

# Optimization of Hydrogen Production Through Methane Steam Reforming in a Membrane Reactor

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**Abstract** — Hydrogen is used as fuel and as raw material in important processes. Steam methane reforming is the main route for hydrogen production with the process being globally endothermic and reversible, which requires operating at high temperatures to achieve satisfactory conversions. Membrane reactors are an interesting alternative since it leads to higher conversions at lower temperatures. In order to consolidate this technology, it is necessary to find the optimal operational conditions. Temperature ( $T$ ), reaction pressure ( $P$ ), permeate pressure ( $P_P$ ), steam to methane molar ratio in the feedstock ( $m$ ) and methane feed flow rate ( $F_{CH_4^0}$ ) were chosen as decision variables. The objective function was defined as the sum of methane conversion and hydrogen recovery. The Flexible Polyhedra method was used as optimization algorithm. Considering the determined optimal conditions, a methane conversion of 99.94% and a recovery of hydrogen of 98.87% were achieved.

**Keywords** — methane steam reforming, membrane reactor, optimization, hydrogen production, Nelder-Mead algorithm.

## I. INTRODUCTION

Hydrogen ( $H_2$ ) is a fuel and an important chemical for the manufacture of many important products. Moreover,  $H_2$  is also consumed in large amounts in oil refineries. In this way, these evidence indicates that the demand for hydrogen will continue to increase in the near future [1,2].

Finding potential sources of energy has become an indispensable challenge. In recent decades, increased environmental pollution and reduced sources of fossil fuels led researchers to seek alternative and environmentally friendly fuel. The hydrogen can be introduced as a suitable alternative energy source [3].

Methane ( $CH_4$ ) is the main constituent of natural gas and is most commonly produced by separating the other components of natural gas [1]. Currently the main industrial source for hydrogen is the steam methane reforming (SMR) since it can achieve the highest  $H_2/CO$  ratio (3) in comparison to other

processes. The overall steam reforming reaction is endothermic and occurs at high temperatures. The total productivity of a hydrogen plant depends heavily on how efficiently the reformer is operated [2,4].

However, due to the high operational costs involved in carrying out the reforming process, theoretical studies of modeling, simulation and optimization have proved to be interesting tools to study the influence of different process variables, making possible the investigation of the best operational conditions [5,6].

The reactions involved in the methane steam reforming are reversible and have an endothermic global mechanism. This results in two severe limitations to the process: the reach of chemical equilibrium and the large amount of energy spent in obtaining the synthesis gas [5,6]. In this context, an alternative is the usage of membrane reactor technology. This process allows the displacement of the chemical equilibrium by means of a continuous withdrawal of the hydrogen, which enables high conversion rates operating at milder temperatures. In these reactors, dense palladium membranes are commonly used, which are considered permeable only to hydrogen [5,8].

In this work, the optimization of the steam methane reforming process for the production of hydrogen in a reactor with  $Ni/Al_2O_3$  catalyst and palladium membrane were studied, using models proposed in the literature [5-8]. The simulation of the mathematical model and the optimization procedure were performed in MATLAB<sup>®</sup>. The objective function was defined as the sum of methane conversion and hydrogen recovery. The decision variables were the reaction temperature ( $T$ ), reaction pressure ( $P$ ), steam to methane molar ratio in the feedstock ( $m$ ), methane flow rate in the feed ( $F_{CH_4^0}$ ), and permeate pressure ( $P_P$ ). The Nelder-Mead algorithm [9] was used to solve the optimization problem.

## II. MATHEMATICAL MODELING

Comparing to traditional chemical reactor models, the analysis of a membrane reactor should consider the additional contribution of mass transfer through the membrane, i.e., the permeation rate must be

considered alongside the expression of the reaction rate [8]. The scheme of a membrane reformer is present in Fig. 1.

In order to best represent the actual behavior of the process, a kinetic permeation model was used. The equations and hypotheses used are described below.

