

# Exergy analysis of a solid oxide fuel cell power plant fed by either ethanol or methane

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## Abstract

The method of exergy analysis is presented for a solid oxide fuel cell (SOFC) power plant involving external steam reforming and fed by methane and ethanol. The parameters for optimal operation of the integrated SOFC plant are specified after minimizing the existing energy and exergy losses. A comparison of methane and ethanol as appropriate fuels for a SOFC-based power plant is provided in terms of efficiency of exergy assuming the minimum allowable (for carbon-free operation) reforming factors for both cases. Then, a parametric analysis provides guidelines for practical design. The analysis employs parameters such as the extension of the steam reforming reaction and the hydrogen utilization in the SOFC and proves that the appropriate adjustment of the plant performance can be achieved by simply interrelating them in order to control the energy losses to environment and the participation of combustion processes in the power cycle. Energy losses from the SOFC stack are found also of negative impact to plant efficiency and are minimized through an appropriate thermal management between the mixtures incoming and outgoing the stack, attaining the adiabatic regime of SOFC operation. It is concluded that the exergy calculations pinpoint the losses accurately and that the exergy analysis gives a better insight of the system's process. © 2004 Elsevier B.V. All rights reserved.

*Keywords:* Optimization; Power plant; Energy; Exergy analysis; SOFC

## 1. Introduction

It is well established by the second law of thermodynamics that it is of great importance not only the amount of the energy but also its quality. “Exergy” is the part of the energy that is transformable to useful work and can be considered as a significant norm for the usefulness of energy, while “anergy” is the competitive energy part that cannot be transformed to work. The estimation of “exergy” and “anergy” allows a qualitative comparison of the engineering systems through an analysis according to the second law of thermodynamics. Ordinary power generation systems transform the chemical energy of a fuel into useful work by passing through the intermediate stage of production of thermal power that is most commonly achieved by processes of combustion, which is the major responsible for significant losses of potential energy that could otherwise be useful in work form as it is an extremely irreversible mechanism [1,2]. From the very beginning of the systematic development of actual electricity generating systems based on fuel

cells, research was focused on the approximation of optimal values of the major operational parameters by considering the first law of thermodynamics (energy analysis). Given that the first law has been generally regarded as capable and sufficient to determine real design optima, the analysis according to the second law was usually underestimated. In fact, it was not until the term “exergy” became a synonym of monetary value when the second law acquired practical significance in the optimization of energy systems [3]. Since this had happened, the “exergy analysis” has been accepted as a sound method for the interpretation of the axiomatic role of the second law in the design and optimization of energy systems in terms of both efficiency and cost, and as a supplementary tool to aid in decision making about the parameters and criteria that may lead to optimality in terms of the impact of engineering systems to environment [3,4].

Ethanol and methane (natural gas) are currently regarded as the most probable solid oxide fuel cell (SOFC) fuels due to a number of considerations dealing with their accessibility and their physical properties [5,6]. Methane was the first fuel that has been investigated on high temperature operating cells both experimentally ([7] and the relative references there) and theoretically [7–9]. Ethanol can be considered as a very promising and reliable fuel option for fuel cells because

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**Nomenclature***Latin letters*

$e$	specific exergy (J/mol)
$E$	total exergy (J)
$F$	Faradays' constant (=96484 J/(mol V))
$h$	specific enthalpy (J/mol)
$Q$	heat flux (J)
$m$	mass flow (kg/s)
$N$	molar flow rate (mol/s)
$p$	pressure (bar)
$R$	universal gas constant (=8.314 J/(mol K))
RF	steam to methane ratio
$s$	specific entropy (J/(mol K))
$T$	temperature (K)
$U_f$	fuel utilization (%)
$W$	work (J)
$x$	molar fraction

*Greek letters*

$\varepsilon$	extension of reforming (%)
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*Subscripts*

0	property at the state of the environment (dead state)
air	indicator of air
D	property destruction
gen	property generated
$i$	indicator of chemical species
in	indicator of inlet
$j$	indicator of individual heat transfer or indicator of the high temperature heat source
max	indicator of maximum allowable quantity
out	indicator of outlet
ref	indicator of reformer
SOFC	indicator of solid oxide fuel cell
th	indicator of heat produced in SOFC

