

INFLUENCE OF NATURAL GAS REFORMING PROCESSES ON THE PERFORMANCE OF A FUEL CELL

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***Abstract.** In the last 10 years, fuel cells have emerged as a promising alternative for electricity generation. Although they present great advantages, such as high efficiency and low emissions, one of their disadvantages is the cost to obtain the hydrogen required for the electrochemical process. Hydrogen for fuel cells is generally obtained from the reforming process of hydrocarbon fuels. Here, two different reforming processes of natural gas are evaluated and compared: steam reforming and autothermal reforming. The autothermal reforming process is conducted under an ideal operational condition, i.e., the operation point is set at the thermoneutrality point, $DH_r=0$. The steam reforming is modelled considering an equilibrium mechanism with two reactions: the reforming itself and the water gas shift reaction. To compare the performance of these reforming processes, a fuel cell is fuelled with the products of the autothermal reforming and steam reforming. The global efficiency, i.e. the ratio between the useful electrical power generated by the cell and the energy (lower heating value) of the natural gas entering the reforming reactor, is the observed parameter.*

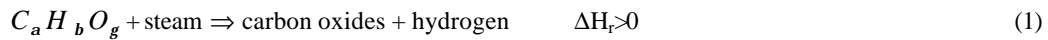
***Keywords.** Reforming Process, Natural Gas, Fuel Cell.*

1. Introduction

The conversion of hydrocarbon fuels into hydrogen for fuel cells is carried out by one of the three major fuel processing alternatives – steam reforming (SR), partial oxidation reforming (PO) and autothermal reforming (ATR).

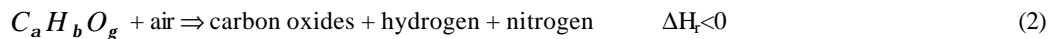
Considering a general hydrocarbon or oxygenate fuel $C_a H_b O_g$, the main characteristics of these three processing routes are (Ahmed et al.,2001):

Steam Reforming:



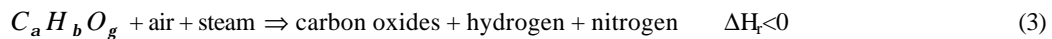
Steam reacts with the fuel in the presence of a catalyst to produce H₂, CO and CO₂. These reformers can deliver relatively high hydrogen concentration in the product gas (>70%) for temperatures at the order of 600°C. The CO and CO₂ can be removed from the product by a variety of reactions and scrubbing techniques. The primary SR reaction is strongly endothermic, and reactor designs are typically limited by heat transfer, rather than by reaction kinetics. Consequently, reactors are designed to promote heat exchange and tend to be large and heavy.

Partial Oxidation:



This reforming process reacts the fuel with sub-stoichiometric amount of oxygen. The partial oxidation reaction results in heat generation (exothermic reaction) and high temperatures, at the order of 1000°C. After this partial oxidation, steam can be injected in the gas mixture to steam-reform the remaining or added hydrocarbon or oxygenate fuel. The oxidation step can be conducted with or without a catalyst.

Autothermal Reforming:



This process combines the heat effects of PO and SR. The SR reaction absorbs part of the heat generated in the oxidation reaction, limiting the maximum temperature in the reactor, resulting in a slightly exothermic process. The process is carried out in the presence of a catalyst, which controls the reaction pathways, determining the extents of oxidation and steam reforming. The lower temperature achieved in this case provides many benefits for the reactor, among others:

- The reactor hardware can be built from a wide choice of materials;
- Lower temperature process needs less insulation, which means less cost;
- During start-up, lower temperature reactor requires less energy to achieve its operating temperature.

One difficulty, not present in the steam reforming, is the control of the optimum amount of air.

Coke formation is a concern in the reforming of hydrocarbon and oxygenate fuels for hydrogen production. It is known that coke formation can be avoided at high temperatures of operation and at high oxygen-to-carbon ratios; however, coke formation is not within the scope of this work.

