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Application of MCFCs for active CO_2 capture within natural gas combined cycles

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Abstract

This paper presents an analysis of the application of Molten Carbonate Fuel Cells (MCFC) in a natural gas fired combined cycle power plant to capture CO_2 from the exhaust of the gas turbine. The gas turbine flue gases are used as cathode feeding for a MCFC, where CO_2 is transferred from the cathode to anode side, concentrating the CO_2 in the anode exhaust. This stream is then sent to a CO_2 removal section consisting either in (i) an oxygen combustion of residual fuel compounds, or (ii) a cryogenic CO_2 removal section, cooling the exhaust stream in the heat recovery steam generator. The MCFC is based on Ansaldo Fuel Cells experience, fed with natural gas processed by an external reformer which is thermally integrated within the FC module. Differently from more conventional approaches to CO_2 capture, it works increasing the plant power output, acting as an active CO_2 concentrator. The plant shows the potential to achieve a CO_2 avoided ranging between 58 and 68%, depending on the configuration while taking advantage from the introduction of the fuel cell, the final electric efficiency is lower from 0.2 to 0.8 points lower than the original combined cycle (57.8% LHV in the most efficient configuration). The power output increases by about 22%, giving a potentially relevant advantage with respect to competitive carbon capture technologies.

Keywords: CO_2 capture , MCFC, combined cycle,

1. Introduction

Reduction of greenhouse gas emissions, and in particular of CO_2 emitted from human activities like power generation, is one of the most important challenges for our modern society. This paper presents an analysis of an advanced power cycle with limited CO_2 emissions, based on the use of Molten Carbonate Fuel Cells (MCFC) for post-combustion capture of CO_2 integrated within a natural gas fuelled gas-steam combined cycle (NGCC) power plant. The application of post combustion capture, with respect to other capture strategies, has the advantage to require limited change to the cycle arrangement so that it can be easily adapted to retrofit existing power plants. On the other hand, CO_2 concentration in NGCC exhaust gases is rather low (about 4%), and conventional post-

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combustion capture concepts typically require the adoption of chemical solvents (amines) to absorb carbon dioxide before the stack. The adoption of such "passive" CO_2 capture processes yields up to 90% carbon dioxide removal but brings about the disadvantage of reducing considerably the plant power output and efficiency, due to the huge amount of thermal energy required to regenerate the chemical solvents. As a matter of fact, because of plant power output reduction consequences of CO_2 capture, the installation of additional power plants must be taken into account, and depending on their type (either based on other CO_2 capture power plants or representative of average power stations), this could partially offset the CO_2 reduction gained on the NGCC.

In the plant presented here, CO_2 is captured thanks to the introduction of an "active" component, the MCFC, which adds power to the plant energy balance while acting as a CO_2 concentrator [1,2]. In the proposed solution, the gas turbine exhausts are used as cathode feeding for a MCFC, where CO_2 and O_2 are transferred (as $CO_3^=$ ions) from the cathode side to the anode side, fed with reformed syngas from natural gas (Figure 1). In such a way CO_2 is concentrated in the anode exhaust gases, making easier its separation. Since while transferring the CO_2, the fuel cell produces "CO_2-free" extra power, the overall energy balance for CO_2 separation becomes positive and the specific emissions [kg_{CO2}/MWh_{el}] can be reduced compared to more conventional methods using chemical absorption such as with amines.

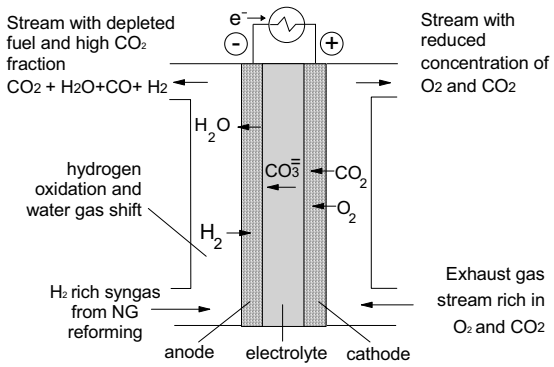

Figure 1: Conceptual scheme of a MCFC fed with externally reformed natural gas.

