An example of innovative application in fuel cell system development: CO2 segregation using Molten Carbonate Fuel Cells

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Abstract

CO_2 is one of the main causes of the greenhouse effect and serious attention is being given to CO_2 abatement at the moment. In this work, the feasibility of segregating CO_2 from the exhaust of a Gas Turbine using a Molten Carbonate Fuel Cell system is studied. In particular, different plant configurations are simulated using a commercial code integrated with proprietary MCFC Fortran blocks. The opportunity of an additional CO_2 separation stage downstream MCFC is also discussed. The results of the simulations are presented and the possibility of producing electrical energy and being able to respect Kyoto Protocol and IPCC environmental requirements is analysed.
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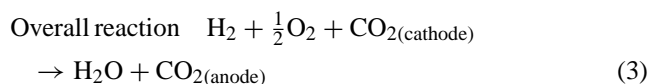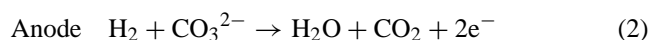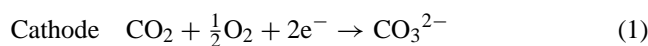*Keywords:* CO_2 abatement; MCFC fuel cells; Plant simulation

1. Introduction

It is well known that Fuel Cells (FCs) are electrochemical devices which directly convert the chemical energy of the fuel into electrical energy [1].

In particular, Molten Carbonate Fuel Cells (MCFCs) demonstrate very high efficiency during experimental tests. This means that at a pre-defined power level a lower fuel consumption is possible in comparison with conventional electrical generators. So, for example, less natural gas or other hydrocarbons are used to produce the primary MCFC fuel, that is H_2, and consequently less CO_2 is sent into the atmosphere, demonstrating that high efficiency makes MCFCs a natural candidate for CO_2 abatement.

Furthermore, MCFCs are the only FC technology that allows high efficiency and CO_2 concentration at the same time, meaning a significant improvement in terms of CO_2 emission per kWh just for existing power plants and an innovative way of separating CO_2 for its final abatement.

This peculiar property is related to the electrochemical reactions that take place inside MCFCs. Specifically, the reactions are the following:

$$\text{Cathode} \quad CO_2 + \tfrac{1}{2}O_2 + 2e^- \rightarrow CO_3^{2-} \tag{1}$$

$$\text{Anode} \quad H_2 + CO_3^{2-} \rightarrow H_2O + CO_2 + 2e^- \tag{2}$$

$$\text{Overall reaction} \quad H_2 + \tfrac{1}{2}O_2 + CO_{2(\text{cathode})}$$
$$\rightarrow H_2O + CO_{2(\text{anode})} \tag{3}$$

where the diffusion species in the electrolyte are carbonate ions, so that CO_2 and O_2 can move from the cathode to the anode selectively.

This important characteristic can be used, for example, to reduce the CO_2 emissions per kWh of a conventional power plant by feeding its exhaust to the MCFC cathodic inlet. The CO_2 is concentrated at the anodic side and then easily separated from this CO_2 richer stream. The CO_2 energy cycle is reported in Fig. 1, coupling the CO_2 removal system with the production of electrical power.

In literature several studies and simulations are available where MCFCs are considered the primary power production devices, emitting a gas with a low CO_2 content into the atmosphere [2–7]. Nevertheless, few studies have been carried out into MCFCs as CO_2 concentrators of exhaust gases [8–12].

The present work specifically concerns the integration of a standard Gas Turbine (GT) with an MCFC system and follows a preliminary study presented by the authors at the International Conference on "Future Energy Systems and Technology for CO_2 Abatement" in Antwerp (Belgium, 2002) [10].

In particular, two plant configurations will be proposed differing in their CO_2 separation stage downstream the MCFC. In fact, the gas composition at the anodic exit mainly contains concentrated CO_2, but also unreacted gases

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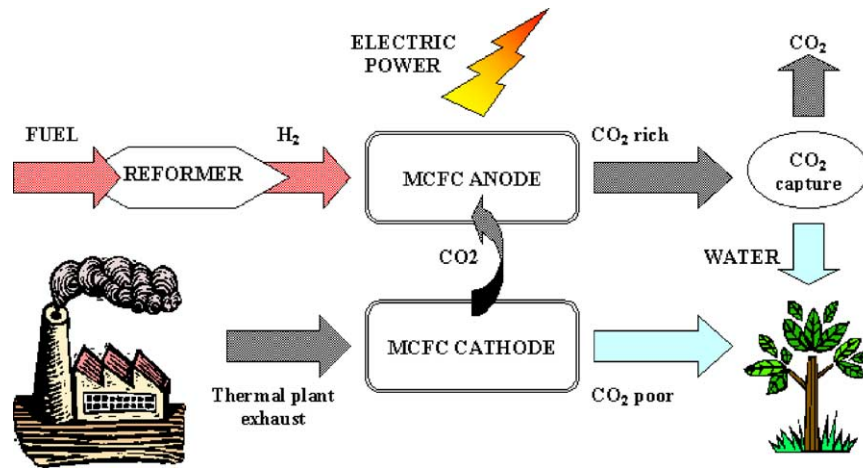fax: +39-010-3532589.
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Fig. 1. Energy cycle based on MCFC application.

and steam, so that the opportunity of coupling an additional CO_2 separation stage downstream MCFC will be discussed and different techniques will be considered.

