Molten Carbonate Fuel Cell as a Reducer of CO_2 Emissions from Gas Turbine Power Plants

Jaroslaw Milewski, Rafal Bernat and Janusz Lewandowski

Abstract A Molten Carbonate Fuel Cell (MCFC) is shown to reduce CO_2 emissions from a Gas Turbine Power Plant (GTPP). The MCFC is placed in the flue gas stream of the gas turbine. The main advantages of this solution are: higher total electricity generated by a hybrid system and reduced CO_2 emissions with power generation efficiency remained the same. The model of the MCFC is given and described. The results obtained show that use of an MCFC could reduce CO_2 emissions by 73.

Keywords CO_2 sequestration · Emissions · Engineering · Fuel cells · Gas turbine · Modeling · Molten carbonate fuel cell · Optimization · Power plants

1 Introduction

Fuel cells are considered to be one of the most prospective electricity sources. They are though to replace mobile phones and computer batteries, become eventual drives for cars, and produce electricity in distributed power plants of larger scale. Various types of fuel cells may be distinguished by different catalysts, different ions being the protone carriers, different operational temperatures and different fuels that may be used. In general, we may recognize low- (e.g. Polymer Exchange Fuel Cells [13]) and high-temperature fuel cells [1] and among the latter Solid Oxide Fuel Cells (SOFC) [9, 15] and Molten Carbonate Fuel Cells (MCFC) [3, 4]. They are both of high

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efficiencies and have the priceless feature of methane utilization—already available fuel [7] including bio-fuels [10]. Others need hydrogen feeding whose production requires significant amount of energy. Additionally, high temperature fuel cell can be coupled to gas turbine for ultra-efficient power generation. Alternatively, the small units based on fuel cells can be utilized as power sources in a Distributed Generation system.

Furthermore, MCFCs enable to concentrate carbon dioxide [11, 17], e.g. from coal [16] or gas fired power plants, and might become a part of a Carbon Capture and Storage system [8]. Operation of MCFC requires flow of CO_3^{2-} as the proton carrier trough the electrolyte. This is achieved by feeding CO_2 to the cathode, where it reacts and flows as CO_3^{2-} to the anode. There, after another reaction, it becomes carbon dioxide again and, after removing water vapor, may be transported as pure gas to the storage point. One may say that MCFCs work as a filter allowing exclusive flow of CO_2 (Fig. 1).

The European Union has placed limits on CO_2 emissions by Member States as a part of its Emission Trading Scheme [2]. This impacts fossil fuel power plants to a significant degree as their emissions are governed by the number of emission allowances they receive from the Member State allocation. Excess CO_2 emissions have to be covered by purchasing extra allowances, which is in effect a penalty. According to the European Energy Exchange, on the 11 of October 2012 it was 7,59 and 7,76 euro/tonne CO_2 for the primary and secondary market respectively. In contrast, undershooting emission limits enables the emitter to sell CO_2 allowances. This is possible to the end of 2012. Then it will be even more strict. From 2013 all emitters will be forced to buy emission allowances from the pool granted to the EU Member. This forces fossil based economies to develop technology adapted to the political situation. CCS is an option. However, one has to consider that carbon dioxide sequestration by, for example wet amine scrubbing requires additional energy. This results in efficiency decrease of the whole system, so in order to produce the same net amount of energy more fuel has to be used. On the contrary, Molten Carbonate Fuel Cells not only separate the gas, but also, simultaneously produce heat and electricity contributing to the total energy generation of the system. They may even increase the efficiency of the whole system.

Keeping in mind that they may as well use many fuels like hydrogen, natural gas, methanol or bio-gas it seems that it is currently feasible to apply them and consider them as extremely competitive.

It is, of course possible to combine a gas turbine with MCFC what will result in a hybrid system (HS) with increased efficiency and decreased carbon dioxide emission. The exhaust gases of a gas turbine power plant consist mainly of nitrogen, oxygen, steam and carbon dioxide. This mixture can be used as the oxidant in the MCFC (cathode feeding).

Negative ions are transferred through the molten electrolyte. Each ion is composed of one molecule of carbon dioxide, one atom of oxygen and two electrons. This means that an adequate ratio of carbon dioxide to oxygen is 2.75 (mass based) or 2.0 (mole based).

