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Techno-economic assessment of membrane-assisted gas switching reforming for pure H₂ production with CO₂ capture

Solomon A. Wassie^{a,b}, Schalk Cloete^c, Vincenzo Spallina^{a,d}, Fausto Gallucci^{a,*}, Shahriar Amini^{b,c}, Martin van Sint Annaland^a

^a Chemical Process Intensification, Eindhoven University of Technology, Department of Chemical Engineering and Chemistry, Eindhoven, The Netherlands

^b Norwegian University of Science and Technology, Department of Energy and Process Engineering, Trondheim, Norway

^c SINTEF Materials and Chemistry, Flow Technology Department, Trondheim, Norway

^d Group of Catalysis and Porous Materials, School of Chemical Engineering and Analytical Science, University of Manchester, Manchester, United Kingdom

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ABSTRACT

Hydrogen has significant potential as a future carbon-free energy carrier. Given that the vast majority of the current global hydrogen is produced from fossil fuels, CO₂ capture and storage (CCS) emerges as a promising strategy for delivering clean hydrogen on a global scale. The primary challenge with CCS is the large energy penalty imposed, but this problem is circumvented by the membrane-assisted gas switching reforming (MA-GSR) technology evaluated in this work. Combined reactor and process simulations showed that the MA-GSR process achieves a similar equivalent H₂ production efficiency as conventional steam methane reforming without CO₂ capture. The results of the process simulations also show that the new MA-GSR concept can achieve a higher H₂ production efficiency than the conventional plant when integrated with CO₂ capture (20% higher). However, a drawback of the MA-GSR concept is the low utilization of the membranes in the system, requiring a large membrane surface area for a given rate of hydrogen production. This makes the economics of the concept highly sensitive to the cost and durability of the H₂ perm-selective membranes. In the base-case, the cost of hydrogen (0.274 €/Nm₃³) was lower than the conventional process with CO₂ capture (0.282 €/Nm₃³), with a cost of CO₂ avoidance of 85.14 €/t_{CO2} instead of 97.06 €/t_{CO2} for the conventional technology. Future technology improvements leading to a threefold reduction in the cost/permeability ratio of H₂ perm-selective membranes can allow the MA-GSR technology to produce hydrogen at a similar cost as conventional steam methane reforming without CO₂ capture.

1. Introduction

Hydrogen is produced as bulk chemical for a wide range of applications, such as ammonia and methanol synthesis, hydro-processing in refineries, metallurgical processes, and as low-emission fuel for gas turbines or fuel cells (Rostrup-Nielsen, 2005; Martinez et al., 2013). If the global policy environment can be aligned more closely with the Paris COP agreement of limiting the global temperature rise “well below 2 °C”, the demand for hydrogen as a clean fuel could increase strongly over the coming decades.

Hydrogen can be produced via different process routes, such as chemical processing of fossil fuels or biomass, electrochemical water splitting using electricity or thermochemical water splitting using heat from nuclear or concentrated solar energy. From an industrial point of view, by far the most widely used route for the production of hydrogen is chemical processing of hydrocarbon feedstocks (mainly natural gas

by steam reforming (Rostrup-Nielsen et al., 2002). Globally, more than 50% of the hydrogen is produced by steam methane reforming (SMR) (Aasberg-Petersen et al., 2001; Meerman et al., 2012). SMR is a highly endothermic process where the reforming reaction is carried out in a multi-tubular fixed bed reactor (called Fired Tubular Reformer – FTR) using an external heat source over a nickel based catalyst (Rostrup-Nielsen et al., 2002; Aasberg-Petersen et al., 2001). This conventional steam reforming process comprises multiple conversion (reactors) and separation units, which includes feedstock pre-treatment and sulphur compound abatement, a high temperature and high-pressure reformer (typically 800–1100 °C, and 15–30 bar), high and low temperature water gas shift reactors and finally H₂ separation in a Pressure Swing Adsorption (PSA) unit to obtain a high H₂ purity (> 99.99%) (Rostrup-Nielsen et al., 2002; Rostrup-Nielsen, 1993; Spallina et al., 2016). To supply the heat needed for the highly endothermic reformer, part of the feed and PSA off-gases are combusted in a furnace. This leads to large

* Corresponding author.

E-mail address: F.Gallucci@tue.nl (F. Gallucci).

List of symbols*Main Symbol definitions*

α	Volume fraction (–)
ρ	Density (kg/m ³)
D	Mass diffusivity (m ² /s)
g	Gravitational acceleration (m/s ²)
h	Specific enthalpy (J/kg)
K_{sg}	Interphase momentum exchange coefficient (kg/m ³ .s)
k	Thermal conductivity (W/m.K)
p	Pressure (Pa)
Q_{pq}	Interphase heat exchange rate (W/m ³)
S	Mass source term (kg/m ³ .s)
S^h	Energy source term (W/m ³)
S^u	Momentum source term (N/m ³)

t	Time (s)
u	Velocity (m/s)
x	Axial distance (m)
Y	Species mass fraction (–)
η_{H_2}	H ₂ production efficiency (–)
$\eta_{th,ref}$	Reference thermal efficiency (–)
$\eta_{el,ref}$	Reference electrical efficiency (–)
$\dot{m}_i$	Mass flow rate of the gas (kg/s)
LHV	Lower heating value (J/kg)

Subscript definitions

g	Gas
i	Species index
q	Phase index
s	Solids

CO₂ emissions (around 0.82 kg_{CO2}/Nm_{H2}³) to the atmosphere (Collodi et al., 2017).

Another widely-known process for H₂ production is Autothermal Methane Reforming (ATR), where some of the steam is replaced by oxygen to achieve autothermal operation through partial oxidation of the fuel. However, one of the main drawbacks of this process is the expensive separation of oxygen from air (Dybkaer, 1995). Dry reforming or partial oxidation of methane offer additional alternatives, although their relatively low H₂/CO ratio makes them less attractive for hydrogen production applications (York et al., 2003; Li and Zhang, 2013). Hence, SMR and ATR are currently the most used technologies for H₂ production from natural gas (Medrano Jimenez, 2017).

However, these processes are associated with significant CO₂ emissions and will need to be equipped with CO₂ capture and storage (CCS) to produce clean hydrogen. CCS is one of the promising technological routes in the energy sector to reduce global CO₂ emissions. Recent projections rely on CCS for 14% of cumulative emission reductions by 2060 in the 2 °C scenario and 18% in a “beyond 2 °C” scenario that is better aligned with the Paris agreement. When excluding emission reductions from efficiency improvements to look only at low-carbon energy supply, the expected contribution of CCS is even 30% (International Energy Agency, 2017).

When CO₂ capture is included in the hydrogen production process, various separation systems may be employed. If the CO₂ is separated from syngas, it is typically separated by methyl diethanolamine (MDEA) scrubber before being sent to the PSA unit. With this approach, around 60% CO₂ capture can be achieved (Martinez et al., 2013; Meerman et al., 2012; Collodi, 2010). The other source of CO₂ emissions is from the FTR furnace vent, where a typical post-combustion capture unit using a monoethanolamine (MEA) absorption is usually employed (Rath, 2010). However, the increased number of process steps and the energy penalty for the solvent regeneration significantly increase the cost of hydrogen production with CO₂ capture (more than 25% increase in cost of hydrogen compared to the conventional process without CO₂ capture) (Damen et al., 2006).

