep units, whereas Pd-MRs are recommended for treating the high CO content streams. In particular, the different sequences analysed are outlined in Fig. 6.

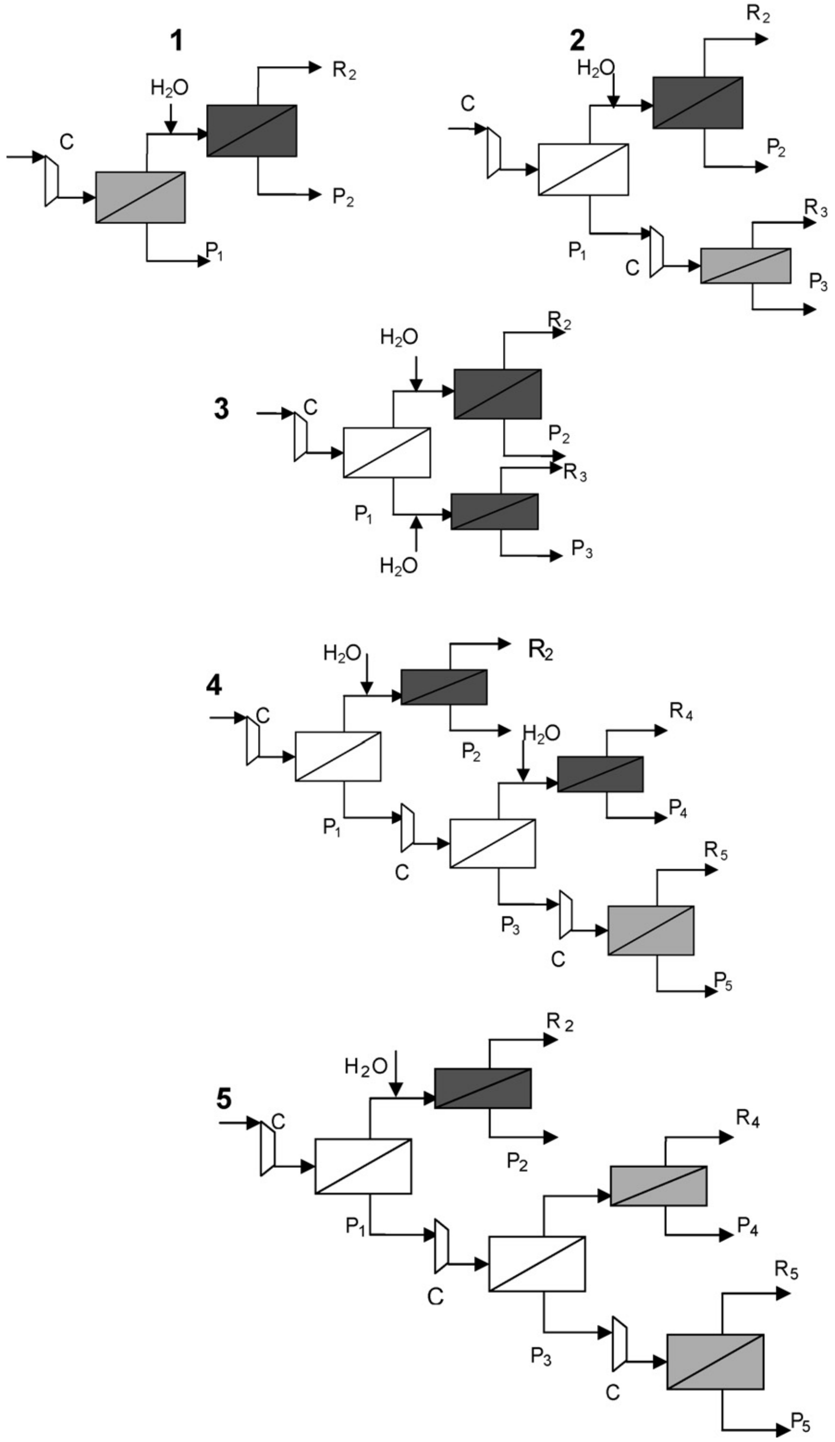

Fig. 6. Sequence of membrane units to meet the separation target. A white box indicates the polymeric unit (Pol-Sep), a grey box represents the Pd-Sep, while a dark grey box refers to Pd-MR.

