

Effect of the Pressure Increasing and Design Parameters on Pd/Ag – based Membrane Reactor Performance

Giovanni Chiappetta^{a*}, Giuseppe Barbieri^a, Enrico Drioli^{a,b}

^a Institute on Membrane Technology (ITM-CNR)

Via P. Bucci cubo 17/c, The University of Calabria - 87036 Arcavacata di Rende (CS)

^b Department of Chemical Engineering and Materials

Via P. Bucci cubo 44/a, The University of Calabria - 87036 Arcavacata di Rende (CS)

In the twenty-first century, hydrogen could have a huge potential since, in order to meet environmental requirements, it is considered the main energy carrier and a candidate to substitute gasoline and diesel as a clean transportation fuel. A novel reforming technology for breaking the equilibrium limitation and to guarantee an economic small scale hydrogen production is the use of a reactor combined to a selective membrane. The hydrogen separation improves with increasing pressure but the maximum is a trade-off between a transport propriety (hydrogen separation) and thermodynamic extent (hydrogen production) which has an opposing pressure dependency. In this paper, the antagonist effect of pressure on *methane steam reforming* reaction equilibrium and hydrogen permeability has been studied in a Pd-based membrane reactor in absence of a sweep gas. Moreover, the influence of the ratio membrane area (A_m) and catalyst volume (V_{cat}) combined to the ratio of the load methane (L_s , limiting reagent) in feed onto membrane area (A_m) has been considered in this study. In the membrane reactor, a increase twofold of the methane conversion was obtained by increasing the ratio A_m/V_{cat} from 0.42 to 2.1 cm^2/cm^3 whereas the L_s/A_m ratio was 11.6 $\text{cm}^3(\text{STP})/(\text{cm}^2\cdot\text{min})$. A methane conversion about three-times as much as thermodynamic equilibrium limit was obtained when the L_s/A_m ratio was reduced to 8.4 $\text{cm}^3(\text{STP})/(\text{cm}^2\cdot\text{min})$. Ultimately, a methane conversion of the 68% and a hydrogen recovery approximately of 43% was reached for a ratio $A_m/V_{cat} = 2.1 \text{ cm}^2/\text{cm}^3$ and $L_s/A_m = 8.4 \text{ cm}^3(\text{STP})\cdot\text{cm}^{-2}\cdot\text{min}^{-1}$ ($T=550^\circ\text{C}$, $P_{feed} = 650 \text{ kPa}$ and at a feed molar ratio of 2.5). A proper combination of the pressure driving force to the load methane, membrane area and catalyst volume can lead to an improvement of the membrane reactor performance.

*Corresponding Author: Tel.: +39 0984 492115; Fax: +39 0984 402103.

E-mail address: g.chiappetta@itm.cnr.it

1. Introduction

The growing demand of energy in many industrial fields and the development of environmental friendly and highly efficient energy processes to reduce the greenhouse gas concentrations in the environment have amplified the potentiality of the hydrogen as the main energy carrier and candidate to substitute gasoline and diesel. In the intermediate and small scale applications as the electrochemical converters (*e.g.* Polymer Electrolyte Membrane Fuel Cell), the hydrogen generates, in a clean way, directly power and produces exclusively water vapour with a higher efficiency (40–50%) than that current (20–35%) with internal combustion engines (Song et al., 2002). The presence of a large quantity of natural gas in the earth and the advantage of existing worldwide production and distribution infrastructure is increasing the interest towards those processes based on conversion/reforming of methane to hydrogen (*e.g.* methane steam reforming) and/or synthesis gas. In the endothermic reforming reactions, the conversion is limited by the thermodynamic equilibrium as a result of their reversible character. These reactions produce a net increase in moles and are disfavoured by high pressure. The conversion of methane is promoted by an increase in temperature (800–950°C) that compensates for high applied pressure (20–30 bar) required for reducing the volume of the equipments (Liguras et al., 2004). Consequently, the energy consumption during the methane steam reforming reaction as well as thermal and mechanical stresses of the materials are relatively high.