Plant layout optimization has to account with operating conditions suitable for long term fuel cell operation. From the CO_2 separation point of view, it has to be considered that the MCFC cannot completely exploit the CO_2 contained in the stream which feeds the cathode, nor to oxidize all the fuel introduced, while maintaining a high conversion efficiency. The first limitation requires to set a compromise between the fraction of CO_2 separated and the plant performance, reaching a balance which is influenced by the choices on the cycle configuration (variation of CO_2 fraction in the cathode stream due to recycling of exhaust streams, use of residual fuel stream in the gas turbine). The second issue is given by the fact that the MCFC generates at anode outlet a stream mainly composed of CO_2 and water but still containing significant fractions of residual, non-oxidized, CO and H_2. Following the results of previous works [3,4], two strategies are compared here to recover the heating value of CO and H_2 while preserving high CO_2 purity in the stream:

- burn CO and H_2 in pure oxygen. Heat released in the combustion is recovered for steam generation in favor of the power plant. This solution will be referred to as "oxyfuel" configuration in the paper.
- remove CO_2 from the more volatile CO and H_2, adopting a removal section composed by a cryogenic plant. Combustible species are then recycled to the power plant. This solution will be referred to as "cryogenic" configuration in the paper.

The proposed plant layout are designed with specific reference to the MCFC technology developed by Ansaldo Fuel Cells and presented in the following section.

2. MCFC technology

The power cycles investigated in this work are based on the integration of Molten Carbonate Fuel Cells which reflect the experience of Ansaldo Fuel Cells on MCFC technology.

Ansaldo Fuel Cell technology is based on its own MCFC stack design, result of several years of steady spending in R&D the Company managed to shift the activity from the initial laboratory-scale to a full-size test approach.

During the last decade, Ansaldo Fuel Cells continued the development of its proprietary MCFC technology based on several key component, specifically the MCFC stack and the Modular integrated reformer: an external reformer strictly integrated to the stack (from the thermal management point of view). The Company has built an in-house significant expertise and know-how for managing also the manufacturing process, starting from the engineering development of the concepts, to the assembly of the final components and also the operation of experimental demonstration plants.

In particular, significant results are the new generation full scale MCFC stacks, the set up in Italy of the Pilot Manufacturing facility, MCFC demonstration plants built and operated in Italy, Spain and Turkey, set up and operation of the full scale experimental area in Italy (Bosco Marengo, Piemonte) with two MCFC test plants for full scale stacks and BoP testing.

Figure 2: Ansaldo MCFC plant at Bosco Marengo site.

Among the most important assumptions regarding MCFC, which influence the layout and performance of the power cycle, it must be evidenced that:

- the maximum temperature at MCFC outlet has been set at 660°C. This influences also the inlet temperatures, given that the temperature rise of the streams feeding the fuel cell must balance the cooling duty for removing heat from the MCFC;
- the minimum CO_2 residual fraction at cathode outlet is set at 1.5%. While this limit is reached in the oxy-fuel solution, since the CO_2 fraction at the inlet is only 3.9%, it is not reached by the cryogenic solution, because of outlet temperature constraints, where burning a recycled stream ahead the fuel cell increases the CO_2 fraction at MCFC inlet at about 5%.

Table 1– MCFC simulation assumptions.

MCFC	
Fuel utilization factor U_f	75%
CO_2 utilization factor U_{CO2}	56-63%
O_2 utilization factor U_{O2}	9.7-12.7%
Steam-to-carbon ratio at anode inlet	3.5
Cell current density i_c	1000 A/m^2
Cell voltage @ nominal conditions	0.746 V
Δp/p anode and cathode streams	3% / 2%
Heat loss to environment (% inlet thermal power)	1%
DC-AC converter efficiency	94%

3. MCFC integrated in NGCC for CO_2 capture

The proposed power cycles are based on a natural gas combined cycle (NGCC), where a MCFC is placed between the gas turbine and the heat recovery steam generator (HRSG). The gas turbine exhaust gases are directly used as cathode feeding for the MCFC, where CO_2 is moved from the cathode to anode side, concentrating the CO_2 in the anode exhaust gases. The fuel cell works at atmospheric pressure and is fed with a syngas generated within the fuel reformer, fed with a mixture of desulphurized[1] and preheated natural gas and low pressure steam extracted from the steam turbine.

