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Residential Solid Oxide Fuel Cell Generator Fuelled by Ethanol: Cell, Stack, and System Modelling with a Preliminary Experiment

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**Abstract**

The flexibility and feasibility of a 5 kW SOFC generator designed for natural gas and fuelled by a non-conventional liquid fuel such as ethanol is analysed. A complete generator model is implemented to predict and determine the main criticalities when ethanol fuel is operated. The main Balance-of-Plant (BoP) units considered are the reformer, the recirculation system based on an ejector, the tubular cells bundles constituting the stack unit, the after-burner zone and the air blower. The electrical and global efficiencies achieved at nominal operating conditions show how ethanol...
maintains generator performance good, while only slightly reducing the system AC efficiency from 48% (achieved by natural gas) to 45%. The effectiveness and flexibility of the recirculation system when changing the fuel is also verified, since a safe steam-to-carbon ratio (STCR) is established after the fuel is switched from natural gas to ethanol. The stack thermal management is analysed in detail and related to the system performances, showing how a high endothermic fuel reforming reaction is required to maintain the overall system efficiency. A preliminary experiment with ethanol feeding the Siemens generator is finally presented. The system response to the new fuel is monitored by several measured parameters and the system regulation is explained.

1. Introduction

Natural gas (NG) is considered the major fuel for SOFCs due to its widespread availability, well-known catalytic reforming techniques to produce hydrogen and carbon monoxide, and reduced costs. Several SOFC systems running on natural gas are already installed, and some of them have already achieved several operating hours with high conversion efficiency rates for electricity production [1,2]. Still, natural gas is a fossil fuel, and its consumption to produce energy implies having a net balance of CO₂ emissions. One attractive feature of SOFC technology is the possibility to operate on different fuels. The relatively high operating temperature permits to have an integrated plant for converting hydrocarbons or alcohols into H₂ and CO, which are subsequently electro-oxidised in a SOFC to produce electricity.

Among the others, fuels that can be derived from a biological path (e.g. biogases or bio-fuels) are of great interest to assure a sustainable energy production since the net carbon dioxide balance emissions is in principle zero. Of course, depending on the particular fuel composition, a proper device for the catalytic reforming (preferably internally integrated into the stack) has to be selected in order to assure both an adequate conversion of the hydrocarbons or alcohols, as well as to prevent carbon deposition on the anode side of the cells.
The physical status of a fuel at environmental pressure and temperature is also a feature to consider when selecting a fuel. The general advantage of liquid fuels is the high specific energy density, which translates directly into easier and more convenient storage and transportation. Especially for maritime transportation and aircrafts (where the fuel volume storage is a significant parameter), liquid fuels are of a great interest. One available option is the use of alcohols (e.g. methanol, ethanol, DME) in an SOFC generator with internal or in-stack fuel reforming to provide power to high energy-demanding auxiliary units [3]. Methanol is a good candidate since it is readily available, but usually a fossil fuel such as natural gas or coal is used as the initial feedstock. Moreover, methanol is toxic and special handling and safety issues must be considered. Ethanol is a very promising candidate as well since it can be produced from renewable resources and has no toxicity issues.

In general, an important issue arising when considering bio-fuels, either gaseous or liquid, is how much energy is actually spent to produce a certain available amount fuel starting from the biomass. The debate was and still is very intense, particularly regarding the ethanol production. In fact, the Well-to-Tank (WTT) value of the first-generation bio-ethanol, is around 1.51 MJ/MJ (mean value obtained from different production pathways), which is still far from the values reached by the traditional fossil fuels (e.g. 0.19 for natural gas) [4]. It has recently been reported [5] that corn ethanol is energy-efficient, as indicated by an energy output/input ratio of 1.34, while other studies state that producing ethanol requires more energy than that stored in the final fuel [6]. Of course, this clearly depends strongly on the specific production pathway selected and the type of starting biomass.

There is still of course a great opportunity to improve the production and distribution paths of bio-fuels, and the second generation is developing fast. In addition, bio-ethanol could reach a good performance level in terms of the «generalised» Tank-to-Wheel (TTW) ratio. As shown in the results of this paper, a good electric and CHP efficiency can be reached when a SOFC is used as the device converting the bio-fuel into electricity and heat.
The consolidated bio-ethanol production technology essentially uses biomass waste as the raw material. Most of the worldwide production relies on the microbial fermentation of sugars (prior to eventually the hydrolysis of the starch-containing compounds to the corresponding sugar). The standard path from sugar (glucose) follows the basic overall reaction:

\[ C_6H_{12}O_6 \rightarrow 2 \text{CH}_3\text{CH}_2\text{OH} + 2 \text{CO}_2 \quad (1) \]

Sugarcane (wide production and use in Brazil) or corn (especially in the US) can be used as feedstock biomass and the two have different ethanol yields per kg of biomass.

Through hydrolysis, a cellulosic biomass is feasible as well, since enzymes capable of hydrolysing cellulose and preparing it for fermentation have been widely discovered and selected. This technology could turn a number of cellulose-containing agricultural by-products such as corn cobs, straw, and sawdust into renewable energy resources. Some enzymes are able to hydrolyse agricultural residues such as corn stover, wheat straw, and sugar cane bagasse as well as energy crops such as switchgrass into fermentable sugars [7].

Ethanol is also relatively easy to convert in hydrogen and carbon monoxide through catalytic steam reforming (which is already generally performed in large SOFC systems to convert natural gas). When bio-ethanol is coupled with a high-energy conversion system, such as an SOFC, a complete sustainable and efficient electricity production is available. For these reasons, an SOFC system fuelled by ethanol is an option worthy of consideration.

2. Scope of this study
The main purpose of this study is to establish a detailed and complete modelling framework of an SOFC generator that is able to consider both hydrocarbons and alcohols as fuel inlet. The model is validated against the real generator operating with tubular cells and running on natural gas. System simulations are performed to show how ethanol could be used to efficiently produce energy (electricity and heat) using an SOFC device as power generator. An experiment with ethanol fuel feeding the real generator is finally performed to check the validity of the simulation results and...
support the main findings. In particular, the generator fuel-flexibility is checked with particular concern to the ejector-based recirculation system and the stack thermal management.

3. Balance-of-Plant of the SOFC system

In this section, the reference case (a generator fuelled by natural gas) and the proposed alternative (a generator running on ethanol fuel) are compared together. A wide range of topics related to the operation with a non-conventional fuel are discussed. For both feeding cases, the BoP is maintained the same; in this way, the fuel flexibility of the generator is assessed while the system design and configuration are kept unchanged.

A complete system model of a 5 kW SOFC generator was developed in the present work. The main modules considered are the fuel processing zone (with a thermally integrated in-stack reformer), the stack unit, the after-burner zone, the ejector-based recirculation system and the cathode air blower.

The SOFC system described is representative of the SFCα6 Siemens Fuel Cell design, of which a prototype unit was installed and has been running at Turbocare Spa (Torino) since April 2006.

The stack consists of 88 tubular cells with a 75 cm active length. The cell design and materials are well known and are reported in [8]. The cells are packed together in a 4 bundles arrangement, each one consisting of 22 tubular cells. Within every bundle, two strings of 11 series-connected cells are connected together in parallel. According to this electrical connection, the voltages produced by the 4 bundles are summed together to provide the overall stack voltage.

Figure 1 - Installation of the 5 kW Siemens Generator in Turbocare Spa

The generator has a nominal AC electric power around 3-3.5 kWel, with a respective DC stack current of 120-150 A and a voltage of 29-26.5 V. The peak power is 5 kW DC. The nominal thermal recovered power is in the range of 2.5-3.1 kWth. The nominal operating temperature of the stack is 970 °C. A scheme of the BoP main modules is presented in Figure 2.

Natural gas is the designed fuel and can be provided directly from the industrial grid, where it is available at pressure of approximately 5 bars. A valve reduces the pressure to a value of 3 bars just
before the generator inlet. As the first step, the fuel enters the desulphuriser, a two reactor beds connected in series, the first one filled with zeolites and the second one with activated carbon. After the cleaning stage, the NG enters the ejector at a pressure that is dependent on the nominal flow. A maximum NG flow of 30 SLPM with an inlet pressure of 2.75 bars is achievable at the ejector inlet.

The fuel flow is heated as it is piped inside the hot-box of the system: measurements provide an inlet ejector temperature of around 700°C. Inside the ejector, the primary fuel (NG) entrains part of the anodic exhaust due to fluid-dynamics effects. By mixing with the latter flow, NG is additionally heated. The recirculation factor of the ejector, and especially the exhaust composition, are strictly dependent on the main operative parameters of the system, which are essentially the Fuel Utilisation [FU] and the current load requested to the stack.

Figure 2 - Basic BoP design of the SOFC generator analysed

In the system BoP is included an auxiliary steam line used mainly for the start-up and partial load operation of the generator. Under these circumstances, the NG flow entering the generator is much reduced from the nominal value and is unable to entrain water (steam) enough from the anode exhaust to accomplish the reforming reactions. Additional steam is therefore externally added to the stack to guarantee a safe operation in terms of carbon deposition (that could affect both the reformer and the cells catalytic activity and long-term integrity).