In particular, steam is always easily separated by means of a condensation stage.

With regard to unreacted gases, in this work we simulated two plants: a first one where they were separated from the CO_2 rich stream resulting from anodic exhaust by a conventional stage of CO_2 separation; and then a second one where they were burnt in O_2 producing additional CO_2 and H_2O. Moreover, these solutions were studied operating at ambient pressure as well as under pressure.

All plants were simulated with Aspen Plus software integrated with proprietary software for the MCFC section simulation. In particular, two specific MCFC modules have been performed in Fortran for stack anodes and cathodes, respectively. These units receive input data from the Aspen convergence loop and give them back modified on the basis of the MCFC electrochemical reactions, the water shift reaction occurring at the anode and the thermal exchange between the anode and cathode.

2. Definition of MCFC operating conditions and constraints

Before analysing the feasibility of this MCFC application, it may be useful to discuss the operating conditions in terms of temperature, gas compositions, pressure, gas flow rates, and current density. In particular, they have also to be analysed in terms of the MCFC operating constraints to be respected for the safe running of a real plant.

The temperatures of MCFC input gas streams have to be of at least 580 °C to guarantee a good ionic conduction inside the cells. On the other hand, maximum local temperatures higher than 700 °C should be avoided because they can cause problems such as electrolyte loss and corrosion. These requirements are respected in the following simula-

tions, and in particular the temperatures of gas entering the MCFC have been fixed at 635 °C.

Concerning the gas compositions, in the present work the gas fed to the cathodic side comes from a GT fuelled with natural gas. For this exhaust, a standard molar composition is assumed: H_2O 7%, N_2 76%, CO_2 3%, O_2 14% [10].

While H_2O and N_2 are inert components in the cathodic process and their content only influences the MCFC thermal management, CO_2 and O_2 are reactants and their concentrations can affect the electrochemical kinetics. In particular, while the kinetics is not affected noticeably by the CO_2 concentration, a low concentration of O_2 can penalise the electrical resistance [11]. Nevertheless, the O_2 concentration here considered can be acceptable.

In addition, the CO_2 concentration to be fed to the cathode is constrained by two other factors: a CO_2 utilisation factor lower than 55% to avoid diffusion limited operating conditions and a CO_2 content higher than 5–6% to avoid secondary reactions. The first constraint has been respected, while, concerning the second one, the CO_2 concentration is slightly lower (about 3%). The latter condition, imposed by GT exhaust composition, could involve MCFC performance penalisation. Specific tests are in progress to investigate this effect.

Usually, then, GT exhaust contains also some trace substances like CO, NO_x, and SO_x. Carbon monoxide burns at the cathode side of the MCFC, producing some additional CO_2 and heat. The CO content is usually very low and its effects can be neglected in this application. On the contrary, the damaging effects of NO_x have often been stated in the literature data, but a general agreement on the maximum admissible level has not yet been reached. At the same time, a recent work [13] shows minima the NO_x effects and shows how MCFCs could have the function of removing NO_x from the oxidant gas. This feature is under study at the moment, while for the application discussed here the NO_x content is assumed not harmful. Finally, sulphur compounds are not here foreseen, but if they are present, a desulphurisation stage may be necessary upstream from the MCFC because they damage the electrode catalyst.

With regard to anodic side, natural gas is considered as primary fuel. As MCFCs need H_2 for electrochemical reactions, a steam reformer to convert the methane into hydrogen is foreseen upstream the anodic side. So, the anodic composition results from thermodynamic equilibrium and involve H_2, H_2O, CO, CO_2, and CH_4.

Moreover, MCFC performance depends on the operating pressure and increases under higher pressure. From the point of view of the system this means that the gas to be fed to the MCFC has to be pressurised to enhance the ability of the fuel cell to transfer CO_2 from the cathode to the anode. On the other hand, pressurisation penalises turbine performance, which is better at the lowest outlet pressure. Therefore, the overall performance of the plant has to account for these two opposite requirements.

In this work, two operating pressure solutions will be discussed for each case studied: the first one considers the possibility of working the MCFC at ambient pressure, the second one considers the MCFC between two expansion stages that allow operation at higher pressure. In particular, a pressure of 3 atm was chosen because higher gain on cell performance in the operating range 2–4 atm is expected.

It is to be observed that the fuel molar flow fed to the plant in the two solutions is different. In particular, taking account that at higher pressure the limiting current density increases and so cells can work at higher utilisation factors without diffusion effects strongly penalising their performance, the H_2 utilisation factor has been fixed at 47% in the atmospheric operation and at the maximum value of 75% in the pressurised solution, reducing consequentially the fuel flow rate being fixed the current density.

In the following calculations, aimed to a feasibility analysis of MCFC/TG coupling in environmental respect, any other influence of pressure is neglected.

