NATURAL GAS STEAM REFORMER INTEGRATED WITH Pd-BASED MEMBRANES: EXPERIMENTAL INVESTIGATION ON PILOT SCALE

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Natural gas steam reforming still represents the most industrially employed technology to produce synthesis gas. Being a strongly endothermic reaction, thermodynamically limited, its coupling with a membrane device for hydrogen separation may enhance hydrocarbon conversion. The feasibility of this option, widely demonstrated on a laboratory scale, it is still to be shown on an industrial one. The aim of this work is to review all the experimental results obtained with an industrial natural gas steam reformer plant, placed in Chieti Scalo (Italy), with a H_2 design capacity of 20 Nm^3/h, coupled, in an open architecture, with Pd and Pd/Ag based membranes for hydrogen separation. This installation represents the first of this type and size in the world

1. INTRODUCTION

Hydrogen can be obtained from different sources as fossil fuels (natural gas reforming, and coal gasification), renewable fuels, algae, vegetables and water. However, nowadays, hydrogen production through steam reforming of natural gas ($CH_4 + H_2O = CO + 3H_2$, $\Delta H^0_{298K} = +206$ kJ/mol) is undoubtedly the most industrially applied process (48% of the total production), mainly for its lower cost. In this process, the steam reforming reaction is followed by the slightly exothermic water gas shift reaction ($CO + H_2O = CO_2 + H_2$, $\Delta H^0_{298K} = -41$ kJ/mol) in which the carbon monoxide is reacted with steam to produce CO_2 and additional H_2.

The major drawback of steam reforming reaction is that as CH_4 is a stable hydrocarbon, owing to the strong endothermicity of this reaction, very high reaction temperatures, around 800°C, are required for its almost total conversion. However, If H_2 is selectively removed from the reaction system, the chemical equilibrium of these reactions may be shifted to the product sides and highly efficient conversion of CH_4 to CO_2 and H_2 can be attained even at low temperatures (Kikuchi et al., 2000).

Significant advantages deriving from the use of membrane reactors are the following: (i) conversion enhancement of equilibrium limited reactions; (ii) achievement of the same performance attained in a traditional reactor at milder operating conditions, such as lower temperature; (iii) reduced capital costs due to the combination of reaction and separation in only one system; (iv) reduced CO_2 emissions in the case of steam reforming (Mendes et al., 2010, Saracco et al., 1999). The number of possible applications of membrane reactors is large, in particular in petrochemical industry or for environmental protection, however their commercial applications are emerging slowly due to a number of practical limitations such as low separation factors, leakage at higher temperature, poisoning of catalyst and mass transfer limitations (Ravanchi et al., 2009).

In particular, for hydrogen separation, the selective membranes can be broadly separated into four categories: polymeric (organic), metallic, carbon and ceramic (the latter three jointly called inorganic). For a long time considerably more effort has been put in development of polymeric membranes than in inorganic membranes. Consequently, polymeric membranes have wide ranging applications and can be bought at relatively low cost. However, interest in inorganic membranes has started to grow in the last decade, since they can operate under higher temperatures than polymeric materials and generally possess superior chemical stability with respect to polymeric materials. Dense metal membranes have attracted the interest of many researchers due to their permselective characteristics that allow complete separation of a component from a gas mixture without requiring a further separation/purification unit. The most widely employed are those based on Pd and Pd-alloy and they operate according to a solution/diffusion mechanism. Several reviews summarize the results obtained with these membranes (Adhikari et al., 2006, Ockwig and Nenoff, 2007, Mendes et al., 2010). The commercialization of pure palladium membranes is still limited by several factors. Above all, the pure Pd membranes undergo the embrittlement phenomenon when exposed to pure hydrogen at temperature lower than 300°C. Such a phenomenon may produce pinholes on the membrane, which will negatively affect the hydrogen permselectivity of the membrane. Furthermore, the pure palladium membranes are deactivated by carbon compounds at temperature higher than 450°C and can be irreversibly poisoned by sulphur compounds. The last major limit is their high cost. All these disadvantages may be overcome by using Pd-alloy membranes, obtained by alloying the Pd with Ni, Cu and in particular Ag (Li et al., 1993).