With regards to the ethanol feeding case study, the steam line is actually used to pump the ethanol into the ejector. This option was selected since it represented the most convenient and easy way to feed the stack with a liquid fuel. A benefit of dealing with a liquid fuel is that the energy required to pump the fuel into the ejector at an adequate pressure is a negligible fraction of the overall stack power output. Thus the ethanol was pumped at room temperature as a liquid towards the ejector and the stack. Before reaching the ejector, the steamer available was used to vaporise it. A more detailed description is reported in the experimental section of this paper.

4. Cell, stack and system modelling of the 5 kW Generator
4.1 Tubular cell model

The Siemens Generator employs cathode-supported tubular cells. The cathode support consists of a 2.2 mm thick doped LaMnO$_3$ layer fabricated by extrusion-sintering. The inner diameter is ~22 cm. The YSZ electrolyte (40 µm), the Ni-YSZ anode (100 µm) and the doped LaCrO$_3$ interconnector (100 µm) layer are successively deposited onto the cathode surface by atmospheric plasma-spraying technique. A thin protective interlayer of CeO$_2$ is deposited between the cathode and the electrolyte using an impregnation technique.

The cathode tube is continuous, generating a seal-less design, where air is always contained on the inside of the cells. Each cell has an uncovered portion of cathode (where no electrolyte or anode are deposited) where the interconnector layer is placed. A nickel felt is attached onto this layer to provide electrical connection with the other stack cells.

Once the cell geometry and materials are defined, the cell voltage characteristics have been modelled as a function of the current load with a detailed polarisation model. Many models of SOFC single cells exist in the literature; those used here as references are reported in [9-11].

The Nernst potential has been calculated as:

$$V_{Nernst} = \frac{R \cdot T}{4 \cdot F} \log \left( \frac{P_{O_2,an}}{P_{O_2,cat}} \right)$$ (2)

where the oxygen partial pressures are evaluated respectively in the fuel and air channels, before the gas mixture enters the diffusion zone inside the porous electrodes. The losses arising from the diffusion of reacting and produced species inside the anode and cathode layers are evaluated as concentration losses, as later described.

Ohmic losses occur due to the flow of electrons or ionic species inside the cells. The electron paths inside the cells’ active layers due to the particular cylinder shape of the cells have been calculated, along with ohmic losses arising in the Ni-felts and the interconnector contact layers between one
The path is circumferential inside the anode and cathode, and radial into the electrolyte, interconnector and felt. The formulas used are those proposed in [12]:

\[
\eta_{\text{ohm,an}} + \eta_{\text{ohm,cat}} = j \cdot \frac{\pi D}{2} \left( \rho_{\text{an}} \frac{l_{\text{an}}}{1} + \rho_{\text{cat}} \frac{l_{\text{cat}}}{2} \right) \frac{1}{2} \pi D \tag{4}
\]

\[
\eta_{\text{ohm,el}} = j \cdot \rho_{\text{el}} \cdot l_{\text{el}} \tag{5}
\]

\[
\eta_{\text{ohm,int,el}} + \eta_{\text{ohm,felt}} = j \cdot \pi D \left( \rho_{\text{int,el}} \frac{l_{\text{int,el}}}{W_{\text{int,el}}} + \rho_{\text{felt}} \frac{l_{\text{felt}}}{W_{\text{felt}}} \right) \tag{6}
\]

Figure 3 shows a schematic view of the electrons migrating from the Ni-felt of a cell to that of the subsequent cell, passing through the anode, cathode and electrolyte layer. The current collector zones (interconnector + felt) are located at each semicircle. A uniform current distribution inside the tube is assumed.

**Figure 3 – Ohmic losses in the tubular cell**

The anodic concentration losses are evaluated with the following expression:

\[
\eta_{\text{eff,an}} = -\frac{RT}{2F} \log \left( \frac{P_{H_2\text{an}}}{P_{H_2\text{an,channel}}} \right) \tag{7}
\]

An analogous expression was derived for the CO diffusion, being this species considered electrochemical active as well as H₂ in the proposed electrochemical model.

The Fick’s law is solved at the anode to account for the partial pressure change of the gas species diffusing through the electrode along the anode thickness direction [13]:

\[
N_i = -D_i^{\text{eff}} \frac{P}{RT} \nabla Y_i \tag{8}
\]

Since a multi-species gas diffusion is present, the diffusion coefficient of each species inside the mixture is calculated as reported in [14]:

\[
\eta_{\text{ohm,el}} = j \cdot \rho_{\text{el}} \cdot l_{\text{el}} \tag{5}
\]
\[ D_{i,m}^{\text{eff}} = \frac{\varepsilon}{\tau} \left[ \frac{1 - \alpha_{i,m} \cdot y_i}{D_{i,m}} + \frac{1}{D_i} \right]^{-1}. \]  

(9)

\( \alpha_{i,m} \) is a dimensionless parameter defined as:

\[ \alpha_{i,m} = 1 - \left( \frac{M_i}{\sum_k M_k / n_{\text{prev1}}} \right). \]  

(10)

where

\[ D_{i,m} = \frac{1 - y_i}{\sum_j y_j / D_j}. \]  

(11)

The dusty-gas model is used at the cathode side \[15\]. The most significant concentration loss occurs here due to the higher thickness of the cathode compared to the anode layer. An higher accuracy is sought when in evaluating this overpotential. The superiority of dusty-gas model with respect to the Fick’s law has been reported in literature \[16\].

The equation for oxygen partial pressure at the cathode/electrolyte interface, considering \( O_2 \) self-diffusion into the cathode layer, takes the following form once solved:

\[ p_{\text{O}_2,\text{cat}}^\text{int} = p_{\text{O}_2,\text{cat}}^\text{out} - \left( p_{\text{O}_2,\text{cat}}^\text{out} - p_{\text{O}_2,\text{channel}}^\text{out} \right) \cdot \exp \left( \frac{\delta_{\text{O}_2} - R \cdot T \cdot j \cdot \tau}{4F \cdot D_{\text{O}_2}^{\text{eff}} \cdot p_{\text{O}_2,\text{cat}}^\text{out}} \right). \]  

(12)

where

\[ \frac{1}{D_{\text{O}_2}^{\text{eff}}} = \frac{\varepsilon_{\text{cat}}}{\tau_{\text{cat}}} \left( \frac{1}{D_{\text{O}_2,K}} + \frac{1}{D_{\text{O}_2,N_2}} \right) \]  

\[ N_j = -D_{\text{O}_2}^{\text{eff}} \frac{\partial p_{\text{O}_2}}{\partial y_j} \]  

\[ \delta_{\text{O}_2} = \frac{D_{\text{O}_2}^{\text{eff}}}{D_{\text{O}_2,K} + D_{\text{O}_2,N_2}}. \]  

(13)

The binary diffusion and Knudsen diffusion coefficients have been calculated according to the Chapman-Enskog kinetic theory \[17\]. For a low-density gas, the binary coefficients are calculated as:

\[ \frac{1}{D_{i+m}^{\text{eff}}} = \frac{\varepsilon_{\text{cat}}}{\tau_{\text{cat}}} \left( \frac{1}{D_{i+m,K}} \right). \]  

(14)
where $p$ is the total pressure (in atm), $\sigma_{AB} = (\sigma_A + \sigma_B)/2$ is the collision diameter (in Å) and $\Omega_{DAB}$ is the ‘collision integral’ for diffusion, based on the Lennard-Jones potential that can be obtained from the dimensionless temperature $kT/\varepsilon_{AB}$, where $\varepsilon_{AB}$ is the Lennard-Jones parameter for the energy of molecular interaction, which is expressed in ergs.

The Knudsen diffusion coefficients are calculated as:

$$D_{Ak} = \frac{2}{3} \left( \frac{8 \cdot R \cdot T}{\pi \cdot M_A} \right)^{1/2} \cdot \frac{1}{2} \cdot \frac{1}{f_{\text{prev}}}. \quad (16)$$

The effective diffusion coefficients are evaluated using the Bousanquet formula, multiplying the binary and Knudsen coefficients for the porosity over tortuosity factor.

The cathodic diffusion overpotential is defined as:

$$\eta_{\text{diff,cat}} = -\frac{RT}{4F} \log \left( \frac{p_{O_2,\text{cat}}^{\text{int}}}{p_{O_2,\text{cat}}^{\text{chan}}} \right). \quad (17)$$

**Table 1 - Parameters for the cell electrochemical model**

The activation overpotentials are derived from the Butler-Volmer equation, which was obtained in its explicit form by means of the hyperbolic sine approximation. The anodic exchange current has been calculated as reported in [18]:

$$j_{0,\text{an}} = \gamma_{an} \cdot \frac{p_{H_2,eq}}{p_{H_2,an}} \cdot \exp \left( -\frac{E_{\text{act,an}}}{R \cdot T} \right) \cdot \frac{N_e}{4} \cdot D_{\text{an}}^{\text{eff}} \cdot \frac{1}{p_{\text{act}}^2} \cdot \nabla V. \quad (18)$$

$$j_{0,\text{cat}} = \gamma_{cat} \cdot \left( \frac{p_{O_2,\text{cat}}^{\text{int}}}{p_{O_2,\text{cat}}^{\text{chan}}} \right)^{1/2} \cdot \exp \left( -\frac{E_{\text{act,cat}}}{R \cdot T} \right). \quad (19)$$

The sum of the anodic and cathodic overpotentials holds the following expression:

$$\eta_{\text{act,an}} + \eta_{\text{act,cat}} = \frac{RT}{2F} \cdot \sinh \left( \frac{j}{j_{0,\text{an}}} \right) + \frac{RT}{4F} \cdot \sinh \left( \frac{j}{j_{0,\text{cat}}} \right). \quad (20)$$

The total cell polarisation can finally be written as:
The set of equations (Eqs. 2-21) provided permits to evaluate the cell polarisation behaviour as a function of the current load requested. The present model was solved for a 1D discretised domain of the tubular cell (see Figure 4). The domain has been divided into equidistant sectors along the tube length, and the polarisation model is solved for each discretised tube element. Because the gases in each solved tube section diffuse in a direction orthogonal to the fuel flow in the channel, a quasi 2-D model is derived. An uniform current distribution along the tube length is assumed. Since both the H₂ and CO coming from the reforming of CH₄ are considered as being electrochemical active species, a value of 3 was assumed as the one expressing that ratio between H₂ and CO reacted to provide the overall current requested. This empirical assumption agrees with the literature [11], and in our case it is supported also by the chromatographic analysis of the stack outlet gas, which were performed routinely during the generator operation.