3.4. Sequence 1

By considering that both Pd-based membrane units are capable to meet the process target, the succession of a Pd-Sep and a Pd-MR has been finalised to reduce the total membrane surface by lowering the H_2 content in the stream fed to the Pd-MR without changing the compression requirements. Thus, in this configuration the syngas mixture has been fed to Pd-Sep, then the retentate stream exiting from it has been processed in a Pd-MR (Fig. 6-1). The relative amount of hydrogen recovered in the Pd-Sep and Pd-MR represents a fundamental aspect. In fact at a fixed pressure value, as the fraction of H_2 recovered in the Pd-Sep increases, the requirement of total membrane surface increases as well. It depends on the exponential growth of the membrane surface in the Pd-Sep that occurs when the stage cut increases as already discussed in the previous section, see Fig. 4. This behaviour is more evident at a low feed pressure (5 atm) where a higher contribution to the total surface is given by the Pd-Sep (Fig. 7a). The possibility to reduce the membrane surface in the system by acting on feed pressure becomes more important as a higher H_2 fractional recovery is required in the Pd-Sep. Thus, if the feed pressure increases from 5 atm to 10 atm at a stage cut of 0.1, the reduction in the membrane surface is about 50%, while at $\theta = 0.3$ it reaches the 90%. Equal surfaces for both Pd-based units are obtained at a stage cut for the Pd-Sep equal to 0.13 and 0.18 at 5 atm and 10 atm, respectively. For what concerns the CO conversion in the Pd-MR, it remains still superior to 90%, due to the specific MR design.

In the retentate streams, a hydrogen molar concentration of 15.8% and 9.8% combined to a ratio H_2/CO of 5.4 and 7.0 has been calculated at 5 atm and 10 atm, respectively. As result, a loss of hydrogen (Ψ) equal to 55% (at 5 atm) and 34% (at 10 atm) has been obtained for this sequence. The same compression power of the single Pd-MR and Pd-Sep is required.

The sequence where the Pd-MR is set before the Pd-Sep has not been analysed because of the low hydrogen concentration in the retentate stream exiting from the Pd-MR for which the hydrogen fractional recovery should require a high membrane surface in the Pd-Sep.

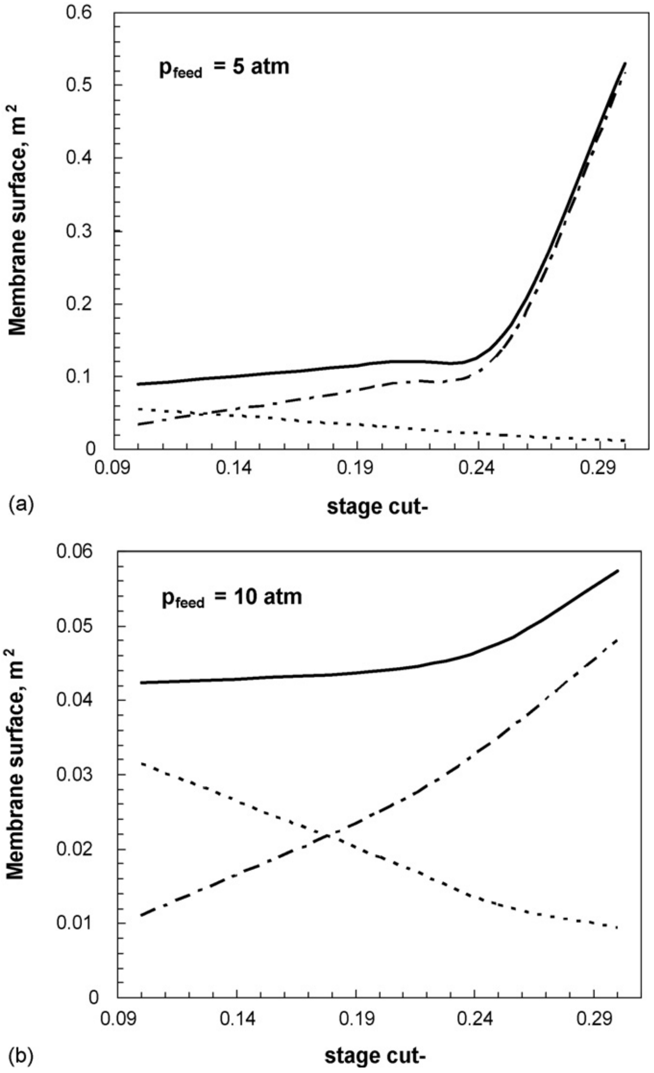

Fig. 7. Membrane surface vs. stage cut at 5 atm (a) and 10 atm (b) for the sequence 1. Dotted lines for Pd-MR, dotted-dashed lines for Pd-Sep, solid lines for the total membrane surface (Pd-MR + Pd-Sep).