Recently, membrane reactors have been proposed as a potentially more cost-effective alternative for hydrogen production with integrated CO₂ capture (York et al., 2003; Zaabout et al., 2013; Zaabout et al., 2015; Gallucci et al., 2008). Using membrane reactors, an ultra-pure H₂ stream can be extracted via the membranes. This in-situ hydrogen extraction shifts the reaction equilibrium to produce more hydrogen, thus allowing operation at much lower temperatures than conventional SMR. As a result, feedstock conversion and H₂ separation can be performed in a single unit that can be operated at lower temperatures (500–700 °C), which decreases the total cost of the system. In an ideal case of infinite membrane surface area and complete vacuum inside the membranes, a relatively pure CO₂ stream (after condensation of the

remaining steam) can be directly obtained for transport and storage.

In this context, Pd-based membranes have been extensively studied because of their high H₂ perm-selectivity and permeability at relatively low temperatures (Zaabout et al., 2013; Zaabout et al., 2015; Medrano et al., 2016a; Gallucci et al., 2013; Fernandez et al., 2016a; Fernandez et al., 2015a). Using Pd-based membranes, De Falco (2018) carried out a performance assessment on a reformer membrane module (RMM) for a hydrogen production plant. In the RMM configurations, after removing CO₂ from the retentate, the remaining hydrogen (after the H₂ separation via membrane modules) and the unconverted gas (CO, CH₄) were used as a fuel in the gas turbine for extra electric power production for the plant. In addition, the exhaust gases after the gas turbine are used to provide the heat of reaction for the reforming unit. These combined effects of hydrogen and electricity production provided a significant reduction in the energy consumption of approximately 10%.

Iaquaniello et al. (2008) also carried out an economic evaluation on a hybrid system based on a Pd-based membrane reformer reactor for hydrogen and electricity production. They reported that the production cost of the hybrid system is 30% lower than the conventional tubular steam reforming technology, and is also 13% lower than a gas-fired cogeneration plant coupled with a conventional hydrogen plant. Jordal et al. (2004) also performed a study on the integration of H₂ separation using Pd and microporous membranes in a gas turbine process for CO₂ capture. It is reported that natural gas combined cycles with an integrated membrane reactor with CO₂ capture can reach a thermal efficiency of up to 48%. Spallina et al. (2016) have shown a strong reduction in the CO₂ avoidance cost (below 10 €/t_{CO2}) by performing a thermodynamic optimization and sensitivity study on the economics of a H₂ production plant using two different membrane-assisted reactor concepts.

New reactor concepts have also been proposed in pursuit of cost effective and environmentally friendly hydrogen production. Among the proposed technologies, chemical looping is believed to be one of the most promising and efficient technologies (Aasberg-Petersen et al., 2001; Ortiz et al., 2011; Ortiz et al., 2010). Chemical looping reforming (CLR) consists of two interconnected reactors, called air reactor and fuel reactor. An oxygen carrier circulates between the two reactors to transfer oxygen from the air to the fuel, so that ATR is achieved without the energy penalty of air separation. As with conventional ATR, the produced syngas requires further processing to produce hydrogen. Efficient utilization of a PSA unit for producing ultra-pure H₂ is not possible, however, since the CLR process cannot efficiently utilize the PSA off-gas fuel. The conventional CLR process is therefore better suited for power production with pre-combustion CO₂ capture (Spallina et al., 2017a; Francisco Morgado et al., 2017), unless using the packed-bed reactor, where the reduction (carried out by the PSA off-gas) and reforming processes can be distinctively separated (Spallina et al., 2017b).

Insertion of H_2 perm-selective membranes into the CLR fuel reactor allows pure hydrogen production and also avoids the need for downstream process units, resulting in a thermodynamically favourable process (Medrano et al., 2014). Nevertheless, high pressure operation (up to 50 bar) is critical for achieving competitive overall energy efficiencies (Spallina et al., 2016). Due to technical challenges related to the solids circulation between the interconnected reactors and separation of solids from the gas stream at elevated pressures, scale-up of a pressurized CLR is expected to be very challenging. To circumvent this challenge, the membrane-assisted chemical looping reforming process is proposed to be carried out in a single dynamically operating fluidized bed reactor, referred to as the membrane-assisted gas switching reforming reactor (MA-GSR).

This MA-GSR reactor concept has been primarily proposed for ultra-pure hydrogen production with integrated CO_2 capture from steam methane reforming. As described in (Wassie et al., 2018), the MA-GSR concept uses: 1) an oxygen carrier, which acts as catalyst and heat carrier to the endothermic reforming reaction and is alternately exposed to fuel/steam (reforming/reduction) and air (oxidation) streams; when air is fed to the reactor, the oxygen carrier is heated by the exothermic solids oxidation reaction; this heat is then utilized in the fuel stage, where endothermic reduction and catalytic reactions regenerate the oxygen carrier and produce syngas; 2) hydrogen perm-selective membranes (thin Pd-based) immersed into the fluidized bed to directly recover pure hydrogen produced during steam-methane reforming and water gas shift reactions. This combination of process units brings a high degree of process intensification with additional benefits in terms of increased process efficiencies (Gallucci et al., 2008).

In this work, a detailed thermodynamic and economic analysis of the novel MA-GSR concept is carried out. Results are benchmarked against the conventional FTR process for hydrogen production with and without CO_2 capture, and sensitivity analyses to the most important process parameters are carried out.

2. The MA-GSR reactor concept

Given the transient nature of the MA-GSR reactor, a cluster of several identical reactors is required to create an overall steady-state process unit. In this study, five reactors are included in the cluster. Each reactor cycles repeatedly through three distinct stages: oxidation, reduction and reforming (Fig. 1). At any given moment, one reactor will be in the oxidation stage, two reactors in the reduction stage and another two reactors in the reforming stage.

In order to maximize the energy efficiency, the residual fuel from the reactors in the reforming stage is directly fed to the reactors in the reduction stage. In this way, all the fuel fed to the system is either extracted as H_2 or combusted to supply heat for the endothermic reforming reaction. Furthermore, the incoming methane stream is diluted with some of the CO_2 and H_2O from the reduction stage. This practice increases the required reactor volume and membrane surface area by 67% relative to a case where the reforming stage is fed with methane and steam at a S/C ratio of 2 because the gas throughput in the reduction and reforming stages increases by about a factor of 2, but this is necessary to avoid carbon deposition problems (Chen et al., 2004; Nielsen and Trimm, 1977; Bartholomew, 2001).

A high degree of CO_2 separation also requires a delay in the switching of the outlet valves relative to the switching of the inlet valves. When the inlet valve is switched to start a new stage, a significant amount of time is required to push out the gases remaining in the reactor from the preceding stage before the outlet valve can switch. This delayed outlet switch combined with the high degree of interconnection between reactor outlets and inlets will require an elaborate system of valves to control the process.