An important aspect to be considered in the realization of a membrane based steam reformer is that the separation modules can be integrated by means of two potential configurations: Membrane Reactor (MR) where selective membrane is assembled directly inside the reaction environment and Reformer and Membrane Module (RMM), where hydrogen selective membrane is assembled downstream to reaction units. Although more compact, MR architecture presents some technical problems related to membrane thermal stability resulting in a reaction temperature lower than maximum allowable membrane temperature (500°C).

Advantages of using steam reforming reactors equipped with H_2 selective membrane, over conventional fixed bed reactor for MSR reaction have been widely recognized and investigated as reviewed by Kikuki et al. 2000, Chen et al. 2006, Matsumura et al. 2008. Conversions in the range of 80-95% were obtained by Shirasaki et al. (2009) during steam reforming of natural gas in a compact MR equipped with Pd-Ag membranes at the following operating conditions: reformer temperature of 495-540°C, pressure of 0.9MPa and steam to carbon ratio 3-3.2. Chen et al. (2006) observed much higher performance of membrane reactor due to the combination of hydrogen ultra-thin permeable Pd-based membrane obtaining 98.8% methane conversion under mild working conditions. Gallucci et al. (2007) achieved 70% MSR methane conversion at 450°C in an oven-heated PBMR equipped with a 50 μm thick Pd-Ag foil membrane. They also summarized several data from recent literature work reporting higher methane conversions performed by integrated steam reforming respect to traditional ones.

The aim of this work is to review all the experimental results obtained with an industrial natural gas steam reformer plant, placed in Chieti Scalo (Italy), with a H_2 design capacity of 20 Nm^3/h, coupled, in an open architecture (Iaquaniello, 2009, Iaquaniello and Salladini, 2011), with three Pd and Pd/Ag based membranes for hydrogen separation. This installation, the first of this type and size, makes it possible to completely understand the potential of selective membrane application in industrial high-temperature chemical processes. This very innovative work was developed in the framework of the Italian FISR Project “Pure hydrogen from natural gas reforming up to total conversion obtained by integrating chemical reaction and membrane separation”, which grouped Italian universities, and the engineering society Tecnimont KT (TKT), cooperating in the development of each critical point of this innovative technology, such as membrane manufacture and assembling and catalyst optimization, resulting in the plant design and operation finally carried out by TKT.

2. PLANT LAYOUT

The plant process scheme is reported in Figure 1a together with a bird-eye view (Figure 1b) of the constructed industrial test plant which covers an area of 1000 m^2. The plant is composed by two-step reformers and two membrane modules working respectively in the temperature range 550-650°C and 400-450°C.

Natural gas is supplied from battery limits or from cylinders at 20 barg. A portion of natural gas is fed through a flow controller to the desulphurisation reactor (DS) for sulphur compounds removal to content lower than 0.1 ppm. The residual is used as fuel gas, reduced at 0.3 barg. The desulphurised feed is mixed with steam, produced separately by a real hot oil boiler, preheated in the convection section and fed to the first reforming stage. More specifically, each reformer module is composed by two main sections: (i) a radiant tube, charged with the catalyst and (ii) a convection section, where heat is recovered from the flue gases, having a temperature higher than 800°C, for preheating and superheating feed and steam.