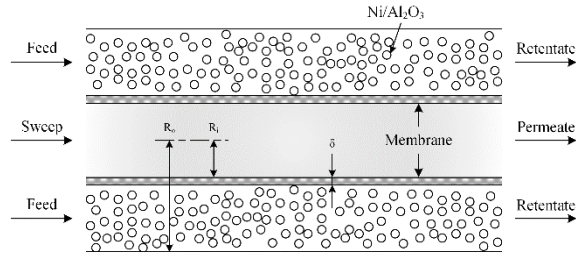


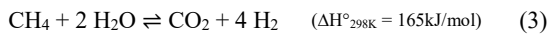
Fig. 1: Membrane reactor scheme considered in this work.

### A. Basic assumptions

- Isothermal and isobaric reaction conditions.
- Steady-state operation.
- Plug flow on both reaction and permeation sides.
- Diffusion is only significant through the membrane.
- Intrinsic kinetics for methane steam reforming and water-gas shift reactions.
- No boundary layer on membrane surfaces.

### B. Equations

Methane steam reforming involves two reversible reactions: the reform reaction (Eq. 1) and water gas shift reaction (Eq. 2). The process overall reaction is presented at Eq. 3 [11].



Reaction rate equations are presented in Eqs. 4, 5 and 6, proposed by Xu and Froment [11], based on the Langmuir-Hinshelwood mechanism, where  $P_j$  is the partial pressure of component  $j$ ,  $k_i$  is the rate constant for reaction  $i$ ,  $K_{e,i}$  is the equilibrium constant of reaction  $i$ ; and  $K_{a,j}$  is the adsorption coefficient for component  $j$ .

$$r_1 = \frac{k_1 (P_{\text{CH}_4} P_{\text{H}_2\text{O}} - P_{\text{H}_2}^3 P_{\text{CO}} / K_{e,1})}{P_{\text{H}_2}^{2,5} (\text{DEN})^2} \quad (4)$$

$$r_2 = \frac{k_2 (P_{\text{CO}} P_{\text{H}_2\text{O}} - P_{\text{H}_2} P_{\text{CO}_2} / K_{e,2})}{P_{\text{H}_2} (\text{DEN})^2} \quad (5)$$

$$r_3 = \frac{k_3 (P_{\text{CH}_4} P_{\text{H}_2\text{O}}^2 - P_{\text{H}_2}^4 P_{\text{CO}_2} / K_{e,3})}{P_{\text{H}_2}^{3,5} (\text{DEN})^2} \quad (6)$$

$$\text{DEN} = 1 + K_{a,\text{CO}} P_{\text{CO}} + K_{a,\text{H}_2} P_{\text{H}_2} + K_{a,\text{CH}_4} P_{\text{CH}_4} + K_{a,\text{H}_2\text{O}} P_{\text{H}_2\text{O}} / P_{\text{H}_2}$$

The partial pressures in the reaction side can be calculated using the Eqs. 7, 8, 9, 10 and 11, where  $P$  is the total pressure,  $X_{\text{CH}_4}$  is the methane conversion,  $Y_{\text{H}_2}$  is the hydrogen recovery; and  $m$  is the steam to methane ratio in the feed [8].

$$P_{\text{CH}_4} = (1 - X_{\text{CH}_4}) / \sigma \quad (7)$$

$$P_{\text{CO}} = (X_{\text{CH}_4} - X_{\text{CO}_2}) / \sigma \quad (8)$$

$$P_{\text{CO}_2} = X_{\text{CO}_2} / \sigma \quad (9)$$

$$P_{\text{H}_2\text{O}} = (m - X_{\text{CH}_4} - X_{\text{CO}_2}) / \sigma \quad (10)$$

$$P_{\text{H}_2} = (\theta_{\text{H}_2}^0 + 3X_{\text{CH}_4} + X_{\text{CO}_2} - Y_{\text{H}_2}) / \sigma \quad (11)$$

$$\sigma = (1 + m + \theta_{\text{H}_2}^0 + 2X_{\text{CH}_4} - Y_{\text{H}_2}) / P$$

Experimentally it is common that the feed is composed only of methane and steam, which mathematically means that  $\theta_{\text{H}_2}^0 = 0$  and makes the hydrogen partial pressure to be zero and the initial rate infinite [7-9]. This can be bypassed by defining an arbitrary input  $\theta_{\text{H}_2}^0$  sufficiently small, such as  $1.0 \times 10^{-6}$ .