The biggest drawback of the MA-GSR configuration is the fact that the membranes are only fully utilized in the reforming stage. Also, the membranes have to withstand the exposure to oxygen in the oxidation

stage. However, given that the oxidation over an oxygen carrier is generally very fast and the oxygen carrier is mostly kept in a highly reduced state, this challenge may be circumvented by positioning the membranes at a safe distance above the reactor inlet so that the O_2 does not reach the membranes (Wassie et al., 2018). As a matter of fact, the authors have performed an experimental test using metallic supported Pd-Ag ($\sim 5 \mu m$) membrane at relatively low pressure (up to 4 bar) and temperature ($550^\circ C$) under the switching conditions and found that the main limitation of the concept is related to the stability of the membranes (Wassie et al., 2018). Due to the continuous exposure of the membranes to thermal cycles and alternating oxidizing and reducing atmospheres, some defects on the selective (Pd) layer have been observed. Particularly the membrane area close to the distributor (bottom part of the membrane) showed extensive modification on the membrane surface compared to the top part. An oxidation of the Pd-based selective layer was observed which forms PdO which in turn results in the formation of pores in the dense Pd layer, while thermal stresses cause a delamination of the selective layer. Based on this result, the authors suggested either to redefine the concept configuration to limit membrane exposure to oxygen (keeping the membranes in a lower O_2 concentration zone) or improve the current-state-of-the-art membranes with higher thermal and mechanical resistance to oxidative atmosphere. However, this study was performed if an improved membrane is developed in the future, the scaled-up MA-GSR reactor could be one of the potential candidate for hydrogen production integrated with CO_2 capture.

To better understand the behaviour of the MA-GSR reactor cluster and to give input to the process simulations, reactor simulations were carried out using a 1D CFD approach, similar to the work of Solsvik et al. (2015). All five reactors in the cluster were simulated simultaneously with the appropriate outlet valve switch delays and connections between reactor outlets and inlets required to correctly capture the system dynamics.

The reactor simulation task is simplified by the fact that H_2 permeation through the membranes is assumed to be the rate-limiting step. Results are therefore primarily influenced by the membrane permeation law employed (Eq. (1)) (Fernandez et al., 2016b). Other model closures influencing the bed voidage, effective reaction rate and axial dispersion are of secondary importance and are therefore only included in the Appendix A.

$$F_{H_2} = \frac{P_0}{t_m} e^{\left(\frac{-E_A}{RT}\right)} (P_{H_2,ret}^{0.74} - P_{H_2,perm}^{0.74}) \quad (1)$$

Where $P_0 = 4.24 \times 10^{-10} \frac{\text{mol}}{\text{smPa}^{0.74}}$, $E_A = 5810 \frac{\text{J}}{\text{mol}}$ and $t_m = 5 \times 10^{-6} \text{ m}$.

Inlet flow specifications to the reactors are given in Table 1. It should be noted that, in practice, a few seconds of steam purging will be implemented directly 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

Fig. 1. A MA-GSR reactor concept showing the inlet and outlet of the three stages alternately executed in the reactor.

Table 1

Inlet specifications to the three reactor stages indicated in Fig. 1.

Stream	Stage time (s)	Mass flux (kg/m ² s)	Temperature (°C)	Composition (mole fraction)	
Air to oxidation stage	250	1.081	518.8	O ₂	0.21
				N ₂	0.79
Residual fuel to reduction stage	500	Outlet from the reforming stage	467.4	H ₂	0.0237
Methane and steam diluted with combustion products to reforming stage	500			CO	0.0039
				CH ₄	0.1935
				H ₂ O	0.3780
				CO ₂	0.3960
				N ₂	0.0049

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.

Each reactor was simulated with a cross sectional area of 1 m² to allow for easy scaling according to the needs of the process simulations. The reactor height was specified at 10 m with membranes occupying the bottom 6 m. The 0.05 m diameter membranes were assumed to be arranged to occupy a volume fraction of 0.25, resulting in a total membrane surface area of 120 m² per m² of reactor cross sectional area (corresponding to 1196 membranes per reactor). A permeate side pressure of 1 bar was implemented and the reactors were operated at 50 bar. The NiO oxygen carrier had a density of 3400 kg/m³, a particle size of 150 µm and an active content of 20% by mass, and was initialized to fill the bottom 6 m of the bed with a volume fraction of 0.4. This oxygen carrier has been successfully tested for gas switching reforming application in previous study (Wassie et al., 2017), and was chosen due to its high catalytic activity and oxygen carrying capacity.

The outlet gas species and temperature profile as well as the hydrogen extraction rate through the membranes are shown in Fig. 2 for one reactor in the cluster. It is immediately evident from the species

plot that a lengthy delay is necessary in the outlet switching valve. For example, the oxidation stage with air starts at 0 s, but substantial N₂ concentrations only reach the outlet after about 100 s. If the outlet valve for the oxidation stage was switched at the same time as the inlet valve such so the reactor outlet gases from 0 to 250 s are released to the atmosphere, a lot of CO₂ would be lost. This would result in unacceptable CO₂ capture performance.

An outlet switch delay time of 120 s was therefore implemented in the simulations. This implies that the outlet gases from the three process stages are represented by the following ranges in Fig. 2: 120–370 s for oxidation, 370–870 s for reduction and 870–1200 s for reforming. As an example, it is clear to see that much less CO₂ will be lost if the outlet gases are released to the atmosphere for 120–370 s in Fig. 2 instead of 0–250 s.

Despite this outlet switch delay, part of the CO₂ from the subsequent reduction and preceding reforming stage is leaving the reactor with the N₂ during the oxidation stage (120–370 s in Fig. 2). This effect is caused by the thorough mixing in a fluidized bed. Undesired mixing can be reduced by making the overall cycle longer, but this strategy will cause larger temperature variations across the cycle. As shown in Fig. 2, the reactor temperature increases during the highly exothermic oxidation stage and decreases during the endothermic reforming stage.

The maximum reactor temperature was specified as 700 °C in view of the thermal stability of the membranes (assuming that the membranes can be operated at high temperature for better heat integration). Given this limit, longer cycles will require a larger drop in temperature during the endothermic reforming stage so that the larger temperature rise during the subsequent highly exothermic oxidation stage can be accommodated. This will however reduce the equilibrium H₂ concentrations and membrane permeability, thereby requiring a larger membrane surface area for a given amount of H₂ extraction. The selected cycle time specified in Table 1 was found to be a good compromise between CO₂ separation efficiency and required membrane surface area.

To supply data for the process simulations, the outlet stream flow rates, temperatures and compositions were averaged for each of the three stages. These average stream properties would be well approximated by a sufficiently large cluster of MA-GSR reactors acting as a steady-state process unit as presented by the authors in (Cloete et al., 2015; Spallina et al., 2015) for chemical looping combustion in IGCC.

3. Process descriptions

The three hydrogen production plant setups that have been selected for techno-economic comparison are briefly discussed in the following sections.