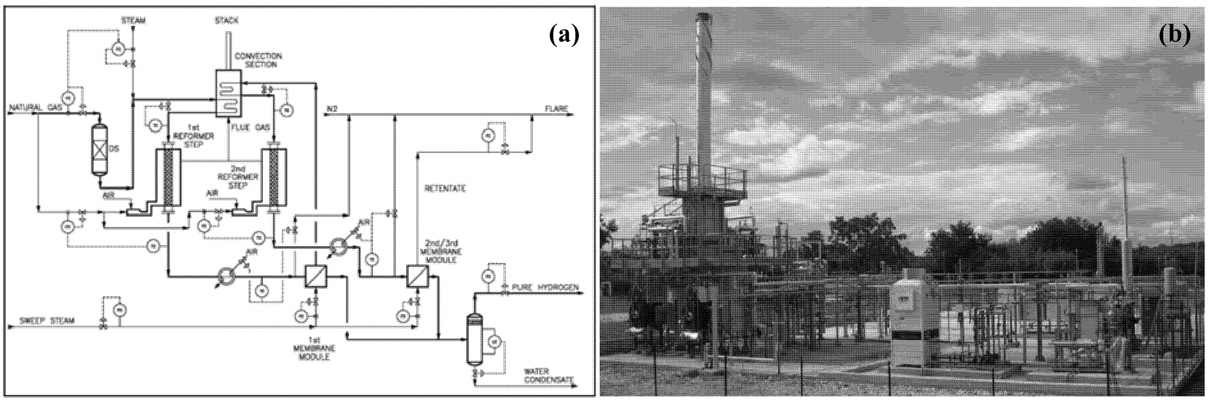

Fig. 1: Process scheme (a) and bird-eye view (b) of the industrial test plant

The design of the radiant chamber differs from the conventional one for the heated length of the reformer tube which is around 3 meter, the tube metallurgy and the contained catalyst. In particular, it must be observed that, owing to the lower operating temperature relevant to the use of this innovative architecture, a low cost stainless steel instead of exotic and quite expensive material as HP25/35 chromium/ nickel alloy was employed.

The reformed gas product from the first reformer is cooled down at the temperature chosen for membrane module operation and enters the first separation module. A retentate, recycled to the second reformer stage and a mixture of H_2 plus sweeping steam, are produced. The second reformer stage is cooled down from 650°C to the temperature chosen for membrane operation and routed to the second separation module. H_2 from both modules are mixed together and sent to final cooling and condensate separation. Retentate from the second stage is sent to the flare. The pressure of both shell and permeate sides are controlled using a back pressure regulators. Both membrane modules are protected using a pressure relief regulator installed on the income lines. All the vent points are connected to main vent system and routed to the flare. Heat of reaction in both reforming steps is provided by two independent hot gas generators in order to set the reforming temperatures as required by the tests.

The main parameters such as the temperatures and pressures before and after each reformer and separation step as well as the pressure drop along the catalytic tube were monitored respectively with K-type thermocouples and differential pressure sensors. A constant flow of the exhaust stream is sent through a cold trap maintained at fixed temperature (0°C) to NDIR analyzers (Uras 14, ABB) for real-time CH_4, CO, CO_2 measurements, while the concentration of H_2 was performed with a thermoconductivity analyser (Caldos 17, ABB).

Four different membrane separators, Pd and Pd/Ag based, able to work at high temperatures, were planned for installation on the prototypal plant. Their main features are summarised in Table 1.

Table 1: Main features and geometry of the membranes (De Falco et al., 2011)

Developer	Substrate/support	Membrane selective layer	Thickness of the selective layer, µm	Manufacturing method	Geometry
ECN	Alumina	Pd	3-9	Electroless deposition	Tubular
Confidential	Alumina	Pd/Ag	2-3	Electroless deposition	Tubular
MRT	Stainless steel	Pd/Ag	25	Proprietary	Planar
Acktar	Stainless steel+alumina	Pd or Pd/Ag	3-5	Reactive sputter deposition	Tubular

In this work the performance of ECN (Figure 2a) and MRT (Figure 2b) membranes was reported. The total installed surfaces were respectively 0.40 and 0.60 m^2.

