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Preliminary design of a MW-class demo system for CO₂ capture with MCFC in a university campus cogeneration plant

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Abstract

One of the most promising, short-term options for efficiently capturing CO_2 from combustion exhaust gases – potentially from any combustion process source - is based on the operating principle of Molten Carbonate Fuel Cells (MCFC): their electrochemical reactions promote the transport of both CO₂ and O₂ molecules from the cathode side (which can be fed with combustion effluents) to the CO₂-rich atmosphere of the anode side (fed with internally reformed natural gas), by means of a CO₃²-ion conducting electrolyte. In the present work, the preliminary design of a 1 MWel MCFC demo plant operating downstream a Combined Heat and Power (CHP) Internal Combustion Engine (ICE) installed at the Politecnico di Milano campus is investigated, with the aim of promoting a valid solution for high efficiency, de-carbonised heat and electricity production. The study envisages two purification strategies for the CO2-rich stream at the MCFC anode outlet: i) the CO2 is separated and compressed in a cryogenic unit and the unconverted fuel is either recycled at the anode inlet or burned and sent to the MCFC cathode inlet ii) the anode exhausts are burned in a catalytic oxy-combustor, increasing both the thermal energy available in the cogeneration unit and the CO₂ concentration in the stream sent to the storage site. Subsequently to a thermodynamic analysis carried out with a 0D model calibrated upon experimental data available for a commercial MCFC unit, the main components are designed by taking into account all the operating constraints of the machines and the CO₂ capture limitations associated to the size of the MCFC modules currently available on the market. Moreover, an economic analysis is performed in order to assess the feasibility of such an installation within the university campus cogeneration grid. As a main finding, the use of MCFCs to capture CO₂ at a distributed generation scale allows reaching interesting energy and environmental performances, highlighted by promising values of the Specific Primary Energy Consumption for CO₂ Avoided (SPECCA=0.9-1.9 MJ/kgCO₂) and Carbon Capture Ratios (CCR=68-84%). Within a mid-term perspective for MCFC specific cost, the economic analyses reveal acceptable values for the cost of electricity and the cost of CO2 avoided, respectively close to 130 €/MWhel and 100 €/tCO₂.

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1. Introduction

MCFCs are being extensively studied for post-combustion Carbon Capture and Storage (CCS) applications [1,2], thanks to their inner capability of transporting CO_2 and O_2 from the exhaust gas stream of a conventional power cycle (cathode side) as reactants to oxidise the fuel (anode side). Decarbonisation of the power generation sector is currently focusing also on small power units installed in medium scale communities supplied with local mini-grids. The novelty of the present work is to apply the MCFC-based post-combustion CCS configuration at a distributed generation scale (<10 MW) in a local Combined Heat and Power (CHP) grid which supplies a university campus, setting up the study of a potential demonstrative installation of this type of power plant.

The main targets of this study are summarised as follows:

- Calibration of a simulation model for a commercial MCFC power plant, taken as a reference for its possible adaptation to the CCS operation
- Design of possible layouts to implement post-combustion CCS to the CHP Internal Combustion Engine (ICE) unit installed at Politecnico di Milano campus, when combined with a commercial-scale MCFC unit
- Assess the energy balances and greenhouse gas emissions of the proposed solutions with respect to the current solution without CCS
- Introduce a techno-economic analysis in order to assess the feasibility of the new installation.

MCFC	Molten Carbonate Fuel Cell
СНР	Combined Heat and Power
CCS	Carbon Capture and Storage
CCR	Carbon Capture Ratio
ICE	Internal Combustion reciprocating Engine
LHV	Lower Heating Value
PES	Primary Energy Saving
SPECCA	Specific Primary Energy Consumption per CO ₂ Avoided

Nomenclature

2. Plant modelling

2.1. Modelling methodology

In this study the system thermodynamic modelling is carried out employing an in-house modular simulation code called "GS"; the software has been developed at the Energy Department of Politecnico di Milano since the early 90's [3]. The plant layout is built by assembling in a coherent network the different components selected in a library containing over 20 basic modules. The thermodynamic and chemical properties are internally calculated using the standards reported in [4,5] for ideal gases and water/steam.