*Superscripts*

CH	indicator of chemical exergy component
e	property referred to the chemical composition of the environment
PH	indicator of physical exergy component

it can be alternatively produced biochemically from biomass [10,11]. Due to the natural availability of bioethanol, it is considered an alternative fuel with positive impact both on economy and environment. Although steam reforming of ethanol has been variously investigated for hydrogen production [12–14], the analysis of ethanol utilization in SOFCs was undertaken recently by Tsiakaras et al. [15].

In the present investigation, the effect of the operational conditions on the theoretical performance of a SOFC system fed by either ethanol or methane is examined. The analysis is oriented to the comparison of these fuels, at optimal op-

erational conditions, in terms of the performance (efficiency and exergy destruction) of the overall system. The present work is devoted to the examination of this specific problem, assuming a stationary power plant comprised of a SOFC, a steam reformer, an afterburner, a vaporizer, a mixer and two heat exchangers. A mathematical model has been developed in order to simulate and optimize all processes involved.

**2. Theory**

Exergy is the maximum work, which can be obtained from a given form of energy using the environmental parameters as the reference state [16]. Exergy is a property depended on both the states of the system and its environment, and, thus, its calculation considers thermal, mechanical and chemical processes. It is obvious that,

$$\text{energy} = \text{exergy} + \text{anergy} \quad (1)$$

The energy balance for a single inlet/outlet device system, by ignoring the changes in kinetic and potential energies, can be expressed as,

$$\sum_j Q_j - W = \left( \sum_i m_i h_i \right)_{\text{inlet}} - \left( \sum_i m_i h_i \right)_{\text{outlet}} \quad (2)$$

where heat flux  $Q_j$  is conventionally positive when its direction is from the environment to the system and work is positive when it is produced by the system. The exergy balance for this system is,

$$E_D = \left( \sum_i m_i e_i \right)_{\text{in}} - \left( \sum_i m_i e_i \right)_{\text{out}} + \sum_j \left( 1 - \frac{T_0}{T_j} \right) Q_j - W \quad (3)$$

where  $E_D = T_0 s_{\text{gen}}$  is the rate of exergy destruction into the device due to irreversibilities and  $e_i$  is the total exergy of each chemical species  $i$ . Note that  $e = \sum_i m_i e_i$  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 [17]. Physical exergy,  $e_i^{\text{PH}}$  can be calculated as

$$e_i^{\text{PH}} = (h - h_0)_i - T_0(s - s_0)_i \quad (4)$$

where

$$(h - h_0)_i = \int_{T_0}^T (C_P)_i dT \quad (5)$$

and

$$(s - s_0)_i = \int_{T_0}^T \frac{(C_P)_i}{T} dT - R \ln \frac{P_i}{P_0} \quad (6)$$

The chemical exergy,  $e_i^{\text{CH}}$ , can be estimated as [17],

$$e_i^{\text{CH}} = -RT_0 \ln \frac{x_i^e P_i}{p_0} \quad (7)$$

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. To simulate the environment, all the values of standard chemical exergy have been selected from literature [18] 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.

### 3. The SOFC system

The flow sheet of the SOFC system consists of a SOFC, a reformer, an afterburner, two pre-heaters and a mixer (see Fig. 2). Fuel and water vapor enter the mixer and are heated in pre-heater 2 before entering the reformer. Due to the incompleteness of the steam reforming, the present analysis assumed a conversion factor that will be described as extension of reforming,  $\varepsilon$ . The gas mixture coming from the reformer enters in the anode compartment of the SOFC where hydrogen reacts with oxygen ions supplied from cathode through the solid electrolyte. A portion of hydrogen should not react to avoid dramatic losses in the electric potential of the SOFC. Moreover, a fraction of the hydrogen entering the SOFC should be allowed to reach the afterburner in order to support the heat demands of the reformer. The afterburner serves to guarantee the energy requirements that should be satisfied by the heat produced from the combustion of non-reacted methane (ethanol) and hydrogen. Finally, two pre-heaters (heat exchangers) were used to increase the thermal contents of air before the SOFC as well as of the fuel/steam mixture before the reformer.

