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Exergetic Optimization on Solid Oxide Fuel Cell Systems

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***Abstract*—**Biogas can be currently considered as an alternative option for electricity production, mainly due to its high energy content (hydrocarbon-rich source), its renewable status and its relatively low utilization cost. Solid Oxide Fuel Cell (SOFC) stacks convert fuel's chemical energy to electricity with high efficiencies and reveal significant advantages on fuel flexibility combined with lower emissions rate, especially when utilize biogas. Electricity production by biogas constitutes a composite problem which incorporates an extensive parametric analysis on numerous dynamic variables. The main scope of the presented study is to propose a detailed thermodynamic model on the optimization of SOFC-based power plants' operation based on fundamental thermodynamics, energy and exergy balances. This model named THERMAS (THERmodynamic MAthematical Simulation model) incorporates each individual process, during electricity production, mathematically simulated for different case studies that represent real life operational conditions. 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 incorporates a specific criterion concluded by the extensive energy analysis to identify the most optimal scenario per simulated system in exergy terms. Therefore, several dynamical parameters as well as several biogas mixture compositions have been taken into account, to cover all the possible incidents. Towards the optimization process in terms of an innovative OPF (OPtimization Factor), presented here, this research study reveals that systems supplied by low methane fuels can be comparable to these supplied by pure methane. To conclude, such an innovative simulation model indicates a perspective on the optimal design of a SOFC stack based system, in the direction of the commercialization of systems utilizing biogas.

***Keywords*—**Biogas, Exergy, Optimization, SOFC.

I. Introduction

IT is of great importance to reclaim the anthropogenic and biogenic by-products (wastes) to produce totally eco-friendly electrical energy without the limitations imposed by usage of fossil fuels. In this context, biogas seems to be a key player in the field of renewable energy sources, since its production by biodegradable materials (organic wastes) is usually totally eco-friendly [1]. More precisely, biogas is a gas mixture, whose main components are methane (CH_4) and carbon dioxide (CO_2), while the gas is saturated with water vapour [2]. Therefore, its final composition depends on the organic source the gas has been produced, as well as the duration of the aforementioned biological processes [3].

One of the main biogas advantages is the possibility to be used in SOFCs, due to their very high operational temperature, which assures increased flexibility on fuel choice [4]. Precisely, SOFCs are devices that directly convert chemical energy of fuel to electricity when fuelled by hydrocarbon rich mixtures [5]. Furthermore, several SOFC-based projects present theoretical energy efficiencies up to 80%-90% when fuelled by pure methane [6], [7], while such a project can achieve satisfactory performance using biogas, even of relatively low methane content [8].

The main aim of the presented study is the use of an innovative detailed thermodynamic model, named THERMAS, in order to simulate and optimize a SOFC-based power plant, fed by biogas of several compositions. The system is supposed to operate under real life conditions without theoretical restrictions on selected parameters. Moreover, an extensive parametric analysis based on fundamental energy and exergy theory has been be carried out, while the novel OPF has been introduced and used as norm for the efficiency of optimization, in terms not only of energy (1st Law of Thermodynamics) but also of exergy (2nd Law of Thermodynamics). This scientific approach offers the opportunity to indicate a wide range of different values for each operational parameter separately, thus allowing for studies in otherwise unexplored operational regimes.

II. Theory

Exergy is actually a thermodynamic property that describes the quality of the produced energy corresponding to the maximum useful work provided by a system during to its reversible transition to a thermodynamic state in equilibrium with its environment [9]. Exergy depends on both the states of the system and its environment, while exergy calculation considers processes of thermal, mechanical and chemical character. More precisely, physical exergy, e_{ph}, expresses the useful work obtainable when the chemical species are brought from the state of the system to the environmental state through physical processes involving only thermal interaction with their environment and can be generally expressed as [10]

$$e_{ph} = m\left\{\int_{T_0}^{T} \tilde{C}_P \, dT - T_0\left[\int_{T_0}^{T} \frac{\tilde{C}_P}{T} \, dT - R \, \ln\left(\frac{P}{P_0}\right)\right]\right\}. \quad (1)$$

where m is the mass per chemical element, P is the pressure and T is the temperature per process while $\tilde{C}_P$ is the mean

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molar isobaric specific heat capacity which corresponds to each chemical element. On the other hand, chemical exergy e_{ch}, expresses the useful work that the chemical species can produce if they are brought reversibly in chemical equilibrium with their environment according to the relation [10]

$$e_{ch} = m_{tot}\left(\sum_i x_i \left(e_0\right)_i + R\ T_0 \sum_i x_i \ln\left(x_i\right)\right). \quad (2)$$

where m_{tot} is the total mass per stream, T_0 is the environmental temperature, x_i is the molar fraction per element and R is the gas constant. Also it is essential to be used an appropriate "exergy reference environment" in order to be estimated the standard chemical exergy e_0.