A novel reforming technology for breaking the equilibrium limitation, for reducing the energy needs and the employment of expensive materials, is the use of a selective membrane in the reactor (*e.g.* Pd-based membranes). The permeation ability of membrane surface combined with the selectivity makes it possible to remove hydrogen from the reaction mixture during the reversible methane reforming reaction and thereby to shift the reaction towards the product side. Palladium alloys are often used in commercial hydrogen separation applications instead of pure palladium. This is due to an enhancement of hydrogen permeation rate in presence of definite metal alloying concentrations that, for the Pd/Ag alloys, reaches a maximum at around 25 wt.%. Membrane reactor (MR) could guarantee an economic small scale hydrogen production. An improved separation can be obtained by increasing the driving force by means of a sweep gas on shell side or by operating at a high reaction pressure on feed side. The study of the effect of pressure to increase hydrogen production, by avoiding the sweep gas use on shell side, is one experimental aspect that has not been treated exhaustively in the membrane reactors literature. Moreover, it is preferable to carry out the reforming reaction at high pressure, in a membrane reactor, for two reasons: the natural gas to the primary reformer of a conventional industrial plant is at high pressure; a high product yield can be accomplished in a reduced reactor volume (fewer palladium membrane surfaces) and this reduces the membrane reactor capital costs. The rate of hydrogen recovery and transport through the membrane increases with increasing pressure but the maximum is a trade-off between the transport propriety (hydrogen separation) and thermodynamic limit (hydrogen production) which have opposing pressure dependencies. In this paper the antagonist effect of pressure on reaction equilibrium and H₂ permeability have been studied in the Pd/Ag 75/25 wt% membrane reactor in absence of sweep gas on shell side. The influence on membrane reactor performance of

the ratio membrane area (A_m) and catalyst volume (V_{cat}) combined to the ratio of the load methane (L_s , limiting reagent) in feed onto membrane area (A_m) has been considered in this study. A suitable combination of the pressure driving force to the load methane, membrane area and catalyst volume can lead to an enhancement of the membrane reactor performance.

2. Experimental Details

In this experimental study, self-supported commercial Pd/Ag 75/25 wt % membranes (Goodfellow, Ltd.) having thickness 100 μm , internal diameter 0.8 mm, outside diameter of 1.0 mm and lengths 3.5 – 8.5 cm have been used in the reactor. The hydrogen permeation measurements have been performed in the temperature range of 360 - 560°C and in the pressure range of 200 – 600 kPa, in absence of sweep gas. The membrane was allocated inside to a Nickel-based catalyst bed (Ni – 3288 E 1/16 3 F of Engelhard: Ni/Al₂O₃/SiO₂: 31% Ni, 39% NiO, 11% Al₂O₃, 19% SiO₂ and surface area 160 m²/g). The size of catalyst particle, having cylindrical geometry, was 1.5 mm. The housing was a stainless steel (SS) tube having an internal diameter of 4 mm, outside diameter of 6 mm. The Pd/Ag membrane was welded on an extremity to a SS-tube representing the permeate side while the other end was closed. The conversion of methane is calculated by means of the following equation:

$$CH_4 \text{ Conversion} = 1 - \frac{F_{CH_4}^{Retentate}}{F_{CH_4}^{Feed}}, [-] \quad (1)$$

A fundamental variable used to evaluate the performance of membrane reactor is the H₂ Recovery Index (RI_{H₂}) that is the amount of hydrogen recovered through the membrane with respect to hydrogen total production:

$$RI_{H_2} = \frac{F_{H_2}^{Permeate}}{F_{H_2}^{Permeate} + F_{H_2}^{Retentate}}, [-] \quad (2)$$

In order to compare the extraction ability of the membrane represented by available surface area with the limiting reagent flow rate (methane), an important ratio is considered in this study:

$$\frac{L_s}{A_m}, [\text{cm}^3 / (\text{cm}^2 \cdot \text{min})] \quad (3)$$

A parameter typical required for the development of a competitive and efficient membrane reactor (Saracco et al., 1999) is the ratio between membrane surface area and the catalyst volume necessary to uphold the reforming reaction:

$$\frac{A_m}{V_{cat}}, [\text{cm}^2 / \text{cm}^3] \quad (4)$$

3. Results and Discussion

During the permeation and characterization tests of the selective palladium membrane, hydrogen pure was fed on retentate side and the flux through the membrane was analyzed by means of a soap bubble flow-meter. The hydrogen transport into Pd- based membrane follows the Sieverts' law. The following hydrogen permeability expression has been obtained:

$$P_{e,H_2} = 1.54 \cdot 10^{-7} \cdot \exp\left(\frac{-13.44}{(R \cdot T)}\right), [\text{mol} \cdot \text{m} / (\text{m}^2 \cdot \text{s} \cdot \text{Pa}^{0.5})] \quad (5)$$

