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ELECTRICITY AND HYDROGEN PRODUCTION BY COGENERATION SYSTEM APPLIED IN A FUEL STATION IN BRAZIL: ENERGY ANALYSIS OF A COMBINED SOFC AND ETHANOL STEAM REFORMING MODEL

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Abstract

A model is presented that hydrogen and electricity are cogenerated by a compact system, regarding operational integration of units of SOFC and Ethanol reformer. This is a model of a simultaneously production of electricity and hydrogen to be applied and allocated strategically in fuel stations, considering the Brazilian conditions that such fuel stations follow marketing and logistics premises that allow to be regularity provided with ethanol biofuel as well are usually near to the consumers. The strategic is the use of the wide network of fuel stations that generally has relevant locations such as urban centers and highways for electricity and hydrogen supply. The objective refers to direct green-hydrogen usage after the processing of ethanol steam reforming, mitigating the usual technical and economics difficult and limitations related to storage and transportation of high volumes of hydrogen that alternatively could be accomplished with ethanol and water, using the proposed model. Concurrently, the same fuel stations would be a green-hydrogen provider, contributing to the reduction of pollution by using ethanol as a biofuel already extremely applied over all the Brazilian territory, attempting to the demands needed. The main novelty of this model refers to combination of three characteristics: (i) high heat produced by the SOFC that could be provided as the energy required for the (ii) endothermic Ethanol reforming, and this fuel is already used throughout (iii) Brazilian territory in fuel stations, which startup to offering also hydrogen and electricity as new products. The full study of this model consists in two papers, that in this first work is presented the thermodynamic analysis, aiming to identify the potential of the energy integration specially related to the SOFC and Reformer functionalities, as a technical feasibility validation. The conclusion of the theoretical results regarding mathematical modelling demonstrates this feasibility, indicating the existence of a minimum energy parity required between SOFC and Ethanol reformer.

Keywords

SOFC, Green-Hydrogen, Ethanol Steam Reforming, Electricity-Generation, Thermodynamic Modeling of Cogeneration

1. Introduction

The research aims to approach four fundamental aspects apparently disassociated, however susceptible to establishing a correlation to produce academic, applicable and technological knowledge. The first aspect concerns the production of hydrogen gas from the ethanol reform which has valid advantages due to the wide availability of this biofuel in almost Brazilian territory (Silva, 2005; Souza, 2005). The second aspect refers to the vast network of fuel stations, comprising around 40,000 commercial establishments distributed throughout Brazil (Fecombustíveis, 2022). The third aspect comprises the current Brazilian energy matrix (according to ANEEL, 2022) that has inconsistencies as such as the recent

variation of rainfall regime, growing demand for electricity, use of fossil fuels (in thermoelectric that represents 20-25% of total generated power). The adequacy of the National Biofuels Policy (2022) that determines the propensity for decentralization and diversification, especially considering the use of green fuels (in definitions of Art. 5, item XII: "decarbonization target: goal set to ensure lower carbon intensity in the national fuel matrix"). Based on this, Brazilian ethanol stands out as a biomass product for reducing or even suppressing carbon dioxide (CO_2) emissions since agricultural production consumes CO_2 itself during the growth of sugarcane (Souza (2018)). And finally, the fourth aspect refers to the future and growing demand for energy service to electric cars (Fontana (2022)) which those cars could be provided with batteries (and thus, requiring additional electricity for recharging) or H_2 in order to provide fuel cells. The electrics' cars could be used for urban shorter distances as well as on long routes such as roads, considering both models of electric car (battery or fuel cell).

Thus, the research proposal is the establishment of a compact station capable of allocation and adaptation in fuel stations that are already supplied with ethanol biofuel. It is simply presented as a possibility to match these four aspects with the primary objective of producing hydrogen gas and distributing electricity. Therefore, the research comprises this broad approach, organized as presented in Figure 1.

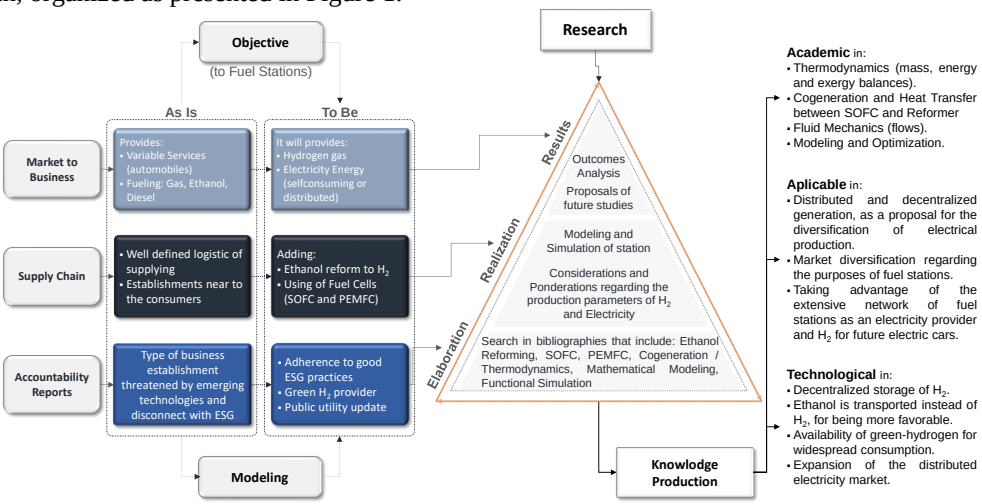


Figure 1: scope and objectives of the research of the aggregate station in fuel stations (elaborated by the author)