In this work, thermochemical models for the steam reforming and autothermal reforming reaction pathways for the production of H₂ from natural gas are presented and solved. The exhaust mixture from the reforming is then used to fuel a typical phosphoric acid fuel cell (PAFC) and its overall efficiency is observed for a few different operation conditions.

In the following, models for the reforming processes and the fuel cell are presented and the results are discussed.

2. Reforming processes

2.1. Autothermal reforming process

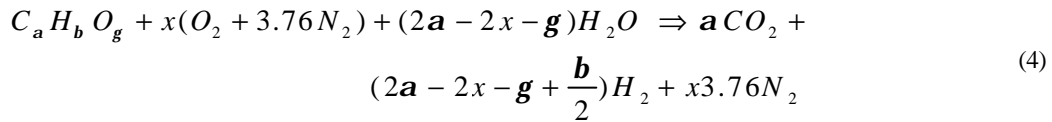
In this section, the *ideal*¹ ATR reaction of natural gas will be described and analyzed in more detail. The simulation of the natural gas ATR reaction presented in this work is based on the autothermal conversion process of methane (CH₄), presented in Ahmed et al (2001).

Table (1) shows the composition of the natural gas considered here.

Table 1. Natural Gas composition

Component	Molar fraction [%]	Mass fraction [%]	LHV [kJ/kmol]
CH ₄	90	82.4	800,000
C ₂ H ₆	6	10.3	1,425,750
N ₂	3	4.8	---
CO ₂	1	2.5	---
Total	100	100	805,545

For an ideal ATR reaction, the global reaction mechanism is represented as:



where x is the air-to-fuel molar ratio.

From the above mechanism, we note that:

- (a) Water required to convert all the carbon into CO₂:

$$2a - 2x - g \quad (5)$$

- (b) Maximum hydrogen yield in the reaction:

$$2a - 2x - g + b/2 \quad (6)$$

- (c) Maximum concentration of hydrogen in the product gas:

$$\frac{(2a - 2x - g + b/2)}{a + (2a - 2x - g + b/2) + 3.76x} * 100 \quad (7)$$

- (d) Heat of reaction at T₀:

$$\Delta H_r = n\Delta H_{f,CO_2} - (2a - 2x - g)\Delta H_{f,H_2O(L)} - \Delta H_{f,fuel} \quad (8)$$

For the natural gas in Table (1), we take $g = 0$.

¹ The products are considered to be only H₂, CO₂ and N₂.

The overall energy balance for the isobaric, isothermal, steady-flow autothermal reactor is:

$$H_R(T_0) + Q_c = H_P(T_r) \quad (9)$$

where T_0 is the inlet temperature, T_r is the reaction (outlet) temperature, H_R and H_P are the total reactants and products enthalpy and Q_c is the total heat transferred to heat the reactants, vaporize the water and to sustain the reaction temperature.

From the energy balance, the reactor efficiency is defined as:

$$h_{reformer} = \frac{LHV_{H_2}(T_r) * n_{H_2}}{LHV_{NG}(T_0) * n_{NG} + Q_c} \quad (10)$$

which is the ratio of the useful energy provided by the H_2 to the energy spent to produce it, assuming that no energy has been recovered from the exhaust streams.

The model is simulated using the computer code *EES* (“*Engineering Equation Solver*”), from Klein et al., (2001). Ideal gas behavior is assumed for all the substances and the global reaction mechanism, Equation (4), is assumed to proceed to equilibrium.

2.1.1. Simulation of the ATR process

In the simulations, we assume a consumption of 1 kmol of natural gas in the reformer, with the inlet streams (fuel + air + water) at standard reference conditions ($P_{in} = 1 \text{ atm}; T_m = 25^\circ\text{C}$).

As it can be seen from equations (4) – (8), for a value of $x = 0$, the global reaction (4) results in steam reforming, while for values of $x = x_c = [a - (g/2) + (b/4)]$, Equation (4) represents the combustion reaction to saturated products. Therefore, it can be concluded that the amount of air has a strong influence in the product composition of the ATR reaction. This is shown in Figure (1).

