

Membranes and molten carbonate fuel cells to capture CO₂ and increment energy production in natural gas power plants

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ABSTRACT

Molten Carbonate Fuel Cells (MCFCs) can be used for concentration of carbon dioxide in Natural Gas Combined Cycles (NGCCs) exhaust gas, at the same time increasing electrical energy: when used in combination with Gas Separation Membranes (GSMs) for final segregation of CO₂, they constitute an interesting carbon capture solution. This paper analyses distributed parameter models for fuel cells and membranes in a global plant simulation, so as to propose an optimized NGCC-MCFC-GSM process configuration that takes into account both fuel cell operational constraints and the specific limitations of membrane technology. The integration obtained produces very good results , presenting in all scenarios better economic

indicators than conventional amine absorption NGCC retrofit. Furthermore, a great margin for performance improvement exists if the fuel cell maximum hot-spot temperature limit is tackled.

1. Introduction

Carbon dioxide is one of the main causes of the greenhouse effect and of climate change, as a result serious attention is being given to the issue of reducing CO₂ emissions deriving from the generation and consumption of electrical energy.

Several solutions exist for reducing the impact of greenhouse gases and mitigating climate change, the most important being the reduction of end use energy consumption. Generation of electrical energy from renewable sources is recognized as a good option, but its financial viability is currently being challenged and it is sometimes unable to satisfy electricity grid demands in terms of continuity, range, peak hours, etc.

Within this scenario, CCS (Carbon Capture and Storage) technology provides an appropriate temporary, short-term, solution for stationary electrical power generation: allowing the continued use of fossil fuels for energy production by reducing their impacts.

Considering the scarce level of public acceptability for CCS applied to coal-fired power plants, it is a recognized fact that, in the short-term, in countries where a step-down from nuclear power generation has occurred (Italy, Japan), or is planned (Germany, Belgium), energy demands are to be met by conventional Natural Gas Combined Cycle (NGCC) power plants.

Natural gas is a relatively abundant fossil fuel, even more true with the recent emergence of non-conventional exploitation techniques (such as fracking): in areas of the world where these types of techniques are allowed, natural gas is currently cheaper than any other fossil energy

source, and its projected reserves could last for centuries¹. Furthermore, when natural gas is fed into state-of-the-art combined cycle power plants, it is converted into electrical energy with a higher efficiency rate and lower specific CO₂ emissions than any other fossil fuel-based technology.

With these facts in mind, it is very likely that conventional NGCC technology will be chosen for a large share of new power plant projects over the next decade, and the addition of a carbon capture unit could render these plants even more attractive.

Over recent years, a wide range of technologies has been studied for post-combustion capture of CO₂ from stationary, fossil-fuelled, electrical power plants. A number of these technologies, such as absorption and membranes, have reached maturity and are used widely in other fields too.

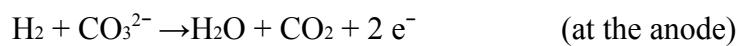
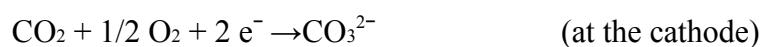
Chemical absorption is already used on a large scale to separate CO₂ from raw natural gas, and is suitable for treating gas streams with low CO₂ concentrations. Most utilized chemical solvents are amine solutions, in particular Monoethanolamine (MEA), however, although economical, it is also toxic and leads to a higher energy penalty due to high desorption energy consumption². Others chemical absorbents currently being studied are carbonates, ammonium and amino acids.

Physical absorption is frequently used for gas streams with high CO₂ concentrations, as physical absorbents (methanol, propylene carbonate, NMP) are ineffective for low concentrations. However the energy required for desorption is less than that required in chemical absorption processes.

With regards to membrane technology, used in a wide range of applications for gas separation, many types of membrane have been analyzed for CO₂ capture: polymeric, inorganic, mixed, hybrid, facilitated transport membranes and capillary membranes, although most for small-scale applications. If scale-up problems were to be resolved, they would offer significant advantages over absorption processes only for flue gases with a CO₂ content exceeding 20%³⁻⁵.

In order to avoid the drawbacks of traditional methods, innovative technologies have been studied (i.e. adsorption into solids, carbonation/calcination cycle) and also the use of MCFCs as CO₂ concentrators.

MCFCs are electrochemical reactors which convert the chemical energy of fuel directly into electrical energy, thus they are able to generate electricity at higher efficiency rates and with lower environmental impact than conventional state-of-the-art power stations. The distinctive feature of MCFCs is that they operate at high temperatures (approx. 923 K), in which molten carbonate is contained in a porous matrix as the electrolyte and gives rise to the following electrochemical reactions:



So O₂ and CO₂ fed through the cathode side form CO₃²⁻ ions which pass through the electrolyte to the anode side where they react with H₂, resulting in the transfer of CO₂ from the cathode to the anode. This demonstrates the advantage of MCFCs in the field of CO₂ capture, in that low concentration CO₂ in the NGCC flue gas can be fed through the cathode and concentrated in the anode exhaust gas, making the final separation process easier⁶⁻⁷.

MCFCs have also been proposed as a useful carbon capture technology in Integrated Gasification Combined Cycles (IGCCs)⁸⁻⁹, however MCFCs require special clean-up provisions to protect them from sulfur poisoning and other impurities: from this point of view, flue gas from a gas-fired power plant is easier to adapt to the requirements of fuel cells.

This being said, MCFCs do not offer a definitive capture solution. Although they have the capacity to concentrate CO₂, they are not able to guarantee high recovery rates or purity levels of the CO₂ recovered. In fact, after separation, the CO₂ has to be transported to the storage site. Storage choice will fall most probably mainly on geological formations, in particular depleted oil and gas fields. Certain studies¹⁰ have shown that the recommended CO₂ concentration for safe transportation and storage is >95.5%.