Differently from a conventional MCFC layout, where the fuel reformer can be heated up by a hot stream generated by the combustion of the anode exhaust together with the cathode exhaust, the two gases are here kept separated in order to avoid CO_2 dilution which was concentrated at the anode.

In the first plant layout (Figure 3), based on the cycle configuration proposed in [3] which has been adapted here to the specific MCFC technology previously presented, an air separation unit (ASU) provides 98% purity oxygen to a burner where the heating value of the spent anode fuel is recovered by producing a hot gas stream which feeds the fuel reformer at the hot side (oxy-combustion temperature is rather high, about 1190°C, so that the option of different integrations will be investigated in a future work). The exhaust stream from the reformer is then cooled in a separate channel of the heat recovery steam generator, avoiding mixing with the cathode exhausts. This stream mainly contains steam and CO_2, so that after water condensation, the content of contaminants in dry CO_2 is lower than 4%[2]. At the cooling end, the CO_2 rich stream is compressed to 80 bar in a 5 stage intercooled compression train followed by a pump that takes the final pressure to 110 bar.

A fraction of steam extracted from the HRSG is used to preheat the fuel feeding the gas turbine and the MCFC.

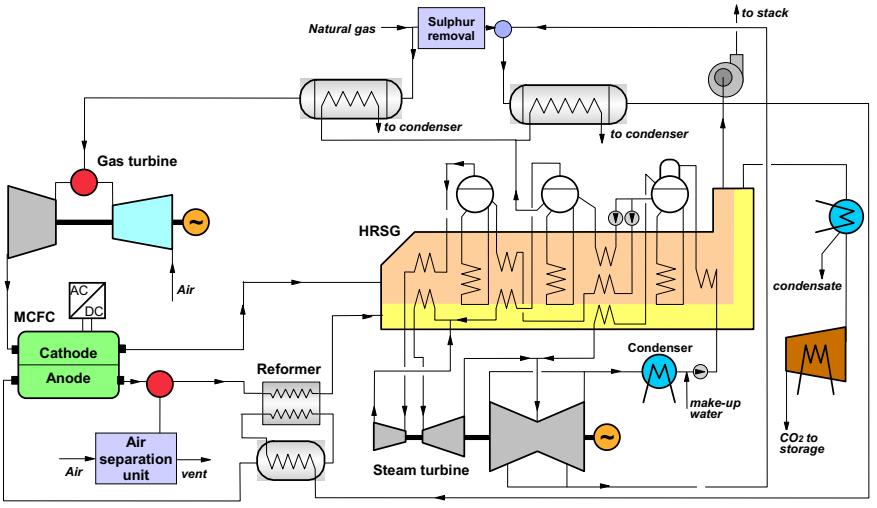

Figure 3. Plant layout with integration of the MCFC in a combined cycle, with CO_2 separation via oxygen combustion.

In the second plant layout (Figure 4), which is derived from the cycle configuration proposed in [4], the cell anode exhaust stream is cooled in the HRSG (heat recovery steam generator) of the combined cycle, then further cooled to ambient temperature and sent to a CO_2 removal section. Considered that the CO_2 concentration of the stream at the MCFC anode outlet is about 80% (dry basis), it is convenient to carry out this separation by means of a

[1] Natural gas can be desulphurized in advance by mean of proper treatment since reformer catalysts and MCFCs do not tolerate the presence of sulfur compounds, including the typical NG odorizers, above 0.5-1 ppmv.