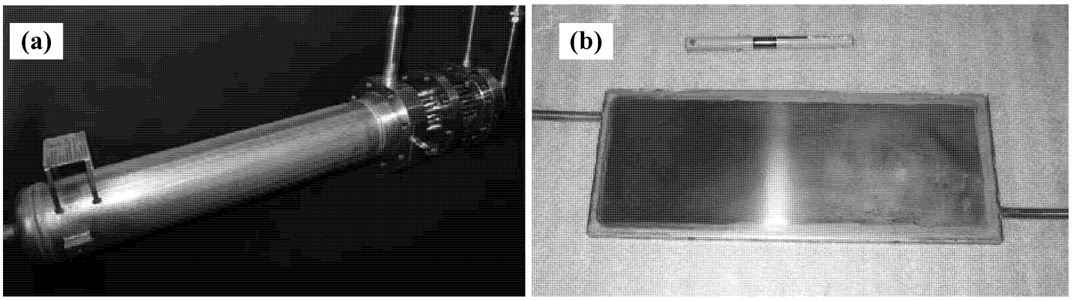

Fig. 2: ECN (a) and MRT (b) membranes

Another innovation of this work is represented by the catalyst employed for the catalytic activity tests. Typically, methane steam reforming catalysts for industrial production of hydrogen and synthesis gas are based on pellets shaped nickel/nickel oxide or cobalt compositions on refractory alumina or supports such as magnesium alumina spinel, often promoted with alkali or alkali-earth compounds to accelerate carbon removal (Faur Ghenciu, 2002). However, also noble metals based catalyst are often employed. Furthermore, the consideration that in the steam reforming process, the kinetics, and therefore the throughput, is limited by the rate at which the heat generated in external burners can be transferred to the catalytic bed where the endothermic reforming reactions take place, led for this plant to the choice of open cells foam structured catalysts, whose particular irregular network may greatly contribute to an intensification of heat and mass transfer along the catalytic bed in both axial and, more important, radial directions. In particular, the catalytic activity tests performed at the University of Salerno in collaboration with TKT in the framework of the above mentioned FISR project, on a pre-pilot scale autothermal reforming reactor showed how such structured supports, in particular when realised with high thermal conductivity materials, may contribute to an enhancement of heat transfer along the catalytic bed resulting in a flattening thermal profile (Palo, 2007; Ciambelli et al., 2007). More specifically, the catalyst loaded in the industrial steam reformer in Chieti Scalo was characterized by a commercial formulation Rh-Pt based (SR10, BASF) deposited on high thermal conductivity SiC open cells foams. Each cylindrical shaped element was 150 mm long with a diameter of 60 mm and twenty-one elements were loaded in each reformer.

The catalytic activity tests were carried out in the following operating conditions: $3.8<(H_2O/CH_4)_w <4.8$, $550°C<T_{reformer}<680°C$, P=10 barg, $4,300\ h^{-1}<GHSV<6,900\ h^{-1}$ where the GHSV value is defined as the ratio between the total gaseous flow rate fed to the reactor (referred to 0°C and 1 atm) and the total catalytic bed volume. For membrane characterization in terms of hydrogen flux and permeability, the following syngas composition was employed (Table 2).

Table 2: Typical syngas composition used for membranes characterization (De Falco et al., 2011)

H_2, vol%	CH_4, vol%	CO_2, vol%	CO, vol%	H_2O, vol%
24-30	6-9	6-9	1-2	54-59

3. PLANT PERFORMANCE

3.1 Overview of previous results

Several catalytic activity tests were performed in order to evaluate respectively the effect of the reformer outlet temperature on CH_4 conversion. The results obtained are reported in Figure 3 (De Falco et al., 2011).

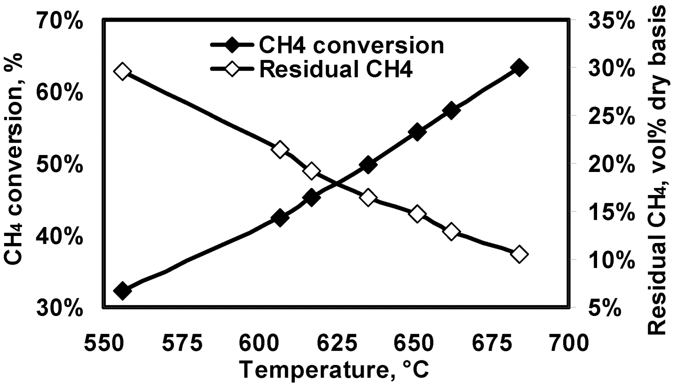

Fig. 3: Effect of reformer outlet temperature on CH_4 conversion

It can be observed a decrease in the residual methane at the reactor outlet and a corresponding increase in methane conversion at increasing the reformer outlet temperature. In particular, it increases from 32% at 550°C to 64% at 680°C. This effect can be explained considering the strong endothermicity of reforming reactions that are favoured at higher temperature. Further catalytic activity tests carried out by changing the GHSV value in the range 4,300-6,900 h^{-1} showed a decrease in methane conversion from 48.7% to 46.5%, since the steam reforming reactions are affected by low contact times (De Falco et al., 2011, De Falco et al., in press). However, in time on stream tests performed over 1000 h, any catalyst deactivation occurred, as evidenced by stable methane conversion over the entire test period.

