Renewable Energy 108 (2017) 1–10

Contents lists available at ScienceDirect

Renewable Energy

journal homepage: www.elsevier.com/locate/renene

Thermodynamic analysis of biogas fed solid oxide fuel cell power plants

George N. Prodromidis, Frank A. Coutelieris*

Department of Environmental & Natural Resources Management, University of Patras, Greece

ARTICLE INFO

Article history:
Received 23 February 2016
Received in revised form
13 February 2017
Accepted 16 February 2017
Available online 20 February 2017

Keywords:
Biogas
Efficiency
Energy
Exergy
Optimization
SOFC

ABSTRACT

The present research study presents the optimization of Solid Oxide Fuel Cell (SOFC) power plants directly fed by biogas. By considering energy and exergy balances for such a system, a detailed thermodynamic model (THERMAS) was designed and implemented. A specific SOFC-based system was selected as case study, equipped with three heat exchangers (preheaters), a reformer, a SOFC-stack system and an afterburner. The use of the simulation tool THERMAS give us the opportunity to investigate all the appropriate parameters that affect system's efficiency based on exergy analysis while incorporating a detailed parametric analysis regarding the whole system. The optimization process relies on the difference between the energy and exergy efficiency by considering an innovative Optimization Factor (OPF) for each simulated system, which is dynamically affected by operational parameters, such as fuel composition, extension of chemical reactions and temperatures. It is found that the use of a pure fuels seems to be meaningless without optimization.

© 2017 Elsevier Ltd. All rights reserved.

1. Introduction

During the last decades, overpopulation and the consequent excessive overconsumption, characterizes the global existing situation, thus producing a huge amount of wastes (agriculture, animal, food, domestic wastes etc.). These billions tons of wastes can be properly managed and treated to avoid environment pollution and simultaneously to be produced enough electrical energy to cover the human needs despite the limitation of the fossil fuels deposits [1].

Under these considerations, biogas a multi-gas mixture, seems to be an important source of renewable energy as it can be produced by the degradation of biodegradable materials, such as organic wastes under the eco-friendly way of anaerobic digestion [2]. Biogas is primarily composed by methane (CH_4) and carbon dioxide (CO_2), while it is saturated with water vapor. By considering the initial organic materials and the time-period for the finalization of the biological process during biogas production, its composition varies. Statistically speaking, it has been shown that the typical values for methane per unit mass of biogas production vary between 50% and 73%, usually attained after a 14 week anaerobic digestion process, while after a 10 week process corresponds to a 40% [1,3]. By concerning carbon dioxide, its values vary from 15% up to 45% and the water vapor from 5% up to 12%, respectively [1,4–6].

Fuel cells are devices that directly convert chemical energy of the feeding fuel to electricity without Carnot limitations [7–9]. As far as biogas is a methane-rich fuel, it stimulates a reliable alternative to fuel options. The increased flexibility on fuel choice that Solid Oxide Fuel Cells (SOFC) advantageously present [10,11], strengthen further biogas utilization in such devices.

Experimental results on SOFC based projects fed with pure methane or ethanol to produce electric energy reveals theoretical energy efficiencies up to 80%–90%, under a totally eco-friendly way [12–14]. Also such a project can achieve satisfactory performance using biogas even with low methane content [15]. Several studies throughout the literature have already examined the economic performance of SOFC systems under different aspects (i.e. the levelized cost of electricity (COE), the biogas cost, the objective function of interest, the power normalized capital cost or the internal rate of return on investment as a function of several operational parameters [16,17]). Also several studies use thermodynamics to perform analysis on SOFC systems combined with heat production [12–14,18] while special effort has been put to investigate the effects of biogas feeding under several assumptions [19].

The basic aim of the presented study is to present a detailed model for the optimization of the operation of SOFC-based power

---

* Corresponding author. Current address: G. Seferi 2, 30100, Agrinio, Greece.
E-mail address: fcoutelieris@upatras.gr (F.A. Coutelieris).

http://dx.doi.org/10.1016/j.renene.2017.02.043
0960-1481/© 2017 Elsevier Ltd. All rights reserved.

plants by using thermodynamics. The optimization is based on fundamental thermodynamics, energy and exergy balances and the corresponding cost analysis. This model has been named THERMAS (THERmodynamic MAthematical Simulation model). In this context, each individual process incorporated in the power production system has been extensively mathematically simulated for different cases that represent real life operational conditions. Therefore, several dynamical parameters as well as several mixture compositions have been taken into account, to cover all the possible incidents. Also THERMAS offers the opportunity to choose a great variety of different values for each operational parameter individually, thus allowing for studies within unexplored and experimentally impossible operational ranges. Finally, THERMAS innovatively introduces exergy efficiency to identify the optimal scenario per system.

2. Theory

The initial fundamental phenomenon which is widely used in engineering and environmental analyses and is required for thorough design and analysis of several physical systems' processes, is based on mass balances. Mathematically, the general mass flow rate balance can be described through the expression [20]:

$$\dot{m}_{in} + \dot{m}_{gen} = \dot{m}_{out} + \dot{m}_{cons} + \dot{m}_{accu} \tag{1}$$

This can be described as the initial criterion to control the proper operation of each device and simultaneously of the whole system during its simulation. Eq. (1) has to be satisfied in each time step of the process, mainly due to the chemical reactions take place that are characterized by different extensions, accordingly to the limitations being put by the materials used and the conditions applied. Obviously, $\dot{m}_{gen}$, $\dot{m}_{cons}$ and $\dot{m}_{accu}$ might be zero, dependent on the simulated case.

Engineering processes are also based on the First Law of Thermodynamics, referred as energy balance theory and for the needs of the current modelling will constitute the second criterion which has to be satisfied for each device. The energy balance of a heat exchanger can be expressed as [21]:

$$T_{in}\left[\sum_i M_i (C_P)_i\right]_{in} = T_{out}\left[\sum_i M_i (C_P)_i\right]_{out} \tag{2}$$

where C_P is the molar specific heat capacity. By assuming ideal gases, this can be calculated through NASA Polynomials with the appropriate specific coefficients for each chemical element [22].

