Hydrogen production with integrated CO₂ capture in a membrane assisted gas switching reforming reactor

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Review Article

Hydrogen production with integrated CO₂ capture in a membrane assisted gas switching reforming reactor: Proof-of-Concept

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ABSTRACT

This paper presents a new membrane reactor concept for ultra-pure hydrogen production with integrated CO₂ capture: the membrane-assisted gas switching reforming (MA-GSR). This concept integrates alternating exothermic and endothermic redox reaction stages in a single fluidized bed consisting of catalytically active oxygen-carrier particles, by switching the feed between air and methane/steam, where the produced hydrogen is selectively removed via Pd-based membranes. This concept results in overall autothermal conditions and allows easier operation at high pressure compared to alternative novel technologies. In this work, the MA-GSR concept is demonstrated at lab scale using four metallic supported membranes (Pd–Ag based) immersed into a fluidized bed consisting of a Ni-based oxygen carrier. The performance of the reactor has been tested under different experimental operating conditions and high methane conversions (>50%) have been obtained, well above the thermodynamic equilibrium conversion of a conventional fluidized bed as a result of the selective H₂ extraction, with (ultra-pure) H₂ recoveries above 20% at relatively low temperatures (<550 °C). These results could be further improved by working at elevated pressures or by integrating more membranes. Even though the concept has been successfully demonstrated, further research is required to develop suitable membranes since post-mortem membrane characterization has revealed defects in the membrane selective layer as a consequence of the frequent exposure to thermal cycles with alternating oxidative and reducing atmospheres.

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Introduction

According to a recent report from the international energy outlook (IEO2016) [1], the total world energy consumption will increase by 48% over the coming three decades, where renewables (2.6%/year) and nuclear power (2.3%/year) will become the fastest growing energy sources. However, this will not reduce our dependency on fossil fuels, which is expected to still account for 78% of the global energy use in 2040. The anthropogenic carbon emissions to the atmosphere as a result of the use of fossil fuels has a very large impact. Nowadays, the CO₂ concentration in the atmosphere is the highest ever measured and several of the effects of the associated climate change are already visible [2,3]. In order to reduce the CO₂ emissions to the atmosphere and improve the efficiency of energy conversion processes, the course of events should be changed, and this can be achieved by developing new climate-neutral technological strategies. One of the possible and promising technological strategies is H₂ production with integrated CO₂ capture under the Carbon Capture and Storage (CCS) route.

Hydrogen is widely considered to be the most viable carbon-free energy carrier for the future [3], in addition to a much broader range of applications in chemical industries (ammonia, methanol, metallurgy, food processing, etc.) without polluting the environment [4,5]. In addition, the H₂ demand is constantly increasing due to the rapid advancement in hydrogen fuel cell technology [6]. However, hydrogen does not exist as a gas on the Earth, but it has to be produced. Currently, almost 90% of hydrogen production comes from fossil fuels, generally via reforming of natural gas or light oil fractions with steam at high temperatures [7,8]. Natural gas reforming is an equilibrium limited endothermic process, which is usually carried out in a multi-tubular fixed bed reactor filled with nickel catalyst pellets, and that has the need of external furnaces to provide the heat of reaction [8–12]. However, this technology is responsible of a large amount of greenhouse gases emissions and local pollutants since part of the fuel (and off-gas from the separation unit) is burnt to supply the heat of reaction. The following are the equilibrium

limited steam methane reforming (SMR) (Eq. (1)) and water gas shift (WGS) (Eq. (2)) reactions that play a role in the production of hydrogen from natural gas:

Autothermal natural gas reforming is regarded as another well-established process for hydrogen production, where partial oxidation of the fuel is used as energy source for overall autothermal operation. However, this process requires pure oxygen delivered by an air separation unit which increases the capital cost and energy consumption of the process [13]. Dry reforming (Eq. (3)) and partial oxidation of methane (Eq. (4)) are also considered as an alternative processes for hydrogen production despite the relatively low hydrogen to carbon ratio in the produced syngas (less attractive for large scale applications) [14,15].

To arrive at a cost effective and environmentally friendly process for hydrogen production, currently more attention is given towards the development of novel reactor concepts for efficient reforming. Among the several different proposed technologies, autothermal chemical looping reforming (CLR) is a promising technology for hydrogen production with integrated CO₂ capture [16]. The typical CLR reactor scheme is similar to the well-known chemical looping combustion (CLC) [17] concept, the major difference being the desired product which is heat in CLC and syngas in CLR. The scheme of a typical chemical looping reformer consists of two interconnected reactors, namely the air reactor and the fuel reactor. In the fuel reactor, the fuel gas is converted into a mixture of CO–CO₂ and H₂ (syngas) by a (supported) metal oxide (MeO) which is reduced to a metal (Me) or a reduced form of MeO, where the reduced oxygen carrier (Me) also acts as a catalyst for the reforming reaction. The metal or reduced oxide is further transferred into the air reactor where it is

oxidized with air via in an exothermic reaction, and the hot, regenerated material is ready to start a new cycle [18]. This process configuration results in inherent separation of CO_2 and N_2 with a much lower energy penalty than conventional CO_2 capture processes [16,17,19].

