

EFCE Excellence Award in Membrane Engineering -Call for nomination 2010

Extended abstract of the PhD thesysis

TITLE OF THE THESIS: "Integrated membrane plant for pure hydrogen production for PEMFC"

Eng. Adele BRUNETTI, Institute of Membrane Technology, ITM-CNR, Via P.Bucci c/o University of Calabria cubo 17/C, 87036 Rende CS. a.brunetti@itm.cnr.it

Summary

Aim of the PhD thesis is the application of the Membrane Engineering in the study of new integrated membrane plant solutions for the production of CO-free hydrogen (CO<10 ppm) for PEMFC (polymer electrolyte membrane fuel cell). Three different solutions for the production/separation/purification of hydrogen by light hydrocarbons, referring particularly to the upgrading of down-streams of reformers, have been proposed as a suitable alternative to the traditional systems. This focus has been done in the optic of integrating the new membrane systems in already existent plants, or in fuel processors on board.

The thesis consists of an experimental and a theoretical analysis of the upgrading stage of the stream coming out by a reformer, consisting particularly in the water gas shift (WGS) reaction, carried out using membrane reactors (MR) with different membrane types. The performances of the systems have been analysed as a function of the operating conditions, paying particular attention to the feed pressure effect on the reduction of the volume and the process yield, expressed in terms of CO conversion and hydrogen recovery. The simulation study allowed to explore the performances of the MR in a wider range of operating conditions and, thus, is an interesting tool for foreseen the MR behaviour under such operating conditions, not often applicable in the lab. It was developed in dimensionless form analysing the results also in terms of Damköhler number, a dimensionless parameter very important in the membrane reactor design since it takes into account the characteristic reaction time and the space time.

The modelling and simulation study was accompanied by a wide experimental campaign for the analysis of the three integrated membrane plant solutions proposed. The water gas shift reaction have been performed in MR using Pd-Ag MR and silica membranes, feeding mixtures of different composition, in order to confirm the results achieved by simulations. Then, in order to verify the technological feasibility of these systems, the reaction/purification units have been integrated with a PEMFC. The performances of the three integrated systems have been analysed and compared in terms of "integrated plant technological efficiency". Two new performance indexes, useful to compare the advantages of a membrane solution with respect to the traditional one, were introduced as new metrics of Membrane Engineering.

Problems addressed

Nowadays, the necessity to release energy production from oil and natural gas as primary energy sources and, more in general, to diversify such sources, in order to assure the supplying, is making more pressing the interest on the innovative technologies. Moreover, the increasing effort on reduction of environmental problems has recently led to the development of clean technologies, designed to enhance both the efficiency and environmental acceptability of energy production, storage and use, in particular for power generation [1]. Since the hydrogen represents, as energetic carrier, a good answer to the growing necessity of new, abundant, clean, safe and renewable energetic sources, its employment as feeding fuel for fuel cells is certainly one of the most attractive aspects for the scientific community. The membrane technology and, in particular, the membrane reactor represent a good answer in this field since they pursue, in the mean time, the maximization of the sources exploitation as well as the compactness of the new systems. The approach followed in this thesis is basically focused on the Membrane Engineering aspects of the process and it pursues the logic of process intensification strategy, a new design philosophy that heads toward most efficient processes, tending to a better exploitation of raw materials, lower energy consumption and, also, plant size reduction. This last point is one of the main aspects to take into account for what concerns the low environmental impact and, thus, represents an important variable to consider in the new production plant design strategies.

State of the art

The stream coming out by a reformer is of highly industrial attractive since it contains around 50% of hydrogen (in dry condition) that might be recovered. Furthermore, the CO present in the stream (40-45%) is usually reduced in the upgrading stage, producing at the mean time, more hydrogen.

In traditional applications, the upgrading of reformat streams is performed by using a multi-stage CO-shift process, with an intermediate carbon dioxide absorption stage and a final CO₂ removal process.



WGS reaction is exothermic and favoured by a low temperature; on the other hand, by reducing the temperature, the catalyst activity decreases, with a consequent lower reaction rate. Therefore, according to the commercial CO shift systems (widely used in petrochemical industry), the traditional process is based on a series of catalytic reactors: firstly, operating at high temperatures (about 350-400 °C), a large portion of carbon monoxide is converted giving hydrogen and CO₂, taking advantage from the high reaction rate; furthermore, operating at low temperature (around 220-300 °C), the carbon monoxide conversion is refined, thus allowing a lower CO final concentration (less than 1% molar) [2]. H₂ rich stream coming out from the last reactor is supplied to a pressure swing adsorption (PSA) unit for the separation of H₂ from the other gases. It must be highlighted that the new utilization of H₂ as feed in fuel cells for mobile power sources requires that the anode inlet gas has a CO concentration lower than 10–20 ppm [3] for avoiding the catalyst poisoning with consequent drops in the cell efficiency. Hence, the purification step of the H₂ produced from hydrocarbon or alcohol reforming, must be very efficient in order to reduce CO level to cell requirements.

In the last few years, the significant developments in membrane science and the vision of process intensification by multifunctional reactors have stimulated a lot of academic and industrial researches [4, 5] in the direction of the development of the WGS reaction in a MR. However, practically no large-scale industrial applications of catalytic MRs have been described yet, due to the relatively high price of membranes (particularly for Pd-based membrane) and, also, to the other factors connected to the building-up stages.