The rate constants ( $k_i$ ), adsorption coefficients ( $K_{a,j}$ ) and equilibrium constants ( $K_{e,i}$ ) are related to temperature according to Eqs. 12, 13 and 14 [9,11].

$$k_i = k_{0,i} \exp \left[ \frac{E_{A,i}}{R} \left( \frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \right] \quad (12)$$

$$K_{a,j} = K_{a,j}^0 \exp \left[ \frac{\Delta H_j}{R} \left( \frac{1}{T_{\text{ref}}} - \frac{1}{T} \right) \right] \quad (13)$$

$$K_{e,i} = \exp \left( \frac{-\Delta_r G^\circ}{RT} \right) \quad (14)$$

$$\text{With: } \begin{cases} \Delta_r G^\circ = \sum_{i,j} v_{ij} G_j^\circ \\ G_j^\circ = A_j + B_j T + C_j T^2 \end{cases}$$

The mass balance of the system can be defined by two differential equations based on the fact that only two of the chemical reactions are independent. Therefore, methane and carbon dioxide conversions are related to the dimensionless length ( $z$ ) according to Eqs. 15 and 16 [9].

$$\frac{dX_{\text{CH}_4}}{dz} = \tau_r (r_1 + r_3) \quad (15)$$

$$\frac{dX_{\text{CO}_2}}{dz} = \tau_r (r_2 + r_3) \quad (16)$$

The reaction contact time ( $\tau_r$ ) is given by Eq. 17,

$$\tau_r = \frac{\rho_B L \pi [R_o^2 - (R_i + \delta)^2]}{F_{CH_4}^0} \quad (17)$$

where  $\rho_B$  is the bed density, L is the reactor length,  $F_{CH_4}^0$  is the methane molar flow rate in the feed,  $R_o$  and  $R_i$  are the internal and external radius, respectively, and  $\delta$  is the membrane thickness.

The bed density ( $\rho_B$ ) can be calculated using the Eq. 18, where  $\rho_{cat}$  is the Ni/Al<sub>2</sub>O<sub>3</sub> density and  $\epsilon$  is the bed porosity.

$$\rho_B = \rho_{cat} (1 - \epsilon) \quad (18)$$

The hydrogen permeation rate through the membrane is defined as Eq. 19, where  $\tau_m$  is a parameter that correlates the membrane surface area with the methane inlet flow rate (Eq. 20),  $P_{H_2}$  is the hydrogen partial pressure in the reaction side and  $P_{H_2,p}$  is the hydrogen partial pressure in the permeate side.

$$\frac{dY_{H_2}}{dz} = \tau_m (P_{H_2}^n - P_{H_2,p}^n) \quad (19)$$

$$\tau_m = \frac{2\pi(R_i + \delta)L\beta}{F_{CH_4}^0 \delta} \quad (20)$$

For a palladium (Pd) membrane with a thickness of 5  $\mu\text{m}$ , the transport mechanism is controlled by the dissociative adsorption of hydrogen in the Pd, and the exponent concerning the driving force of permeability (n) is equal to 1 [5].