In the CLR process, the produced syngas must go through additional steps to be shifted to H_2 and CO_2 and separated in a subsequent shift reactors (WGS) and a pressure swing adsorption unit, if pure H_2 is the desired end-product [20,21]. However, the downstream process steps can potentially be integrated into one, if hydrogen perm-selective membranes (Pd-based) are introduced into the reactor resulting in a thermodynamically favorable process [22]. Thus, with this process modification: an ultra-pure H_2 stream can be extracted via membranes leading to conditions beyond the conventional thermodynamic equilibrium; and, in the ideal case of a very large installed membrane surface area, a pure CO_2 stream at the reactor outlet can be obtained (after steam condensation). The outlet CO_2 stream (from the fuel reactor) together with the N_2 stream from the air reactor can also potentially generate additional revenue streams for the plant.

Operation at elevated pressures is very important in the demonstration of the real potential of the highly intensified membrane-assisted CLR process in order to achieve a competitive overall energy efficiency. High pressure operation enables a more homogeneous fluidization with better mass transfer rates [23], increases the driving force across the membrane which reduces the surface area required for a given fuel throughput and allows for a higher permeate side pressure, requiring less hydrogen compression, generates a high pressure CO_2 outlet stream for efficient compression, transport and storage by reducing the capital cost associated with compression of the product stream. However, due to the technical challenges related to the solid circulation between interconnected fluidized bed reactors and the separation of solids from the gas stream (cyclone), scaling up of a pressurized interconnected fluidized bed CLR would be very difficult and costly. In order to simplify process scaling-up and control under elevated pressure operation, it is proposed to carry out the membrane-assisted CLR process in a single dynamically operated fluidized bed reactor, referred to as a membrane-assisted gas switching reforming reactor (MA-GSR). The GSR concept has already been experimentally demonstrated at lower pressures without immersed membranes [24] and this work extends the concept to the membrane-assisted reforming application.

The MA-GSR reactor concept combines ultra-pure hydrogen production with integrated CO_2 capture from steam methane reforming by the use of (Fig. 1): (i) an oxygen carrier, which acts as catalyst and heat carrier to the endothermic reforming reaction and is periodically exposed to fuel/steam and air streams. When air is fed to the reactor, the oxygen carrier is heated by the exothermic solids oxidation reaction to be utilized in the fuel stage, where endothermic reduction and catalytic reactions regenerate the oxygen carrier and produce syngas. (ii) hydrogen perm-selective membranes (thin Pd-based) immersed into the fluidized suspension to directly recover pure hydrogen generated during steam-methane reforming and water gas shift reactions. This method of hydrogen recovery has two important advantages: firstly, the

Fig. 1 – Schematic view of the MA-GSR system.

integration of hydrogen production and separation (and purification) into one single step and secondly, a complete shift in the Water-Gas-Shift reaction, resulting in complete and constant conversion of fuel at a lower and gradually varying reaction temperature. This combination of process units brings a high degree of process intensification with additional benefits in terms of increased process efficiencies [25].

This paper describes the experimental demonstration of pure hydrogen production in a lab-scale MA-GSR reactor. The prime objective is to demonstrate the reactor concept by examining the hydrogen permeation flux and reactor performance under both steam methane reforming (SMR) and autothermal reforming (ATR) operating conditions. Experimental results investigating the influence of the reactor temperature, oxygen carrier utilization, steam-to-carbon ratio and operating pressure on the reactor performance will be presented and discussed after the description of the experimental setup and procedures.

Experimental MA-GSR process

Experimental setup and methods

A schematic process flow diagram of the membrane-assisted gas switching reforming reactor and auxiliary utilities used in this study is shown in Fig. 2. The fluidized bed membrane reactor is 10 cm in diameter and has a total length of 1 m, and is placed inside an electric oven supplied by ELICRA. To avoid particle losses, a conical freeboard is installed on top of the reactor, which in turn helps in hanging the membranes that are to be immersed in the catalytic bed. A metallic porous plate distributor of 7 mm thickness and 40 micron average pore size supports the fluidized bed inside the reactor. Gases

Fig. 2 – Schematic process flow diagrams of MA-GSR reactor and auxiliary components.

are fed from the bottom of the reactor using mass flow controllers supplied by Bronkhorst b.v. Water is fed into the system using a diaphragm metering pump (STEPDOS 03RC) equipped with an external evaporator to generate steam. To avoid steam condensation, electrical tracing is installed at the inlet and outlet lines of the reactor. Gas composition at the reactor outlet is measured with an in-line IR/TCD gas analyzer (Sick S710). In order to avoid damages of the analyzer, a condenser (to remove all water) and filters (15 μm pore size) are installed upstream of the analyzer. The installation is equipped with safety relief valves and gas sensors in case of overpressure or gas leaks during operation.

Four metallic supported Pd–Ag membranes have been immersed inside the fluidized bed for selective separation of H_2 . These membranes have been prepared at Tecnalia Research (ES) by an electroless plating technique as reported elsewhere [26]. The selective layer was around 4–5 μm thick and was deposited onto a surface-treated Hastelloy X porous support of

3/8" O.D. and 13.5 cm in length (supplied by Mott Corporation). In order to avoid intermetallic diffusion of the metals of the support towards the Pd–Ag layer, a thin ceramic barrier was deposited between the support and the selective layer as can be clearly discerned from the cross-section Scanning Electron Microscope (SEM) image given in Fig. 3b. Before the deposition of the selective layer, the porous support was welded at both sides with dense Inconel tubes (by Mott corporation) to close one side of the tube (dead-end configuration) and to facilitate the sealing on the other side of the tube. A picture of one of the membranes used in this work is depicted in Fig. 3a.