During biogas reforming the total energy balance can be described as [22,23]:

$$T_{in}\left[\sum_i M_i (C_P)_i\right]_{in} + [Q_{burn}]_{ref} + |\Delta H_{WGS}| = T_{out}\left[\sum_i M_i (C_P)_i\right]_{out} + \Delta H_{ref} \tag{3}$$

where $[Q_{burn}]_{ref}$ is the extra thermal energy supplied by the afterburner for the finalization of the reforming process. The enthalpy changes, ΔH_{WGS} and ΔH_{ref} are characterized by positive or negative values due to the exothermic and endothermic character of each reaction, respectively.

As concern the considered SOFC-stack system modelling, we must underline the absence of an extra thermal energy term and the presence of exothermic reactions, while an extra energy term is derived by the produced electric load, W_{el}. Also, regarding the afterburner's operation, it is necessary to consider the environmental thermal losses, $[Q_{burn}]_{env}$, and the supplied thermal energy to the reformer, $[Q_{burn}]_{ref}$, as well as the enthalpy changes due to the several exothermic reactions. The above presented energy balance theory is followed as well in both SOFC-stack system and afterburner, as reveal Eq. (4) and Eq. (5) respectively:

$$T_{in}\left[\sum_i M_i (C_P)_i\right]_{in} + |\Delta H_{H_2}| + |\Delta H_{CO}| = T_{out}\left[\sum_i M_i (C_P)_i\right]_{out} + W_{el} \tag{4}$$

$$T_{in}\left[\sum_i M_i (C_P)_i\right]_{in} + |\Delta H_{burn}| = T_{out}\left[\sum_i M_i (C_P)_i\right]_{out} + [Q_{burn}]_{ref} + [Q_{burn}]_{env} \tag{5}$$

From the very beginning of the systematic development of 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 balance theory). In fact, it was followed until the second law of thermodynamics acquired practical significance in the optimization of energy systems [23]. Since then, 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 conversion systems in terms of efficiency [14]. Also it constitutes a supplementary tool to aim in decision making about the operational parameters and criteria that may lead to optimal system's operation.

Mentioning that exergy is actually a thermodynamic property that describes the maximum useful work provided by a system during to its reversible transition to a thermodynamic state in equilibrium with its environment, it seems to play a crucial role during simulation process [24]. The exergy analysis (availability analysis) determines in general the location, cause and magnitude of energy resource waste and loss [25]. Exergy depends on both the states of the system and its environment while exergy calculation considers processes of thermal, mechanical and chemical character and it is convenient, however, to be separated into two terms. More precisely, physical exergy, e_{ph}, expresses the useful work that a chemical component can produce if it is brought reversibly from the state of the system to the "restricted dead state", which is a state in thermal and mechanical equilibrium with the environment and can be generally expressed as [26]:

$$e_{ph} = \int_{T_0}^{T} C_P\, dT - T_0\left[\int_{T_0}^{T} \frac{C_P}{T}\, dT - R\ln\left(\frac{P}{P_0}\right)\right] \tag{6}$$

On the other hand, chemical exergy e_{ch}, expresses the useful work that the chemical elements can produce if it is brought reversibly in chemical equilibrium with the environment. It is essential to be used an appropriate "exergy reference environment" in order to be estimated the standard chemical exergy e_0 according to the relation [26]:

$$e_{ch} = M_{tot}\left(\sum_i x_i (e_0)_i + RT_0 \sum_i x_i \ln x_i\right) \tag{7}$$

As far as the characteristics of each device are unique, the aforementioned approach has to be mathematically modelled for all the processes in each operational step. The exergy balance of a heat exchanging process in a SOFC based system, during present simulations, can be expressed as [26]:

$$\left[\sum_k\left[M_{tot}\Delta T\sum_i x_i\left(C_P^e\right)_i\right]\right]_{in} = \left[\sum_k\left[M_{tot}\Delta T\sum_i x_i\left(C_P^e\right)_i\right]\right]_{out} + I \tag{8}$$

This incorporates only the physical exergy balance due to the absence of any chemical reaction, while the heat transfer over a finite temperature difference leads to an irreversibility rate, I, during its operation.

Accordingly, the exergy balance of the biogas reforming process, can be mathematically described in THERMAS as [26]:

$$\left[\sum_k\left(e_{ch}+M_{tot}\Delta T\sum_i x_i\left(C_P^e\right)_i\right)\right]_{in} + e^Q = \left[e_{ch}+M_{tot}\Delta T\sum_i x_i\left(C_P^e\right)_i\right]_{out} + I \tag{9}$$

where C_P^e (kJ kmol^{-1} K^{-1}) is the mean isobaric exergy capacity which separately calculated for each chemical species through a curve fitting process by using Lagrange interpolation method [27]. The above expression incorporates the amount of chemical exergy in each stream as well as an extra exergy term associated with heat transfer, e^Q as follows [26]:

$$e^Q = [Q_{burn}]_{ref}\frac{T_{SOFC}-T_0}{T_{SOFC}} \tag{10}$$

The afterburner and the SOFC-stack follow the same mathematical approach for their exergy balance but with some appreciable differences. The afterburner's exergy balance is characterized by an extra term which incorporates the irreversibility rate associated with heat losses and can be expressed as [26]:

$$I^Q = \left([Q_{burn}]_{ref} + [Q_{burn}]_{env}\right)\frac{T_{burn}-T_0}{T_{burn}} \tag{11}$$

As concern the SOFC system modelling, it is characterized by the chemical exergy of the reactants of the chemical reactions taking place in the stack that is transformed to electrical energy and can be directly calculated, as follows [26]:

$$W_{el} = \sum_r\left[-\left(H_{prod}-TS_{prod}\right) + \left(H_{react}-TS_{react}\right)\right] \tag{12}$$

where H is the enthalpy and S the entropy terms, both calculated by NASA polynomials [22].

3. Simulations

The above presented theory has been integrated in a computational innovative software tool, named THERMAS, which was designed from scratch to simulate and optimize biogas fed systems including reforming and fuel cells of various types. The combination of mass, energy and exergy balances, as previously described constitutes the main core of THERMAS modelling. This fundamental analysis is combined with the opportunity to dynamically specify all the operational parameters (fuel's composition, mass flowrates, temperature at each device and branch as well as all the reaction-relative parameters separately), in accordance to each unit architecture and the user's needs, in order to eliminate the irreversible exergy destruction in the system.