2. **Process Description and Modeling**

The primordial objective aims to establish the modelling parameters, starting from the projection of obtaining 1 kg of hydrogen gas from the reform process. The reference for measuring hydrogen gas by mass (kilogram-kg) is made according to the North American standard NIST Handbook 130 (2022) which exactly determines the sale of hydrogen gas in kg for vehicle supply. As Vaughn (2021), an automobile (usable fuel cells) adds a capacity tank in the order of 3 kg up to 5 kg of H_2. Figure 2 shows the schematic model of the hydrogen and electricity production unit, and Figure 3 shows the station design of a container which aims to accommodate all components and subsystems.

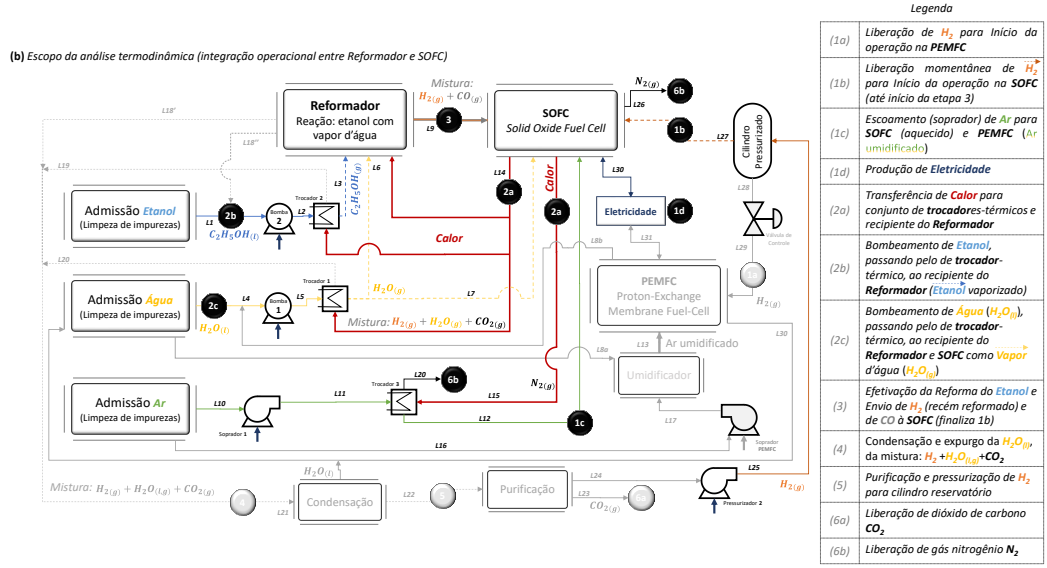


Figure 2: Schematic diagram of the Station as a hydrogen gas and electricity production unit, considering the interaction and sequencing of processes and components, explained in the frame-legend on the right (author's prepared)

Figure 3: CAD illustration with the project of a station in a fuel-station and container (author's prepared)

The simultaneous production of electricity and hydrogen gas allows the possibility of a balance in terms of profit, considering the economic value of commercialization of both products. Thus, the structuring of the model with two cells, one SOFC and another PEMFC results from the rapid activation of the PEMFC, providing an immediate supply of electricity (according to Boccaletti *et al.*, 2006, the PEMFC requires less than one minute for an immediate start against between 20 and 30 minutes for SOFC). With this, it will be possible to provide a joint supply of electricity and cogenerated heat to reform the ethanol, producing hydrogen.

This work's objective in modelling is the calculations inherent to operational interaction between the reformer and SOFC in which the thermodynamic analysis permeates both equipment individually and the form of integration of these. All mathematical modelling is calculated via EES® (*Engineering Equation Solver*).

