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Co-production of hydrogen and electricity from autothermal reforming of natural gas by means of Pd-Ag membranes

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Abstract

In this paper, the use of two Water Gas Shift (WGS) Hydrogen Separator Membrane Reactors (HSMRs) is proposed downstream of a natural gas Autothermal Reformer (ATR), for hydrogen and electricity co-production with low carbon dioxide emissions. Starting from an advanced ATR plant based on state-of-the-art technologies with carbon capture, a novel configuration is proposed. Application of HSMRs allows a significant layout simplification and the reduction of the number of components. Hydrogen separation by means of membrane reactors allows carbon capture higher than 99% compared to 87% of the reference case. Simulation results show that the membrane based power plant achieves higher equivalent fuel conversion efficiency even with a significant amount of electricity produced. Moreover, the innovative solution allows to produce electricity and hydrogen at different ratio without affecting the overall performances.

Keywords: Hydrogen production; Natural gas reforming; CCS; Selective membranes; HSMR; WGS; Autothermal reforming.

1. Introduction

Hydrogen Separator Membrane Reactors (HSMRs) allow simultaneous production and separation of hydrogen from a reacting stream. They are based on selective membranes, i.e. media with different permeability to various species. In particular, a thin Pd-Ag dense layer applied on a porous support is considered: Pd-Ag alloy is permeable only to hydrogen, leading to pure hydrogen separation, while the porous support increases mechanical strength as well as permeance. Thanks to the continuous separation of hydrogen from the reacting stream, which is at chemical equilibrium, WGS reaction advances, increasing hydrogen production beyond standard equilibrium yield.

Several studies analyze the integration of HSMRs in IGCC, Natural Gas Steam Reforming (NGSR) and Partial Oxidation (NGPO) plants, mainly in conjunction with CO_2 Capture and Storage (CCS). In this paper, the use of a

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Water Gas Shift (WGS) HSMR is proposed downstream of the Autothermal Reforming (ATR) of natural gas (NG), for the co-production of hydrogen and electricity with CCS.