Inorganic membranes for H₂-separation have been developed using various materials, such as palladium and its alloys, ceramics, silica and alumina, etc. Many of them and, in particular, palladium-alloy membranes were successfully used for hydrogen production/separation also for the WGS reaction because of the infinite H₂ selectivity which allows a pure H₂ stream, not requiring further separations [6, 7, 8, 9,10, 11] to be recovered. Among the first studies, Seok and Hwang [12] evaluated the performance of the WGS reaction by using as membrane Vycor glass coated with ruthenium (III) chloride trihydrate. The highest CO conversion obtained was 85% (equilibrium value 99.9%) at relatively low temperature (170°C) and a sweep factor equal to 10 feeding only CO and water. Complete conversion (100%) was obtained by Kikuchi et al. [13] and by Uemiya et al. [14] at 400 K using a tube in tube MR, in which the inner tube consisted of a thin palladium film, also by using a sweep factor equal to 10. Tosti et al. [15] developed a WGS membrane reactor with a Pd-Ag film (50 microns thick) coated on the inside wall of a ceramic porous tube and achieved reaction conversions close to 100% (well above the equilibrium value of 80%), owing to a high sweep gas flow rate. However, among the various advantages listed above, palladium – alloy membranes have shown some important drawbacks, such as high costs, degradation of H₂ separation performance [16], [7], which pushed the research also to consider other materials. Ceramic materials, on the other hands, can be hopefully expected to be membrane materials of high stability at high temperatures, even they exhibit finite H₂ selectivity. Costa *et al.* [17] proposed the WGS reaction carried out in a membrane reactor with a ceramic membrane. Rather than the Pd-Ag based membrane reactors where the CO conversion increases monotonically with the H₂ removal through the membrane, the CO conversion reached a maximum. This behaviour can be assigned to finite selectivity of the membrane which allows also to the reactants to permeate. In the last years, considerable attention was attracted by silica membranes for the production of hydrogen streams free of CO for feeding PEMFCs [18, 19, 20, 21]. Silica membranes exhibit lower module costs, high permeating fluxes, no

inhibition effects by chemical species, and high thermal stability, on the contrary to Pd-based membranes generally used for H₂-separation. Therefore, they appear attractive for hydrogen purification. However, the improvement of H₂ selectivity of this membrane type often corresponded to the reduction of the membrane permeability. Since permeance is normally enhanced through the reduction of selectivity, a balance between permeance and selectivity is essential to achieve optimum performances. The presence of an intermediate layer between the active layer and the support tube improved both permeance and selectivity.

The majority of the studies presented in the literature propose the use of sweep gas to promote the H₂ permeation, whereas only a small part combines the use of a slightly high feed pressure at the sweep gas for improving the permeation.

Key scientific and technological innovation

One of the main innovations of this thesis is the assignment of the role of driving force of the process exclusively to the feed pressure, whereas no sweep gas is used.

The main advantages offered by this choice are:

- 1) the achievement of a pure H₂ stream in the permeate side, not requiring further separation steps
- 2) the achievement of a retentate stream already concentrated and compressed in CO₂, therefore easily recoverable
- 3) the reduction of the membrane reactor volume.

The three integrated membrane plant solutions proposed in the thesis are the following (Figure 1):

- *Solution A*: Integrated membrane plant constituted by two stages: the first is a membrane reactor with a porous stainless steel supported silica membrane in which the WGS reaction takes place. A purification step with a Pd-Ag membrane for the removal of the residual CO permeated through the silica membrane has been placed in series on the permeate stream coming out by the membrane reactor.
- *Solution B*: Integrated membrane plant constituted by a single reaction/purification stage consisting in a Pd-Ag membrane reactor where the WGS reaction is carried out. In dependence of the feed composition, an innovative MR configuration has been proposed in order to assure the best exploitation of the whole membrane area.
- *Solution C*: Integrated membrane plant constituted by a single Pd-Ag purification step.

The permeate coming out by the three integrated solutions is then directly fed to a PEMFC and the performances of the whole systems have been evaluated in terms of efficiency, stability, etc.

Two different membrane types have been considered: porous stainless steel silica membranes prepared by KRICT (Membrane and Separation Research Center, Korea Research Institute of Chemical Technology, 305-600 Daejeon, South Korea) and Pd-Ag commercial membranes. The main difference within them is the gas permeation selectivity; Pd-Ag membrane shows infinite hydrogen selectivity and, thus, allows the recovery of a pure H₂ stream in the permeate. On the contrary, the selectivity offered by the silica membrane is finite, thus, the stream recovered in the permeate contains also other species. Therefore, it requires, a further purification steps before supplying a PEMFC. However, since the silica membranes results to be less expensive than the Pd-Ag one, it was considered interesting to study its application in an integrated membrane plant solution.