The following equations related to hydrogen permeation through the membrane were also defined (Eqs. 21, 22, 23) [5,8,9],

$$\beta = \beta_0 \exp\left(\frac{-E_{A,P}}{RT}\right) \quad (21)$$

$$P_{H_2,p} = \frac{Y_{H_2} P_P}{(Y_{H_2} + \theta_1)} \quad (22)$$

$$\theta_1 = \frac{F_1^0}{F_{CH_4}^0} \quad (23)$$

where  $\beta$  is the permeance of palladium membrane,  $P_P$  is the permeate pressure and  $\theta_1$  is the sweeping gas to methane molar ratio in the feed.

The percent of recovery hydrogen in the optimal operating conditions was calculated by Eq. 24.

$$Y_{H_2} (\%) = \frac{Y_{H_2}}{4 X_{CH_4}} \times 100 \quad (24)$$

Tables 1, 2 and 3 display the values of the parameters and constants used in the model.

TABLE I: PARAMETERS VALUE USED AND MEANING [7,9].

Symbol	Value	Description
$R_i$ (cm)	2.540	Internal radius (without membrane)
$R_o$ (cm)	6.350	External radius
$\epsilon$	0.500	Bed porosity
$\rho_{cat}$ (Kg m <sup>-3</sup> )	2,100	Catalyst density
L (m)	7.000	Reactor length
n	1.000	Exponent of permeance rate
$\theta_{H_2}$	$1.0 \times 10^{-6}$	Hydrogen/methane ratio
$F_1^0$ (Kmol h <sup>-1</sup> )	10.000	Sweeping gas flow
$\delta$ ( $\mu\text{m}$ )	5.000	Membrane thickness

TABLE II: KINETIC PARAMETERS AND PERMEANCE OF PD MEMBRANE USED IN SIMULATION [7,9].

Parameter	Pre-exponential factor	$E_A$ or $\Delta H$ (kJ mol <sup>-1</sup> )
$k_1$ (kmol bar <sup>0.5</sup> kg <sup>-1</sup> h <sup>-1</sup> )	$1.8 \times 10^{-4}$	240.10
$k_2$ (kmol kg <sup>-1</sup> h <sup>-1</sup> bar <sup>-1</sup> )	7.600	67.13
$k_3$ (kmol bar <sup>0.5</sup> kg <sup>-1</sup> h <sup>-1</sup> )	$2.2 \times 10^{-5}$	243.9
$K_{a,CH_4}$ (bar <sup>-1</sup> )	$1.8 \times 10^{-1}$	-38.28
$K_{a,H_2O}$ (-)	0.400	88.68
$K_{a,CO}$ (bar <sup>-1</sup> )	40.900	-70.65
$K_{a,H_2}$ (bar <sup>-1</sup> )	$2.9 \times 10^{-2}$	-82.90
$\beta$ (m <sup>3</sup> m <sup>-2</sup> h <sup>-1</sup> bar <sup>-0.5</sup> )	$1.776 \times 10^{-2}$	-15.70

TABLE III: PARAMETERS USED FOR THE CALCULATION OF EQUILIBRIUM CONSTANTS [9].

Element	Constant	Value
CH <sub>4</sub>	$A_j$ (kJ mol <sup>-1</sup> )	-75.3
	$B_j$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$7.6 \times 10^{-2}$
	$C_j$ (kJ mol <sup>-1</sup> K <sup>-2</sup> )	$1.9 \times 10^{-5}$
H <sub>2</sub> O	$A_j$ (kJ mol <sup>-1</sup> )	-241.7
	$B_j$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$4.2 \times 10^{-2}$
	$C_j$ (kJ mol <sup>-1</sup> K <sup>-2</sup> )	$7.4 \times 10^{-6}$
CO	$A_j$ (kJ mol <sup>-1</sup> )	-109.9
	$B_j$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$-9.2 \times 10^{-2}$
	$C_j$ (kJ mol <sup>-1</sup> K <sup>-2</sup> )	$1.5 \times 10^{-6}$
CO <sub>2</sub>	$A_j$ (kJ mol <sup>-1</sup> )	-393.4
	$B_j$ (kJ mol <sup>-1</sup> K <sup>-1</sup> )	$3.8 \times 10^{-3}$
	$C_j$ (kJ mol <sup>-1</sup> K <sup>-2</sup> )	$1.3 \times 10^{-6}$

### C. Boundary conditions

$$z = 0; X_{CH_4} = X_{CO_2} = Y_{H_2} = 0.$$

**D. Numerical simulation**

The system of differential equations was solved numerically using "ode15s" integrator in MATLAB® 2008, which is suitable for the resolution of stiff problems. The proposed model was validated using experimental data from Shu et al. [8].

