



Efficient low CO₂ emissions power generation by mixed conducting membranes

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Summary

The integration of gas separation membranes in the energy sector has the potential to provide novel plant configurations that achieve improved performance at lower investment costs than conventional designs.

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 O₂ and H₂ separation by using a new deposition technique "Plasma Spraying – Thin Film" (PS-TF) in combination with nano-porous, highly catalytic layers.

This poster presents a portion of the results achieved in the performance assessment analysis of large scale power plants carried out by Politecnico di Milano and Foster Wheeler Italiana. With a focus limited to natural gas fired combined cycles with pre-combustion CO₂ capture, a comparison of plant configurations implementing membranes versus arrangements based on commercially available technologies is presented. Calculations were carried out with the code GS, developed at the Department of Energy of the Politecnico di Milano and ASPEN Plus™. Membrane operating conditions adopted in this work come from indication derived from DEMOYS experimental activities.

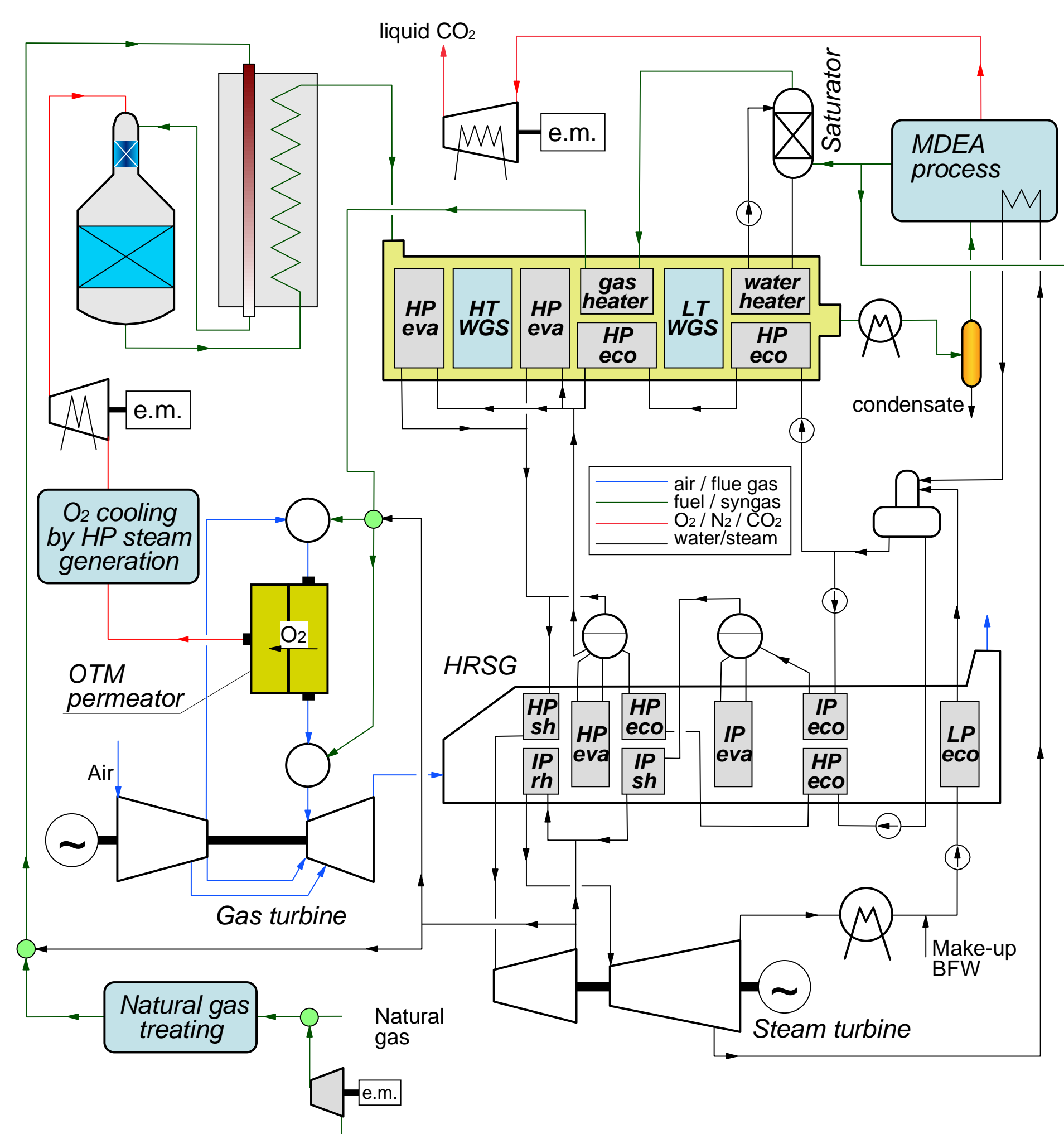
Cases without membranes

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

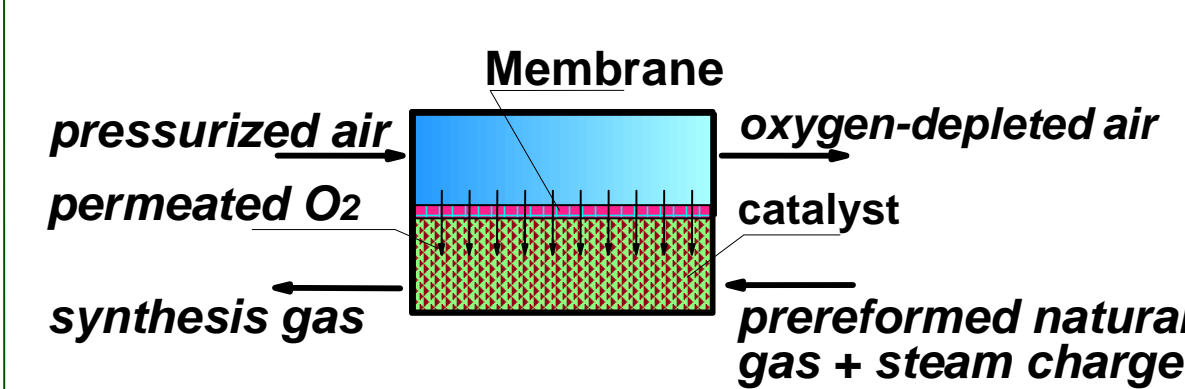
- NGCC (Natural Gas Combined Cycles): reference technology for power generation plants without CO₂ capture
- ABAR (Air Blown ATR with CO₂ capture) plant featuring:
 - methane steam reforming in an air blown Auto Thermal Reactor (ATR)
 - CO conversion to CO₂ in a two stage water gas shift reactor
 - pre-combustion CO₂ by absorption with MDEA solvent
 - H₂ rich syngas fueled combined cycle
- CAAR (Cryogenic ASU + ATR with CO₂ capture): plant configuration similar to ABAR, but featuring O₂ blown ATR. Oxygen provided from a cryogenic Air Separation Unit (ASU)

Cases with O₂ membranes

OMAR plant flow diagram shown in this box can be conceptually divided into the five following sections: 1) the natural gas treating section; 2) the hydrogen production section; 3) the O₂ production and compression system based on a membrane permeator operating at 950°C; 4) the MDEA-based absorption process that separates CO₂ from the H₂-rich syngas; 5) the combined cycle based power island.