### 4. Results and discussion

A mathematical model and FORTRAN code have been developed in order to simulate the processes involved in the plant described above. This simulation program was able to calculate the flow rate, the temperature, the energy and the exergy in every branch of the plant as well as the exergy destruction appearing in the individual units. The outlet exergy efficiency of the electrical work as percentage of the standard chemical exergy of the fuel and the energy efficiency of the electrical work as percentage of the chemical energy of the fuel could be also calculated. Finally, the model optimized also the system for obtaining the maximum efficiency. In order to calculate the exact temperatures in the devices of the power cycle, an iterative method has been employed taking into account the variation of the thermal capacities with temperature [19].

Under the assumption of ideal thermal exchange between the streams of gas mixture from the output of reformer and pre-heated air upstream the SOFC, it is obvious that an infinite number of equivalent scenarios with different temperatures of these streams may result in the same plant efficiency. Accordingly, the first law analysis is unable to specify an optimal operative scheme regarding the temperatures of the

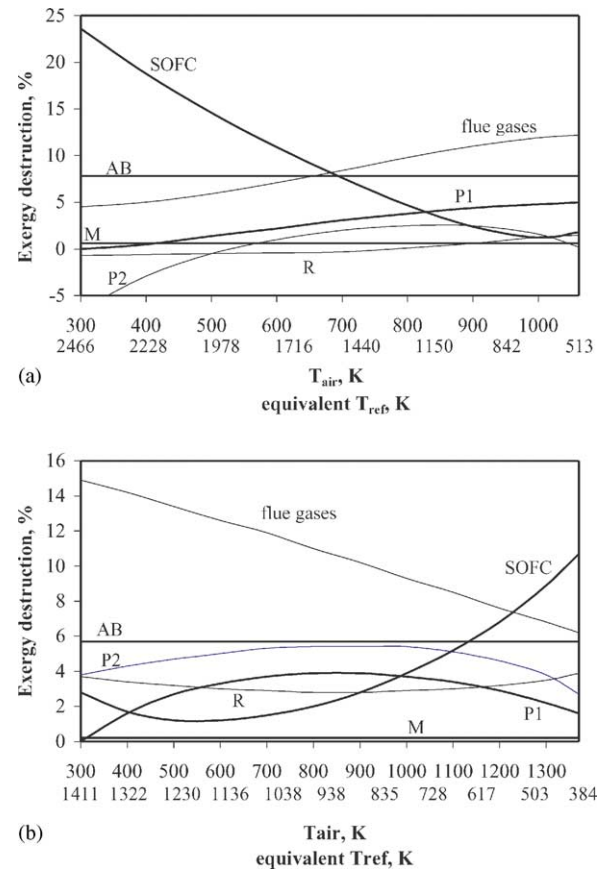


Fig. 1. Allocation of exergy costs in the units of the methane (a) and ethanol (b) optimally designed SOFC plant at all equivalent schemes for temperatures of pre-heated air and reformat ( $T_{sofc} = 1200$  K,  $\varepsilon = \varepsilon_0$ ,  $U = U_0$ , RF is 2.2 for methane and 3 for ethanol). M: mixer; P1: pre-heater 1; P2: pre-heater 2; AB: after burner; R: reformer.

reforming reaction and air pre-heating. To overcome this weakness, the “exergy analysis” may be applied as shown in Fig. 1a and b, where the cases of a power plant fed by methane (a) and ethanol (b) are considered. In both cases, the design parameters of the reforming temperature and air pre-heating may be specified according to the necessity for cost-effective plant operation, allocating the exergy costs of the individual units of the plant. Although exergy destruction due to dissipative phenomena (friction, chemical reaction, heat transfer, thermal losses) is irreversibly lost, exergy losses may be considered exploitable by an appropriate engine. Therefore, different scenarios of Fig. 1 result in different allocations of exergy costs in the devices of the plant attributed to friction heat transfer through finite temperature differences and chemical reactions. Since, the afterburner is optimally designed to operate with zero energy losses, participation of combustion in the power cycle is minimized and so is associated exergy destruction. For the case of a methane-fed power plant, it is interesting to observe that the dependence of the individual exergy costs on  $T_{air}$  and the equivalent  $T_{ref}$  differs significantly from those obtained for the ethanol plant. Indeed, a significantly large