Quantitatively, it was decided to treat an exhaust of about 2430 kmol/h coming from a 4.6-MW gas turbine. With reference to standard Ansaldo Fuel Cells modules [10], this feeding is suitable to feed MCFC stacks for a nominal power of about 2 MW as a function of the operating conditions.

So, taking account of MCFC characteristics, an operating current density of 1000 A/m^2 was chosen for the following preliminary evaluation of the behaviour of the system, guaranteeing a CO_2 utilisation factor lower than 55%.

Fuel flow rates in the range of 60–100 kmol/h were selected for the two pressure operating modes in order to guarantee the above discussed H_2 utilisation factors.

3. MCFC plant simulation with downstream conventional CO_2 separation

3.1. Plant scheme description

The scheme of the proposed plant with a conventional separation stage downstream MCFC is reported in Fig. 2 for ambient pressure operation.

Starting from the left hand side, the methane fuel (FUELIN) is preheated (FUEL) and then fed to a reformer (REFIN) together with steam (STEAM) in excess.
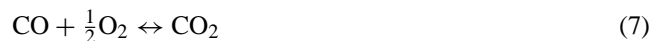
At the reformer the following reactions occur:

$$CH_4 + H_2O \leftrightarrow 3H_2 + CO \tag{4}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{5}$$

The endothermic reforming process receives heat from a catalytic burner to guarantee a sufficient H_2 production and an outlet stream (REFOUT) at about 700 °C.

Before entering the cells the REFOUT temperature is reduced to 635 °C and then fed to the anode (ANIN). In the same way, the temperature of the stream entering the cathode (CATIN) is guaranteed at 635 °C by means of a preheating stage applied to the gas turbine exhaust (TURBOUT), which is assumed at 450 °C.

So as above mentioned, the gas composition at the anodic exit (ANOUT) contains concentrated CO_2, unreacted gases (CO, H_2, CH_4) and steam. The steam (H_2O) is removed by a simple condensation stage. Then, any possible traces of unreacted gases (UNRE) are separated from the CO_2 by means of a conventional method in the block SEP2 and, together with the gas coming from the cathode (CATOUT), are fed to a catalytic burner, where the following reactions occur:

$$H_2 + \frac{1}{2}O_2 \leftrightarrow H_2O \tag{6}$$

$$CO + \frac{1}{2}O_2 \leftrightarrow CO_2 \tag{7}$$

$$CH_4 + 2O_2 \leftrightarrow CO_2 + 2H_2O \tag{8}$$

The gas at the burner outlet (BURNOUT) is used to produce the steam necessary for the reformer and then discharged into the atmosphere (ATMOUT).

In the solution under pressure, an expansion stage has to be considered.

Concerning the stage of CO_2 separation downstream MCFC section, even if the selection of a specific method is not object of this work, it could be added that the specific characteristics of the stream to be treated will be to taken into account for the choice: high temperature, low pressure, and high CO_2 concentration.

For example, a recent study has shown that a MEA (Mono-Ethanol–Amine) aqueous solution can capture up to 90% of CO_2, if the CO_2 concentration is low (up to 14%) [14], however this traditional process could be not suitable at high CO_2 concentration. An alternative solution could be the HP (Hot Potassium carbonate) process, which takes advantage of high CO_2 partial pressure [15] and works with high efficiency at low pressure and high temperature.

