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Effect of reforming on the overall efficiency of a solid oxide fuel-cell based power plant system fed by methane

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Abstract: In the present work, energy and exergy system analysis are used to estimate the thermodynamic performance of a SOFC system fuelled by methane. More precisely, the present work examines in detail the influence of the presence or absence of the reformer within the whole apparatus and the consequent energy and exergy losses due to the reforming process. The Reforming-SOFC-PP system consists of the SOFC stack, a reformer, an afterburner, two preheaters, a vaporiser and a mixer. Methane and steam are mixed in the mixer and are heated in one preheater up to the operational temperature of the reformer. On the other hand, the Direct-Methane-SOFC-PP consists of the SOFC stack and only two preheaters. The heat produced in SOFC was enough to heat the fuel and the air entering SOFC up to a temperature adequate for the efficient operation of the power plant. It was found that the exergetic efficiency for the Direct-Methane-SOFC-PP is very high (92.5%) compared with that obtained by assuming Reforming-SOFC-PP (66.9%). This, approximately 34%, difference is mainly because of the fewer devices that the Direct-Methane-SOFC-PP consists of, which leads towards the minimisation of the exergetic consumption. Under this respect, the non-reforming case could be considered as the upper limit for the efficiency's of the reforming case, and, obviously, every modification will result in lower efficiencies. Finally, it was stressed that the influence of the fuel utilisation on the cell output is positive in the direction of the maximisation of the energetic and exergetic efficiency.

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1 Introduction

Solid oxide fuel-cell based power plants (SOFC-PPs) constitute a very promising technology, which offers many advantages over conventional methods of power generation, including higher efficiencies and reduced emissions, and, thus, it has attracted significant interest in the area of environmental-friendly technology (Li, 2002; Minh and Takahashi, 1995; Stambouli and Traversa, 2002). Commercialisation of SOFCs is related to endeavours to increase SOFC stack performance using cheap materials and appropriate fuel processing. Therefore, when designing a SOFC plant, the need for optimisation of both operational conditions and fuel recovery is more than necessary in order to ensure economic feasibility. To realise its full potential, utilisation of SOFCs for practical power generation requires optimisation to reflect on the maximisation of the efficiency of the fuel exploitation and therefore, some optimisation criteria must be applied. These criteria should be based not only on the often misleading quantitative considerations of the first law of thermodynamics, but also on the evaluation of the qualitative availability of energy for transformation into useful work according to 'exergy analysis'.

SOFCs can be fuelled by almost every organic compound which contains a significant amount of hydrogen. The possibility of a reforming SOFC-PP system has been examined both theoretically and experimentally (Demin et al., 1992; Hassmann and Rippel, 1998; Wiese et al., 1999; Yanhui and Diyong, 2001) and some pilot units have already been installed. Since the by-products of the electrochemical reaction in a fuel cell are water and a significant amount of heat, effective thermal management is one of the important problems for all types of fuel cells. An important technical case results by considering the possibility of avoiding the steam reforming process. The directly fed SOFC stack would be the case presenting maximum efficiency because the steam supply should not be necessary and, therefore, some devices would not be needed.

In the present work, energy and exergy system analysis are used to estimate the thermodynamic performance of a SOFC power plant fuelled by methane. More precisely, the present work examines in detail the influence of the presence or not of the reformer within the whole apparatus and the consequent energy and exergy losses due to the reforming process.

2   Theory

Exergy is the maximum work that can be obtained from a given form of energy using the environmental parameters as the reference state while 'anergy' is the competitive energy part (Bejan et al., 1996; Caton, 2000; Kotas, 1985). Both of them can be considered as a direct consequence of the second law of thermodynamics and they establish a qualitative comparison of the engineering systems in terms of efficiency and exergy destruction sinks.