The final separation stage can be performed using, for example, Gas Separation Membranes (GSMs). This technology offers certain advantages: operation is continuous without sorbent materials; installation is relatively small; system has competitive potential in comparison with energy requirements of absorption process as soon as CO₂ concentration exceeds 20% (a condition that occurs when MCFC is used).

Following this process scheme, the present paper extends a previous contribution from the group¹¹, presenting a model-based feasibility study of a modified NGCC integrated with MCFCs for post-combustion CO₂ concentration and GSMs for CO₂ separation.

An essential feature of the work is that, unlike simplified studies based on assumed fixed MCFC and GSM performances, here both MCFC and GSM models are based on intermediate fidelity distributed parameter models previously developed by the group¹²⁻¹³. These models are integrated into a global plant simulation in order to define an optimized process that takes into

account both fuel cell operational constraints (maximum temperature, fuel and CO₂ utilization, steam-to-carbon ratio), and the specific limitations of membrane technology (CO₂ and inert gas driving forces, pinch points).

This study approach is adopted to provide a more reliable feasibility analysis as discussed here.

2. Process configurations

2.1 Reference power plant

A reference, state-of-the-art, NGCC plant with a standard 800 MW electrical output, based on open literature and commercial manufacturer data, was taken as the base case. The process model is based on box units for the open cycle (OC) and the steam cycle (SC), as shown in Figure 1.

The OC unit is represented as a simple recuperated Brayton cycle, including a gas compressor, recuperator, burner and expander. Here the natural gas stream, S02-Fig.1, is compressed together with the air, S01-Fig.1, up to the pressure of 3 Mpa. It is then thermally heated by the hot turbine exhaust in the recuperator, completely oxidized in the burner, and finally allowed to expand in the gas turbine.

The compressor power is estimated on the basis of non-interrefrigerated single-stage compression, operating with a compression ratio equal to 29.6, an isentropic efficiency of 85 % and a mechanical efficiency of 98%.

The turbine isentropic efficiency is 89.2 %, the mechanical efficiency is 98%.

The electrical efficiency for conversion from shaft mechanical power is assumed to be 99%.

The recuperator thermal transport coefficient is set to obtain reasonable cold / hot temperature approaches for gas/gas heat transfer in the range of 230 K.

The temperature of the OC discharge stream, S05-Fig.1, is reported in open literature as 849 K. This value was matched by manipulating the fresh air inflow, resulting in a turbine exhaust CO₂ molar fraction of about 3.8%.

The turbine inlet temperature is also calculated but this value has little physical meaning here, as the simplified model does not represent accurately the thermodynamic cycle, but rather imitates its nominal operating point and sensitivity behaviors.

The sensible heat of the OC discharge stream, S05-Fig.1, is then exploited to produce steam in the heat recovery steam generator (HRSG) for the SC unit. This part of the plant is represented by a simple conversion of the thermal energy available when the expander exhaust is cooled down to a flue gas (S08-Fig.1) temperature of 381 K. The efficiency of this conversion is assumed to be 34.8%, so equalling the combined cycle energy conversion efficiency.

2.2 Integrated plant proposal

Integration of the base NGCC power plant with a CO₂ concentration / separation MCFC-GSM unit is obtained by interposing latter unit between the OC and the SC to treat the high-temperature OC exhaust, as shown in Figure 2.

The increased pressure drops due to the additional MCFC unit was accounted for by applying an efficiency penalty as a linear function of the counter-pressure, with a proportionality constant of 0.03 % / hPa based on previous art.

In the proposed integration, a small purge stream (S10-Fig.2) containing some unreacted hydrogen and CO is recycled back to the OC, so that the overall fuel fed to the OC is S04-Fig.2.

The OC exhaust (S05-Fig.2) is sent to the MCFC-GSM unit to reduce its CO₂ content before being expelled as flue gas (S13-Fig.2), while the concentrated CO₂ stream (S12-Fig.2) is sent to transportation and then to storage. The actual fuel for the MCFC is provided by another amount of natural gas (S09-Fig.2) which is fed into the MCFC-GSM unit and converted here into hydrogen in a reformer.

It needs to be noted that MCFC fuel needs to be desulfurized to a much severer specification than that commonly applying to natural gas, in order to prevent contamination of the MCFCs¹⁴⁻¹⁵. So a proper desulfurization step must be foreseen upstream of the system, treating also the natural gas (S02-Fig.2) fed to the OC, as the same sulfur tolerance problem exists with regards to the OC exhaust stream (S05-Fig.2), and it is easier to remove sulfur compounds from a tiny fuel stream than from a huge flue gas stream.

The medium pressure steam required for reforming this fuel (S03-Fig.2) is obtained from the steam cycle, in this way eliminating the need for a steam production subsystem to be attached to the fuel cell unit.