The membranes were completely immersed inside the fluidized bed. The permeated gas from the four membranes is combined into a single line, which in turn is connected to a vacuum pump to enhance the driving force for H_2 separation. The amount of gas permeation is measured using a HoriBatec VP4 film flow meter. This allows the quantification of several parameters that are used as indicators of the

Fig. 3 – a) Metallic supported membrane welded to dense Inconel 600 tube b) cross sectional SEM image of a ~5 microns thick Pd–Ag membrane supported on ceramic coated Hastelloy X porous tube [27].

performance of the novel reactor concept. In particular, the methane conversion (using the gas analyzer), the Hydrogen Recovery Factor (HRF) and the Separation Factor (SF) as given in Eqs (5)–(7). The HRF is an indication of the amount of (ultra-pure) hydrogen obtained through the membranes compared to the total amount of hydrogen that could maximally be produced from the feed and it is strongly depended on the methane conversion. Thus, this parameter is an important overall performance measure of the MA-GSR concept. On the other hand, the separation factor refers to the amount of hydrogen permeated compared to the total amount of hydrogen actually produced during reaction, thus it gives a measurement on the performance of the membranes only.

$$\text{Methane conversion : } X_{CH_4} = \frac{F_{CH_4, in} - F_{CH_4, out}}{F_{CH_4, in}} \quad (5)$$

$$\text{Hydrogen Recovery Factor : } HRF = \frac{F_{H_2, permeated}}{4F_{CH_4, in}} \quad (6)$$

$$\text{Separation Factor: } SF = \frac{F_{H_2, permeated}}{F_{H_2, total}} \quad (7)$$

The solid phase is a NiO/Al₂O₃ oxygen carrier/catalyst prepared at VITO (Belgium) with a mean particle size of 200 μm and apparent density of 1950 kg/m³. It has 37% (weight) NiO content and its minimum fluidization velocity has been measured at different temperatures using the standard pressure drop method (the fluidization velocity is non-dimensionalized as U_0/U_{mf}). This material has been tested before in the literature for gas switching and reforming systems and more information can be found in a previous work [24,28].

Experimental procedure and description

Before the actual demonstration of the MA-GSR concept, a detailed investigation on the behavior of the membranes and their potential interaction with the solid phase has been carried out. At first, the inside of the membranes was pressurized

to 0.5 bar overpressure with helium and submerged in ethanol in order to identify possible defects on the membrane. In this test, no bubble formation was observed from the Pd–Ag layer or the welding points, thus excluding large pinholes on the membrane surface or leakages at the sealings. Afterwards, the membrane stability (to investigate possible interactions between the Pd–Ag alloy and the support and thus the performance of the interdiffusion layer) and permeation tests at different temperatures (400 °C–525 °C) and pressures (1 bar–2 bar) were performed with the membranes placed inside the experimental setup devoid of the solids phase. For these tests, the reactor was heated up with 2 °C/min heating rate in a N₂ atmosphere, and then single gas permeation tests for H₂ and N₂ were performed every day for 10 days to evaluate the ideal H₂/N₂ perm-selectivity to check the stability. The membranes showed a stable average hydrogen permeance ($\sim 8.05 \cdot 10^{-7} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$) over the tested period; the average N₂ leakage through the metallic supported membranes was also relatively stable, which resulted in an ideal perm-selectivity of more than 11,000. These results are in line with the findings by Ref. [29] for metallic supported Pd-based membranes in a fluidized bed reactor.

After these tests, the membranes were cooled down to room temperature in N₂ and the reactor was filled with 2.4 kg of active oxygen carrier. This leads to a bed height of 18 cm, which means that the membranes are completely submerged in the bed. The catalytic bed is then heated up to the required temperatures at a heating rate of 2 °C/min while fluidizing the bed with N₂. A decrease in H₂ permeance (by 15%) has been measured under fluidization conditions compared to permeances measured in the setup without particles. This decrease might be associated with thermal stresses (the porosity of the support might be modified upon heating which can increase mass transfer resistances) as the membrane has been exposed to a cooling-heating cycle during catalyst feeding, which was also observed in the study of [29], or due to densification of the emulsion phase near the membranes with a corresponding increase in mass transfer resistances.

Subsequently, SMR and GSR (autothermal reforming) tests were performed under different operating conditions. In case of the SMR tests, external heat supply was applied to investigate the performance of the bubbling fluidized bed membrane reactor (with and without hydrogen extraction via the membranes) in terms of methane conversion, HRF and SF as a function of temperature and pressure. The results have been compared with the thermodynamic equilibrium predictions using Aspen Plus® as described in the work of Medrano et al. [29]. In this experimental campaign, the oxygen carrier was first reduced with hydrogen, and then CH₄ and steam were fed to carry out the reforming reaction.