For a specified control volume and by ignoring changes in kinetic and potential energies, the energy balance can be expressed as follows (Bejan et al., 1996; Caton, 2000; Kotas, 1985):

$$\sum_j \dot{Q}_j - \dot{W} = \left(\sum_i \dot{m}_i h_i \right)_{inlet} - \left(\sum_i \dot{m}_i h_i \right)_{outlet} \tag{1}$$

where Q_j is the heat flux from the environment to the system, W is the power produced by the system, m_i is the mass flow rate and h_i is the specific enthalpy of the species i, respectively. On the other hand, exergy balance for this system is (Bejan et al., 1996; Caton, 2000; Kotas, 1985),

$$\left(\sum_i \dot{m}_i e_i \right)_{inlet} - \left(\sum_i \dot{m}_i e_i \right)_{exit} + \sum_j \left(1 - \frac{T_0}{T_j} \right) \dot{Q}_j - \dot{W} = T_0 s_{gen} \tag{2}$$

where $T_0 s_{gen}$ is the rate of exergy destruction of the system due to irreversibilities: heat dissipation, mixing, chemical reactions etc. (Gouy–Stondola theorem), and e_i is the total exergy of each chemical species i. In fact, $\sum_i \dot{m}_i e_i$ is the sum of the physical and chemical exergy components that are associated with the physical and chemical properties of the stream of matter, respectively (Bejan et al., 1996). More precisely, the physical exergy, e_i^{PH}, expresses the useful work that the chemical component i can produce if it is brought reversibly from the state of the system to the 'restricted dead state' that is a state in thermal and mechanical equilibrium with the environment. Therefore, physical exergy can be expressed as:

$$e_i^{PH} = (h - h_0)_i - T_0 (s - s_0)_i \tag{3}$$

where

$$(h - h_0)_i = \int_{T_0}^{T} (C_P)_i \, dT \tag{4}$$

and

$$(s - s_0)_i = \int_{T_0}^{T} \frac{(C_P)_i}{T} dT - R \ln \frac{p_i}{p_0}. \tag{5}$$

On the other hand, chemical exergy, e_i^{CH}, expresses the useful work that the chemical species i can produce if it is brought reversibly in chemical equilibrium with the environment. It is apparent that the chemical species comprising the system should be referred to the properties of a suitable selected set of environmental substances. Accordingly, an appropriate 'exergy reference environment' is usually used in order

to estimate the standard chemical exergy e_i^{CH} according to the relation (Kotas, 1985):

$$e_i^{CH} = -RT_0 \ln \frac{x_i^e p}{p_0} \tag{6}$$

where x_i^e is the molar fraction of the gas i in the standard reference environment, $T_0 = 298.15\,K$ and $p_0 = 1.013\,bar$. In this work, the 'standard reference environment' proposed by Szargut et al. (1988) has been adopted, assuming an environmental composition of 75.67% N_2, 20.35% O_2, 0.03% CO_2, 3.03% $H_2O_{(g)}$ and 0.92% Ar in volume basis at $T_0 = 298.13\,K$ and $p_0 = 1.013\,bar$.

## 3   The power plant system

The flow sheet of the external reformer SOFC-PP system that has been taken under consideration in the present study is presented in Figure 1(a) and it is analogous to that studied in Bedringas et al. (1997). It consists of the SOFC stack, a reformer, an afterburner, two preheaters, a vaporiser and a mixer. Methane and steam are mixed in the mixer and are heated in preheater 2 up to the operational temperature of the reformer. The reaction of methane steam reforming can be written (Douvartzides et al., 2003) as:

$$CH_4 + H_2O \rightarrow CO_2 + H_2 + 802.6\ kJ/mol\ of\ CH_4. \tag{7}$$
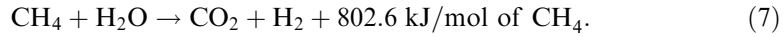
Figure 1   Efficiency maximisation for reforming-SOF-PP system with fuel utilisation $U_f = 73\%$ (a) and direct-methane-SOFC-PP with $U_f = 99\%$ (b). Steam to methane ratio RF = 2.2
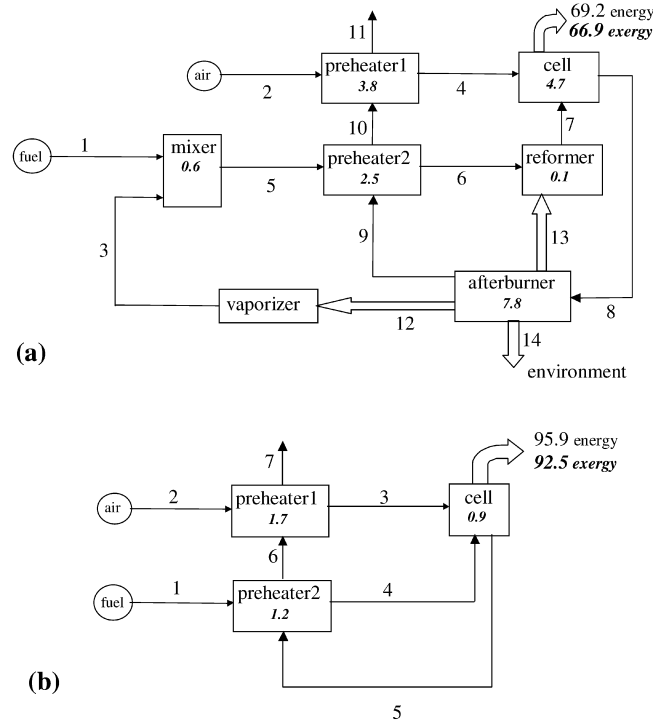
Because of the high stability of the methane molecule, the above reaction requires an environment of adequate heat supply at temperature between 800 and 1200 K. The reformed gas mixture enters the anode of the SOFC stack where hydrogen reacts with oxygen ions supplied from the cathode through the solid electrolyte, as follows:

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- + Q_{th} \tag{8}$$
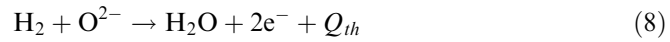
where Q_{th} is the heat produced in SOFC. In the present analysis, it is supposed that the extension of reaction (8) is lower than 100% and, thus, the factor of fuel (hydrogen) utilisation, U_f, is also employed. The reformer and the vaporiser are heated by the afterburner while preheater 1 is used to increase the temperature of the incoming air from 278 K close to the operational temperature of the SOFC.

The case of direct methane supply is considered assuming the configuration of Figure 1(b). In this case, most of the devices of Figure 1(a) can be excluded, since there is no demand for steam or additional heat supply. Therefore, the apparatus consists only of two preheaters and the fuel cell. The flue gases coming from the SOFC heat the fuel in preheater 2 up to the SOFCs operational temperature. The same heat source is also used to heat the air entering the cell.

4 Results and discussion

A mathematical model has been developed in order to simulate the processes involved in the plant described above. This simulation programme is able to calculate the flow rate, the temperature, the energy and the exergy in every branch of the plant as well as the irreversibilities appearing in the individual units. The energy efficiency of the electrical work as a percentage of the chemical energy of the fuel and the outlet exergy efficiency of the electrical work as a percentage of the standard chemical exergy of the fuel were also calculated. The influence of the independent variables (namely: reforming factor, extension of reforming, fuel utilisation, air excess, temperature of reforming and operational temperature of fuel cell) to the final efficiency of the system are recognised and optimised. Optimisation of the system requires the maximisation of the energetic action of the reformer and the SOFC by minimising entropy generation (exergy losses) due to chemical reactions, heat transfer and wastes of unexploited energy. Optimisation of driving forces for heat transfer phenomena has been applied with parallel minimisation of the participation of the combustion process.

Figure 1 presents the operational flow sheets of the Reforming-SOFC-PP system (a) and for Direct-Methane-SOFC-PP (b) for RF = 2.2 and stoichiometric analogy for air. The extension of reforming in Figure 1(a) has been set to $\varepsilon = 99\%$ and the fuel utilisation $U_f = 73\%$ (Douvartzides et al., 2003) while in the case of Direct-Methane-SOFC-PP is can reach the value of 99%. The basic parameters (temperature, mass flow rate, composition of the gas mixture), as well as the energy and exergy, are presented in Tables 1(a) and 1(b) for the positions 1–14 indicated by plain numbers in Figure 1(a) and in Tables 2(a) and 2(b) for positions 1–7 of Figure 1(b). The bold italic numbers presented in the devices of both figures represent the exergy destruction occurred in these devices. The temperatures of any device, as well as the mass flow rate in any branch of the apparatus, have been adjusted so that maximum