Further improvements resulting in an enhanced overall plant performance were provided by membrane integration. A comparison of methane conversion obtained in the absence or in the presence of membranes for hydrogen separation is reported in Figure 4 as a function of GHSV values. The results are collected over 200 h of operation at 10 barg and at a reformer outlet temperature ranging between 610-620°C (De Falco et al., submitted, De Falco et al., 2011).

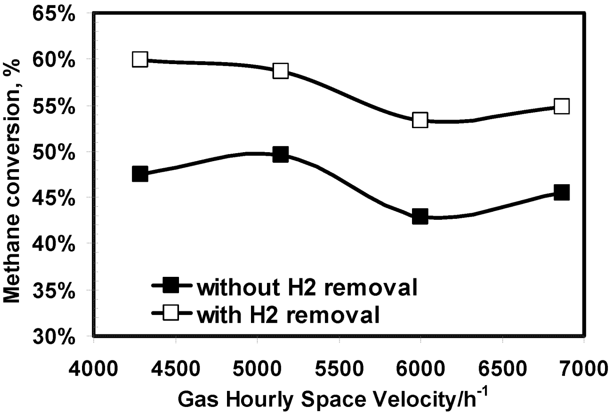

Fig. 4: Effect of hydrogen removal on plant performance at changing the gas hourly space velocity

All these catalytic activity tests enabled for a membranes permeability characterization. In particular, by assuming the Arrhenius law for the dependence of permeability from temperature and the Sievert-Fick's law for hydrogen flux expression (Ockwig and Nenoff, 2007), the following results were obtained for ECN and MRT membranes (Table 3, De Falco et al., 2011):

Table 3: Permeability membranes characterisation results (De Falco et al., 2011)

Membrane	A, kmol/(m h $kPa^{0.5}$)	Ea, kJ/mol	Permeability at 450°C, kmol/(m h $kPa^{0.5}$)
ECN	1.72×10^{-1}	77	4.67×10^{-7}
MRT	5.75×10^{-4}	35.3	1.61×10^{-6}

Further parametric studies enabled to predict the overall CH_4 conversion with a larger membrane surface (A) as parameter (De Falco et al., 2011). By assuming the same ECN membrane permeance of 30 Nm^3/m^2 h $bar^{0.5}$ at 430°C, CH_4 conversion was found to be enhanced with an increase in the reforming temperature and membrane area. In particular, the membrane area can be increased to achieve the same conversion at lower reformer temperature (methane conversion of 60% can be achieved at 603°C with $A=1.2m^2$, at 623°C with $A=0.4m^2$). Methane conversion increases more slowly when the membrane area exceeds $0.8m^2$. At 620°C such increase ranges from 11 to 19 point percent respectively, with a membrane surface of $0.4m^2$ and $0.8m^2$.

3.2 Influence of membrane thickness on plant performance

Starting from permeability expression obtained for ECN and MRT membranes, a parametric study was also carried out for these membranes by changing the thickness of the separation layer at different operating reformer temperature. The experimental results obtained for ECN membrane are reported in Figure 5. In the figure, the results obtained from literature review are also reported.