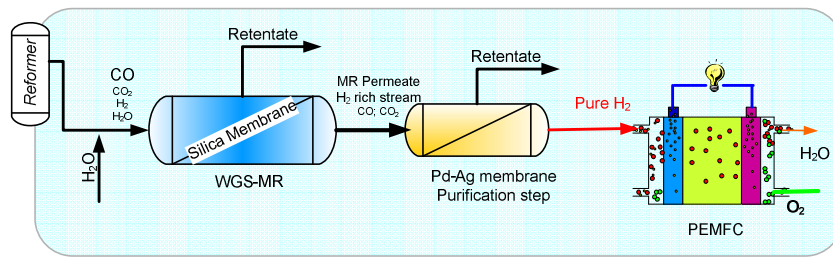
The main objective of this thesis is to demonstrate the technological feasibility and the related advantages of substituting a single-stage membrane reactor to the multistage traditional process. This can be done since this membrane technology allows the reaction and the H₂ separation to be performed in the same unit.

Generally, the use of a membrane reactor in the upgrading process implies several advantages with respect to the traditional operation, such as:

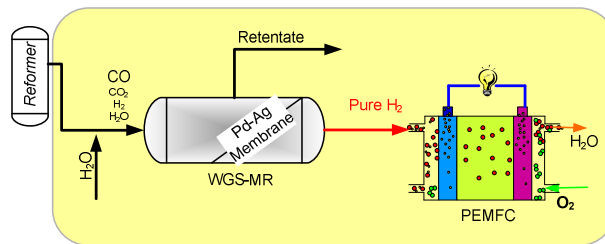
- Exceeding of the equilibrium of a traditional reactor (TR), owing to the selective removal of H₂ from the reaction volume
- Shifting of the inverse reaction rate
- Increasing of residence time of reactants

- Rich/pure hydrogen stream recovered in the permeate (depending on the type of membrane used, as explained in the following)
- Positive effect of feed pressure on CO conversion

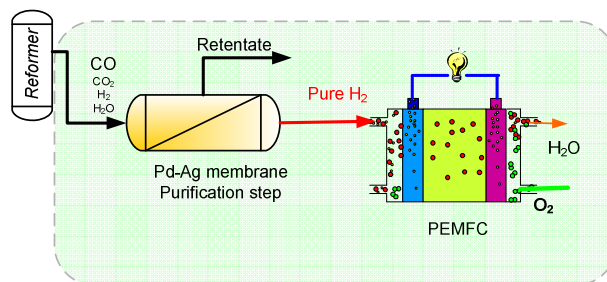
However, these advantages are strictly connected to the type of membrane housed in the MR.



Solution A



Solution B



Solution C

Figure 1 – Integrated membrane plant solutions

WGS is a reaction limited by thermodynamic equilibrium and it is not influenced by the reaction pressure from a thermodynamic point of view, since it is developed without changes in the mole number. In the case of the upgrading of a syngas mixture, the conversion is further limited by the presence of reaction products (H_2 and CO_2) and the maximum conversion achievable in a TR (TREC) is very low (30-40%), in the temperature range investigated in this work (270-330°C). The MR allows significantly higher conversion to be obtained owing to the positive effect of the feed pressure on the selective removal of the hydrogen through the membrane.

Applications, implementations and results

Modelling and simulation [22]

Before starting the experimental analysis, the WGS reaction performed in the MR (considering both the cases of *solution A* and *B*) was studied by means of 1D non-isothermal model using, as main design parameter, Damköhler's number (Da), the ratio of characteristic times of flow rate and reaction. The simulations were carried out for two feed mixtures (Mixture 1: 50% CO , 50% H_2O ; Mixture 2: 20% CO , 20% H_2O , 10% CO_2 , 50% H_2) in a temperature range of 220-320°C, with a feed pressure ranging 200 to 1,500 kPa which allows a good H_2 recovery index (up to 95%) and a retentate stream rich (up to 80%) in CO_2 . By calculations it was found that a Da around 1 assures a better exploitation of the catalytic bed and a better reactants management as well as a good exploitation of the whole membrane area (Figure 2). In this condition, considering the syngas stream, a CO conversion up to 75% and a RI up to 90% were achieved at a high feed pressure (i.e., 1,500 kPa) (Figure 3).

The Volume index (VI) and Conversion index (CI) are introduced for the first time and proposed as simple tools analysing the volume reduction or improved conversion shown by MRs; both index lead to the catalyst amount and reactor size being reduced. In particular, VI represents an important parameter in installing new plants. Future plants should be characterized by low sizes and high productivities: the VI is an indicator of the compactness of MR and it compares the MR reaction volume with that of a TR, necessary to achieve a set conversion. VI ranges from 0 to 1. A low VI means that the reaction volume, required by an MR to reach a set CO conversion, is too much lower than that required by a TR. As a consequence, the catalyst weight necessary in MR is reduced. For the WGS reaction, VI is a decreasing function of the feed pressure as shown in Figure 4. MR reaction volume is 25% of that of a TR, therefore VI is equal to 1/4 when an equimolecular mixture is fed at 1,500 kPa and a final conversion of ~80% (corresponding to 90% of the TREC) is considered. A high feed pressure implies that more H₂ permeates through the membrane, shifting the reaction toward further CO conversion.