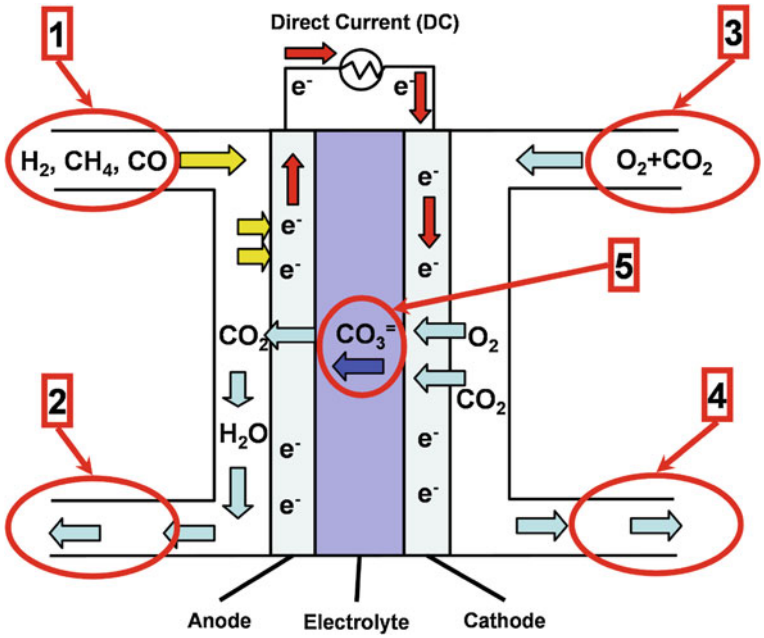


Fig. 1 Working principles of MCFC; *1* fuel input, *2* mixture of CO_2, H_2 and H_2O, *3* oxidant input, *4* exhaust, *5* ions of CO_3^{2-}

Table 1 Exhaust gas composition

Component	Mass fraction (%)	Mole fraction (%)
CO_2	5.2	3.4
H_2O	4.1	6.6
O_2	15.3	13.6
N_2	74.0	75.4
Ar	1.4	1.0
CO_2/O_2	0.34	0.25

The typical gas turbine flue gas composition is shown in Table 1. The ratio of carbon dioxide to oxygen is hence 0.25 (mole based) and 0.34 (mass based). This means that flue gas contains an insufficient quantity of oxygen to trap all CO_2.

2 Mathematical Model and Optimization

As for many other engineering applications, mathematical modeling is the basic method for analyzing fuel cells systems. In order to model system elements correctly, a zero-dimensional approach was used. The parameters, that are considered to be the most significant ones in the modeling process, are briefly presented below. The model

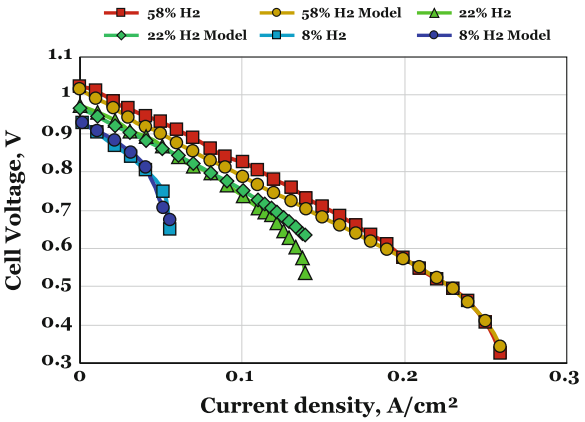
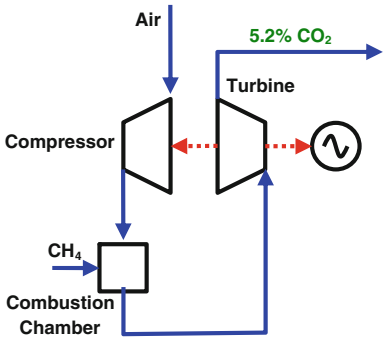


Fig. 2 Experimental and simulations data at different H_2 molar fractions, experimental data taken from [14]

Fig. 3 GTPP system



that used here is a new conceptual, alternative mathematical model of an MCFC [12]. The discrepancy between the model and experimental data given by Morita and alia are presented in the Fig. 2. It is conspicuous that it is valid for different hydrogen compositions—the error is marginal.

However, the MCFC is only a part of the plant thats emissions are to be reduced. The analyzed, sole gas turbine system is presented in the Fig. 3 (Table 2).

In the system the compressed air is delivered to the combustion chamber where fuel (natural gas) is combusted. Hot gas expands in the gas turbine and is rejected to the atmosphere. The mathematical model of the GTPP was created based on three main assumptions:

- air compressor isentropic efficiency: 79 %
- gas turbine isentropic efficiency: 88 %
- no pressure drops across the combustion chamber.