2. Background and scope

A previous study [1], identified an interesting plant configuration (Fig. 1) for the co-production of hydrogen and electricity from NG, with low CO_2 emissions. Such a plant was entirely based on commercial available technologies: an oxygen blown ATR, two-step WGS for CO conversion, aMDEA-based CO_2 absorption and the following compression up to 150 bar, hydrogen purification through Pressure Swing Absorption (PSA) and delivery at 60 bar, compression and water saturation for the PSA purge gas and its use as fuel for a state-of-the-art "frame-F"-based combined cycle.. The configuration was characterized by a tight integration among the fuel conversion section, the syngas purification island and the power section. Assuming for the key parameters values aligned with the state-of-the-art of the various technologies involved, a fuel conversion efficiency of 64.3% and a net electric efficiency of 8.0% were achieved on Lower Heating Value (LHV) basis. Moreover, 86.9% of the carbon content of NG was captured and made available for geological sequestration. A second law analysis for this plat configuration showed that it was almost as much efficient as the best Fired Tubal Reforming (FTR) plant considered in the same study, with the advantage of reaching a much higher carbon capture.
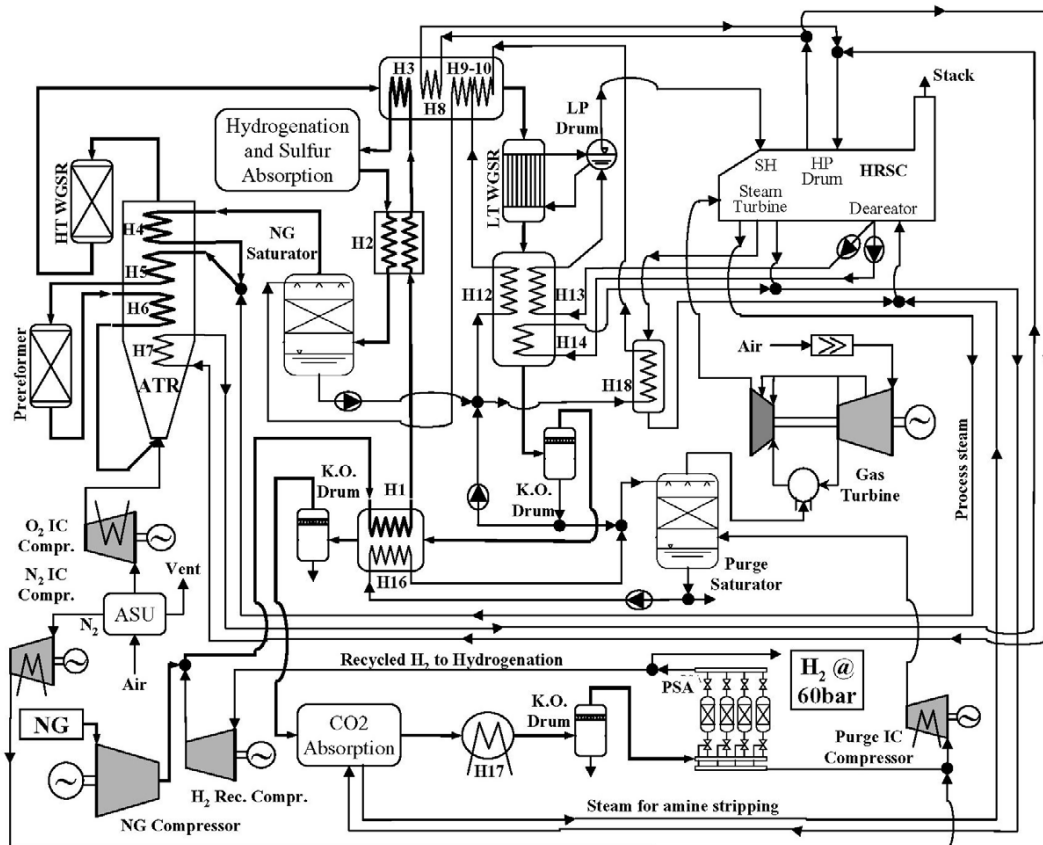

Figure 1. Schematic configuration of the reference plant [1].

These appealing performances have suggested the use of such a plant configuration as basis for further studies, and in particular for the development of innovative technologies that can replace any conventional technology adopted in the original scheme. The syngas purification island is, by far, the most complicated section of the plant, involving an aMDEA-based absorption system for CO_2 capture, the sequential compression and drying system, a PSA system for hydrogen purification and another compression system for bringing the PSA purge gas pressure at a level suitable for feeding the Gas Turbine (GT). A membrane based purification system can greatly simplify the plant layout with consequent advantages in terms of performances and capital cost reduction.

The plant configuration here proposed (Fig. 2) is based on a reforming island that is similar to the conventional solution above presented: an oxygen blown ATR converts NG into hydrogen and carbon monoxide; the oxygen is supplied by a dedicated Air Separation Unit (ASU) followed by an oxygen intercooled compressor. Heat management is carried out through an evaporative quench boiler right after the ATR, and sequential regenerative heat exchangers. Hydrogen production and separation requires three different reactors: first a conventional adiabatic Water Gas Shift reactor to increase hydrogen partial pressure and to sustain most of the heat produced from the reaction and two HSMR to separate hydrogen from the reacting stream.