Along the tube, the anodic and cathodic gas mixtures change composition according to Faraday’s law. At the generic tube element along the domain, the following equations hold:

\[ \frac{1}{N} (I_{H_2,J} + I_{CO,J}) = I_{\text{cell}} \]  \hspace{1cm} (22)

\[ n_{H_2,J+1} = n_{H_2,J} - \frac{3}{4} \cdot \left( \frac{I_{\text{cell}}}{N} \right) \]  \hspace{1cm} (23)

\[ n_{H_2,J+1} = n_{H_2,J} - \frac{3}{4} \cdot \left( \frac{I_{\text{cell}}}{N} \right) \]  \hspace{1cm} (24)

\[ n_{CO,J+1} = n_{CO,J} - \frac{1}{4} \cdot \left( \frac{I_{\text{cell}}}{N} \right) \]  \hspace{1cm} (25)

\[ n_{O_2,J+1} = n_{O_2,J} - \frac{1}{4} \cdot \left( \frac{I_{\text{cell}}}{N} \right) \]  \hspace{1cm} (26)

\[ n_{n_{\text{act},J+1}} = n_{n_{\text{act},J}} \]  \hspace{1cm} (27)

Figure 4 - Fuel and air flows along the tubular cell.
The value representative of the cell voltage is the mean of the voltage values calculated at each discretised sector (or element) along the tube length.

In Table 1 the main geometrical, microstructural and electrochemical parameters used as an input to solve the tubular cell model are reported.

4.2 Stack model

Each tubular cell is assumed to work under the same identical conditions to the other cells inside the stack and with the same performances. Thus, the polarisation model presented in Section 4.1 is solved just for one cell, and the results obtained are extended to every cell in the stack. As mentioned in Section 3, the total number of cells is 88, and they are stacked together in bundles of 22 cells each. A schematic view of the electrical connection among the cells inside a bundle is reported in Figure 5. The terminal cells at both sides of the bundle are welded to current-collecting metallic sheets. Referring to the electrical arrangement described before, the same current is flowing in each bundle being all connected together in series. Therefore the overall stack current output is the double of that flowing in each cell. When measuring the generator stack voltage (the only voltage measurement available for the real generator), the cells average voltage can be obtained by dividing the former voltage by 44 (which is half of the total number of cells within the stack).

Figure 5 - Cells arrangement inside a bundle

The stack is air-cooled, which means that air in excess to the stoichiometric quantity needed for the electrochemical reactions is used to cool the stack. The stack thermal balance is solved to evaluate the stoichiometric air excess.

The heat internally produced by the stack is calculated as:

\[ Q_{\text{stack}} = Q_{\text{react}} + Q_{\text{loss}} = T_{\text{stack}} \cdot \Delta S_{\text{stack}} + Q_{\text{loss}} \]  
\[ (28) \]

The two heat source terms in Eq. 28 are respectively defined as:

\[ T_{\text{stack}} \cdot \Delta S_{\text{stack}} = \Delta H_{\text{stack}} - \Delta G_{\text{stack}} \]

\[ Q_{\text{loss}} = I_{\text{stack}} \left( \frac{\Delta G_{\text{fuel/2O_2}}}{} \frac{y_{\text{fuel}}}{2} \left( \frac{T_{\text{stack}} \cdot y_{\text{fuel}}}{2 \cdot F} - V(I) \right) \right) \]  
\[ (29) \]
The first equation refers to the entropic heat of reaction, arising from the electrochemical oxidation of H$_2$ and CO in H$_2$O and CO$_2$ respectively, while the second term is related to the irreversibilities originated by the cells’ overvoltages.

The air excess ratio is the parameter used to control the stack temperature; it can be calculated solving the energy balance equations around a control volume representative of the stack itself; the following expression is obtained for the air excess ratio:

$$\lambda_{air} = \frac{Q_{stack} + Q_{ref} + Q_{fuel}}{n_{air,stack} \cdot \varepsilon_{F,#} \cdot (T_{stack} - T_{air,inlet})}$$  \hspace{1cm} (30)

The stack air inlet temperature has been set to 750 °C, as measured during the real generator operation. A particular feature of the Siemens BoP is the air pre-heating zone, which is integrated into the stack ‘hot-box’. The cathode inlet air enters the generator at the upper side. As the air heads down towards the stack, it encounters the after-burner unit, just located at the top of generator. In this way, the inlet air, before entering the stack, is preheated to the temperature mentioned before.

4.3 System model

Several works on the modelling of a complete SOFC system are available in literature. Notably are those reported in [19-25]; among these, only Riensche et al. [19,20], Marsano et al. [21], Milewski et al. [22] and Campanari [23] have included an ejector model in their simulations. Of these, just Marsano included a detailed fluid-dynamic description of the ejector-based recirculation system, and accounted in his model for a detailed ejector geometry.

The other equations required to describe the generator behaviour consist of mass and energy balances throughout each component of the BoP, coupled to the electrochemical balances and reactions previously described for the stack (which are basically the Faraday’s law and an electrochemical polarisation model of the tubular cell). A simple combustion model for the after-burner is used for the stack exhaust burning.
Since gas mixtures are generally present throughout the system (namely CH₄, C₂H₅OH, H₂, CO, H₂O, CO₂, O₂, N₂), detailed polynomial fitting functions for the specific heats, enthalpies, entropies and Gibbs function values are considered according to the thermochemical data available from the literature [26,27].

4.3.1 Ejector

The ejector is one of the most important components of the BoP since a proper management of anode recirculation mechanism is crucial to safely operate the generator. The ejector is required to provide the reformer with a sufficient amount of steam, which has to be enough to fully reformate the NG hydrocarbons (of which CH₄ is the most abundant) as well as to avoid carbon deposition on the catalyst present in the reformer or in the piping within the generator. The ejector behaviour for SOFC applications is well described in [21,28-30]. The fluid-dynamic equations used in this work are those proposed by Zhu et al. [28,29]. The ejector has a nozzle where the fuel (natural gas or NGEtOH/H₂O as in our case) is injected at a relatively high pressure and accelerated at sonic velocities (Ma > 1). The fuel flow (‘primary flow’) is thus able to entrain a secondary flow, which is a fraction of the total anodic exhaust produced into the stack. The entrainment is mainly due to the combined effects of viscous forces and a local pressure differential occurring at the nozzle outlet between the primary and the secondary flows. The model considered solves the conservation equations (of mass, momentum and energy) at the main sections of the ejector. The assumption of the fuel reaching a Ma > 1 at the nozzle outlet is used to determine the velocity profile of the secondary flow between the primary/secondary streams boundary and the wall. This assumption was verified observing that the inlet fuel pressure measured at the nozzle inlet was always such to enable a critical flow through the nozzle, which indeed means having a Ma = 1 at the nozzle throat. Further detail on this aspects are nicely reported in the extensive work on ejectors developed by De Chant [31]. The mass flow of the entrained secondary stream is finally determined integrating the radial velocity profile over the available flow area and multiplying it over the density [28].
Besides the fuel nozzle area, the ejector includes a mixing zone, where the two flows have time and space enough to get homogeneous before entering the reformer/stack zone, and a diffuser which converts part of the dynamic pressure of the flow into static pressure in order to overcome the reformer and stack fuel compartment pressure drops. A schematic design of the ejector is reported in Figure 6.

**Figure 6 - Ejector scheme**

The primary flow is accelerated in the nozzle (just convergent in our design) to obtain high entrainment ratios of the secondary flow: the anodic exhaust. The molar entrainment ratio of the ejector is hence defined as the ratio between the recirculated flow (a fraction of the total anodic exhaust) and the incoming fresh fuel:

\[
\omega = \frac{n_s}{n_f} = \frac{f_{\text{recirc}} \cdot R_{\text{exhaust}}}{n_f}
\]

_Since_ an ejector is generally designed to operate at supersonic speeds, the inlet primary fuel flow passing through the nozzle can be expressed by the following relation:

\[
G_{\text{fuel}} = \sqrt{f_{\text{fuel}} \cdot k \cdot R \left( \frac{2}{k+1} \right)^{\frac{k+1}{k-1}} \rho_{\text{fuel}} \cdot A_t \cdot \sqrt{T_{\text{fuel}}}}
\]

The previous equation expresses the critical mass flowing into a nozzle of a defined geometry (where \( A_t \) represents the throat area of the nozzle), _once_ provided the thermodynamic properties of the fluid. By _substituting_ the ideal gas law into the density term, the pressure term becomes explicit.