3. **Methodological Approaches**

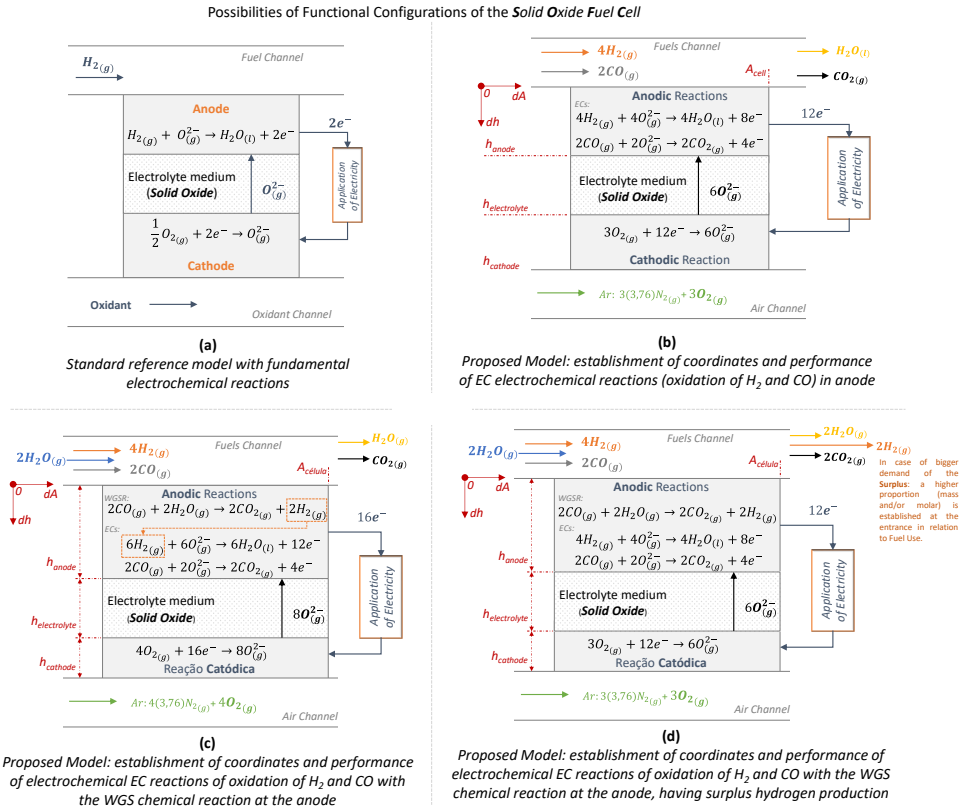
3.1. **Initial Considerations**

Observing the schematic diagram of the model in Figure 2, standout the steps 2-a, 2-b, 2-c and 3 in which are established flows in steady regime between reformer and SOFC, regarding respectively: thermal transfer from the reformer to SOFC, ethanol vaporization, water vaporization and the flowing from reformer to SOFC of the mixture of hydrogen, steam and carbon monoxide. Therefore, those steps are objectively configured as a cogeneration situation once there is the correlated and simultaneous production of various products, such as heat, electricity and hydrogen.

Conceptually (Gomes, 2020), cogeneration is defined as the simultaneous production of energies in various forms, such as electrical, mechanical and thermal (useful), coming from a single source such as fossil fuels (oil, coal, natural gas) extractives, renewable fuels from biomass (ethanol, methanol and biogas and various organic sources, such as planting or decomposition), wind and solar. From this definition, a project of cogeneration of electric energy and thermal energy is presented from the combined production of hydrogen gas in which a process of steam reform of ethanol occurs with heat from a fuel cell (SOFC).

3.2. **Operational Integration between the Reformer and SOFC**

Regarding the operation of SOFC, according to Leal (2003) and Nakashima (2021), it becomes inherent to this the release of energy at high temperatures since electrolyte promotes the best ionic conduction at high temperatures. Khan et al. (2021) highlights that SOFC's operation at a high temperature enables rapid electrolytic reaction and results in high-quality heat as a byproduct which can be used in cogeneration. Functionally, SOFC can be demonstrated from various configurations, according to Figure 4 in terms of chemical reactions.



(a)
Standard reference model with fundamental electrochemical reactions

(b)
Proposed Model: establishment of coordinates and performance of EC electrochemical reactions (oxidation of H_2 and CO) in anode

(c)
Proposed Model: establishment of coordinates and performance of electrochemical EC reactions of oxidation of H_2 and CO with the WGS chemical reaction at the anode

(d)
Proposed Model: establishment of coordinates and performance of electrochemical EC reactions of oxidation of H_2 and CO with the WGS chemical reaction at the anode, having surplus hydrogen production

Figure 4: Functional Representation of SOFC (elaborated by the author with the reference of Souza, 2018)

SOFC cells present the property of BETAFC, which consists of the relationship between the electricity generated with the heat also generated, called as β_{FC} this concept refers to fuel cells as cogeneration properties (Leal, 2003). There are some authors (Wiranarongkorn *et al*., 2019; Facci *et al*., 2017 and Silva *et al*., 2016) that indicate the use of β_{FC} inverted, relating the amount of heat generated to the electricity produced (usually defined as *HoP*: *heat-to-power ratio* or *CHP*: *Combined Heat and Power*).

According to Camargo (2004), Khan *et al.* (2021) and Aguiar *et al*. (2004;2005) the SOFC presents itself as an energy conversion device with electric efficiency of 45%~55%, providing electricity and heat useful for cogeneration. For this work, considering the classifications related to SOFC and reformer interaction, the project proposed of the model is better defined as IIR-SOFC (Indirect Internal Reform), which the caveat that the overall reform process is bipartite wherein the reformer has the only occurrence of the reaction of reform with water vapor, called as SRR (Steaming Reform Reactions) and the shift reaction (called WGSR: Water Gas Shift Reactions or simply WGS reaction) occurs directly and internally in the SOFC anode, together with the EC (electrochemical) reactions of hydrogen and carbon monoxide oxidations, as described in Figure 4 (proposed model c) and better detailed in Figure 5 in terms of reformer and SOFC interaction.