3.1. Reference plants: steam reforming of natural gas with and without CO₂ capture

Conventional natural gas steam reforming in a FTR process has been considered as benchmark technology as described in Martinez et al. (2013). The layout of this reference plant (shown in Fig. 3), is described

Fig. 2. Gas species mole fractions and temperature of the stream exiting from one reactor, as well as the rate of hydrogen extraction through the membranes as a function of time. The reactor was cycled through oxidation (0–250 s), reduction (250–750 s) and reforming (750–1250 s).

Fig. 3. Schematic description of a reference fired tubular plant for H₂ production without CO₂ capture.

in detail in the work of Spallina et al. (2016). In this configuration, the natural gas is first heated (365 °C) and sent to the desulphurization unit, where H₂S is removed using ZnO. The natural gas is then mixed with H₂O to the desired S/C ratio (3.4) and is pre-reformed in an adiabatic pre-reformer at 490 °C over a Ni-based catalyst. The pre-reforming is required to remove higher hydrocarbons from the natural gas (to reduce excessive carbon formation) and reduce the heat duty of the reforming section. Subsequently, the pre-reformed gas passes through a secondary pre-heater (620 °C) and is fed to an externally heated fired tubular reformer where the natural gas is converted into syngas at 890 °C and 32.7 bar in tubes filled with a Ni-based catalyst. The S/C ratio for the reformer is selected based on industrial experiences for H₂ production using SMR (Dybkiær and Aasberg-Petersen, 2016; Farshchi Tabrizi et al., 2015) and to avoid Ni-based catalyst deactivation (Yang et al., 2016).

The produced syngas is then cooled down (338 °C) while producing

high pressure steam (at 100 bar and 485 °C) for the process. The syngas is subsequently sent to a WGS reactor operated between 330 and 430 °C with an Fe-Cr based catalyst and is converted into CO₂ and H₂. For this reference plant (without CO₂ capture), a single-stage WGS reactor is used as the remaining unconverted CO is sent back to the furnace of the reformer. The shifted syngas mixture is subsequently cooled down to atmospheric temperature to condense the steam and the H₂ rich syngas is supplied to a Pressure Swing Adsorption (PSA) unit with 89% recovery efficiency providing higher than 99.999% H₂ purity. The produced H₂ is compressed to the final delivery.

The PSA-off gas mixed with part of the natural gas is combusted in the reformer furnace to supply heat for the endothermic reforming reaction. The remaining waste heat is fully integrated in the system as shown Fig. 3 and the steam produced is sent to a steam turbine to produce electricity. In addition, part of the intermediate pressure steam is also sent to the process to meet the desired S/C ratio.

Fig. 4. Schematic description of a reference fired tubular plant for H₂ production with CO₂ capture.

The fired tubular reforming plant with CO₂ capture is the second benchmark configuration (Fig. 4) (Spallina et al., 2016). The same H₂ output and similar layout to the conventional FTR plant is used with main difference being the presence of the carbon sequestration. In this configuration, the syngas is shifted in two WGS stages (HT-and LT-WGS) to maximize the CO₂ and H₂ production. The LT-WGS reaction is performed at around 213 °C using a Cu-Zn catalyst on an Al₂O₃ support achieving CO conversions higher than 98%. Then, the H₂ rich mixture is cooled down to ambient temperature to condense H₂O, and the CO₂ is separated from the H₂ using a methyldiethanol amine (MDEA) absorption unit. MDEA as a solvent was selected considering the intermediate CO₂ partial pressure and the limited heat input for solvent regeneration. The separated CO₂ stream is then compressed and sent for long term storage. The remaining H₂-rich off-gas from the absorption unit is combusted with pre-heated air to provide heat for the reforming reaction, producing combustion products with a low CO₂ content. The rest of the H₂ rich gas is sent to the PSA for further purification.

3.2. Membrane assisted gas switching reforming (MA-GSR)

The MA-GSR concept has recently been presented by the authors (Wassie et al., 2018). The plant configuration of this new reactor concept is depicted in Fig. 5. The three stages (oxidation, reduction and reforming as depicted in Fig. 1) are simulated as steady state process units under the assumption that a cluster of dynamically cycled MA-GSR reactors can achieve sufficiently steady operation.

Specifically, the reactor operated in oxidation is fed by air (#11) while the reactor operated in reduction is fed with the retentate from the reforming stage (#5). In this configuration, a combination of steam/dry reforming occurs using natural gas, steam and recycled $\text{CO}_2/\text{H}_2\text{O}$ from the reduction stage (which also increase the CH_4 dilution to control the carbon deposition) (#4). In the reduction stage (RED), the inlet gas (mainly H_2 , CO) reacts with a metal oxide (NiO supported on Al_2O_3) to form H_2O and CO_2 (#6), which does not need any downstream separation treatment. This stream is used to pre-heat the fuel and, after H_2O condensation, compressed and sent for long term storage (#8).

In the reforming stage (REF), the reduced Ni acts as a catalyst for the SMR and WGS reactions; the produced H_2 during the REF stage permeates through the membranes and hence the methane conversion

is enhanced. The H_2 from the permeate side (#14) is cooled down to ambient temperature while producing part of the steam required for the process, and then compressed for the final use (#15).

In order to reach high pressure (50 bar), an inter-cooled air compression is adopted to avoid too high temperatures at the compressor outlet to compress air (#9) to the feeding conditions at the OXI stage. After the OXI stage, the exiting O_2 depleted air (#12) is used first to generate part of the steam required for the process and then expanded before sent to the stack (#13).

As discussed earlier, the MA-GSR concept leads to some undesired mixing between fuel and nitrogen when the gas feed is switched between the three stages (OXI-RED-REF). This effect is directly captured in the reactor simulations, thus ensuring that the resulting reduction in CO₂ capture efficiency is correctly accounted for in the process simulations.

4. Main assumptions and methodology

The procedures and the main assumptions used for the thermodynamic and economic assessment of this study have been taken from (Spallina et al., 2016; Martinez et al., 2013; Chiesa et al., 2011) and the EBTF report (Anon., 2011). From the EBTF report, assumptions regarding the heat exchangers, reactors, CO₂ compression and purification, steam cycle and turbomachines were taken.

In view of the thermodynamic analysis, each plant transfers the chemical energy input from the natural gas into H_2 , electricity, heat (as steam export) and releases some of the CO_2 to the environment, with the rest being captured and stored. To facilitate a direct comparison between the selected reference plants and the new concept, the same amount and composition of natural gas input is chosen. A high degree of heat integration is included in each plant to maximize heat extraction from all outgoing streams for the purpose of increased H_2 production, electricity production or steam generation. To quantify the plant performance, different indices have been selected based on the approach used by (Martínez et al., 2013) and are defined and explained below.

$$\text{H}_2 \text{ production efficiency } \eta_{\text{H}_2} = \frac{\dot{m}_{\text{H}_2} \text{LHV}_{\text{H}_2}}{\dot{m}_{\text{NG}} \text{LHV}_{\text{NG}}} \quad (2)$$

Fig. 5. Schematic description of the MA-GSR plant for H_2 production with CO_2 capture.

Table 2

Performance of the MA-GSR plant and comparison to the benchmark of Steam Methane Reforming with and without CO₂ capture.