In this context and by following a realistic approach, THERMAS introduces an innovative optimization process based on the difference between energy and exergy efficiency rather than on the reduction of environmental thermal losses, as widely used [14]. Ideally, a system is completely "optimized" when entirely transforms the entering chemical energy into useful work, i.e. when it is characterized by almost zero energy wastes during operation. The rate of optimization (optimization level) is actually described by the difference between energy and exergy efficiency, which can be expressed by an innovative optimization factor (OPF), being incorporated in THERMAS software. This factor can be characterized by either positive or negative values, as presented here:

$$OPF = (\eta_{en}-\eta_{ex})100 \quad \text{with} \quad -100 < OPF \le 100 \quad \text{and} \quad \eta_{en} \neq 0 \tag{13}$$

OPF tents to zero for optimal system's operation, since exergy efficiency (i.e. useful work divided by useful energy entered the system) approximates energy efficiency in that case. Obviously a system which is out of order is also described by a zero OPF value, not characterized as optimized due to zero energy production, which corresponds to an optimization process that is actually meaningless. Additionally, the upper limit of the above presented factor characterizes a heating system (i.e. a wood burning stove) where the entire internal energy of the initial fuel transforms into heat, contrary to the lower limit which represents a system with low energy potential, transformed almost totally into useful work. OPF could be considered as a powerful engineering tool since it adequately describes both the energetic and exergetic behavior of the system, allowing therefore for an ease control of all the operational parameters.

In order to be investigated a simulated theoretical operation of a biogas fed system based on a SOFC-stack, the design of a real life scenario was inevitable, as Fig. 1 presents. In such a case, the entire fuel feeding system of the ongoing simulated scenario consisting of biogas (mixture of methane and carbon dioxide with a low moisture content), air and water keeps separate inlet streams for these components, each passing throughout a heat exchanger to reach the desirable functional temperature. Furthermore, the major part of the entire system is constituted by an internal reforming biogas device, combined with a fuel cell stack (Fig. 1). To finalize the theoretical layout under real life prospects for such an established system an afterburner was used to offer extra thermal energy, being necessary for the continuous operation of the whole process.

From chemistry point of view, the system is characterized by methane steam reforming (Eq. (14a)) and water gas-shift reaction (WGS) (Eq. (14b)) which takes place in the reformer's bulk phase (i.e. constant extension approx. 100%), as they are presented in Refs. [12–14]:

$$CH_4 + H_2O \rightarrow CO + 3\,H_2 \quad \Delta H_0 = 206\ \text{kJ mol}^{-1} \tag{14a}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H_0 = -41.2\ \text{kJ mol}^{-1} \tag{14b}$$

Simultaneously, the entire chemical process in the SOFC core is described by hydrogen and carbon monoxide electrochemical oxidization reactions [12–14]:

$$H_2 + \frac{1}{2}\,O_2 \rightarrow H_2O + 2e^- \quad \Delta H_0 = -241.8\ \text{kJ mol}^{-1} \tag{15a}$$

$$CO + \frac{1}{2}\,O_2 \rightarrow CO_2 + 2e^- \quad \Delta H_0 = -283\ \text{kJ mol}^{-1} \tag{15b}$$

It is important to mention that by involving the real life operation of such a system in THERMAS software tool can lead the research to unexplored pathways which experimentally is hard to

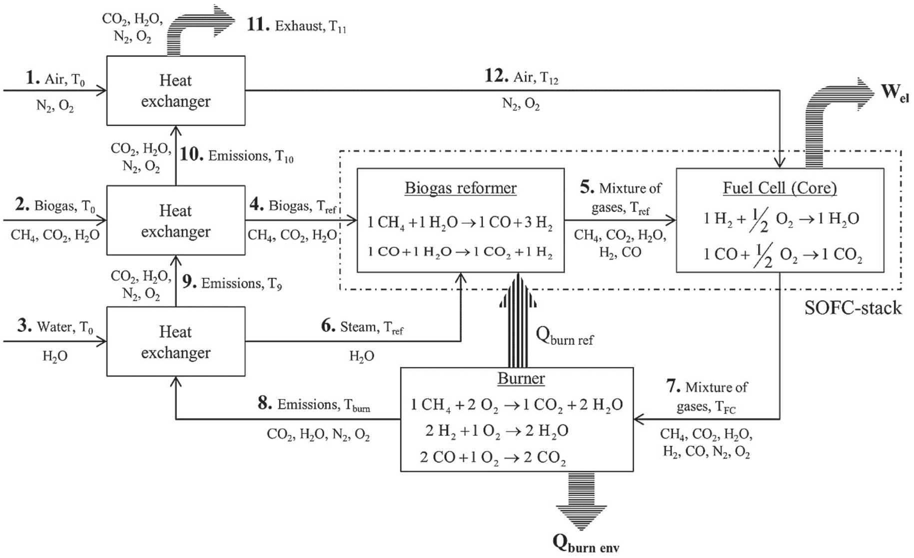

Fig. 1. Schematic flowchart of the simulated system.

be investigated due to the arisen restrictions during the real life design of such a system.

4. Results & discussion

Since previous research attempts incorporate specific computational models based on exergy theory under several theoretical operational assumptions and simultaneously deal with several scenarios which entirely use pure fuels (i.e. either methane or ethanol), the current research study, apart from incorporating an innovative simulation software tool under a more realistic point of view, aims at describing an optimization process by calculating the factor OPF, as defined above.

4.1. Validation

A pure methane fed case study presented by Douvatzides et al. [14] is similar to the present project (see Fig. 1) and supported by two preheaters, each designed for air and steam-methane mixture respectively, a SOFC-stack system and an afterburner, as supportive device, has already been simulated under several theoretical restrictions.

The values of the operational parameters used in THERMAS when simulating a pure methane scenario, are the same as those used by Douvatzides et al. [14], in order to assure that the results are directly comparable. Under this respect the simulated system is characterized by: a) separate air and methane-steam flows equal to 17.6 kg s^{-1} at 800 K and 3.5 kg s^{-1} at 1160 K temperature, respectively, b) reformer's and afterburner's operational temperature varying between 1150 K and 1200 K and c) extensions of chemical reactions [Eqs. (14a) and (15a)] equal approx. to 95%. For the needs of this validation, water gas shift [Eq. (14b)] and carbon monoxide electrochemical oxidization [Eq. (15b)] reactions were neglected, as in Ref. [14].

