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Efficient low CO_2 emissions power generation by mixed conducting membranes

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Abstract

This papers aims at the performance assessment of large scale, natural gas fired power plants where O_2 and H_2 separation membranes developed inside the DEMOYS project are implemented to make pre-combustion CO_2 removal less energy demanding and more cost effective. Three different plant configurations are considered. Their heat and mass balance have been simulated and performance compared versus those achievable by equivalent plants based on commercially available technologies.

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Keywords: natural gas, combined cycles, pre-combustion CO_2 capture, steam reforming, oxygen separation membranes, hydrogen separation membranes

1. Introduction

The integration of gas separation membranes in the energy sector has been actively investigated in the recent years because it has the potential to provide novel plant configurations that achieve improved performance at lower investment costs than conventional designs. In particular, carbon capture is probably the most promising application of membranes in the energy sector. Therefore extensive research programs finalized to CCS focused on different membrane technologies, able to permeate different chemical species, relying on different transport mechanisms and operating at different temperatures.

DEMOYS (Dense Membranes for Efficient Oxygen and Hydrogen Separation) is a project co-financed by the European Commission run by a consortium, led by RSE, joining 15 partners from 6 European countries. The project essentially aims at the development of thin mixed conducting membranes for O_2

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and H_2 separation by using a new deposition technique "Plasma Spraying – Thin Film" (PS-TF) in combination with nano-porous, highly catalytic layers. In the frame of the activities of the DEMOYS project, Politecnico di Milano and Foster Wheeler Italiana are in charge of performance assessment and economic evaluation of large scale plants implementing these kinds of membranes. To this purpose, they accomplished (in collaboration with the Institute of Power Engineering of Poland) an accurate literature review to map all the possible options to implement membranes developed by DEMOYS in coal and natural gas fired plant, both for power generation or hydrogen production. This paper presents a portion of the results achieved in the analysis carried out, specifically the part focusing on natural gas fired power plants.

Oxy-combustion of natural gas can be adopted as an option to exploit the oxygen separation membranes in future power generation plants with CO_2 capture. The configuration based on OTM (Oxygen Transport Membrane) most widely assessed in literature is the AZEP (advanced zero emission power plant) concept, essentially an externally fired gas turbine cycle [1,2]. The main drawback of this configuration lies in the requirement of high temperature ceramic heat exchanger in order to attain temperatures at turbine inlet high enough to fully exploit the capabilities of state-of-the-art combustion turbines. To overcome this hurdle, different configurations have been proposed. For instance Yantovski and co-authors [3] proposed a plant where a CO_2 stream flows as sweep gas on the permeate side of an OTM and collects oxygen. The CO_2/O_2 stream is used as oxidant in a natural gas combustor which produces a high temperature flow which is expanded in a turbine. In this way, the maximum cycle temperature is no longer restricted by the heat exchanger limit but only by the turbine limit, with consistent advantages in term of efficiency. However, in this case the turbine expands almost pure CO_2 hence requiring a completely new design. The development of ceramic heat exchangers and CO_2 turbines poses additional feasibility issues to the ones related to the manufacture of the membrane module. For this reason, the implementation of OTM in oxyfuel combined cycle has not been considered in the DEMOYS project, that instead only deals with pre-combustion CO_2 removal.

With a focus limited to natural gas fired combined cycles with pre-combustion CO_2 capture, the paper therefore aims to set up a performance comparison based on homogeneous assumptions of plant configurations implementing membranes versus arrangements based on commercially available technology.

2. Plant configurations

A wide spectrum of plant configurations has been simulated to evaluate the benefits deriving from the integration of high temperature, mixed conducting O_2 or H_2 separation membranes into power generation plants and to provide input for process scale-up and cost assessment. Reference is made to power plants based on F class, ~260÷280 MW gas turbine. Plant configurations considered for the analysis are illustrated in the following.