Process	Benchmark	Benchmark	MA-GSR
CO ₂ capture technologies	N/A	CA-MDEA	H ₂ O cond
T _{ref} [°C]/P _{ref} [bar]/SC/P _{perm} [bar]	890/32/2.7/-	890/32/4/-	662/50/ 2.1/1
NG flow rate [kg/s]	2.62	2.81	2.62
NG thermal input [MW _{LHV,NG}]	121.94	130.79	121.94
Steam-to-carbon ratio	2.7	4	2.1
H ₂ mass flow rate [kg/s]	0.75	0.75	0.91
Electricity production/consumption			
Air compressor-Air/exh Fan [MW _{el}]	−0.68	−0.91	−5.73
Gas turbine [MW _{el}]	−	−	6.84
H ₂ compressors [MW _{el}]	−2.27	−2.28	−9.00
CO ₂ compressors [MW _{el}]	−	−2.23	−0.28
Steam turbine [MW _{el}]	3.27	3.79	−
Pumps [MW _{el}]	−0.21	−0.29	−0.03
Other auxiliaries [MW _{el}]	−0.05	−0.15	−0.09
Net electric power [MW _{el}]	0.07	−2.07	−8.29
Steam export (160 °C, 6 bar) [kg/s]	4.02	0.27	0.65
H ₂ production efficiency η_{H_2} (H _{2,LHV} /NG _{LHV})	0.74	0.69	0.89
Equivalent NG input $m_{NG,eq}$ [kg/s]	2.41	2.88	2.89
H ₂ yield [mol _{H2} /mol _{eq,CH4}]	2.49	2.48	2.97
Eq. H ₂ production efficiency $\eta_{H_2,eq}$ (H _{2,LHV} /NG _{eq,LHV})	0.81	0.67	0.81
Heat rate (HR) [Gcal/kNm ₃ H ₂]	3.24	3.79	3.05
CO ₂ specific emission E_{CO_2} [kg _{CO2} /Nm ₃ H ₂]	0.82	0.14	0.14
Equivalent CO ₂ specific emission $E_{CO_2,eq}$ [kg _{CO2} /Nm ₃ H ₂]	0.76	0.16	0.20
Eq. CO ₂ avoided (CCR _{eq}) [%]	−	79	72
SPECCA _{eq} [MJ/kgCO ₂]	−	4.57	0.02

$$\text{Equivalent natural gas flow rate } \dot{m}_{NG,eq} = \dot{m}_{NG} - \frac{Q_{th}}{\eta_{th,ref} LHV_{NG}} - \frac{W_{el}}{\eta_{el,ref} LHV_{NG}}$$

$$\eta_{th,ref} = 0.9; \eta_{el,ref} = 0.583 \quad (3)$$

$$\text{Steam export } Q_{th} = \dot{m}_{steam,export} (h_{steam@6bar} - h_{liqsat@6bar}) \quad (4)$$

$$\text{Equivalent H}_2 \text{ production efficiency } \eta_{H_2,eq} = \frac{\dot{m}_{H_2,LHV,H_2}}{\dot{m}_{NG,eq} LHV_{NG}} \quad (5)$$

$$\text{CO}_2 \text{ specific emissions } E_{CO_2} = \frac{\dot{m}_{CO_2,vent}}{\dot{m}_{H_2,LHV,H_2}} \quad (6)$$

$$\text{Equivalent CO}_2 \text{ specific emissions } E_{CO_2,eq} = \frac{\dot{m}_{CO_2,vent} - Q_{th} E_{th,ref} - W_{el} E_{el,ref}}{\dot{m}_{H_2,LHV,H_2}}$$

$$E_{th,ref} = 63.3 \left[\frac{\text{gCO}_2}{\text{MJ}_{th}} \right]; E_{el,ref} = 97.7 \left[\frac{\text{gCO}_2}{\text{MJ}_{el}} \right] \quad (7)$$

$$\text{Carbon Capture Ratio } CCR = \frac{\dot{m}_{CO_2,scr}}{\dot{m}_{NG} LHV_{NG} + E_{NG}} \quad (8)$$

$$\text{Equivalent Carbon Capture Ratio } CCR_{eq} = \frac{\dot{m}_{CO_2,scr}}{\dot{m}_{NG} LHV_{NG} + E_{NG} - Q_{th} E_{th,ref} - W_{el} E_{el,ref}} \quad (9)$$

$$\text{Equivalent Specific Primary Energy Consumption for CO}_2 \text{ Avoided } SPECCA_{eq} = \frac{\frac{1}{\eta_{H_2,eq}} - \frac{1}{\eta_{H_2,eq,ref}}}{E_{CO_2,eq,ref} - E_{CO_2,eq}} * 1000 \left[\frac{\text{MJ}}{\text{kgCO}_2} \right] \quad (10)$$

$$\text{Total energy consumption or Heat rate } HR_{tot} = \frac{\dot{m}_{NG} LHV_{NG} - Q_{th} - W_{el}}{\dot{N}_{H_2} * 22.414} \left[\frac{\text{Gcal}_{NG}}{\text{km}^3 \text{H}_2} \right] \quad (11)$$

$$\text{Cost of H}_2 \text{ COH} = \frac{(TPC * CCF) + C_{O \& M,fix} + (C_{O \& M,var} * h_{eq})}{\dot{N}_{H_2} * 22.414 * 3600 * h_{eq}} \left[\frac{\text{€}}{\text{Nm}^3 \text{H}_2} \right] \quad (12)$$

In addition to H₂, the plant can also produce net electrical plant power (the difference between electricity produced and accessories

electric consumption) and the heat output for steam import/export (Eq. (4)). Considering the electricity and heat contribution, an equivalent natural gas thermal input has been defined (Eq. (3)). This parameter represents the actual natural gas used for hydrogen production. Based on the equivalent natural gas input, other equivalent terms have been defined. These parameters provide information for proper comparison between plants that are working at different conditions.

Regarding the cost assessment, several references have been used to estimate the cost of components (Manzolini et al., 2006; Manzolini et al., 2013; Baasel, 1976; Campanari et al., 2014). The fluidized bed reactors cost has been determined based on (Peters and Timmerhaus, 2018) while the cost of the syngas coolers were determined with Aspen Exchanger Design and Rating. The standard exponential scaling law has been used to determine the equipment cost of the whole system. Each equipment cost has then been updated to the designed plant size and cost actualized based on the chemical engineering cost index. In addition to the cost estimation of components, the cost of hydrogen (COH) was also calculated to compare the selected process plants. The cost of hydrogen was determined using the methodology provided by global CCS institute (Rubin, 2012) as indicated in Eq. (12).

