Performance model of a Proton Exchange Membrane (PEM) fuel cell operating in steady-state conditions with Aspen HYSYS®

Angelo Di Domenico[a], Paolo Vitulli[b], Francesca Mennilli[a], Mosè Rossi[a], Gabriele Comodi[a]

[a] Marche Polytechnic University, Department of Industrial Engineering and Mathematical Sciences, Ancona, Italy, s1096334@studenti.univpm.it
[b] Marche Polytechnic University, Department of Information Engineering, Ancona, Italy, p.vitulli@pm.univpm.it
[a] Marche Polytechnic University, Department of Industrial Engineering and Mathematical Sciences, Ancona, Italy, f.mennilli@pm.univpm.it
[a] Marche Polytechnic University, Department of Industrial Engineering and Mathematical Sciences, Ancona, Italy, mose.rossi@staff.univpm.it, CA
[a] Marche Polytechnic University, Department of Industrial Engineering and Mathematical Sciences, Ancona, Italy, g.comodi@staff.univpm.it

Abstract:

Nowadays, Hydrogen is considered an important energy vector through which the decarbonization process can be carried out if it is produced by Water electrolysis using renewables. Then, Hydrogen is stored for performing medium- and long-term storage, which is suggested for those sources that face considerable electricity production variability throughout the days/months like renewables, and sent to Fuel Cells (FCs) for producing again electricity. The coupling of the electrolyzer, storage, and FC constitutes an integrated Hydrogen system. This work presents a model of a 5 kW-Proton Exchange Membrane Fuel Cell (PEMFC), which has been developed in Aspen HYSYS®, to evaluate its performance by varying its operating conditions (e.g., current density, temperature, and pressure). The simulation is based on the determination of a semi-empirical mathematical model of the electric potential related to a single 25 cm^2 cell through the regression of experimental data taken from the scientific literature. Normal Root Mean Square Errors (NRMSEs) were obtained by the comparison between the results of the electric potential model of the single cell and the experimental ones, showing a good agreement. The model developed in Aspen HYSYS® allows to predict the behaviour of the PEMFC by identifying the optimal conditions in terms of temperature and pressure. Results showed that the PEMFC performance improves by increasing the temperature up to 80°C, while it is not suggested to operate at pressure values higher than 3 atm due to a lower net electric power and overall system electric efficiency.

Keywords:

Aspen HYSYS®, Fuel cell modeling, Green Hydrogen, Proton Exchange Membrane Fuel Cell.

1. Introduction

In recent years, the issue of environmental sustainability has become increasingly important. Problems related to both pollution and global warming led the international community to pay more attention to the research of new technologies for energy production through the exploitation of renewable sources. In the context of the ecological transition, Hydrogen can play a fundamental role; indeed, governments and companies have focused on this type of chemical element to further contribute to the decarbonization process. Hydrogen is an energy carrier, and it has a higher energy density than fossil fuels. Because of its properties, it represents a valid solution for energy storage and production; in the latter case, Fuel Cells (FCs) use Hydrogen to produce electricity without pollutant emissions.

Nowadays, FCs have considerable attention as they constitute the key technology for further deploying this type of energy carrier [1]. Among the different types, Proton Exchange Membrane Fuel Cells (PEMFCs) are

https://doi.org/10.52202/069564-0100

mostly applied in automotive and small stationary applications due to their high electric efficiency, power density, and reliability. In a PEMFC, the fuel is Hydrogen that reacts with the Oxygen contained in the air to generate electricity, Water, and heat. Electrochemical reactions as well as the transport of ions, electrons, energy, and species in gas and liquid phases across a heterogeneous media are involved. However, this technology is currently developing to further increase its efficiency and applicability ranges, especially when dealing with cogeneration purposes in both residential and industrial sectors [2-4].