In case of GSR (autothermal reforming), the reactor was first heated up (with a ramp rate of 2 °C/min) externally to an initial desired temperature, called Temperature at the Start of Reduction (TSR), before the start of the gas switching experiments. The autothermal operation of the GSR process is then carried out, while the heaters are turned off. At first, the gaseous fuel (20% CH₄ and 60% steam balanced with N₂) is fed to the reactor to complete the oxygen carrier reduction/reforming reactions, which leads to a temperature drop until the Temperature at the End of Reduction (TER). This step is then followed by feeding the reactor with air for a certain period of time to re-oxidize the oxygen carrier in a highly exothermic reaction and bring back the bed to the TSR. The maximum temperature rise can be calculated with Eq. (8). One minute of purging with nitrogen was applied between the air and fuel stages to prevent direct contact between fuel and air. It is worth mentioning that, in practice, a few seconds of steam purging will be implemented before and after the oxidation stage to prevent any explosion hazard from direct mixing of air and fuel in the feed lines to the reactor. Once the gases enter the reactor, no explosion hazard exists since the oxygen carrier very rapidly consumes both oxygen and fuel, and heat released from exothermic combustion reactions is very rapidly absorbed in the high heat capacity of the oxygen carrier. The cycle time of the GSR operation was varied to investigate the effect of degree of oxygen carrier utilization. Generally, the influences of different operating parameters have been studied for both SMR and GSR. All the details regarding the conditions of the experiments conducted in the GSR system are summarized in Table 1.

$$\text{Temperature rise : } \Delta T = \text{TSR} - \text{TER} \quad (8)$$

Table 1 – Experimental conditions for tests carried out in the MA-GSR reactor setup.

Parameter	Configuration	
	FBR	MA-GSR
Temperature [°C]	400–550	450–550
U ₀ /U _{mf} (fluidization velocity/minimum fluidization velocity)	3–5	3–5
Inlet pressure [bar]	1–4	1–4
Oxygen-to-Carbon (O/C) ratio	–	0.5
Steam-to-Carbon (S/C) ratio	2–3	2–3
Oxidation time [min]	–	2–8
Oxidation: reduction ratio	–	1:2
Permeate pressure [mbar]	8	8

In order to interpret the results obtained during the tests listed in Table 1, post-mortem membrane characterization has also been carried out by means of different measurement techniques. The surface and cross-section of the membrane at different axial locations were analyzed with a JEOLJSM-6330F SEM-EDX (Energy dispersive X-ray spectroscopy) equipment. The elemental composition of the surface has also been analyzed using X-ray photo-electron spectroscopy (XPS). Data were recorded on a Kratos AXIS Ultra spectrometer equipped with a monochromatic AlK α X-ray source and a delay-line detector (DLD). Spectra were obtained using an aluminum anode (h ν = 1486.6 eV) operating at 150 W, with survey scans at a constant pass energy of 160 eV and region scans at a constant pass energy of 40 eV. The background pressure was 2·10^{−9} mbar. CasaXPS data processing software was used for peak fitting and quantification, where all binding energies were referenced to the C 1s line at 284.6 eV. The surface composition was estimated from the integrated intensities corrected by atomic sensitivity factors. The results will be discussed in the next section.

Results and discussion

The results will be presented and discussed in three main parts: i) a brief investigation on the performance of the MA-GSR reactor with/without hydrogen extraction and compared with thermodynamic equilibrium predictions; ii) an experimental demonstration of a full transient MA-GSR cycle; and iii) post-mortem membrane characterization.

Reactor performance under steam methane reforming

The steam methane reforming reaction was first carried out with all the permeate sides of the membranes closed to evaluate the performance of the reactor as a standard fluidized bed reactor (FBR) without gas extraction through the membranes. Once it reached steady state operation, the permeate side was opened and the vacuum pump was connected to increase the hydrogen flux via the membranes to investigate the performance of the fluidized bed membrane reactor configuration (FBMR). Fig. 4 shows a typical transient profile of the retentate gas composition together with the achieved methane conversion. It can be seen that the methane conversion increases as a consequence of the H₂ extraction through the membranes thereby increasing the methane conversion.

Very similar gas concentration profiles have been obtained for the other experimental conditions tested during SMR experiments, both with and without H₂ extraction. Fig. 5 gives a summary of the results for the different operating conditions investigated, while it also presents a comparison with the thermodynamic equilibrium calculated with Aspen for the fluidized bed and the fluidized bed membrane reactor configuration. As can be seen, the experimental conversion is slightly below the thermodynamic equilibrium for both reactor configurations. For these tests, due to the presence of the membranes, the fresh oxygen carrier was reduced with H₂ (for 2 h) at a relatively low temperature of 400 °C, and then the SMR reaction was carried out. However, additional tests

Fig. 4 – Retentate compositions and methane conversion during steam methane reforming with and without H_2 extraction through membranes with a feed stream: S:C of 3, P of 4 bar, T of 475 °C and $U_o = 3U_{mf}$ m/s.

Fig. 5 – Methane conversion as a function of temperature (at 1.6 bar) (a), pressure (b) and separation factor (SF) and hydrogen recovery factor (HRF) as a function of temperature (c), pressure (d) for the two reactor configuration under steam methane reforming conditions.

showed that this was not sufficient to fully reduce the NiO to Ni so that maximum catalytic activity is achieved. When the 2 h reduction was carried out at 700 °C (without membranes) instead of 400 °C, the thermodynamic equilibrium is achieved

in all cases (Fig. 6), thus confirming that higher temperatures are required to fully reduce the oxygen carrier. This is an important finding for the MA-GSR concept (discussed in the following section) where the oxygen carrier is oxidized and

reduced in each cycle, but the temperature needs to be limited to protect the membranes. It is also worth mentioning that, for all the tests carried out in this work, the carbon imbalance was verified and was found to be typically around 5% (relative error). This error is many associated with the gas analyzer and the nitrogen dilution applied. Moreover, in further experiments during GSR reaction CO_2 was not detected during the oxidation step with air, thus the possibility of catalyst deactivation because of carbon formation is discarded.