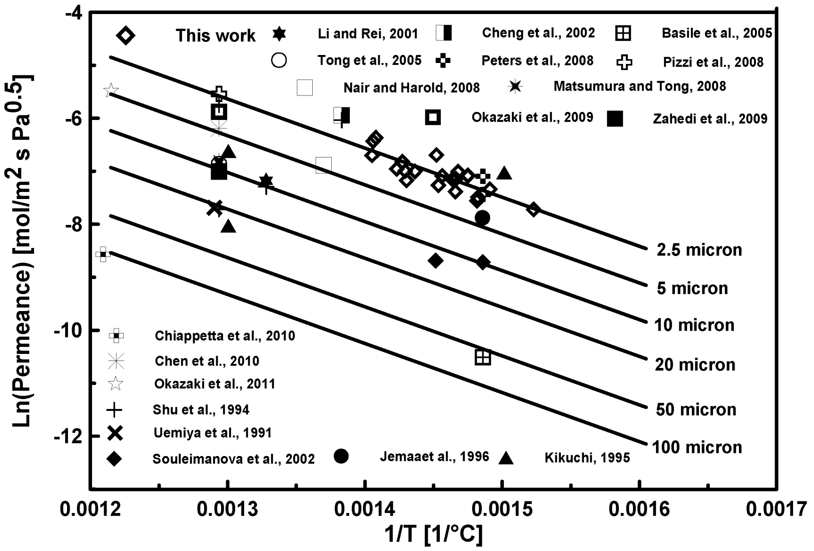

Fig. 5: Effect of membrane thickness on ECN membrane permeance

Obviously, the thickness of the separation layer greatly affects the membrane permeance which resulted lowered from 2.12×10^{-4} to 5.3×10^{-6} at 350°C and from 7.85×10^{-3} to 1.96×10^{-4} at 550°C by increasing the thickness of the separation layer from 2.5 to 100 micron. The obtained results pointed out on the continuous industrial efforts aiming to develop composite membrane made of a very thin Pd layer. It is worth nothing that reducing the selective layer thickness allows membrane cost to be decreased (decreasing the Pd thickness by a factor two reduces the total Pd cost by a factor four) and increasing the hydrogen flux, which is in inverse proportion with the film thickness. On the other side, a too high decrease in the selective film thickness may result in an excessive embrittlement of the membrane which becomes too mechanically fragile for the condition of high temperature catalytic processes.

The obtained results were employed by the authors to predict the CH_4 conversion at the different selective layer thickness even at lower value than those reported in Figure 5. The experimental operating conditions were the following: P_{ref}=10 barg, $(H_2O/CH_4)_w$ =4.8, P_{perm}=0.4 barg, T_{mem}=430°C. The CH_4 conversion evaluation was carried out by commercial process flow modelling (PRO II) integrated with a subroutine to simulate membrane behaviour. The results are reported in Figure 6.

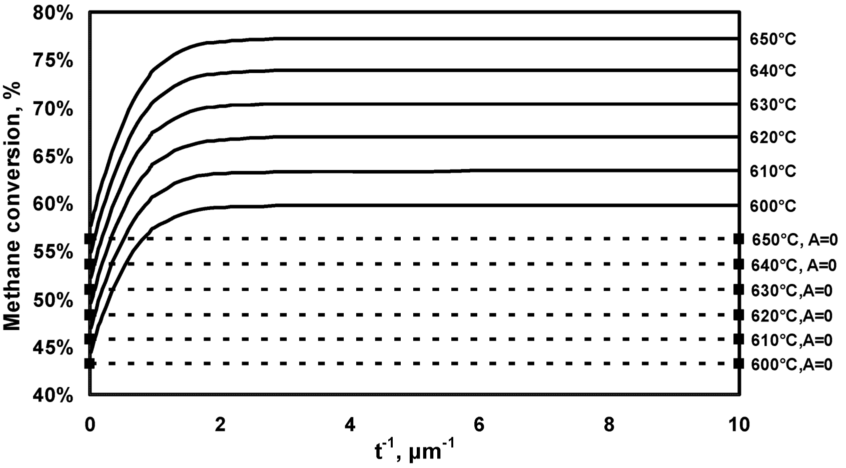

Fig. 6: Effect of membrane thickness on CH_4 conversion (ECN membrane)

At each operating temperature investigated, the decrease of membrane thickness resulted in higher methane conversion. In particular, at 630°C, a reduction of membrane thickness from 2.5 micron to 0.5 micron may enhance methane conversion of 10% due to the higher hydrogen removal. It is interesting to note that thickness thinner than 0.5 micron have no more significant effect on the overall performance. Such a thickness could be considered as the technological limit to be overcome. Similar results were obtained for MRT membrane (Figures 7 and 8).