To better understand the phenomena behind the operation of FCs, several experiments have been carried out so far and interesting results have been already reported in the scientific literature; however, numerical models aiming to resemble the behaviour of FCs, according to their typology, would fasten and further contribute to the development of this technology, being less time consuming and less economically demanding as well. Among the most known simulation environments, Aspen Technology® is one of the most used since it allows to easily design, manage, and integrate several parts of a system in one macro-system as well as provide preliminary data of how it would run. In this regard, Beheshti et al. [5] developed an Aspen Plus® model to simulate the behavior of an integrated gasification system with a PEMFC stack by coupling the Aspen Plus® software with dedicated FORTRAN subroutines. Effects of critical parameters (e.g., current density, feed gas humidity, equivalence ratio, steam/biomass ratio, and biomass moisture content) on the cell potential and gasification efficiency have been discussed. Results showed that a higher feed humidity at the cathode side is more favorable for the improvement of the voltage output, while the biomass moisture content has a negative impact on the cell potential. Barelli et al. [6] studied a micro-cogeneration Combined Heat and Power (μCHP) energy system based on a PEMFC to evaluate both the performance and energy/economic feasibility of the system to fulfil the thermal and electrical demands of apartments. A zero-dimensional model of the PEMFC has been developed in Aspen Plus® and simulations at different operating conditions have been carried out. Subsequently, optimal operating conditions of the PEMFC have been identified; in particular, these operating conditions have been obtained by fixing constraints to the electricity production/supply as well as to the return temperature and pressure of hot Water at 105 °C and 2 atm, respectively. Zuliani et al. [7] carried out a performance analysis of a 1 kW-High Temperature PEM Fuel Cell (HT-PEMFC). The performance of this FC has been predicted through a zero-dimensional, semi-empirical model implemented in FORTRAN and subsequently integrated into Aspen Plus®. The aim of the work was to perform an energy analysis to investigate how the system operates at partial load operating conditions and assess the difference with Low-Temperature PEM Fuel Cell-based (LT-PEMFC) systems. Results showed that a more reliable balance of plant is obtained with HT-PEMFCs than LT-PEMFCs, while the system efficiency is unchanged.

To the authors' knowledge, as also previously discussed, there are several models of FCs in Aspen Plus® available in the scientific literature, but no references have been found on PEMFCs modeling with Aspen HYSYS®. Aspen Plus® is mostly used with fine chemistry, general chemistry, electrolytes, and polymer modeling, while Aspen HYSYS® is devoted to resemble petrochemical refining, oil assays, and all related industries, thus having wider use in chemical applications. Thus, the modeling of a PEMFC block in this kind of environment can be of interest to those researchers/scientists that would like to use this specific model in a more complex chemical system since it would be easier to be embedded.

This work consists of the development of a numerical model in Aspen HYSYS® related to a stack of a 5 kW-Proton Exchange Membrane Fuel Cell (PEMFC), whose experimental data are available in [8], to study its behaviour by changing its operating conditions (e.g., current density, temperature, and pressure). In particular, the model could be considered as a starting point for then applying an optimization procedure to optimally manage the electricity production of PEMFCs according to a specific load trend. The paper is structured as follows: Section 2 presents the used methodology to analytically model the FC stack, as well as provides an overview of the Aspen HYSYS® model [9]. Section 3 is devoted to the results obtained from the simulations at different operating conditions (e.g., current density, temperature, and pressure). Finally, Section 4 reports the conclusions of the work.

2. Methodology

The models that describe the behaviour of a FC by varying the operating conditions (e.g., current density, temperature, and pressure) typically include the analysis of the following quantities: i) electric potential, ii) net electrical power generation, iii) electrical efficiency, and iv) heat power production. The present analysis has been carried out by considering the experimental data of [8]. The regression of the experimental data allowed to develop a model to predict the performance of the analysed PEMFC. After the validation of the numerical results with the experimental ones, the characteristics of the PEMFC (e.g., dimensions and the number of cells) have been scaled up to analyse the performance of the same PEMFC having a power output of 5 kW. This FC has a stack consisting of 72 cells in series, each of them having an area of 196 cm^2. The modelling of

https://doi.org/10.52202/069564-0100

the PEMFC involves mathematical relationships, thus resulting from empirical or semi-empirical analyses. Figure 1 shows the block diagram that sums up the eight steps used in the present methodology to carry out this study. It is worth noting that some of these steps have been performed in parallel and, for this reason, they have been placed in the same row.