efficiency can be obtained. The output efficiency for the Direct-Methane-SOFC-PP is higher than the efficiency obtained by assuming Reforming-SOFC-PP system (92.5 to 69.2%, i.e. ∼34%). In fact, the efficiency of the non-reforming case is the upper limit for the efficiency of the reforming case, and, obviously, every modification will result in lower efficiencies. This behaviour can be explained because, in the case of Direct-Methane-SOFC-PP, combustion, reforming and fuel-steam mixing are completely avoided and, thus, the exergy losses of the power cycle are reduced due to the absence of additional chemical reactions, such as reforming, as well as because of the absence of steam in the flow paths. Under this respect, exergy destruction occurs only due to stream-to-stream heat exchanges that can be optimised by using the appropriate air and fuel preheating.

The influence of the fuel utilisation is presented in Figure 2 for both cases. Fuel utilisation can attain extremely high values in the Direct-Methane-SOFC-PP (up to 98%) while it is limited at 78% for the case of Reforming-SOFC-PP. The power output of the SOFC system is obviously positively affected, in an almost identical linear manner, by the increases of fuel utilisation for both cases. It is obvious that the influence of U_f should be only on the devices that are related to electrochemical reactions, i.e. it affects the reformer, the fuel cell and the afterburner. This influence is positive in the direction of efficiency maximisation because the energy dissipations of the whole system become lower as U_f reaches higher values. Therefore, the case of Direct-Methane-SOFC-PP has a competitive advantage compared with the Reforming-SOFC-PP case, since it presents significantly higher energy and exergy efficiency.

Table 1(a) The major parameters at the positions denoted in Figure 1(a)

Position	T(K)	m (kg/sec)	Energy (%)	Exergy (%)
1	298	1	100	100
2	298	17.6	0	0
3	298	2.5	0	2.4
4	800	17.6	18.9	7.6
5	298	3.5	100	101.8
6	1165	3.5	115.5	110
7	1050	21.1	136	124.9
8	1200	21.1	87.5	61
9	1200	21.1	53.3	31.9
10	947	21.1	37.7	21.1
11	617	21.1	18.8	9.8
12	–	–	12	6.4
13	–	–	20.5	14.5
14	–	–	0	0

Table 1(b) The compositions at the positions denoted in Figure 1(a)

| Position	Mixture composition (%)					
	N_2	O_2	CO_2	H_2O	CH_4	H_2
1	0	0	0	0	100	0
2	75.6	20.3	0.03	3.03	0	0
3	0	0	0	0	100	0
4	75.6	20.3	0.03	3.03	0	0
5	0	0	0	68.8	31.2	0
6	0	0	0	68.8	31.2	0
7	0	0	19.1	4.3	0.2	76.4
8	55.2	4.1	7.4	25.3	0.1	7.9
9	57.5	0	7.7	34.8	0	0
10	57.5	0	7.7	34.8	0	0
11	57.5	0	7.7	34.8	0	0
12	–	–	–	–	–	–
13	–	–	–	–	–	–
14	–	–	–	–	–	–

Table 2(a) The major parameters at the positions denoted in Figure 1(b)

Position	T(K)	m (kg/sec)	Energy (%)	Exergy (%)
1	298	1	100	100
2	298	17.6	0	0
3	1200	17.6	35.1	18.5
4	1075	1	101.9	100.2
5	1200	18.6	41.1	26.1
6	1162	18.6	39.2	24.7
7	411	18.6	4.1	4.6

Table 2(b) The compositions at the positions denoted in Figure 1(b)

Position	Mixture composition (%)					
	N_2	O_2	CO_2	H_2O	CH_4	H_2
1	0	0	0	0	100	0
2	75.6	20.3	0.03	3.03	0	0
3	75.6	20.3	0.03	3.03	0	0
4	0	0	0	0	100	0
5	69.3	0.2	9.2	21.2	0.1	0
6	69.3	0.2	9.2	21.2	0.1	0
7	69.3	0.2	9.2	21.2	0.1	0