2.1. Oxygen Separation Membrane Permeator + ATR with CO2 capture (OMAR).

The plant flow diagram of this configuration is shown in fig. 1. It can be conceptually divided into the four following sections:

1) A natural gas treating section where NG is first hydrogenated to convert organic sulfur to H_2S, then desulfurized in a zinc oxide bed and finally moisturized in a column where natural gas is in direct contact with water heated up by using low-grade heat from syngas cooling or HRSG.
2) A hydrogen production section where a CO/H_2 rich stream is first produced by methane steam reforming in an oxygen blown, nickel-based catalytic autothermal reactor (ATR). The ATR is preceded by pre-reformer where a similar catalyst decomposes complex hydrocarbons to avoid cracking in the main reactor and to feed it with a uniform stream independently of the composition of the primary feed-

stock. The adoption of a heat exchange catalytic pre-reformer is suggested by thermodynamic and operational reasons: achievement of the highest conversion efficiency is critical in a competitive electric market and, being the pre-reforming process endothermic for natural gas, it allows an efficient recovery of high temperature heat released by cooling syngas exiting the ATR. Pre-reformer operating temperature is usually set according to pressure and charge composition in order to respect strict limits about catalyst deactivation and carbon deposit. In this case, an outlet temperature of 700°C was assumed, according to industrial practice [4]. Syngas produced by steam reforming has an elevated concentration of carbon monoxide and it is therefore treated to promote water gas shift (WGS) reaction that allows reallocating the heating value of syngas to hydrogen and eventually produce a carbon-free fuel. Since the WGS reaction is favored at low temperature, it is convenient to carry out the overall process in a two-stage process with intermediate cooling.

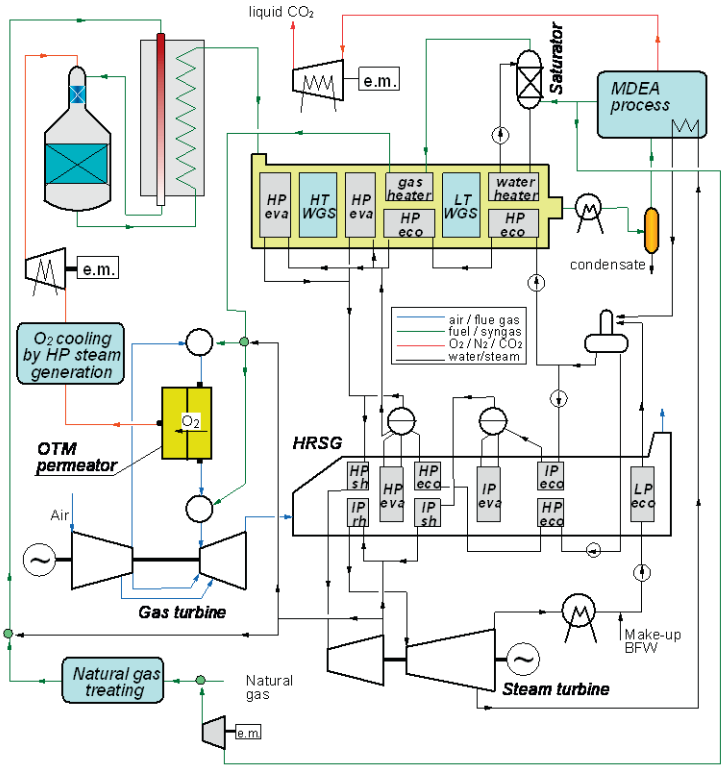

Fig.1 – Plant flow diagram of the OMAR configuration.

3) An oxygen production and compression system. The plant integrates a membrane permeator that produces the oxygen for the ATR. The air stream at the gas turbine compressor outlet is heated up to the operating temperature of the membrane (850°C) by burning a fraction of the H_2 rich syngas in a combustor placed before the permeator. Oxygen is extracted on the permeate side without any sweep gas at a pressure of 1.05 bar. It is cooled down to ambient temperature by recovering heat for steam production and it is sent to an intercooled compression train that takes it to the pressure required to feed the ATR.
4) A CO_2 island where carbon dioxide is separated from the H_2-rich syngas by means of a MDEA-based absorption process. In the process a significant flow rate of LP steam is used to provide heat for

MDEA regeneration that is partly accomplished by thermal stripping. The CO_2 is recovered at the stripper outlet at 1.1 bar, with more than 99% purity (dry basis). No additional purification process is therefore needed and the stream is simply dehydrated and taken to the delivery pressure (150 bar).