Each component is modelled by means of 0D approach; in particular, the MCFC model performs the calculation of the stack operating conditions (i.e., average voltage, overpotential losses, power output) using the values of inlet pressure, composition, mass flow rate, temperature and average current density. The polarisation curve of the stack is

calibrated against experimental data reported in *Spinelli et al., 2015* [1], in which a CCS operation is explored using a commercial stack manufactured by FuelCell Energy (USA).

The cell operation depends, among other effects, on the fuel utilisation factor and on the nature of the kinetic reactions on the anode side. In this study, the Steam Methane Reforming (SMR) and Water Gas Shift (WGS) reactions are assumed to reach full conversion and the thermodynamic equilibrium composition respectively. With reference to the FuelCell Energy module, the stack is fed through reforming layers in which Indirect Internal Reforming (IIR) takes place along with a partial fuel pre-heating; these reaction layers are thermally integrated within the stack but are non-electrochemically active. Subsequently, the resulting syngas is split and supplied to the cell layers in which additional Direct Internal Reforming (DIR) occur in parallel with the electrochemical reactions:

$H_2 + CO_3^{2-} \to CO_2 + H_2O + 2e^-$ 0.50 ₂ + CO ₂ + 2e ⁻ $\to CO_3^{2-}$	$\Delta H_r^{\circ} = -286 kJ mol^{-1}$
$CH_4 + H_2 0 \rightleftharpoons CO + 3H_2$	$\Delta H_r^\circ = +206 \ kJ \ mol^{-1}$
$CO + H_2O \rightleftharpoons CO_2 + H_2$	$\Delta H_r^{\circ} = -41 kJ mol^{-1}$

Summarizing all the effects, and taking into account the consumption of H_2 ultimately oxidized at the anode, the cell performs a complete internal reforming of the fuel. As far as the modelling of the CO₂ purification and compression systems is concerned, the need for more advanced state equations compels using a different simulation software. Due to the extensive experience with these systems [6], AspenPlus is employed to simulate both the CO₂ cryogenic purification section and the compression system. Table 1 summarises all the main assumptions of each component used in the simulation.

Ambient conditions				
Temperature [°C]	15.0			
Pressure [bar]	1.013			
Relative Humidity [%]	60.0			
Natural Gas ch	emical properties			
Molar composition [%mol]	CH ₄ : 89.0, CO ₂ : 2.0, C ₂ H ₆ : 7.0, C ₃ H ₈ : 1.1, N ₂ : 0.89			
LHV [MJ/kg]	46.477			
М	CFC			
Module gross power output [kW]	300.0			
Active area [m ² /module]	270.0			
Anode stream inlet temperature [K]	723.15			
Cathode stream inlet temperature [K]	853.15			
Fuel utilisation factor (once-through) [%]	75.0			
S/C at anode inlet*	2.0			
Anode inlet pressure [bar]	1.11			
Cathode inlet pressure [bar]	1.10			
Minimum CO_2 at cathode outlet $[v/v\%]$	1.0			
Anode and cathode channels pressure losses [%]	2.0/3.0			
DC/AC electrical efficiency [%]	94.0			
Heat loss [% of inlet fuel LHV]	1.0			
CO ₂ compr	ession system			
Equation of state	Peng-Robinson [7]			
Flash temperature [°C]	-54.0			
Minimum ΔT in cryogenic heat exchanger [°C]	2.0			
Inter-cooled volumetric compressors number [-]	5			
Hydraulic/mechanical/electric efficiency [%]	64.0 / 94.0 / 94.0			
Inter-coolers outlet temperature [°C]	25			
Inter-coolers pressure losses [%]	1% of inlet pressure			
Liquid CO ₂ conditions at pump inlet	20 °C, 89.1 bar			
Liquid CO ₂ to storage	150 bar			
Burner				
Combustion efficiency [%]	99.0			
Oxidant pressure loss $\Delta p/p_{in}$ [%]	1.0			
Compressor isentropic efficiency [%]**	80.0			

Table 1 - Main simulation assumptions

Compressor mechanical-electrical efficiency [%]**	94.0			
Heat Exchangers				
Hot and cold side $\Delta p/p_{in}$ [%]	2.0			
Heat losses pre-heater [% of heat transferred]	0.7			
Heat losses recuperator [% of heat transferred]	0.5			
Effectiveness per-heater [%]	60.0			
Effectiveness recuperator [%]	90.0			
Minimum gas-evaporating water ΔT (pinch-point) [°C]	10			
Minimum ΔT in gas—water heat exchangers [°C]	15			
Minimum ΔT in gas—gas heat exchangers [°C]	30			
Miscellaneous				
Minimum exhaust temperature at stack [°C]	80.0			
Air fan isentropic efficiency [%]	80.0			
Air fan mechanical-electrical efficiency [%]	94.0			

