Abstract

In this paper, an exergoeconomic analysis of a PEM fuel cell using a styrene ethylene propylene styrene (seps) copolymer synthetized membrane was performed. The calculations were done on typical fuel cell operating voltages in order to determine their effects on the exergetic efficiency and cost of the fuel cell. Regression models were found for destroyed exergy, exergetic efficiency and exergetic cost with $R^2$ of 0.99, 0.98 and 0.99 respectively. The results showed a maximum efficiency of 32% and the minimum exergy cost of the fuel cell was 30 $/GJ$. Furthermore, lower capital cost of the fuel cell, annual O & M cost and hydrogen cost could contribute to a reduction in the exergy cost. Thus, a significant improvement in the overall process could be achieved.

Keywords: PEM fuel cell, destroyed exergy, exergetic efficiency; exergetic cost; exergoeconomics

Introduction

In recent years, more than 80% of the world's energy needs have been covered by
energy transformations based on fossil fuels, being oil, coal and natural gas the most commonly used sources [1]. Over population and excessive use of these fuels are responsible for environmental pressures as global warming, oceans acidification, damage to health, etc [2]. Facing this global scenery of energy insufficiency and environmental problems, researchers have been developing other types of alternative energies that adjust to actual necessities to improve the quality of life, reduce costs, etc. One of these alternatives are the proton exchange membrane fuel cells (PEMFC), which are devices that use the chemical energy of a fuel, in a clean and efficient way to produce electrical energy with little or no CO₂ production [3]. A PEMFC consists of two electrodes (anode and cathode), which are composed of bipolar plates and current collector plates. Sandwiched between these is the membrane electrode assembly (MEA), as shown in Fig. 1 [4]. The MEA is typically composed of five layers, two gas diffusion layers (GDL), two catalyst layers, and an ion conductive membrane in the middle, that in this research was previously synthetized in laboratory using seps copolymer.

![Fig.1. PEMFC diagram](image)

In nowdays, scientists have reached the knowledge for the synthesis of different membranes and other parts of fuel cells, in order to reduce the cost of production and operation of these equipments [5]. However, the thermodynamic study of cell performance has been left out, which is the objective of this article. The exergoeconomic analysis is based on the application of the second law of thermodynamics and economic analysis to a process. The second law has proved to be a powerful tool for the optimization of industrial systems and the exergoeconomics allows to transform the losses of energy into money, which is a decisive factor in any industrial process [6]. The aim of this study is to develop an exergoeconomic analysis to determine the exergetic efficiency and the exergetic cost of a fuel cells at established operating conditions.

**Methodology**

**Fuel cell Test**

A 25 cm² active area lab-scale fuel cell designed and constructed was used to run the different experiments. Each electrode, the anode and cathode each consists of a
base, current collector plate, bipolar plate and gaskets. The bases, constructed of aluminum 6061, are the main structure used to fasten the fuel cell together. The bipolar plates are fabricated from graphite, which has good chemical stability, strength, and electrical conductivity as well as relatively low cost. The polymer membrane was synthesized from seps copolymer, which was previously sulfonated during 2 hours and loaded with 2% of TiO₂. The anode and cathode electrodes of 5 cm x 5 cm, have 20% of Platinum in Coal and the diffusing layers had a dimension of 5 cm x 5 cm. Hydrogen and air were fed to the fuel cell with volumetric flows of 0.1341 L • min⁻¹ and 0.3619 L • min⁻¹. Condition were measured over a range of current densities (0.1 - 1.0 A/cm², stepping every 0.1 A/cm²).