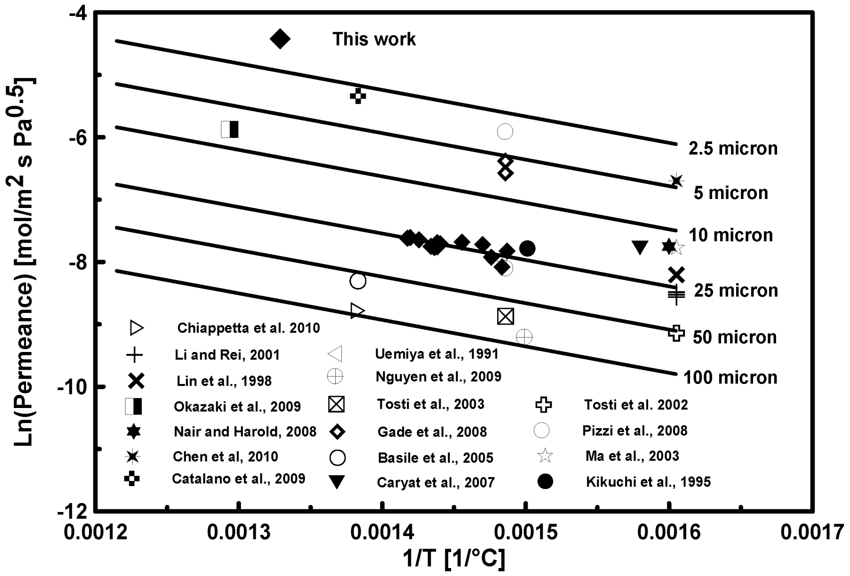

Fig. 7: Effect of membrane thickness on MRT membrane permeance

For MRT membrane, a decrease of the permeance from 2.22 x 10^{-3} to 5.55 x 10^{-5} at 350°C and from 1.16 x 10^{-2} to 2.91 x 10^{-4} at 550°C by increasing the thickness of the separation layer from 2.5 to 100 micron, was observed. It is interesting to note that owing to higher intrinsic permeability shown by MRT membrane, any significant improvement in CH_4 conversion are observed for selective layer thickness lower than 5 micron.

The experimental results show that in order to obtain a good performance in terms of hydrogen recovery is necessary to realize a compromise between membrane permeability and selective layer thickness. In particular, optimizing the preparation procedure with an improvement in membrane permeability enables to be independent to some extent, on membrane thickness, which nowadays still represents an issue in membrane manufacture forcing to the choice of a determined preparation technique such as physical sputtering.

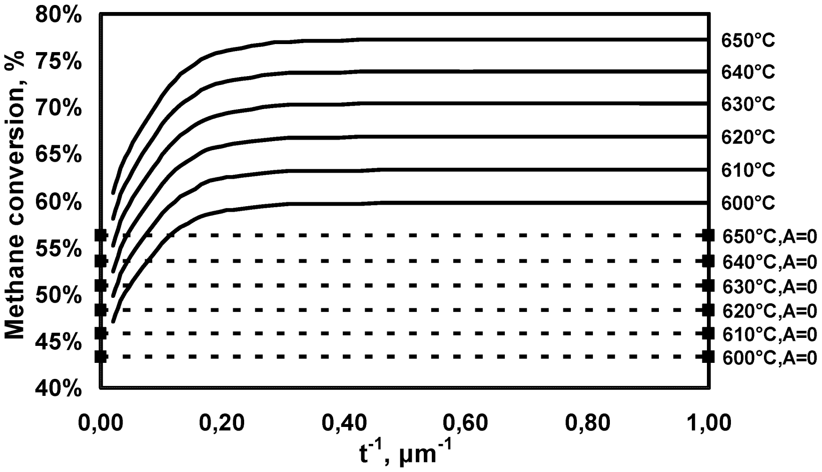

Fig. 8: Effect of membrane thickness on CH_4 conversion (MRT membrane)

4. CONCLUSIONS

The experimental results obtained for a pilot scale (20 Nm^3/h H_2 capacity) natural gas steam reformer integrated with three membranes for hydrogen separation in an open architecture show that with such an architecture and with Pd and Pd/Ag based membranes it is possible to reach CH_4 conversion higher than 90% with a permeated H_2 flux of 300 Nm^3/m^2 h $bar^{0.5}$.

The achievement of this goal shows the industrial feasibility of this option up to now demonstrated only on a laboratory scale, even if the last gap to be overcome for the technology commercialization is represented by the optimization of membrane preparation procedure with enhancement of their stability.

ACKNOWLEDGEMENTS

This work was carried out within the framework of the project entitled “Pure hydrogen from natural gas reforming up to total conversion obtained by integrating chemical reaction and membrane separation”, funded by MIUR (FISR DM 17/12/2002)-Italy.

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