In any case, it is to be noticed the important advantage of a strongly reduced flow rate to be treated in comparison to a conventional separation stage applied directly to the GT exhaust, so as discussed in the following.
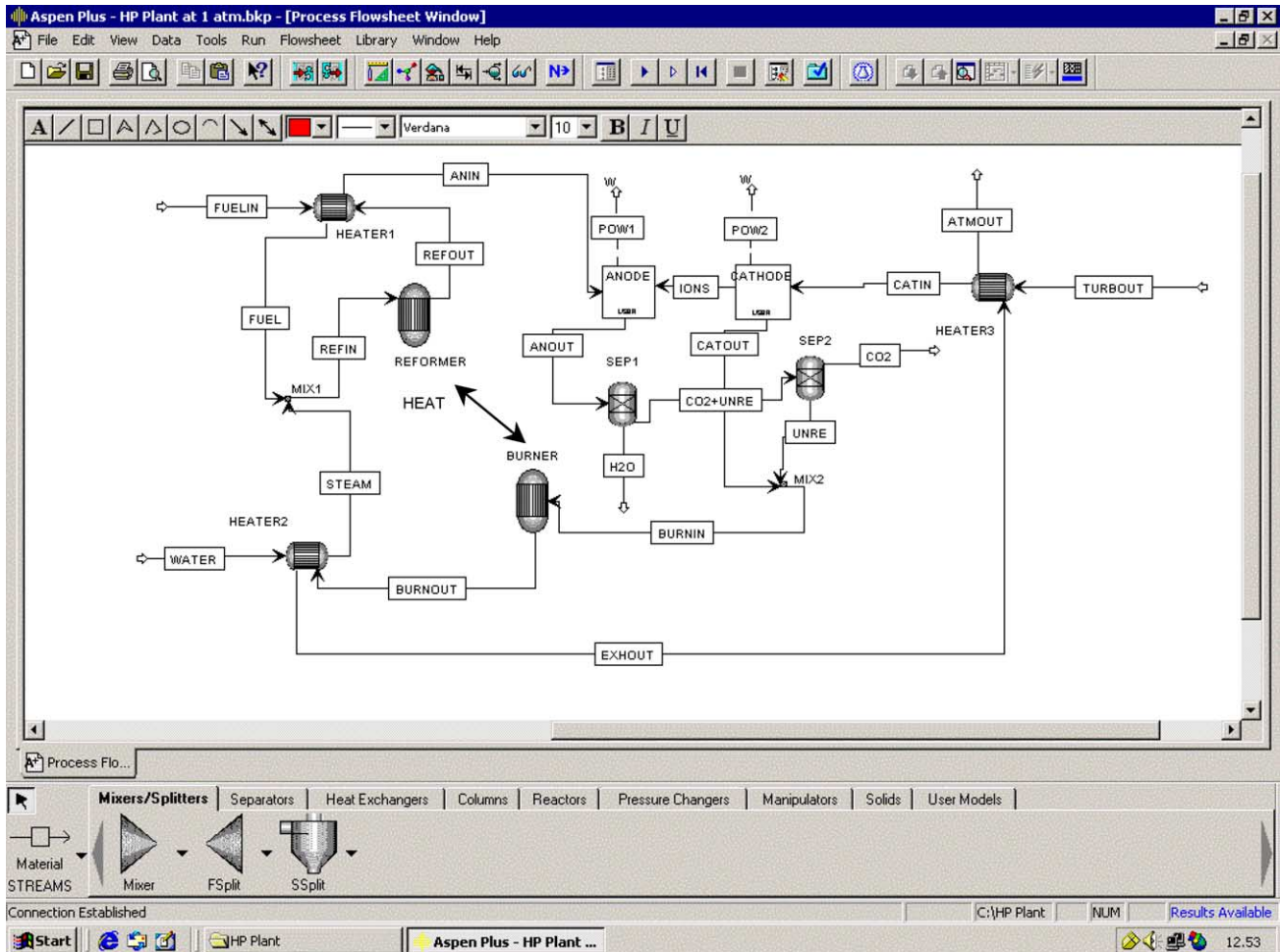
Fig. 2. Integration of GT, MCFC and a conventional CO_2 separation stage: plant scheme for operation at 1 atm.

3.2. Main results

First aim of this simulation activity was to study the advantages of MCFC/GT coupling in terms of CO_2 emissions and evaluate if a conventional CO_2 separation stage needs to be added. So, a parametric analysis was carried out in order to evaluate the effects of the efficiency of a possible CO_2 conventional separation downstream the burner, taking account of environmental requirements of the Kyoto Protocol [16] and the more restrictive ones of the Intergovernmental Panel on Climate Change (IPCC) [17].

Figs. 3 and 4 show the parametric analysis results in terms of CO_2 molar flow discharged in atmosphere versus the efficiency of CO_2 separation in plants working at 1 and 3 atm, respectively.

If the CO_2 separation stage is not present (efficiency = 0%), the effects of a simple MCFC/GT integration are shown: in both simulations Kyoto Protocol requirements are respected. In fact, taking account of the additional power generated by the MCFC, the CO_2 emission per kWh is reduced from 16.2 to 14.7 mol CO_2/kWh ($\approx$9%) working at 1 atm and from 16.2 to 13.4 mol CO_2/kWh ($\approx$17%) working at 3 atm, while the Kyoto Protocol established an 8%

CO_2 reduction for European countries between 2008 and 2012 [16].

This result underlines the suitability of MCFCs to reduce CO_2 emissions.

However, to meet the more restrictive requirements of the IPCC [17], CO_2 separation efficiency has to be high enough to reduce the CO_2 emission per kWh from 16.2 to 6.5 mol CO_2/kWh ($\approx$60%).
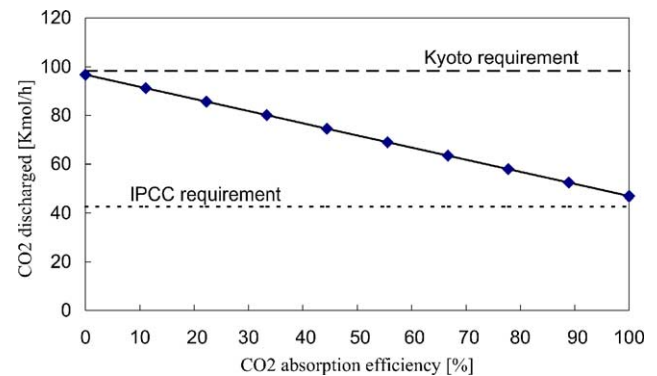

Fig. 3. Parametric analysis @ 1 atm of CO_2 discharged vs. conventional separation stage efficiency.

Fig. 4. Parametric analysis @ 3 atm of CO_2 discharged vs. conventional separation stage efficiency.