Mathematical exergy models
The exergetic efficiency of a cell as shown in Fig. 2, is the relationship between the output work (\(\dot{W}\)), divided by the difference of exergy between the reactants and the products, which may be calculated by equations (1) and (2):

![Exergy diagram of a pem fuel cell](image)

\[
\varepsilon = \frac{\text{Electrical output}}{(\text{Exergy})_R - (\text{Exergy})_P} \quad (1)
\]

\[
\varepsilon = \frac{\dot{W}}{(E_{\text{air}, R} + E_{\text{H}_2, R}) - (E_{\text{air}, P} + E_{\text{H}_2O, P})} \quad (2)
\]

where \(E_{\text{air}, R}, E_{\text{H}_2, R}, E_{\text{air}, P}, E_{\text{H}_2O, P}\) are the total exergy of reagents (air and fuel) and air and water as products respectively. Assuming negligible kinetic and potential energy in the fuel cell, the total transfer of exergy per unit mass for each reactant and product consists of the sum of physical and chemical exergy. Physical exergy is associated with the temperature and pressure of the reagents and products of the fuel cell. Mathematically it may be described as:

\[
e^{PH} = (h - h_o) - T_o (s - s_o) \quad (3)
\]

where \(h_o, s_o\) are enthalpy and entropy evaluated at standard conditions, respectively. Considering involved gases as ideals, the physical exergy may also be expressed as:
\[ e^{PH} = C_p T_o \left[ \frac{T}{T_o} - 1 - \ln \left( \frac{T}{T_o} \right) + \ln \left( \frac{P}{P_o} \right)^{k-1} \right] \quad (4) \]

The chemical exergy is related to the deviation of the composition of the system and its surroundings. For simplicity, the exergy will be calculated at standard conditions \( T_o = 298K \) and \( P_o = 1 \text{ atm} \). The chemical exergy of produced air may be calculated in terms of the mole fraction of each component in the mixture (\( x \)) using the following equation:

\[ e^{CH} = \sum x_n e_n^{CH} + RT_o \sum x_n \ln x_n \quad (5) \]

where \( e_n \) is the standard exergy and \( x_n \) the fraction of components in every stream [7].

Depending on the output power (\( W \)), the voltage of cell (\( V \)), the stoichiometric ratio of air, the mass flow of reactants and products may be easily calculated using the equation used by Larminie and Dicks [8]. First the value of \( \lambda \) must be calculated using the following equation:

\[ \lambda = \frac{\text{O}_2 \text{ mols}}{\text{H}_2 \text{ mols}} \]

The air and fuel mass flows may be evaluated by the following equations:

\[ \dot{m}_{\text{air}, R} = 3.57 \times 10^{-7} \left( \frac{\lambda W}{V} \right) \quad (7) \]

\[ \dot{m}_{\text{H}_2 R} = 1.05 \times 10^{-8} \left( \frac{W}{V} \right) \quad (8) \]

The mass flow of produced air is the difference between the initial oxygen and the consumed oxygen by the reaction with hydrogen to produce water, so:

\[ \dot{m}_{\text{air}, P} = 3.57 \times 10^{-7} \left( \frac{\lambda W}{V} \right) - 8.29 \times 10^{-8} \left( \frac{W}{V} \right) \quad (9) \]

The flow of produced water can be calculated by the expression:

\[ \dot{m}_{\text{H}_2O, P} = 9.34 \times 10^{-7} \left( \frac{\lambda W}{V} \right) - 8.29 \times 10^{-8} \left( \frac{W}{V} \right) \quad (10) \]

Total exergy of the reactants and products can be determined using the following equations, where mass flows and exergies equations (3) to (10) were replaced:

\[ \dot{e}_{\text{H}_2 R} = \dot{m}_{\text{H}_2 R} e_{\text{H}_2 R} = \dot{m}_{\text{H}_2 R} (e^{CH} + e^{PH})_{\text{H}_2 R} \quad (11) \]
\[ P_{\text{air,R}} = m_{\text{air,R}} e_{\text{air,R}} = m_{\text{air,R}} (e^{CH} + e^{PH})_{\text{air,R}} \]  
\[ (12) \]
\[ \dot{E}_{\text{H}_2O,P} = \dot{m}_{\text{H}_2O,P} e_{\text{H}_2O,P} = \dot{m}_{\text{H}_2O,P} (e^{CH} + e^{PH})_{\text{H}_2O,P} \]  
\[ (13) \]
\[ \dot{E}_{\text{air,P}} = \dot{m}_{\text{air,P}} e_{\text{air,P}} = \dot{m}_{\text{air,P}} (e^{CH} + e^{PH})_{\text{air,P}} \]  
\[ (14) \]