3.5. Sequence 2

In the sequence 2, the syngas mixture has been at first fed to the polymeric membrane stage, then the permeate stream, after a compression at the same feed pressure, has been treated in a Pd-Sep while the retentate stream has been processed in a Pd-MR (Fig. 6-2). This arrangement allows each Pd-based unit to operate in the most favourable conditions. Thus, a stage cut of 0.1 has been chosen for the polymeric membrane unit in order to enrich in hydrogen the permeate stream to feed in the Pd-Sep and to process in the Pd-MR a retentate stream containing a high CO amount. Once more as feed pressure increases, membrane surface decreases for all the units. A double of the operating pressure determines a reduction of two thirds for the polymeric surface and around 40% for the total Pd surface. Referring to the only Pd-based units, the saving of membrane surface with

Table 5
Membrane surface requirement to recover the 90% of H_2 at 99.9995% purity level as a function of the feed pressure for the sequence 2

p_{feed} (atm)	Compression power (hp)	Membrane surface (m^2)			Partial H_2 recovery (%)	
		Pol-Sep	Pd-Sep	Pd-MR	Pd-Sep	Pd-MR
5	0.087	0.061	0.011	0.047	18	72
			0.058			
10	0.119	0.021	0.0044	0.03	19	71
			0.0344			

Table 6
Hydrogen loss in retentate streams at different feed pressure

p_{feed} (atm)	Hydrogen loss, Ψ (%)	
	R_3	R_2
5	0.42	25.1
10	0.87	28.4

respect to the best conditions in sequence 1 results of 35% and 20% at 5 atm and 10 atm, respectively. In this case the CO conversion in Pd-MR is equal to 95% and 96% at 5 atm and 10 atm. However, a negative aspect with respect to the previous sequence is represented by the necessity to compress the permeate stream exiting from polymeric unit at the same feed pressure (5 atm or 10 atm) before its processing into the Pd-Sep. In Table 5 the values of membrane surface required in the integrated system (distinguishing the different contributions) are summarized. An increase of compression power of 10% with respect to the sequence 1 has been calculated at both feed pressure levels.

As regard to the concentration of the retentate streams, it is relevant to observe as a large part of the hydrogen is lost on the lumen side of the membrane reactor whereas in the Pd-Sep this loss is less important (see Table 6). Furthermore the (relative) amount of H_2 and CO results significantly different into the retentate streams exiting from the two Pd membrane units as a consequence of a drastically lower CO content in the Pd-MR due to a high conversion. However, the H_2 concentration results higher in the retentate of the Pd separator where the dilution effect of water vapour is absent.

3.6. Sequence 3

The possibility to enhance the H_2 content, allowing the simultaneous abatement of CO, can be achieved by setting two Pd-MRs on the gas streams exiting from the Pol-Sep. Therefore, in this sequence the syngas mixture has been at first fed to the polymeric membrane stage, then both permeate and retentate streams have been treated without further compression in two Pd-MRs (Fig. 6-3). In order to avoid the compression of the permeate exiting from the polymeric stage, this stream has been processed in a membrane reactor operating at atmospheric pressure. In this case a stage cut value of 0.6 relative to the polymeric unit has been selected for a better distribution of both feed flow rate and composition to the Pd-based membrane units. This choice allows to keep high CO conversions in both membrane reactors. In fact, a conversion of 95.2% is attained in a Pd-MR at 1 atm, while in the membrane reactor operating at high pressure a conversion higher than 99.5% is reached.

As showed in Table 7, despite the high conversion values, this arrangement requires higher membrane surfaces for both polymeric and Pd-based units with respect to the sequences analysed previously. Furthermore, the working pressure has a little influence on the membrane surface requirement. The global H_2 amount lost in the lumen of the membrane reactors is equal to 12.5% and 8.5% at 5 atm and 10 atm, respectively. The average H_2/CO ratio in the retentate streams is around 5.