It indicates that the hydrogen permeating transport is an activated process in agreement to Arrhenius' law. This expression is well-matched with the experimental expressions reported in literature by Buxbaum et al., 1996. The operating conditions used during reaction tests were the following:

Table 1 – Operating conditions

Temperature, °C	400 – 600
Feed Pressure, kPa	600 – 800
Permeate Pressure, kPa	100
H ₂ O /CH ₄ (m) feed molar ratio	2 – 3
Gas Hourly Space Velocity (GHSV), h ⁻¹	1200 – 4200
Catalyst weight, g	0.5

Since the membrane was thoroughly compromised at 600 °C, it has been decided to carry out the reaction tests at 550°C.

At a fixed value of $L_s/A_m=11.6 \text{ cm}^3/(\text{cm}^2 \cdot \text{min})$ and feed pressure, an increase A_m/V_{cat} from 0.42 to 2.1 cm^2/cm^3 produced an increase of about 50 % for methane conversion and a similar improvement per cent of RI_{H_2} . At $A_m/V_{\text{cat}} = 0.42 \text{ cm}^2/\text{cm}^3$, the membrane is not able to counterbalance the large hydrogen production caused by the presence of a high catalyst mass. This means that the membrane has not an adequate material exchange surface, at a fixed limiting reagent in the feed. Instead, at an A_m/V_{cat} value of 2.1 cm^2/cm^3 , a reduced methane flow rate (L_s) with respect to membrane area (8.4 $\text{cm}^3/(\text{cm}^2 \cdot \text{min})$) points out that a large amount of methane reacts in presence of a high exchange surface.

As shown in fig. 1, the hydrogen recovery increases versus the feed pressure as well as the conversion methane. For a diminution of L_s/A_m equal to the 27%, the RI_{H_2} is increased of the 33% when the hydrogen driving force has a low value whereas, at a higher driving force, this improvement is not substantial (25%) since the recovery is already high and the steam reforming reaction is not thermodynamically favoured.

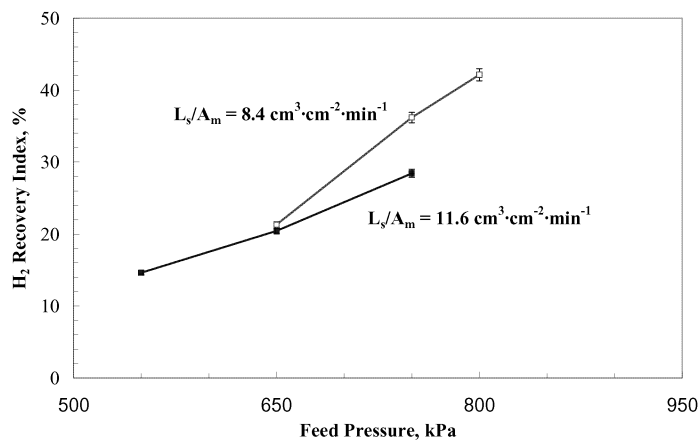


Figure 1 – H_2 Recovery Index as a function of Feed Pressure. Operating conditions: $GHSV = 4200 \text{ h}^{-1}$; $m = 2.5$; $T = 550^\circ\text{C}$.

As shown in fig. 2, the methane conversion increases as the feed pressure enhances, at each feed molar ratio. At 800 kPa, the methane conversion is approximately 62% higher than thermodynamic equilibrium conversion for a conventional reactor. However, it achieves a value of 68%, at $m = 2.5$, and the hydrogen recovered on permeate side is 43% with respect to the amount produced.