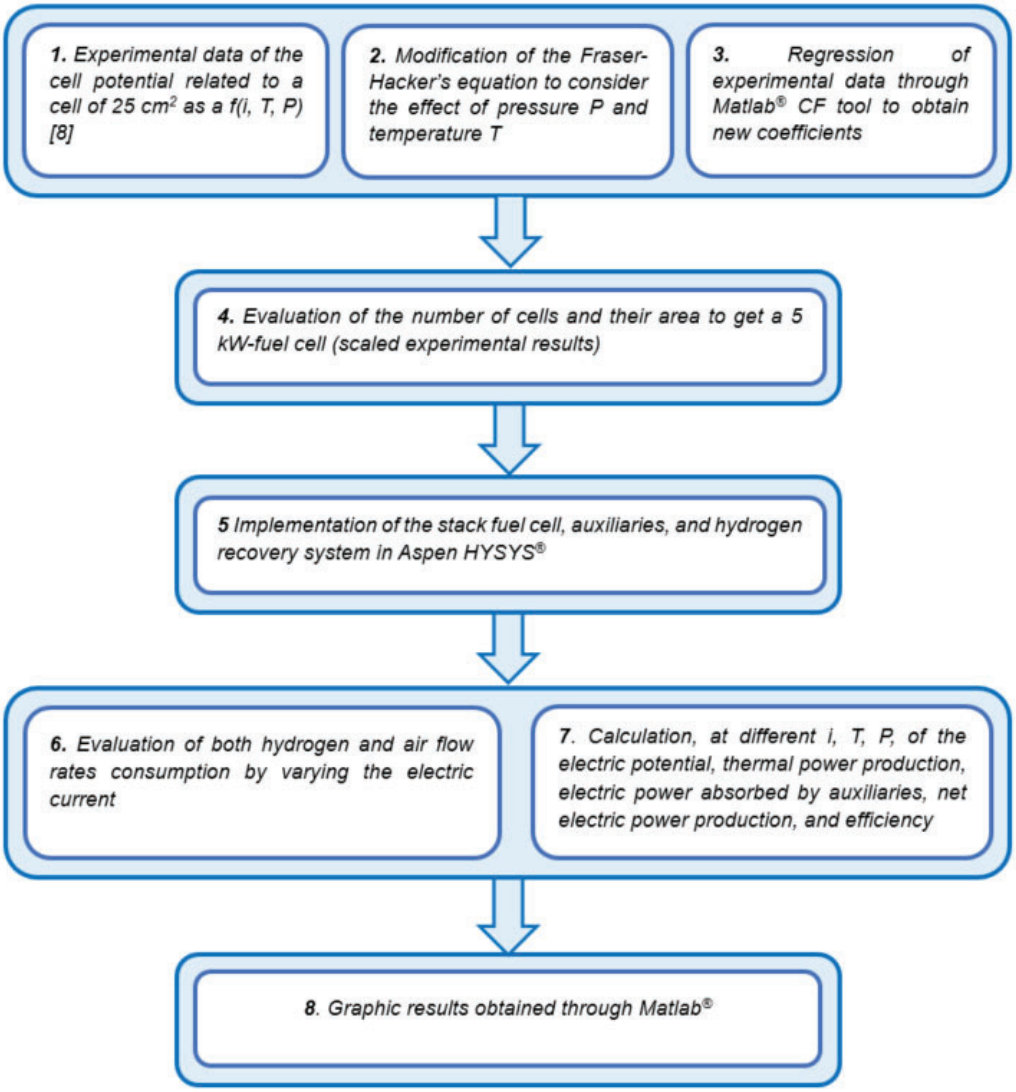


Figure 1. Block diagram with the eight steps used in the present methodology.

The polarization curve that describes the relationship between the output voltage and the current density is a good indicator of the FC performance. The most known semi-empirical fuel cell model to draw up the trend of the electric potential as a function of the current density is Fraser-Hacker's one [10], which is reported in Eq. 1:

$$E_{cell} = E_{rev} - b \cdot log\left(\frac{i+i_{int}}{i_0}\right) - R \cdot i - m \cdot e^{(n \cdot i)} \quad (1)$$

where E_{rev} [V] is the reversible cell voltage and it is computed as a function of the cell temperature and the partial pressures of the active species according to the Nernst's equation, *b* [V] is the charge transfer overvoltage fitting parameter (V), i_{int} and i_0 [A·cm^{-2}] are charge transfer overvoltage fitting parameters, *R* [Ω·cm^2] represents the Ohmic overvoltage fitting parameter, *m* and *n* are mass transport overvoltage fitting parameter [10] that represent the mass transport limitations and the rapid decrease of *E* while increasing *i*, respectively. The reversible thermodynamic voltage E_{rev} is calculated from the modified Nernst's equation that considers both temperature and pressure dependence [11]:

$$E_{rev} = E^0 \cdot \frac{\Delta \hat{s}}{n_e \cdot R}(T - T_0) - \frac{R_g \cdot T}{n \cdot F} \cdot ln\left(\frac{a_{H_2 0}}{a_{H_2} \cdot a_{02}^{1/2}}\right) \quad (2)$$

where E^0 is equal to 1.229 V and it is the standard-state reversible cell voltage, Δŝ is the reaction entropy (assuming that it is independent of the temperature and it is equal to -163.28 J·mol^{-1}·K^{-1}), R_g is the universal constant of the gases (8.314 J·mol^{-1}·K^{-1}), *n* is the number of electrons transferred in the chemical reaction (2 mol_{e^-}/mol_{H2}), *F* is the Faraday's constant (96,485 C/mol), a_x is the activity of *x* that for an ideal gas becomes $a_x = p_x/p_O$ (where p_x is the partial pressure of *x*, p_o is the standard pressure of 1 atm [11].