The heat required to sustain endothermic reforming reactions is provided by high temperature heat recovery by the pressurized burner in the Brayton. The reasoning is that the natural gas burner can be adapted to deliver heat at the high thermal level required. In fact, the adiabatic

combustion temperature for the natural gas composition considered is 2177 K, however the gas turbine cannot tolerate such a high heat level. As a result , in the base case NGCC plant, gases are diluted to a high degree in excess air (in a ratio of 2.5 times the stoichiometrically required air). If the heat required for reforming were to be extracted from the natural gas burner at a constant fresh air inflow mass rate, the turbine inlet temperature (TIT) would be reduced too much (by about 77 K), but by reducing the fresh air inflow the TIT can be almost totally restored to its value in the reference NGCC plant. Furthermore, the turbine outlet temperature (TOT) after the recuperator (849 K in the reference NGCC power plant) is incompatible with the MCFC anode inlet temperature limit (873 K)¹⁶ : to increase the temperature, it makes sense to remove the recuperator from the Brayton cycle so that the OC exhaust temperature is equal to the TOT. These changes should not impact the performance of the gas turbine cycle; as a matter of fact, reducing the air flow reduces the size and cost of the rotating turbomachinery (air compressor, turbine), and concentrates the CO₂ in the flue gas which makes its final concentration easier. In particular, by reducing the fresh air by about 13%, it is possible to match the TIT with the material constraints and the TOT with MCFC limits, increasing electrical efficiency by about 1%, and concentrating the CO₂ in the OC exhaust from 3.8 % up to 4.4 % in moles. Heat recovery from the turbine burner to the reformer and the increase in OC exhaust temperature also make addition of a post-firing step unnecessary¹⁷.

The exhaust from the MCFC cathode (S11-Fig.2), with a temperature of 957 K, can proceed to the steam cycle (SC-Fig.2).

The water from the MCFC-GSM unit (S06-Fig.2) is in large part recycled to the SC (S07-Fig.2) for steam generation, while excess waste water (S08-Fig.2) is ready for discharging.

The purge (S10-Fig.2) from the semi-closed anodic recycle loop is sent to the gas compressor / burner in the OC section, eliminating the need to provide a dedicated burner.

As a result, the whole plant is independent and self-contained, not requiring any external auxiliary equipment to feed the energy demands of the additional carbon capture unit.

2.3 Concentration-separation unit and constraints

The MCFC unit geometry was configured in accordance with Greppi et al.¹², i.e. stacks of 300 planar cells of approx. 0.7 m².

The relevant constraints that have been observed to guarantee safe operation of the MCFC¹² are:

- Temperature: maximum inside the stack = 963 K; cathodic inlet = 863 K; anodic inlet = 873 K;
- Reactions: fuel-cell current density = 1500 A/m²; hydrogen-to-carbon atomic ratio at reformer inlet = 2.5; fuel utilization factor (in terms of CO + H₂) < 75%; O₂ utilization factor < 20%; CO₂ utilization factor < 60%;
- Composition: O₂ molar fraction at the cathode inlet > 8%; H₂ molar fraction at the anode outlet > 6%; CO₂ molar fraction at the cathode inlet > 4%.

For specific applications serving for CO₂ capture, the CO₂ “conversion” or “utilization factor” in MCFC terminology becomes the so-called CO₂ “separation yield”. Consequently, in some recent studies¹⁸⁻¹⁹, CO₂ utilization has been pushed up to 90%, 75% and 95%, respectively. However, earlier data from authors has invited more conservative values²⁰, and more recent experimental data²¹⁻²² available for high CO₂ utilization in low CO₂ concentration streams

seems to indicate a high sensitivity to low CO₂ concentrations - constituting a strong argument for caution. In addition, using a distributed parameter model for the fuel cell plane, it becomes apparent that fuel and CO₂ utilizations are “dependent” constraints, in the sense that the maximum temperature inside the stack is the actual limiting factor, as discussed in the chapter relating to the results.

Therefore, in this work, the base design values for the fuel and CO₂ utilizations were assumed to be 54.5% and 58.1%, respectively, providing good performance and enforcement of temperature constraints.

The process scheme shown in Figure 3 is a refinement of the scheme used in a previous work¹¹, where a standard hybrid MCFC-Gas Turbine system was adapted to make it suitable in a CO₂ concentration application. The main changes w.r.t. Ferrari et al.¹¹ are:

- detailed model of membrane unit for CO₂ separation inserted;
- air burner eliminated, anode purge recycled to the gas compressor / burner in the OC section.

The diluted CO₂-carrying stream, highlighted in black, enters (S09-Fig.3) and leaves the MCFC cathode side (S11-Fig.3) after transferring part of the CO₂ to the anode side.

The anode inlet (S08-Fig.3) is the reformatte (S07-Fig.3) cooled down in the recuperator REGHEX. The anode outlet (S10-Fig.3) is mostly composed of unreacted steam vapor, CO₂ and non-condensable gases (H₂ and CO), so it is not mixed together with the cathode outlet, as is the case in conventional GT-hybrid systems. After a pre-cooling phase in the recuperator COND, which is designed to keep the temperature approaches realistically greater than 115 K,

the pre-cooled anode outlet (S12-Fig.3) is first condensed atmospherically in SEP, then the dry gas (S13-Fig.3) proceeds to the membrane unit.

Together with the atmospheric condensate (S14-Fig.3), some additional water (S17-Fig.3) is condensed in the membrane unit during the compression steps, resulting in the combined condensate stream S18-Fig.3.

CO₂ on the other hand is separated (S16-Fig.3) in the two-stage pressurized GSM unit. The residual anodic outlet (S15-Fig.3), depleted in water and CO₂, is rich in H₂ and CO. After reheating in the heat recovery COND (S19-Fig.3), it is recycled as much as possible back to the reformer (S03-Fig.3) to exploit the unreacted H₂ and CO. This recycling has the added benefit of reusing the water already in the vapor state as a reactant in the reformer, without the need for vaporization, however it causes a 70% increase in anode gas flow from 14.6 to 24.7 kmol/h per stack, and this will render necessary geometry adaptations in the stack. On the other hand, the increased anode flow actually reduces the imbalance in volume flows between the two sides of the cell, reducing the cathode to anode side volume flow ratio from 15 to 8.3, which should make pressure distribution control easier, preventing cross-over²³.

The anode recycling to the reformer is set to 95.6% so that even if the once-through fuel utilization factor consumed by electrochemical reactions is set to 54.5%, the system conversion results as higher than 95%.