The first HSMR separates pure hydrogen for the pipeline, thus it is arranged in a cross-flow configuration with no use of sweep gas, while the second one produces hydrogen to feed the GT: in this case, nitrogen taken from ASU is used, after water saturation, as sweep gas in order to limit NO_X production. Moreover, the sweep gas reduces membrane surface area and allows the extraction of almost all the hydrogen theoretically producible via WGS from the reacting stream.
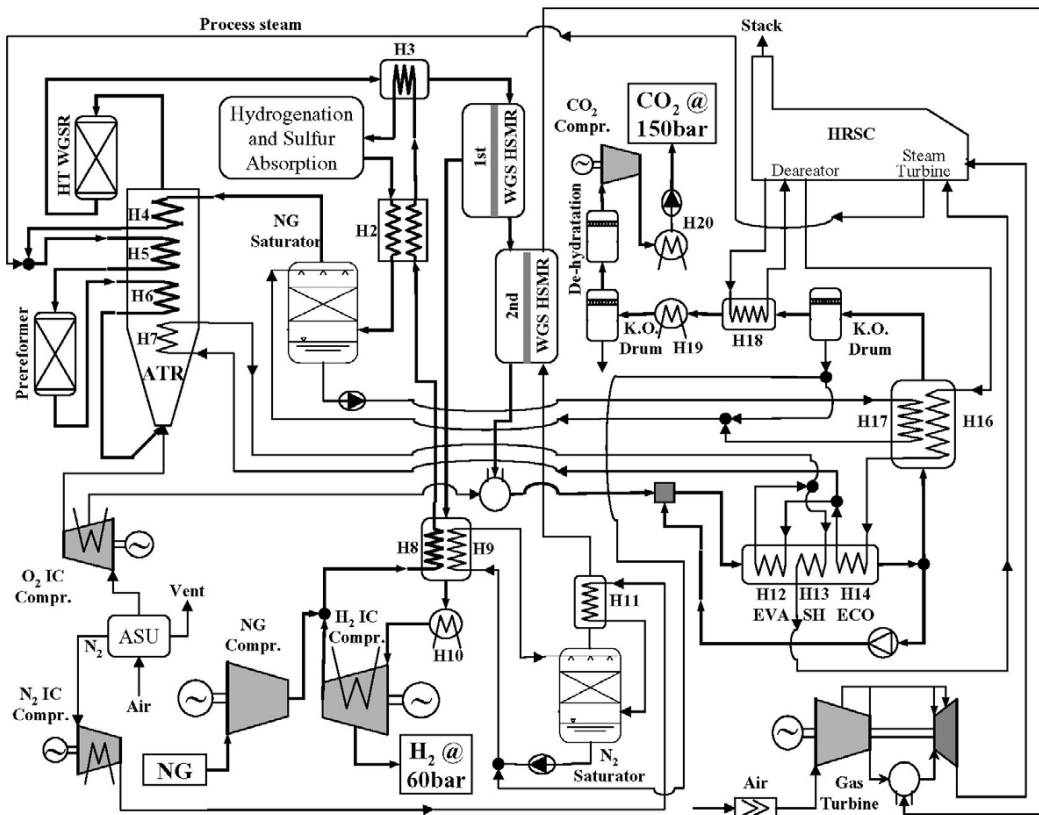

Figure 2. Schematic configuration of the membrane-based plant.

3. Plant configurations and basic assumptions

Both the original plant and the new configuration have been simulated adopting a coherent set of assumptions, in order to evaluate all the significant differences in performance due to the sole technologies. The new configuration is represented in Fig. 2 and from the NG delivery point to the first adiabatic WGS reactor is identical to the reference plant. For NG, a standard North America composition (Tab. 1) has been assumed, as well as a conventional delivery pressure of 50 bar, which is insufficient for feeding directly the fuel conversion system and needs the adoption of a compressor. In fact, the reforming pressure, set at 70 bar, has been chosen for the reference plant in order to obtain pure hydrogen from the PSA at 60 bar avoiding the hydrogen compression; for simplicity, the same assumption is taken also for the innovative case based on HSMR. Moreover, previous studies showed economic benefits for membrane based systems to work at high pressure [2,3].

In both plants, after compression, NG is mixed with a small quantity of pure hydrogen, coming from the final product stream, with the purpose of reaching a hydrogen concentration of 2% by volume in the process gas. This concentration is necessary for hydrogenation and desulphurization, which are realized by means of a catalytic process and sulfur absorption over zinc-oxide beds at 380°C. Process gas is then cooled down (in the heat exchanger H2 in Fig. 1 and 2), in order to reach a temperature suitable for water saturation. This solution has been chosen because allows recovering a significant fraction of the low temperature heat that is largely available. Water saturation adds an important amount of steam into the process gas, bringing the molar Steam to Carbon ratio (S/C)[2] in the reference and in the membrane-based schemes to 0.5 and 0.7 respectively. More is the steam added by means of water saturation, less is the steam that needs to be bled from the steam cycle with benefits on electric efficiency. The final S/C for the reference plant has been set to 2.1. This is the maximum value that can be reached without occurring in appreciable penalties from the electric generation standpoint. In fact, increasing the S/C above 2.1 implies reducing the steam superheating, with the consequent derating of the steam cycle performances. Instead, for the membrane based plant, an initial value of 1.75 is assumed; a sensitivity analysis on this parameter will be performed and presented in results section.