It is possible to substitute the constants in Eq. 2 so that the reversible voltage can be also described as a function of both temperature and pressure:

$$E_{rev} = 1.229 - 8.46 \cdot 10^{-4}(T - 298.15) - 4.31 \cdot 10^{-5} \cdot T \cdot ln\left(\frac{1}{p_{H2} \cdot p_{O2}^{1/2}}\right) \quad (3)$$

Fraser-Hacker's equation (Eq. 1) considers only the dependence of the electric potential on the current density [7]. An important step of the present work was the modification of Fraser-Hacker's equation to consider the dependence of the electric potential, as well as the current density, temperature, and pressure. The modified equation is the following:

$$V = E_{rev} - \left(b_t + b_p\right) \cdot log\,10\frac{\left(i + i_{lt} + i_{lp}\right)}{\left(i_{0t} + i_{0p}\right)} - \left(r_t + r_p\right) \cdot i - \left(m_t + m_p\right) \cdot e^{[(n_t + n_p) * i]} \quad (4)$$

where the parameters with the subscript *t* indicate that they are temperature dependent, while those with the subscript *p* indicate that they are pressure dependent. The dependence of each parameter on both temperature and pressure was derived through the regression of the experimental data of [8], and it has been carried out with the Matlab® Curve Fitting Tool.

The process simulation of the entire system has been developed using Aspen HYSYS® [9]. Regarding the implementation of the model, it is required to identify both involved elements and chemical compounds, the components of the PEMFC, and the methodology to calculate the thermophysical properties of the streams. The selected fluid package is the "*Peng-Robinson*" one [9]. The oxidation-reduction reaction is defined as a *"Conversion reaction"* that takes place in the conversion reactor (CRV-100, see Figure 2), which constitutes the electrode. The mixture of Hydrogen and Oxygen, called reaction gas, is sent to the second component that acts as a membrane (X-100, see Figure 2) and it is capable of perfectly separating the excess of Hydrogen that has not reacted and then recirculating towards the *Mixer*. Based on the thermodynamic operating conditions in terms of both temperature and pressure, the spreadsheet evaluates the value of the main electrochemical and thermochemical equations that define the reaction products and the electrical power produced. Through the spreadsheet, the equations that allow to calculate the fundamental outputs of the model have been implemented such as the stack electric potential, the electrical power produced, the electrical efficiency, and the thermal power to be disposed of. Other relationships have also been implemented such as Faraday's equation (5) for calculating the flow rate of Hydrogen consumed $\dot{n}_{H_2}$ as a function of electric current *I*.

$$\dot{n}_{H_2} = \frac{I \cdot N_{cell}}{2 \cdot F} \quad (5)$$

https://doi.org/10.52202/069564-0100

where N_{cell} is the number of cells that constitute the stack and F is Faraday's constant, equal to 96,485 C/mol.

The stack electric potential V_{stack} is implemented in the spreadsheet starting from Eq. 4. Eq. 3 is preferred to calculate the reversible potential for ease of implementation. Eq.s 3 and 4 refer to the cell potential, thus to obtain the stack potential the number of cells in series is multiplied by the cell potential. The calculation of the electric potential allows the calculation of the other variables of interest. The net electric power of the PEMFC, $\dot{W}_{el}$, is calculated as the product of its electrical voltage and the electric current minus the electric power required by the air compressor, $\dot{W}_{ac}$. It is worth noting that the electric power of the air compressor is calculated by Aspen HYSYS® and depends on both the pressure ratio and the Hydrogen flow rate. The air compressor allows to maintain the air pressure in the stack equal to that of the Hydrogen, as well as to maintain a stoichiometric ratio between the anode and the cathode.

$$\dot{W}_{el} = \dot{V_{stack}} \cdot I - \dot{W}_{ac} \tag{6}$$

The electric efficiency η_{el} is expressed as the ratio of the net electric power generated by the FC, $\dot{W}_{el}$, and the product between the Lower Heating Value (LHV) of Hydrogen and its molar flow $\dot{n}_{H_2}$ as described in Eq. 5:

$$\eta_{el} = \frac{\dot{W_{el}}}{LHV_{H_2} \cdot \dot{n}_{H_2}} = \frac{V_{stack}}{V_{LHV}} \tag{7}$$

The generated heat power that has to be disposed of $\dot{Q}$ depends on the difference between the thermoneutral potential of the reaction V_{LHV} and the electric stack potential. *T*he thermoneutral potential is related to the Hydrogen Lower Heating Value (LHV) and it is equal to 1.25 V.