TPC is the total plant cost which has been determined following the procedure described in the EBTF report. The procedure is based on a Bottom-Up Approach (BUA) which involves breaking down the whole plant into basic components and adding installation and indirect costs. The COH is also computed using the first year Carrying Charge Factor (CCF) which represents the total plant cost distribution per annum over the life time of the plant. Different financial parameters (Anon., 2011; DOE/NETL, 2010) have been used to calculate the CCF of the MA-GSR plant, and was found to be 0.1533. For the CCF analysis, the fraction of loan (60%) and equity of the capital (40%) and their corresponding interests (8.5%, and 20%, respectively) have been considered as intermediate values between high and low risk investment. In addition, 3 years of construction time with three stages of instalment, operating lifetime of 25 years while the lifetime of catalysts and oxygen carrier of 5 years, inflation rate of 3%, tax rate of 35% and 20 years of depreciation were assumed (DOE/NETL, 2010; Flavio et al., 2011). As shown in Eq. (12), by multiplying the total plant cost and CCF, the incidence of the total cost in a year of production of the plant can be determined. The $C_{O \& M,fix}$ and $C_{O \& M,var}$ are the fixed and variable operating and maintenance costs, respectively, while h_{eq} is the equivalent working hours, with a plant availability assumed to be 90%.

5. Results and discussion

The discussion on the results are divided into two main parts. In the first part, the performance of the MA-GSR plant is reported and compared to the benchmarks. In the second part, the economic evaluation of the plants will be presented and discussed.

5.1. Analysis of plant performance

The energy balance and performance indices of the novel MA-GSR

and the reference plants for hydrogen production are summarized and presented in Table 2. The reforming efficiencies of the benchmark technologies are respectively 74% and 69%. This difference is due to the larger H₂O content used for the reforming (to maximize the carbon-to-CO₂ conversion) and the cost of CO₂ capture. Overall, 79% of CO₂ is captured, with a resulting SPECCA_{eq} of 4.57 MJ_{LHV}/kgCO₂.

Compared to the conventional plants with/without CO₂ capture, the new MA-GSR technology provides a higher hydrogen production

efficiency of 89%, i.e. 15–20%-points higher than the benchmarks. This is primary due to the limited amount of sensible heat in the depleted air stream from the oxidation stage. Two factors limit the sensible heat: the MA-GSR process requires only the stoichiometric amount of oxygen for autothermal reforming and the maximum temperature of all the gases in the MA-GSR never exceed the maximum temperature ($\sim 700^\circ\text{C}$) significantly reducing the sensible heat of the gases at the reactor outlet.

Since the permeate pressure of H_2 is 1 bar, high energy costs for compression are required. When all energy consumptions are taken into account, the equivalent H_2 production efficiency of the MA-GSR decreased to a value of 81%, while, in the case of the benchmark plant without CO_2 capture it increases to 81% as a result of the remaining steam to export. The equivalent H_2 production efficiency of the reference plant with CO_2 capture is also decreased by 2% which is mainly related to the energy consumption for CO_2 compression. The equivalent H_2 production efficiency of the MA-GSR concept therefore remains 14%-points higher than the benchmark case with CO_2 capture.

In terms of electricity consumption, the air compressor consumption is partly compensated by the expander production for all the cases, yet the hydrogen compressors are a substantial electricity consumer, particularly in the case of the MA-GSR. The CO_2 compressor energy demand of MA-GSR is lower in comparison to the reference system with CO_2 capture because the CO_2 is available at high pressure due to the higher reforming pressure. On the other hand, the steam export is significantly lower in MA-GSR and the reference plant with CO_2 capture compared to the reference plant without CO_2 capture. This is due to the fact that, in the case of MA-GSR, the steam produced by the waste heat is mostly consumed by the process itself while, in the benchmark case, the steam is required for the MDEA reboiler.

In view of CO_2 emissions (E_{CO_2}), the MA-GSR achieves almost similar specific CO_2 emissions compared to the conventional system with CO_2 capture. The main reason for the direct CO_2 emissions in case of the MA-GSR is the mixing of the outlet gas during the switching operation (mainly during the oxidation stage). The equivalent specific CO_2 emission is higher in the MA-GSR compared to the conventional system with CO_2 capture due to the higher net electricity consumption. Nevertheless, 72% of equivalent CO_2 avoidance can be obtained, where the remaining 28% corresponds to the electricity consumption for compressors and the direct emissions due to the gas mixing. Furthermore, the total heat rate and $\text{SPECCA}_{\text{eq}}$ are much lower in MA-GSR compared to the reference plant with CO_2 capture (0.02 vs 4.57). The low value of $\text{SPECCA}_{\text{eq}}$ indicates that using the MA-GSR would not add any additional energy penalization with respect to the conventional

H_2 production plant (in which CO_2 capture is not integrated).

As discussed earlier, the CO_2 avoidance of the MA-GSR concept can be increased by deploying longer cycle times. This will lead to lower reforming temperatures, however, requiring a larger membrane surface area for the same amount of H_2 extraction. Alternatively, a large amount of thermal mass can be included in the reactor, decreasing the rate of temperature variation shown in Fig. 2. This will allow for longer cycle times without lowering the average reforming temperature, but will also increase reactor costs.

In Table 3, the thermodynamic conditions of the streams depicted in Fig. 5 are presented for the case at 662°C reforming temperature; S/C ratio of 2.1; and 50/1 bar of feed/permeate pressure.

5.2. Economic assessment

An economic evaluation of the MA-GSR concept has been performed and compared with the benchmark technologies. The results of the economic analysis are shown in Table 4 (based on membrane cost of 7911 €/m^2). The percentage contribution of the main components to the Bare Erected Cost (BEC) has been listed. In the listing, the Total Overnight Cost (TOC) is defined according to NETL (DOE/NETL, 2010).

As can be observed in Table 4, the total overnight cost of the proposed concept is the highest compared to the reference plants. The most expensive unit of the MA-GSR plant is represented by the separation unit (membranes) with associated cost of around 48% of the BEC. As discussed earlier, due to the intrinsic dynamic operation, each reactor requires a certain number of membranes, and therefore about 60% of the membranes are not continuously operated (see the H_2 extraction rate plot in Fig. 2). This may represent a positive point for the lifetime of the membrane provided that the changes in dynamic operation (thermal and chemical cycles) would not affect the lifetime of the membrane. Nowadays, the membranes withstand temperature changes of 100°C (Fernandez et al., 2015b; Medrano et al., 2016b), while in the presence of O_2 the current state-of-the-art Pd-based membranes easily lose the Pd layer (Wassie et al., 2018; Roa and Way, 2005), indicating that the type of membrane or its composition needs to be improved. As a result, the separation unit in the MA-GSR process (membranes) is 5.3 times more expensive than the benchmark without CO_2 capture (PSA) and 2.2 times more expensive than the benchmark with CO_2 capture (PSA and MDEA).

This large membrane cost unfortunately cancels out most of the efficiency advantage of the MA-GSR concept. Specifically, the cost of hydrogen from the MA-GSR concept is 0.274 €/Nm_2^3 which is more than the benchmark reformer without CO_2 capture (0.216 €/Nm_2^3) and

Table 3
Thermodynamic data of the selected streams represented in Fig. 5.