In a general context, the reactions to the reform are known and widely cited (Fiuza, 2005; Silva, 2005; Souza, 2005; Braga, 2014), which there are presented as the basis of the global reaction to the ethanol reform (with steam or water vapor) as Equation 1.

$$C_2H_5OH_{(g)} + 3\ H_2O_{(g)} \leftrightarrow 2CO_{2(g)} + 6H_{2_{(g)}} \tag{1}$$

The proportion of three mols of steam for one mol of ethanol corresponds to the best molar ratio between the reagents to optimize the obtaining of hydrogen (Silva, 2015). Also, Souza (2018) comments that it is important to note that ethanol should have very low sulfur rates because this can contaminate the reforming catalyst. Defined in stochiometric and energetic equilibrium (Moran and Shapiro, 2009) and Souza, 2018), the such global reaction can be dismembered according to:

- Steam Reforming Reaction - SRR:

$$C_2H_5OH_{(g)} + \ H_2O_{(g)} \leftrightarrow 2CO_{(g)} + 4H_{2_{(g)}} \rightarrow \ \Delta h^0_{298K} = 255{,}7\ \frac{kJ}{mol_{4H_2}} \tag{2}$$

- Water Gas Shift Reaction - WGSR:

$$2CO_{(g)} + 2H_2O_{(g)} \leftrightarrow 2CO_{2_{(g)}} + 2H_{2_{(g)}} \rightarrow \Delta h^0_{298K} = -82{,}3\ \frac{kJ}{mol_{2H_2}} \quad (3)$$

- The reaction of decompositions of ethanol to methane:

$$C_2H_5OH_{(g)} \leftrightarrow CO_{(g)} + CH_{4_{(g)}} + H_{2_{(g)}} \rightarrow \Delta h^0_{298K} = 49{,}6\ \frac{kJ}{mol_{H_2}} \quad (4)$$

- Reaction of *Bouduard*:

$$CH_{4_{(g)}} \leftrightarrow C_{(s)} + 2H_{2_{(g)}} \rightarrow \Delta h^0_{298K} = 75\ \frac{kJ}{mol_{2H_2}} \quad (5)$$

However, according to Figure 5 it is noted that the SRR reaction actually occurs in the reformer, and the WGS reaction is included in the simultaneous reactions in the anode.

According to Figure 4 (proposed model 'b'), the following electrochemical reactions are estimated:

- 1st Anodic Reaction: $4H_{2_{(g)}} + 4O^{2-}_{(g)} \rightarrow 4H_2O_{(g)} + 8e^- \rightarrow \Delta h^0_{298K} = -1964\ \frac{kJ}{mol}$ (6)
- 2nd Anodic Reaction: $2CO_{(g)} + 2O^{2-}_{(g)} \rightarrow 2CO_{2_{(g)}} + 4e^- \rightarrow \Delta h^0_{298K} = -1064\ \frac{kJ}{mol}$ (7)

Finally, the cathodic reaction (Equation 8) occurs concerning anodic reactions in the balance of chemical species.

$$3H_{2_{(g)}} + 12e^- \leftrightarrow 6O^{2-}_{(g)} \quad (8)$$

According to Bao et al. (2016a;2016b;2014) and O'Brien et al. (2012), the hydrogen oxidation reaction (1st anodic reaction, Eq. 6) presents a chemical kinetics 2.5 times faster and more favorable than the oxidation reaction of carbon monoxide (2nd anodic reaction, Eq. 7), thus making it more conducive to occurrence in terms of prevalence. Furthermore, the WGS reaction (Eq. 3), considering that there is the reagent $H_2O_{(g)}$ present (explained in Figures 2 and 4), also presents much faster kinetics compared to the 2nd anodic reaction (7) and possibly similar to the 1st anodic reaction (6). However, several factors influence the dynamics of these reactions such as catalyst material used, temperature (the higher, favors WGSR) and quantities of reagents.

From this study and observing Figure 4 (model C) it is exactly observed the mixing ratio of the CO/H_2 fuel in the proportion 25/75, in molar terms. In model D of Figure 4 and Figure 5 due to the excess production of H_2, the proportion between CO/H_2 is 33/64 in molar terms, considering the WGSR chemical equilibrium hypothesis. In terms of mass, the relationship between CO/H_2 tends to be greater than the CO component of this synthesis gas, which in theory, reinforces the occurrence of WGSR in order to guard against the possibility of the occurrence of the *Bouduard* reaction, regardless of the material to be adopted for the anode. Another relevant aspect observable in Figure 5 refers to the exothermic characteristic of the electrochemical reactions of hydrogen oxidation (1st anodic reaction), oxidation of carbon monoxide (2nd anodic reaction) and the WGS reaction, which corroborates heat transfer and cogeneration with the reformer reactor.