$$\dot{Q} = (V_{LHV} - V_{stack}) \cdot N_{cell} \cdot I \tag{8}$$

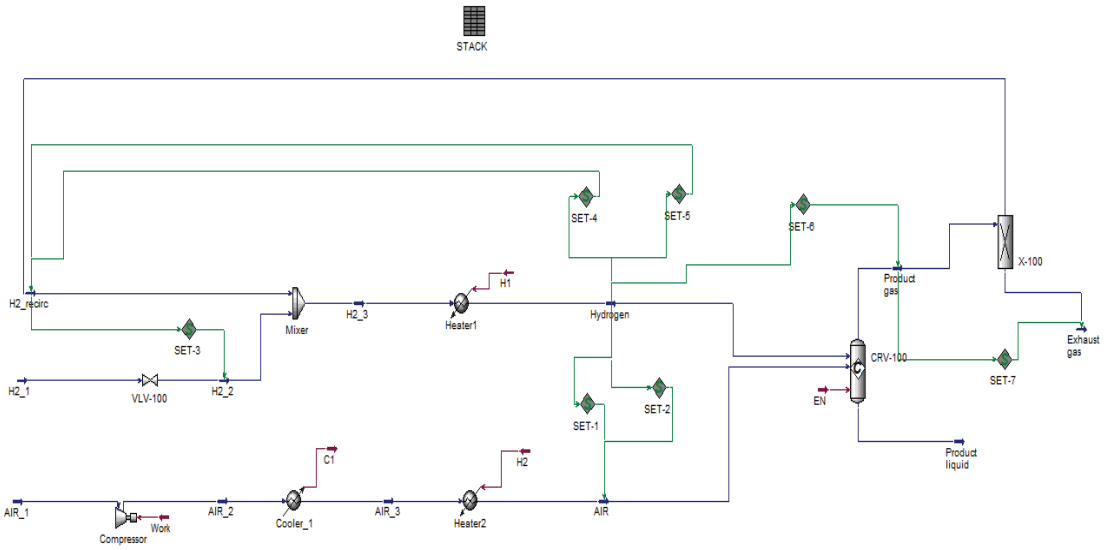


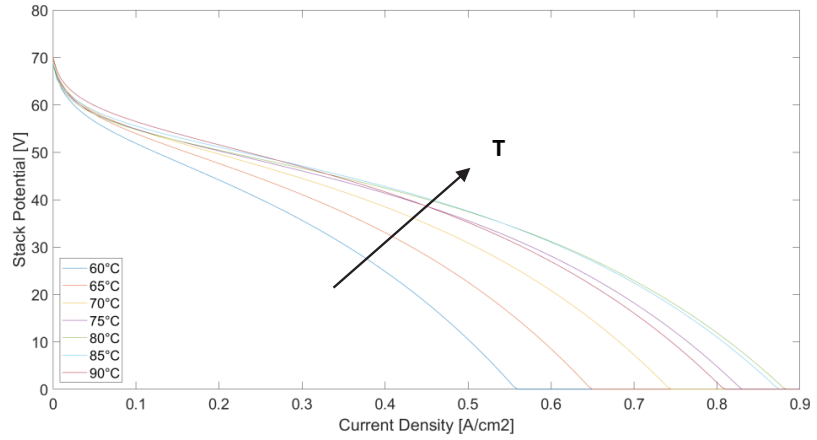
Figure 2. Model of a PEMFC developed in Aspen HYSYS®.

The trends of the performance variables such as temperature, pressure, and current density variation have been obtained by setting up “for cycles” in Aspen HYSYS® called “nested case studies”, which allow to study the trend of multiple dependent variables as a function of multiple independent variables. The numerical results of the analysis were processed in Matlab® to obtain the graphs shown in the next section.

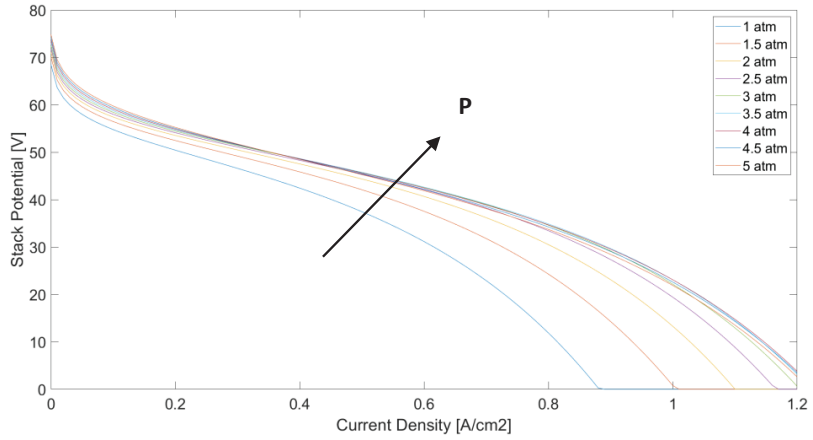
https://doi.org/10.52202/069564-0100

3. Results and comments

The results of the PEMFC performance are evaluated as a function of the current density (range of 0-0.9 A/cm^2), and they depend either on the temperature (range of 60-90°C with steps of 5°C) or the pressure (range of 1-5 atm with steps of 0.5 atm). Precisely, Figure 3, Figure 4, Figure 5, and Figure 6 show the stack electric potential curve, the electric power curve, the electric efficiency curve, and the produced heat trend, respectively.