Table 2 Nominal parameters of GT power plant [6]

Name	Value
Air compressor inlet pressure (MPa)	0.1
Air compressor inlet temperature (°C)	15
Pressure ratio	17.1
Fuel	Natural gas
Fuel mass flow (kg/s)	4.0
Turbine inlet temperature (°C)	1210
Exhaust gas mass flow (kg/s)	213
Turbine outlet temperature (°C)	587
GT Power (MW)	65
GT Efficiency (LHV) (%)	33
CO_2 annually emission (Gg/a)	250
Relative emission of CO_2 (kg/MWh)	609
CO_2 mass flow (kg/s)	11

In order to make the model more real a commercial gas turbine unit was chosen to analyze [6]. Nominal parameters of the GTPP and exhaust gas composition are shown in Tables 1 and 3, respectively.

To compose a CO_3^{2-} ion, it is necessary to split a half mole of O_2 with one mole of CO_2. Adequate mass and molar ratios of CO_2 to O_2 (for capture all carbon dioxide) are 1.38 and 2, respectively. However, from data given in Table 1 it seems that, theoretically, all CO_2 could be captured (some of the oxygen will be simply rejected to the atmosphere).

All analyzed cases were optimized with the objective function being total power generation efficiency. Nevertheless, there is room for discussion as to the choice of this as the objective function of the optimizing process [19]. While the main task of an MCFC is to capture CO_2 from flue gas, it also increases total power generation due to its higher efficiency compared with that of the steam cycle (44 vs. 30 %).

The size of the MCFC installed at the flue gas rejection pipelines can be varied in wide range. From the other hand the same fuel utilization ratio can be realized by fuel cells of different size. There are three main parameters which determine the MCFC size: fuel utilization factor, maximum current density and inlet fuel flow. At least two from these three parameters determine the size of the MCFC. The stack fuel utilization factor was chosen at constant level of 90 %. The maximum current density and fuel mass flow were taken as primary variables of the optimizing process.

Optimized parameters:

- MCFC fuel mass flow
- The value of i_{max} in the range 0.06–0.3 A/cm^2
- Heat Exchanger efficiency in the range 0–85 %.

The optimizing process was carried out with the temperature inside the stack below 750 °C.

3 Gas Turbine Power Plant with MCFC

Two cases of gas turbine power plant with the MCFC were investigated. Case 1 concerns a situation when there is no intervention in GTTP cycle. It means that MCFC is added at GTPP outlet stream. Case 2 concerns the situation when heat exchangers before combustion chamber are added to the GTPP. These heat exchangers are fed by MCFC exhaust streams. This case, however, seems to be very difficult to apply in reality. It is obvious, that due to the design of gas turbines, there is not enough space to fix heat exchangers just after the compressor. We also have to consider that relatively low CO_2 content in flue gas results in low MCFC efficiency (about 34 % (based on Lower Heating Value, LHV)). Therefore, another option to compose low efficient MCFC with high efficient Combined Cycle Gas Turbine (with efficiency about 55 %) seems to be unreasonable and this case was not investigated.

The CO_2 reduction emission factor is defined as follows:

$$\eta_{CO_2} = 1 - \frac{\dot{m}_{CO_2,out}}{\dot{m}_{CO_2,in}} \tag{1}$$

where: $\dot{m}$—mass flow, kg/s; out—MCFC outlet cathode stream; in—MCFC inlet cathode stream.

What should be the objective of the optimizing process is not obvious. The MCFC is installed to capture the CO_2, from this point of view the quantity of captured CO_2 should be maximized. But on the other side, the MCFC utilizes the same fuel as the gas turbine and produces electricity and heat. From that reason both analyzed cases were optimized to obtain maximum system efficiency.

We have to remember that the fuel cells system itself is not the only equipment that has to be installed in order to separate CO_2. Additionally, we need a CO_2 separator, a catalytic burner, and a DC/AC converter. The CO_2 separator is a water cooled heat exchanger that cools down the gases that are rejected from the fuel cell. The condensate is then taken away purifying the flue gases stream to carbon dioxide only. The catalytic burner is fed by pure oxygen to utilize the rest of methane, hydrogen and carbon oxide. Naturally, oxygen extraction (e.g. from air) requires energy. The production of one kilogram of oxygen at atmospheric pressure requires from 200 to 300 kJ. The mean value of 250 kJ was taken into calculations, what is included in the model and decreases the system efficiency depending on the amount of consumed oxygen.