After water saturation, the process gas is further preheated (in H4), then mixed with the steam bled from the steam cycle, heated up to 670°C (in H5) and fed to an adiabatic prereformer. Here, some endothermic reforming reactions take place, causing an appreciable temperature drop that allows an additional heat recovery from the reformed syngas (in H6), before feeding the process gas into the ATR.

The ATR is fed with the process gas (a mixture of methane and steam, with small quantities of other species: H_2, CO, etc…) and almost pure oxygen. The flowrate of oxygen is regulated in order to achieve a prefixed value of reforming temperature, which in this case has been assumed equal to 950°C. Higher is the reforming temperature, higher is the methane conversion and the efficiency of the process. However, reforming temperature for ATRs is limited by the resistance of the catalyst that is placed immediately after the first reaction zone. In the cases considered, a quench boiler is inserted right after the ATR to quickly cool the reformate down to a temperature of about 750°C as because of, given the high values of S/C adopted, this can be acceptable.

After two regenerative heat exchangers, the reformate is sent to an adiabatic WGS reactor where most of the CO, about 60%, is converted into CO_2. From this point on, the two schemes present substantial differences.

In the conventional solution, after a first cooling section, a low temperature water gas shift reactor is required to convert the remaining CO. CO_2 as well as H_2 separations are carried out at ambient temperature with conventional technologies as aMDEA absorption and PSA. The purge gas from PSA is then mixed with some nitrogen coming from the ASU, compressed, saturated with water, and used as fuel for the GT. The cooling section required to bring the reformate at ambient temperature consists of water heating for saturators and the Heat Recovery Steam Cycle (HRSC), as well as High Pressure (HP) and Low Pressure (LP) steam generations. PSA purge gas dilution with nitrogen is necessary to limit NO_X formation in the GT combustor.

In the innovative solution, the syngas is sent to the HSMRs right after the high temperature WGS reactor: in the first, pure hydrogen is produced for the pipeline at 60 bar, while in the second a hydrogen-nitrogen-water fuel mixture is extracted to feed the GT.

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[2] Molar ratio between the total amount of water added to the process gas and its carbon content.

The backpressure of the first HSMR is set to get a H_2 minimum pressure difference across the membrane of 2 bar. This value seems to be a good compromise between the membrane surface area requirement and the hydrogen compression work for the pipeline. The most important performance parameter for a membrane reactor is the Hydrogen Recovery Factor (HRF) defined as the ratio between the quantity of hydrogen permeated and the maximum quantity of hydrogen plus the amount theoretically producible via WGS from the feeding stream. As base case, an HRF of 50% has been assumed. This, with the syngas composition resulting from the assumptions of S/C = 1.75 and 950°C for the reforming temperature, leads to a backpressure of 22 bar in the first HSMR.

On the contrary, the backpressure of the second HSMR is fixed by GT combustor. For this reason, assuming a fuel overpressure of 50%, the backpressure is 23.25 bar. Sweep gas flowrate has been set to limit the molar fraction of hydrogen in the fuel mixture at 50%, value that implies a stoichiometric flame temperature compatible with an acceptable NO_X production [8]. The HRF for the second membrane reactor is calculated in order to have a H_2 minimum pressure difference of 2 bar.