region of solutions is found to violate the second law by means of negative exergy destruction rates in the reformer and the pre-heater 2. This seems plausible by observing that air pre-heated at low temperatures requires extremely high equivalent temperatures for reforming. As a consequence, air must be pre-heated above 800 K and the reformat must be produced at temperatures lower than 1150 K in order the plant to operate optimally.

Due to these constraints, Fig. 2 provides a thermodynamically feasible optimal operation configuration with the specific operation conditions that maximize energy and exergy efficiencies, assuming the reforming reaction at about 1100 K. As shown, exergy loss within the flue gases is 9.8% and 12.4% of the chemical exergy of the fuel, respectively, and exhaust-gas temperature may be used for useful

purposes (heating rooms, water, etc.). Further, the major exergy sink of the plant is the afterburner with exergy destruction rate equal to 7.8 and 5.7%, respectively, due to highly irreversible spontaneous combustion process. It is important to notice that this rate of exergy destruction in the afterburner is the minimum possible for the example under consideration, as it corresponds to zero energy losses. Finally, it should be stressed that avoidable exergy destruction near the output (electrical power) of the plant has greater impact on the efficiency and cost of electricity than avoidable exergy destruction of the same magnitude in a unit near the inputs (fuel, steam, air) according to the Gouy-Studola theorem [20]. Since the major devices that contribute on electricity generation are the reformer and the SOFC, a scenario of low exergy costs in these units is preferable