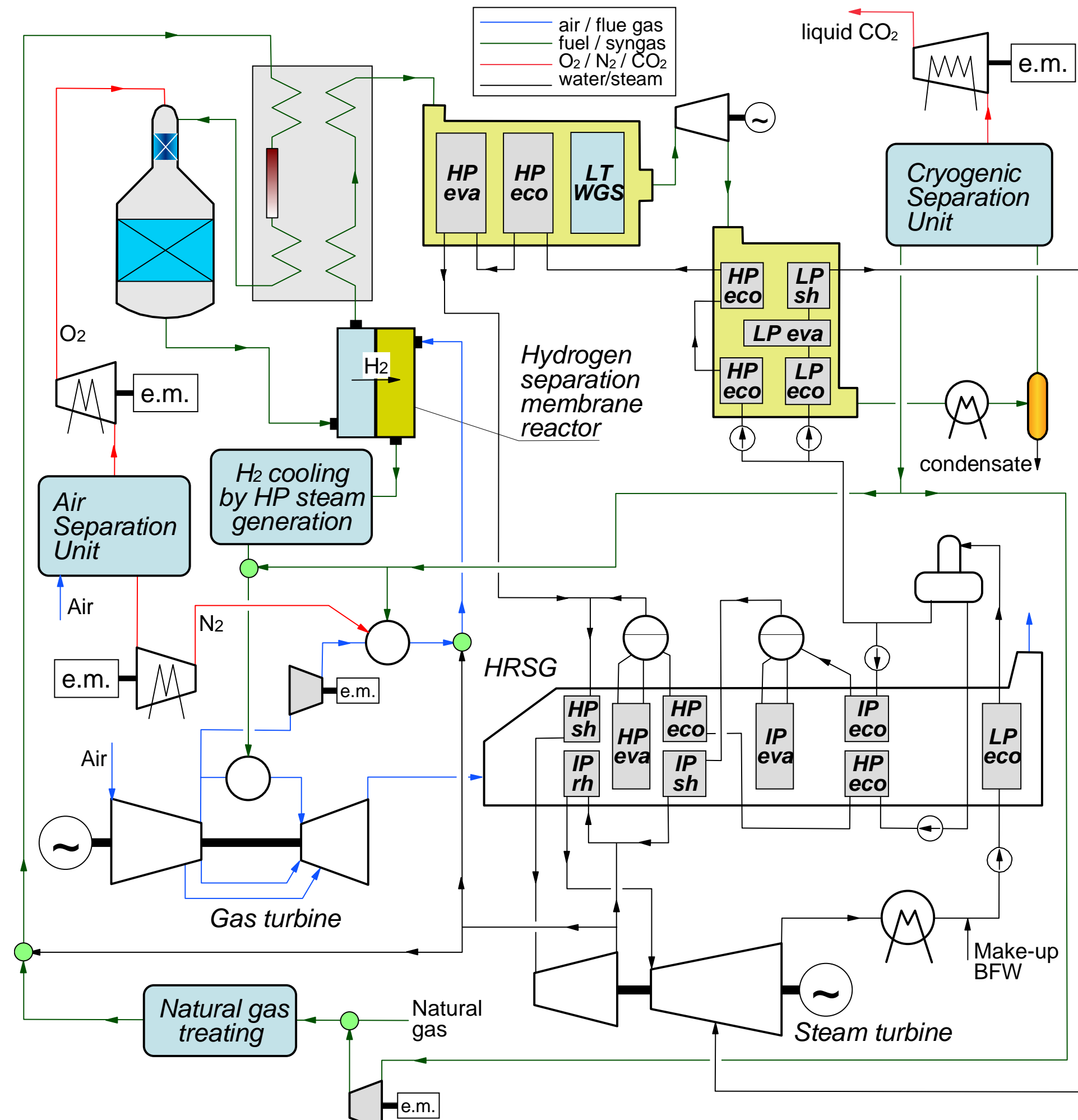


OMCR plant includes a catalytic partial oxidation (CPO) reactor. Since in a CPO reactor all the reactions occurring in an ATR (partial and complete combustion, methane steam reforming, water gas shift) take place in heterogeneous phase, it can be directly integrated with an OTM (see figure below). This reduces O₂ compression work compared to OMAR. Moreover, due to reactions on the permeate side, O₂ partial pressure is virtually zero enhancing O₂ permeation and lowering the membrane surface.