The retentate stream, rich in CH_4 (molar concentration is about 10%), CO_2 and H_2O, with some H_2 and CO, is combusted using O_2 bled from the same oxygen compressor that supplies the ATR. Such a stream still presents an appreciable energy content, and its combustion in almost pure O_2 is very important for the system efficiency, as well as for the CO_2 quality. Flue gas, mainly a mixture of CO_2 and water, is gas quenched to about 1200 – 1300°C by means of a flue gas recirculation. This solution aims to balance the HP steam production and superheating outside the Heat Recovery Steam Generator (HRSG), since the maximum temperature of gas admissible for superheaters has been assumed at 1000°C. Recirculated gas is split from the main flow after a first stage of feedwater preheating, just before reaching the mixture dew point. The condensation of syngas water content releases a large amount of heat, which is recovered heating up steam cycle feedwater and the water for the NG saturator. Condensate recovery produces an excess of hot water with respect to the needs of makeup for the two saturators. After cooling down to 35°C and water knock-out, the CO_2 stream is dehydratated, compressed, liquefied and pumped to the pressure of 150 bar.

4. Methodology

Heat and material balances have been estimated by a computer code (GS³) developed at Department of Energy - Politecnico di Milano, which is capable to assess performances of gas/steam cycles for power production [4-7]. All chemical reactions have been simulated with the chemical equilibrium approach. Full equilibrium has been assumed at the exit of the ATR and for the WGS, reaction, while the conversion of CH_4 in the pre-reformer has been limited in order to obtain an approach difference in temperature with respect to the adiabatic equilibrium situation of 10°C. At the selected reforming conditions, low CH_4 conversions are reached at the ATR exit, this is mainly due to the high reforming pressure that has been assumed. The base case of the innovative configuration reaches a CH_4 conversion of only 80%.

NG specification is based on the pipeline quality gas from Canada and north USA reserves [9]. Oxygen is produced in a stand-alone ASU with a purity of 98% (with 0.67% N_2 and 1.33% of Ar) at atmospheric pressure. ASU has been modeled as a black-box splitter with a fixed power demand of 0.295 kWh/kg of pure O_2.

The sizes of plants, i.e. the flowrates of NG, have been determined case by case in order to maintain GT at full load. Power island is based on the same GT considered in the original work [1]: a GE 7FA calibrated on 2003 performances. Hydrogen mixtures are fuels with low volumetric heat values and their use to feed a gas turbine imposes the reduction of air flow at compressor inlet in order to limit the increase in pressure ratio and prevent exceeding stall limits. Our off-design simulations of GT is based on the assumption of constant pressure ratio and lower air flow: a solution that is somewhat intermediate between what is most desirable - constant air flow, higher pressure ratio - and most unfavourable - lower air flow and lower pressure ratio. Moreover, the combusted gases produced by hydrogen mixtures impose more severe working conditions for the turbine than in normal cycling, due to higher heat transfer coefficients. With the same Turbine Inlet Temperature (TIT), a higher coolant flow is

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³ This code treats all material streams assuming the models of ideal gas and ideal condensate respectively for all gas, condensate and mixture streams, with the exception of pure water/steam whose thermodynamic properties are evaluated according with IAPWS97 routines.

consequently required. Our code accounts also for this effect, but the feasibility of increased cooling flows should be verified.

CO_2 compression section, simulated with Aspen Plus™[4], consists of a compressor, a glycol-based dryer and a pump. In the reference plant an intercooled compressor is required, and CO_2 dehydratation takes place at an intermediate stage; in the innovative plant CO_2 mixture is already available at a pressure of about 60 bar, thus it is firstly dehydratated and then compressed in a single stage - radial compressor. In both cases liquefaction takes place at 90 bar, 20°C, and a small chiller is accounted for this purpose. A pump brings CO_2 pressure up to 150 bar, ready for delivery. In the reference plant the total electric consumption for CO_2 absorption and compression was 440 kJ/kg of pure CO_2, while in the innovative plant the CO_2 compression section presents a total electric consumption of about 32 kJ/kg of pure CO_2.

Main calculation assumptions are reported in Table 1.

Table 1. Main calculation assumptions.

