EXERGY ANALYSIS OF BIOGAS-FED SOFC

G. Fragoyiannis, D. Mytakis and F.A. Coutelieris

Department of Environmental & Natural Resources Management, University of Patras, Seferi 2, 30100, Agrinio, Greece, Tel: +302641074196; Fax: +30 2641074176, fcoutelieris@upatras.gr

ABSTRACT

Fuel cells are highly efficient energy conversion systems that have recently gained significant interest in terms of both science and applications. Exergy analysis is adopted here for a power plant involving SOFC with external steam reforming that is fuelled by modeled biogas/steam mixtures. The electrical efficiency has been estimated and the effect of various operational parameters on the process efficiency has been investigated. The optimal operation parameters of the integrated SOFC plant are specified by pinpointing and minimizing the existing losses, while a parametric analysis has been also performed to provide guidelines for practical design.

KEYWORDS

SOFC, biogas, Power plant, Energy, Exergy analysis.

1 INTRODUCTION

From the very beginning of the systematic development of actual electricity generating systems based on fuel cells, research was guided by endeavors to approximate their optimal theoretical patterns of operation as dictated by the first law of thermodynamics. Given that the first law (energy) analysis 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. 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 (Rosen &Dincer, 2001).

Biogas is a renewable fuel containing 50 – 80 %v CH4 diluted by 50 – 20 %v CO2 reforming agent. Only 10 % of the readily exploitable biogas resources are estimated to be used today due to the local nature of biogas production, which implies the use of internal combustion engines of small nominal power and low electrical conversion. Moreover, landfill biogas (almost 80 % of current biogas production) often contains less than 50 % CH4, hindering its use in conventional power systems. On the contrary, solid oxide fuel cells (SOFCs) can be directly fed with CH4/H2O mixtures and by-pass the need to pre-reform biogas or to eliminate CO through successive catalytic reactors (Singhal & Kendall, 2003). Internal steam reforming is the dominant route for biogas-fed SOFCs commercialization, while only few preliminary studies, mostly triggered by the prospects of direct biogas SOFC applications, had examined internal dry reforming (Yentekakis, 2006, Shiratori et al., 2008).

In general, the advantageous position of fuel cells as highly efficient energy conversion systems has been indemnified by numerous projects for installation in central or distributed power plants (see for example Bedringas et al., 1997). Accumulation of experience from these early fuel cell programs revealed that it would be useful to recognize the exergetic optimization criteria for effective performance, as these could allow engineering modifications to attain optima unconceivable from energy conservation law. The present work is devoted to the examination of this specific problem, assuming a stationary power plant fed by biogas and comprised of a SOFC with the ability of internal steam reforming, while peripheral devices were also considered.

2 ENERGY AND EXERGY BALANCES

Exergy is the thermodynamic property that describes the “useful energy” content, or the “work producing potential” of a system at a certain state (Kotas, 1985). Hence, exergy can be calculated assuming the reversible thermal, mechanical and chemical transition of the system to a state that is in equilibrium with its environment. A clarification of the exergy concept can be presented by considering a one inlet – one outlet device as a system with a flow of a mixture of i chemical species of known composition at elevated temperature and high pressure. The energy balance for this system, ignoring the changes in kinetic and potential energies, may be expressed as

$$\sum_j \dot{Q}_j - \dot{W} = \left(\sum_i \dot{m}_i h_i\right)_{in} - \left(\sum_i \dot{m}_i h_i\right)_{out} \qquad (1)$$

where $\dot{Q}_j$ is the heat flux from the environment to the system, $\dot{W}$ is the power produced by the system, $\dot{m}_i$ is the mass flowrate and h_i is the specific enthalpy of the species i, respectively. On the other hand, the exergy balance for this system is,

$$\sum_{i=1}^{p}\left(1-\frac{T_0}{T_i}\right)\dot{Q}_i + \sum_{i=1}^{n}[(\bar{h}_i - T_0\bar{s}_i)_{in} - \mu_{0,i}]\,\dot{N}_{i,in} = \dot{W} + \sum_{i=1}^{n}[(\bar{h}_i - T_0\bar{s}_i)_{out} - \mu_{0,i}]\,\dot{N}_{i,out} + T_0\,\dot{s}_{gen} \qquad (2)$$

where $T_0\,\dot{s}_{gen}$ is the rate of exergy destruction in the system due to the irreversibility (heat dissipation, mixing, chemical reactions etc.), $\dot{N}_{i,in}$ and $\dot{N}_{i,out}$ are molar flow rates and the bar over some quantities of Eq. (2) denotes averaged quantities referred to mixture of chemical species. The first term of the left hand side of Eq. (2) describes the exergy in heat flows and the second the exergy in inlet mass flows. The second term of the right hand side describes the exergy in outlet mass flows.