The fact that the reactions (Equations 2 and 3) of the reform are split between the reformer and the SOFC anode is justified precisely by the prevention of the reactions of decomposition of ethanol in methane, *the Bouduard* reaction (Equation 5), considering this harmful to SOFC, because it presents solid carbon which is adhered to the constituent material of the anode, impairing and subsequently hindering the correct operational functioning of the full anode. According to Souza (2018), there are suitable catalysts for the reform in the SRR (based on Radio and Nickel) which are not appropriate for WGSR, which would also justify the SSR reaction occurring in the reformer and WGSR in the SOFC anode. O'Brien et al. (2012) and Souza (2018) comments that the mere presence of $H_2O_{(g)}$ in the anode provides the prevention of *Bouduard's* reaction. Despite this, according to Dogdibegovic et al. (2021) in empirical experimental tests the nickel-based catalyst (Ni) used in the formulation Ni-$Sm_{0.20}Ce_{0.80}The_{2-\delta}$ (Ni-SDCN40), presents the lack of carbon deposit in an experiment of direct internal ethanol reform at SOFC, with this material as electrode-anode. Even so, the reformer's function is defined with the peculiarity that the complete consumption of the volume of ethanol occurs, producing 1 kg of $H_{2_{(g)}}$ and the respective volume of carbon monoxide $CO_{(g)}$. Thus, these species are drained to SOFC in the form of fuels, allowing the corresponding electrolytic reaction as demonstrated in Figure 5. According to Aguiar *et al.* (2004) and Souza (2018), SOFC fully accepts carbon monoxide as fuel which is considerable in order to consume this species in the whole process, since it is characterized by being a pollutant. Bao et al. (2016a) also comments that one of SOFC's considerable operational advantages is precisely the flexibility of fuels to be used.

3.3. **Mass Balance and Thermodynamic Analysis of Ethanol Reform**

The mass and energy balance begins from the chemical reaction SSR (Equation 2), considering the obtaining of 1 kg of hydrogen. Table 1 shows the respective mass balance of the chemical species.

Table 1: Mass Balance of the Reaction of Equation 2

Species Chemistry (Eq. 2)	Mass-Molar $\overline{M}\left[\frac{kg}{kmol}\right]$	Stochiometric coefficient	Mass m [kg] de of each species of 1 kg_{H_2}	n [$kmol$] corresponding to 1 kg_{H_2}	Specific volume $v\left[\frac{Nm^3}{kg}\right]$	Volume [Nm^3] of each species of 1 kg_{H_2}
1st Reagent: **Ethanol** $C_2H_5OH_{(g)}$	46.069	1	5.7145	0.1240	0.00124	0.0071
2nd Reagent: **Water** $H_2O_{(g)}$	18.015	1	2.2346	0.1240	0.0006432	0.0014
1st Product: **carbon monoxide** $CO_{(g)}$	28.01	2	6.9469	0.2480	0.8103	5.6291
2nd Product: **Hydrogen** $H_{2_{(g)}}$	2.016	4	**1.00** (Reference)	0.4960	11.2714	11.2714

Noted that from the reference value of $1\ kg_{H_2}$ as one of the products of the reaction, there are necessary reagents $5.7145\ kg_{C_2H_5OH_{(g)}}$ and $2.2346\ kg_{H_2O_{(g)}}$, the mass of $6.9469\ kg_{CO_{(g)}}$ is a complementary product of Equation 2. The mass-molar and volume-specific data highlighted in Table 1 are obtained respectively from Van Wylen et al. (1995) and EES®.

As already indicated in Figure 5, the reaction of Equation 2 is highly endothermic, obtaining $\Delta h^0_{298K} = 255{,}772.0\ \frac{kJ}{kmol}$ (variation of the formation enthalpy, configuring the heat necessary to perform the reaction), obtained from Equation 9 that uses the ambient reference (temperature of 25°C and pressure of 101.3 kPa).

$$Q_{reação} = Q_{Produtos} - Q_{Reagentes} = \left(2\overline{h}_{f_{CO_{(g)}}} + 4\overline{h}_{f_{H_{2(g)}}}\right) - \left(\overline{h}_{f_{C_2H_5OH_{(g)}}} + \overline{h}_{f_{H_2O_{(g)}}}\right) = 255{,}772\ \left[\frac{kJ}{kmol}\right] \quad (9)/(10)$$

Using the data provided in Table 1 it is observed $n_{H_2} = 0.496\ kmol$ that allows the calculation of the energy transferred or available from SOFC for the reform process, according to Equation 11.

$$Q_{SOFC \rightarrow Reform} = \frac{1}{4} 255{,}772 \left[\frac{kJ}{kmol}\right] \times 0.496\ [kmol] = 31{,}715.7\ kJ \quad (11)$$

Equation 11 refers to the heat required (or energy demand) for the production and obtaining of 1 kg of hydrogen for 1 mol de $H_{2_{(g)}}$, considering the reaction to the reform. For this ratio, Equation 11 is divided by the stoichiometric coefficient corresponding to the hydrogen species, according to Table 1.