Additionally, effects of temperature, pressure, and steam to methane ratio in methane conversion using a membrane reactor (MR) and a non-membrane reactor (PBR), were evaluated under the same operating conditions in order to compare the efficiency of both reactors.

**III. FORMULATION OF THE OPTIMIZATION PROBLEM**

Many works in literature present the study of certain variables influence in the process, mainly the conversion of methane [5,7-9]. Among the variables that affect the performance of a membrane reactor to produce hydrogen from the steam methane reforming, the following were chosen as decision variables:

- Temperature (T).
- Reaction pressure (P).
- Steam to methane molar ratio of steam to methane (m).
- Methane flow rate in the feed ( $F_{CH_4}^0$ ).
- Permeate pressure ( $P_p$ ).

It is desired to obtain maximum conversion of methane associated with a high recovery of hydrogen. Therefore, the objective function is defined as displayed in Eq. 25, with  $\phi$  representing the decision variables,  $\phi = (T, P, m, F_{CH_4}^0, P_p)$ .

$$F_{obj}(\phi) = X_{CH_4} + Y_{H_2} \tag{25}$$

In this way, the optimization problem can be written in the form of Eq. 26:

$$\begin{aligned}
 & \text{maximize } F_{obj}(\phi) \\
 & \text{s.t. } \begin{cases} 600 \leq T \text{ (K)} \leq 900 \\ 1 \leq P \text{ (bar)} \leq 10 \\ 1 \leq m \leq 5 \\ 1 \leq F_{CH_4}^0 \text{ (kmol h}^{-1}\text{)} \leq 5 \\ 0.5 \leq P_p \text{ (bar)} \leq 3 \\ \text{Eqs. (4-23)} \end{cases} \tag{26}
 \end{aligned}$$

Inequality constraints were established according to the physical and economically feasible ranges of the process according to the literature [4-9]. Equality constraints are all equations that compose the mathematical model.

To solve the optimization problem, MATLAB® software and Nelder-Mead algorithm were used. Nelder-Mead is a deterministic method of direct search that, starting from an initial polyhedron, seeks to improve the worst vertex by reflecting it in relation to the centroid of the "n" best vertices. It is allowed to perform non-isometric reflection, expansion or external contraction, as well as internal contraction of the polyhedron. If none of these steps produce an improvement, the polyhedron is reduced and the process is restarted [11].

The initial estimate given to the algorithm was based on the literature [5,7-9] and is present in Eq. 27.

$$x_0 = [800 \ 10 \ 3 \ 1 \ 0.5] \tag{27}$$

**IV. RESULTS**

The validation of the model used in this process is displayed in Fig. 2.

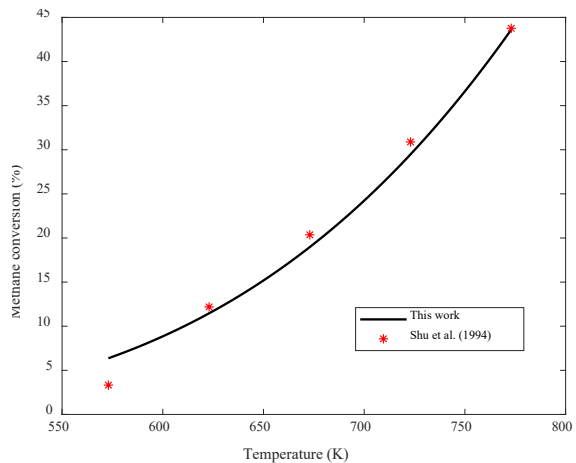


Fig. 2: Validation of the model using experimental data from Shu et al. [8] ( $P = 1.36$  bar;  $F_{CH_4}^0 = 9.9 \times 10^{-5}$  kmol h<sup>-1</sup>;  $m = 3$ ;  $P_p = 1.01$  bar;  $\theta_1 = 1$ ;  $\delta = 20$   $\mu$ m).