A purge (S04-Fig.3) is necessary from this semi-closed anodic recycle loop, because it may accumulate incondensable inert gases (N₂, Ar...) originally present in the natural gas feed.

The supplemental water required to fulfill the H-to-C ratio is provided in the form of medium pressure steam (S02-Fig.3), then mixed with the natural gas (S01-Fig.3) and with the anode

recycle (S03-Fig.3), resulting in a total feed (S05-Fig.3) which is heated up (S06-Fig.3) in the recuperator REGHEX and finally reformed. As discussed previously, the reformer requires an external heat supply to sustain the endothermic reforming reactions, which are maintained at 1008 K.

As to the separator unit downstream of the MCFCs, it consists of a two-stage pressurized gas separation membrane unit.

Its design, shown in Figure 4, was partly based on the solution proposed in Figure 6b of Deng and Hägg²⁴ for the capture of CO₂ in a CH₄-rich stream within the framework of biogas upgrading.

The stream fed to the membrane system⁴, based on the flue gas from an average 600 MWe coal-fired power plant, was compared with our stream (see Table S1 in the Supporting Information). Due to the MCFC CO₂-concentrating effect, the membrane separation sizing for the 800 MW NGCC has a 4-fold lower feed flow and a 3.6-fold higher CO₂ concentration than the reference. The membrane permeability and selectivities are based on data from Merkel et al. works^{4,25} (see Table S2 in the Supporting Information). These selectivities are consistent with those reported by Chen et al.²⁶: 12.9 and 41.1, respectively, for CO₂ / H₂ and CO₂ / N₂, for a polymer / ionic liquid blend.

3. Modeling and tools

The feasibility analysis has been performed assuming the inlet fluid compositions reported in Table 1.

The modeling key hypotheses include i) ideal gas law; ii) ambient conditions corresponding to 15°C and 1 atm; iii) entirely adiabatic combustion of hydrogen, methane and ethane in the burner; iv) 33 K temperature approach to equilibrium for all reactions in the REFORMER; v) negligible REFORMER and REGHEX pressure drops.

A summary of the key input data is given in Table S3 (Supporting Information).

The modeling tool used to perform the process simulations was LIBPF²⁷ version 1.0.1015. To make it possible to perform a trial-and-error design procedure to find the optimum operating parameters, we have adopted the intermediate fidelity modeling approach for the MCFC and GMS units.

On a typical workstation, the calculation time for the intermediate-fidelity model is in the range of minutes for the first execution, and about 2 seconds for subsequent evaluations. In the case of the detailed model, about one hour is required for the first execution and a few minutes for subsequent evaluations.

As far as concerns the MCFC model¹², it consists of a coarsely discretized distributed parameter model for planar, rectangular, MCFCs, which allows temperature inhomogeneities on the cell plane to be calculated with relatively little computational effort. The results are not the same as those obtained from a detailed model, but they can be reconciled at the nominal operating point using three empirical correction parameters : i) temperature approach for the reformer; ii) offset tension ; iii) offset-heat duty.

These empirical parameters have been calibrated for the reference working point and extrapolated for a wider domain in the sensitivity studies; therefore the usual warning applies

that the sensitivity results are qualitative in nature and are not meant to predict in detail the quantitative system behavior.

The gas separation membrane is represented by a distributed parameter model obtained by replicating ten LIBPF units of type Membrane12Cstr. The latter is a free flow, concentrated parameter, perfectly mixed unit with one inlet and two outlets (no permeate-side sweep provision). The resolution of Membrane12Cstr is based on an adimensional implicit formulation solved for the total stage cut as the only unknown¹³.

The results obtained from the simulation were analyzed in order to find the best solution to the problem of reducing GHG emissions from stationary electrical power generation. However it is not straightforward to identify the best criterion on the basis of the various quantitative indicators available, and taking into account the non-quantifiable factors. For this reason, particular attention was dedicated to choosing the right indicators as evaluation tools.

In fact, when the chosen indicator is the abatement cost, the “gas plant CCS retrofit” results as the least attractive GHG-reducing technology as indicated in McKinsey work²⁸, which reports an abatement cost of approx. 60 € / tCO₂e.

Nevertheless, the abatement cost takes into account only two of the three measurable factors involved - cost and GHG emission reduction - but it fails to take into account the third factor - conversion efficiency - and its impact on non-renewable fossil resource consumption. Other non-quantifiable criteria also, such as technical feasibility, electricity market compatibility and public acceptability are not accounted for.

Another useful indicator is SPECCA (Specific Primary Energy Consumption for CO₂ Avoided)²⁹, that accounts for reduction of greenhouse gas emissions and fossil resource

consumption. On the other hand, this indicator neglects costs and, of course, all non-quantifiable requirements.

In this paper, we present results using a set of five different indicators:

- Energy conversion efficiency (LHV base)
- Specific CO₂ emission, kgCO₂ / kWh
- Abatement cost, € / tCO₂e
- SPECCA, MJLHV/kgCO₂
- COE (cost of energy), €/MWhel

which must be evaluated as a whole, together with non-quantifiable requirements, based on the understanding that no unique “best” solution exists, but that one or other solution may be better depending on local conditions, timing, constraints, opportunities etc.

It should be noted that the abatement cost and cost of energy are mutually exclusive: the abatement cost shifts all additional costs for capture to the separated ton of CO₂, as if the electricity market in no way compensates for these costs. The cost of energy shifts all additional costs to the kWh produced, again as if no incentives whatsoever were in place to reward the separated ton of CO₂. In reality, both the electricity price and CO₂ emission cost are determined by their respective markets, deriving from the complex interplay between renewables, ageing high-emission conventional plants, and newer plants based on competing capture technologies. The approach adopted in the Financial Sustainability section below, is to compare the abatement cost with a given scenario for the CO₂ emission cost, resulting in a reward or penalty for the energy cost.