**Destroyed exergy**

The destroyed exergy (\( E_{\text{des}} \)) represents the wasted potential of work, it is also called irreversibility or lost work [9]. For this study, the destroyed exergy was calculated using this relationship:

\[ E_{\text{des}} = \dot{E}_{\text{H}_2R} + \dot{E}_{\text{air,R}} - \dot{E}_{\text{H}_2O,P} - \dot{E}_{\text{air,P}} - W \]  
\[ (15) \]

**Exergy cost**

The exergy cost of a PEM fuel cell is defined as the ratio of the difference between the exergetic cost rate (cost per unit time) of streams entering and exiting the fuel cell plus the capital investment and operation and maintenance cost of the fuel cell to the electrical power output. The exergy cost represents an average cost per unit exergy[10][7]. To calculate the exergy cost of a fuel cell, the following expression may be used:

\[ C_{\text{H}_2O} \dot{E}_{\text{H}_2O,P} + C_{\text{air}} \dot{E}_{\text{air,P}} + C_W W = C_{\text{air}} \dot{E}_{\text{air,R}} + C_{\text{H}_2} \dot{E}_{\text{H}_2,R} + Z_{\text{FC}} \]  
\[ (16) \]

The exergy cost of the cell power may be determined by clearing \( C_W \) like this:

\[ C_W = \frac{C_{\text{air}} \dot{E}_{\text{air,R}} + C_{\text{H}_2} \dot{E}_{\text{H}_2,R} - C_{\text{H}_2O} \dot{E}_{\text{H}_2O,P} - C_{\text{air}} \dot{E}_{\text{air,P}} + Z_{\text{FC}}}{W} \]  
\[ ($GJ$) \]  
\[ (17) \]

where: \( Z_{\text{FC}} \) is the total investment cost of the fuel cell, which is a function of investment cost of capital \( Z_{\text{Cl}} \) and of the investment and maintenance cost of the cell \( Z_{\text{O&M}} \)

\[ Z_{\text{FC}} = Z_{\text{Cl}} + Z_{\text{O&M}} \]  
\[ (18) \]

The cost of capital of the cell was calculated in terms of the annual cost of capital, the capacity factor and the power of the cell as follows:

\[ Z_{\text{Cl}} = \frac{ACCW}{CFx8760(\frac{h}{yr})3600(\frac{s}{h})} \]  
\[ ($/s$) \]  
\[ (19) \]

Where the capacity factor of the cell (CF) was estimated as 0.9. The annual cost of the capital (ACC) was calculated in terms of the cost of the cell CFC and the recovery factor of the investment (CRF), which is the equivalent annual cost equivalent in the number of years (ny) of an investment at an annual interest rate (ir)
\[ \text{ACC} = C_{FR} \text{CRF} \]  
\[ \text{CRF} = \frac{i_r (1+i_r)^{ny}}{(1+i_r)^{ny} - 1} \]

with an annual interest rate of 7% and a life time of 5 years, the capital recovery factor CRF is 0.244 yr⁻¹. With an average cost of the cell of 1200 $/kW and an annual cost O&M of 100 $/kW based on the high costs of these equipment [7]. The operation and maintenance cost \( Z(\text{O&M}) \) can be expressed as:

\[ Z^{\text{O&M}} = \frac{C^{\text{O&M}W}}{8760 \left( \frac{3600}{h} \right)^{3600} \left( \frac{2}{h} \right)} \text{($$/s)} \]