In general, the results noticeably show that the equilibrium constraint is circumvented by the H_2 separation through the membranes. Specifically, Fig. 5 shows that the presence of membranes increases the methane conversion beyond the equilibrium that can be achieved without membranes. This effect is more prominent when the driving force for H_2 permeation is increased (higher pressure) or the membrane permeability is increased (higher temperature).

The separation factor (SF) and the hydrogen recovery factor (HRF) have also been determined for the different experimental conditions as they give an indication on the membrane and reactor performance. The results for these two parameters are also presented in Fig. 5. The flux through the membranes has obviously a significant effect on the overall membrane reactor performance, as it controls the final equilibrium gas composition. An increased hydrogen recovery factor and separation factor will result in less hydrogen bypass in the retentate gas and hence improved reactor performance. These two parameters are also influenced by the driving force that exists in the system: the amount of hydrogen produced (from the reaction), the amount of inert gas fed (inlet conditions), and the operating pressure. Moreover, according to Medrano et al. [29], who used a similar metallic supported Pd–Ag membrane, the mixing of hydrogen with other gas components may induce mass transfer resistances (lowering the separation factor) that can largely influence the H_2 permeance. It can be observed in Fig. 5 that the HRF and SF are very low compared to an ideal recovery and separation factor (which is supposed to be 100% in case of full methane conversion). Due to lower methane conversion

(lower recovery factor) and inert gas fed (N_2 as carrier gas for the analyzer), the partial pressure of H_2 in the bed is rather low, which hampers the driving force for H_2 permeation, thus influencing the SF and HRF. An increase in the operating temperature leads to higher methane conversions, consequently higher hydrogen partial pressures in the bed. This implies higher HRF's as observed in Fig. 5. However, since the reaction is carried out at low pressures, there is a limitation in the minimum driving force for H_2 separation, which restricts the increase in the SF ($\approx 21\%$). On the other hand, an increase in pressure imparts a significant effect on both HRF and SF. As can be concluded from Fig. 5, operation at a higher pressure leads to higher hydrogen separations and recovery factors, which is related to the increased driving force. As expected, an increase in pressure leads to a decrease in methane conversion according to the thermodynamic equilibrium. However, this limitation is overcome in a membrane reactor since hydrogen separation brings the process to conditions beyond thermodynamic restrictions. Thus, it can be concluded that the efficiency of the membrane assisted steam methane reforming system can be maximized by operating at higher pressure.

Demonstration of membrane assisted gas switching reforming (MA-GSR)

In this section the MA-GSR concept is demonstrated. As briefly outlined earlier, this concept operates on a repeating cycle of oxidation, purge, reduction/reforming, purge. At first, the effect of the oxidation and reduction times (oxidation to reduction time ratio was kept constant) has been investigated in order to find the optimum operating conditions achieving autothermal operation. Relatively short cycle times will emphasize the effect of the constant purge in between the stages with a corresponding decrease in overall performance because of some mixing of products with the purge gas. On the other hand, longer cycles will lead to a larger amount of temperature variation across the cycle, which will reduce the temperature of the reforming stage, given that the maximum

Fig. 6 – Experimental methane conversion and the corresponding thermodynamic equilibrium (from Aspen®) at different temperatures (at 1.6 bar) (a) and inlet flowrates (b) under steam methane reforming conditions (after the catalyst is reduced at higher temperature).

reactor temperature is fixed by the membranes. Lower reforming temperatures will lead to lower methane conversion and membrane permeability. Very long cycle times can also result in incomplete air conversion. Slippage of oxygen has the undesirable effects of increasing the amount of heat removed by the outgoing gases and increasing the oxygen concentration around the membranes (leading to faster membrane degradation). Following this investigation, the effect of operating pressure on the overall performance is studied at the optimum cycle configuration.

As for the steam methane reforming, the autothermal MA-GSR demonstration has also been investigated for the two reactor configurations, with and without H_2 extraction via the perm-selective membranes. A typical (MA-)GSR test measurement is shown in Fig. 7, where the transient temperature profile and the retentate gas composition over six redox cycles are presented. The first three cycles correspond to the GSR reaction with the permeate side closed, while the last three cycles are carried out with the MA-GSR configuration, thus with H_2 extraction. The figure shows that autothermal operation can be achieved by switching the gas feed (CH_4 /steam and air) periodically. For these cases the oven temperature was set at a lower set-point than the desired working temperature (around 40°C far from the predicted end temperature

of reforming). During the GSR experiments the reactor temperature decreases gradually due to the highly endothermic reduction and reforming reactions during the fuel stage, but it increases back to the starting target temperature (or TSR) when air is fed during the oxidation stage (bottom Fig. 7).