Even if the characteristics of each device are unique, a general approach on the exergy balance can be mathematically modelled in general for all the processes in each operational step. The expression which has to be satisfied in a SOFC based system for each device separately, while ignoring kinetic and potential energies during the present simulations (THERMAS modelling), can be described as [10]

$$\left[\sum_k\left(e_{ch} + m_{tot}\Delta T\sum_i x_i\left(\tilde{C}_P^e\right)_i\right)\right]_{in} + e^Q = \left[\sum_k\left(e_{ch} + m_{tot}\Delta T\sum_i x_i\left(\tilde{C}_P^e\right)_i\right)\right]_{out} + I + W_{el}. \quad (3)$$

where e^Q is an exergy term associated with heat transfer when a device interchange energy with its environment, I is the irreversibility rate associated with heat losses which describes the amount of exergy destruction, while $\tilde{C}_P^e$ is the mean isobaric exergy capacity calculated for each chemical element as in [10]. Finally, the term W_{el} in (3) represents the amount of chemical energy which transforms into electricity, directly calculated as [11]

$$W_{el} = \sum_i\left[-\left(H_{prod} - T\ S_{prod}\right) + \left(H_{react} - T\ S_{react}\right)\right]. \quad (4)$$

where H is the enthalpy and S the entropy terms, both calculated by NASA polynomials [12].

The innovation of the present study is in describing an optimization process by incorporating OPF. Actually, OPF value describes the difference between the entire amount of produced energy and the useful one (i.e. exergy). Ideally, a system which entirely transforms fuel chemical energy into electricity can be considered as optimized due to the almost zero energy wastes during its operational process, while a combustion chamber is characterized by a high *OPF* value (equal to approx. 100), due to the irreversible processes occurring. By taking into account the difference between energy and exergy efficiency, THERMAS was designed to characterize the optimization level of each simulated case study, by using

$$OPF = \left(n_{en} - n_{ex}\right)100, \text{ with } -100 < OPF \le 100 \text{ and } n_{en} \ne 0. \quad (5)$$

where n_{en} and n_{ex} correspond to energetic and exergetic efficiency, respectively. Although OPF is able to attain positive and negative values, the present study uses its absolute value, for presentation purposes.

To describe optimization behavior, 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. Under this respect, 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.

III. The SOFC-Based System

The considered biogas-fed power plant is based on a SOFC-stack was designed under real life operational scenarios. This allows for presenting a system capable to interact with its environment. This system will be our case study for optimization effects, regarding its effectiveness on electricity production, in terms of both energy and exergy efficiency.

The flow sheet of the SOFC system consists of a SOFC, a reformer, an afterburner and several pre-heaters (Fig. 1). Biogas and steam enter the system through individual pre-heaters 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. The gas mixture coming from the reformer along with the appropriate oxygen (O_2) (air) enters the SOFC where hydrogen (H_2) and carbon monoxide (CO) react to produce electricity, while a fraction of the active reactants should be allowed to reach the afterburner in order to support the heat demands of the system. Finally, a heat exchanger is used to increase the thermal contents of air before the SOFC as well as of the fuel/steam paths before the reformer. Also it is worth mentioning that in the simulated scenarios, the water vapor and CO_2 content may vary from 5% up to 15% and from 15% up to 45%, respectively [13], [14].

It is worth noticing that all the different temperatures T, as presented in Fig. 1 can individually be adjusted during simulation processes, while the several *Q* symbols referred to the interchangeable thermal amount of energy during its operation. Also from chemistry point of view, it is must be underlined that biogas reforming also includes the water gas-shift reaction (WGS), occurring in the bulk phase. Also, the operational temperatures per stream and of all devices can dynamically change, accordingly to the architecture of the system.