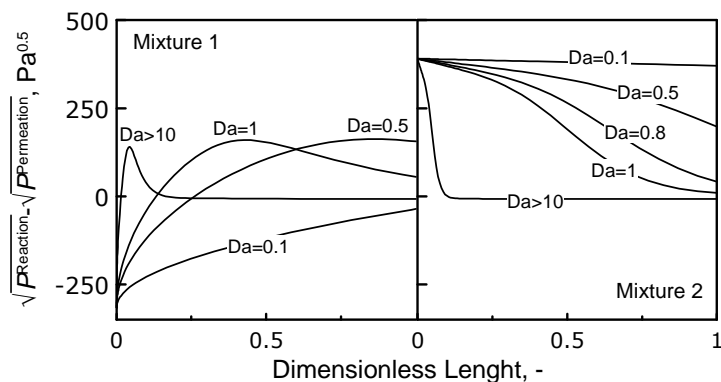


Figure 2 - Sievert's driving force profiles as a function of dimensionless length at different Da values. Furnace temperature = 280°C. Feed pressure = 1,000 kPa.

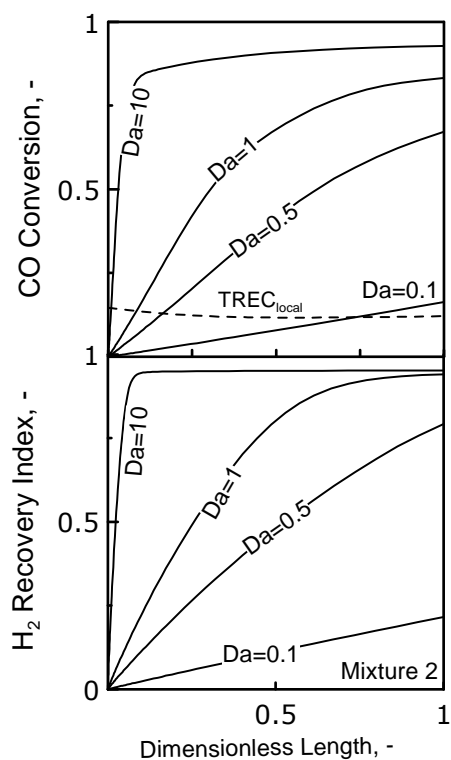


Figure 3 - CO Conversion and H₂ Recovery Index profiles as a function of dimensionless length at different Da . Furnace temperature = 280°C. Feed pressure = 1,000 kPa.

Therefore, for achieving a set conversion, at a higher feed pressure corresponds a lower catalyst requirement. If the mixture containing mainly reactants (mixture 1) is fed to MR for achieving the 80% of CO conversion, at 600 kPa the MR reaction volume size to the 75% of the TR one. Increasing the feed pressure, at 1,500 kPa the VI goes down to 25%. Therefore, the catalyst amount necessary to reach a suitable conversion is drastically reduced with clear gain also in terms of plant size reduction. When the reformat stream (mixture 2) is fed to the MR, the VI is too much lower, being the TREC up to 15%. Therefore the catalyst volume required to reach the 90% of the TREC varies from 40% at 500 kPa to 10% at 1,500 kPa.

From the evaluation of VI considering also membranes different than Pd-Ag such as silica ones, it was observed that in all cases the MR offers better performance than TR. At high feed pressure, the reaction volume of the MR with the silica membrane was calculated to be one half of the TR volume at the same operating conditions, but higher than that of a Pd-Ag MR. This effect is mainly due to the fact that the Pd-Ag membrane shows an infinite hydrogen permselectivity, whereas a microporous membrane is permeable also to the other gases, hence more catalyst volume is required for reaching the same CO conversion (Figure 5).

CI, comparing the conversion achieved in a MR and a TR, for a set reaction volume, gives an evaluation of the gain in terms of conversion. Also the *CI* ranges from 0 to 1. A high *CI* implies relevant gain in terms of conversion achieved in an MR with respect to the conventional reactor one, with the same reaction volume, meaning better raw material exploitation and lower wastes. A *CI* equal to 7 was reached using the reformat stream: 50% H₂; 10% CO₂; 20% CO; 20% H₂O.

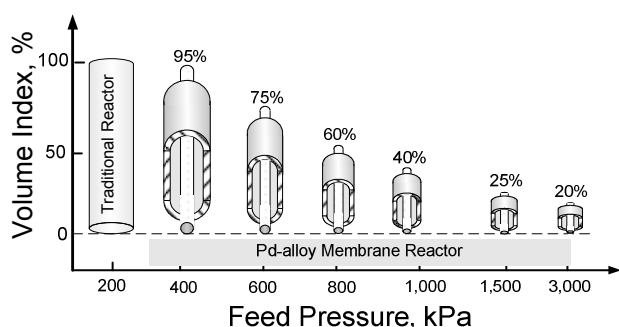


Figure 4 – Volume Index as a function of Feed pressure.

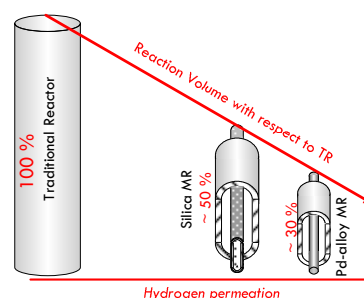


Figure 5 - Reaction volume reduction for different membrane types.