As stated before, the ejector has the task of providing enough steam for reforming the NG. Rather than using an external water source, the steam produced by the electrochemical oxidation of \( \text{H}_2 \) is internally “recycled”, and part of it is transferred from the stack zone to the reformer zone. At the top of the anodic chamber containing the tubular cells, a duct is placed in such a way to permit part of the anodic exhaust to reach the ejector. The exhaust anodic gas consists of a mixture of unspent fuel (\( \text{H}_2, \text{CO} \)), whose quantity depends on the FU of the generator, and by-products of the
electrochemical reactions (H₂O, CO₂). Since the driving force to entrain the exhaust gas is provided by the accelerated primary fuel (NG) through the ejector nozzle, once the ejector geometry is fixed, the fraction of the anodic exhaust recirculated depends on its molar composition and on the thermodynamic state and mass flow of the primary stream.

4.3.2 Reformer and after-burner

The component where the reforming of NG takes place to produce hydrogen and carbon monoxide is the so-called ‘in-stack reformer’. The reformer is placed just between the two central bundles of the generator. The BoP has been designed in such a way that the high endothermic reforming reactions receive heat directly from the bundles where heat sources are actually located. The heat exchanged between the reformer and the stack bundles is predominately ruled by radiative phenomena. Since the reformer is receiving heat from the stack, its average temperature is always lower than that of the stack. In our calculations, the reforming equilibrium reactions have been carried out at a temperature of 800 °C. This temperature can be regarded as an average between the reformer inlet and outlet temperature.

A chemical equilibrium software provided by NASA [24], based on the minimisation of the Gibbs free energy, has been used to determine the equilibrium composition of the flow entering the reformer (fresh fuel + anodic recirculated flow). The NASA code, written in FORTRAN, has been built into a Matlab© code, which we developed to solve all of the equations reported in the present work.

The reformer is catalysed by Ni-Al-Mg pellets through which the fuel mixture flows. In the real plant operation, up to 95% of the methane fuel is known to be converted inside the reformer. The rest is converted directly over the cells’ anode surface. In our calculations, the methane is allowed to react entirely in the reformer. The reformer is treated as being completely selective towards H₂O in the methane conversion reactions, while the CO₂ remains unreacted. In this way, a full steam reforming reaction takes place, while dry-reforming is completely inhibited even if the CO₂ is available as significant fraction in the recirculated flow. CH₄ is by itself thermodynamically more...
favoured to choose steam rather than CO$_2$ if both available, for its conversion in H$_2$ and CO, but of course is the catalyst chosen inside the reformer that determines the reactions taking place inside it.

Our assumption is therefore supported by the particular catalyst known to be available in the reformer. The reformer selectivity has been intrinsically taken into account in our model as a non-reacting CO$_2$ was constrained within the equilibrium routine solved for calculating the reformer outlet composition.

The fraction of the anodic exhaust that is not recirculated join the exhaust air in the upper part of the stack module, the after-burner-zone.

The after-burner section is the region where the hot exhaust cathodic air and the non-recirculated fraction of the anodic exhaust mix together in a combustion chamber. What actually burns are the H$_2$ and CO not consumed by the electrochemical reactions within the stack. The combustion is therefore strictly related to the generator FU. The combustion has been modelled again by a tool available within the NASA program CEA [24], assuming a constant volume and pressure combustion, which is highly representative of what actually takes place in the after-burner region of the generator.

A final consideration has to be made for some internal combustion of H$_2$ and CO inside the stack, which introduces the concept of fuel consumption (FC). Inside a stack, some air leaks into the anode chamber due to imperfect sealing between the anode and cathode compartments. This phenomenon is due to the alumina structure holding the tubes in place, which is not completely gastight. The FC is defined as the overall fraction of H$_2$ and CO consumed inside the stack, either by electrochemical or combustion processes, while the FU just takes into account the electrochemical consumption. For the 5 kW Generator, the FC is estimated to be around 3% higher than the FU.

Once the leak is fixed, the fuel flow and the operating FU automatically determine the overall amount of H$_2$ and CO burning inside the stack. This kind of direct internal combustion inside the stack has a detrimental effect not just in terms of wasted fuel, but also in terms of thermal management of the stack itself. The combusted H$_2$ and CO generate more heat that if they were
converted electrochemically. We accounted for this phenomenon in our model, and its effect on the air excess is not negligible. Actually taking into account this aspect, the calculated air excess ratio was in a better agreement with the value experienced by the generator during its real operation.

### 4.4 Model validation

The complete system model has been validated against experimental data available from the 5 kW Siemens generator. The output stack voltage provided by the model matches that of the real system at an operation point within the nominal range of the generator (120 A of stack current and an FU of 85%), as well as in a wide interval of off-design points, with a stack current ranging from 100 to 170 A. The voltages predicted by the model reproduce the experimental ones with a maximum relative error of 2%.

The model has been validated for the reference case (NG feeding) also verifying a close match between the modelled and the real generator in terms of other significant operating, such as \( \lambda \), \( W_{el,DC} \), \( f_{recirc} \) and \( STCR \), which were either available from the BoP design or directly measured during the generator operational life.

In particular, the excess air ratio requested by the stack to keep its temperature constant at 970 °C was calculated by the model with value very close to the real measured one (3.47 against an experimental value of 3.34, at 120 A).

### 5 System simulation results

The model described in the previous section was solved iteratively to compute the ejector module, an initial guess over the anode recirculated molar fraction was necessary. At each iteration step, the exhaust molar composition is corrected and updated until convergence is reached. A schematic diagram of the iteration step within the system model is shown in Figure 7.

**Figure 7 - Schematic sheet describing the iteration step for determining the molar composition of the anodic exhaust**
The results of the system model numerical simulations that illustrate the main energy fluxes exchanged within the SOFC generator with two different fuels feeding, methane and ethanol, are respectively reported in Figures 8-9. The simulations are evaluated both at a stack current of 120 A.

5.1 System modelling of the 5kW generator fuelled by natural gas (reference case)

The system simulation results of the generator running on natural gas are reported in Figure 8. It can be observed how the generator is working with a safe STCR, over 2.5, and an air excess ratio that is relatively low due to the highly endothermic reaction of the methane reforming. The power ratio of the plant (defined as net AC electrical power output over thermal one) is ~ 1.15.

Figure 8 - Detailed flow-sheet with natural gas reference case

The net electrical AC efficiency is over 48%, which is close to the value observed in the real plant. Actually, a value around 44-45% is measured in the real configuration, essentially because of bad inverter efficiency, while in the model a value as high as 95% was used.

The temperature of the anodic exhaust reaching the ejector has was taken at 925 °C rather than the 970 °C of the stack. This correction has been used to match the real operation of the generator, where the anodic exhaust cools down slightly before reaching the ejector. The temperature of the mixed flow at the outside of the ejector is calculated using this corrected temperature. An identical assumption has been made for the ethanol case, where again the secondary ejector flow was set at 925 °C.

Regarding the fuel temperature at the ejector inlet, again a temperature of 700 °C was experimentally derived. The fuel pipe reaching the ejector passes before through the combustion zone of the stack (the after-burner), where is heated near the temperature indicated above.

A correct determination of the ejector inlet flows’ temperatures is fundamental when solving the ejector model to correctly evaluate the thermodynamic state of the inlet flows.
As a concluding remark on this section, each flow cooling or heating inside the generator ‘hot-box’ has always been accounted for in such a way as to preserve the consistency of the energy conservation principle.

5.2 System modelling of the 5kW generator fuelled by ethanol

The simulation results for the ethanol feeding are reported in Figure 9. Ethanol is provided to the stack through a pump that extracts the liquid fuel from a reservoir tank and conveys it to a vaporiser (steamer of the actual BoP). The power absorbed by this component is a negligible fraction of the electric output of the plant. A favourable feature of dealing with liquid fuels is the possibility of having a pump instead of a compressor to flow the fuel into the ejector, with an associated enthalpy change much lower than that required when compressing a gas.

Figure 9 - Detailed flow-sheet with ethanol feeding

By comparing the two flow sheets in Figures 8 and 9, it can be concluded that the ethanol feeding produces overall system performances comparable with those achieved with the reference natural gas fuel. The net AC efficiency drops of about 3 points when the fuel is switched from natural gas to pure ethanol. An higher LHV to produce the same overall quantity of stack current is required by the ethanol fuel. This accounts for ~1.5% of efficiency loss. The remaining loss arises from the higher power consumption of the blower due to the increased air excess of the ethanol-fuelled stack.

The local Nernst voltage curves for NG and EtOH under a stack current of 120 A are reported in Figure 10. The curves have of course a similar trend, where the voltage drop observed is related to the gradual consumption along the tube of the reactive moles due to the electrochemical reactions occurring in the cell. Apart from the terminal region of the tube, the Nernst cell voltage is always higher for ethanol than for methane. The lower STCR achieved with ethanol means a less-diluted anode fuel which consequently brings a slower descent of the open circuit voltage as the fuel reactive moles (H₂ and CO) are depleted along the tubular cell channel. Nevertheless, at the tube...
end the lower local FU obtained with the ethanol feeding is responsible for the more pronounced local Nernst voltage drop (see section 5.3 for a detailed explanation of the local FU).