Based on the energy and exergy balances of Eqs. (1) and (2), the analysis of the power plant is possible given the exact definition of the physical and chemical properties of each stream of matter and the environment. For the purposes of this work, the “standard reference environment” proposed by Szargut et al. (1988) has been adopted and an environmental composition of 75.67% N2, 20.35% O2, 0.03% CO2, 3.03% H2O(g) and 0.92% Ar in volume basis was assumed at T_0 = 298.13 K and p_0 = 1.013 bar.

3 THE POWER PLANT

The architecture of the system that has been taken under consideration in the present study is presented in Figure 1. A range of biogas/steam mixtures of constant molar flowrate (2.9 10^{-6} mol/sec) were fed to the anode compartment in parallel (co-flow) to a cathodic air flowrate (4.0 10^{-5} mol/sec), adequate to ensure a slight variation of the oxygen content, throughout the unit volume. The, preheated at 1073 K in a heat exchanger biogas/steam mixtures are mixed with steam in the mixer before supply the cell and internally reformed through the linearly independent reactions of steam reforming and water gas shift (WGS):

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

$$CO + H_2O \leftrightarrow CO_2 + H2 \tag{4}$$

The anodic electro-oxidation of both H2 and CO at the triple phase boundary is given as:

$$H_2 + CO + 2O^{2-} \rightarrow H_2O + CO_2 + 4e^- \tag{5}$$

Although only one device is actually required for both reforming and electro-oxidation, it is necessary to distinguish reformer from fuel cell, in terms of processing, as presented in Figure 1. In order to express the incompleteness of the above mentioned reforming process, the extensions of reforming, ε_{CH4} were used as conversion factors of reaction (3). It is also assumed that reaction (5) takes place with an extent below 100% by employing the factor of hydrogen utilization, U. In practice, a portion of hydrogen would not react in the SOFC since the cell voltage adjusts to the lowest chemical potentials for the gas mixture at the exit of the anode. Unreformed methane and residual hydrogen are considered to undergo complete combustion in the burner providing heat for vaporization and reforming. The reformer and the vaporizer are heated by the burner while a heat exchanger is used to increase the temperature of the incoming air. A part of the heat produced in the burner is released to the environment. Finally, the overall energy efficiency (η_I, %) is defined as the ratio of the produced electrical work to the lower heating value of biogas and the overall exergy efficiency (η_{II}, %) as the ratio of the produced electrical work to the standard chemical exergy of biogas. Obviously, the aforementioned values depend on biogas composition.

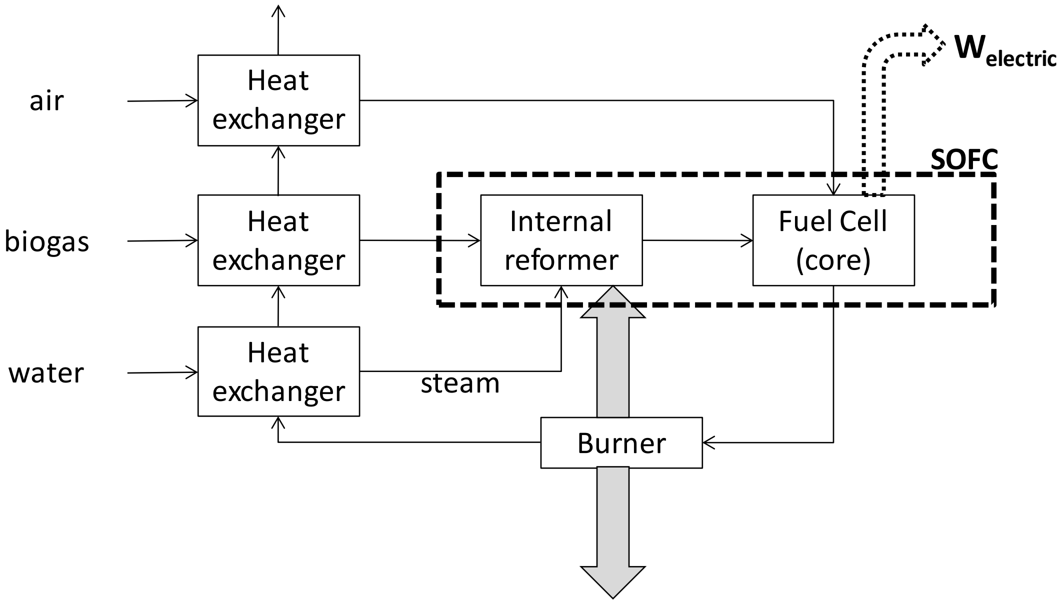


Figure 1: Schematic representation of the plant configuration.