ATR			ASU and oxygen compressor	
Reforming temperature, °C	950		O_2 purity, %$_{vol.}$	98.0
Reforming pressure, bar	70.0		Electrical consumption, kWh/kg of pure O_2	0.295
S/C ratio	1.5 - 2.1		Pressure of O_2 and N_2 delivered by ASU, bar	1.05
Pressure drop, %	4.0		Polytropic efficiency of O_2 compressor, %	82.0
ΔT at exit, due to thermal losses, °C	4.0		O_2 maximum temp. during compression, °C	210
Pre-reformer			**Gas Turbine GE 7FA (2003 nominal data)**	
ΔT chemical approach, °C	10.0		Air flow, kg/s	432
Pressure drop, %	2.0		Pressure ratio	15.5
ΔT at exit, due to thermal losses, °C	2.0		Total Inlet Temperature (TIT-our estimate), °C	1316
Hydrogen Separator Membrane Reactor (HSMR)			Power output, MW	171.7
Minimum H_2 pressure difference, bar	2		Net electrical efficiency, %$_{LHV}$	36.2
Heat Exchangers			**Steam Cycle**	
ΔT pinch point for evaporator, °C	10		Steam evaporation pressures (HP/IP/LP), bar	130-140/30/4
ΔT$_{min}$ for gas-liquid heat transfer, °C	15		SH and RH temperature, °C	565
ΔT$_{min}$ for gas-gas heat transfer, °C	30		Condensation pressure, bar	0.05
ΔT$_{min}$ for humid gas - dry gas heat transfer, °C	20		**Other assumptions**	
ΔT$_{min}$ for humid gas - water heat transfer, °C	5		N_2 compressor polytropic efficiency, %	85.0
Pressure drop gas stream, %	0.5		Fuel compressors polytropic efficiency, %	77.0
Pressure drop water stream, %	2-4		Fuel maximum temp. during compression, °C	210
Thermal losses, % of heat transferred	0.7		Pumps hydraulic efficiency, %	75.0
CO₂ compression			Motor drivers electric-organic efficiency, %	94.0
Final delivery pressure, bar	150		Generator efficiency, %	98.7
Temp. for CO_2 liquefaction (@90 bar), °C	20		BOP electric autoconsumption / heat released to the environment, %	1.5
Compressor isentropic eff. (single group), %	82.0			

Natural gas composition (by volume): CH_4 94.9%; C_2H_6 2.5%; C_3H_8 0.2%; C_{4+} 0.1; CO_2 0.7%; N_2 1.5%. LHV 47.6 MJ/kg.

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[4] This commercial code offers several models for the evaluation of thermodynamic properties. In our simulations, Peng-Robinson equation of state has been used, assuming default values for the binary interaction parameters.

Comparisons among the two plants in the different conditions considered are performed on the basis of three LHV-based indexes: electrical efficiency (η_{el}), fuel conversion (η_{H2}) and equivalent fuel conversion efficiency (η_{eq}), given respectively by:

$$\eta_{el} = \frac{P_{el}}{\dot{m}_{NG} \cdot LHV_{NG}} \tag{1}$$

$$\eta_{H2} = \frac{\dot{m}_{H2} \cdot LHV_{H2}}{\dot{m}_{NG} \cdot LHV_{NG}} \tag{2}$$

$$\eta_{eq} = \frac{\eta_{H2}}{1 - \eta_{el}/\eta_{el,std}} \tag{3}$$

Equivalent fuel conversion is defined by splitting the NG consumption into a quota chargeable to electric production and the remaining part to hydrogen. The first contribution is calculated assuming a standard electric efficiency ($\eta_{el,std}$) for power plants with carbon capture, while the second contribution is calculated by difference (this is coherent with the fact that considered plants produce mainly hydrogen rather than electricity). The value of 47% has been taken as standard electric efficiency. It corresponds to the performance of a combined cycle based on the same GT turbine considered, decreased by an efficiency penalty of ten percentage points, which is typical of conventional post-combustion technology with 85% of carbon capture [10]. This assumption has a strong influence on final results and while it is quite suited for the evaluation of the reference plant (i.e. carbon capture ratio of 86.9%), it penalizes the innovative plant that achieves an appreciable higher carbon capture (above 99%).