*S/C value has been calculated vs. reactive carbon-based molecules (i.e., total carbon except CO2)

** when present

2.2. Reference CHP plant

Figure 1 represents the layout of the reference MCFC-based CHP plant without CCS. The system aims at reproducing a simplified configuration of the 1400 kW_{el} (AC) commercial module currently proposed by FuelCell Energy, which will be taken as baseline to compare the proposed systems with CCS. The system is based on the use of 4 MCFC stacks (each of the capacity of approximately 350 kW), here represented as a lumped unit, and features a natural gas supply (point no. 9) which, subsequently to an appropriate desulphurisation stage, is pre-heated and humidified prior being fed to the stack reforming layers (not represented for simplicity) and anodic compartment.





Fuel conversion in the anodic reactions is characterised by a fixed utilisation factor, as reported in Table 1. The remaining un-oxidised fuel is burnt in a catalytic combustor and the exhaust gases, featuring a CO_2 and O_2 content of approximately 18% and 6% respectively, are fed to the MCFC cathode. The cathode exhausts, leaner in CO_2 content, are used for heat recovery purposes within the cycle and to produce additional thermal power for external uses. Note that the simulations carried out in this work are performed assuming the air mass flow rate at the system inlet as constant, hence the natural gas and water supply flow rates change accordingly in order to maintain the imposed operating conditions of the MCFC stack.

The cell current density (with a nominal value of 1400 A/m^2) is selected to ensure a cell operating voltage above 0.69-0.7 V, according to the manufacturer's advice, to avoid difficulties in the cell thermal management and incurring in thermo-chemical instability of the molten carbonates which constitute the electrolyte.

2.3. CCS configurations

The analysis developed in this work investigates two post-combustion CCS configurations, designed to retrofit the Jenbacher J612 2 MW natural gas fed internal combustion engine installed at the Politecnico di Milano "Leonardo da

Vinci" campus. The exhaust gases of the ICE, in nominal operating conditions, are at ambient pressure and relatively low temperature (\approx 120°C); however, an additional cooling and dehydration step is beneficial for two reasons: i) it increases the carbon concentration at the MCFC cathode inlet; ii) it reduces the power consumption of the downstream blower. Subsequently, the system envisages a pre-heating section in order to reach the cathodic inlet conditions (T=580°C, p=1.1 bar). The anodic inlet stream is made up of humidified natural gas, with a nominal steam-to-carbon (S/C) ratio of 2.0 (see Table 1). Note that the water flow rate required to ensure an adequate S/C ratio is obtained from the condensation of the water content in the ICE exhaust gases, hence allowing for a net zero water consumption of the MCFC system.

The two CCS configurations proposed herein differ for the different CO_2 purification section. In particular, case A exploits the use of a single-flash cryogenic section, whilst case B is based on the oxy-combustion of the anode off-gas stream, thus requiring only a CO_2 compression system for CO_2 liquefaction in view of transportation and storage (or re-utilization). In the following, a more detailed description of the two systems is presented.

2.3.1. Case A: MCFC + cryogenic section

The plant layout of case A is reported in Figure 2. Note that the cathodic pre-heating is performed first exploiting the cathode outlet stream and then by means of a catalytic combustor which oxidises the remaining fuel of the anodic stream separated within the CO_2 purification section. The cathode inlet stream is characterised by a CO_2 and O_2 molar fractions respectively equal to 4.79% and 11.47%, which guarantees the compliance of the MCFC operating condition constraints listed in Table 1.



Figure 2 - Case A: MCFC post-combustion system with cryogenic CO2 purification section

The anodic inlet stream is pre-heated using the available heat from the anode off-gas stream, which needs to be cooled down to ambient conditions prior being sent to the cryogenic purification section. The heat recovery section exploits both the anode and cathode off-gas streams to produce low temperature useful heat for district heating and to meet the thermal load demands of the campus buildings surrounding the generation plant. The cathode stream, lean in CO_2 content ($\approx 1.55\%$), is then vented to the environment, whilst the anode stream is sent to the cryogenic section.