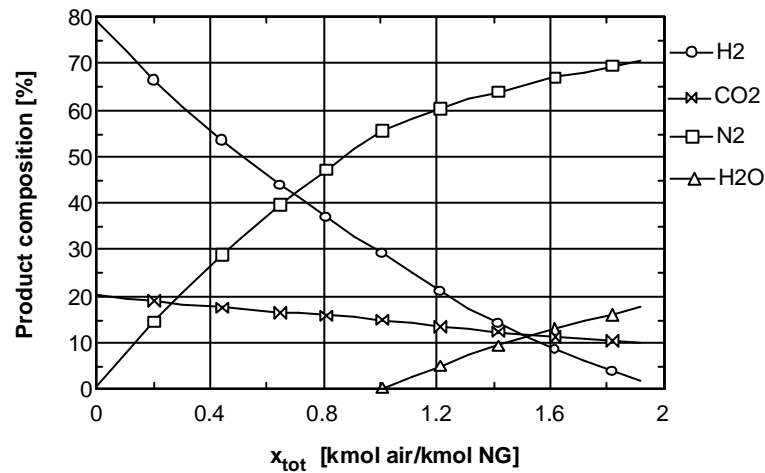
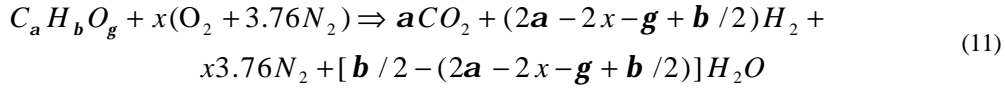


Figure 1. Product composition as a function of reactant air

The maximum amount of H_2 is formed when there is no air present. For the natural gas used, $x_c = 2$.

When $x > 1$, water is formed since the amount of air is just enough to convert all the carbon to CO_2 . Thus, as shown in Equation (11), water is no longer required as reactant in the ATR reaction.



When $x \leq 1$, the air present in the reaction is assumed just enough to convert the carbon of the fuel to CO. Then, water is used to convert CO to CO₂.

Figure (2) shows the effect of the air-to-fuel ratio on the heat of reaction defined as $\Delta H_r = \Delta H_P - \Delta H_R$. For $x = 0$ the ATR reaction is strongly endothermic ($\Delta H_{r,298K} > 0$). Increasing the air-to-fuel ratio, the reaction becomes progressively less endothermic, achieving the thermoneutral point ($\Delta H_{r,298K} = 0$) at $x = x_0 = 0.4446$. For $x > x_0$ the reaction becomes increasingly exothermic ($\Delta H_{r,298K} < 0$). Beyond $x = 1$, water is formed and the reaction becomes more exothermic when water is allowed to condense. Here it is assumed that water is present in the products in the vapor phase.

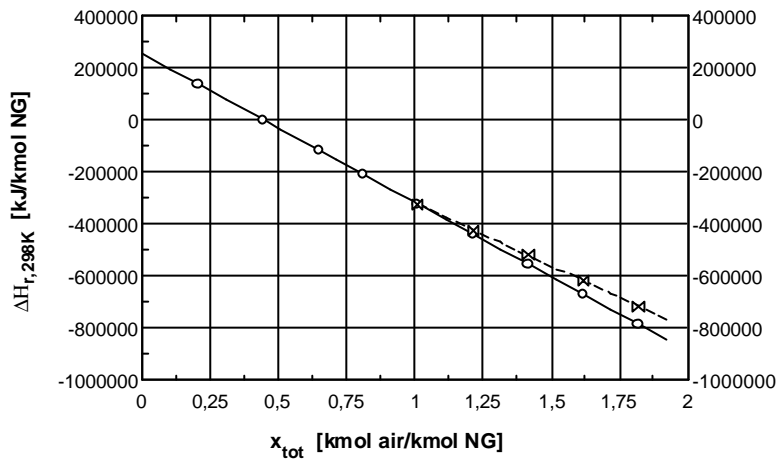


Figure 2. Heat of ATR reaction of natural gas as a function of the air-to-fuel ratio.