The retentate gas composition shows the conversion of CH_4 to CO_2 (and H_2O) in the first stage by the gas-solid (oxidized oxygen carrier) reduction reaction and then a large production of H_2 through catalytic steam methane reforming reaction. As expected, the catalytic reforming reaction is facilitated as the oxygen content in the oxygen carrier material is reduced, which provides free metallic nickel sites to catalyze the steam-methane reforming reaction. When comparing the first three cycles with the last three, a change in the gas concentration profiles can be seen as consequence of the selective H_2 removal. Remarkably, this does not influence the temperature profiles over the cycles, concluding that in the MA-GSR configuration autothermal operation can be achieved.

Similar oxidation/reduction cycles were performed to study the effects of the degree of oxidation and pressure on the reactor performance, and the results have been time-averaged over the three complete redox cycles for both configurations (with/without membranes). Similar to the SMR

Fig. 7 – Transient retentate gas compositions (top) and the corresponding temperature profile (bottom) at 3 bar, TSR of 550°C , S:C of 3, and $U_o = 3U_{mf}$, O:C ratio of 0.5, oxidation time of 6 min, Oxidation:reduction time ratio of 1:2.

analysis, the methane conversion in the autothermal GSR concept has been compared with the computed thermodynamic equilibrium at the corresponding temperature at the end of reforming. As explained earlier, the degree of oxidation was controlled by adjusting the duration of the air/fuel stage time. A longer cycle means a longer oxidation and reduction time, which thus corresponds to a higher oxygen carrier conversion. Fig. 8 shows the effects of the oxidation time on the reactor performance (in terms of average methane conversion) and the average temperature rise per cycle.

As can be seen from the figure, the lower the oxidation time (short cycle), the higher the methane conversion. This is explained by the fact that at shorter cycle times, the reduction/reforming reactions taken place at a temperature closer to the TSR (maximum working temperature). On the other hand, when the oxidation time increases, the methane conversion slightly decreases; this is again due to the decrease in the reforming temperature resulting from the longer reduction/reforming stage (as reduction/reforming stage time is changed proportionally) and cold feed gases (which need to be heated up to the reactor operating temperature). However, in an industrial scale reactor, the larger reactor temperature

variation can be reduced by implementing a heat integration system (pre-heating the incoming gas via heat exchange with the hot depleted O_2 and N_2 stream) and reducing the heat losses by implementing improved insulation.

Similar to the SMR system, the methane conversion (without membranes) obtained is close to the thermodynamic equilibrium, and when the membrane reactor configuration is activated, there is a clear displacement of the equilibrium as a result of the hydrogen extraction through the membranes. However, as observed in the SMR system, there is again a deviation between the experimental results and the predicted thermodynamic equilibrium for both configurations. This is again attributed to the relatively slow gas-solid reaction kinetics for the reduction of the NiO to the free Ni sites for the catalytic reforming reaction (as described in Section [Reactor performance under steam methane reforming](#)). The performance of the membranes was also compared in terms of HRF and SF. For different oxidation times, the trends were fairly similar and found to be almost constant for all the cases with a HRF of around 9% and a SF of 31%.

As discussed earlier, longer cycle times have detrimental effects in terms of lower reforming temperatures and the possibility of O_2 slip that removes heat from the reactor and can damage the membranes. This is clearly illustrated by the temperature rise per cycle profile in Fig. 8b, where an optimum temperature rise during the redox cycle is obtained for a cycle time of 6 min. In case of longer oxidation times, the TSR value will drop in each cycle, thus leading to a constant temperature decrease over time (like in the case of 8 min). The temperature rise during oxidation stage increases as the oxidation time increases due to the higher heat generation, however, after a certain period of time the temperature rise decreases as the O_2 slip starts occurring thereby increases the heat removal.

In addition to the effect of oxidation time, the influence of operating pressure on the autothermal GSR reactor performance is evaluated. Table 2 gives a summary of the different operating conditions used in a relatively high-pressure autothermal gas switching reforming tests.

The results clearly show the increase in the hydrogen recovery and separation factor at higher pressure due to the increased hydrogen permeation. This is also reflected in the CH_4 conversion that decreased from 3 bar to 4 bar in the GSR case (due to equilibrium limitations), but increased from 3 to 4 bar for the MA-GSR case (due to a larger driving force for H_2 permeation). The experimentally determined methane conversion during the GSR configuration was close to the thermodynamically predicted conversion in the FBR configuration. Remarkably, the methane conversion during the MA-GSR configuration was higher at the same operating conditions. Comparing the equilibrium conversion of methane (FBMR) and the conversion obtained during the experiments in the membrane-assisted switching configuration, a significant increase has been detected. In addition, comparing the SF and HRF with the steady state SMR results at the same operating conditions, the SF and HRF in the membrane-assisted switching configuration was 20% and 16% respectively, higher than the SMR system.

During the entire set of SMR and GSR experiments, the average ideal H_2/N_2 perm-selectivity of the membranes was

Fig. 8 – Autothermal methane conversion as a function of oxidation time (a) and corresponding temperature rise as a function of normalized time (b) at 1.6 bar, TSR of 485 °C, S:C of 3, and Oxidation:Reduction time of 1:2.

Table 2 – Summary of autothermal GSR/MAGSR reactor performance at two different pressures.