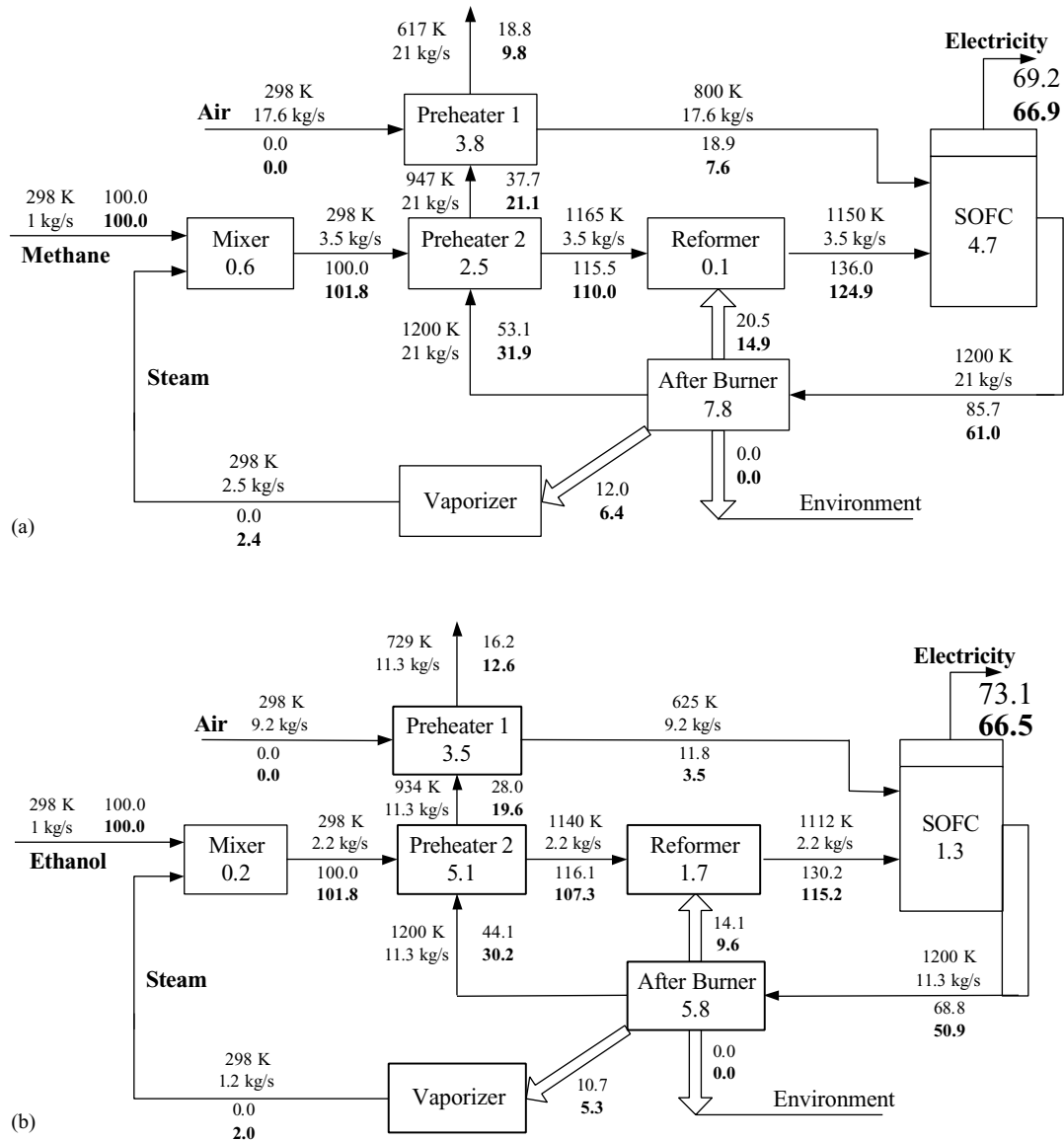


Fig. 2. Optimal configuration of the methane (a) and ethanol (b) fed SOFC plant for stoichiometric air,  $\varepsilon = \varepsilon_0$ ,  $U = U_0$ . RF is 2.2 for methane and 3 for ethanol. Plain text stands for energy values and bold stands for exergy ones.