5) A power island where decarbonized fuel is burned in an advanced combined cycle. The current gas turbine technology does not allow burning the H_2 rich syngas in premixed combustor so that additional dilution of the hydrogen fuel is required to achieve an acceptable value for NO_X emissions. In this plant configuration, dilution can only rely on steam mixing given that no pure nitrogen stream is available in the plant. IP steam is therefore derived from the steam turbine to take the stoichiometric adiabatic flame temperature to 2300 K assumed as acceptable value for NO_X emissions.

2.2. Oxygen Separation Membrane + CPO with CO_2 capture (OMCR)

This configuration includes a catalytic partial oxidation (CPO) reactor instead of an ATR. Working principles of the CPO are actually exactly the same as the ATR, with the difference that all the reactions occur in heterogeneous phase. Therefore a CPO reactor does not have the typical burner of the ATR technology and the charge (hydrocarbons, oxidizer and optionally steam) is directly sent to the catalytic zone where the following reactions take place at the same time: partial and complete combustion, methane steam reforming, water gas shift. Catalysts used for CPO are usually based on noble metals (Pt, Pd, Rh, Ir) [5] and allow a very short contact time (in the range 0.1÷10 ms) which turns out in high space velocity and the possibility to design very compact reactors that is the main advantage sought by developing this technology. In theory, a CPO reactor can be used also in combination with an OTM permeator like in the previous configuration, but significant advantages can be achieved by integrating an OTM membrane in a CPO reactor, as shown in the figure 2.

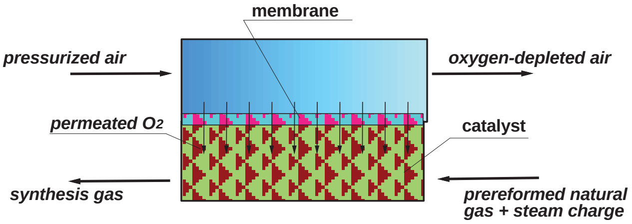

Fig.2 – Schematics of the Oxygen Transport Membrane Catalytic Partial Oxidizer implemented in the OMCR configuration.

In this case O_2 partial pressure on the permeate side is virtually zero since permeated O_2 promptly reacts with the methane / steam charge to produce hydrogen. This greatly enhances O_2 permeation and allows drastically reducing the membrane surface (and consequently its cost). Moreover, compared to the OMAR configuration, two main advantages can be attained in term of electric efficiency. First, pure oxygen compression is not needed, leading to reduced equipment and parasitic energy consumption. Then, oxygen is mixed to reactants at high temperature, so that less methane is burned to achieve the required temperature at the reactor exit. The resulting cold gas efficiency is higher, meaning that more energy is available to the gas turbine combustor. The combined result is that efficiency grows by about 1.2 points. One point to outline is that in the OMCR case, the operating temperature of the membrane is the same of the reactor and we arbitrarily assumed that the membrane can operate at 1050°C to maintain the same reforming reactor outlet temperature of the previous case.

2.3. ATR + Hydrogen Separation Membrane Reformer with CO_2 capture (ARHS)

In this plant configuration the reforming reactor in split in two parts as illustrated in fig. 3. Placing a hydrogen separation membrane reactor (HSMR) after the ATR allows moving toward products equilibrium of steam reforming and water gas shift reactions. The main advantage arising from this configuration is that ATR can operate at a lower S/C ratio, since the HT-WGS reactor (which sets specific limits on the S/C) is no more required just because of the enhancement of the WGS reaction achieved inside the HMSR. To make easy H_2 permeation through the membrane, steam reforming is carried out at higher pressure (58 bar) than in the previous cases and a sweep gas is flowing on the permeate side. The sweep gas is produced by burning a fraction of the fuel stream separated in the cryogenic separation unit with a stoichiometric amount of air as to avoid having oxygen on the reactor permeate side. Nitrogen from the ASU and additional steam are mixed to the sweep stream to increase dilution and moderate the combustion temperature to the operating condition of the HSMR (850°C). It is worth noting that in this case no significant heat exchange is required in the membrane reactor. Therefore membrane operations appear less challenging than in most of the alternative HSMR arrangements proposed in the literature, where heat transfer surfaces are needed in the membrane module [6-7] or the heat to sustain the steam reforming reaction is exchanged through the membrane itself [8-9].