Conditions	GSR	MAGSR	FBR	FBMR
Pressure [bar]	3			
Oxidation time [min]	6			
Temperature at the end of reforming [°C]	508	508	508	508
Temperature rise [°C]	71.40	71.40	—	—
CH ₄ conversion [%]	32.26	42.50	36.55	45.78
HRF [%]	—	19.37	—	
SF [%]	—	35.80	—	
Pressure [bar]	4			
Oxidation time [min]	6			
Temperature at the end of reforming [°C]	516	518	516	518
Temperature rise [°C]	69	68.20	—	—
CH ₄ conversion [%]	30.65	49.75	34.80	47.08
HRF [%]	—	25.99	—	
SF [%]	—	51.8	—	

thermal, mechanical and chemical resistances. However, it should be mentioned that, a long term thermal stability tests under the same operating conditions while keeping the membranes in a lower O₂ concentration zone is still of high importance. As a matter of fact, a long-term stability test on similar membranes under reforming conditions was already conducted by Medrano et al. [29] and it has been shown that the membranes were quite stable in terms of hydrogen permselectivity (higher than 200,000 has been measured) for more than 800 h. However, the stability against redox cycling needs to be further improved.

Post-mortem characterization

The possible defects on the surface of the membranes were evaluated by pressurizing (1 bar) the inside of the membrane with He and submerging them in ethanol. Bubbles were observed on the membrane layer, particularly at the bottom

Table 3 – EDX analysis of the different sections of the tested membrane as indicated in Fig. 10d, e & f.

Spectrum	C	O	Al	Ni	Pd	Ag	Si	Cr	Fe	Zr	Mo
Bottom surface of the membrane (picture “d”)											
Spot 1		4.50	1.10	14.87	79.53						
Spot 2		34.05	16.46	24.47	24.44	0.57					
Cross sectional composition of the middle part of the membrane (picture “e”)											
Spot 1		10.50	1.97	19.83	67.57	0.13					
Spot 2		33.21	18.20	23.32	23.96	0.23			1.08		
Spot 3		2.83		1.77	89.56	4.65			1.20		
Spot 4		25.39	11.90	2.20	50.41	2.31	1.36		2.73	3.70	
Spot 5	14.56	1.51		40.15			0.85	18.88	16.08		7.97
Top surface of the membrane (picture “d”)											
Spot 1		3.54	0.51	0.42	90.29	5.24					
Spot 2		4.90	0.78	1.08	89.91	3.33					

measured and it was found that at the end of this work it was only 150, which is a much lower value compared to the initial average ideal perm-selectivity of 11,000. This decrease is directly associated with an increase in the N₂ permeation (leakage) via the membranes, since the H₂ permeance remained constant over the experiments once they were immersed in the catalytic bed. In this work, the purity of the permeate was not analyzed, thus for the calculations it was assumed that all the gas permeated corresponded to H₂. Once all the experiments were concluded, the membranes were removed from the setup and a modification on the membrane surface was observed, thus indicating the need for detailed post-mortem characterization. These observations indicate that the membranes suffer from the gas switching operation, either by thermal stresses, oxidation of the Pd-based selective layer, or a combination of both effects. However, the main objective of this work is the demonstration of the MA-GSR concept, rather than evaluation of the membrane performance. Nevertheless, this is also an indication that the concept configuration needs to be redefined to limit the membrane exposure to oxygen (e.g. keeping the membranes in zones with lower O₂ concentration) and/or the existing membranes need further improvement in terms of improved

(dead-end zone) and middle part. While with the “fresh” membranes bubbles were not detected on the surface (as discussed in Section [Experimental setup and methods](#).) and the measured He permeation was zero, in this case an average permeation of 7–8 mL/min was measured. This indicates that pinholes were formed on the surface of the Pd layer. Based on this, further membrane characterization has been performed.

For membrane characterization, cross-sectional and surface SEM-EDX analysis on one of the used membranes has been carried out. The membrane was divided into three different sections along the height as shown in [Fig. 9](#). It has to be noted that two distinctive colors were observed on the membrane surface: a darker color at the dead-end of the membrane (near to the distributor) and the original silver color on the top part of the layer.

Cross-section and surface SEM images of the tested membrane are shown in [Fig. 10](#), where defects can clearly be observed. [Fig. 10a](#) shows an increment in Pd membrane thickness ($\approx 7 \mu\text{m}$) and the development of a number of black spots. This is due to the formation of PdO which is confirmed by the EDX analysis. As expected, the PdO formation is very extensive at the lower part of the membrane compared to the top and the middle sections. Another aspect that has been

Fig. 9 – Picture of a membrane used and the different locations analyzed by SEM-EDX shown in red: the bottom part of the membrane (near the distributor of the fluidized bed) is represented by (a), the interface between dark and the silver colored (the middle part of the membrane) by (b) and the top part of the membrane is represented by (c). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 10 – SEM images of the membrane after use under SMR and autothermal reforming reactive conditions: (a) cross-sectional image of the bottom part (corresponds to “a” of Fig. 9); (b) cross-sectional image of the middle part (corresponds to “b” of Fig. 9); (c) cross-sectional image of the top part (corresponds to “c” of Fig. 9); (d) and (f) indicates the membrane surface of the bottom and top part, respectively; (e) the cross-sectional image of the interface (middle) see (Table 3).

observed is the delamination (shown in Fig. 10b) of the Pd layer from the support creating a serpentine structure. This delamination is observed particularly at the interface between bottom and top part (between the dark and silver colored), which is most likely to be related to the high thermal cycle (thermal expansion) exposure. At the top of the membrane, a thinner black layer is observed onto the Pd layer, indicating also the formation of PdO (although in a much lower extent). Remarkably, the Pd layer presents several defects as voids are

created in the ideally dense Pd layer, which might indicate migration of Pd from the layer to form the PdO.