As the membrane reactor, that processes the permeate stream exiting from the polymeric stage, works at a pressure higher than 1 atm, its size decreases. In more detail, for this reactor at 5 atm the membrane surface is five times lower while at 10 atm it is 8.2 times lower. With reference to the overall Pd surface a saving of 60% and 70% is achieved at 5 atm and 10 atm, respectively. However, since an additional compression step is necessary, this new arrangement can be directly compared to the sequence 2. For this last sequence both the membrane surface and the compression power are still lower. In particular, concerning the saving in the compression (−31% for both feed pressure values), it is due to a lower flow-rate in the second compression step.

3.7. Sequence 4

A higher hydrogen enrichment in the permeate stream of a two-stage polymeric membrane system has been investigated in this specific configuration, where the syngas mixture has been

Table 7
Membrane surface requirement to recover the 90% of H_2 at 99.9995% purity level as a function of the feed pressure for the sequence 3

p_{feed} (atm)	Compression power (hp)	Membrane surface (m^2)			Partial H_2 recovery (%)	
		Pol-sep	Pd-$MR_{1\text{ atm}}$	Pd-MR	Pd-$MR_{1\text{ atm}}$	Pd-MR
5	0.079	1.77	0.157	0.044	49	41
			0.201			
10	0.108	0.64	0.157	0.038	49	41
			0.195			

Table 8
CO conversion and membrane surface requirement to recover the 90% of H_2 at 99.9995% purity level as a function of the feed pressure for the sequence 4

p_{feed} (atm)	Compression power (hp)	Membrane surface (m^2)					Conversion (%)	
		Pol-Sep_1	Pol-Sep_2	Pd-MR_1	Pd-MR_2	Pd-Sep_2	Pd-MR_1	Pd-MR_2
5	0.107	0.191	0.022	0.038	0.0063	0.0085	95.4	70.5
		0.213			**0.0528**			
10	0.146	0.063	0.009	0.0251	0.0063	0.0036	96.1	74.8
		0.072			**0.035**			

Table 9
Hydrogen loss in retentate streams at different feed pressure

p_{feed} (atm)	Ψ (%)		
	R_2	R_4	R_5
5	23.9	2.7	1.8
10	29.9	1.2	1.9

Table 10
Hydrogen loss in retentate streams at different feed pressure

p_{feed} (atm)	Ψ (%)		
	R_2	R_4	R_5
5	23.9	12.9	1.8
10	29.9	16.1	1.9

processed in membrane units arranged in cascade (Fig. 6-4). The retentate streams have been processed in Pd-MRs while the permeate stream exiting from the second membrane stage, after a re-compression at the same feed pressure value, has been treated in a Pd-Sep. This sequence is a natural extension of the sequence 2 since it replaces the polymeric single with a two-stage membrane system in order to enrich in H_2 the permeate side. In analogy with the sequence 2, the global stage cut investigated for the polymeric units is equal to 0.1, obtained as product of $\theta_1 = 0.25$ and $\theta_2 = 0.4$. At both feed pressure values, the contribution to the global H_2 recovery (90%) is divided for about 60% in the permeate stream exiting from Pd-MR_1 (P_2 stream), about 20% in Pd-Sep (P_4 stream), the rest in P_5 stream. This configuration is characterised by an increase of the polymeric membrane surface with respect the sequence 2 for both pressure values considered (about 3.5 times), but it results more convenient at 5 atm for what concerns the Pd-membrane surface, see Table 8. On the contrary, at 10 atm the Pd membrane surface is similar for these two sequences. A drawback of this arrangement is the necessity of two compression steps on the permeate stream (+35% and +23% of compression power at both feed pressures with respect to sequences 1 and 2, respectively) while a benefit is represented by the availability of retentate streams at high pressure and different H_2 content for a further use in the plant.

As to the hydrogen lost, it is straight to observe in Table 9 that a large part of it occurs in the MR processing the retentate from the 1st polymeric stage (R_2 in Fig. 6-4) at both feed pressures. On the other hand, the stream exiting from the Pd separator (R_5 in Fig. 6-4), characterised by a high pressure and a low flow-rate, contains hydrogen at a high purity level eventually profitable in an additional unit.