The stream exiting the membrane feed side (retentate stream) is first cooled, treated in a low temperature shift reactor to further increase CO conversion and expanded to recover energy before the CO_2 separation unit. Thanks to H_2 removal, the CO_2 concentration is higher than in the previous configurations illustrated so that CO_2 separation can conveniently be accomplished in a cryogenic separation unit with a lower energy cost than a MDEA process.

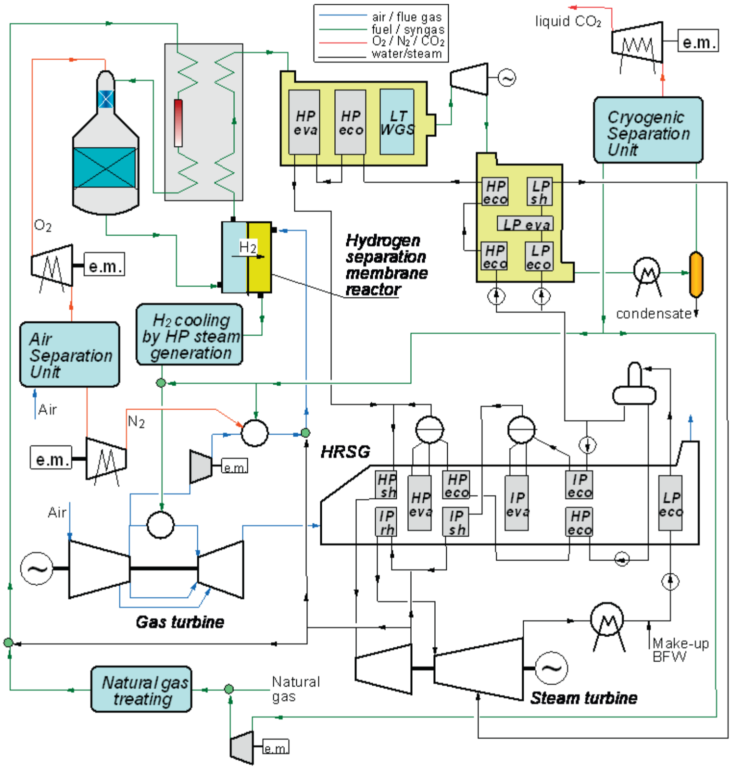

Fig.3 – Plant flow diagram of the ARHS configuration.

2.4. Reference plants without membranes.

Three more plant configurations without membranes integration have been considered as terms of comparison:

- CAAR (Cryogenic ASU + ATR with CO_2 capture) has a plant configuration similar to the OMAR, except that oxygen for reforming comes from a cryogenic air separation unit rather than the oxygen permeator. The considerable flow rate of nitrogen available (at zero energy cost) from the ASU, is compressed and used to dilute the H_2 fuel for NO_X prevention, reducing the efficiency decay compared to steam dilution. This configuration represents the most direct comparison term for the membrane base configurations considered before.
- ABAR (Air Blown ATR with CO_2 capture) relies on a process similar to the previous cases, except that the O_2 required for autothermal reforming is provided by adding air rather than pure oxygen. Intrinsic advantage of this solution is that it allows removing the ASU, an expensive ancillary plant in terms of energy and economic requirements. On the other hand, this solution suffers from some drawbacks. The most important is that much more steam is drawn from the steam turbine to comply with the limits imposed by the HT-WGS operations. A steam to carbon (S/C) ratio of 2.98 (vs. 1.94 of the CAAR case) in the reforming input charge was set to comply with a minimum steam to dry gas ratio of 0.5 at the inlet of the high temperature WGS reactor. This large steam to carbon ratio also brings about that an operating temperature of 950°C is enough to attain a good methane conversion in the ATR and optimal for plant efficiency. Additional disadvantages of the ABAR configuration are lower cold gas efficiency of the reforming process, and a lower concentration of the CO_2 in the stream sent to the AGR unit that slightly increases the energy consumption for CO_2 separation.
  Plant flow diagram of this configuration is essentially the same previously described by the same authors in [10]. The more conservative assumption on the steam to dry gas in the HT-WGS gives explanation of the different performance compared to the previous work.
- NGCC (Natural Gas Combined Cycles) has been finally considered as reference technology of the power generation plants without CO_2 capture.