The continuous line is the result when the product water is in the liquid phase, while the dashed line is the result for the product water in the vapor phase.

However, due to reaction kinetic limitations (Ahmed et al., 2001), the reformer must not operate at temperatures below 600°C (873K). In this case, the reforming process efficiency will be affected by the additional energy (Q_c) that must be supplied to keep $T_{out} = 873K$. Hence, the thermoneutral point as well as the heat of reaction take different values when compared to those from Figure (2). Figure (3) plots the global energy consumed in the reformer and the enthalpies of reactants and products as a function of the reactant air for $T_{out} = 873K$.

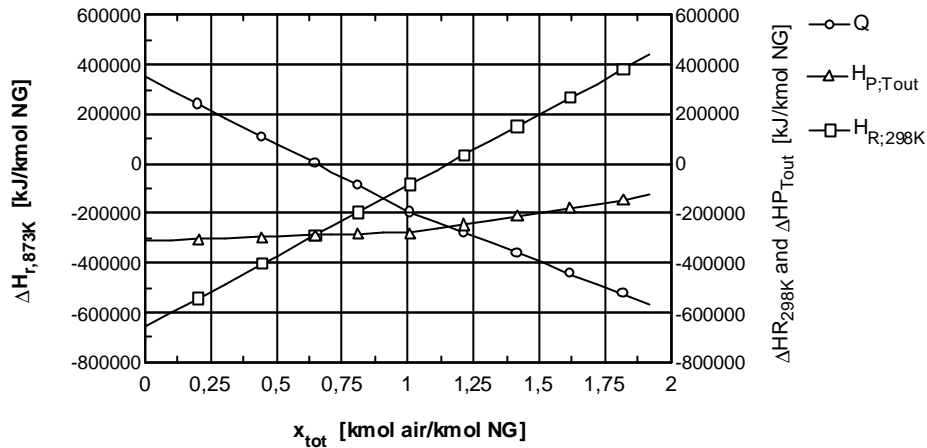


Figure 3. Heat of reaction and enthalpies of reactants and products as a function of the air-to-fuel molar ratio

In this case, the thermoneutral point is at $x = x_{0,873K} = 0.6463$.

Figure (4) shows the effect of x on $h_{reformer}$ and on the amount of hydrogen produced. Following Equation (9), the reformer efficiency achieves its maximum when $Q_c = 0$, for the reaction occurring at 298K. This occurs at the thermoneutral point $x = x_{0,298K} = 0.4446$, when $h_{reformer} = 78.18\%$.

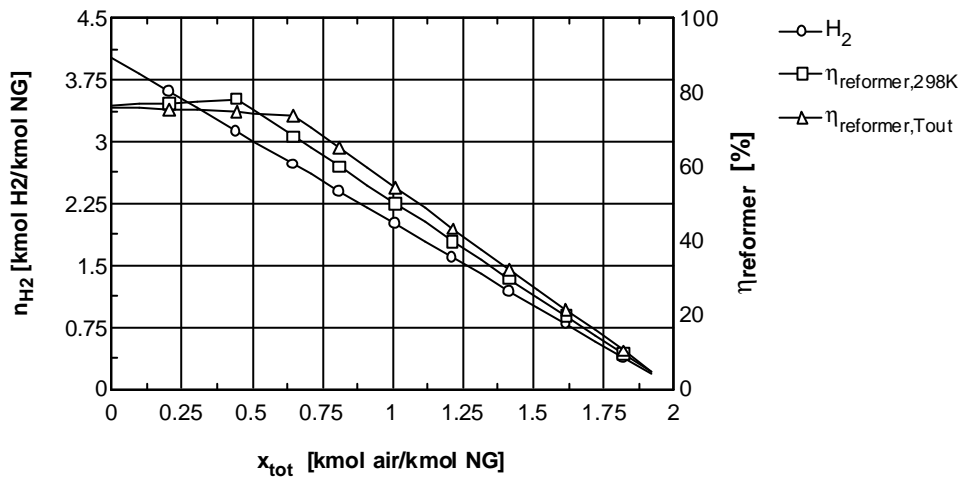


Figure 4. Reforming process efficiency and hydrogen produced as a function of air-to-fuel ratio