As far as the cryogenic section is concerned, a revised version of the system presented in *Campanari et al.*, 2016 [8] is considered, focusing on a simplification which can be reasonably adapted to the small size of the proposed installation. In particular, with respect to the original solution, the system proposed here is characterised by a single flash layout working at -54°C. The CO₂ stream entering the cryogenic section is firstly dehydrated and then compressed in a train of three inter-cooled volumetric compressors up to the maximum pressure of the system (i.e., 20 bar). The vapour fraction, rich in H₂ and CO, is throttled to ambient conditions in a three stages iso-enthalpic lamination process; this stream is then fed to the catalytic combustor to pre-heat the cathode inlet stream. On the other hand, the liquid fraction is compressed in a two-stage inter-cooled volumetric compressor up to 90 bar and then pumped to 150 bar.

2.3.2. Case B: MCFC + oxy-fuel combustion

The second proposed solution features an oxy-fuel combustion process of the anodic off-gas stream in order to ultimate the CO_2 purification prior the final compression and liquefaction. Figure 3 depicts the layout of case B. It is noticeable that the anodic off-gas stream is burned in an oxy-fuel burner fed with pure oxygen; moreover, a partial CO_2 recycle from the CO_2 compression system to the oxy-fuel burner is considered, aiming to control the high temperatures which are expected at point #19 in the figure (i.e., maximum temperature approx. 700°C). Note that, due to the limited size of the considered application, a local production of the required oxygen is not pondered feasible; hence oxygen is envisaged to be delivered to the plant site by an external supplier and stored locally in cryogenic tanks, periodically refilled. The burner outlet stream features a composition rich in CO_2 and H_2O , respectively 73.2% and 26.6%, which, subsequently to a heat recovery section and a dehydration stage, shall be sent to the CO_2 compression system.



Figure 3 – Case B: MCFC post-combustion system with oxy-fuel combustion and CO_2 compression section

3. Results and discussion

The proposed configurations are investigated from a technical and economical perspective, in order to perform a preliminary feasibility study of the installation of such systems. In the following, the overall thermodynamic and greenhouse gas performance parameters, resulting from the design of the main components of the systems and the preliminary economic evaluation are summarised.

3.1. Overall thermodynamic performance

Table 2 presents the operating conditions and overall performance of the MCFC system for case A and B (top rows), and those of the overall plant including the ICE (bottom rows). The reader should refer to *Campnari et al., 2016* [8] for a complete description of the performance and greenhouse gas emission parameters reported in Table 2. Note that in both cases the proposed design is characterised by the employment of two 'standard' 350 kW MCFC modules based on the manufacturer commercial line (which are used both within 300 kW and 1.4 MW net power output units), assuming a total active area of 540 m². The operating current density is fixed, in nominal load conditions, in order to comply the mentioned constraints on minimum cell voltage and to optimise the trade-off between plant thermodynamic efficiency and Carbon Capture Ratio (CCR); in fact, the CCR increases at higher current densities because of the higher achievable CO₂ utilisation factors. On the other hand, the power consumptions for the cryogenic and CO₂ compression systems increase accordingly.

Parameter	Units	Case A	Case B
i	A/m2	1400.0	1500.0
V	V	0.697	0.693
CO_2 cathode inlet	%	4.79	4.74
CO_2 cathode outlet	%	1.55	1.25
₩ _{el} gross MCFC	kW	527.0	561.0
Active area	m ²	540.0	540.0
<i>₩_{el}</i> cryo/compr. CO ₂	kW	160.0	113.0
₩ _{el} fan	kW	55.0	50.0
\dot{W}_{el} net MCFC	kW	280.0	350.0
η_{el} MCFC	%	34.05	31.51
\dot{Q}_{NG} (LHV)	kW	5329.0	5638.0
\dot{W}_{el} (ICE+MCFC), net	kW	2282.0	2358.0
¢ CHΡ	kW	2090.0	2283.0
η_{el}	%	42.82	41.83
η_{th}	%	39.22	40.49
E_{CO_2}	$kg_{CO_2} MWh_{el}^{-1}$	123.0	95.0
CCR	%	73.76	80.11
SPECCA	$MJ kg_{CO_2}^{-1}$	0.909	1.395
PES	%	22.6	22.3

Table 2 - Summary of main thermodynamic and greenhouse gas emission performance of the new proposed MCFC-based CCS systems

Note that the solutions proposed here envisage the cooling down of the ICE exhaust gases from approximately 120°C to 30°C in order to reduce the power consumptions of the blower and increase the concentration of CO_2 at the MCFC cathode inlet. It is assumed the availability of water from a cooling tower as a heat sink to reach the desired temperature through a gas-water heat exchanger.