**Figure 10 - Comparison of the calculated Nernst voltage along the fuel channel (cell tube length) for both natural gas and ethanol feeding**

With reference to the ethanol feeding case, the ejector recirculation system is able in principle to provide enough water for the reforming reaction, thus avoiding the need for an external water source; as explained with further detail later in this section, the lower STCR achieved by the ethanol fuel is essentially due to a different exhaust molar composition (richer in CO) established in the anodic exhaust.

The lowered STCR achieved is enough to avoid carbon deposition from equilibrium thermodynamic considerations, but its value is just located on the lower bound of a safety range, which generally lies between 2 and 2.5. A possible way to compensate for a too low STCR, without changing the ejector design, could be directly mixing some water with the ethanol feeding stream. Since water and ethanol have very similar vaporisation points, they could be easily mixed together when in the liquid phase, and subsequently vaporised and conveyed together to the ejector nozzle (this will be actually the solution adopted by the Authors in the experimental part of this work).

From the simulations results obtained, a mass entrainment ratio of ~8 is obtained with NG, while a much lower value of ~3 is obtained with EtOH. The main reason is that when EtOH is used as a fuel, the primary flow in the ejector nozzle is almost doubled on a mass basis, consequently the available flow area for the secondary stream is significantly decreased, and eventually a reduced entrained secondary flow is obtained (values of 11.0e-4 kg s⁻¹ and 7.7e-4 kg s⁻¹ are respectively obtained for NG and EtOH).

The following considerations explain with some more detail why the primary flow increases while changing the inlet fuel. Ethanol and natural gas have a molecular weight ratio of 46:16, while 2:3 is the ratio established to produce the same amount of electricity regardless of the fuel used (for a...
better clarification on this peculiar feature see Section 6.1 as well). These two ratios should be multiplied together to get the NG:EtOH mass flow inlet ratio. A value close to 2 is obtained, exactly meaning that an almost doubled mass flow passing through the ejector nozzle is established when the fuel is changed from NG to EtOH.

We have now clarified the reasons behind a different mass entrainment ratio between the NG and the EtOH fuels. Nevertheless, the ejector entrainment ratio would be more meaningful if expressed on a molar basis, being the STCR defined on the very same basis. Under the assumption (quite realistic according to our calculations) that the average molecular weight of the anodic exhaust is identical between NG and EtOH, the mass entrainment ratio achieved for each fuel can be related to the molar one by simply multiplying the former ratio for the molar ratio of the two fuels (which is 2:3, according to the strategy of keeping constant the electricity produced by the generator and thus the H\textsubscript{2}-equivalents number entering the stack). If the value obtained is multiplied over the ratio of secondary mass flows established by each fuel (which is 7.65:11, as reported before), a value close to 1 is now found, meaning that eventually almost the same molar entrainment ratio is obtained for both the fuel feeding cases, consistently also to what reported in Figure 8 and 9.

In Table 2 the molar entrainment ratios and the molar compositions of the recirculated flow for both NG and EtOH are reported. The water entrained by the ejector normalised to the molar flow of fuel entering into the stack is reported as well; from now on this parameter will be defined as the H\textsubscript{2}O stoichiometry of the ejector. Otherwise, the STCR is defined according to the following formula:

$$ \text{STCR} = \frac{y_{\text{H}_2O} \cdot n_{\text{in},\text{recire}}}{n_{\text{fuel}} + y_{\text{CO}} \cdot n_{\text{in},\text{recire}}} \tag{33} $$

The difference between the two parameters lies in that the STCR accounts also for the CO in its definition, being this species potentially able to produce carbon deposition as well as CH\textsubscript{4}.

As shown in Table 2, provided that methane and ethanol require the same stoichiometric amount of water in the reforming process, the H\textsubscript{2}O stoichiometry achieved for both fuels is...
essentially the same. The fact of having a lower ST CR for the ethanol is only due to the higher amount of CO present in its anode exhaust gas, as already mentioned before.

Table 2 - Molar compositions of the recirculated flow entrained by the ejector and total steam fraction recirculated normalised to the primary flow entering the ejector itself

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The power ratio is ~ 1 for the ethanol fuel, meaning that almost the same amounts of electrical and thermal powers are generated. The air excess \( \lambda \) is almost 40% higher than the NG reference fuel, due to an overall less endothermic reaction in the reformer zone. This aspect is further analysed and explained in more detail in the next section, where some experimental evidence is brought to show how the reformer increases its mean temperature due to the presence of a less endothermic reaction when ethanol replaces NG flow.

5.3 Local FU of the generator

An useful and meaningful parameter to monitor within the stack is the local FU achieved. The values calculated for the NG and EtOH are respectively 78.0% and 82.4%.

In what follows, we briefly derive an expression of local FU in terms of the other significant parameters of the generator.

The local FU is defined as:

\[
FU_{local} = \frac{I_{TOT}/2F}{n_{H2,CO}} = \frac{FU \cdot (1 - f_{rec})}{1 - FU \cdot f_{rec}}
\]

(34)

The expression in Eq. 34 is derived considering that the molar flow reaching the cell \( (n_{H2,CO}) \) in terms of \( H_2 \) and \( CO \) is the sum of two contributions: i) the inlet methane converted in the reformer, and ii) the \( H_2 \) and \( CO \) present in the recirculated anodic flow. This term is then written as:

\[
n_{H2,CO}^{\text{local}} = n_{H2,CO}^{\text{CH}_4} + f_{rec} \cdot n_{H2,CO}^{\text{CH}_4} \cdot (1 - FU_{local})
\]

(35)

The global FU is defined as:

\[
FU_{local} = \frac{I_{TOT}/2F}{n_{H2,CO}} = \frac{FU \cdot (1 - f_{rec})}{1 - FU \cdot f_{rec}}
\]

(32f)

(34f)

(37f)
Combining Eqs. 35 and 36 yields the expression reported in Eq. 34.

The local FU is useful to define the fuel utilisation which is effectively experienced by a stack where an anodic exhaust ‘recycling’ (or recirculation) is carried out. Since the ethanol-fuelled generator brings a lower recirculation fraction of the anodic exhaust, a less diluted fuel enters the stack. This has a positive effect on the Nernst voltage (as pointed out before). At the same time, the Nernst voltage is sensitive to the FU (the latter increasing, the former decreasing). The local Nernst voltage behaviour for the ethanol fuel (as observed in Figure 10) brings with it exactly these two contrasting effects (higher local FU, but with a less diluted fuel).

6 The preliminary experiment with ethanol fuel

6.1 Experimental

The SFC 5 kW system has been tested for few hours with a mixture of ethanol and water. During the experiment, the ethanol mixture has been progressively replacing the NG nominal flow. The latter can be calculated once the stack DC current, operating FU and fuel composition are known. The overall fuel flow required by the stack at a specified current load and FU is given by the following formula:

\[
\frac{n_{\text{fuel}}}{F} = \frac{I_{\text{TOT}}}{2F} n_{\text{cell}} \cdot \frac{1}{H_{\text{ref,max}} / \text{FU}}
\]

(37)

In the above expression, the stack current is related to the molar flow of inlet fuel. The H2-equivalents is a value characteristic of each fuel or fuel mixture. By definition, the number of H2-equivalents expresses how many reactive moles are obtained by an un-reformed fuel mol undertaking a complete steam reforming reaction:

\[
C_2H_5 + x \cdot H_2O \rightarrow x \cdot CO + (y/2 + x) \cdot H_2
\]

(38)
NG is a mixture of various hydrocarbons plus some $\text{N}_2$ and $\text{CO}_2$ in small amounts. The composition varies from site to site, and significant differences in the methane content subsist over the different countries. From the data records on the NG composition available in Turbocare Spa (IT – Torino), the gas from the grid contained on average a methane fraction of ~ 91-92%.

For simplicity, we always considered the NG as composed of just methane in all our simulations. This of course leads to some inaccuracy in the results obtained. Nevertheless the error was estimated to be less than 1% in the evaluation of the system efficiencies.

The basic idea under which part of the nominal NG flow has been replaced with EtOH was to provide the generator always with the same amount of $\text{H}_2$-equivalents. The reforming reactions of methane and ethanol are respectively the following:

$$\text{CH}_4 + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}, \quad \Delta H^0_{\text{298 K}} = -206.33 \text{ kJ mol}^{-1} \quad (39)$$

$$\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} \rightarrow 3\text{H}_2 + \text{CO}, \quad \Delta H^0_{\text{298 K}} = -256.79 \text{ kJ mol}^{-1} \quad (40)$$

It is trivial to see how 1 mole of fully steam-reformed ethanol gives 6 $\text{H}_2$-equivalent reactive moles ($\text{H}_2$+$\text{CO}$) compared to the 4 provided by the methane undertaking the same kind of reforming reaction. The 6:4 ratio obtained is also the one driving the switch from NG to ethanol fuel.