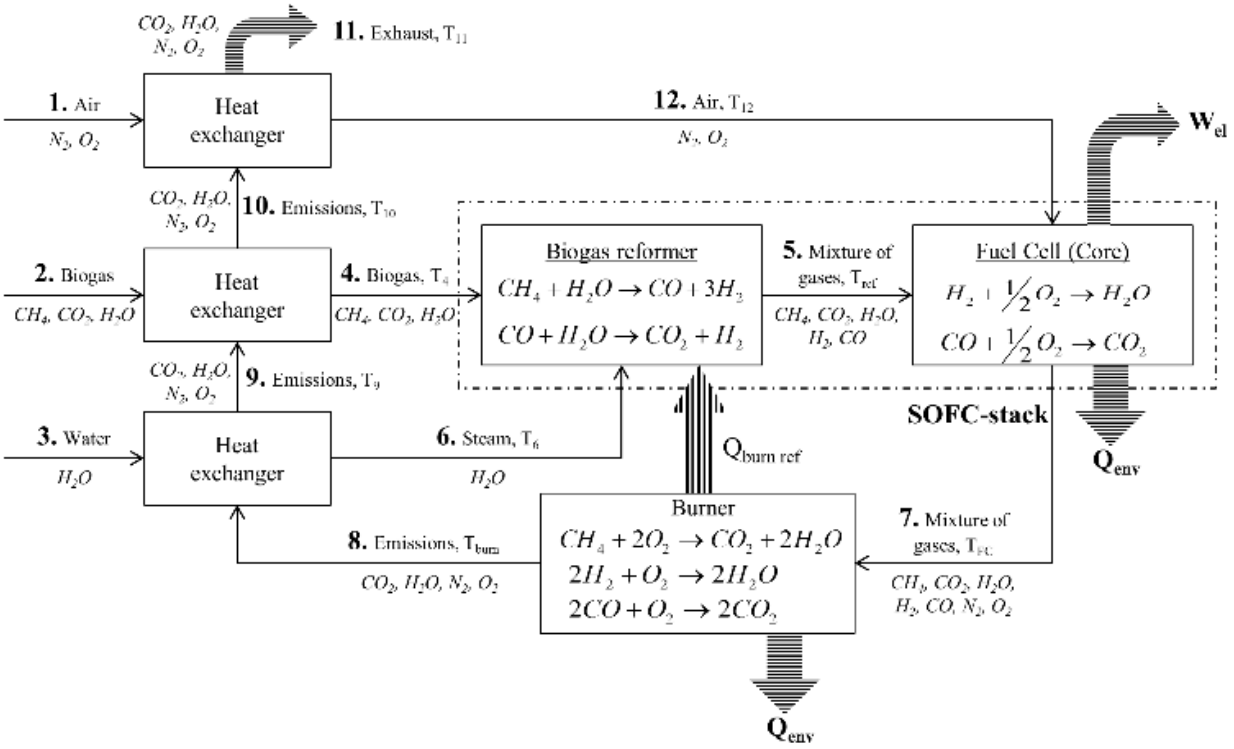

Fig. 1 Flow chart of the power plant

IV. Results & Discussion

By considering the above analysis, the presented simulation tool predicts realistic operational results by incorporating the fundamental thermodynamics. In order to examine the operation and specifically the optimization level for such a system, a constant input biogas mass flux of 1 kg sec^{-1} has been considered in any case, while steam and air flows were the stoichiometric ones. For obtaining directly comparable results, the individual operational temperatures of the main devices have been adjusted for maximum energetic and exergetic efficiency. It will be also examined the effect of the chemical reactions occurring in the reformer and the fuel cell, as analytically presented in Fig. 1. Moreover, the water vapor approaches an average value of 10%, except otherwise clearly stated [13], [14].

The use of THERMAS model offers the opportunity to dynamically change the extensions of each chemical reaction. To start with, an accurate correlation between real life operation and theoretical simulation of a CH_4 case study is characterized by a low extension of the electrochemical oxidization reaction of CO (anode of SOFC), at approx. 15%, with a validation up to 1/4 of the extension of the H_2 reaction [15]. Obviously, the contribution of *CO* to electricity production and its influence on *OPF* of such a system is of low importance, since almost all the available *CO* seems to be consumed through the WGS reaction, as depicted in Fig 2, where OPF is of nearly constant behavior with CO reaction extension. More precisely, for all the presented scenarios when the electrochemical oxidization of CO, in fuel cell device, drops from 15% up to 0% the *OPF* is slightly differentiated at approx. less than 1%.

The extension of the WGS reaction has been also considered, where it is found that this chemical reaction influences the optimization level of the system under a more drastically way compared to the previous examined reaction, as presented in Fig. 3. This result underlines the significance of WGS reaction on H_2 production. Starting from approx. 95%, the extension of WGS reaction varies up to approx. 30% (Fig. 3). Obviously, OPF decreases with the extension in any case. More precisely, for hydrocarbons reach feed-streams OPF decrease by 6%, while for non-purified fuels this destruction approximates 2%, as depicted in Fig. 3.