a)

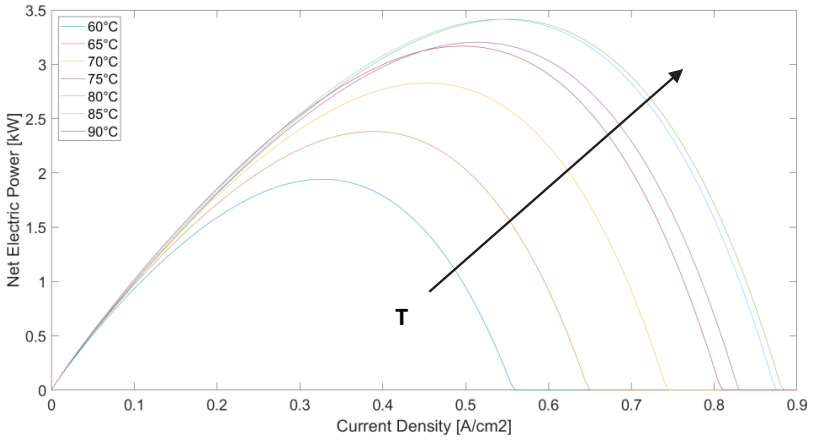


b)

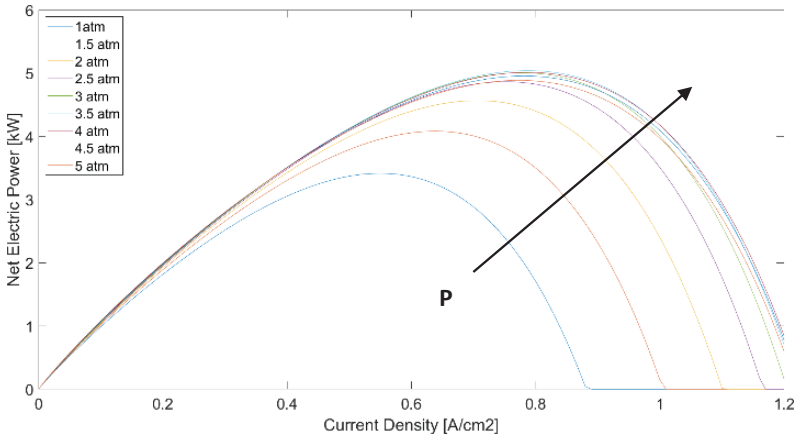
Figure 3. (a) The electric stack potential as a function of both the current density and the temperature (pressure equal to 1 atm), and of (b) both the current density and the pressure (temperature equal to 80°C).

The results confirm the positive effect on the stack performance of increasing both the temperature and the pressure. Figure 3a highlights that the performance of the FC improves while increasing the temperature up to 80°C; beyond this value, it starts to lower due to membrane hydration issues linked to a decrease of the relative humidity in the reaction environment. Polarization curves at different operating pressures show that the performance improves while increasing the pressure (see Figure 3b). The polarization curves undergo a positive increase while increasing the pressure as it produces high partial pressures of the reactants near the electrodes, thus improving the transport phenomena and the solubility of gases in the electrolyte as well.

https://doi.org/10.52202/069564-0100



a)



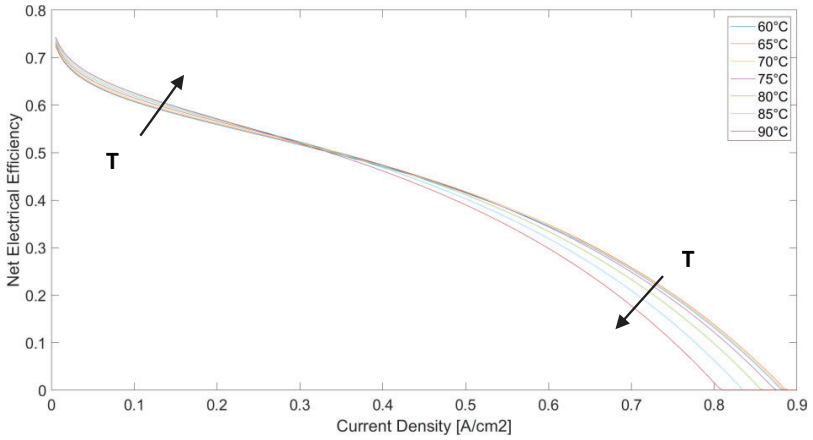
b)

Figure 4. (a) The net electric power as a function of both the current density and the temperature (pressure 1 atm) and of (b) both the current density and the pressure (temperature 80°C).