[2] According to reference literature on CO_2 geological sequestration [5], it ensures that the stream can be sent to long term storage in saline aquifers without further purification treatments.

cryogenic compression – liquefaction process, where the temperature is made low enough that most of the CO_2 is condensed and separated by gravity from the gaseous combustible species included in the mixture which have a much lower boiling point [6]. The anode stream at the HRSG exit is therefore cooled down to the ambient temperature and then enters the separation and compression process, which has already been discussed in detail in [4].

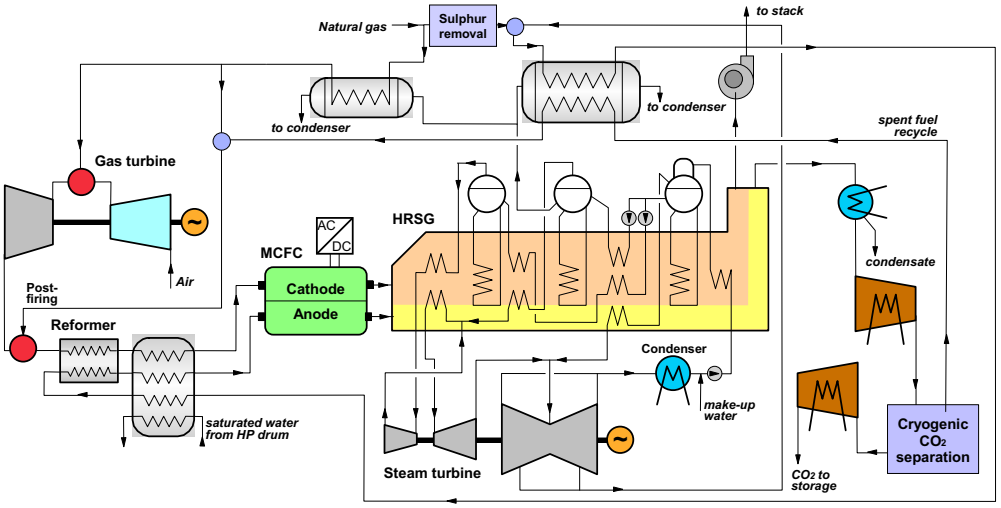

Figure 4. Plant layout showing the integration of the MCFC in a combined cycle, with cryogenic CO_2 separation.

The remaining spent fuel is recycled and burned to increase the temperature of the exhaust stream coming from the gas turbine, which is then used to heat up the fuel reformer. NG has to be added in order to achieve a temperature of 750°C at the hot side of the reformer reactor to enhance the endothermic reforming reactions. Gas turbine and spent fuel are preheated with saturated water bled from the IP drum of the HRSG.

In both configurations, the cathode exhaust stream is cooled by the HRSG, so that the MCFC operates in a hybrid configuration releasing exhaust heat to the steam bottoming cycle. This allows improving the efficiency (at least before CO_2 capture, as will be clarified in the discussion of results) with respect to the level of the original combined cycle. Moreover, in both cases the cooled exhaust gas can be sent to the stack (as shown in Figure 3 and Figure 4) or partially recycled to increase the CO_2 concentration on the MCFC cathode side and enhance the fraction of CO_2 captured; this option, which has been considered in previous works [3,4] based on internal reforming type MCFCs, is not addressed here because exceed the proper range of operating conditions.

4. Methodology

Heat and material balances have been estimated by a proprietary computer code (GS) developed by the Gecos group at the Department of Energy of Politecnico di Milano to assess the performance of gas/steam cycles and fuel cell systems. The plant scheme is reproduced by assembling in a coherent network the different components selected in a library containing over 20 basic modules, whose models have been previously implemented. Built-in rules allow predicting turbomachines (gas and steam turbines, compressors) efficiency as a function of their operating conditions, while the turbine cooled expansion is calculated by a stage by stage model [7-10]. Energy balance of the CO_2 cryogenic and compression section are simulated with ASPEN Plus™ [11].

The main design assumptions used in simulations are reported in Table 2.