Solution A [23] & Solution C [24]: Experimental analysis

The MR of the *Solution A* is constituted by a silica membrane prepared with the soaking-rolling procedure by a Korean partner [19], with the aim of improving the H₂ membrane selectivity. Firstly, the membrane transport properties were measured; Permeance of all species (H₂:9.7-29; CO: 0.3-1.1; CO₂ 0.4-1.5 nmol/m²sPa) and ideal separation factor (H₂/CO, H₂/CO₂ and H₂/N₂) ranging from 15 to 40 and separation factors (H₂/CO=20-45), showed no dependence on the permeation driving force. Furthermore, no inhibition effect of other gases on the hydrogen flux was observed.

Then, MR was successfully used in WGS reaction. The CO conversion was an increasing function of the temperature and always exceeded the one of TR and, at a temperature higher than 250°C, also the TREC (TR equilibrium conversion) limit. However, the conversion presented a maximum as a function of the reaction pressure at high reaction temperature (280°C): at 6 bar it was lower than that at 4 bar (Figure 6).

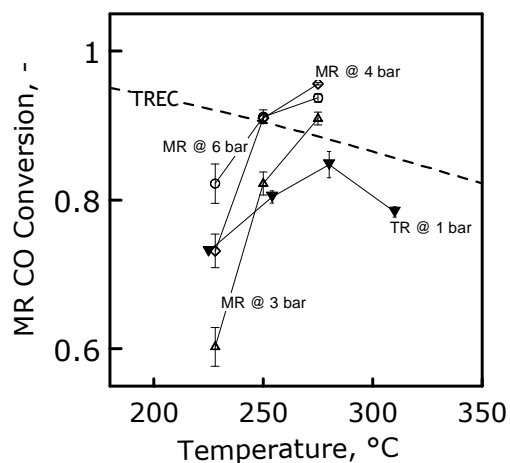


Figure 6 - MR CO Conversion as a function of Temperature at different P^{Reaction}. GHSV = 2000h⁻¹.

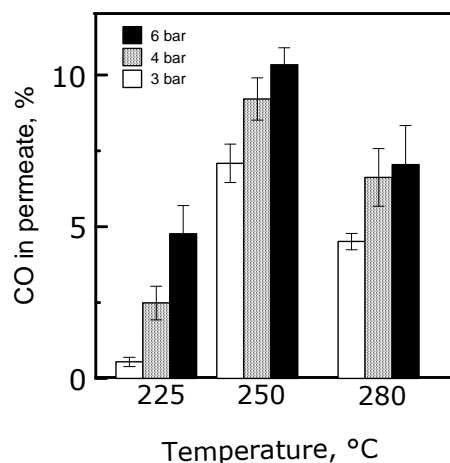


Figure 7 – CO content in permeate stream as a function of Temperature at different P^{Reaction}.

Since a pressure increase favours the permeation, on one hand a higher H₂ removal takes place from the reaction volume, on the other hand the reactant removal also occurs with a consequent lower CO conversion. This behaviour was more visible at a high temperature, since it positively affects the reaction and the permeation: the reactant permeation competes with reaction, depleting the CO conversion. By increasing temperature, the competitive permeation mechanism increased and, at 280°C and 6 bar, prevailed over the reaction. the CO content in the permeate stream ranged 1 to 10%, therefore the permeate H₂ rich stream couldn't be directly supplied a PEM-FC and a further

purification step was added for the residual CO reduction (Figure 7). However, the silica MR gave interesting results in terms of improved CO conversion with respect to TR one.

The permeate stream of the silica MR, containing at worst 10% of CO and around 10% of CO₂ was fed to a Pd-Ag purification module. The performances of this purification stage were studied also feeding the stream coming out from the reformer, by-passing the MR (*Solution C*).

The Pd-Ag membrane module was characterized by means of permeation tests with pure and gas mixture in the range of 300-450°C and 200-650 kPa, analysing the CO poisoning effect on the hydrogen permeation. Depending on the feed mixture considered and on the operating conditions the H₂ recovery ranges 50-95%.

The pure H₂ permeate stream was then supplied to a commercial PEMFC and the whole process was evaluated also in terms of efficiencies of the PEMFC and of the integrated plant, analysing the effect of the operating conditions changes to the MR on the whole integrated system (Figure 8).