However, for the reaction occurring at 873K, the maximum efficiency is obtained at $x = 0$, when $h_{reformer} = 75.97\%$. Therefore, the highest efficiency is no longer achieved at the thermoneutral point $x_{0,873K}$, which gives a value of $h_{reformer} = 73.85\%$. As it can be seen in Equation (10), this behavior is explained by the influence of the reaction temperature over the lower heating value of H_2 and over the extra

energy Q_c . By analyzing Figure (4), we conclude that the higher the operation temperature, the higher is the decrease of Q_c as compared to the decrease in the lower heating value of H_2 .

At the thermoneutral point, $\Delta HR = \Delta HP$. Below the thermoneutral point, when the reaction is endothermic, the extra energy Q_c supplied to the reaction must be equal to the heat of the endothermic reaction $\Delta H_{r,T}$ so that the reaction can occur. Beyond the thermoneutral point, when the reaction becomes exothermic, the extra energy Q_c is no longer required to perform the ATR reaction at any temperature, therefore we take $Q_c = 0$ for $x \geq x_0$ in Figure (4), which simplify the reactor design, since cooling system is not necessary. In addition, if the reactor is to operate in the range where $x < x_0$, heating system would be necessary.

Each fraction composing the global heat Q_c is shown in Figure (5) for $x = 0$. These different fractions are:

- Latent heat to vaporize liquid water from 298K to vapour at 298K;
- Sensible heat to heat the water vapour from 298K to $T = T_{out}$;
- Sensible heat to heat the fuel from 298K to $T = T_{out}$;
- Sensible heat to heat the products from the adiabatic flame temperature to $T = T_{out}$.

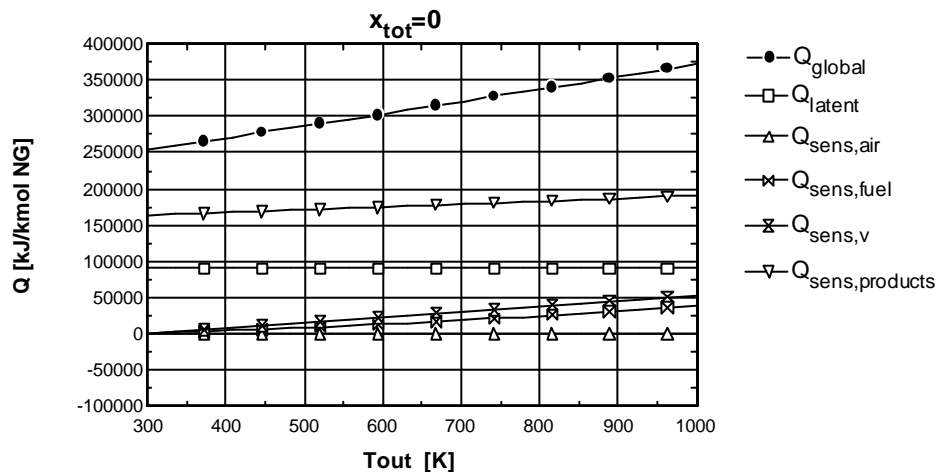


Figure 5. Heat of reaction as a function of reaction temperature.

From Figure (5) we note that the global heat is formed basically by the water latent heat and the sensible heat needed to heat the products of the reforming reaction from the adiabatic temperature to the operational temperature T_{out} . The reactants sensible heat is approximately negligible.