In assessing the plant performance, reference is made to a "state of the art" combined cycle (NGCC) based on a Siemens SGT5-4000F (V94.3A) gas turbine [12], which also defines the plant size and natural gas input. Slight variations in GT operating conditions occurs due to the higher expander back pressure necessary to avoid sub-atmospheric pressure within the fuel cell. This variation does not entail relevant changes except that a small decrease

of the power output is expected as a consequence of the higher turbine exhaust pressure. Conditions at turbine admission and other design parameters of the bottoming steam cycles are kept the same for all the plants considered.

Table 2– Main assumptions adopted for plant simulations.

Ambient conditions	15 °C / 1.013 bar / 60% RH
Air composition, dry molar fraction (%)	N_2 78.08%, CO_2 0.04%, Ar 0.93%, O_2 20.95%
Gas turbine	
Pressure ratio	17.0
Gas mass flow rate at the turbine inlet	672.6 kg/s
TIT	1335 °C
Pressure loss at inlet	1 kPa
Steam cycle	
Pressure levels, bar	130,30,7.5
Maximum temperature SH e RH	565 °C
Pinch, subcooling, approach ΔT	10/5/25 °C
Condensing pressure	0.048 bar (32 °C)
Turbine Isentropic efficiency (HP/IP/LP)	92/94/88 %
Pumps efficiency	70%
HRSG – Heat exchangers thermal losses	0.7 % of thermal input
HRSG pressure losses	4 kPa
Gas turbine and steam cycle	
Generator efficiency	98.7%
Mechanical efficiency	99.6%
Power consumed for heat rejection	0.8% of heat released
Air Separation Unit	
Oxygen Purity	98%
Oxygen outlet pressure	1.05 bar
Energy consumption for O_2 production	0.295 $kWh_{el}/kg_{PURE\ O2}$
CO_2 separation and compression	
Final delivery pressure	110 bar
Compressor isentropic efficiency	85%
Temperature for CO_2 liquefaction	25°C
Pressure drop for intercoolers and dryer	1.0%
Pump efficiency	75%

The MCFC is simulated through a lumped-volume model which requires to assign the reactant properties at FC inlet (temperature, pressure, chemical composition and mass flow) and the utilization factor for CO_2 (U_{CO2}, or alternatively U_{O2} regarding oxygen consumption) inside the fuel cell. U_{CO2} is defined as the ratio between the flow rate of CO_2 transferred through the cell as carbonate $CO_3^=$ ions and the CO_2 flow rate introduced at the cathode inlet.

The cell voltage is calculated starting from the reversible Nernst potential, and considering the cell losses, proportional to the cell current density, split among the anode and cathode overpotential (depending on reactant composition and temperature) and the ohmic resistance (ionic and electronic resistance, with an Arrhenius type expression depending on temperature). Details about the assumed model are given in [3].

Choice of current density is a critical aspect to define the plant performance since this parameter heavily affects the efficiency of a fuel cell. For a given current output, the cell active area A is actually set as a compromise between costs and efficiency, which are both increasing with the cell area, being the MCFC efficiency and cell voltage higher at low current densities. For the purpose of this work, the cell current density is fixed at 1000 A/m^2 in combination with a fuel utilization factor of 75%; the resulting cell voltage is 0.744 V and the total cell area is about 111000 m^2.

5. Results

The most important results in terms of energy balances are given in Table 3. The table shows in the first two columns the energy balances of the reference NGCC and of a reference NGCC+MCFC power cycle analogue to the one of Figure 3 but without CO_2 separation[3], which can be used as a reference to evaluate the performance of the two proposed cycles of Figure 3 and Figure 4.

[3] In this case, it is not necessary to rely on an oxygen combustion to complete the anode exhaust oxidation, which is simply carried out burning the residual fuel together with the cathode exhaust stream. The hot stream resulting from this combustion

When comparing the results of the different power cycles, a measure of the energy cost related to CO_2 capture is given by the Specific Primary Energy Consumption for CO_2 Avoided (SPECCA), which is defined as:

$$SPECCA = \frac{HR - HR_{REF}}{E_{REF} - E} = \frac{3600 \cdot \left(\frac{1}{\eta} - \frac{1}{\eta_{REF}} \right)}{E_{REF} - E} \quad (1)$$

where:

- HR is the heat rate of the plant, expressed in kJ_{LHV}/kWh_{el}
- E is the specific CO_2 emission rate, expressed in kg_{CO2}/kWh_{el}
- REF is the NGCC+MCFC reference case for electricity production without carbon capture.