#N	T	P	m	N	MW	Composition (Vol.%)								LHV	
	$^\circ\text{C}$	bar	kg/s	kmol/s	kg/kmol	C_2^+	CH_4	CO	CO_2	H_2	H_2O	N_2	O_2	MJ/kg	MJ/kmol
1	15	75	2.62	0.15	18.02	8.11	89	0	2	0	0	0.89	0	46.5	837.8
2	365	75	2.62	0.15	18.02	8.11	89	0	2	0	0	0.89	0	46.5	837.8
3	485	51	22.43	0.79	28.33	1.49	16.36	0.00	39.37	0.38	39.92	2.47	0.00	5.47	154.96
4	467.1	50.5	22.43	0.81	27.76	0	18.17	0.38	39.2	2.32	37.5	2.42	0	5.49	152.58
5	664.2	49.5	21.9	0.62	35.24	0	2.81	8.33	64.5	4.04	17.04	3.28	0	1.59	55.91
6	676.3	49.5	22.35	0.61	36.84	0	0	0	72.8	0	23	4.2	0	0	0
7	296.03	47	6.28	0.17	36.84	0	0	0	72.8	0	23	4.2	0	0	0
8	30	110	5.51	0.13	43.12	0	0	0	95.4	0	0	4.5	0	0	0
9	25	1.01	10.91	0.38	28.85	0	0	0	0	0	0	79	21	0	0
10	30	1.85	10.91	0.38	28.85	0	0	0	0	0	0	79	21	0	0
11	518.77	50	10.91	0.38	28.85	0	0	0	0	0	0	79	21	0	0
12	685	49.5	9.07	0.33	29.36	0	0	0	10.83	0	3.83	85.34	0	0	0
13	75.37	1	9.07	0.33	29.36	0	0	0	10.83	0	3.83	85.34	0	0	0
14	662.89	1	0.91	0.45	2.02	0	0	0	0	1	0	0	0	119.91	241.72
15	30	150	0.9	0.45	2.02	0	0	0	0	0	0	0	0	119.91	241.72
16	301.88	47	17.17	0.475	36.19	0	0	0	0.68	0	0.28	0.04	0	0	0
17	354.52	52	3.87	0.22	18.02	0	0	0	0	0	1	0	0	0	0

Table 4

Economic evaluation of the MA-GSR plant and comparison to the benchmark of Steam Methane Reforming with and without CO₂ capture.

Process	Benchmark	Benchmark	MA-GSR
CO ₂ capture technologies	N/A	CA-MDEA	H ₂ O cond
T _{ref} [°C]/P _{ref} [bar]/SC/P _{perm} [bar]	890/32/2.7/-	890/32/4/-	662/50/2.1/1
MA-GSR reactor geometry			
Reactor diameter [m]			3.5
Reactor length [m]			10
Number of reactors			5
Membrane length [m]			6
Membrane diameter [m]			0.05
Number of membranes			5984
Economic evaluation			
Bare Erected Cost [M€] (% of tot BEC)			
Reactors	10.56 (27.3%)	11.11 (18.7%)	25.13 (27.4%)
Convective cooling HEX	10.67 (27.6%)	13.27 (22.3%)	5.73 (6.2%)
Turbomachines	3.42 (8.8%)	3.7 (6.3%)	2.13 (2.3%)
H ₂ compressors	1.46 (3.8%)	1.38 (2.3%)	5.71 (6.2%)
Syngas coolers & heat rejection	4.17 (10.8%)	6.58 (11.1%)	7.70 (8.4%)
PSA unit	8.45 (21.8%)	5.9 (10.0%)	–
MDEA unit	–	14.29 (24.1%)	–
CO ₂ compressors	–	3.12 (5.2%)	0.69 (0.8%)
H ₂ membranes	–	–	44.62 (48.7%)
Total Overnight Cost x CCF [M €/y]	14.15	21.70	33.18
O&M fixed (others) [M€/y]	6.60	9.75	10.10
O&M variable (90% plant availability) [M€/y]			
Water (process + cooling)	0.63	0.82	0.36
Natural Gas	31.67	33.97	31.67
Steam export	–1.37	–0.09	–1.01
Electricity	–0.02	1.14	4.99
H ₂ mass flow rate [kg/s]	0.75	0.75	0.91
Cost of Hydrogen (COH) [€/Nm _{H2}]	0.216	0.282	0.274
COH _{variablecost} [€/Nm _{H2}]	0.129	0.150	0.124
COH _{fixedcost} [€/Nm _{H2}]	0.087	0.132	0.150
Cost of CO ₂ avoided [€/tCO ₂]		97.06	85.14
Cost of CO ₂ avoided equiv. em. [€/tCO _{2,eq}]		110.00	105.31

slightly less expensive than the reference technology with CO₂ capture (0.282 €/Nm_{H2}). Based on the thermodynamic and economic evaluation, the variable costs are higher than the fixed costs for both reference plants, especially for the case with CO₂ capture due to the high fuel cost (related to the lower efficiency). In the MA-GSR plant, the higher energy demand for compression (import of electricity) increases the operating cost, while the membrane replacement cost significantly contributes in the fixed cost (the base case is based on a lifetime of 2 years (Damle et al., 2010) and a cost recovery of 80% due to the Pd and support recycling).

Due to the large impact of membrane costs on the process

economics and the uncertainties involved in the cost and durability of H₂ perm-selective membranes in fluidized beds, a sensitivity analysis to important membrane-related assumptions is presented in Fig. 6. The figure shows that the MA-GSR plant outperforms the reference plant with CO₂ capture provided that the price of the membranes remains below 9500 €/m² (the current status of the end-user cost of a thin membrane with metallic support is 1000 \$/ft² (Damle et al., 2005), however the DOE target is the end-user cost of less than 500 \$/ft² (Damle et al., 2005)). Moreover, it is remarkable that, if the cost of membranes drops to 30% of the current price, the cost of hydrogen for the new concept would be even lower than the conventional system without CO₂ capture. It should be noted that these effects can also be achieved by future developments that increase membrane permeability so that a smaller membrane surface area is required.

Secondly, Fig. 6 shows that poor membrane durability will have a strong negative effect on process economics, especially when the membrane lifetime reduces below 1 year. Improved durability beyond the base-case assumption of 2 years only has a moderate positive effect. A high membrane recovery factor is also important to the economics of the MA-GSR process. The COH exceeds that of the conventional MDEA process if less than 70% of the membrane cost is recovered in the replacement process.

Finally, the effect of natural gas (NG) cost and the discount rate applied to the capital investment on the COH is also evaluated in Fig. 7 (the cost of imported electricity is not varied with NG cost). When the cost of NG goes from 2 €/GJ (current price of NG in Saudi Arabia is 1.18 €/GJ (IMF, 2017)) to 18 €/GJ (high fuel cost scenario), the COH increases steeply for the reference plant with CO₂ capture (with a slope of 0.016) compared to the MA-GSR (slope of 0.012) and the conventional without CO₂ capture (slope of 0.014). It is therefore clear that the high efficiency of the MA-GSR concept makes it less sensitive to high natural gas prices than the benchmarks.

Given the large capital requirement of the MA-GSR process, Fig. 7 shows a high sensitivity to the discount rate compared to the conventional process without CO₂ capture. Naturally, lower discount rates favour capital intensive, but highly efficient technologies like MA-GSR. A discount rate of only 5% brings the COH of MA-GSR within 5% of the conventional process without CO₂ capture. Such low discount rates are not impossible over coming decades, given the current record low benchmark interest rates and the potential of favourable climate policies to greatly reduce investment risks. For example, favourable policies in Germany resulted in real weighted average cost of capital in the range of 2.8–4.1% (Kost et al., 2013) for wind, utility-scale solar and biomass plants.