Fig. 4 shows that at 3 atm, a CO_2 separation efficiency of about 94% allows the achievement of CO_2 reduction requested by IPCC. On the contrary, in the simulation at 1 atm (Fig. 3) not even 100% efficiency is sufficient, even if the emission reduction is very high ($\approx$56%). This is due to the low fuel utilisation factor assumed in the MCFC and the consequent combustion which involve the emission of 7.1 mol CO_2/kWh.

Tables 1 and 2 show the main simulation results at the different studied pressures assuming a total CO_2 separation from burner exhaust.

Operating at 1 atm (Table 1), the calculations show that 27.6 kmol/h of CO_2, which would otherwise be discharged into the atmosphere, can be captured thanks to this MCFC integrated solution. Therefore, the CO_2 content reduction is about 37%, when the turbine

Table 1
Simulation results of plant @ 1 atm with 100% efficiency CO_2 conventional separation stage

Streams	T (°C)	CH_4 (kmol/h)	CO (kmol/h)	CO_2 (kmol/h)	H_2 (kmol/h)	H_2O (kmol/h)	N_2 (kmol/h)	O_2 (kmol/h)	TOT (kmol/h)
FUELIN	137	14.1	0	0	0	78.1	0	0	100.4
REFIN	661	22.3							
REFOUT	700		11.1	10.7	76.2	45.5			143.9
ANIN	635	0.4							
ANOUT	671		11.8	49.8	35.8	86			183.8
TURBOUT	450			74.4				344.2	2432.5
CATIN	635	0	0		0	168.1	1845.8		
CATOUT	667			34.6				324.3	2372.8
CO_2 + INCO	671	0.4	11.8	49.8	35.8	0	0	0	97.8
BURNIN	667			34.6		168.1	1845.8	324.3	2420.8
BURNOUT	764	0	0	46.8	0	204.6		299.8	2397
ATMOUT	695								

Table 2
Simulation results of plant @ 3 atm with 100% efficiency CO_2 conventional separation stage

Streams	T (°C)	CH_4 (kmol/h)	CO (kmol/h)	CO_2 (kmol/h)	H_2 (kmol/h)	H_2O (kmol/h)	N_2 (kmol/h)	O_2 (kmol/h)	TOT (kmol/h)
FUELIN	137	14.1	0	0	0	49.4	0	0	63.5
REFIN	603								
REFOUT	700		5.9	6.6	44.1	30.3			88.5
ANIN	635	1.6							
ANOUT	672		3	49.3	7.2	67.1			128.2
TURBOUT	450			74.4				344.2	2432.5
CATIN	635	0	0		0	168.1	1845.8		
CATOUT	667			34.6				324.3	2372.8
CO_2 + INCO	672	1.6	3	49.3	7.2	0	0	0	61.1
BURNIN	667			34.6		168.1	1845.8	324.3	2384.6
BURNOUT	680	0	0	39.2	0	178.4		316.1	2379.5
ATMOUT	638								

outlet and the exhaust outlet to the atmosphere are compared.

At the same time, the CO_2 is concentrated in the anodic outlet stream, achieving a molar concentration of 27% that, after a simple condensation step, can be increased to about 51%.

The results at 3 atm (Table 2) show that about 35.2 kmol/h of CO_2 can be captured and the CO_2 emission per kWh can be reduced to 5.9 mol CO_2/kWh ($\approx$63%).

The CO_2 molar concentration in the anodic outlet stream is 38% before the condensation stage and then 81%, demonstrating the capacity of MCFCs to act as CO_2 concentrators.

Moreover, in terms of heat recovery, the calculations put in evidence that, operating at 1 atm, the stream discharged into the atmosphere has still enough heat to preheating the GT exhaust before entering the MCFC cathodic side. This is not possible in the pressurised case, as the higher MCFC efficiency involves a lower content of unreacted gases to be oxidised in the burner.

Finally, it is to be observed how, in comparison to a possible direct treatment of the GT exhaust, this plant solution presents the advantage that the flow rate to be treated is strongly reduced (from 2432 kmol/h down to 128–180 kmol/h) and its CO_2 concentration increased (from 3% up to 27–38%).

4. MCFC plant simulation with downstream unreacted gas combustion in O_2

4.1. Plant scheme description

A second plant configuration was simulated where unreacted gases coming from the anodic outlet are burnt in oxygen separately from the cathodic flow rate.

The scheme for operation at ambient pressure is presented in Fig. 5.