where: \( C^{\text{O&M}} \) is the annual cost of operation and maintenance of the fuel cell. The properties of the fuel cell with the operating conditions and their related cost are shown in table 1.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard temperature, ( T_0 )</td>
<td>298 K</td>
</tr>
<tr>
<td>Standard Pressure, ( P_0 )</td>
<td>1 atm</td>
</tr>
<tr>
<td>Average specific heat of the air, ( C_p )</td>
<td>1.005 kJ/kg·K</td>
</tr>
<tr>
<td>Average specific heat of the Hydrogen, ( C_p )</td>
<td>14.3 kJ/kg·K</td>
</tr>
<tr>
<td>Specific power ratio air and Hydrogen, ( k )</td>
<td>1.4</td>
</tr>
<tr>
<td>Water enthalpy at standard conditions, ( h_w )</td>
<td>104.88 kJ/kg</td>
</tr>
<tr>
<td>Water entropy at standard conditions, ( s_w )</td>
<td>0.3674 kJ/kmol</td>
</tr>
<tr>
<td>Enthalpy of product air at standard condition, ( h_{pa} )</td>
<td>-21,120.0 kJ/kmol</td>
</tr>
<tr>
<td>Entropy of air in product at standard conditions, ( s_{pa} )</td>
<td>129.17 kJ/kmol·K</td>
</tr>
<tr>
<td>Air stoichiometry, ( \lambda )</td>
<td>5.397</td>
</tr>
<tr>
<td>Hydrogen cost, ( C_{H_2} )</td>
<td>10 $$/GJ</td>
</tr>
<tr>
<td>Water cost, ( C_{H_2O} )</td>
<td>1 $$/m³</td>
</tr>
<tr>
<td>Air cost, ( C_{air} )</td>
<td>0.011 $$/kg</td>
</tr>
<tr>
<td>Fuel cell cost (capital cost)</td>
<td>1200 $$/kW</td>
</tr>
<tr>
<td>Capacity Factor of the Fuel Cell</td>
<td>0.9</td>
</tr>
<tr>
<td>Fuel cell life time</td>
<td>5 years</td>
</tr>
<tr>
<td>Average annual interest rate</td>
<td>7 %</td>
</tr>
<tr>
<td>Annual operation and maintenance cost (O&amp;M)</td>
<td>100 $$/kW</td>
</tr>
</tbody>
</table>

**Results**

**Performance test**
The fuel cell was tested at a temperature of 70 °C in a range of 0.1-1 A/cm² of current density, the values are depicted in fig. 3.
Pem fuel cell performance assessment

Fig. 3 Polarization and power curve

The cell reached a power density of around 60 mW • cm⁻², the power density obtained is lower than obtained in other studies [11], [12] that recorded power density values between 600 and 4000 mW • cm⁻².

At a temperature of 70°C, the stoichiometric ratio of air (λ) was calculated applying equation (6), where λ equals to 5.4 was obtained. These results are depicted in fig. 4, as shown the mass flows of the reacting gases increase as the voltage decreases and the power in the cell increases, these behaviors are similar to those reported by Abdulkareem [13] (see fig. 4).

Fig. 4. Mass flows in the fuel cell

Hydrogen and air flows fed into the cell were taken constant, for the hydrogen 2.7x10⁻⁷ kg/s and for air 3.33x10⁻⁵ kg/s. Physical exergies remained constant because temperature and pressure factors were constant during the experimental tests. Using experimental data, the chemical exergy of each reagent and product stream was obtained for every point of the polarization curve. Equation 11 to 14 were used to calculate the total exergy of each stream, this requires multiplying each flow by the sum of chemical and physical exergy of each stream. With these
values, equation 15 was applied to calculate the destroyed exergy in the fuel cell in
the stipulated current density range. Plotting destroyed exergy data versus the
current fig. 6 was obtained. Analyzing this data, was obtained the following
regression model.

\[ \text{Ex}_{\text{dest}} = 4.2 \cdot 10^{-3} - 1.81 \cdot 10^{-4}\text{Current} + 6.59 \cdot 10^{-6}\text{Current}^2 \]  

(23)

This regression showed a \( R^2 \) of 0.99 and an adjusted \( R^2 \) of 0.98, which indicates
that the data fit well with this quadratic regression model in the cell's operating
range. This regression model achieved a minimum destroyed exergy value equal to
\( 2.96 \cdot 10^{-3} \text{kW} \) when the current has a value of 13.73 A.