Finally, the financial costs have been calculated using a simplified approach . It was found that the cost of electricity and the CO₂ abatement cost²⁹ could be equaled in both reference NGCC and the NGCC-MCFC-GSM plants using a simple coefficient to compute the OPEX, excluding the feedstock (natural gas) cost, as a yearly 13.6% fraction of the CAPEX. This coefficient can be interpreted as the sum of 8% interest and approx. 5.6% for depreciation, labor, and maintenance.

4. Results

4.1 Performance

Conventional NGCC power plants already have comparatively low specific CO₂ emissions, in the range of 0.357 kgCO₂ / kWh. For comparison with Polimi report²⁹, a removal efficiency of 86% is applied to the Advanced Super Critical (ASC) pulverized bituminous coal test case, bringing the specific CO₂ emission down from 0.763 to 0.105 kgCO₂ / kWh. To achieve a comparable specific CO₂ emission from the NGCC, a removal efficiency of 70.6% would be sufficient.

However, due to the constraints on the MCFC CO₂ utilization factor and consequently on the CO₂ separation yield, a 70% reduction in specific CO₂ emissions cannot be guaranteed today using this technology, as discussed above. For this reason, in this work, we will keep to a realistic removal efficiency of approx. 58%, while the path to follow to increase the removal efficiency further is outlined in the Conclusion section.

For the purposes of making comparisons, it is useful to present here the performance of NGCC for capture using traditional post-combustion technologies based on chemical solvents²⁹:

- Energy conversion efficiency (LHV base): 49.9 %, 8.4 % less than 58.3 % base case
- Specific CO₂ emission: 0.036 kgCO₂ / kWh, 90% less than 0.352 kgCO₂ / kWh
- Abatement cost: 47.6 € / tCO₂e
- SPECCA: 3.3 MJLHV/kgCO₂
- COE (cost of energy): 69 €/MWhel, up 28 % from 54 €/MWhel

A summary of the results for non-economical indicators is shown in Table 2. It is interesting to note that the NGCC retrofitted with conventional amine separation has a 15% lower net electricity output. The proposed NGCC-MCFC-GSM configuration, on the other hand, has a 27% higher net electricity output due to the reduced energy costs of separation from a concentrated stream, and the additional power output from the MCFCs. In the reference NGCC plant, the OC contributes 72.4% of the total net electricity output, while the remaining 26.4 is supplied by the SC. In the proposed configuration, the net power is split as OC 58.4%, SC 28.5 % and MCFC 13.1%. The energy cost of separation is given by the compression power consumption in the membrane unit of 34 MW, corresponding to 3.2 % of the overall plant energy turnover.

4.2 Sensitivity analysis

A few degrees of freedom have been allocated to keep certain results within the required boundaries:

- the number of stacks was manipulated to set the stack CO + H₂ utilization factor, which can be used to study different working points of the system;

- the fresh air to the OC was manipulated to match the desired TOT, which must be set to the value 863 K compatible with the cathode inlet;
- the water condensate split ratio was manipulated to set the desired H-to-C ratio at the reformer inlet.

After these three additional equations were added, the parameters below could be optimized, and the sensitivity of the constrained results and of the key performance parameters on them could be studied:

- total membrane area;
- membrane pressure level;
- membrane area ratio;
- stack CO + H₂ utilization factor;
- natural gas feed to OC and MCFCs;
- anode recycle purge split ratio.

The total membrane area and the membrane pressure level both behave in very similarly: both have a heavy impact on the anode recycle and the SPECCA. The maximum stack temperature also is affected. Generally speaking, a higher total membrane area or pressure reduces anode recycle and favors SPECCA, energy conversion efficiency and the maximum temperature, but reduces the CO₂ purity due to the limited selectivity between CO₂ and other components in the anode off-gas.

Increasing the membrane area ratio (ratio of the second membrane to the first membrane) is beneficial to all indicators, but results in a linear decrease of CO₂ purity and recovery.

The stack CO + H₂ utilization factor also benefits all indicators, but violates the maximum stack gas temperature constraint, as can be seen from the plot shown in Figure 5. For example, if the utilization factor is increased from a nominal value of 54.5% to 80%, reducing the NG fed to the MCFC and maintaining the same current density, the SPECCA is reduced from 2.42 to 1.17, the electrical efficiency increases from 52.5% to 54.5%, and the system CO₂ recovery increases from 58.1% to 61%. Unfortunately, the maximum stack gas temperature also increases from 962 to 978 K, which is unacceptable. The increase in stack temperature is attributable, in part, to the increased heat release from the irreversible reactions, and in part to the reduction in cooling due to sensible heat removal caused by the reduced anode flow.

CO₂ recovery can be controlled by changing the ratio of natural gas fed to the OC and MCFC. For example, if the natural gas fed to the OC is kept constant, increasing the natural gas fed to the MCFC for a constant fuel utilization factor, increases CO₂ recovery. There is a penalty to pay because the SPECCA and electrical efficiency indicators are impacted, and again the maximum stack temperature constraint is reached. For example, if the same CO₂ specific emission of 0.105 kgCO₂ / kWh is targeted as for the Advanced Super Critical pulverized bituminous coal test case²⁹ with a removal efficiency of 86%, then the natural gas fed to the FC must be increased by 19%, increasing the SPECCA to arrive at 3.69, reducing the electrical efficiency to 49.6% and bringing the maximum stack temperature above acceptable limits to 983 K.