By considering the above operational values, Fig. 2 presents the results from both theoretical simulation processes. The previous one can be described through the bold line while THERMAS can be schematically presented by the dashed line. Throughout the analysis of Fig. 2 can be easily mentioned that by increasing the SOFC-stack temperature (T_{SOFC}) from 800 K up to 1200 K the exergetic efficiency constitutes a linear function of the temperature while following negative identical slope (see Fig. 2), caused by the increasing conversion of useful energy into thermal losses.

Also, in order to be additionally supported the validation process of THERMAS modelling, it is worth noticing that both theoretical approaches (the previous one [14] vs THERMAS) are characterized by almost identical temperature in stream 11 (T_{11}, see Fig. 1) for the emitted gas mixture, equal to 617 K (old model) and 617.6 K (THERMAS). By finalizing the validation analysis, it has to be highlighted a rate of correction of 10.68% for exergetic efficiency compared to the old model, as Fig. 2 presents. This difference emerges from the fact that THERMAS adopts a more realistic approach on the thermal losses which could not tent to zero as it has been considered in the old model [14]. In order to present an optimal system, Douvatzides et al. [14] incorporated an extra atomizer device, during the operation of such a system (Fig. 1), supplied by the entire amount of the extra produced thermal energy by the afterburner to reduce the environmental thermal losses and the irreversibility rate, which influences the exergy destruction.

To conclude, the successful validation process reveals that the temperatures of the flue gases (T_{11}, see Fig. 1) calculated through both computational tools are almost identical, with a negligible difference of 0.1%, while the exergetic efficiency follows the same behavior under the same theoretical limitations.

4.2. Optimization

By considering the above analysis some serious misunderstandings arise which have to be investigated and various operating parameters should be examined and determined from scratch in order to totally evaluate the entire behavior of such a system under real life conditions. The presented modelling tool seems to have the ability to predict realistic operational results by incorporating the entire energy and exergy theory as it is presented previously.

Moreover, in order to finalize the energy and exergy analysis of several biogas fed systems, it is important to mention the general calculations on the different chemical properties which can dynamically change accordingly to the operational temperatures per chemical element for several processes in each simulated case study. As concern the energy part calculations, it is essential to analytically discuss the general expressions for enthalpy H (J),

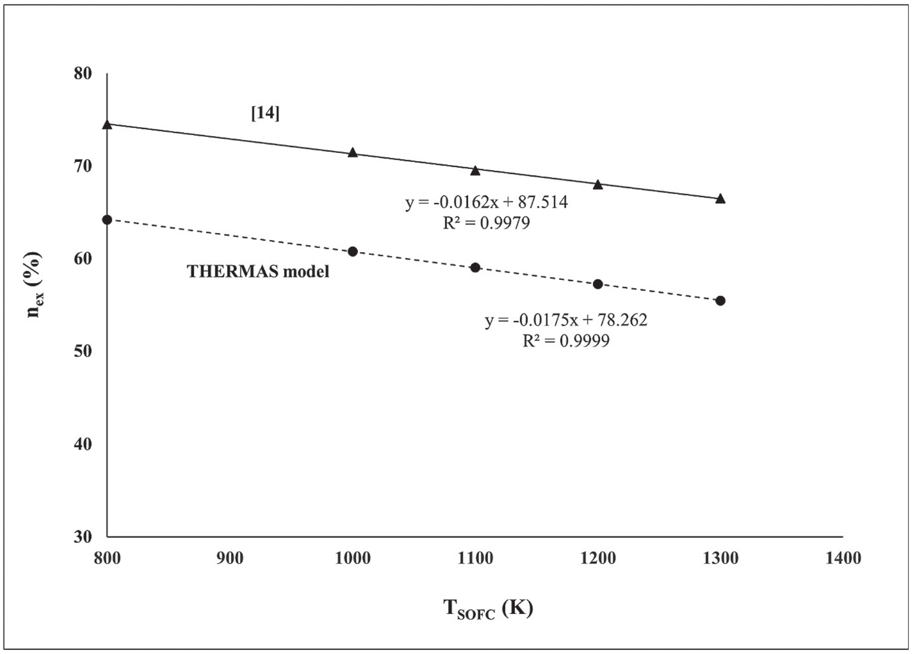

Fig. 2. Validation of THERMAS model against results in Ref. [14].

entropy S (J) and molar isobaric specific heat capacity C_P (J kmol^{-1} K^{-1}), as they are presented through eq. (16–18), respectively [22]:

$$\frac{H}{RT} = A_1 + A_2\frac{T}{2} + A_3\frac{T^2}{3} + A_4\frac{T^3}{4} + A_5\frac{T^4}{5} + A_6\frac{1}{T} \tag{16}$$

$$\frac{S}{R} = A_1 \ln T + A_2 T + A_3\frac{T^2}{2} + A_4\frac{T^3}{3} + A_5\frac{T^4}{4} + A_7 \tag{17}$$

$$\frac{C_P}{R} = A_1 + A_2 T + A_3 T^2 + A_4 T^3 + A_5 T^4 \tag{18}$$

where R is the gas constant, (8.1344 J mol^{-1} K^{-1}), T (K) is the temperature and A_1 up to A_7 are the numerical coefficients which characterize each chemical element [22].

Regarding exergy calculations, the standard chemical exergy e^0 (J mol^{-1}) [26] was considered constant for each chemical element per stream (see Fig. 1), as well as the mean isobaric exergy capacity C_P^e (J mol^{-1} K^{-1}) through a curve fitting process by using Lagrange interpolation method to attain the temperature variations [26,27].

4.2.1. *Effect of biogas composition*

In order to optimize such a system, it is essential to choose realistic values for several fuel compositions (Table 1). The simulations reveal that a system supplied by almost pure methane [14] presents energy efficiency approx. 96.07%, while the useful energy (exergy) equals to 59.02%, as Fig. 3 shows. This specific system presents an OPF equal to 37.06 and cannot be characterized as optimized, even if the energetic efficiency is over 90%. A SOFC-stack system which uses a low methane content fuel can more properly manage the initial internal energy by optimizing its operational characteristics and, as depicted in Fig. 3, Scenario 1 & 2 present an increased exergetic efficiency (useful energy) compared to the initial not optimized scenario (i.e. ~99%).