One may not forget that installation of MCFC at gas turbine outlet results in back pressure drop of about 1 %. It decreases the efficiency of the GTPP from 33 to 32 % (Fig. 4).

Parameters obtained during the optimizing process are given in Table 3. It is easily visible that in both cases quite high values of CO_2 reduction are achievable.

The MCFC-GTPP in Case 2 was created by adding two heat exchangers (see Fig. 5). The heat exchangers have a role to recover exhaust heat from MCFC outlet

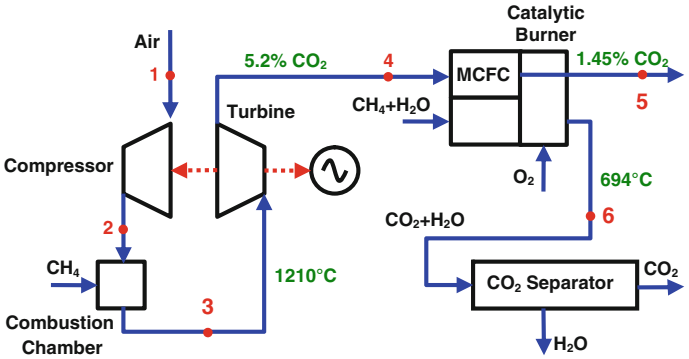


Fig. 4 GTPP-MCFC system—case 1

Table 3 Nominal parameters of GTPP-MCFC

Name	Case 1	Case 2
GTPP-MCFC power (total power) (MW)	80	77
GTPP power/total power (%)	81	82
MCFC power/total power (%)	19	18
GTPP-MCFC efficiency (LHV) (%)	33	40
CO_2 emission reduction factor (%)	73	91
Annual CO_2 emission (Gg/a)	67	18
Relative CO_2 emission (kg/MWh)	132	37
MCFC efficiency (LHV) (%)	34	36
GTPP efficiency (LHV) (%)	32	41
Fuel utilization factor (%)	90	90
Average cell voltage (mV)	513	486
Current density (mA/cm^2)	29.5	29.6
Oxygen mass flow (kg/s)	0.2	0.2
MCFC/GTPP fuel ratio	0.52	0.65

streams. Note that the GTPP efficiency would increase with a recuperative heat exchanger when no MCFC is installed as well.

The system was optimized with the same conditions like Case 1. Nominal parameters of Case 2 of GTPP-MCFC system are given in Table.

GTPP-MCFC Case 2 generates slightly less power in comparison with Case 1. During the simulations a constant value of Turbine Inlet Temperature (TIT) was assumed. The implementation of heat exchangers means lower fuel mass flow demanded by the combustion chamber.

A reduction of the CO_2 emission of 91 % is obtained. Simultaneously, electric efficiency is increased to 40 % (LHV) what gives the relative emission of CO_2 of 37 kg/MWh.