The gas turbine exhaust is preheated and fed to the cathodic side, while the methane is reformed and then fed to
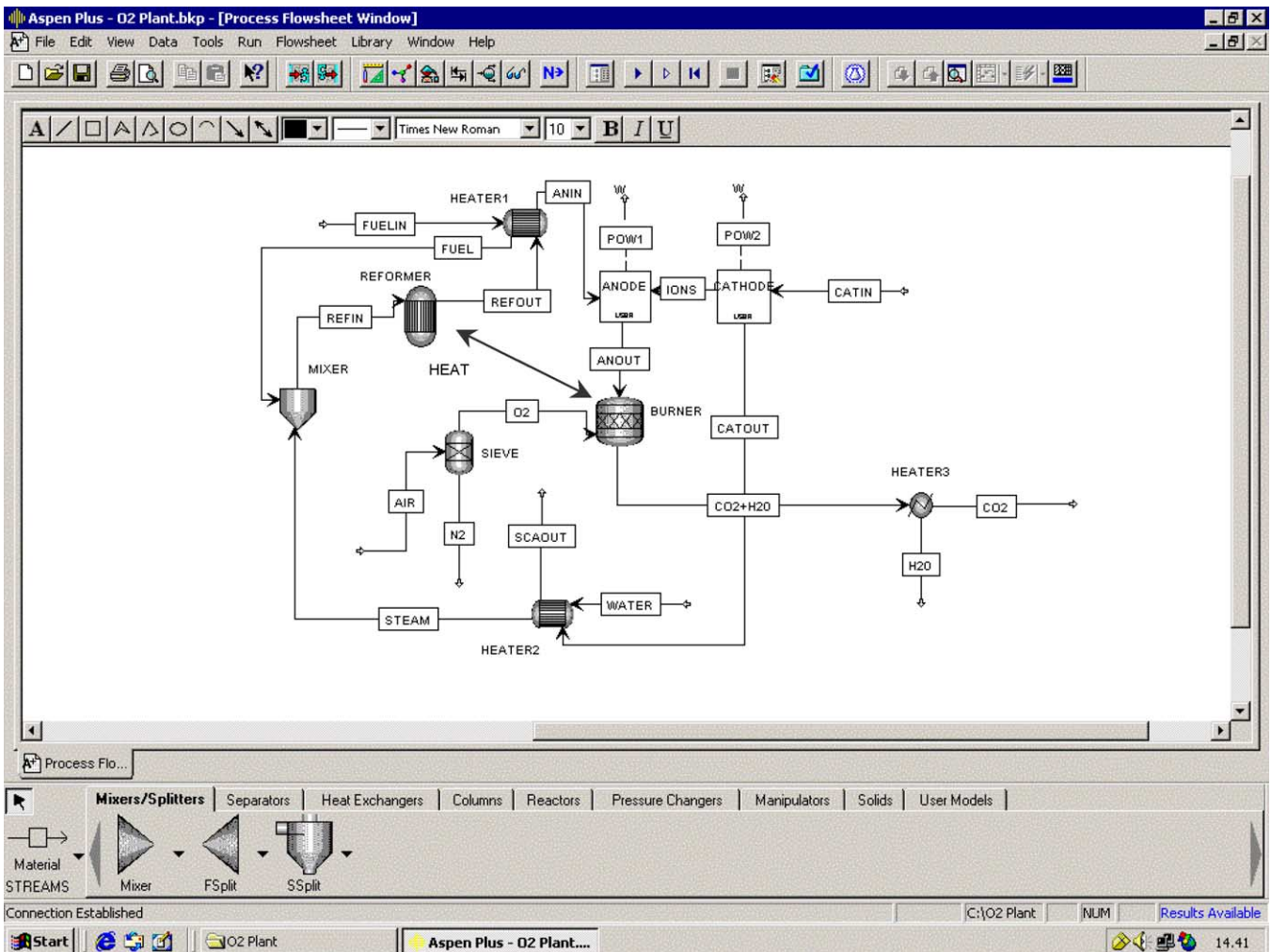

Fig. 5. Integration of GT, MCFC and anodic catalytic burner for CO_2 separation: plant scheme for operation at 1 atm.

Table 3
Simulation results of plant with anodic catalytic burner for CO_2 separation

CO_2 molar fraction	Simulation at 1 atm			Simulation at 3 atm		
	ANOUT stream	$CO_2 + H_2O$ stream	CO_2 stream	ANOUT stream	$CO_2 + H_2O$ stream	CO_2 stream
Pure O_2	0.27	0.34	0.97	0.38	0.41	0.99
Commercial O_2 (92% O_2–8% N_2)	0.27	0.32	0.86	0.38	0.41	0.94
Air (21% O_2–79% N_2)	0.27	0.22	0.39	0.38	0.33	0.63

the anodic side passing through the same blocks described in Section 3.1.

The units after the cell exit are different from those of the plant previously analysed.

Firstly, the gas coming from the cathode (CATOUT) heats the water to produce steam for the reformer and then is directly discharged into the atmosphere.

Secondly, the anodic exhaust (ANOUT), which is rich in CO_2, is burnt in oxygen, thanks to a catalytic burner that allows the complete combustion of the unreacted gases in the reactions (6), (7), and (8).The oxygen necessary for combustion (O_2) can be fed pure, commercial, or in air.

For commercial oxygen, a typical concentration of 92% was assumed taking account of the separation efficiency of, for example, molecular sieves.

The water is separated from burner exhaust ($CO_2 + H_2O$) by means of a condensation stage.

Also in this case, in the solution under pressure an expansion stage has to be added.

4.2. Main results

In this proposed plant solution, the cathodic exhaust is directly discharged into the atmosphere, while the burner exhaust is not.

By this way, the CO_2 emission per kWh are strongly reduced from 16.2 to 5.2 mol CO_2/kWh ($\approx$68%), if the GT and the GT/MCFC integration are compared, and IPCC requirements are accomplished.