The limitation of the inlet fuel purification in methane is followed by an expected decrement of the energy efficiency for a SOFC-based system and simultaneously by a more accurate management of the useful energy through THERMAS model, as Fig. 3 reveals. The present research work innovatively reveals that systems supplied by low methane fuels (<60%, 3rd and 4th scenario) are characterized by a higher exergetic efficiency than the energetic one. Even if the entire internal energy of a poor fuel is limited, can be efficiently managed and the amount of the energy which can be transformed into useful electric work remains unexpectedly in high levels compared, to the destructed one (a.k.a anergy).

To conclude, the use of a pure fuel seems to be meaningless without optimization. This is valid, as far as at least one configuration exists (Scenario 2 with 70% CH_4), where OPF is improved to 5.49 (Fig. 3) in comparison with relative results using pure CH_4 [14].

4.2.2. *Effect of chemical reactions' extensions*

Throughout the above analysis the optimized Scenario 2, which

Table 1
Biogas compositions produced under real life conditions and simulated scenarios through THERMAS model.

Scenarios	Biogas (mixture of gases) 1 kg s^{-1}			Water (kg s^{-1})	Air (kg s^{-1})
	CH_4 wt%	CO_2 wt%	$H_2O_{(g)}$ wt%	$H_2O_{(g)}$	$O_2 + N_2$
Initial [9]	99	0.5	0.5	2.5	17.6
Scenario 1.	80	10	10		
Scenario 2.	70	20	10		
Scenario 3.	60	30	10		
Scenario 4.	50	40	10		

where wt% is the percentage by weight.

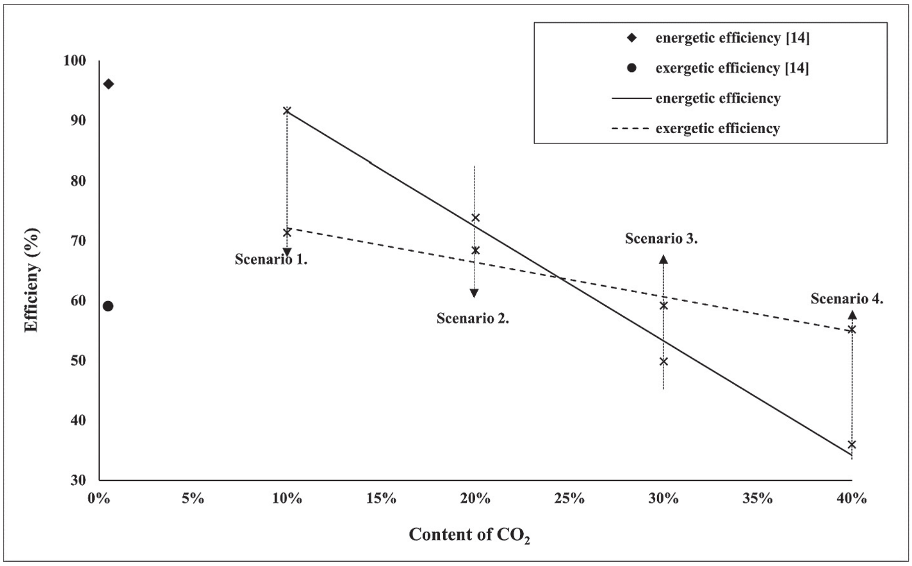

Fig. 3. Energetic and exergetic efficiencies of the optimized scenarios as presented in Table 1.

is characterized by energy and exergy efficiency equal to 73.87% and 68.38%, respectively, and simultaneously by an improved OPF at 5.49 compared to 37.06 for the initial scenario, will constitute the basis in the present study, in order to investigate how several operational parameters influence the optimization process.

The use of THERMAS model offers the opportunity to dynamically change the extensions of three main chemical reactions for each simulated power plant, as they are presented by Eqs. (14a, 15a &15b). An accurate correlation between real life operation and theoretical simulation is characterized by: a) the already mentioned almost constant extension of the WGS reaction [Eq. (14b)], at ~100% and b) the extension of the electrochemical oxidization reaction of CO (anode of SOFC) [Eq. (15b)], at ~15%, with a validation up to 1/4 of the extension of the hydrogen reaction [28]. Obviously the contribution of CO to electricity production is minor, since WGS reaction seems to consume almost all the available toxic carbon monoxide.

By considering the above presented values, Fig. 4 depicts that the increasing of methane-steam reforming reaction's extension, drastically improves the n_{en} and n_{ex}, up to 73.87% and 68.38%, respectively. OPF equals to 5.49, being also improved compared to the initial one (37.06). Almost the same behavior characterized by similar changes on the OPF can be mentioned for the system by analysing Fig. 5, while the hydrogen electrochemical oxidization reaction [Eq. (15a)] is increased up to 90%. To conclude by innovatively enabling the WGS reaction in THERMAS model, a slightly destruction on the OPF is observed, which can be characterized as meaningless due to the greatly increased of both efficiencies, n_{en} and n_{ex} by 20.08% and 15.43% respectively, as Fig. 4 presents.

4.2.3. *Effect of temperatures*

By considering the most optimal scenario, each operational temperature of the main individual units has to be investigated. The SOFC-stack temperature influences not only the energetic efficiency, but also advances the destruction of the OPF during optimization process, as Fig. 6 presents. It is worth noticing that by lowering this temperature, the OPF is destructed with an almost equal rate as the energetic efficiency increases. A higher energetically efficient system ($n_{en} \geq 70\%$) is more important to be followed by an optimized OPF (i.e. limited energy losses) rather than be characterized by increased energy efficiency in absolute terms without respect to the exergy efficiency (i.e. useful work).

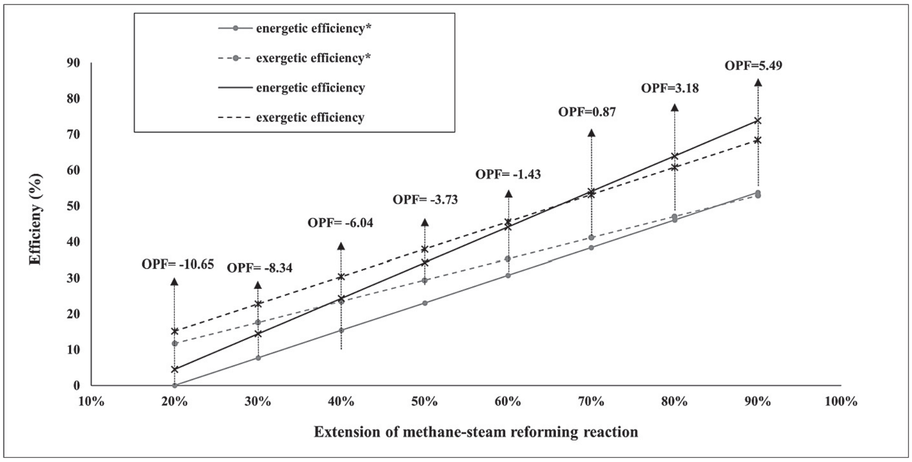

Fig. 4. The effect of methane-steam reforming reaction on system's behavior. *calculations under the assumption of a zero WGS reaction's extension ($\varepsilon_{WGS} = 0\%$).