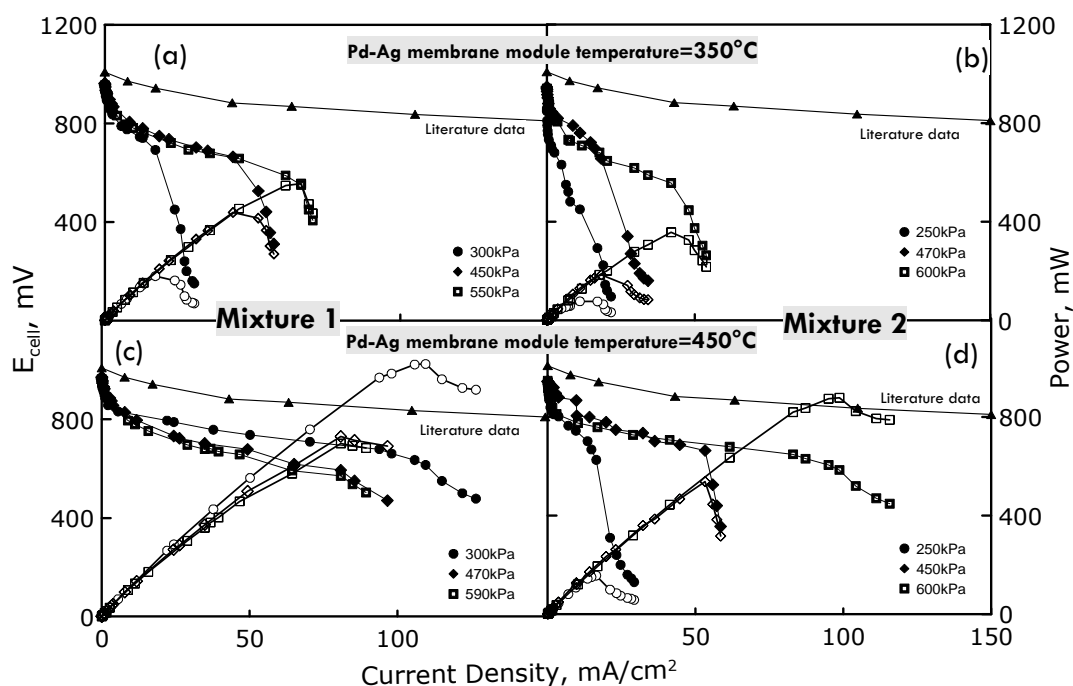


Figure 8 – Potentiometric measurements. Voltage (full symbols) and power (open symbols) as a function of current density at different operating conditions of the Pd-Ag membrane purification step. Literature data (full triangle)²⁵

Good and stable performances were realized in terms of power, voltage and current. A good agreement of experimental data obtained feeding H₂ by cylinder and by Pd-Ag membrane purification step was obtained confirming no performance loss when the PEMFC was fed by the membrane purification step. An independence of the PEMFC actual efficiency by the Pd-Ag membrane purification step operating conditions was observed, whereas a significant dependence was shown on the integrated membrane plant efficiency. This efficiency was calculated as the ratio between the H₂ actually converted in current and the H₂ totally fed/produced in the whole integrated system. It ranged from 40-85% for the *Solution C*, whereas it was significantly lower for the *Solution A* (ca. 35%). This is mainly due to the low H₂ recovery and, thus to the huge amount of H₂ loss in the retentate, measured with the MR, which does not exceed 35%.

Solution B: Experimental analysis [26, 27]

The *Solution B* is constituted by a single stage of reaction/purification consisting of a Pd-Ag MR. In dependence on the composition of the feed, the MR has been used in two different configurations:

- innovative configuration, where the tubular membrane is located only in the second part of the catalytic bed, whereas the first part works as a TR. This configuration is suitable for feed streams containing mainly CO and H₂O and few amount of products and when no sweep gas is used (as in the present study) (Figure 9-right side).

- typical configuration, suitable for the feed streams containing apart from reactants, also H₂ and CO₂ in relevant percentage, where the tubular membrane is allocated along the catalytic bed, having the same length of the shell (Figure 9-left side).

A fundamental aspect in the Pd-alloy MR use is the good exploitation of the whole available membrane area, which improves the global MR performance, assuring a higher CO conversion and, also, further H₂ recovered in the permeate side. However, the hydrogen permeated is a linear function of the driving force, therefore, when the feed stream is constituted mainly by reactants, in the first part of MR the H₂ partial pressure starts from zero since it is not present in the feed stream, but it is only produced by reaction. As a consequence, in this reactor section the H₂ partial pressure is very low, implying a bad utilization of the first part of the membrane area and, thus, a worsening of the MR performance with lower H₂ recovery and lower CO conversion. To avoid this problem, in this thesis a different MR configuration was proposed: the Pd-based membrane is located only in the second part of the catalytic bed: the reaction starts at the reactor entrance producing H₂ and its permeation starts in the second part of the MR, where its partial pressure is high.

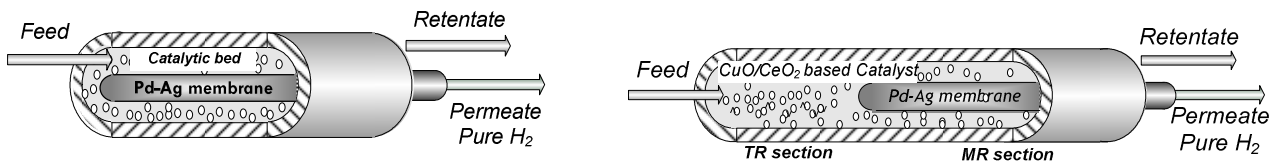


Figure 9 – Dimensionless partial pressure profiles as a function of dimensionless length for a typical and an innovative MR configuration.

The CO conversion achieved during the experiments (at 280-320°C and up to 600 kPa) was much higher than TR one operating in the same conditions, significantly exceeded also the thermodynamic equilibrium value of a TR (TREC). A conversion of 93% was measured at 300°C and 600 kPa operating at 2000 h⁻¹(Figure 10); 70% of the H₂ produced by reaction was collected as a pure permeate stream.