Figure 7 shows the exergetic efficiency versus current data obtained from eq. 1 and
2. With the values, it was possible to obtain the following quadratic regression
model between current and efficiency (see Fig.7)

An \( R^2 \) equal to 0.98 was achieved by the cell, which indicates a good fit of the data
to this regression model. The model obeys the formula:
Efficiency = 4,398 + 4,135 \cdot \text{Current} - 0,150 \cdot \text{Current}^2 \quad (24)

After analyzing the first and second derivatives of the regression model, the maximum exergy efficiency was obtained at a current of 13.78 A. The reached efficiency of 32.89\%, is lower than reached by authors like Kazim [14], who obtained values around of 46\%, this efficiency might be improved if the flows are optimized. Equation 17 was used to evaluate the exergy cost using the values shown in Table 1. The process of the cell in terms of exergy costs may be represented like Fig. 8.

\[
\text{Total cost of PMFC}_{\text{PC}}
\]

\[
\begin{align*}
\text{Air (C}_{\text{air}} \ \dot{e}_{\text{air}}) & \rightarrow \text{Air (C}_{\text{air}} \ \dot{e}_{\text{air}}) \\
\text{H}_2 (C_{\text{H}_2} \ \dot{e}_{\text{H}_2}) & \rightarrow \text{H}_2O (C_{\text{H}_2O} \ \dot{e}_{\text{H}_2O}) \\
\text{Power (C}_p \ W) & 
\end{align*}
\]

Fig.8 Schematic of exergy costs in a fuel cell

The values of fuel and fuel cell cost were obtained from studies prior to this project. The exergetic cost was calculated using equations from (17) to (22). Graphically the exergy cost behavior of the PEM fuel cell with SEPS copolymer membranes is depicted in Fig.9.

\[
\text{Cost} = 21,778 + \frac{119.045}{\text{Current}} 
\]

Fig.9. Regression model for the exergetic cost

Statistical analysis leads to the following mathematical formulation:
The regression model has a good fit of the data, presented in $R^2$ of 0.99. Figure 9 showed that the exergy cost tends to reach a constant minimum value of $\$ 30/\text{GJ}$ by increasing the current density during the experimentation. This value is lower than those reached by Kazim [10], who obtained values between 58 and 63 $$/\text{GJ}. This could be caused by the low cost of the fuel cell, because it was made in our university and does not have a high commercial value that would logically increase the cost of the equipment.

An analysis to evaluate the convenience of investing in order to improve energy performance of a process, is the investment per power exergy unit plot. In this, the ratio investment over the exergy of the products ($Z/X_p$) versus the ratio destroyed exergy over exergy of products ($X_d/X_p$) are plotted (see Fig.10).

![Investment per power exergy unit](chart.png)

As shown in Fig.10, the ratio of capital investment to destroyed exergy is inversely proportional, this indicates that investing in the fuel cell system will reduce the destroyed exergy tends, taking advantage of the availability of the system and may improve the exergetic efficiency of the fuel cell [15]

**Conclusions**

It was found that the fuel cell achieved a power density of around 60 mW•cm$^{-2}$. For the exergy destruction of the system was found a quadratic regression model with an $R^2$ of 0.979. This regression model achieved a minimum destroyed exergy value equal to $2.96 \times 10^{-3}$ kW, when the current had a value of 13.73 A in the operating range. In the case of the exergetic efficiency of the cell, was found a quadratic regression model with an $R^2$ of 0.98, from which was observed a maximum exergy efficiency of 32.89% at a current of 13.78 A. The exergy cost tends to reach a constant minimum value of $\$ 30/\text{GJ}$ by increasing the current intensity in the experimental range of operation. It was established that, if the fuel cell is upgraded in its operating system, the destroyed exergy will decrease and the efficiency of the overall system will reach better values than the actual ones.
References


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