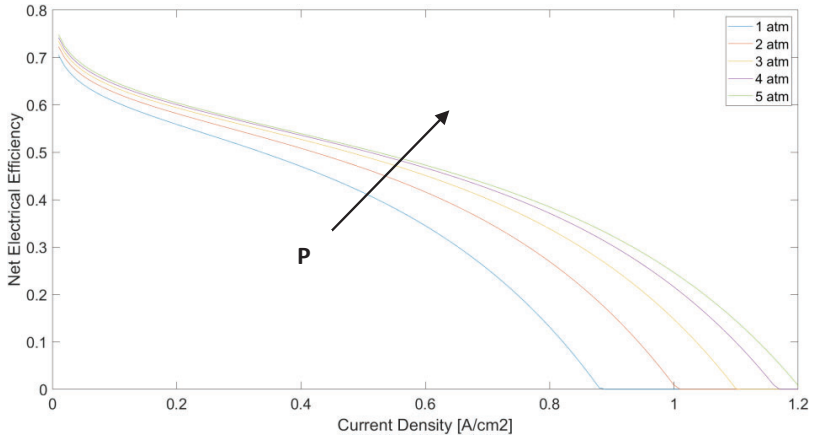
As it can be noticed in Figure 4a, the net electrical power of the stack improves while increasing the temperature up to 80°C, and then decreases due to the lower electrical potential caused by hydration problems. The net electric power also shows an initial increase with the current density (range 0-0.3 A/cm^2), while it starts to decrease afterward due to the prevalence of the effects due to overvoltage losses.

Figure 4b shows the same trend while changing the operating pressure of the fuel cell, being almost unchanged with pressure values equal to or greater than 3 atm; indeed, higher pressures make the energy power of the compressor increase, thus balancing the electrical production and keeping fixed the net electric power at a constant value.

https://doi.org/10.52202/069564-0100



a)

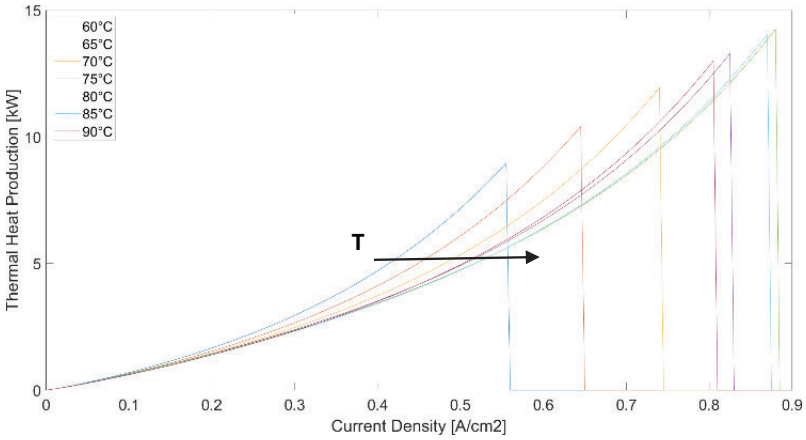


b)

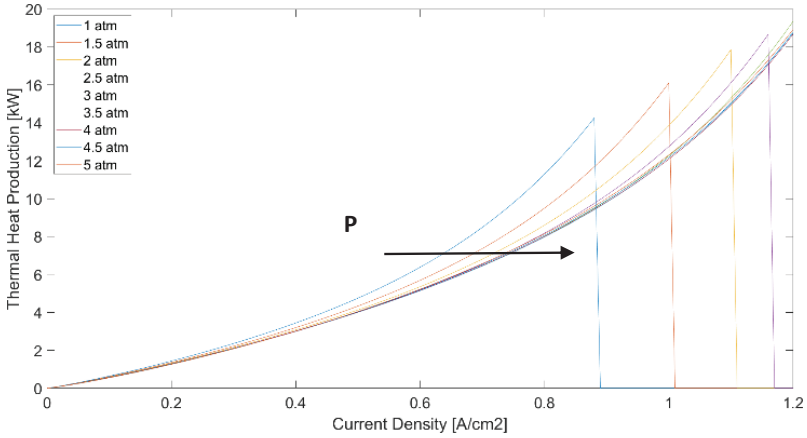
Figure 5. The net electric efficiency as a function of both the current density and the temperature (pressure of 1 atm), and (b) both the current density and the pressure (temperature of 80°C).

Figure 5 shows that the trend of the net electric efficiency depends on the electric potential as it is the result of the ratio between the latter and the thermoneutral potential referred to the LHV, which it can be considered constant in the analysed temperature and pressure ranges.

https://doi.org/10.52202/069564-0100



a)



b)

Figure 6. (a) The thermal heat production as a function of both the current density and the temperature (pressure of 1 atm), and (b) both the current density and the pressure (temperature of 80°C).