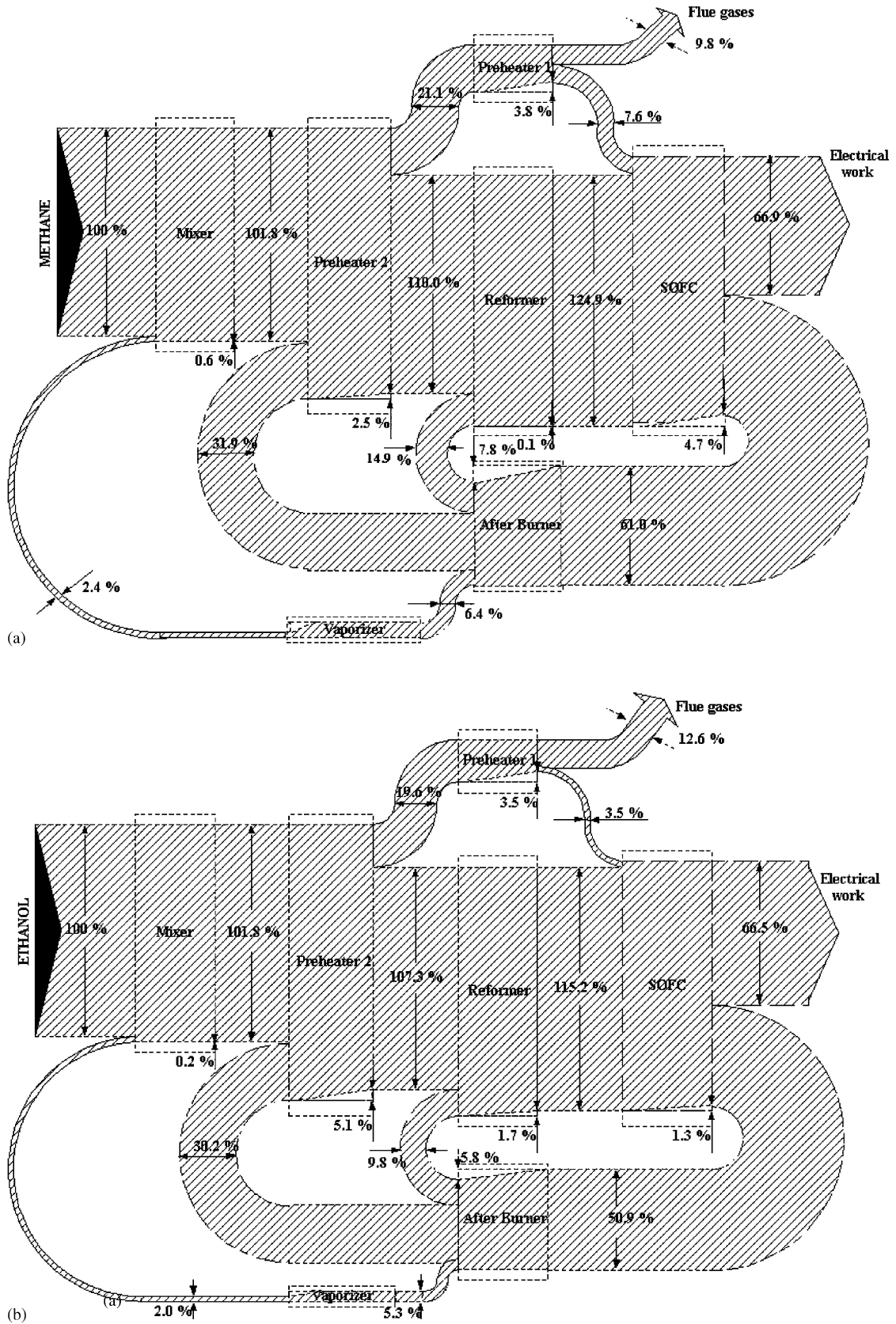


Fig. 3. Grassman diagrams of methane (a) and ethanol (b) fueled SOFC plants (comparison of optimal designs).

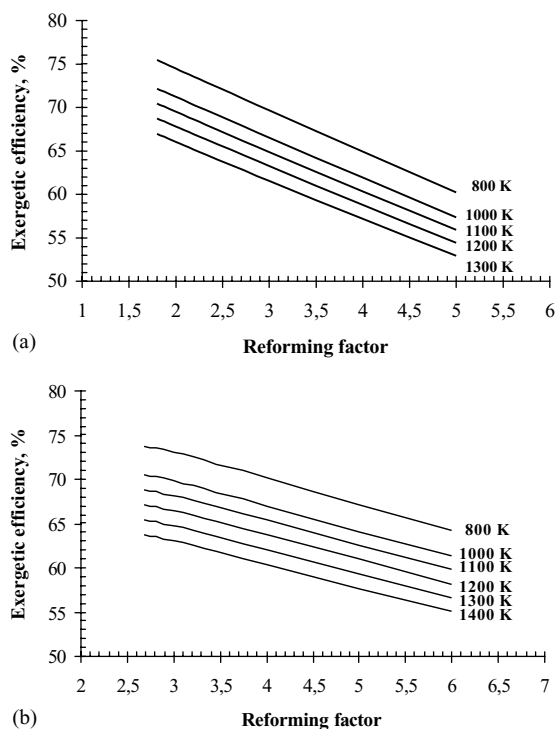


Fig. 4. Effect of the reforming factor on the optimum exergetic efficiency of a methane (a) and ethanol (b) SOFC plant of the plant for various temperatures.

than a scenario involving low exergy costs in devices close to the plant inputs. In terms of exergy, a comparison of the cases of methane and ethanol is provided for their optimal designs by the Grassman (exergy flow) diagrams of Fig. 3.