Hence, based on the size of a 10" container it is possible to obtain the reformer with serial cylinders (catalytic beds) with cross-sectional diameters ranging from 5 mm to 25.4 mm, for example. As the sizing of the reformer is not the direct scope of this work, it is reasonably estimated in $200\ \frac{Nm^3}{h}$ as reference, however the productivity could be parameterized in $350\ \frac{Nm^3}{h}$, as a safety coefficient of the energy dimensioning which it becomes possible to estimate the time of 116 seconds, regarding the theoretical necessary period to produce $1\ kg_{H_2}$, as presented in Equation 12.

$$\Delta t_{\ 1\ kg_{H_2}} = \frac{Prod.Cap.}{v_{H_2}} \left[\frac{Nm^3}{h} \times \frac{kg}{Nm^3}\right] = \frac{350}{11.2714} = 31.05\ \left[\frac{kg}{h}\right] \times \frac{1}{3600} \left[\frac{h}{s}\right] \cong 0.0086\ \left[\frac{kg}{s}\right] \xrightarrow{1\ kg_{H_2}} 116\ s \quad (12)$$

Therefore, the result of Equation 12 corresponds to the theoretical period to obtain 1 kg of H_2 which $350\ \frac{Nm^3}{h}$ is the referenced as the productive capacity applied, becoming an important definition related to the productive mass flow of hydrogen to precisely model the energy flows between SOFC and the reformer.

From Equations 11 and 12 it is possible to determine the theoretical power of energy transfer between SOFC and Reformer, according to Equation 13.

$$P_{Reform\ 1\ kg_{H_{2(g)}}} = \frac{Q_{VC}}{\Delta t} \left[\frac{kJ}{s}\right] = \frac{31{,}715.7}{116} = 273.145\ kW \quad (13)$$

It is also necessary to define the heat transfer rate for the heat exchangers regarding the purpose of heating to vaporize ethanol and water previously pumped. Then drain into the reformer's container (catalytic bed of the reactor), according to Figure 5, corresponding in steps 2b and 2c.

As mentioned in section 3.2, the cells of type SOFC presents the property of BETAFC (Leal, 2003) that consists of the relationship between the electricity generated with the heat also generated, called as β_{FC}, and thus this relationship is established in Equation 14.

$$\beta_{FC} = \frac{\boldsymbol{Electricity\ Produced\ (EP)}}{\boldsymbol{Heat\ Generated\ (HG)}} \tag{14}$$

Considering the results of Table 2, as well as Boccaletti *et al*. (2006), quoting an experimental SOFC of $200\ kW$ that there is a plundering (or stack) of 20 units in series of the PEN set [electrode-**P**ositive→ **E**lectrolytic→ electrode-**N**egative; according to the denomination in Aguiar et al. (2004), Bao et al. (2016a) and Li et al. (2010)] which presents the feasibility of obtaining a SOFC with this need for an electrical generation with heat cogeneration. Camargo (2004) also cites practical examples of models with SOFC for electricity generation with $250\ kW$ operational power. Thus, it is determined the modelling of a SOFC that $\beta_{FC} = 0.42$ (as an estimate), providing $248.5\ kW_e$ electricity.

Table 2: Simulation of β_{FC} and EP (via Equation 15) from HG (Equation 13)

Heat Generated (HG)	β_{FC} *Suggested*	**Electricity Produced** (EP)
$590.35\ kW_T$ $\left(\underset{[Eq.13]}{273.15\ kW_{Ref}} + \underset{[Eq.14c]}{317.20\ kW_{Air}}\right)$	1.00	$590.35\ kW_e$
	0.50	$295.17\ kW_e$
	0.42	$\mathbf{248.50\ kW_e}$
	0.30	$177.10\ kW_e$
	0.15	$88.55\ kW_e$

It is also necessary to analyses the energy balance regarding the reactor of the reformer; considering that it is defined as the theoretical transfer of thermal energy of approximately $452\ kW$ from SOFC. Thus, theoretically the reaction of Equation 2 occurs respecting that Gibbs' free energy variation is zero [Silva (2005), Souza (2005), Braga (2014)], establishing a chemical equilibrium of the reaction, defining that the reagents are fully transformed into the products, as demonstrated in Equation 2. Equation 15 demonstrates this relationship.

$$\Delta G = \Delta H - T\Delta S \mid \Delta G = 0 \Longrightarrow T = \frac{\Delta H}{\Delta S} \tag{15}$$

Calculating, the equation 16 obtained the theoretical temperature necessary for Equation 2 of reform reactor.

$$T_{Reactor} = 570.67\ K\ (297.52\ °C) \tag{16}$$

According to Silva (2005), the temperature propriety implies the most significant influence of the reaction of Equation 2, considering that the degree of dissociation α stabilizes at the unit value exactly at 600 K. Regarding the pressure, this demonstrates physical property that does not favor the reaction of Equation 2, and therefore the ambient pressure is maintained (in theoretical terms, because depending on the configuration of the characteristics or proprieties of the fluid-mechanic, could be observed pressure gradients from convective acceleration, which is inherent to the variations in the cross-section of the flowing ducts, according to Panton, 2013).

Based on Silva *et al.* (2009) it applies Gibbs' free energy minimization method via Lagrange multipliers which establishes the temperature between 600 K to 700 K as the most suitable for maximized hydrogen production. It is observed, applying Equation 9, a positive variation of approximately 6% in the necessary heat, for the effectiveness of the reaction of Equation 2 in chemical equilibrium, adopting the temperature indicated. However, the ambient reference is adopted because it is fixed, considering the possibility of variation in the reactor's temperature.