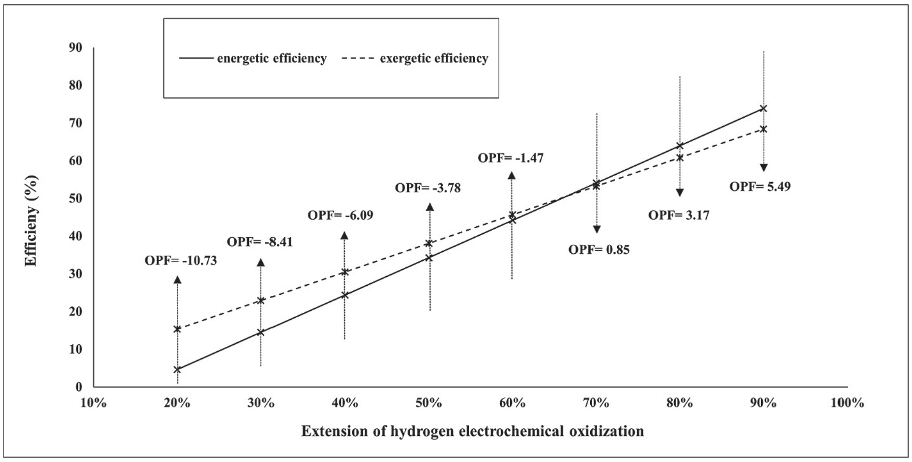

Fig. 5. The effect of hydrogen electrochemical oxidization on system's behavior.

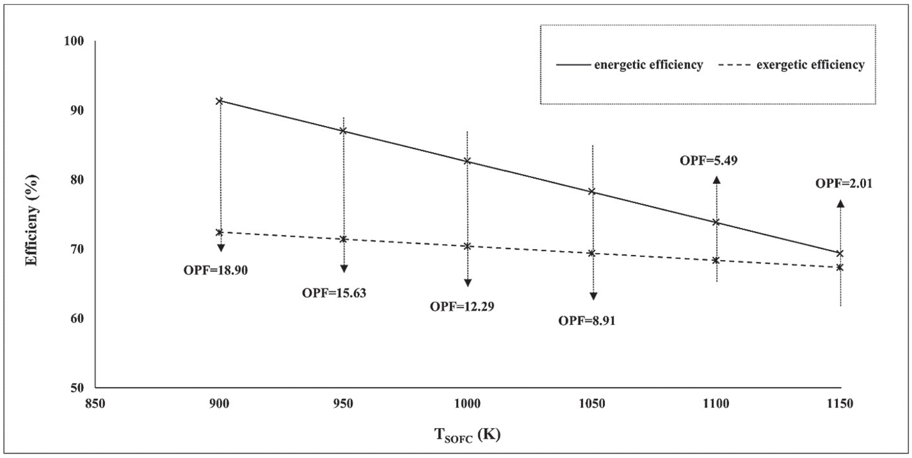

Fig. 6. Influence of SOFC temperature on system's optimization.

The afterburner's temperature is not capable to drastically influence the system's efficiency due to its supportive character. Under this prospect the only remaining parameter which can play a crucial role during optimization process, is the methane reforming temperature, T_{ref}. An extended analysis on this variable (see Fig. 7) reveals that by lowering T_{ref} the internal energy of reformer's products is limited and its useful rate transformed into W_{el} is also reduced and influences the n_{en} of the entire system, while the amount of the useful work (exergy) is kept almost constant and has no effect on n_{ex}. This behavior is

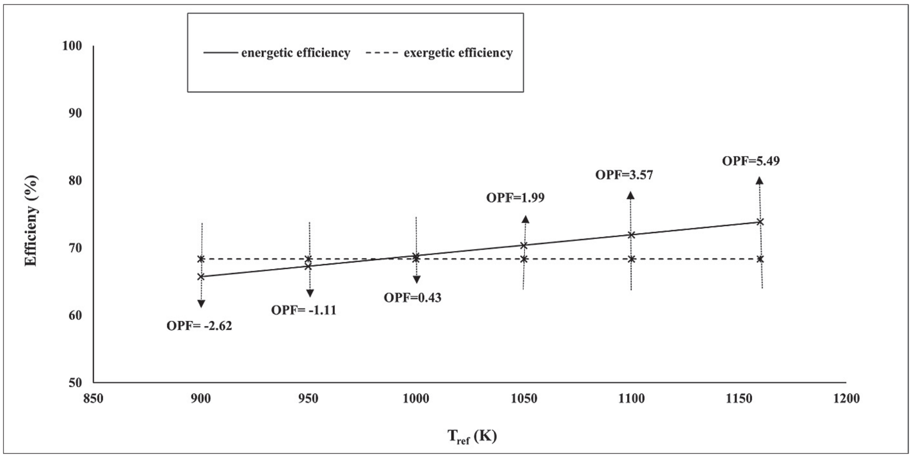

Fig. 7. Influence of the reformer's temperature on system's optimization.