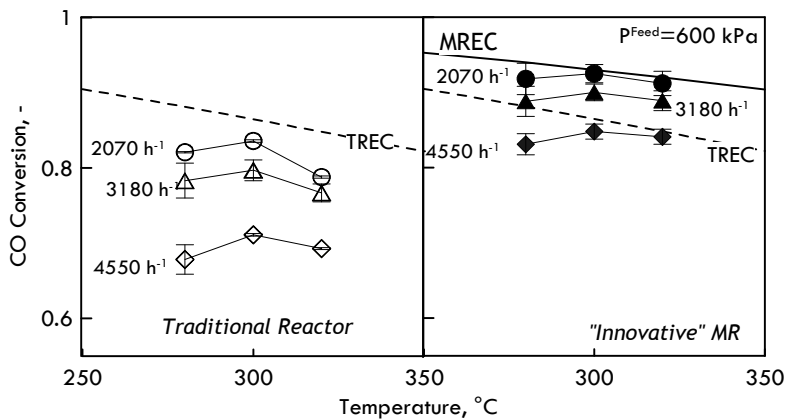


Figure 10 - CO Conversion as a function of Temperature at three different GHSV: 2070 h⁻¹; 3180 h⁻¹; 4550 h⁻¹.

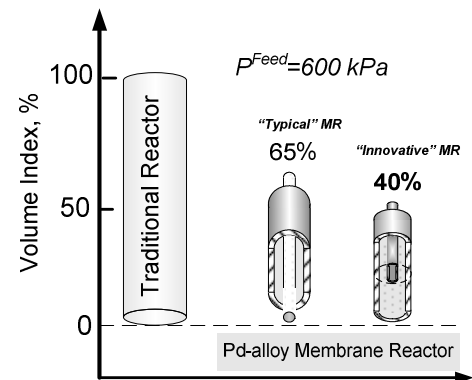


Figure 11 – Comparison of the Volume Index within “typical” MR and innovative MR configurations.

A significant reduction of the volume required to achieve the same CO conversion was shown by the innovative MR configuration with respect to the “typical” one. In fact, the reaction volume (equivalent to the catalyst volume) required by the innovative MR was 40% (at 600 kPa and 280°C) of that of TR, instead of the 65% of the typical MR (Figure 11).

When the feed stream contains also products, the typical configuration can be used, since the H₂ partial pressure is enough for starting the permeation at the inlet side of the MR. A syngas mixture (CO 45%; H₂ 50%; CO₂ 4%; N₂ balance) was upgraded in one-stage using a Pd-Ag membrane (60 micrometers thick) in typical configuration. The thermodynamics and the further limitation due to the H₂ presence (50%) in the feed stream did not limit WGS reaction in the MR: the measured CO conversion of 90% (Figure 12) was 3-4 times higher than that of a TR, greatly exceeding the equilibrium conversion of a TR (36%). The MR showed satisfactory performance also at high GHSV, achieving a CO conversion at least 3 times higher than TR (Figure 13). This means the possibility of processing a higher feed flow rate with the same catalyst volume, obtaining, in any

case, a high CO conversion and good H₂ recovery (Figure 13). The improvement of CO conversion and hydrogen recovery was more relevant at higher feed pressure, which being responsible for the driving force promoting H₂ permeation, showed two significant effects on the system: the first, 80% of H₂ stream was recovered as pure on the permeate side; the second, the retentate stream is already compressed and rich in CO₂ which can be more easily captured.

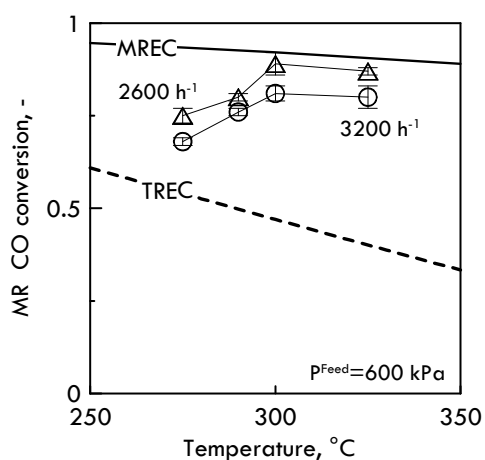


Figure 12 - MR CO conversion in an MR at 600 kPa as a function of temperature

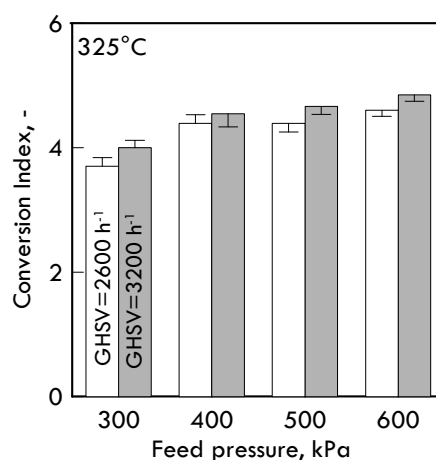


Figure 13 - Conversion index as a function of feed pressure at two GHSVs at 325°C.

Concluding remarks

The most important results obtained in this thesis were:

- Improvement of CO conversion, always higher than traditional reactor and also exceeding the thermodynamic equilibrium conversion, in particular, at high pressure.
- High recovery of pure hydrogen permeate streams, not requiring further separation loads before feeding a PEMFC.
- Reduction of reaction volume with respect to TR one.

The high feed pressure allowed the reaction volume of the membrane reactors to be drastically reduced, acting positively on CO conversion. This result has been also confirmed by the simulation analysis studied in a wider range of feed pressure with respect to the experiments. It was found that, for example, at 280°C and 15 bar the reaction volume of a Pd-Ag MR was around 25% of a TR, in the same operating conditions, for a set CO conversion.