3. Results

The energy balance and the main results of the simulations are reported in Table 1. In order to merge the results on electric efficiency and specific emissions, the specific primary energy consumption for CO_2 avoided (SPECCA) [11] has been calculated by eq.1:

$$\mathrm{SPECCA}\left[\frac{\mathrm{MJ}}{\mathrm{kg}_{\mathrm{CO2}}}\right]=\frac{\left(\frac{1}{\eta}-\frac{1}{\eta_{\mathrm{ref}}}\right)\times 3600}{E_{\mathrm{ref}}-E} \qquad (1)$$

where η is the net electric efficiency of system and E is the CO_2 specific emission (kg_{CO2}/MWh_{el}) of the system with CO_2 capture, while subscript (ref) refers to the reference natural gas fired combined cycles without CO_2 capture.

For the power plants using pre-combustion CO_2 capture commercial technologies, electric efficiency penalties of 12-12.5% points have been calculated, with 88-91% reduction of specific emissions with respect to the natural gas-fired combined cycle (NGCC) without CO_2 capture. The CAAR case, which adopts an O_2-blown ATR, shows a 0.5 percentage point advantage in efficiency with respect to the air-blown ATR-based ABAR case. This difference is mainly due to the higher S/C and the consequently lower steam turbine power output, which is only partly compensated by the avoided consumptions for oxygen production by cryogenic air distillation. Such a high S/C is the consequence of the 0.5 steam to dry gas ratio assumed at the HT-WGS inlet, which penalizes the cases based on air-blown ATR, where the syngas dilution with N_2 lead to higher dry gas flow rates per kg of natural gas processed.

The adoption of the OTMs leads to improved electric efficiencies in both the OMAR and the OMCR layouts (+1.5 and 2.7% points with respect to CAAR), thanks to the avoided electric consumption of the cryogenic ASU and to the good thermal integration in the gas turbine cycle. The CPO-based OMCR plant shows the highest efficiency (+1.2% points vs. OMAR), due to the avoided consumption for O_2 compression and the better thermodynamic integration, in which pure O_2 is consumed at high temperature within the membrane module. The prompt consumption of the oxygen permeated is also beneficial for the membrane area, since it leads to minimum Δp_{O2} between the two sides higher than the permeation only OTM. Both OTM-based plants allow reducing CO_2 specific emission by almost 90%. As a result, SPECCA of 3.8-4.4 MJ_{LHV}/kg_{CO2} are obtained, 15-30% lower than the reference cases.

The ARHS case, based on HTM technology, shows the best performance among all the cases assessed. A net electric efficiency of 49.7%, with 87% of CO_2 avoided and SPECCA of 3.4 MJ_{LHV}/kg_{CO2} have been obtained. Such good performance is mainly due to the high gross power output and the low consumption for CO_2 separation and compression, which is based on a cryogenic process delivering high pressure CO_2 to the final intercooled compressors. Such values compensate the parasitic consumption associated to O_2 production.

Table 1 Results of the simulations of the plants assessed.