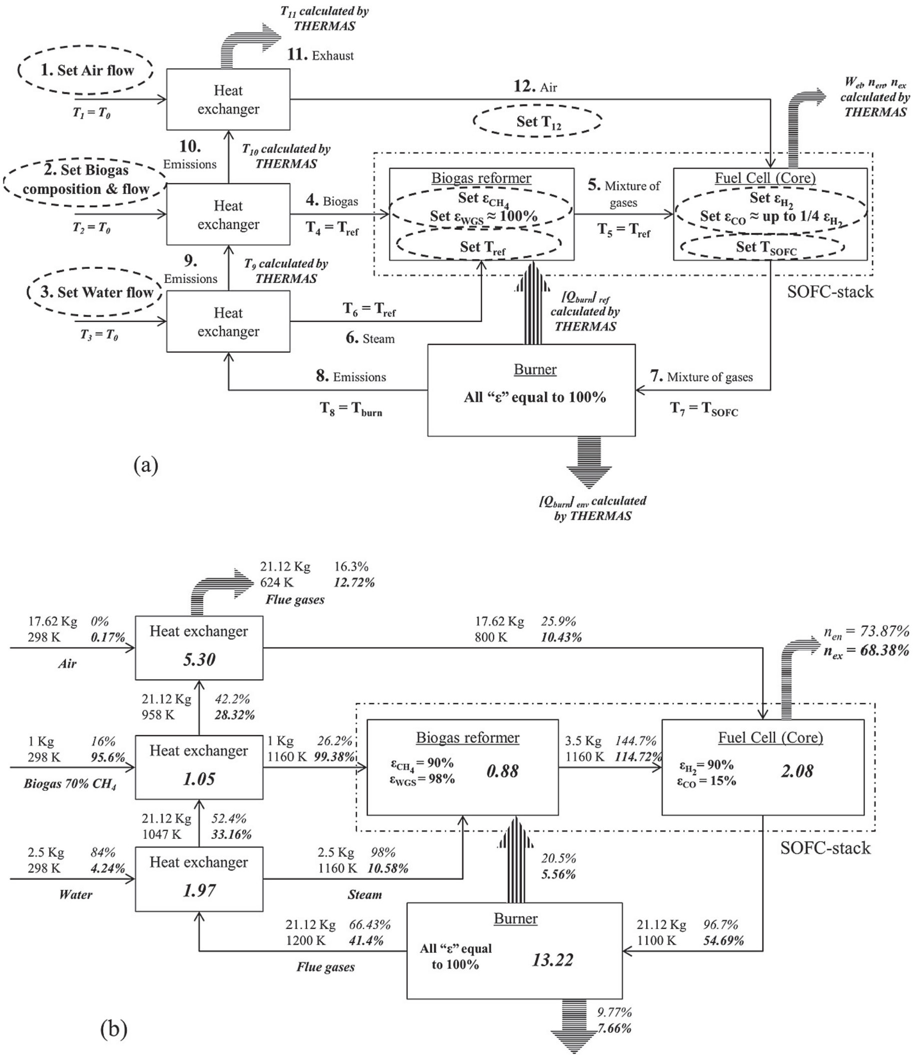

Fig. 8. Optimization methodology (a) and optimal configuration (b). Italic plain text stands for energy values and italic bold stands for exergy values.

followed by an optimized OPF while lowering methane reforming temperature.

4.3. Optimization strategy

The above presented parametric analysis can be schematically described through Fig. 8a and organized by following the dash circled strategic steps that lead to an optimum scenario for each simulated case study. Precisely, this methodology concludes to the best proposed Scenario 2 (see Table 2) which presents 9.36% better exergetic efficiency with an optimized OPF equal to 5.49, even if the energetic efficiency is lowered by 22.20% compared with the theoretical power plant in Ref. [14].

Table 2
Optimized results for scenarios as simulated through THERMAS.

Fuel composition	Initial scenario [9]	Scenario 2.	Comments
	See Table 1		
n_{en}	96.07%	73.87%	Higher is better
n_{ex}	59.02%	68.38%	Higher is better
OPF	37.06	5.49	Lower is better (near zero)

This optimal case study is schematically provided through Fig. 8b. As presented, the total exergy losses correspond to 20.38% of the exergy entering the system, which may be used to cover several thermal needs. Exergy destruction during reforming is limited due to the preheating. Although all the inlet gases are found in an equal temperature during the reforming process, the level of the exergy destruction is found approximately zero (=0.88%) due to the stable environment inside the reformer. This fact saves chemical energy that could be converted to electricity in the fuel cell, where the exergy destruction is also kept in low levels (=2.08%) compared to afterburner. The increasing exergy destruction rate of the fuel cell compared to the reformer is expected due to the combustion of the carbon monoxide [Eq. (15b)]. Furthermore, the exergy destruction in the after burner is 13.22%, being the highest among all the devices, as also expected. It has to be underlined this value is represented by the summation of its total thermal losses. Finally, our work reveals that the most crucial parameters for an optimized scenario, besides the initial fuel composition and the engagement of WGS reaction, are the temperature of both SOFC-stack and the reformer, which influence the energetic efficiency while the exergy is slightly change during simulation process.

5. Conclusion

This research study is based on the design of an innovative software tool, namely THERMAS, which incorporates fundamental energy and exergy theory analysis under more realistic approaches (WGS reaction, CO utilization in F.C., etc.). Different SOFC-stack based scenarios fed by biogas of any composition are simulated and extensively studied, on the optimal operation, compared to an existing one which was supported by purified fuels. After performing an extensive parametric analysis towards an optimization process in terms of OPF, the present study innovatively reveals that systems supplied by low methane fuels might be characterized by higher exergetic efficiencies than energetic ones. In this context, the use of pure fuels with increasing production costs in such a SOFC-based system seems sounds meaningless without optimization. It is also worth mentioning that, the overall performance of the electric production process slightly limited by enabling the WGS reaction, as actual operation indicates. The carbon monoxide consumed during reforming process, does not significantly contribute to the electric load production due to its very limited amount available in the fuel cell. In optimal conditions, temperatures of reformer and fuel cell must be constantly equal and simultaneously higher than 1000 K, while afterburner's temperature seems not to play such an important role to the system's efficiency due to its supportive character. To conclude, such an innovative simulation model indicates a potential solution for the optimal design of a SOFC-stack based system in the direction of the commercialization of systems which use hydrocarbon fuels, like biogas, produced by real life eco-friendly processes like anaerobic digestion.

Acknowledgments

The present research work was finalized through the framework ["Iky Fellowships Of Excellence For Postgraduate Studies In Greece-Siemens Program"].