If the same CO₂ recovery is targeted as in the previous example, but the stack CO + H₂ utilization factor is increased to 80%, with an increase in natural gas fed to FC of 8.6% w.r.t.

the base case, to 1316 kmol/h, then the performance indicators are very positive: SPECCA 1.23, electrical efficiency 54.2%, CO₂ utilization in the stack 66.9%; net power split is OC 56%, SC 29.3 % and MCFC 14.7%. Unfortunately, the maximum stack temperature of 988 K is way beyond acceptable limits.

The anode recycle purge split ratio quite obviously controls the anode recycle flow rate. It increases CO₂ recovery and purity, but impacts negatively on the other indicators. After a certain threshold is surpassed (approx. 98.5%) the subsequent degradation is dramatic, presumably due to accumulation of inerts in the anode recycle. At the nominal point, the anode recycle purge split ratio was set to a value (95.64%) that allows CO₂ of the required purity to be obtained (95.5%).

In conclusion, the sensitivity effects of the H-to-C ratio have also been studied, although strictly speaking it does not represent a degree of freedom since it should be bound to the constrained value of 2.5. It turns out that it has no significant effect on the maximum stack temperature and CO₂ purity and recovery, but impacts energy conversion efficiency and SPECCA. Reducing the H-to-C ratio from 2.5 to 2 would increase efficiency by 0.9 % and reduce the SPECCA from 2.42 to 1.91. However, unfortunately, reducing the H-to-C ratio increases the risk of char deposition and fouling therefore this option cannot be pursued further.

4.3 Financial sustainability

For the CAPEX of conventional NGCC plants in the 800 MW_{el} range, Finkenrath³⁰ reports 960 \$/kW_{el} installed and Polimi work²⁹ 759 €/kW_{el}. The intermediate value of 747 €/kW_{el} at a €/\$ exchange rate of 1.3 has been chosen. The CAPEX for the OC / SC sections in the proposed configuration was downsized by 13% to account for the reduced flows.

The target system-cost for stationary MCFC applications with powers above 100 kW_{el} in the time frame 2009 – 2012³¹ is 1500 – 5000 €/kW_{el} installed. While, the latest installation costs for MCFC systems are in the range 3000 – 4000 €/kW_{el}³² depending on scale, but the long-term target is under 1100 €/kW. For the purposes of this work, the value of 1500 €/kW_{el} was chosen.

For the membrane system, Merkel et al.⁴ extrapolates a membrane skid cost of 50 \$/m² - an order of magnitude less than today's commercial gas separation membrane - based on the low operating pressure, absence of flammable or corrosive gases, large scale and similarity with certain large-scale, reverse osmosis, systems. When compared with Merkel et al.⁴, the membrane area is much less (by a factor of 14), but the compression installed power and energy consumption is comparable; therefore a more conservative value of 250 \$/m² was used for the membrane skid cost, for the same installation factor of 1.6, and compression equipment balance-of-plant \$500/kW as the reference.

The resulting CAPEX for the proposed configuration is 858 M€, see Table 3, that represents an increase of 43% with respect to the reference NGCC power plant. But considering the higher net electricity output, the specific CAPEX is 848 €/kW, which reflects an increase of only 13%.

The simplified approach described above was used to compute the OPEX, excluding the natural gas cost as a yearly 13.6% fraction of the CAPEX.

The cost of natural gas is a very uncertain parameter: geographical differences are huge and future projections ridden with uncertainty. The current US price at the Henry Hub is back at the same nominal prices of ten years ago: 1.89 €/GJ_{th}. The IEA report¹ uses three scenarios: OECD Europe at 7.48 €/GJ_{th}, United States at 5.65 €/GJ_{th}, and “long-term energy crunch” at 15.33 €/GJ_{th}, while elsewhere²⁹ the value of 6.5 €/GJ_{th} is used. Considering that the proposed

configuration involves a scale-up of an existing, but pre-commercial, technology (MCFC) and a new application for a mature technology (gas membranes), its implementation will probably occur in one or more decades from now. Given the 25-year lifetime for this type of plant, it is likely that over a 50-year timescale, increased world consumption will push natural gas prices up. In this work, the cost of natural gas has been considered a sensitivity parameter, between the OECD Europe¹ and “long-term energy crunch” scenarios.

As to the price of carbon dioxide emission, currently at an all-time-low of 6 €/tCO₂e, the recent press³³ release from EU commissioner for Climate Action, Connie Hedegaard, hints at a revised approach for the third phase (2013-2020) of the EU Emissions Trading System (ETS), which could bring the price back to the baseline value of 25 €/tCO₂e, or even to the higher level of 40 €/tCO₂e. In this work, the ETS price is also a sensitivity parameter, varying between the baseline and higher levels.

Taking into consideration the above discussions, for cost abatement we propose two scenarios based on the natural gas price parameter. Similarly, for the COE (Cost Of Energy) including ETS, we propose four scenarios based on both the cost of ETS and the natural gas price parameter. We present these two scenarios and four scenarios for the two NGCC options, plants NGCC-MEA and NGCC-MCFC-GSM, in Table 4. The comparison highlights the economic advantage of the NGCC-MCFC-GSM solution.

5. Conclusions

The configuration proposed requires substantial changes in the NGCC components, so that it cannot be considered as a retrofit technology for existing plants. However, due to its modularity, it could be applied to small plants.

This work underlines the fact that MCFC and GSM integration within NGCC plants is synergistic, each component serving a dual purpose:

- OC produces energy and provides high-temperature heat recovery to sustain reforming;
- SC produces energy and the medium-pressure steam required for reforming;
- MCFCs concentrate the CO₂ and produce energy;
- GSMS separate the CO₂ and recover the unconverted syngas components (CO, H₂).