5. Results

Energy balances for the two solutions are reported in Table 2. Reference plant requires a higher thermal input of about 50% to fuel the GT compared to the innovative solution proposed: the amount of hydrogen remaining in the syngas after PSA is much lower than the amount left by the first HSMR, which has a 50% HRF. The membrane-based plant converts much more fuel into electricity and consequently produces less hydrogen than the reference plant. The costs for producing more electricity are represented by higher electric consumptions of the oxygen production and compression, and other auxiliaries. Moreover, the membrane technology requires an hydrogen compressor, but implies significant savings for CO_2 compression, which more than compensate the hydrogen compression work.

Although the great difference in terms of hydrogen and electricity outputs of the plants, similar equivalent fuel conversion are achieved. This behavior can be explained by the high quality of thermal integration and heat recovery performed in the innovative plant.

A sensitivity analysis on S/C ratio as well as the amount of hydrogen separated in the first HSMR is carried out. Results are summarized in Fig. 3.

Increasing S/C ratio increases methane conversion in the ATR and, consequently, the hydrogen yield (at higher S/C ratio, curves move towards higher hydrogen production percentage). The same results can be achieved also by increasing the amount of hydrogen separated in the first HSMR (HRF from 45 to 55% are investigated). However, the η_{eq} is only significantly affected by S/C ratio: the variation of the amount of hydrogen separated in the first HSMR has almost no consequence on it. Another interesting result is the maximum of η_{eq} at 50% HRF for

Tab. 2 Thermodynamic results

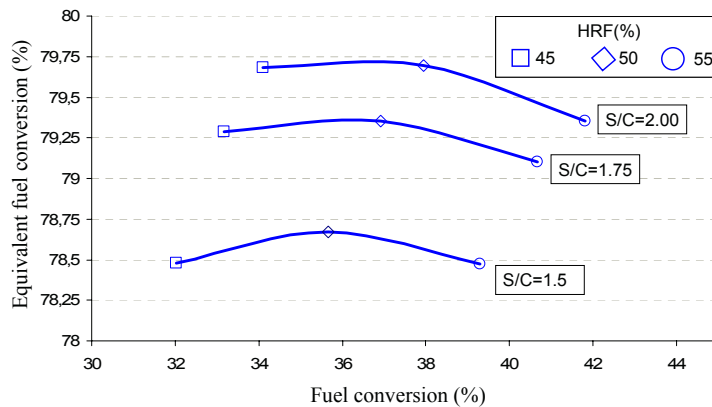|	Reference Plant	Membrane-based plant
S/C	2.1	1.75
NG input, MW$_{LHV}$	1913.5	1237.9
Electric balance as NG input percentage		
GT output	10.0	15.9
ST output	4.9	17.9
CO_2 compression	-2.1	-0.2
H$_2$ compression	-	-0.6
ASU + O$_2$ comp.	-3.0	-4.8
Other auxiliaries	-1.7	-2.2
Net electric output (η_{el})	8.0	25.1
Hydrogen prod. (η_{H2})	64.3	36.9
$\eta_{eq.}$	77.6	79.4
Carbon Capture Ratio	86.9	100.0

Figure 3. Performances of the membrane-based plant for different S/C values and various HRF of the first HSMR.

each case analyzed. This means that the innovative plant proposed, beyond its higher simplicity, is at least as flexible as the reference plant that has the very same trend: hydrogen and electricity can be produced at different ratio without significantly affecting equivalent fuel conversion efficiency.

6. Conclusions

This work compares two different plants for co-production of electricity and hydrogen: the first is based on commercial available technologies, while the second integrates in the fuel conversion section two innovative WGS HSMRs for simultaneous hydrogen production and separation. Membrane-based purification system simplifies the plant layout leading to potential advantages in terms of capital cost reduction.

Results show that the membrane based power plant achieves higher equivalent fuel conversion efficiency even with a significant amount of electricity produced. Moreover, the innovative solution allows to produce electricity and hydrogen at different ratio without affecting the overall performances.

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