For the reformer operating at 873K and $x = x_{0,873K} = 0.6463$, Figure (4) shows the production of an amount of H_2 corresponding to $2.727 \frac{\text{kmol}H_2}{\text{kmolNG}}$. The difference between the reformer efficiencies operating at $x = 0$ and at $x = x_0$ is not significant, only 2.12%, suggesting that investment in a more complex reactor operating at $x = 0$ is not necessary, even at the expense of efficiency, therefore, the reaction is set to occur at the thermoneutral point, $x = x_0$.

2.2. Steam reforming process

The steam reforming is modelled considering a mechanism with three reactions, Equations (12-14), namely methane reforming reaction, ethane reforming reaction and shifting (water-gas) reaction. This mechanism was used by Massardo and Lubelli (2001) in the absence of the ethane reforming.



The equilibrium constant (k) at atmospheric pressure, for reactions 12 to 14 is expressed as:

$$\ln k = -\frac{\Delta G^0}{RT} \quad (15)$$

Table (2) presents the equilibrium constants for each reaction at $T = 600^\circ C$ (Massardo and Lubelli, 2001).

Table 2. Equilibrium constants k for the reforming reactions at $600^\circ C$ and atmospheric pressure.

Reaction	k
Methane reforming, Eq. (16)	21,71
Ethane reforming, Eq. (17)	37,78
Shift reaction, Eq. (18)	5,79

The amounts of methane, ethane and carbon monoxide needed to balance reactions 12 to 14 in equilibrium conditions are given by the solution of:

$$k_{methane} = \frac{\left(\frac{x - 2y - w}{\dot{n}_{total} + 2x + 4y} \right) \cdot \left(\frac{3x + 5y + w}{\dot{n}_{total} + 2x + 4y} \right)^3}{\left(\frac{\dot{n}_{CH_4} - x}{\dot{n}_{total} + 2x + 4y} \right) \cdot \left(\frac{\dot{n}_{H_2O} - x - 2y - w}{\dot{n}_{total} + 2x + 4y} \right)} \quad (16)$$

$$k_{ethane} = \frac{\left(\frac{3x + 5y + w}{\dot{n}_{total} + 2x + 4y} \right)^5 \cdot \left(\frac{x + 2y - w}{\dot{n}_{total} + 2x + 4y} \right)^2}{\left(\frac{\dot{n}_{C_2H_6} - w}{\dot{n}_{total} + 2x + 4y} \right) \cdot \left(\frac{\dot{n}_{H_2O} - x - 2y - w}{\dot{n}_{total} + 2x + 4y} \right)} \quad (17)$$

$$k_{shift} = \frac{\left(\frac{3x + 5y + w}{\dot{n}_{total} + 2x + 4y} \right) \cdot \left(\frac{\dot{n}_{CO_2} + w}{\dot{n}_{total} + 2x + 4y} \right)}{\left(\frac{x + 2w - w}{\dot{n}_{total} + 2x + 4y} \right) \cdot \left(\frac{\dot{n}_{H_2O} - x - 2y - w}{\dot{n}_{total} + 2x + 4y} \right)} \quad (18)$$

where \dot{n}_{total} is the molar flow of reformed gases [kmol/s], \dot{n}_{CH_4} is the molar flow of methane in the reformer inlet [kmol/s], $\dot{n}_{C_2H_6}$ is the molar flow of ethane in the reformer inlet [kmol/s] and \dot{n}_{CO_2} is the molar flow of carbon dioxide in the reformer inlet [kmol/s].

The total molar flow of the reformed gases is obtained from the molar flow of natural gas and the steam to carbon ratio (S/C=3).

Once the amounts of methane, ethane and carbon monoxide reacted are known, the composition of the products exiting the reformer are calculated, from the Law of Mass Action for Equations (16) to (18).

Table (3) shows the composition of the reformer products for inlet temperature $T_{in} = 100^\circ C$, outlet temperature $T_{out} = 600^\circ C$ and pressure $P = 1 \text{ atm}$.