The good integration results in a valid technical compromise which is reflected in the economic indicators that outperform the conventional amine absorption NGCC retrofit in all scenarios. The advantage becomes proportionally greater in “long-term energy crunch” scenarios because the proposed configuration is very good in terms of reduced impact on electrical conversion efficiency, i.e. fossil fuel consumption.

Even if on the basis of several simplified assumptions, which could be the object of further analyses, such as the impact of the desulfurization phase discussed, or the increase of OPEX due to MCFC and GSM maintenance, the results are nevertheless quite promising.

It needs to be added that there could be a great margin for improvement by increasing fuel and CO₂ utilization factors. In this case, the limits due to diffusion effects for high conversion factors - nowadays a critical point in MCFC technology development – need to be analyzed in detail using a proper kinetics model . This work has highlighted that the maximum hot-spot temperature in fuel cells is the main process limitation. This problem could be resolved in a general way, for example, by improving the flow distribution in the cell plane¹⁶ while for the specific process, a cooled cathode recycle could be introduced.

The intermediate fidelity distributed parameter models for fuel cells and membranes, implemented in the LIBPF process simulation library, played a key role in accelerating the process of understanding the complex interactions between the subsystems, and obtaining an optimized configuration compliant with all constraints.

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FIGURES

Figure 1. Process flow diagram for the reference NGCC power plant (LIBPF model NGCC)

Figure 2. Process flow diagram for the NGCC-MCFC-GMS integration (LIBPF model NGFCCC)

Figure 3. Process flow diagram for the MCFC unit (LIBPF model NGFCCC:FC)

Figure 4. Process flow diagram for the GSM unit (LIBPF model NGFCCC:FC:MM)

Figure 5. Sensitivity analysis results for a change in stack fuel utilization factor

TABLES

Component	Mol fraction in natural gas	Mol fraction in air
CH ₄	88.63%	-
C ₂ H ₆	7.34%	-
CO ₂	0.43%	0.0249 %
N ₂	3.61%	79.01 %
O ₂	-	19.75 %
H ₂ O	-	1.207 %

Table 1. Inlet fluid compositions

	NGCC reference	NGCC-MEA	NGCC-MCFC-GSM
Net electricity output, MW	806	687	1012
CO ₂ capture efficiency	-	90%	58.1%
Energy conversion efficiency (LHV base)	56.8%	48.4%	52.5%

Efficiency loss	-	8.4%	4.3%
Specific CO ₂ emission, kgCO ₂ / kWh	0.356	0.036	0.149
SPECCA, MJLHV/kgCO ₂	-	3.43	2.53

Table 2. Non-economical indicator results

	CAPEX, M€	Cost fraction
OC / SC	523	61%
MCFC subsystem	249	29%
GSM	85	10%
TOTAL	858	100%

Table 3. CAPEX for proposed configuration

		NGCC-MEA	NGCC-MCFC-GSM
Specific CAPEX, €/kW _{el} installed		1248	848
Cost surplus w.r.t. reference NGCC plant, specific CAPEX base		67%	13%
Natural gas price	Abatement cost, € / tCO _{2e}	53.2	27.5

OECD Europe (7.48 €/GJ _{th})	COE with ETS baseline (25 €/ tCO ₂ e), €/MWh _{el}	78.6	70.0
	COE with ETS aggressive (40 €/ tCO ₂ e), €/MWh _{el}	79.1	72.3
Natural gas price “Long-term energy crunch” (15.33 €/GJ _{th})	Abatement cost, € / tCO ₂ e	77.3	45.3
	COE with ETS baseline (25 €/ tCO ₂ e), €/MWh _{el}	131.0	118.4
	COE with ETS aggressive (40 €/ tCO ₂ e), €/MWh _{el}	131.5	120.6

Table 4. Economic indicator results

ASSOCIATED CONTENT

The C++ source code and special-purpose process simulator installer for Microsoft Windows operating systems for all configurations presented can be downloaded from this location: : http://www.dicca.unige.it/pert/LIBPF_it.unige_mcfcccs.zip.

Supporting Information. Additional tables. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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REFERENCES

- (1) International Energy Agency Are we entering a golden age of gas? *Special report, World Energy Outlook 2011*, <http://www.worldenergyoutlook.org/goldenageofgas/>
- (2) Ma'mun, S.; Svendsen, H.F.; Hoff, K.A.; Juliussen O. Selection of new absorbents for carbon dioxide capture. *Energ Convers Manage* 2007, 48, 251.
- (3) Brunetti, A.; Scura, F.; Barbieri, G.; Drioli, E. Membrane technologies for CO₂ separation. *J Membrane Sci* 2010, 359, 1-2, 115.
- (4) Merkel, T. C.; Lin, H.; Wei, X.; Baker, R. Power plant post-combustion carbon dioxide capture: An opportunity for membranes. *J Membrane Sci* 2010, 359, 1-2, 126.
- (5) Zhao, L.; Riensche, E.; Blum, L.; Stolten, D. Multi-stage gas separation membrane processes used in post-combustion capture: Energetic and economic analyses. *J Membrane Sci* 2010, 359, 1-2, 160.
- (6) Amorelli, A.; Wilkinson, M.B.; Bedont, P.; Capobianco, P.; Marcenaro, B.; Parodi, F.; Torazza, A. An experimental investigation into the use of molten carbonate fuel cells to capture CO₂ from gas turbine exhaust gases. *Proceedings of GHGT-6*, paper F3-4, Kyoto, Japan, 2002.
- (7) Lusardi M.; Bosio B.; Arato E. An example of innovative application in fuel cell system development: CO₂ segregation using Molten Carbonate Fuel Cells. *J. Power Sources* 2004, 131, 1-2, 351.
- (8) Spallina, V.; Romano, M.C.; Campanari, S.; Lozza, G. Application of MCFC in Coal Gasification Plants for High Efficiency CO₂ Capture, *J Eng Gas Turb Power* 2012, 134, 1, 011701.