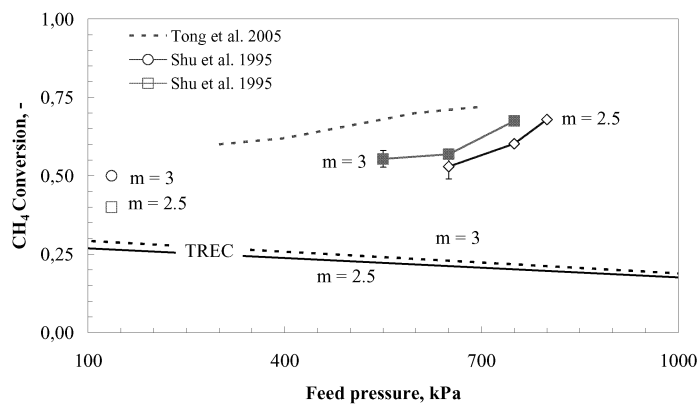


Figure 2 – Methane Conversion as a function of Feed Pressure. Operating conditions: $A_m/V_{cat} = 2.1 \text{ cm}^2/\text{cm}^3$; $L_s/A_m = 8.4 \text{ cm}^3/(\text{cm}^2 \cdot \text{min})$; $T = 550^\circ\text{C}$; $GHSV = 4200 \text{ h}^{-1}$.

This is agreement with the experimental Tong and Matsumura's work, 2005 in which the reaction tests have been carried out, in presence of a sweep gas stream, for a Pd/Ag-based membrane having a thickness of 11 μm but with both a A_m/V_{cat} ratio of 3.8 cm^2/cm^3 and value of GHSV equal to 3360 h^{-1} (feed pressure range of 100-700 kPa). A high hydrogen recovery improves the methane conversion. With respect to a membrane characterized from $A_m/V_{\text{cat}} = 2.1 \text{ cm}^2/\text{cm}^3$ and $L_s/A_m = 11.6 \text{ cm}^3/(\text{cm}^2 \cdot \text{min})$, at 650 kPa, methane conversion increases of the 20% for $m = 3$ and 50% for $m=2.5$, respectively.

4. Conclusions

In the membrane reactor, an increase of the methane conversion equal to 50% was obtained by increasing the ratio A_m/V_{cat} from 0.42 to 2.1 cm^2/cm^3 whereas the L_s/A_m ratio was 11.6 $\text{cm}^3(\text{STP})/(\text{cm}^2 \cdot \text{min})$. A methane conversion about three-times as much as thermodynamic equilibrium limit (for a conventional reforming reactor) was obtained when the L_s/A_m ratio was reduced to 8.4 $\text{cm}^3(\text{STP})/(\text{cm}^2 \cdot \text{min})$. Ultimately, a methane conversion of the 68% and a hydrogen recovery approximately of 43% was reached for a ratio $A_m/V_{\text{cat}} = 2.1 \text{ cm}^2/\text{cm}^3$ and $L_s/A_m = 8.4 \text{ cm}^3(\text{STP}) \cdot \text{cm}^2 \cdot \text{min}^{-1}$ ($T=550^\circ\text{C}$, $P_{\text{feed}} = 650 \text{ kPa}$ and at a feed molar ratio of 2.5). A high pressure favours the hydrogen transport through the membrane and allows for using a reduced membrane surface. Notwithstanding the compression expenses are high, however the use of a sweep gas stream on permeate side adds a supplementary cost for the hydrogen separation steps subsequent to the reactor. The hydrogen permeability coupled to the required membrane area represents an important parameter to realize the most advantageous combination of the *methane steam reforming* reaction and hydrogen permeation in membrane reactor. Proper combinations of the pressure driving force to the load methane, membrane area and catalyst volume, respectively, can lead to an improvement of the membrane reactor performance.

References

- Buxbaum R.E., Kinney A.B., 1996, Hydrogen Transport through Tubular Membranes of Palladium-Coated Tantalum and Niobium, I&EC Research 35, 530-537.
- Liguras D.K., Goundani K., Verykios X.E., 2004, Production of hydrogen for fuel cells by catalytic partial oxidation of ethanol over structured Ni catalysts, J. Power Sources 130, 30-37.
- Saracco G., Neomagus H.W.J.P., Versteeg G.F., Van Swaaij W.P.M., 1999, High-temperature membrane reactors: potential and problems, Chemical Engineering Science 54, 1997-2017.
- Shu J., Grandjean B.P.A., Kaliaguine S., 1995, Asymmetric Pd-Ag stainless steel catalytic membranes for methane steam reforming, Catalysis Today 25, 327-332.
- Song C., 2002, Fuel processing for low-temperature and high-temperature fuel cells: Challenges, and opportunities for sustainable development in the 21st century, Catalysis Today 77, 17-49.
- Tong J., Matsumura Y., 2005, Effect of catalytic activity on methane steam reforming in hydrogen-permeable membrane reactor, Applied Catalysis A: General 286, 226-231.