4. **Results and Discussions**

4.1. **Energy Analysis of electrochemical reactions and WGSR**

Two functions of the free energy variation are possible to be obtained in order to comparatively evaluate the hypothetical situation in which there is only the occurrence of electrochemical anodic reactions (Equations 6 and 7) that the mass of $6{,}9469\ kg_{CO_{(g)}}$ from the reform, it would be totally consumed via oxidation of carbon monoxide, thus being the stochiometric balance different from the one expressed in Table 8. With that, Figure 7 defines the relationship between

temperature and Gibbs' free energy variation in the SOFC, established in kilowatts using the theoretical term, as expressed in Equation 12.

$$\Delta G^{SOFC^{EC}} = -632602 - T(-164{,}64) \tag{17a}$$

Observation in Figure 7, for only the EC (**e**lectro**c**hemical) reactions, it is noted that the theoretical temperature with the variation of Gibbs free energy, in the condition of chemical equilibrium, equal to zero (a requirement that all reagents become products of the reactions of Equations 6 and 7). It would be 3,842.33 K or 3,569.18°C which would make any equipment unfeasible because it is extremely high, making it difficult to apply functional materials at viable costs. However, it is also noted that a range between 900K, 1100 K and 1300 K would be the normal intervals, or even less, considering the SOFC at intermediate temperature (Aguiar et al. (2004)). From Equation 50a, based on Equation 16, it is noted that the part corresponding to enthalpy variation ΔH, specifically the anodic (and cathodic) 1st and 2nd reactions is negative. Denoting that such reactions characterized as exothermic, and thus contribute to the global increase in the temperature of SOFC, which is evaluated as beneficial since the excess production of thermal energy can be transferred to the reformer, enabling this cogeneration system.

From the same analysis, Equation 16, the function of variation of Gibbs free energy is based on the 1st anodic reaction, the 2nd anodic reaction and the WGS chemical reaction; and the 2nd anodic and WGS reactions have the distribution of carbon monoxide mass. Obtaining then, the Equation 17b, which is also inserted in Figure 5, establishes the relationship between Gibbs free energy variation in kilowatts and SOFC temperature.

$$\Delta G^{SOFC^{EC+WGS}} = -544670 - T(-141{,}70) \tag{17b}$$

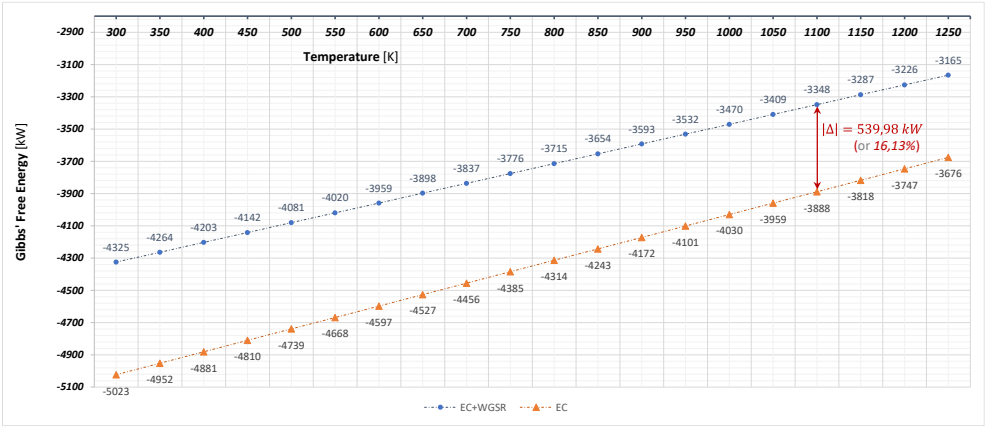


Figure 5: Gibbs Free Energy Variation by Temperature in SOFC (EC and EC+WGS reactions)

Comparing the graphs on both lines (EC: which has only the electrochemical oxidation reactions of hydrogen and carbon monoxide, and EC+WGSR: containing the same electrochemical reactions added of the WGSR), it is possible to verify a common point highlighted to both, referring to for example the temperature of 1100 K (826,85°C), in which the variation of Gibbs' free energy ΔG is, in absolutes-terms, under for the line containing the EC+WGS reactions which denotes the prevalence of WGSR in the anode concerning the reaction (equivalent to the 2nd anodic reaction), since the 1st anodic reaction is common to both scenarios, implies greater feasibility of achieving chemical balance for WGSR in relation than 2nd anodic reaction.

4.2. **SOFC Feasibility Analysis with hydrogen oxidation, carbon monoxide oxidation and WGSR for Heat and Electricity generation**

An analysis is expressed in Table 10, regarding the work and theoretical heat in 821.5 K obtained in SOFC's anode, compared than the Table 3 theoretical data of the minimum values of 248.50 kW of work and 590.35 kW of heat, with which the cogeneration of heat, electricity, and hydrogen (1 kg) between SOFC and reformer becomes operational. As explained in the Table 10 the value of 248.50 kW is adjusted to 465.84 kW. As the theoretical values of work and heat, being respectively 3691.41 kW and 4678.11 kW are higher than the minimum values demanded, in which 465.84 kW the required work represents 12.62% of the available theoretical work and 590.35 kW demanded heat, represents the same 12.62% of the theoretical work available.