- (9) Greppi, P.; Bosio, B.; Arato, E. Feasibility of the integration of a molten carbonate fuel-cell system and an integrated gasification combined cycle. *Int J Hydrogen Energ* 2009, 34, 20, 8664.
- (10) De Visser, E.; Hendriks, C.; Barrio, M.; Mølnvik , M.J.; De Koeijer, G.; Liljemark, S.; Le Gallo, Y. Dynamis CO₂ quality recommendation. *Int J Greenh Gas Con* 2008, 2, 478.
- (11) Ferrari, E.; Greppi, P.; Bosio, B. Molten Carbonate Fuel Cells integration with a Natural Gas Combined Cycle power plant for CO₂ capture. *Proceedings of EFC2011 European Fuel Cell - Piero Lunghi Conference & Exhibition*, Rome, Italy, 2011.
- (12) Greppi, P.; Bosio, B.; Arato, E. A steady-state simulation tool for MCFC systems suitable for on-line applications. *Int J Hydrogen Energ* 2008, 33, 6327.
- (13) Greppi, P.; Arato, E.; Bosio, B. Rapporto PERT3: Membrane modelling, ENEA Report RdS/2011/99 http://www.enea.it/it/Ricerca_sviluppo/ricerca-di-sistema-elettrico/biomasse/produzione-di-energia-da-biomasse-e-scarti/report#2008.
- (14) Scattolini, A.; Bosio, B. Theoretical and experimental investigation of MCFC performance, HYSYDays – 1st World Congress of Young Scientists on Hydrogen, Torino, 2005.
- (15) Di Giulio, N.; Bosio, B.; Cigolotti, V.; Nam, S.W. Experimental and theoretical analysis of H₂S effects on MCFCs. *Int J Hydrogen Energ* 2012, doi:10.1016/j.ijhydene.2012.03.086.
- (16) Bosio, B.; Marra, D.; Arato, E. Thermal Management of the Molten Carbonate Fuel Cell Plane. *J Power Sources* 2010, 195, 15, 4826.

- (17) Campanari, S.; Chiesa, P.; Manzolini, G.; Giannotti, A.; Parodi, F.; Bedont, P.; Federici, F. Application of MCFCs for active CO₂ capture within natural gas combined cycles. *En. Procedia* 2011, 4, 1235.
- (18) Ghezel-Ayagh, H. Combined power generation and carbon sequestration using direct fuel cell. Scientific/Technical Report, FuelCell Energy 2006.
- (19) Campanari, S.; Chiesa, P.; Manzolini, G. CO₂ capture from combined cycles integrated with Molten Carbonate Fuel Cells. *Int J Greenh Gas Con* 2010, 4, 441.
- (20) Arato, E.; Bosio, B.; Costa, P.; Parodi, F. Preliminary experimental and theoretical analysis of limit performance of molten carbonate fuel cells. *J Power Sources* 2001, 102, 74.
- (21) Discepoli, G.; Cinti, G.; Penchini, D.; Sisani, E.; Desideri, U. Experimental test of carbon capture from cogeneration plant with MCFC coupled, *Proceedings of European Fuel Cell - Piero Lunghi Conference & Exhibition*, Rome, Italy, 2011, 370.
- (22) Giannotti , A.; Passalacqua, B.; Puddu, C. MCFC system configuration for CCS application. *Proceedings of European Fuel Cell - Piero Lunghi Conference & Exhibition*, Rome, Italy, 2011, 30.
- (23) Bosio, B.; Costamagna, P.; Parodi, F. Modeling and experimentation of molten carbonate fuel cell reactors in a scale-up process, *Chem Eng Sci* 1999, 54, 2907.
- (24) Deng, L.; Hägg, M.B. Techno-economic evaluation of biogas upgrading process using CO₂ facilitated transport membrane. *Int J Greenh Gas Con* 2010, 4, 638.
- (25) Merkel, T. Private communication

(26) Chen, H.Z.; Li, P.; Chung, T.S. PVDF/ionic liquid polymer blends with superior separation performance for removing CO₂ from hydrogen and flue gas. *Int J Hydrogen Energ* 2012, 37, 16, 11796.

(27) Greppi, P. LIBPF: a library for process flowsheeting in C++. *Proceedings of the international Mediterranean modelling multiconference. 2nd European Modeling and Simulation Symposium*. Barcellona, Spain, 2006, 1, 435.

(28) McKinsey&Company, Pathways to a Low-Carbon Economy, version 2 of the Global Greenhouse Gas Abatement Cost Curve, 2009.

(29) Politecnico di Milano, Alstom UK, European best practice guidelines for assessment of CO₂ capture technologies. *Report D 4.9 of EU FP7 project CAESAR CArbon-free Electricity by SEWGS: Advanced materials, Reactor-, and process design*, 2011.

(30) Finkenrath, M. Cost and performance of Carbon Dioxide from Power generation. *International Energy Agency Working paper*, 2011.

(31) European hydrogen and fuel cell technology platform (HFP) implementation plan – status 2006. Endorsed by the HFP Advisory Council on January 19, 2007.

(32) Bosio, B.; Arato, E.; Greppi, P. Technology Applications of Molten Carbonate Fuel Cells. in *Fuel Cell Science and Engineering: Materials, Processes, Systems and Technology*; ed. Stolten, D. and Emonts, B., Wiley-VCH 2012 , 67.

(33) European Commission Emissions Trading: Commission prepares for change of the timing for auctions of emission allowances, July 25th 2012,
<http://europa.eu/rapid/pressReleasesAction.do?reference=IP/12/850>