Figure 6 shows an increase in the thermal power while increasing the current density. As it can be noticed, although the curves seem to drop down sharply toward zero beyond certain current density values, the jump in thermal power production depends on the lack of data available from [8]. The thermal power production decreases while increasing the temperature due to the higher electric potential; however, it increases with temperatures higher than 80°C. The thermal power production, considering the same current density values, decreases as the pressure increases due to the increase of the electric potential.

4. Conclusions

The present work shows the development of a PEMFC model with Aspen HYSYS® to evaluate its performance in terms of electrical potential, net electric power, electric efficiency, and thermal power production by changing its operating conditions in terms of current density, temperature, and pressure. The semi-empirical model developed by modifying Fraser-Hacker's equation showed a good agreement with experimental data taken from [5]. Aspen HYSYS® has proved to be a valid tool to simulate FCs, thus allowing to evaluate the performance of a 5 kW-PEMFC under different operating conditions, starting from the mathematical model developed for the single cell.

https://doi.org/10.52202/069564-0100

Results confirmed the positive effect on the FC stack performance by increasing both temperature and pressure. Indeed, the performance of the FC improves with increasing temperatures up to 80°C; beyond this value, it lowers mainly due to membrane hydration issues. Furthermore, the performance improves with increasing pressure as it enhances the transport phenomena and the solubility of gases in the electrolyte. Consequently, the net electrical power of the stack improves with increasing temperatures up to 80°C, while it decreases due to hydration problems. Regarding the influence of pressure, a pressure equal to or greater than 3 atm leads to higher energy consumption of the air compressor and thus to a lower net electric power and overall system electric efficiency. Regarding thermal power production, the increase of both temperature and pressure leads to its decrease due to a higher electric potential.

The simulation of the PEMFC performed with Aspen HYSYS® allowed to make other evaluations that have not been reported here. A further step of the work could be the coupling of this system with the models of both the electrolyzer and the storage system to form an integrated Hydrogen system, which can provide flexibility to the current electric network increasingly fed by renewables.

References

[1] Andrew Dicks, James Larminie, *Fuel Cell Systems Explained*, II Edition, John Wiley & Sons Ltd, The Atrium, Southern Gate, Chichester, West Sussex PO19 8SQ, England, 2003, ISBN 0-470-84857-X.

[2] Adam Weber, Sivagaminathan Balasubramanian, Prodip Das, Chapter 2 - Proton Exchange Membrane Fuel Cells, Advances in Chemical Engineering, 41, 2012, 65-144, https://doi.org/10.1016/B978-0-12-386874-9.00003-8.

[3] Yun Wang, Daniela Fernanda Ruiz Diaz, Ken Chen, Zhe Wang, Xavier Cordobes Adroher, Materials, technological status, and fundamentals of PEM fuel cells - A review, materialstoday, 32, 2020, 178-203, https://doi.org/10.1016/j.mattod.2019.06.005.

[4] Horng-Wen Wu, A review of recent development: Transport and performance modeling of PEM fuel cells, Applied Energy, 165, 2016, 81-106, https://doi.org/10.1016/j.apenergy.2015.12.075.

[5] S. M. Beheshti, H. Ghassemi, R. Shahsavan-Markadeh, An advanced biomass gasification-proton exchange membrane fuel cell system for power generation, Journal of Cleaner Production, 112, 2016, 995-1000, https://doi.org/10.1016/j.jclepro.2015.05.106.

[6] L. Barelli, G. Bidini, F. Gallorini, A. Ottaviani, An energetic-exergetic analysis of a residential CHP system based on PEM fuel cell, Applied Energy, 88(12), 2011, 4334-4342, https://doi.org/10.1016/j.apenergy.2011.04.059.

[7] Nicola Zuliani, Rodolfo Taccani, Microcogeneration system based on HTPEM fuel cell fueled with natural gas: Performance analysis, Applied Energy, 97, 2012, 802–808, https://doi.org/10.1016/j.apenergy.2011.12.089.

[8] Qiangu Yan, H. Toghiani, Heath Causey, Steady state and dynamic performance of proton exchange membrane fuel cells (PEMFCs) under various operating conditions and load changes, Mississippi State University, United States, 2006.

[9] Aspen Technology, Aspen HYSYS Property Packages Overview and Best Practices for Optimum Simulation.

[10] Viktor Hacker, An empirical fuel cell polarization curve fitting equation for small current densities and no-load operation, Journal of Applied Electrochemistry, Graz University of Technology, April 2008.

[11] Dong Hao, Jianping Shen, Yongping Hou, Yi Zhou, and Hong Wang, *An Improved Empirical Fuel Cell Polarization Curve Model Based on Review Analysis,* Hindawi Publishing Corporation International Journal of Chemical Engineering, Volume 2016, Article ID 4109204.

 https://doi.org/10.52202/069564-0100