4 RESULTS & DISCUSSION

Fully-customizable modular software, based on the above mentioned mathematical principles, has been developed to simulate the processes that take place in the described system. This program represents the power plant with a circuit-like structure consisted of nodes and connection branches. Each separate device of the system is assumed to be a node of the equivalent circuit. The most significant independent variables that affect on the efficiency have been considered to be the extension of reforming (ε_{CH4}) and the fuel utilization (U). The flow, the temperature, the energy and the exergy in every branch as well as the irriversibilities in every node were calculated as functions of these operational parameters with high accuracy (error < 0.1%). For the calculation of the exact temperatures in the sites of the power cycle, an iterative method has been employed by considering the variation of the thermal capacities with temperature.

Table 1 presents the operational flow-sheet of the system, where all the operational parameters (namely, the temperatures of any device as well as the mass flow-rate in any branch of the apparatus) have been justified so that maximum efficiency can be obtained. This maximization procedure aims at the satisfaction of the following criteria:

I. Air temperature just before the fuel cell should be as closer to the operational temperature of the cell as it can
II. Thermal energy and exergy releases from burner to environment should be minimal.
III. Temperature of flue gases must be minimized, as well.

It is obvious that all the above criteria are satisfied by the operational procedures described in the present work.

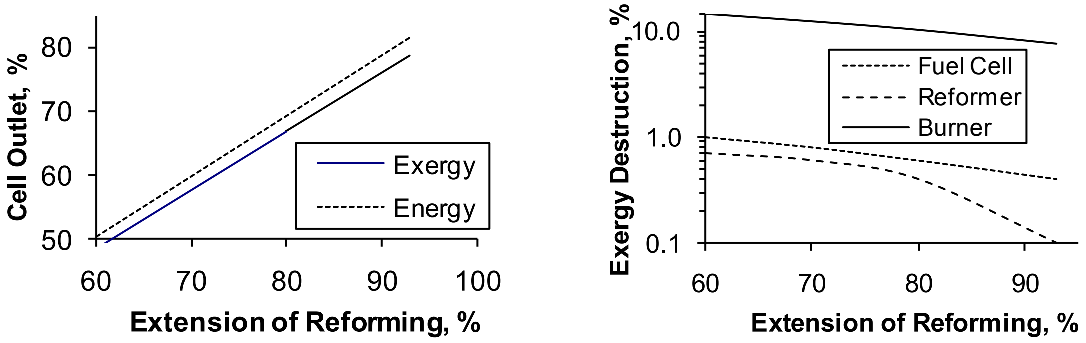
Table 1: Operational Flowchart

Branch	**Flowrate (moles/s)**	**Temperature (K)**	**Energy (% of Biogas HHV)**	**Exergy (% of Biogas Standard Chemical Exergy)**
1	3.7 X 10^{-6}	298	100	100
2	4.0 X 10^{-5}	298	0	0
3	3.2 X 10^{-6}	298	0	0
4	3.7 X 10^{-6}	1073	112.3	107.6
5	1.1 X 10^{-5}	1073	131.2	121.4
6	3.2 X 10^{-6}	1073	27.0	15.5
7	4.0 X 10^{-5}	1045	82.8	59.5
8	4.0 X 10^{-5}	1200	51.2	30.8
9	4.0 X 10^{-5}	1199	39.1	22.3
10	4.0 X 10^{-5}	1186	16.4	10.9
11	4.0 X 10^{-5}	1132	6.1	4.8
12	4.0 X 10^{-5}	1065	22.7	16.0

Device	**Energy Balance (% of Biogas HHV)**	**Exergy destructed (% of Biogas Standard Chemical Exergy)**
Heat Exchanger 1	0	0.5
Heat Exchanger 2	0	2.4
Heat Exchanger 3	0	3.0
Reformer	0	0.1
Fuel Cell	0	0.4
Burner	0	7.9
Electricity Produced	**81.3**	**78.5**