Table 3. Composition of the products for the steam reforming of natural gas at $T_{in} = 100^\circ C$, $T_{out} = 600^\circ C$ and $P = 1 \text{ atm}$.

Chemical species	Molar fraction [%]	
	Reformer inlet	Reformer outlet
CH ₄	24.3	0.4
C ₂ H ₆	1.6	~0
CO ₂	0.3	11.2
N ₂	0.8	0.5
H ₂ O	73.0	18.8
CO	0	6.4
H ₂	0	62.7

3. Results

In order to compare the performance of the two reforming processes, the reformed gases from both processes are used to fuel a 200 kW_{el} phosphoric acid fuel cell (PAFC). The parameter evaluated is the electrical efficiency, which is defined as the ratio of the output electrical power from the cell over the total energy spent to produce the hydrogen and to power the cell. Considering that natural gas is the only fuel used:

$$h_{PAFC} = \frac{\dot{W}_{el}}{n_{NG} * LHV_{NG} + Q_c} * 100 \quad (19)$$

In order to produce its nominal electrical power ($\dot{W}_{el} = 200 \text{ kW}$), the PAFC requires 0.002579 kmol/s of hydrogen (Matelli, 2001). Table (4) presents the natural gas consumption, reformer efficiency, the PAFC efficiency and the additional energy consumed, for both reforming processes.

Table 4. Natural gas consumption, reformer efficiency, PAFC efficiency and additional energy consumed.

Reforming process	\dot{m}_{NG} [kg/s]	$h_{reformer}$ [%]	h_{PAFC} [%]	Q_c [kW]
Autothermal	0.01523	73.9	28.5	0
Steam	0.01269	86.6	32.8	16.1

The autothermal reformer operates at the thermoneutral condition ($Q_c = 0$). The steam reformer requires 16.1 kW of external heating. However, it produces more hydrogen per mol of natural gas, thus resulting in higher reforming and cell efficiency when compared to the autothermal reformer.

4. Conclusions

The conversion of hydrocarbon fuels into hydrogen for fuel cells is carried out by one of the three major fuel processing alternatives – steam reforming (SR), partial oxidation reforming (PO) and autothermal reforming (ATR). Here, two different reforming processes of natural gas were evaluated and compared: steam reforming and autothermal reforming. The autothermal reforming process is conducted under an ideal operational condition, i.e., the operation point is set at the thermoneutrality point, $\Delta H_r = 0$. The steam reforming is modeled considering an equilibrium mechanism with two reactions: the reforming itself and the water gas shift reaction. To compare the performance of these reforming processes, a fuel cell is fuelled with the products of the autothermal reforming and steam reforming. The global efficiency, i.e. the ratio between the useful electrical power generated by the cell and the energy (lower heating value) of the natural gas entering the reforming reactor, is the observed parameter.

From the results obtained we can conclude that:

1. At the operational condition of 298K, the autothermal reforming has its maximum efficiency at the thermoneutral point, $x = x_0$. As the operational temperature is increased this maximum becomes progressively less pronounced. At the operational temperature of 873K the maximum efficiency shifts to $x = 0$. However, the difference between the efficiencies at $x = 0$ and $x = x_0$ is only about 2.12%. Considering that operation at the thermoneutral point requires considerably less equipment (e.g., heat exchangers), this is a more favourable condition to operate.
2. The SR efficiency is about 12.7% greater than the ATR efficiency. This occurs because the SR yields the highest concentration of hydrogen in the product gas per mol of fuel. However, this higher concentration has a very small effect in the Nernst potential in the fuel cell, which varies with the log of the concentrations. Consequently, the overall efficiency of the SR fuel cell is only 4.3% greater than the overall efficiency of the ATR fuel cell.
3. The SR requires heat exchangers, while the ATR requires an air line. We did not evaluate which system is more expensive or troublesome to operate. Also, we note that the efficiency advantage of the SR might be easily overshadowed by kinetic and heat transfer limitations.

5. References

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