Figure 2   Dependence of the cell outlet (energy and exergy efficiencies) of reforming-SOFC-PP (a) and direct-methane-SOFC-PP (b) on the fuel utilisation. $T_{SOFC} = 1200\,K$
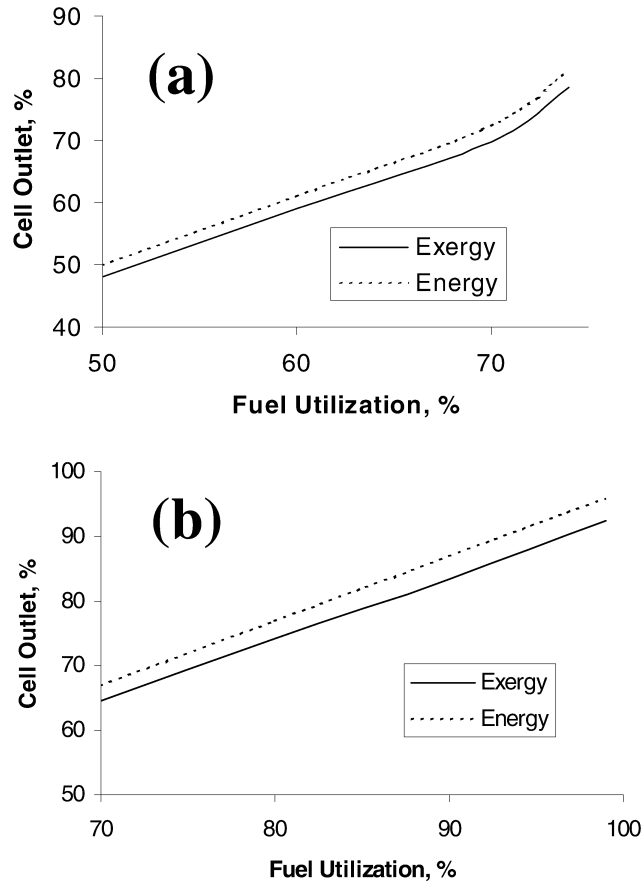
5   Conclusions

The present investigation focused on the maximisation of energetic and exergetic efficiencies of a SOFC-based power plant fed with methane. Initially, a power plant with external steam reforming, an afterburner, a vaporiser and two heat exchangers, was considered. It also compared with the case of a SOFC power plant where the fuel is directly utilised in the fuel cell without having been previously reformed. Based on mathematical optimisation techniques, useful information is deduced about the individual parameters and the independent variables that may lead to optimality according to the first and second law of thermodynamics. Allocation of exergy destruction is applied to determine optimally controlled unit operations. It was found that the case of Direct-Methane-SOFC-PP represents the upper limit for the efficiency of the Reforming-SOFC-PP according to the second law of thermodynamics, presenting an increment in the efficiency of about 34%.

Nomenclature

$(C_P)_i$	heat capacity
ε	extension of reforming
e_i, e_i^{CH}, e_i^{PH}	total, chemical and physical exergy of species i, respectively
h	specific enthalpy
h_i	specific enthalpy of species i,
h_0	specific enthalpy at the 'dead state'
j	position indicator
$\dot{m}_i$	mass flow of species i
p	pressure
p_0	pressure at the 'dead state' ($= 1.013\,\text{bar}$)
$\dot{Q}_j$	heat flux at position j
Q_{th}	heat produced in SOFC
R	gas constant
RF	steam to methane ratio ($=$ reforming factor)
s	specific entropy
s_0	specific entropy at the 'dead state'
s_{gen}	specific entropy generated
T	temperature
T_0	temperature at the 'dead state' ($= 298.15\,\text{K}$)
T_{SOFC}	temperature of Solid Oxide Fuel Cell
U_f	fuel utilisation
$\dot{W}$	power produced
x_i^e	molar fraction of the species i

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