In particular, the cells capture 39.8 kmol/h of CO_2, involving a CO_2 content reduction of about 53%, comparing the turbine outlet, and a discharged CO_2 molar concentration of about 1.5%.

These results are valid for both atmospheric and pressurised systems. Nevertheless, the operation at ambient pressure implies a lower efficiency in terms of fuel consumption, so that there are more unreacted gases which are oxidised in the burner and the quantity of CO_2 captured after the condensation stage is higher. In addition, this significant combustion involves that the condensation stage allows for greater heat recovery than in the pressurised case (about 5 MW @ 1 atm and 2 MW @ 3 atm).

Another important aspect is that, as anodic exhaust does not contain N_2, the choice of the oxidant to be fed to the burner strongly affects the concentration of the segregated CO_2. In fact, if pure oxygen in stoichiometric proportion is

fed to the burner, the stream coming out contains only CO_2 and H_2O, so that a simple condensation stage is sufficient to separate H_2O and pure CO_2.

Otherwise, more nitrogen enters the burner and more the final CO_2 concentration is lower, in fact the condensation stage separates H_2O from a mixture of CO_2 and N_2. For example, the simulations with air imply a CO_2 segregated concentration of about 1/3 in the simulations at 1 atm and of about 2/3 in the one at 3 atm.

The main related results are reported in Table 3.

The concentration of the segregated CO_2 is important for its final utilisation, so that the choice among these solution has to be decided also on the basis of the specific final CO_2 use apart from the environmental effects and economic considerations.

For example, in terms of CO_2 emissions, the solution at ambient pressure and with air as oxidant is very attractive and also the cheapest, however the segregated CO_2 is very diluted and a proper utilisation has to be considered.

Actually the final use of the concentrated CO_2 is an environmental problem of topical interest. Some references about this subject are reported in the Appendix A.

5. Conclusions

The feasibility of concentrating CO_2 and producing additional clean energy using MCFCs has been presented by means of plant simulation results obtained with Aspen Plus and integrated proper MCFC Fortran blocks.

In particular, the effects on CO_2 emissions have been studied considering the integration of an MCFC section downstream a GT. Different solutions have been proposed and analysed assuming operation at atmospheric pressure as well as under pressure (3 atm). A comparison of the results obtained in the considered case studies is summarised in Fig. 6.

In any case, the suitability of MCFC/GT integration to reduce CO_2 emissions has been demonstrated, as Kyoto Protocol requirements are always accomplished.

Nevertheless, the instructions of the IPCC in terms of CO_2 reduction for an effective stabilisation of the global climate are more restrictive. In order to respect these requirements, it has been shown that, in plants where anodic and cathodic exhausts are burnt together before discharging into the atmosphere, the operation under pressure is necessary and an additional CO_2 separation stage with an efficiency of
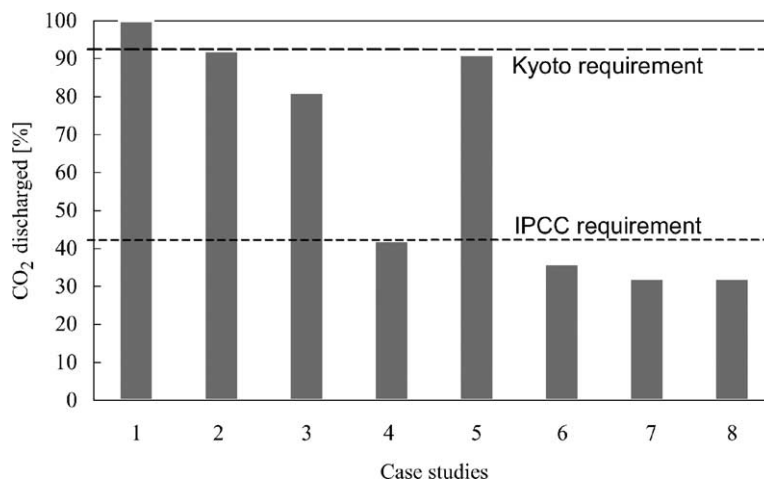
Fig. 6. Comparison of results in the simulated case studies in terms of CO_2 emissions (mol CO_2/kWh emitted per mol CO_2/kWh coming from gas turbine). Nomenclature: 1 = GT; 2 = GT + MCFC @ 1 atm—plant scheme of Fig. 2; 3, GT + MCFC @ 3 atm—plant scheme of Fig. 2; 4, GT + MCFC + 94% CO_2 conventional separation @ 3 atm; 5, GT + MCFC + 100% CO_2 conventional separation @ 1 atm; 6, GT + MCFC + 100% CO_2 conventional separation @ 3 atm; 7, GT + MCFC @ 1 atm—plant scheme of Fig. 5; 8, GT + MCFC @ 3 atm—plant scheme of Fig. 5.

about 90% needs at the anodic exit. In this case a conventional separation system can be used, like absorption into a solvent. However, in comparison to a possible direct treatment of the GT exhaust, this solution presents the advantage that the flow rate to be treated is strongly reduced (from 2432 kmol/h down to 128–180 kmol/h) and its CO_2 concentration increased (from 3% up to 27–38%). Moreover, additional clean electrical power is produced by MCFC.