Looking at the reactions listed above, the enthalpy reaction for EtOH reforming is higher than for CH$_4$; but, since for each CH$_4$ mole just 4.6 EtOH moles are needed, the heat absorbed by the fuel reforming changes with this ratio as well. Considering that the $\text{H}_2$-equivalent moles are kept the same in both feeding cases, the heat of the reforming reactions for NG is 1.2 higher than that required to reformate EtOH. Therefore, fuelling the stack with ethanol reduces the heat sink of the reforming reaction. As a direct consequence, a higher air mass flow is necessary to keep the temperature constant inside the various cell bundles (this aspect is also clear from the system simulation results reported in Figures 8 and 9, where the EtOH feeding case requires a $\lambda_{\text{air}}$ of 5 against a 3.5 value attained by NG).

The ethanol was not flowed pure to the stack, rather an EtOH/H$_2$O mixture was used. The water/ethanol ratio has been set in order to operate the system in safe conditions towards the carbon reaction.
deposition. In Figure 11, using the CEA chemical equilibrium software [24], the mixture equilibrium composition as a function of temperature are plotted for a liquid volumetric EtOH/H2O ratio of 60/40 (the ratio shifts to 33.3/66.7 with the species in the gas phase). The graph shows how the water content in the mixture is already enough to suppress carbon deposition at temperatures above 600 °C.

**Figure 11 - Equilibrium compositions of an ethanol/water mixture in a volumetric ratio 60/40 at different temperatures**

At the stack’s nominal operating condition (120 Amps), the ethanol supplied was ~ 3.5 SLPM, while the total EtOH/H2O mixture was almost 11 SLPM; the NG flow was correspondingly decreased to less than 6 SLPM.

The EtOH/H2O mixture has been supplied through the steam line of the generator; this line was already installed from the beginning in the BoP to provide external steam during start-up and shut-down procedures and at off-load operation. Under these circumstances, either the anodic recirculation flow rich in H2O or CO2 is not available or low, to guarantee a safe steam reforming of the NG. The external water reservoir was with the liquid EtOH/H2O mixture. The latter was vaporised in the steamer and pumped to the stack ejector inlet with a volumetric pump. A schematic view of the experiment set-up is shown in Figure 12.

**Figure 12 - Schematic view of the 5 kW Generator to respect of the fuel and air feeding flows**

The choice of passing the EtOH/H2O mixture into the ejector is worthy of discussion because the steam already present in the EtOH mixture is enough to suppress carbon deposition at the reformer temperature, as mentioned before. Figure 13 reports the carbon boundary of the ethanol steam reforming reaction calculated using again thermodynamic equilibrium considerations. At 700 °C, 2 mol of H2O are sufficient to suppress carbon deposition, while even less are required as the temperature grows. Since this was a preliminary experiment, our choice was motivated by safety, meaning that a high amount of H2O to suppress carbon deposition was voluntarily injected along with the EtOH fuel. The extra steam provided with the exhaust flow recirculated by the ejector.
satisfied our safe operation requirement. In addition, it has been reported that ethanol steam-reforming in H₂ and CO is more difficult than methane reforming [32].

Obviously this extra-safe operating condition reduced stack performances, since an excessively high water dilution of reformed fuel negatively affects the Nernst voltage of the fuel mixture entering the stack anode compartment as well as increases the cell overvoltages. This point is discussed in more detail in the next section, where the experimental results are reported.

Figure 13 - Carbon boundary for the ethanol steam reforming

6.2 Results

In Figure 14, the NG and EtOH flow are plotted along with the measured ejector primary pressure. As already described before, the fuel feeding strategy was to gradually substitute the NG flow with EtOH while keeping constant the H₂-equivalents produced respectively by the two fuels, and assuming a complete steam reforming reaction occurring. Thus the mixture entering the ejector (primary flow) consisted partly of NG from the grid and partly vaporised EtOH/H₂O. A complete substitution of NG with ethanol maintaining the nominal stack current load was not possible due to a limitation on the maximum capacity of the pump extracting the liquid fuel from the tank. A maximum EtOH volumetric flow of 15 cc min⁻¹ was achieved. In terms of H₂-equivalents, at the maximum EtOH feeding, half of the generator current load was provided by ethanol, while the remaining half was covered by NG.

Figure 14 - Ejector pressure increase during EtOH/H₂O mixture feeding

In Figure 14, the volumetric flows of NG and EtOH (60% vol. of EtOH tank mixture) are plotted against the volumetric EtOH/H₂O mixture pumped from the liquid reservoir tank. The graph reports the approximate behaviour of the water finally present in the EtOH/H₂O/NG conveyed into the stack during the experiment. The initial water content in the primary fuel is due to the water already present inside the EtOH/H₂O feeding tank. After the ejector, due to the mixing with the recirculated fraction of the anodic exhaust, the overall water content further increases. The hypothesis that the
normalised molar steam flow entrained by the primary flow is constant. In Figure 15, the H\textsubscript{2}O stoichiometry behaviour is plotted against an increasing EtOH/H\textsubscript{2}O feeding. As stated before, the H\textsubscript{2}O stoichiometry represents the actual steam available in the final mixture flowing into the ejector over the stoichiometric water needed for the steam reforming reaction of the NG or EtOH (it should be noted that both fuels need only 1 mol of H\textsubscript{2}O for accomplishing the conversion reactions).

The hypothesis made can be only partially justified from what is reported in Table 2, where very similar values for the entrainment ratios and steam-to-fuel ratios are achieved regardless of the fuel. In the experiment, the ethanol is already pre-mixed with some water from the liquid reservoir tank. With respect to the pure ethanol feeding modelled before, now we have an even further increased mass flow entering the fuel nozzle. Such an increased mass flow could actually prevent a proper entrainment of the secondary flow. This is the reason why the assumption of a constant molar entrainment ratio of the ejector during the ethanol experiment, can not certainly considered a conservative one. The H\textsubscript{2}O stoichiometry value reported in Figure 15 is probably somewhat higher than the value actually experienced by the reformer.

Figure 15 - Water stoichiometry in the NG/EtOH mixture reaching the stack

According to Figure 15, and to our recommendations about the not-conservative feature of our assumption on the ejector entrainment during the experiment, the steam excess in the fuel flow entering the stack could be regarded as only slightly increased in respect of the nominal NG feeding. This aspect should produce a negative effect on the stack voltage, as already outlined, which is indeed confirmed by the experimental data in terms of a decrease of the stack voltage. In Figure 15, it is evident how the stack voltage reaches a minimum when the EtOH/H\textsubscript{2}O mixture is at the maximum level. The voltage loss is quite limited, though: less than 1 V is lost when partly switching the fuel from NG to EtOH as in our experiment. During the experiment, the stack current was kept constant managing the generator control system to force the stack to provide a set amount of current. The system demonstrated the ability to convert the new fuel into H\textsubscript{2} and CO and to
provide the requested current. This represents only a preliminary result and longer experiments should be carried out to fully demonstrate the fuel flexibility of the generator. The durability of the reformer against a new fuel and the possible formation of carbon deposits in a long-term period are aspects that should be addressed with more detail in the future.

The 1 V loss could be also partially ascribed to a not proper or full conversion of the EtOH stream inside the reformer and the stack. Nevertheless, the increased water dilution of the fuel seems to be a much more plausible explanation. If a not proper catalytic conversion of ethanol was occurring, a more pronounced stack voltage loss and instable generator behaviour would have been observed.

Figure 16 - Behaviour of stack voltage during the EtOH/H2O feeding experiment

In Figure 17, the voltage behaviour for each stack string is reported (each bundle is divided into two strings electrically connected in parallel for a total number of 4 bundles inside the stack: the 4 voltages for the generator that can be read in the system data logger are representative of each bundle voltage). The zoom is now on a wider time interval than in Figure 16. Two EtOH testing phases can be distinguished. The first one was just a short trial, while the second one is the experiment discussed and reported in Figure 16. Referring again to Figure 17, it is interesting to see to what extent the string voltages were perturbed each time the ethanol fuel began to flow into the stack.

Figure 17 - Comparison of string voltages during the EtOH/H2O feeding experiment

In Figure 18, on the same time interval as Figure 17, the stack current and voltage are reported during the experiment. As mentioned before, the current was kept constant during the experiment. The increase in the last part of it occurs when the EtOH flow has already reached its maximum and the NG nominal flow is restored. Regarding the behaviour of the generator control system, the current is generally defined as an external input that the stack is forced to match. However, when the voltage goes down below the set value, the control system automatically reduces the current requested to the stack. In Figure 18, is shown how the current was effectively kept constant during
the ethanol feeding to value only slightly lower than that achieved by NG before the EtOH feeding perturbations.

Figure 18 - Stack voltage and current behaviour

Figure 19 reports the temperature drop across the reformer as measured during the ethanol feeding. The temperature decreases across this component due to the endothermic reforming reactions occurring in it. Since the steam reforming of EtOH normalised to the H₂-equivalents is somewhat less endothermic than that of methane (as previously predicted by the system modelling results as well as by simple thermodynamic calculations on the enthalpies of reaction), a less pronounced temperature drop is indeed observed in the reformer, providing experimental evidence to our previous calculations. It is worth to note how the temperature drop is the lowest when the EtOH feeding is the highest, as we expected.