As can be discerned from the table, a high amount of oxygen on the Pd layer has been found at the bottom and middle area of the membrane, while the top surface of the membrane is mostly Pd. This is a clear indication of the oxidation of the Pd surface during the oxidation stage, especially at lower parts of the membrane where higher partial pressures of O₂ are expected. In addition, nickel and aluminum have been found

Table 4 – Elementary analysis on the surface of the membrane using XPS.

Identifier	Ni 2p	O 1s	Ag 3d	Pd 3d	C 1s	Zr 3d	Si 2p	Y 3p	Al 2p
Bottom surface of the membrane									
Inner layer	1.31	23.18	10.57	40.76	4.56	7.63	7.66	1.11	0.00
Top layer	19.87	37.35	0.21	0.72	9.35	0.01	2.81	0.08	28.24
Middle surface of the membrane									
Inner layer	1.76	21.47	11.78	37.30	4.84	11.80	5.07	1.70	0.66
Top layer	0.69	34.83	1.38	7.13	9.29	0.02	2.51	0.03	23.89
Top surface of the membrane									
Inner layer	0.15	19.35	12.23	49.00	4.11	8.78	3.04	1.22	0.00
Top layer	0.58	28.67	6.69	32.41	6.99	0.00	9.73	0.05	9.49

on the surface at the bottom and middle part of the membrane. Ni and Al originate from the catalyst and seems that these materials have become attached to the membrane surface. Fig. 10e show that the membrane surface is clearly damaged and a number of small openings were created, where even finer Ni and Al elements from the catalyst were able to be detected in the surface (see spectrum 1). These results show obvious defects on the surface, which can be associated to the significant decrease in perm-selectivity observed after the reactive tests.

Furthermore, in order to determine whether the oxygen penetrates completely into the Pd layer, or whether there is inter-metallic diffusion from the support towards the membrane, one of the membranes has been peeled and both the inner and outer part of the Pd layer have been analyzed by XPS analysis. The results of this analysis are summarized in Table 4, and they confirm the EDX results: a higher amount of oxygen and a lower amount of Pd are detected on the top layer of the membrane surface, particularly at the bottom and middle sections.

From the XPS analyses, it can also be observed that when peeling the Pd layer, part of the ceramic barrier is also removed since Zr, Si and Y (YSZ) are clearly detected in the inner part of the layer. This inner part has a common Pd–Ag composition at the various locations, and the oxygen observed is mostly related to the oxides of the ceramic layer. However, a small fraction of Ni is detected, which can be associated to intermetallic diffusion. Particularly, the content of Ni is slightly higher at the bottom and middle parts, where higher temperature gradients are expected during the GSR experiments. In fact, as already observed in previous works [29], diffusion of the metals from the support towards the Pd layer is increased when working at higher temperatures.

On the other hand, the results obtained for the outer part of the Pd layer are in good agreement with the observations from the EDX analyses. In particular, it is observed that the O/Pd ratio decreases when moving from the bottom of the membrane towards the top. In this case, the oxygen measured can be from the PdO layer formed onto the Pd layer, or from catalyst embedded in the pores of the top surface. Overall, it can be concluded that the top layer of the membrane cannot withstand the harsh ATR conditions and that important defects are observed and measured. On the other hand, the inner part of the membrane remained with similar properties as an original membrane. Therefore, improved membranes are needed for this MA-GSR concept in order to protect the top layer. A possibility could be the use of protective layers or pore

filled membranes, where the Pd is embedded in the pores of the support, thus reducing the interaction with the gas (and solid) phase of the catalytic bed.

Conclusions

In this work, a novel reactor concept for ultra-pure H₂ production integrating CO₂ capture has been proposed and demonstrated experimentally at different operating conditions. The concept is based on consecutive reduction/oxidation cycles of a metal (oxide) to provide autothermal operation, where in the reduction stage H₂ is produced and recovered via H₂-selective membranes.

Good reproducibility of the cycles has been observed during MA-GSR experiments and the temperature oscillations between reduction and oxidation cycles have confirmed virtual autothermal conditions. Compared to GSR experiments, the use of membranes clearly enhances the methane conversion at similar experimental conditions. Fuel conversions up to 50% with a hydrogen recovery factor of 26% and separation factors above 50% have been achieved at a relatively low temperature (~500 °C). However, the experiments were not carried out at optimal conditions for fuel reforming in membrane reactors, meaning that the efficiency of this concept can be largely improved if working at higher temperatures and pressures (and installed membrane area).

The main limitation of this concept is related to the stability of the membranes, which are continuously exposed to thermal cycles and alternating oxidative and reducing atmospheres. In fact, it has been observed that they cannot withstand these harsh conditions and defects are created on the Pd layer surface. In particular, the formation of PdO results in the formation of pores in the dense Pd layer, while thermal stresses are responsible for delamination of the selective layer. Therefore, more investigation and development is needed to improve the performance of these membranes in order to optimize and scale-up the MA-GSR concept.

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