3.8. Sequence 5

This sequence differs from the sequence 4 only for the presence of a Pd-Sep instead of Pd-MR on the retentate stream exiting from the 2nd polymeric stage (Fig. 6-5). This choice is justified by the high H_2 concentration in this stream that in a MR lowers significantly the CO conversion. In terms of Pd membrane surface, this option is more convenient at 10 atm, while it becomes less favourable at 5 atm. In fact at 5 atm, the substitution of the MR_2 with the Pd separator produces an increase of Pd surface of the 30% (+4% on the total Pd membrane surface) while at 10 atm it causes a decrease of Pd surface of the 55% (−10% on the total Pd membrane surface). In addition an increased loss of hydrogen has been evaluated at both feed pressure values as reported in Table 10 for the stream R_4.

However, if a higher H_2 global recovery (>90%) is required at a low feed pressure, the sequences 4 and 5 result significantly advantageous in terms of membrane surface and H_2 loss with respect to the previous configurations. As shown in Table 11, that summarizes the performance of the different sequences inves-

Table 11
Summary of the performance achievable in different integrated membrane system sequences

Sequences	Compression power ($\times 10^3$ hp)	Total membrane surface ($\times 10^2$ m^2)		Ψ (%)
		Polymer	Palladium	
$p_{feed} = 5$ atm				
Single Pd-Sep	79	–	130	10
Single Pd-MR	79	–	11.8	12
1	79	–	9	55
2	87	6.1	5.8	25.5
3	79	177	20.1	12.5
3_{bis}	126	177	7.5	12.8
4	107	21.3	5.3	28.4
5	107	21.3	5.5	38.6
$p_{feed} = 10$ atm				
Single Pd-Sep	108	–	19	10
Single Pd-MR	108	–	9	18
1	108	–	4.2	34
2	119	2.1	3.4	29.3
3	108	64	19.5	8.5
3_{bis}	173	64	5.7	7.3
4	146	7.2	3.5	33
5	146	7.2	3.2	47.9

tigated in this work, the sequences 4 and 5 require the same compression power.

4. Conclusions

In this work the potential of different integrated membrane systems has been evaluated to recover hydrogen (90% of the feed value) at a high purity level (99.9995 mol%) and reduce as possible the CO content in the retentate stream, by controlling the expensive Pd membrane surface and compression power.

A preliminary analysis has regarded the comparison between the performance of two different commercial polymeric membranes characterised by different permeation rate and selectivity values. The results have shown that, at the same operative conditions, the polyimide type A membrane allows to achieve a higher H_2 purity but requiring a higher membrane surface than the type B–H. Furthermore, single and two-stage polymeric membrane configurations are not capable to achieve the separation goal if they operate at feed pressures down to 10 atm.

For both Pd-based membrane units, a single stage meets the separation target but their performance changes as a function of membrane surface and compression power (e.g. 5 atm and 10 atm). However a membrane reactor working at 1 atm cannot be proposed for this purpose whatever is its size.

The use of integrated membrane systems has been just investigated for reducing the membrane surface and/or the compression power required to meet the separation target. High conversion values for the Pd-MRs are attained as a low H_2 content is present in the feed stream whereas this circumstance results extremely negative for the operations of polymeric and Pd-based separators. Thus for the reference syngas stream, the combination of a Pd-Sep followed by a Pd-MR is more appropriate than the reverse sequence.

The use of a polymeric unit allows a better division of the syngas stream for the Pd-based units with a saving in membrane surface for these last units.

The screening among all the sequences considered in this work, taking into account that the cost of the palladium membranes is significantly higher than polymeric ones, has been also performed considering the compression power and H_2 losses. Therefore, when a low driving force is available (e.g. 5 atm), the combination that seems to be the most convenient assumes that the syngas mixture is first fed to the two-stage polymeric membrane unit, then the permeate stream, after its re-compression, is further treated in a Pd-Sep while the retentate streams are processed in two Pd-MRs (sequence 4). On the contrary, at 10 atm the sequence 2 becomes competitive with the sequence 5 in view of the fact that the reduction in membrane surface is overbalanced by an increase of compression power and H_2 losses.

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