	NGCC	ABAR	CAAR	OMAR	OMCR	ARHS	ABAR, TIT–	ARHS, TIT–
ATR/CPO temperature, °C		950	1050	1050	1050	923	950	923
S/C ratio at pre-reformer inlet		2.97	1.9	1.9	2.0	1.5	2.97	1.5
Min. feed-permeate $\Delta p_{O2/H2}$, bar				1.39	2.30	3.84		3.84
Membrane feed temperature, °C				850.0	1049.9	923.2		923.2
Membrane retentate temp., °C				850.0	1049.9	850.1		850.1
Gas turbine TIT, °C		1360	1360	1360	1360	1360	1261	1261
Gas turbine gross power, MW	277.2	301.8	325.3	304.4	302.4	322.6	248.9	267.8
Gas turbine auxiliaries, MW	-5.25	-5.72	-6.16	-5.77	-5.72	-6.11	-4.72	-5.07
Steam turbine gross power, MW	143.9	110.6	120.0	128.3	122.9	162.2	97.8	144.9
ASU, MW			-17.83			-19.63		-17.38
Air booster compressor, MW		-10.49				-1.40	-9.24	-1.24
Syngas expander						3.30		2.92
N_2 compressor, MW			-19.25			-30.10		-26.63
O_2 compressor, MW				-8.00		-1.31		-1.16
H_2 compressor, MW		-0.04	-0.02	-0.03	-0.02	-0.12	-0.03	-0.11
MDEA plant auxiliaries, MW		-4.68	-4.66	-4.73	-4.64		-4.14	
CO_2 compression, MW		-15.00	-14.96	-14.74	-14.88	-5.57	-13.27	-4.93
Steam cycle pumps, MW	-1.70	-3.64	-3.72	-3.56	-3.62	-4.01	-3.28	-3.56
Aux. for heat rejection, MW	-1.89	-1.94	-1.79	-1.79	-1.60	-1.93	-1.77	-1.81
Net electric power, MW	412.3	370.9	376.9	394.1	394.7	417.9	310.3	353.7
Thermal input, MW_{LHV}	709.9	814.6	818.2	829.4	809.9	840.3	720.3	743.7
Cold gas efficiency, %		92.10	91.57	91.9	94.45	89.84	92.11	89.84
Net electric efficiency,%	58.08	45.53	46.06	47.52	48.74	49.73	43.07	47.56
Carbon capture ratio, %		92.56	90.28	90.32	90.28	88.95	92.57	89.20
Specific emission, g_{CO2}/kWh_e	353.9	32.9	42.5	41.0	40.1	44.7	34.7	45.7
CO_2 avoided, %		90.7	88.0	88.4	88.7	87.4	90.2	87.1
SPECCA, MJ_{LHV}/kg_{CO2}		5.32	5.20	4.40	3.79	3.37	6.77	4.45

All the cases presented have been calculated considering a high TIT (1360°C), in line with state-of-the-art natural gas-fired F-class machines. Such a calculation should be considered as representative of a future scenario, where a sufficiently wide market of H_2-fired turbines will justify dedicated development of these machines. Thus, additional calculations have been carried out for the ABAR and the ARHS layouts, considering a more conservative assumption, typical of today syngas and H_2-fired turbines which are essentially adaption from natural gas designed machines. An efficiency penalty of over 2% points has been obtained with respect to the high TIT plants, leading to an increase of the SPECCA index of about 30%.

4. Conclusions

Three plant layouts based on high temperature mixed conducting membranes for O_2 and H_2 separation have been assessed in this work and compared to reference pre-combustion CO_2 capture plants based on conventional technologies. The calculations showed that the integration of membranes may lead to very interesting advantages in terms of improved efficiency and lower energy penalties for CO_2 avoidance.

The integration in a CPO reactor seems the best option for OTMs, thanks to the optimal thermodynamic integration of the O_2 production and utilization processes. In addition, the lowest membrane area are expected in this case, thanks to the prompt consumption of the permeated O_2 and its virtually zero partial pressure on the permeate side.

The integration of hydrogen membranes after an O_2-blown ATR represents the highest efficiency solution assessed in this work. An electric efficiency of 49.7%, about 4% points higher than the reference plants, and a SPECCA index of 3.4 MJ_{LHV}/kg_{CO2} have been obtained.

The importance of a proper development of high performance H_2-fired turbines has been highlighted by the calculations. Such a development, which can be expected if a sufficient market subsists in the future, is of primary importance to have high plant efficiencies and improve competitiveness toward post-combustion capture technologies.

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