6. Conclusions

This work has presented a techno-economic assessment of a novel membrane-based chemical looping reforming plant, dynamically operated for hydrogen production with integrated CO₂ capture. As a new concept, it shows a high increase in the performance of the plant in

Fig. 6. Sensitivity of the COH to membrane cost (a) (at 2 years of membrane lifetime and 80% of recovery factor), lifetime (b) (at 7911 €/m² cost of membrane and 80% of recovery factor) and recovery factor (c) (at 2 years of membrane lifetime and 7911 €/m² cost of membrane).

Fig. 7. Sensitivity of the COH to natural gas price (a) and discount rate (b).

terms of reforming efficiency and CO₂ capture rate. In-situ extraction of hydrogen via H₂ perm-selective membranes also has a favourable effect on the reaction equilibrium, thereby allowing to operate the reactor modules below 700 °C. Since no external solids circulation is required (as for conventional chemical looping reforming in fluidized bed reactors), high pressure operation is relatively easy to accomplish. The modular nature of the concept can also accelerate the scale-up process as well as the possible use of the system at smaller scale where the current conventional H₂ production SMR plant results in a H₂ production cost of about 0.36–0.55 €/Nm³ (in a range of 50–190 Nm³/h), while in case of future onsite generation with electrolyzers the COH will increase to 0.53–0.85 €/Nm³ (Melaina and Penev, 2013).

The primary challenge associated with this concept is the low utilization rate of the membranes in the reactor, making the economics of the concept highly sensitive to the cost and durability of the H₂ perm-selective membranes. However, even in the base-case scenario, the MA-GSR concept returned a marginally lower cost of hydrogen than conventional steam methane reforming with CO₂ capture. It is possible that

future developments in membrane science can deliver cheaper, more permeable and more durable membranes. If a threefold reduction in the cost/permeability ratio of the membranes can be achieved, the cost of hydrogen from the MA-GSR process with CO₂ capture and compression falls below that of the conventional steam methane reforming process without CO₂ capture.

In conclusion, the MA-GSR concept can be a promising technology for future clean hydrogen production from fossil fuels, provided that significant future cost reductions can be achieved in the field of H₂ perm-selective membranes.

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Appendix A

The reactor model employed to understand the behaviour of the MA-GSR concept is based on the filtered Two Fluid Model approach (Igci et al., 2008; Holloway and Sundaresan, 2012). In this approach, the conservation equations for mass, momentum, species and energy are solved with appropriate closures for drag and reactions. This filtered approach models the presence of mesoscale structures (clusters and bubbles) occurring in fluidized beds, so that these structures do not need to be resolved on a fine and computationally expensive mesh.

The model setup is almost identical to 3D simulations of a large-scale gas switching combustion reactor performed in an earlier work by the authors (Cloete et al., 2017), and readers are referred to this work for more details. Conservation equations are rewritten in 1D space below for easy reference.

$$\frac{\partial}{\partial t}(\alpha_q \rho_q) + \frac{\partial}{\partial x}(\alpha_q \rho_q u_q) = \alpha_q S_q \quad (13)$$

$$\frac{\partial}{\partial t}(\alpha_g \rho_g u_g) + \frac{\partial}{\partial x}(\alpha_g \rho_g u_g u_g) = -\alpha_g \frac{\partial p}{\partial x} + \alpha_g \rho_g g + K_{sg}(u_s - u_g) + S_g^u \quad (14)$$

$$\frac{\partial}{\partial t}(\alpha_s \rho_s \vec{v}_s) + \frac{\partial}{\partial x}(\alpha_s \rho_s u_s u_s) = -\alpha_s \frac{\partial p}{\partial x} - \frac{\partial p_s}{\partial x} + \alpha_s \rho_s g + K_{sg}(u_g - u_s) + S_s^u \quad (15)$$

$$\frac{\partial}{\partial t}(\alpha_q \rho_q h_q) + \frac{\partial}{\partial x}(\alpha_q \rho_q u_q h_q) = -\alpha_q \frac{\partial p_q}{\partial t} + \frac{\partial}{\partial x} \left(-k_s \frac{\partial T}{\partial x} \right) + Q_{pq} + S_q^h \quad (16)$$

$$\frac{\partial}{\partial t}(\alpha_q \rho_q Y_{q,i}) + \frac{\partial}{\partial x}(\alpha_q \rho_q u_q Y_{q,i}) = \frac{\partial}{\partial x} \left(-\alpha_q D_{s,q} \frac{\partial Y_{q,i}}{\partial x} \right) + \alpha_q S_{q,i} \quad (17)$$

The present study differs in two ways: the conservation equations are solved only in one direction (1D simulations) and specialized models for axial solids mixing are included because the large-scale recirculating flow patterns in fluidized beds cannot be resolved in 1D space. These axial mixing models are outlined below in the form of an effective diffusion coefficient (D_s in Eq. (17)) and thermal conductivity (k_s in Eq. (16)) for the solids phase (Matsen, 1985; Lee and Kim, 1990):

$$D_s = 1.058(U_0 - U_{mf})d_r \left(\frac{gd_r}{U_0 - U_{mf}} \right)^{0.653} Ar^{-0.368} \quad (18)$$

$$k_s = (1 - \varepsilon)\rho_s C_{p,s} D_s \quad (19)$$

$$U_{mf} = \frac{(\sqrt{27.2^2 + 0.0408Ar} - 27.2)\mu_g}{\rho_g d_s} \quad (20)$$

$$Ar = \frac{d_s^3 g \rho_g (\rho_s - \rho_g)}{\mu_g^2} \quad (21)$$

Here, U_0 is the superficial fluidization velocity, U_{mf} is the minimum fluidization velocity, $d_r = 3.5m$ is the reactor diameter, g is the gravitational constant, ε is the bed voidage, ρ_s and ρ_g are the densities of the solids and gas phases, $C_{p,s}$ is the solids heat capacity, μ_g is the gas dynamic viscosity, and d_s is the particle size.

Other closures include the interphase momentum exchange coefficient (K_{gs} in Eqs. (14) & (15)) and mesoscale solids pressure (p_s in Eq. (15)) (Cloete et al., 2013). These closures influence the expansion of the 1D particle bed. Interphase heat exchange is described by the Gunn equation (Gunn, 1978), although thermal equilibrium between gas and solids would also be a good assumption due to the very fast heat transfer typical in fluidized beds.

The source terms at the end of Eqs. (13)–(17) are determined by the reaction rate closures implemented. Catalytic and heterogeneous reaction rates are fully described in an earlier work (Francisco Morgado et al., 2017), where the reaction kinetics are taken from works of Abad et al. (2007), Xu and Froment (1989) and Oliveira et al. (2010). Rate equations are modified with an effectiveness factor that accounts for unresolved bubble-to-emulsion mass transfer limitations (Holloway and Sundaresan, 2012). Four heterogeneous and three solid catalysed reactions are included as outlined below.

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