Case with H₂ membranes

ARHS plant shown in this box features a two stage reforming reactor. The O₂ blown ATR is followed by a hydrogen separation membrane reactor (HSMR) that allows moving toward products equilibrium of steam reforming and water gas shift reactions. ATR reactor can therefore operate at a lower temperature and 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 HSMR.



To make easier the H₂ permeation through the membrane, steam reforming is carried out at higher pressure (58 bar). The sweep gas is produced by burning in air the incondensable off-gas from the cryogenic separation unit. This stream is then mixed with nitrogen from ASU and IP steam to achieve a ~50% H₂ concentration at the permeate side outlet

	NGCC	ABAR	ABAR**	CAAR	OMAR	OMCR	ARHS	ARHS**
ATR/CPO temperature, °C		950	950	1050	1050	1050	923	923
S/C ratio at pre-reformer inlet		2.97	2.97	1.9	1.9	2	1.5	1.5
Min. feed-permeate Δp _{O₂/H₂} , bar					1.39	2.3	3.84	3.84
Membrane feed temperature, °C					850	1049.9	923.2	923.2
Membrane retentate temp., °C					850	1049.9	850.1	850.1
Gas turbine TIT, °C		1360	1261	1360	1360	1360	1360	1261
Gas turbine net power, MW	272.0	296.1	244.2	319.1	298.6	296.7	316.5	262.7
Steam turbine net power, MW	140.3	114.2	101.1	123.7	131.9	126.5	166.2	148.5
ASU, MW				-17.83			-19.63	-17.38
Air booster compressor, MW		-10.5	-9.2				-1.4	-1.2
CO ₂ compression, MW		-15.0	-13.3	-15.0	-14.7	-14.9	-5.6	-4.9
MDEA plant auxiliaries, MW		-4.7	-4.1	-4.7	-4.7	-4.6		
Other auxiliaries, MW		0.0	0.0	-19.3	-8.0	0.0	-28.2	-25.0
Net electric power, MW	412.3	370.9	310.3	376.9	394.1	394.7	417.9	353.7
Cold gas efficiency, %		92.1	92.1	91.6	91.9	94.5	89.8	89.8
Net electric efficiency, %	58.08	45.53	43.07	46.06	47.52	48.74	49.73	47.56
Specific emission, g _{CO₂} /kWh _e	353.9	32.9	34.7	42.5	41.0	40.1	44.7	45.7
SPECCA*, MJ _{LHV} /kg _{CO₂}		5.32	6.77	5.20	4.40	3.79	3.37	4.45

Results

Three plant layouts based on high temperature mixed conducting membranes for O₂ and H₂ separation have been assessed in this work and compared to reference pre-combustion CO₂ capture plants based on conventional technologies. The calculations show that the integration of membranes may lead to very interesting advantages in terms of efficiency improvement and lower energy penalties for CO₂ avoidance.

More in detail:

- Integration in a CPO (Catalytic Partial Oxidation) reactor seems the best option for OTMs. In addition, the lowest membrane area is expected in this case, thanks to the prompt reaction of the permeated O₂ that reduces virtually to zero the partial pressure on the permeate side.
- Integration of hydrogen membranes after an O₂-blown ATR yields the highest efficiency among the arrangements considered. An electric efficiency of 49.7%, about 4 percentage points more than the ABAR plant, and a SPECCA index of 3.4 MJ_{LHV}/kg_{CO₂} can be obtained.
- High performance turbines improve plant efficiency of 1.5 percentage points with respect to the present commercial H₂-fired units. Such a development, expected if a sufficient market will exist in the future, has a primary importance to improve competitiveness of pre-combustion CO₂ capture technologies.

$$SPECCA = \frac{(1/\eta - 1/\eta_{ref}) \times 3600}{(E_{ref} - E)}$$

* The SPECCA measures the energy cost related to CO₂ capture accounting for penalty efficiency as well as for the CO₂ avoided
 ** Gas turbine is calculated according to more conservative assumptions, typical of today syngas and H₂-fired turbines