Figure 19 - Reformer temperature drop during the ethanol experiment

In Figure 20, the temperature behaviour of different regions inside the generator is reported. For the reasons already discussed before, the temperature drop across the reformer decreases when ethanol replaces methane. Regarding the absolute temperature of the inlet reformer, it increases. This temperature is related to the mixing of the fresh fuel and the recirculated flow occurring in the ejector. Such an increase could be explained by a hotter recirculated exhaust coming from the stack.

Figure 20 - Generator temperatures behaviour during the ethanol experiment

The air stoichiometry (air excess ratio) is reported in the same graph. The generator control system varies this parameter in such a way as to keep the stack temperature constant. Since a less endothermic reforming reaction is taking place, the stack temperature would increase if the air excess ratio would remain the same when switching the fuel from methane to ethanol. This effect is avoided by the control system increasing the air flow into the stack, leading to an augmented cooling of the generator. The air flow in the generator (and consequently the air stoichiometry
number) is also regulated by the control system to avoid an excessively high temperature increase in the after-burner zone. As reported in Figure 20, when ethanol was provided to the stack, the burner temperature increased by ~ 30 °C. The increased air flow in the stack could therefore have occurred to compensate for this phenomenon. From Figure 20, and according to the temperatures and airflow behaviours measured, the second option looks like as the more plausible. In fact, there is some evidence on how the after burner temperature compensation brought an extra-cooling of the stack at the end of the experiment.

Figure 21 shows how the measured AC efficiency of the system varies during the ethanol experiment. The efficiency reaches its minimum when the ethanol flow is at its maximum, following the behaviour of the voltage. The decrease is only around 1%, underlining how ethanol could substitute methane without any appreciable system performance modifications.

**Figure 21.** Generator electrical AC efficiency behaviour during the EtOH experiment

**Conclusions**

An SOFC tubular generator has been studied and modelled in detail. The main system components and the stack polarisation behaviour have been accounted for within the model. Among the system components, particular consideration was dedicated to the ejector and its role inside the generator as a whole.

The ejector flexibility to a fuel such as ethanol has been theoretically predicted. A safe generator operation could be guaranteed in terms of STCR with the new fuel. The thermal management of the stack and its link to the reforming of the inlet fuel has been clearly established: it has been shown how a fuel alternative to NG could be used successfully, without significantly degrading the system performance, provided that a high endothermic conversion of the fuel within the reformer occurs.

According to our analysis, a multi-fuel generator running both on natural gas and ethanol could be feasible. Concerning the actual BoP, the only critical aspect identified is represented by the catalyst.
reformer, whose stability and reforming activity against fuels different from NG should be proven on the long run.

A preliminary experiment was finally performed to verify what predicted by the system numerical simulations and prove the feasibility of ethanol as a fuel for a SOFC generator. A good integration of this fuel has been verified with respect to the ejector recirculation system and the stack thermal balance. In particular, the reformer behaviour was qualitatively in agreement with what theoretically expected. The electrical efficiency achieved by an ethanol-fuelled SOFC system is comparable to that of an NG fuelled one. In addition, a SOFC generator capable of running on multi-fuels shows to be a viable option.
Nomenclature

\( A_t \)  
throat area of fuel nozzle inside the ejector / m\(^2\)

BoP  
balance-of-plant

\( D \)  
mean tubular cell mean diameter / m

\( D_i \)  
diffusion coefficient of species \( i \) / cm\(^2\) s\(^{-1}\)

\( D_{Kn} \)  
Knudsen diffusion coefficient of species \( i \) / cm\(^2\) s\(^{-1}\)

\( E \)  
activation energy / J mol\(^{-1}\)

EtOH  
abbreviation for ethanol

\( F \)  
Faraday constant / 96485 C s\(^{-1}\)

\( f_{	ext{loss}} \)  
frictional loss coefficient

\( F_{\text{recirc}} \)  
recirculated fraction of the anodic exhaust

\( FU \)  
(global) fuel utilisation (referring to the inlet NG flow)

\( FU_{\text{local}} \)  
effective fuel utilisation experienced by the stack

\( G_{\text{an,exhaust}} \)  
exhaust anodic flow exiting the stack / kg s\(^{-1}\)

\( G_{\text{fu}} \)  
fuel flow into the ejector / kg s\(^{-1}\)

\( G_{\text{ref}} \)  
mixed fuel flow entering the reformer / kg s\(^{-1}\)

\( G_{\text{stack,inlet}} \)  
reformed fuel flow entering the stack anode side / kg s\(^{-1}\)

\( H_{2,\text{eq}} \)  
\( H_2 \)-equivalents

\( H_2O \)  
stoichiometry: moles of \( H_2O \) (steam) over stoichiometric moles of \( H_2O \) for reforming a selected fuel

\( I \)  
electric current / A

\( I_{\text{CELL}} \)  
electric current of a single cell / A

\( I_{\text{TOT}} \)  
total current requested/produced by all the stack cells ( = \( n_{\text{cells}} \cdot I_{\text{cell}} \)) / A

\( j \)  
current density /A cm\(^{-2}\)

\( j_{\text{an}} \)  
anodic exchange current density / A cm\(^{-2}\)

\( j_{\text{cat}} \)  
cathodic exchange current density / A cm\(^{-2}\)

\( k \)  
ksentropic coefficient of the ideal gas

\( l \)  
cell layer thickness / m

\( LHV \)  
low heating value / W

\( M \)  
molecular weight of species \( i \) / g mol\(^{-1}\)

\( Ma \)  
Mach number

\( n_{\text{cells}} \)  
total number of tubular cells inside the stack ( = 88)

\( N \)  
total number of discretised steps for solving the 1D cell domain

\( n_{\text{i}} \)  
molar flow of species \( i \) / mol s\(^{-1}\)

\( p \)  
absolute pressure / Pa

\( Q_{\text{comb}} \)  
heat generated from the combustion of exhaust \( H_2 \) and CO in the after-burner / W

\( Q_{\text{evap}} \)  
heat required to evaporate the liquid fuel in the tank / W

\( Q_{\text{fuel}} \)  
heat required to heat the fuel at the stack temperature / W

\( Q_{\text{loss}} \)  
heat generated by irreversibilities of the stack polarisation / W

\( Q_{\text{react}} \)  
heat generated by the oxidation of \( H_2 \) and CO inside the stack / W

\( Q_{\text{ref}} \)  
heat required by the reformer / W

\( Q_{\text{stack}} \)  
overall internally heat produced by the stack / W

\( r \)  
mean pore radius / m

\( \text{SLPM} \)  
standard litre per minute

\( \text{STCR} \)  
steam-to-carbon ratio

\( T_{\text{stack}} \)  
operating temperature of the stack / °C

\( V \)  
voltage / V

\( w \)  
interconnector width / m
\( W_{th} \) available thermal power form the stack / W
\( y_i \) molar fraction of species \( i \)
\( \varepsilon \) electrode porosity
\( \eta \) cell overvoltage / V
\( \lambda_{air} \) air excess
\( \rho \) gas density (kg m\(^{-3}\)) / electronic resistivity (ohm m) in Eqs. 3-6
\( \tau \) electrode tortuosity
\( \omega \) ejector molar entrainment ratio

**Subscripts and superscripts**

act activation
an anode
cat cathode
cat channel gas channel (outside the electrodes diffusion layer)
diff diffusion
e ly electrolyte
eq equivalent
telt Ni-felt
int interface (electrode/electrolyte)
ter inter interconnector
phm ohmic
ox oxidant
pore electrode pore
recirc recirculation
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\[ n_{H_2,i+1} = n_{H_2,i} - I_{H_2,i} = n_{H_2,i} - \frac{3/4 \cdot (I_{\text{CELL}} / N)}{2 \cdot F} \]  
\[ n_{H_2O,i+1} = n_{H_2O,i} + \frac{3/4 I_{\text{CELL}}}{2 \cdot F} \]  
\[ n_{CO,i+1} = n_{CO,i} - (I_{\text{CELL}} / N - I_{H_2,i}) = n_{CO,i} - \frac{1/4 I_{\text{CELL}}}{2F} \]  
\[ n_{CO_2,i+1} = n_{CO_2,i} + \frac{1/4 I_{\text{CELL}}}{2 \cdot F} \]  
\[ n_{O_2,i+1} = n_{O_2,i} - \frac{I_{\text{CELL}}}{4 \cdot F} \]  

\[ \begin{aligned} T_{\text{stack}} \cdot \Delta S_{\text{stack}} &= \Delta H_{\text{stack}} - \Delta G_{\text{stack}} \\ Q_{\text{loss}} &= I_{\text{stack}} \cdot \left( \frac{\Delta G_{\text{fuel}(H_2, CO)}(T_{\text{stack}}, y_{\text{fuel}})}{2 \cdot F} \right) - V(I). \end{aligned} \]  

is linked to the thermal balance of the stack.
\[
\lambda_{\text{air}} = \frac{Q_{\text{stack}} + Q_{\text{ref}} + Q_{\text{fuel}}}{n_{\text{air,tech}} \cdot c_{p,\text{air}} (T_{\text{stack}} - T_{\text{air, inlet}})}
\]

Page 13: Justified, Don't adjust right indent when grid is defined, Line spacing: Double, Don't adjust space between Latin and Asian text, Don't adjust space between Asian text and numbers

through the top area of the generator

before reaching the cells.