As alternative solution, only cathodic exhaust can be discharged into the atmosphere. This flow rate consists in the GT exhaust purified thanks to the capability of MCFC to remove CO_2 and transfer it to the anode.

By this way also IPCC requirements are met.

In this second plant configuration, the oxidation of anodic exhaust can be completed in a catalytic burner in order to obtain CO_2 and H_2O easily separable by condensation. The oxygen necessary for combustion can be fed pure, commercial, or in air, and this oxidant choice strongly affects the final concentration of the segregated CO_2 (from 39 up to 99%).

However, it is shown that CO_2 can achieves a concentration of 51–81% also after a simple condensation stage downstream anodic side, confirming the capacity of MCFCs to act as CO_2 concentrators.

The CO_2 concentration is very important when final use of the segregated CO_2 is considered. The latter is today an environmental problem of topical interest and just some references about this subject have been reported in the Appendix A.

Therefore, the choice among the different solutions proposed will depend on the environmental goals as well as on plant problems and economic aspects, so that this work is proposed as a basis for more detailed investigations on this MCFC application. However, the performed calculations have demonstrated that MCFC are clean power generation systems very promising in terms of CO_2 abatement.

Acknowledgements

Appendix A. Some references about concentrated CO_2 utilisation

Many studies on further utilisations of carbon dioxide [18–23], in addition to traditional uses (such as production of ice, fizzy mineral water, fire-fighting equipment, . . .), have been carried out in recent years in order to reduce the emissions in atmosphere.

Hence, present work can provide useful information for different industrial applications: a brief summary of already proposed or innovative utilisations of CO_2 gaseous streams is given below.

A relatively new technology to store concentrated CO_2 has been developed for utilisations of continuous CO_2 production: CO_2 can be pumped into submarine cavities from which it cannot escape. Some researchers of the British Geological Survey have attempted to use this solution in North Sea submarine cavities where a great quantity of CO_2 (five thousand tons) has been trapped since 1996. The spaces under the sea could contain 600 thousand million tons of CO_2. If 1% of this volume were used, it could trap the yearly emissions of 900 coal-fired or gas power stations. However,

in September 2002, a pilot project for CO_2 storage in the depths of the ocean was stopped due to the risk of upsetting the ecological equilibrium [18].

Alternatively, concentrated CO_2 can be stored in oil-fields or natural gas-fields, where the extraction of the oil or gas has left space. Natural gas is used to produce hydrogen and electricity, and both processes produce CO_2, which can be captured and stored in the space left by the natural gas (for example, submarine cavities). In particular, the CO_2 pressure could be used to lift the natural gas [19].

The feasibility of further innovative utilisations of low flow rate of diluted CO_2 gaseous streams can also be investigated.

For instance, CO_2 coming from industrial exhausts could be utilised in *greenhouses* to maximize plant growth. In fact, in greenhouses plants have an inadequate supply of CO_2 (atmospheric molar concentration is about 0.03%) in their natural environment and the addition of CO_2 could be useful for their growth [20]. If the CO_2 molar concentration is higher, the plants will consume CO_2 for chlorophyll photosynthesis until saturation point (about 0.005%), when there is equilibrium between photosynthesis and breathing. In addition, a higher light intensity requires a higher CO_2 molar concentration to reach saturation. In other words, if there is more light, a plant can better exploit a higher CO_2 molar concentration. A deeper investigation could be made to identify plants which are more suitable for this application.

With regard to plant growth application, we consider the case of the alga *Spirulina Platensis* (S.P.) [21], which is used in the production of beauty cream. Carbon dioxide can effectively be removed from exhaust gas emissions by simply bubbling them into an S.P. culture, unless NO_x and/or SO_x inhibitions occur [22]. In fact, large amounts of CO_2 could be employed in the growth of photosynthetic organisms such as photoautotrophic cyanobacteria like Spirulina, which would much faster CO_2 fixation than eukaryotic organisms.

The ability of S.P. to grow on carbon dioxide or a mixture of bicarbonate/carbonate has been compared under light irradiation conditions [23]. Inorganic carbon is preferentially assimilated in the form of bicarbonate and its utilization efficiency depends either on the pH (8.5–10.5) of the final biomass level. During growth the production of a mole of Spirulina corresponds to the consumption of two moles of bicarbonate. The substitution of the carbon source with carbon dioxide requires the addition of NaOH to establish the pH. The comparison of the culture of Schlosser [23] ($NaHCO_3$, Na_2CO_3, ...) and the culture of CO_2 underlines an increase of growth and productivity in the latter case. Feeding Spirulina with a greater quantity of CO_2 allows it to grow better. Furthermore, this type of feeding requires a pH correction only during the start-up, because afterwards the growing Spirulina neutralises the acidity caused by CO_2 bubbling.

In spite of this applications, the use of captured CO_2 represents an open problem and its utilization is linked to the ratio between costs and benefits. It is necessary to improve and increase these uses, also in innovative applications, because the quantity of CO_2 segregated will increase due to the need of continuous and more efficient separation of CO_2 from industrial exhausts.

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