Table 2 – Results of plant simulations.

		Plant without CO_2 capture		NGCC+ MCFC plant with CO_2 capture	
		Reference NGCC	NGCC + MCFC	Oxyfuel CO_2 capture	Cryogenic CO_2 removal
MFCF U_A/U_F	%	-	62.5/75	62.5/75	55.9/75
Temperature at MCFC outlet	°C	-	656.5	656.4	660.0
CO_2 at cathode outlet	%	-	1.519	1.519	2.284
MCFC current density	A/m^2	-	1000	1000	1000
MCFC cell voltage	V	-	0.744	0.744	0.746
MCFC active area	m^2	-	111016	110916	129300
MCFC electric output	MW_{el}	-	77.64	77.57	90.67
GT electric output	MW_{el}	281.32	277.23	276.98	276.98
ST electric output	MW_{el}	135.59	166.73	166.26	211.69
Blower power consumption	MW_{el}	-	-5.14	-1.21	-2.84
ASU power consumption	MW_{el}	-	-	-3.72	-
CO_2 compression	MW_{el}	-	-	-13.20	-19.06
Other auxiliaries	MW_{el}	-1.76	-1.88	-2.39	-2.93
Net power output	MW_{el}	415.15	514.58	500.28	554.50
Fuel input to GT(1)	MW_{th}	715.59	709.80	709.10	709.10
Fuel input to MCFC(1)	MW_{th}	-	155.88	155.76	175.12
Fuel for post-firing(1)	MW_{th}	-	-	-	84.58
Total fuel input(1)	MW_{th}	715.59	865.68	864.86	968.80
Net electric efficiency	%	58.01	59.44	57.84	57.24
CO_2 emissions	g_{CO2}/kWh_{el}	351.03	347.33	111.14	147.99
CO_2 avoided	%	N/A	N/A	68.00	57.39
SPECCA	MJ/kg_{CO2}	N/A	N/A	0.71	1.17

(1) Thermal power calculated on LHV basis.

The proposed cycles feature relevant advantages with respect to competitive CCS solutions, also based on other fuel cell technologies, allowing to:

- keep a very high plant net electrical efficiency: the efficiency loss after CO_2 capture is limited to 1.6% points and 2.2% points with the oxyfuel configuration and the cryogenic solution, respectively;
- limit the role of the fuel cell in the overall energy balances with respect to other kind of FC-gas turbine hybrid cycles [9,10], with positive expected impact on the plant investment costs which would otherwise suffer the very high specific costs (€/kW) of fuel cells; the power output of the fuel cell is here about 15% of the total net power output;
- increase the plant power output from 20 to 30% with respect to the original combined cycle;
- substantially reduce the energy consumption for CO_2 capture with respect to conventional post combustion capture strategies. The SPECCA index shows very low values, ranging between 0.7 and 1.2 MJ/kg_{CO2}, much

process is then cooled down in the HRSG. Apart from this difference, the cycle layout is equal to the one of Fig. 2. The complete layout of this cycle is not shown here for brevity.

lower than those typical of conventional CO_2 capture approaches (a literature review [3] showed that post-combustion CO_2 removal by amines in a conventional NGCC allows an average carbon capture of 90% with an electric efficiency decay of about 8 percentage points, resulting in a SPECCA of about 3.3 MJ/kgCO_2).