Nevertheless, the polarisation of the stack when ethanol fuel is feeding the generator is actually slightly higher than for NG. Under the hypothesis of a proper reforming of ethanol, the fuel quantity in both feeding cases is such as to preserve the overall H\textsubscript{2}\,-
equivalents entering the system. Thus, the Nernst voltage of the stack should not be affected significantly. This aspect has been analysed in more detail by drawing the Nernst voltage along the fuel channel (which corresponds to the cell tube length) for both fuel cases.

\[
STCR = \frac{y_{\text{H}_2\text{O}} \cdot n_{\text{an,recirc}}}{n_{\text{fuel}} + y_{\text{CO}} \cdot n_{\text{an,recirc}}}
\]

For the fuels considered here, t

is also accounted for in the STCR number
\[ FU = \frac{I_{\text{TOT}}}{n_{CH_4}} \]  

That is, the energy of FU causes it to achieve a state in which...
In this sense, \( t \) generates two, but which sum together and finally produce an overall positive effect on the Nernst voltage (as observed in Figure 10).

Figure 10 - Comparison of the calculated Nernst voltage along the fuel channel (cell tube length) for both natural gas and ethanol feeding.
NG flow

According to the standard procedure employed while operating the generator, the fuel
is determined upon DC load, FU of the generator, and type of fuel entering it.

For simplicity, we refer here just to methane as a fuel (even if the real fuel is natural gas); the methane is thus

\[ n_{CH_4} = \frac{I_{stack} / 2 \cdot n_{cells} \cdot \frac{1}{2 \cdot F \cdot H_{2,eq}}}{FU} \]  

(37)
reactive species

Two factors can modify Eq. 37: i) the effective fuel consumption (FC), which is greater
than the FU, since some air leakage occurs inside the stack (the denominator of Eq. 37
should in fact be FC instead of FU); ii) the stack NG flow is not pure methane, thus the
effective inlet molar composition of the fuel gas should be taken into account to calculate
the exact number of H\textsubscript{2}-equivalents. The modifications due to these two effects are
relatively low, because the air leaks inside the generator are rather low and the relative
error committed in considering just methane as the fuel flow is lower than 1\% when
evaluating \(H_{2,eq}\).

of fuels; it has to be taken into account to determine the primary inlet fuel necessary to
satisfy a certain stack current of the generator.

stack fuel removed and
an overall fuel mixture that was able to provide the stack with the same amount of equivalent reactive moles of H$_2$ of the nominal NG flow, while undertaking a full steam-reforming.

Taking a closer observation at the...
C₂H₅OH + H₂O → 4H₂ + 2CO, (∆H_{react} (298 K) = 256.79 kJ mol⁻¹).

(40)

that a

, when fully steam-reformed

moles

per mole of steam-reformed

is

ratio

es

, thus maintaining the number of H₂-equivalents constant.

/ 

in-stack

imposed
reforming
required
for a NG
feeding than for an
feeding
aspect
fully evident in
4.7 instead
of
with NG
In terms of the ethanol fuel mixture
chosen with respect to carbo long, but the value decrease.

and also
confirming

the

predictions

s

various
during the ethanol experiment are

reformer

is diminishe
d

About

is shown to
that happens
therefore
- Temperature
also since this is the parameter managing the stack temperature.
behaves and the reformer is thermally integrated into the stack.
it makes sense that the
should increase
increased
Actually, t
so
In Figure 21, it is also interesting to observe how the inlet reformer temperature behaves similarly to that of the after-burner. The reformer temperature is governed by the fuel inlet temperature and the anodic exhaust temperature. If we consider the fuel inlet temperature to be constant, the anodic exhaust temperature is the one really affecting and governing that of the inlet reformer zone. We should also consider that the anodic exhaust has basically the same temperature of the stack at the upper region. That is why there is a correlation between the stack upper temperature and the after-burner temperature. Thus, we can conclude that the latter temperature depends on what comes from the stack in terms of anodic exhaust, and the observed matching trend between the inlet reformer and after-burner zone temperatures finds its explanation. Of course a gap subsists between the two, and it is due to the combustion taking place in the after-burner.

**Figure 21 - After-burner and stack temperature behaviour**

The local FU has been evaluated for both fuel feeding cases and as related to stack performances.

One issue to note is that with respect to the current system design,
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R.C.,

J.M.,

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<td>composition of the anodic exhaust</td>
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<td>17</td>
<td>Comparison of string voltages during the EtOH/H2O feeding experiment</td>
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<td>18</td>
<td>Stack voltage and current behaviour</td>
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<td>Reformer temperature drop during the ethanol experiment</td>
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<td>23</td>
<td>Basic BoP design of the SOFC generator analysed</td>
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<td>Ohmic losses in the tubular cell</td>
<td>8</td>
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<td>25</td>
<td>Fuel and air flows along the tubular cell</td>
<td>11</td>
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<td>26</td>
<td>Cells arrangement inside a bundle</td>
<td>12</td>
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<td>27</td>
<td>Ejector scheme</td>
<td>15</td>
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<td>29</td>
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<td>19</td>
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<tr>
<td>30</td>
<td>Detailed flow-sheet with ethanol feeding</td>
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<tr>
<th>Ejector volumetric entrainment ratio 'NG feeding':</th>
<th>5.53</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anodic molar exhaust composition:</td>
<td></td>
</tr>
<tr>
<td>H₂ [%]    CO [%]    H₂O [%]    CO₂ [%]</td>
<td></td>
</tr>
<tr>
<td>16        4          52         28</td>
<td></td>
</tr>
<tr>
<td>Mol(H₂O)/Mol(fuel_in):</td>
<td>2.9</td>
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</table>

<table>
<thead>
<tr>
<th>Ejector volumetric entrainment ratio 'EtOH feeding':</th>
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</thead>
<tbody>
<tr>
<td>Anodic molar exhaust composition:</td>
<td></td>
</tr>
<tr>
<td>H₂ [%]    CO [%]    H₂O [%]    CO₂ [%]</td>
<td></td>
</tr>
<tr>
<td>5         13         56         26</td>
<td></td>
</tr>
<tr>
<td>Mol(H₂O)/Mol(fuel_in):</td>
<td>3.0</td>
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</table>
## Tubular Cell - Model Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
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<tbody>
<tr>
<td>Cathode inner diameter / mm</td>
<td>21.7</td>
</tr>
<tr>
<td>Mean tube diameter / mm</td>
<td>24</td>
</tr>
<tr>
<td>Cathode thickness / µm</td>
<td>2200</td>
</tr>
<tr>
<td>Electrolyte thickness / µm</td>
<td>40</td>
</tr>
<tr>
<td>Anode thickness / µm</td>
<td>100</td>
</tr>
<tr>
<td>Interconnector thickness / µm</td>
<td>100</td>
</tr>
<tr>
<td>Interconnector width / cm</td>
<td>1.3</td>
</tr>
<tr>
<td>Ni-felt thickness / cm</td>
<td>0.5</td>
</tr>
<tr>
<td>Tubular cell length / cm</td>
<td>75</td>
</tr>
<tr>
<td>Cell active area / cm²</td>
<td>400</td>
</tr>
<tr>
<td>( \rho_{el,cat} / \Omega \text{m} )</td>
<td>( 0.008114 \times \exp(500/T) )</td>
</tr>
<tr>
<td>( \rho_{el,ely} / \Omega \text{m} )</td>
<td>( 0.00294 \times \exp(10350/T) )</td>
</tr>
<tr>
<td>( \rho_{el,an} / \Omega \text{m} )</td>
<td>( 0.00298 \times \exp(-1392/T) )</td>
</tr>
<tr>
<td>( \rho_{el,inter} / \Omega \text{m} )</td>
<td>( 0.1256 \times \exp(4690/T) )</td>
</tr>
<tr>
<td>( \rho_{el,felt} / \Omega \text{m} )</td>
<td>-</td>
</tr>
<tr>
<td>( \gamma_{an} / \text{A m}^{-2} )</td>
<td>( 7 \times 10^8 )</td>
</tr>
<tr>
<td>( \gamma_{cat} / \text{A m}^{-2} )</td>
<td>( 5.5 \times 10^8 )</td>
</tr>
<tr>
<td>( E_{act,an} / \text{kJ mol}^{-1} )</td>
<td>100</td>
</tr>
<tr>
<td>( E_{act,cat} / \text{kJ mol}^{-1} )</td>
<td>120</td>
</tr>
<tr>
<td>( \varepsilon_{an} ) (anode porosity)</td>
<td>0.3</td>
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<tr>
<td>( \tau_{an} ) (anode tortuosity)</td>
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<tr>
<td>( \varepsilon_{cat} ) (cathode porosity)</td>
<td>0.4</td>
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<tr>
<td>( \tau_{cat} ) (cathode tortuosity)</td>
<td>4</td>
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<tr>
<td>( r_{pore,an} ) (mean cathode pores radius)</td>
<td>3</td>
</tr>
<tr>
<td>( r_{pore,cat} ) (mean cathode pores radius)</td>
<td>15</td>
</tr>
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</table>

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Figure 3 – Ohmic losses in the tubular cell
Figure 4 - Fuel and air flows along the tubular cell
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Figure 6. Ejector scheme
254x190mm (96 x 96 DPI)
Figure 7. Schematic sheet describing the iteration step for determining the molar composition of the anodic exhaust.

701x533mm (96 x 96 DPI)
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