Fig. 4 illustrates the effect of the reforming factor on the second law efficiency of the work output for several operational temperatures of the SOFC. Note that  $T_{\text{sofc}}$  has been considered as a desired initial parameter known a priori by the designer of the plant. It pictures that higher temperatures correspond to lower efficiencies, as operation of SOFC at low temperature corresponds to lower energy losses in the SOFC. It is worth noticing that efficiencies calculated in the case of a methane-fed SOFC are higher than those of an ethanol-fed one for any reforming factor and temperature because the methane's content in exergy, expressed by the ratio of hydrogen per carbon atoms, is higher than this ethanol and, therefore, the theoretical efficiency should be higher, too. Finally, it should be also mentioned that the lower the reforming factor, the higher the efficiency and this is an additional reason for the higher efficiencies produced in the case of methane as this fuel allows lower reforming factors than those of ethanol (1.486–2.68).

By reminding the allocation of exergy costs according to Fig. 1, it would be useful to recognize the effect of the reforming factor on the equivalent temperatures of the reformat and air together with its effect on the individual exergy costs of each unit. Fig. 5 provides the effect of the reforming factor on the equivalence of the temperatures of

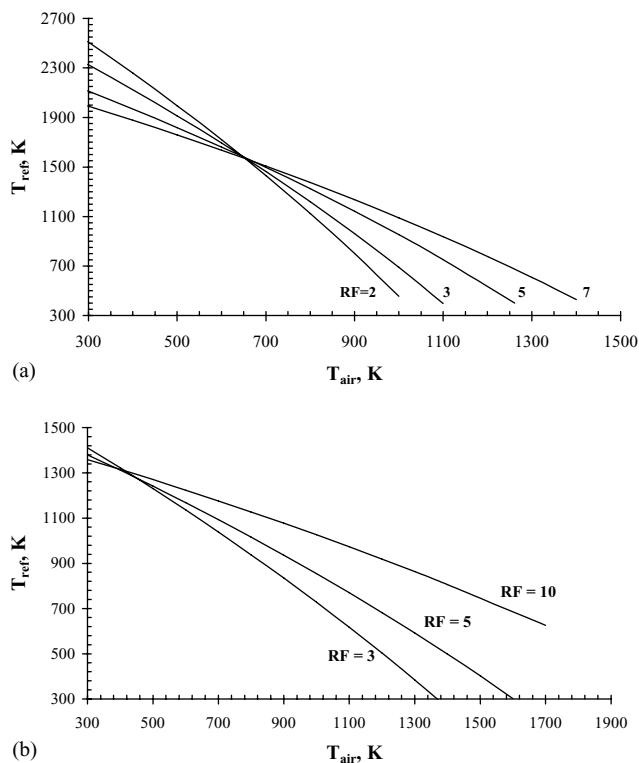


Fig. 5. Effect of the reforming factor on the equivalence of the temperature of the reformat and the pre-heated air for the methane (a) and ethanol (b) fed SOFC power plant.

the reformat,  $T_{\text{ref}}$ , and pre-heated air,  $T_{\text{air}}$  for both the cases where methane and ethanol are used to fed the plant. Since an increment of the reforming factor induces higher energy requirements from the vaporizer, the zero-loss burner balance provides lower plant efficiency. However, it is shown here that the increment of the reforming factor does not favor the overall performance of the plant, especially for the cases of compounds exhibiting high reactivity for reforming at low temperatures such as ethanol. This is not only due to its effect on efficiency but also due to suppressing of the range of feasible temperatures for reforming.

## 5. Conclusions

The present investigation depicted an optimization strategy for a SOFC power plant with external steam reforming, an afterburner, a vaporizer and two heat exchangers, which operates with either methane or ethanol. The energy conservation law and the exergy analysis were combined to specify an optimal scheme of operation and the effect of specific parameters to the convergence to it. Based on a mathematical model, useful information were deduced about the individual parameters and the independent variables that may lead to optimality according to the first and second law of thermodynamics. On the basis of available technical knowledge and experience on materials and catalytic activities,

the analysis reveals the method of integration of the plant configuration in terms of the principal operational parameters for feasible and cost-effective operation. Based on the optimization method, a parametric analysis was presented, engineering modifications were indexed and a general plan of decision-making has been developed. Methane-fed SOFC presents higher efficiency than this of ethanol-fed one for any allowable temperature and reforming factor.

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