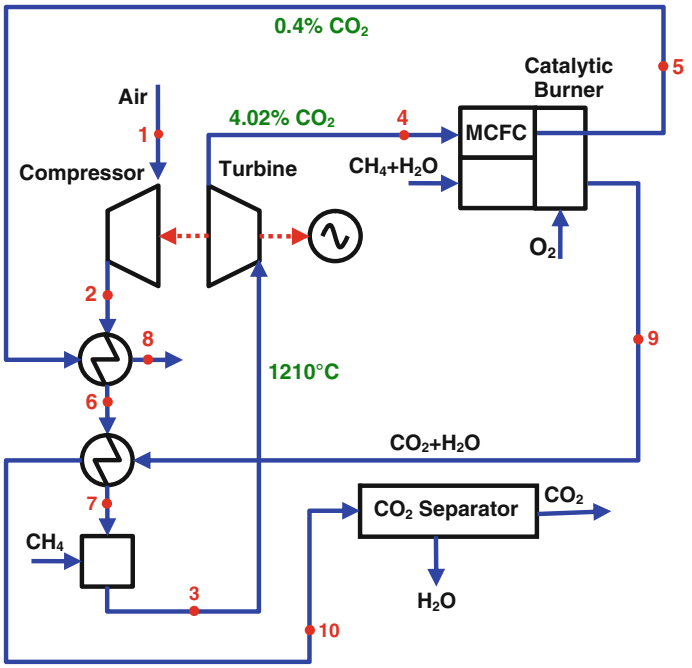


Fig. 5 GTPP-MCFC system—case 2

4 Experimental Investigation

After the mathematical model was created, there arose the need to check the possibility of CO_2 separation in practice. The laboratory of Institute of Heat Engineering at Warsaw University of Technology holds proper apparatus necessary for such investigation. Similar investigations are also being proceed in other research laboratories (e.g. [5, 18]). The MCFC tested has a planar area of 100 cm^2 where the anode was a porous (55 %) Ni structure with thickness of 0.76 mm, the cathode a porous (60 %) nickel oxide structure with thickness of 0.7 mm and the electrolyte a lithium carbonate and potassium carbonate—$(Li_2CO_3)_{0.62}(K_2CO_3)_{0.38}$—mixture (three matrices of 0.3 mm each, in total 0.9 mm). The electrode-electrolyte matrix is sandwiched between the two opposing separator plates and the fuel and oxidant flow concurrently in opposing channels. The cathodic and anodic current collectors were made in the form of stainless steel embossed sheets. The cell was tested in the experimental facility, in which the cell was held in a vessel and it was possible to set up and control each operating parameter. The vaporizer system provides measurement and control of the water vapor directed to the anode and cathode. The temperature of the system is subject to external control, and local temperatures collected by thermocouples, present in various positions on the cell, are processed by the PC board. Proprietary software allows one to easily view and manipulate the

Table 4 Main parameters of the experiments performed

Variant	Fed to	Flow ($ml/min/cm^2$)	H_2 (%)	H_2O (%)	N_2 (%)	Air (%)	CO_2 (%)
GT flue gases	Anode	2.29	70	13	–	–	17
+ reference point	Cathode	36.14	–	6.7	24.5	65.4	3.4
GT flue gases	Anode	1.97	70	13	–	–	17
+ reference point (optimized)	Cathode	38.22	–	6.7	24.5	65.4	3.4

condition and performance of the system. The cell fabrication was concluded by the first heat up ("cell conditioning") during which the components assumed their final form. The cells were operated at atmospheric pressure with the same reference point gas compositions and flow rates. The fuel gas $(H_2)_{80}(CO_2)_{20}$ and the oxidant gas $(Air)_{70}(CO_2)_{30}$ were fed. The cell voltage is directly measured at the two electrodes and its value is processed by a National Instruments board. The cell resistance was measured by using a HIOKI 3560 AC mW HiTESTER (four wires, 1 kHz). The gas composition and flow rates were controlled by a set of mass flow controllers. The gases and water flow rate are measured and controlled by Brooks 5850E Digital Mass Flow Controllers, chosen for their high accuracy and for their ability to be managed by software through serial PC ports. For load demand DC electronic load (SAE Electronic Conversion SRL) was used. Three series of tests were performed at 650 °C, the temperature kept constant on the cell plane using heating plates equipped with three electric heater each. A first one aimed to analyze the simplest case, in which just flue gases are fed into cathode side The laboratory tests were conducted at operational temperature of 650 °C and the necessary parameters, i.e. CO_2 and H_2 mass flows, voltage and current, were measured among others (Table 4).

Two cases were analyzed—one where the flue gases were directly fed on the fuel cell working on nominal parameters and the other, where the MCFC was optimized to obtain higher efficiency and CO_2 reduction rate. The voltage/current characteristic for the investigated fuel cell is presented in the Fig. 6a.

The results proved that concentration of carbon dioxide for its further separation from the flue gases is possible.

The graph shows typical performance of a Molten Carbonate Fuel Cell. However, the most important issue for this chapter is the possibility to extract carbon dioxide from the flue gases of a gas turbine power plant. The research carried out in the laboratory proved this to be possible. As one may observe in the Fig. 6b reduction rate of CO_2 from the gas turbine exhaust gases of more than 60 % was achieved. This, obviously, varies with the load that the fuel cell is subject to.

Naturally, the laboratory stand may not be compared with industrial, large-scale installations. Its operation parameters differ greatly, when compared with pilot-scale installations. For example, the efficiency of the MW-scale fuel cell systems is much greater than the one of the single, investigated cell (Fig. 7). The difference is equal to, more or less, 15 % points. Due to the small size of the equipment used it was

not possible to clearly determine the feasibility and economic profitability of such solutions. Nevertheless, it is certain that it is possible to concentrate and extract quite pure carbon dioxide from GTPP flue gases using Molten Carbonate Fuel Cells. Moreover, if a larger-scale installation would be used for this case, it could increase electricity and heat production of the whole system. This is a priceless advantage comparing to other ways of CO_2 capture.