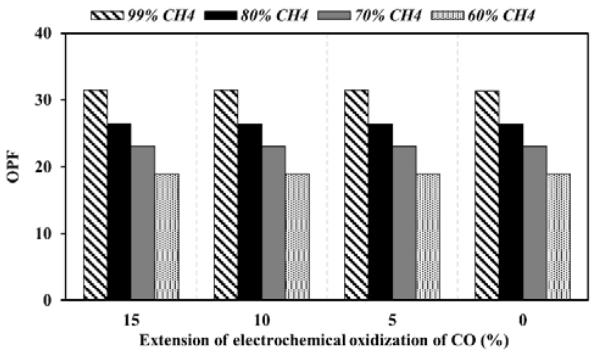

Fig. 2 The effect of electrochemical oxidization of CO on the OPF

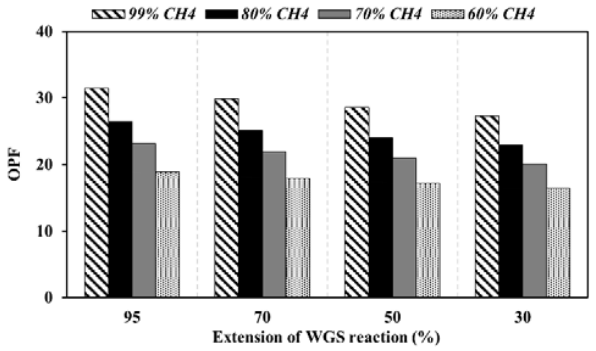

Fig. 3 The effect of WGS reaction on the OPF

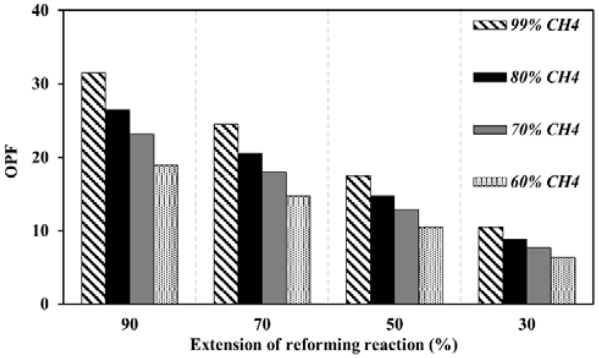

Fig. 4 The effect of CH_4 reforming reaction on OPF

Fig. 4 presents the impact of reforming reaction on the optimization process, where the level of the optimization presents a remarkably different behavior in any case (scenarios). Specifically, OPF presents a remarkably better behavior while lowering the extension of the specific reaction from 90% up to 30%, in each case. Specifically, by changing WGS extension when pure CH_4 is used, the optimization level varies from 31.46 to 10.49, while for 60% enriched fuel in CH_4 this range is drastically restricted between 18.93 and 6.31. It is also worth noticing that the extension of the H_2 electrochemical oxidization in the fuel cell has almost an identical impact on system's overall behavior. More precisely, OPF follows the same trends as in Fig. 4, where lower OPF values correspond to better optimized scenarios. In other words, systems fed by non-purified fuels can efficiently manage the fuel's chemical energy due to fact that this corresponds to a lower energy potential stored in the initial fuel's composition. Practically, this means that the lower the energetic content of the fuel, the higher the necessity for optimized operation since the role of thermal losses (wastes) becomes more significant, even when hydrocarbons rich fuels are used.

V. Conclusion

This extensive research study introduces an innovative software tool, namely THERMAS, which incorporates fundamental thermodynamics. OPF has been also introduced to quantify the significance of optimization in the operation of such a system. By including a parametric analysis on chemical reactions' extension in several simulated scenarios, was clearly revealed the importance of optimization process, which is actually inevitable. Also during simulation processes it was revealed that a SOFC-based system can be efficiently viable by using non-purified fuels as they produced through physical processes. Furthermore, such an innovative simulation tool, like THERMAS, can indicate a potential solution for the optimal design of a SOFC-stack based system in the direction of the commercialization of systems fed by hydrocarbons.

TABLE I
Nomenclature

Symbol	Quantity	Conversion from CGPM to SI [a]
$\tilde{C}_P$	mean isobaric specific heat capacity	J mol^{-1} K^{-1}
$\tilde{C}_P^e$	mean isobaric exergy capacity	J mol^{-1} K^{-1}
e_{ch}	chemical exergy	J
e_{ph}	physical exergy	J
e_0	standard chemical exergy	J
e^Q	exergy associated with heat transfer	J
H_{prod}, H_{react}	enthalpy of produced chemical element, enthalpy of a reactant chemical element	J
I	irreversibility rate	J
m, m_{tot}	mass per element, mass per stream	moles
n_{en}, n_{ex}	energy efficiency, exergy efficiency	%
P, P_0	pressure, environmental pressure	atm, 1 atm $\rightarrow$ 1.01 $\times$ 10^5 Pa
R	gas constant	8.1344 J mol^{-1} K^{-1}
S_{prod}, S_{react}	entropy of produced chemical element, entropy of a reactant chemical element	J
T, T_0	temperature, environmental temperature	K
W_{el}	electric energy	J
x	molar fraction	
ΔT	temperature difference	K
Indicators	**Quantity**	
i	chemical elements	
in	input stream of a device	
k	streams throughout a device	
out	output stream of a device	
r	number of chemical reactions	

[a] CGPM to SI; atm = atmosphere; J = joule, K = kelvin, mol = mole, Pa = pascal.

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