Nomenclature

Latin symbols

C_P	Molar Isobaric Specific Heat Capacity (J mol^{-1} K^{-1})
C_P^e	Mean Isobaric Exergy Capacity (kJ kmol^{-1} K^{-1})
E	Exergy (J)
e^Q	Exergy associated with heat transfer (J)
H	Enthalpy (J)
I	Irreversibility rate (J)
I^Q	Irreversibility rate due to heat losses (J)
M	Mass (moles)
$\dot{m}$	Mass flow rate (kg s^{-1})
n	Efficiency (%)
OPF	Optimization factor
P	Pressure (atm)
Q	Thermal energy (J)
R	Gas constant, 8.1344 (J mol^{-1} K^{-1})
S	Entropy (J)
T	Temperature (K)
W_{el}	Electric energy (J)
x	Molar fraction

Greek symbols

ΔH	Enthalpy of formation (kJ mol^{-1})
ΔT	Temperature difference (K)
ε	Extension of a reaction (%)

Subscripts

0	property at the state of the environment
accu	accumulation
burn	afterburner
CO	carbon monoxide
ch	chemical
cons	consumption
en	energy
env	environment
ex	exergy
gen	generation
H_2	hydrogen
i	Chemical elements
in	input
k	Streams throughout a device
out	output
ph	physical
prod	Products (chemical elements)
r	Number of chemical reactions
react	Reactants (chemical elements)
ref	reformer
SOFC	SOFC-stack system
tot	Total amount of components
WGS	water gas shift

References

[1] V. Schroeder, B. Schalau, M. Molnarne, Explosion protection in biogas and hybrid power plants, Proced. Eng. 84 (2014) 259–272.

[2] S. Shokri, Biogas technology, applications, perspectives and implications, Int. J. Agric. Sci. Res. 2 (2011) 53–60.

[3] B. Sitorusa, Sukandarb, S.D. Panjaitan, Biogas recovery from anaerobic digestion process of mixed fruit-vegetable wastes, Energy Proced. 32 (2013) 176–182.

[4] C.H. Vanegas, J. Bartlett, Green energy from marine algae: biogas production and composition from the anaerobic digestion of Irish seaweed species, Environ. Technol. 34 (2013) 2277–2283.

[5] R. Zhanga, H.M. El-Mashada, K. Hartmana, F. Wanga, G. Liua, C. Choateb, P. Gambleb, Characterization of food waste as feedstock for anaerobic digestion, Bioresour. Technol. 98 (2007) 929–935.

[6] M. Farooque, J. Daly, T. Leo, C. Pais, R. Venkataraman, J. Wang, Direct fuel cell experience on renewable biogas, ECS Trans. 30 (2011) 261–270.

[7] S. Trogisch, J. Hoffmann, L. Daza Bertrand, Operation of molten carbonate fuel cells with different biogas sources: a challenging approach for field trials, J. Power Sources 145 (2005) 632–638.

[8] J. Van herle, Y. Membrez, O. Bucheli, Biogas as a fuel source for SOFC co-generators, J. Power Sources 127 (2004) 300–312.

[9] R. Bove, P. Lunghi, Experimental comparison of MCFC performance using three different biogas types and methane, J. Power Sources 145 (2005) 588–593.

[10] U. Desideri, L. Barelli, Handbook of Clean Energy Systems, Chapter: Solid Oxide Fuel Cell (SOFC), John Wiley & Sons, Ltd., J.Yan, U.Desideri.

[11] D. Papurello, A. Lanzini, L. Tognana, S. Silvestri, M. Santarelli, Waste to energy: exploitation of biogas from organic waste in a 500 Wel solid oxide fuel cell (SOFC) stack, Energy 85 (2015).

[12] S.L. Douvartzides, F.A. Coutelieris, P.E. Tsiakaras, On the systematic optimization of ethanol fed SOFC-based electricity generating systems in terms of energy and exergy, J. Power Sources 114 (2003) 203–212.

[13] S.L. Douvartzides, F.A. Coutelieris, A.K. Demin, P.E. Tsiakaras, Electricity from ethanol fed SOFCs: the expectations for sustainable development and technological benefits, Int. J. Hydrogen Energy 29 (2004) 375–379.

[14] S. Douvartzides, F. Coutelieris, P. Tsiakaras, Exergy analysis of a solid oxide fuel cell power plant fed by either ethanol or methane, J. Power Sources 131 (2004) 224–230.

[15] Y. Yi, A.D. Rao, J. Brouwer, G.S. Samuelsen, Fuel flexibility study of an integrated 25kW SOFC reformer system, J. Power Sources 144 (2005) 67–76.

[16] A. Trendewicz, R.J. Braun, Techno-economic analysis of solid oxide fuel cell-based combined heat and power systems for biogas utilization at wastewater treatment facilities, J. Power Sources 233 (2013) 380–393.

[17] N.S. Siefert, S. Litster, Exergy & economic analysis of biogas fuelled solid oxide fuel cell systems, J. Power Sources 272 (2014) 386–397.

[18] A.V. Akkaya, H.H. Erdem, B. Sahin, An analysis of SOFC/GT CHP system based on exergetic performance criteria, Int. J. Hydrogen Energy 33 (2008) 2566–2577.

[19] F. Zabihian, A.S. Fung, Performance analysis of hybrid solid oxide fuel cell and gas turbine cycle: application of alternative fuels, Energy Convers. Manag. 76 (2013) 571–580.

[20] D.M. Himmelblau, Basic Principles and Calculations in Chemical Engineering, second ed., Prentice Hall, New Jersey, 1967.
[21] R.H. Perry, D.W. Green, Perry's Chemical Engineers' Handbook, seventh ed., McGraw-Hill, New York, 1999.
[22] B.J. McBride, S. Gordon, M.A. Reno, Coefficient for Calculating Thermodynamic and Transport Properties of Individual Species, NASA TM-4513, USA, 1993.
[23] A. Bejan, G. Tsatsaronis, M. Moran, Thermal design and Optimization, first ed., John Wiley & Sons, 1996.
[24] Y. Cengel, M. Boles, Thermodynamics: an Engineering Approach, fourth ed., McGraw-Hill, New York, 2002.
[25] M. Moran, G. Tsatsaronis, in: Frank Kreith (Ed.), Engineering Thermodynamics, the CRC Handbook of Thermal Engineering, CRC Press, Boca Raton, 2000.
[26] T.J. Kotas, The Exergy Method of Thermal Plant Analysis, Krieger, Florida, 1995.
[27] S. Chapra, R. Canale, Numerical Methods for Engineers, sixth ed., McGraw-Hill, New York, 2010.
[28] E. Vakouftsi, G. Marnellos, C. Athanassiou, F.A. Coutelieris, CFD modeling of a biogas fuelled SOFC, Solid State Ion. 192 (2011) 458–463.