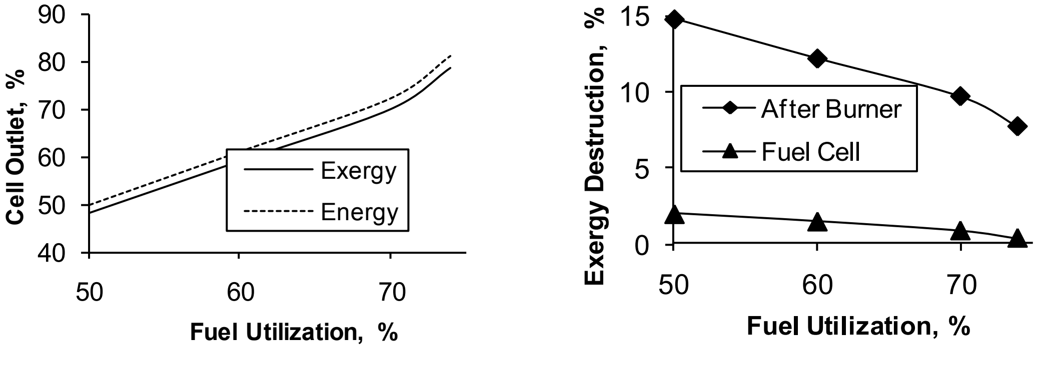
The influence of the extension of reforming as well as of the fuel utilization is presented in the following Figures. Power output of the fuel cell system is obviously positively affected by the increases of both the extension of the reforming and fuel utilization (see Figures 2a & 3a).

Furthermore, fuel utilization affects on cell outlet in an almost identical linear manner for values lower than 70% while a quite higher increment rate is presented as U values reach their upper limit (74%). It is obvious that the influence of these two parameters should be only on the devices that are related to reforming and electrochemical reactions. Thus, (see Figure 2b) its increase affects on the reformer, the fuel cell and the burner. This influence is positive in the direction of the efficiency maximization because the higher the ε_{CH4}, the richer in hydrogen the gas mixture that fed the cell and, thus, the lower the energy dissipations of the whole system. It must be noted that ε_{CH4} is limited at 93% because higher values correspond to conditions where the burner becomes insufficient for the coverage of the total energy needs of the system. System response to the variations of the fuel utilization is quite analogous (see Figure 3b). The only significant difference can be focused on the limit of the increament, which is 78%.



(a) **(b)**

Figure 3: Extension of reforming influence on cell outlet (a) and exergy destruction (b) (U = 78%, Tair = 1040K, CH4/CO2/H20=30/30/40).



(a) **(b)**

Figure 4: fuel utilization influence on cell outlet (a) and exergy destruction (b) (ε_{CH4} = 93%, Tair = 1040K, CH4/CO2/H20=30/30/40).

5 CONCLUSIONS

The overall performance of a fuel cell system fed by biogas according to the first and the second law of thermodynamics, is presented here. The analysis was directed to the optimization of the operational condition, while both energy and exergy balances as functions of the principal operational parameters have been postulated and used. A computer program with advanced optimization abilities was developed and used for simulation purposes. After the optimization took place, efficiencies of the order of 81.3% of the low heating value and 78.5% of the standard chemical exergy of biogas are obtained.

6 REFERENCES

Bedringas, K.W., Ertesvag, I.S., Byggstoyl, S., Magnussen, B.F. (1997) Exergy analysis of solid-oxide fuel-cell systems. *Energy*, 22, 403-412.

Kotas, T.J. (1985). *The exergy method of thermal plant analysis*. London: Butterworths.

Rosen, M.A., Dincer, I. (2001). Exergy as the confluence of energy, environment and sustainable development. *Exergy An International Journal*, 1, 3-13.

Shiratori, Y., Oshima, T., Sasaki, K. (2008). Feasibility of direct-biogas SOFC. *International Journal of Hydrogen Energy,* 33, 6316-6321.

Singhal, S.C., Kendall, K. (2003). *High Temperature Solid Oxide Fuel Cells*. New York: Elsevier.

Szargut, J., Morris, D.R., Steward, F.R. (1988)). *Exergy analysis of thermal, chemical and metallurgical processes*. New York: Hemisphere.

Yentekakis I.V. (2006). Open- and closed-circuit study of an intermediate temperature SOFC directly fueled with simulated biogas mixtures. *Journal of Power Sources,* 160, 422–425.