In Table 10 a final data is needed, regarding the effective estimation of work and heat generated by the SOFC, because the values of the Maximum Theoretical Reversible are the theorical top amounts able to be reached as reversible process that in practical terms is not valid, being so the Maximum Theoretical Reversible work and heat just a numerical reference of the maximum capacity of the SOFC. Therefore, in order to determinate the effective estimation of work and heat, the

calculation is conducted using the almost of the equations demonstrated in section 3.4.2 and Table 6 (Appendix II), though in some case a data observed in literature review it is used as reference, as materials characteristics demonstrated in Table 3. The effective estimation reflects the electrical efficiency of 0.5 (referenced by Camargo, 2021). In Table 11, considering the size (area) of the PEN and the number of stacks.

Table 3: SOFC: comparison of Energy Demands: estimated with the minimum (Table 3) required

Energy demand	**Work** (Electricity generated)	**Heat** (generated)
Minimal Parity Required	465.84 kW	590.35 kW
Considerations for calculation:	*The Minimal Parity Required (MPR) is obtained using the Equations 13, 14c and 15 as also demonstrated in Table 3, being the work and heat respectively of* 248.50 kW *and* 590.35 kW*. However, those values were obtained considering the called* β_{FC} *(BETAFC, obtained in Table 3 as* $\beta_{FC} = 0.4209$*, and explained in Equation 15 and section 3.2), and as mentioned the conception of the* β_{FC} *is similar of the definition of the thermal efficiency (Equation 47b, previous obtained as* ${\varepsilon_T}^{EC+WGSR} = 0.7891$*). Based on, the value of work (electricity generated) is adjusted to* 465.84 kW *instead the previously* 248.50 kW *demonstrated in Table 3, applying then the* ${\varepsilon_T}^{EC+WGSR}$ *as obtained in Equation 47b as the* ${\beta'}_{FC} = 0.7891$ *(BETAFC adjusted). Although, the thermal energy of* 590.35 kW *maintain the same obtained in Table 3 and it represents the transferred thermal-energy from SOFC to Ethanol reformer (SRR) in order to obtain in that 1 kg of* H_2*, regarding the reformer temperature informed in Equation 17 and the residence time of Equation 12.*	
Maximum Theoretical Reversible	3,691.41 kW	4,678.11 kW
Considerations for calculation:	*Applying firstly the Gibbs free energy function (Equation 16) of the combined reactions 49a, 49b and 3 (respectively demonstrates in tables 7, 8 and 9 in terms of stoichiometric and mass balances) occurred in anode in the reference temperature of* 821.5 K*, the maximum theoretical reversible work and heat generated in SOFC are obtained secondly using the Equations 47a and 47b, regarding the additional definition that* $W_{out} = -\Delta G$ *and* $Q_{in} = -\Delta H$*.*	
Effective Estimation	1,658.12 kW	2,110.11 kW
Considerations for calculation:	*Referencing the section 3.4.2.1, applied Equation 23 and Equations (24↔27) does not used and inserted the data of referenced materials (Bao et al. [26], Nakashima [14], Aguiar et al. [16,17] and Ranjbar et al. [35]) considered empirical data for Ni-YSZ (Nickel with YSZ: yttria-stabilized zirconia) on the anode, YSZ-SDC (SDC: samaria-doped-ceria,* $Sm_{0.2}Ce_{0.8}O_{1.9}$*) in the electrolyte and LSC-SDC (LSC:* $La_{0.6}Sr_{0.4}CoO_{3-\delta}$*) in the cathode; regarding the characteristics as such as porosity (average pore radius), tortuosity and molar weight, especially considering diffusivity (binary, effective binary and Knudsen).* *Referencing the sections 3.4.2.2 and 3.4.2.3, applied the Equations: 28, 29a, 30, 31, 33.* *Referencing the section 3.4.2.4, applied the Equations: 34, 35c, 36, 37a, 38a, 39, 40, 41b, 43, 44.* *Referencing the section 3.4.2.5, applied the Equations: 45b, 46, 47a, 48b.*	

5. **Conclusions**

Reviewing, the results researched and concluded are based on a model proposed and designed as a compact system that produces hydrogen and electricity from Ethanol steam reforming allied to integration of a SOFC (fuel cell made of solid-oxide electrolyte membrane), assembled in fuel station regularly supplied with this biofuel that the fuel cell allows the supplying of heat to the reformer and hence, the reformer produces the fuel (syngas) to the SOFC.

The main novelty of this model proposed is establish a synergy with those devices (reformer and SOFC) in terms of own major characteristics: reform demands heat-energy and SOFC generates as byproduct heat-energy. Based on, the assumption of a feasible operational integration between ethanol reformer and SOFC is correctly attested, and so there is a valid possibility of a rapid improvement of the infrastructure in Brazil basis (or another place that offers ethanol as fuel, as for example exists in USA), for the future and carbon-free electrified automobiles fleet, offering for that hydrogen and electricity directly from fuel-stations.

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