At first sight the separated CO_2 fraction obtained by the proposed solution (in the range 56-70%) does not reach the declared 90% level of competitive technologies like amine separation. However, further analysis reveals a different picture [13] coming from the consideration that the proposed solution avoids the necessity of building additional power plants for compensating the lower power output which typically affects competitive "passive" technologies. Depending on a scenario where the loss of power of a "passive" plant would be compensated by renewables or other CCS plants (keeping the full advantage of CO_2 reduction), or oppositely by the average CO_2 emitting power park (substantially reducing the gain due to additional CO_2 emitted elsewhere), the comparison could be upset in full favour of the MCFC system [13]. By this point of view an advantage of the proposed solution is that it is completely independent on this scenarios, since it allows increasing the plant power output with "CO_2-free" extra power.

6. Conclusions

This paper has discussed the analysis of the application of Molten Carbonate Fuel Cells (MCFC) in natural gas fired combined cycles to capture CO_2 from the exhaust of the gas turbine. The gas turbine flue gases are used as cathode feeding for a MCFC, based on Ansaldo Fuel Cells experience, fed with natural gas processed by an external reformer. The MCFC acts as an active CO_2 concentrator, where CO_2 is transferred and concentrated from the cathode to anode side, while producing additional power. The cell anode exhaust is sent to a CO_2 removal section consisting in an oxygen combustion of residual fuel compounds or a cryogenic CO_2 removal section, cooling the exhaust stream in the heat recovery steam generator. The plant shows the potential to achieve a CO_2 avoided ranging between 58 and 68% (depending on the configuration), while taking advantage from the introduction of the fuel cell the final electric efficiency can be close or few points lower than the original combined cycle (0.2% LHV in the most efficient configuration), and the power output increases by about 20%, giving a potentially relevant advantage with respect to competitive carbon capture technologies typically featuring a relevant net power output decay. Moreover, the role of the fuel cell on the overall power balances is limited to 15%, leaving the majority of power to conventional components, improving the possibility of achieving a low plant specific cost (€/kW).

References

[1] Amorelli A. et al. "An experimental investigation into the use of molten carbonate fuel cells to capture CO_2 from gas turbine exhaust gases", Energy, Vol. 29, pp. 1279–1284, 2004.
[2] Campanari S. "Carbon dioxide separation from high temperature fuel cell power plants" J. of Power Sources, Vol. 112/1 pp. 273-289, 2002.
[3] Campanari S., Chiesa P., Manzolini G. "CO_2 capture from combined cycles integrated with Molten Carbonate Fuel Cells", Int. J. Greenhouse Gas Control Vol.4(3), pp. 441-451, 2010.
[4] Chiesa P., Campanari S., Manzolini G. "CO_2 cryogenic separation from combined cycles integrated with Molten Carbonate Fuel Cells", Int. J. of Hydrogen Energy, in press.
[5] Caesar Project, Deliverable 4.6: "Common Framework Definition Document", Public Report, 2009
[6] J Davison, K Thambimuthu - Proceedings of GHGT, 2004 paper 597- uregina.ca
[7] "Software Presentation: GS (Gas-Steam cycles)", http://www.gecos.polimi.it/software/gs.html, 2009.
[8] Chiesa P., Macchi E., "A thermodynamic analysis of different options to break 60% electric efficiency in combined cycle power plants" J Eng Gas Turb Power, 126, 770-785, 2004.
[9] Romano M., Campanari S., Spallina V. , Lozza G. "SOFC-based hybrid cycle integrated with a coal gasification plant", ASME Turbo Expo, GT2009-59551, Orlando, USA, 2009.
[10] Campanari S., Iora P., Macchi E., Silva P. "Thermodynamic analysis of integrated MCFC / Gas Turbine cycles for multi-MW scale power generation", ASME J. of Fuel Cell Science and Technology, Vol. 4, pp. 308-316, 2007.
[11] Aspen Plus version 2006.5, Aspen Technology, Inc., Cambridge, Massachusetts U.S.A.
[12] Gas Turbine World "GTW Handbook", Pequot Publication, Vol. 27, 2009.
[13] F. Federici, "Molten Carbonate Fuel Cells, an opportunity for CO_2 capture", Oral Presentation at 11th Grove Fuel Cell Symposium (2009), London (UK).