The comparison of the two cycles shows a higher MCFC efficiency for case A, mainly related to the presence of the anodic recycle which allows increasing the overall fuel utilisation factor; on the other hand, case A is characterised by a higher power consumption of the cryogenic plant compared to the compression system in case B. These differences entail a higher CCR for case B, which however comes at a higher expense; the Specific Primary Energy Consumption for CO_2 Avoided (SPECCA) is higher in case B than in A.

3.2. Preliminary economic analysis

The preliminary economic analysis results are summarised in Table 3. The main outcomes confirm that the MCFC modules constitute the biggest cost of the total investment (i.e., 62-63%), based on an assumed 'mid-term perspective' specific cost of 1620 €/kW. Other investment costs are assumed based on the experience discussed in previous analyses [1,9]. Note that the variable costs are approximately constant in the two cases, since no relevant electric efficiency differences are found. The plant lifetime is assumed of 20 years and the MCFC stack replacement time is set at 10 years (again consistently with a mid-term perspective), assuming 8000 h/y of operation. Moreover, 55% of the investment is considered as debt with discount and inflation rates of 7% and 2%, respectively.

Once the COE is known, an estimation of the Cost of CO₂ Avoided (CCA) and the Cost of CO₂ Captured (CCC) is possible for the overall system (ICE+MCFC). The current ICE power plant is taken as a reference case without CCS. It is interesting to note that the obtained CCA is close to the target value of $100 \notin ton_{CO_2}^{-1}$ typical of conventional CCS technologies (i.e., solvents-based CCS [10]). Moreover, the values of CCA and CCC are very similar thanks to the additional electric power production which the MCFC ensure, hence reducing the efficiency penalty of the CCS process, compared to the no CCS case.

Parameter	Units	Case A	Case B
MCFC	k€	1002.0	1002.0
BoP	k€	375.0	450.0
CO ₂ compression	k€	216.0	159.0
Total investment	k€	1593.0	1611.0
O&M	$\in MWh_{el}^{-1}$	15.0	16.0
Fuel	$\in MWh_{el}^{-1}$	62.0	64.0
COE	$\in MWh_{el}^{-1}$	130.0	132.0
CCA	$\notin ton_{CO_2}^{-1}$	107.0	104.0
CCC	$\notin ton_{co}^{-1}$	105.0	102.0

Table 3 - Economic analysis of the new proposed MCFC-based CCS systems

4. Conclusions

This work proposes a techno-economic feasibility study for the installation of a demonstration plant for distributed generation and post-combustion MCFC-based CCS system, which could be placed downstream the exhaust line of a 2 MW CHP ICE currently installed at the campus Leonardo da Vinci at Politecnico di Milano. Two configurations are proposed, which differ on the CO₂ purification technology: i) case A - MCFC + cryogenic purification section; ii) case B - MCFC + oxy-fuel combustor and CO₂ compression system. The main thermodynamic and economic results suggest the following:

- The design of the MCFC system envisages the use of two FuelCell Energy 350 kW modules, processing the exhaust gases of the ICE in the cathodic compartment. The two modules achieve a net electric efficiency of 34% and 31.5% for the two cases in CCS mode, corresponding to an electric power output of 280 kW and 350 kW in addition to the current ICE plant.
- The CCS system allows achieving a CCR between 73% and 80% with respect to the system without CCS. Moreover, the SPECCA parameter ranges between 0.9 and 1.4, thus suggesting promising results, especially when considering the limited size of the plant.
- The economic analysis shows that the investment cost of the post-combustion system is dominated by the cost of the MCFC modules (approx. 63% of the total investment). Moreover, the resulting CCA is close to that typical of more conventional CCS systems, i.e., 104-107 € ton_{CO₂}.

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