- For a first evaluation of the effective feasibility of the integrated system, the permeate stream coming out by each integrated plant solution was connected with a PEMFC as a the final user. The possibility to use the hydrogen produced for feeding the PEMFC was confirmed. The hydrogen stream produced was pure, no drops in the PEMFC performance were observed, being assured a stable permeate flow rate for more than 500 h.
- Comparing the three integrated plant solutions, the Solution B, consisting of a single stage MR with a Pd-Ag membrane, resulted the most convenient in terms of overall performance as well as of reaction volume reduction. Even, in fact, the Pd-Ag membrane significantly affects the fixed plant costs, however this plant scheme does not require further separations and implies a reduction of the footprint occupied by the plant also considering the large reduction of the catalyst amount.

Globally, the integrated plant solutions showed good results in terms of improved reactants conversions, high H₂ recovery and, also, technological plant efficiency. They, thus, might represent a suitable alternative to the traditional hydrogen production plants and a valid solution for the “clean energy” production in already existent plants or in fuel processors on board.

References

- [1] Wadhvani S., Wadhvani A.K., Agarwal R.B., First International Conference on Clean Coal Technologies for Our Future, Chia Laguna, Sardinia, Italy, 21-23 October 2002
- [2] Raggio G., Pettinau A., Orsini A., Fadda M., Cocco D., Deiana P., Pelizza M.L., Marengo M., Second International Conference on Clean Coal Technologies for Our Future, Castiadas, Sardinia, Italy, 10-12 May 2005
- [3] Barbir F., *Solar Energy*, 78, 2005, 661-669
- [4] Dittmeyer R., Höllein V., Daub K., *Journal of Molecular Catalysis A: Chemical*, 173, (2001) 135–184
- [5] Stankiewicz A., *Chem. Eng., Proc.*, 42, (2003), 137-144
- [6] Shu J., Grandjean B.P.A., Van Neste A., Kaliaguine S., *Can. J. Chem. Eng.*, 69, 1991, 1036-1048.
- [7] Lewis F. A., Academic Press, London, New York, 1967
- [8] Uemiyama S., Sato N., Inoue H., Ando H., Kikuchi E., *Ind. Eng. Chem. Res.*, 30, 1991, 585-589.
- [9] Paglieri S.N., Way J.D., *Separation Purification Methods*, 31, 2002, 1–169
- [10] Arstad B., Venvik H., Klette H., Walmsley J.C., Tucho W. M., Holmestad R., Holmen A., Bredesen R., *Catalysis Today*, 118, 1-2, 2006, 63-72
- [11] Bredesen R., Jordal K., Bolland O., *Chemical Engineering and Processing*, 43, 9, 2004, 1129-1158
- [12] Seok D.R., Hwang S.T., in Misono M., Morooka Y., Kimura S. (Eds.), "Future Opportunities in Catalytic and Separation Technology", Elsevier, Amsterdam, 1990, 248–267
- [13] Kikuchi E., Uemiyama C., *Chemistry Letters*, (1989), 189-192
- [14] Uemiyama C., *Ind. Eng. Chem. Res.*, (1991), 80, 585-589
- [15] Tosti S., Basile A., Chiappetta G., Rizzello C., Violante V., *Chemical Engineering Journal*, 93, 2003, 23–30
- [16] Shu J., Grandjean B.P.A., Van Neste A., Kaliaguine S., *Can. J. Chem. Eng.* 69 (1991) 1036
- [17] Giessler S., Jordan L., Diniz da Costa J.C., Lu G. Q., *Separation and purification technology*, 2003, 32, 255-264
- [18] Sea B.-K., Watsnabe M., Kuskabe K., Morooka S., Kim S.-S., *Gas Separation and Purification*, 10, (1996), 187-195
- [19] Lee D.-W., Lee Y.-G., Lee K.-H., Study on the variation of the morphology and separation behavior of the stainless steel supported membrane at high temperature, *Journal of membrane science*, 220, (2003), 137-153
- [20] Kanezashi M., Asaeda M., *Journal of Membrane Science*, 271, (2006) 86-93
- [21] Lee D.-W., Lee Y.-G., Sea B., Ihm S.-K., Lee K.-H., *Journal of Membrane Science* 236 (2004) 53–63
- [22] Brunetti A., Caravella C., Barbieri G., Drioli E., *Journal on membrane science*, 2007, Vol 306/1-2 pp 329-340
- [23] Brunetti A., Barbieri G., Drioli E., Granato T., Lee K.- H., *Chemical Engineering Science*, 62, 2007, 5621-5626
- [24] Brunetti A., Barbieri G., Drioli E., *Chemical Engineering and Processing*, 47 (2008), pp. 1081–1089
- [25] Passalacqua E., Lufrano F., Squadrito G., Patti A., Giorni L., *Electrochimica Acta* (2001), 46, 799 - 805
- [26] Barbieri G., Brunetti A., Tricoli G., Drioli E., *Journal of Power Sources*, 182 (2008), 160–167
- [27] Brunetti A., Barbieri G., Drioli E., *Chem. Eng. Sci.*, 2009, 64, 3448-3454