5 Final Remarks

The CO_2 emission reduction factor and CO_2 relative emission were used to compare the systems. These values for all analyzed cases are given in the Table 5. The MCFC could reduce the CO_2 emission from gas turbine power plant exhaust by more than 70 %. The relative CO_2 emission decreases more significantly because the MCFC produces additional power.

Relatively low efficiency of the MCFC is caused by low CO_2 content at gas turbine exhaust, which gives low maximum cell voltage. The combination of MCFC with GTPP requires higher investment costs. However, common CO_2 separation methods also require capital investment and, instead of producing energy they consume it.

Moreover, application of the MCFC in a Gas Turbine Power Plant gives a relatively high reduction in CO_2 emissions. The relative CO_2 emission of the GTPP is estimated at 609 kg_{CO_2}/MWh while in contrast the MCFC-GTPP hybrid system has an emission rate of 135 kg_{CO_2}/MWh. The quantity of CO_2 emitted by the MCFC-GTPP is 73 % lower than is the case with the GTPP.

As mentioned earlier, all cases were optimized to achieve maximum power generation efficiency. However, this may be open to challenge if it is accepted that the main task of the MCFC is to limit CO_2 emissions, which would result in the CO_2 emission reduction factor being used as the objective function of the optimizing process. If this factor is optimized the cell voltage at last cell can fall below zero and the MCFC will work as a CO_2 concentrator only. At the very least, the MCFC

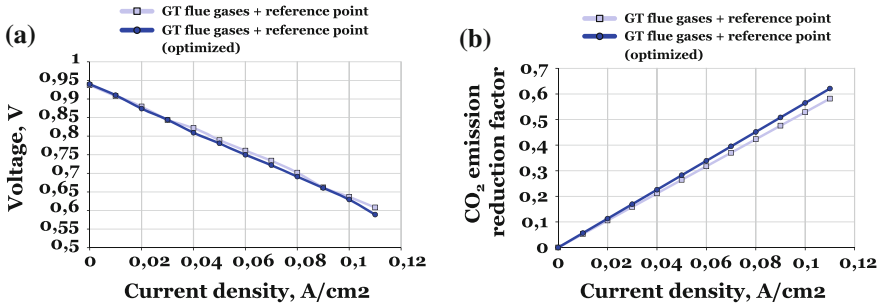


Fig. 6 Results of the experiments. **a** Voltage to current density for the investigated fuel cell. **b** CO_2 reduction rate

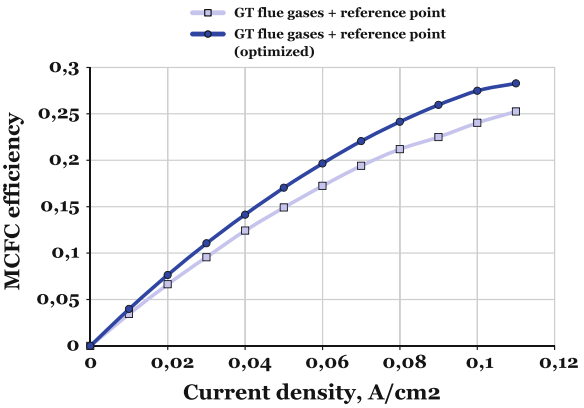


Fig. 7 Efficiency of the MCFC

Table 5 Main parameters of analyzed systems

Name	GTPP	Case 1	Case 2
$MCFC_{fuel\ flow}/GT_{fuel\ flow}$ (%)	0	29	45
System efficiency (%)	33	33	40
CO_2 emission reduction factor (%)	0	73	91
MCFC/GTPP fuel ratio	0	0.52	0.65
Relative CO_2 emission (kg/MWh)	609	135	37
Annual CO_2 emission (Gg/a)	250	68	18
Total system power (MW)	65	80	77

would generate no power, and might even consume some. However, the main task of a power plant is power generation; hence hybrid system efficiency was chosen as the objective function for optimization.

It should be borne in mind that prices of tradeable CO_2 allowances are relatively constant at present, which affords opportunity to realize profits from carbon trading.

Important technical issues such as sulfur or dust resistances of the MCFC fell outside the remit of this paper, although they can evidently limit the application of MCFCs in gas turbine power plants.

MCFCs could be profitably used in existing power plants which have been given CO_2 limits. MCFCs could potentially decrease CO_2 emissions, leaving the power generation capacity of the system at least the same, if not greater.

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