It is observed that the model gives a good representation of the process and conforms to the experimental data in these operating conditions. Therefore, this model was chosen to determine the optimal operational parameters. The effects of temperature on methane conversion in the membrane reactor (MR) and in the conventional reactor (PBR), considering the same operating conditions are presented in Fig. 3.

It is observed that the increase in temperature provided an increase in conversion for both reactors. However, the membrane reactor was able to reach higher methane conversions at lower operating temperature. At 870 K, the membrane reactor achieved total conversion while the PBR conversion reached 32.4%.

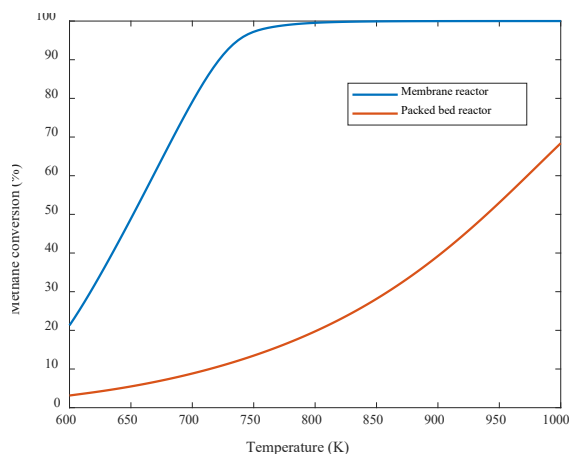


Fig. 3: Comparison of CH<sub>4</sub> conversion with temperature variation in different types of reactors (P = 10 bar; F<sub>CH<sub>4</sub></sub><sup>0</sup> = 1 kmol h<sup>-1</sup>; m = 3).

The highest conversion obtained in the membrane reactor is justified by the fact that steam methane reforming is a highly endothermic reaction limited by chemical equilibrium, requiring high temperatures to obtain a satisfactory conversion. The process in membrane reactors allows the displacement of the chemical equilibrium by means of the continuous withdrawal of the hydrogen, which enables high conversion rates at lower temperatures [5].

The methane conversion obtained by changing the reaction pressure and maintaining the same operating conditions in the membrane reactor (MR) and in the non-membrane reactor (PBR) is presented in Fig. 4.

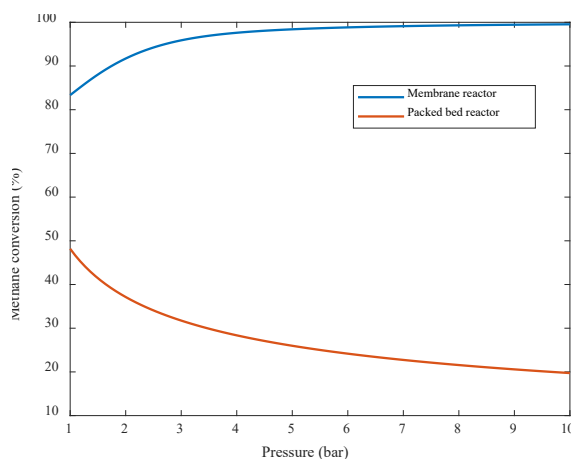


Fig. 4: Comparison of CH<sub>4</sub> conversion with pressure variation in different reactor types (T = 800 K; F<sub>CH<sub>4</sub></sub><sup>0</sup> = 1 kmol h<sup>-1</sup>; m = 3).

In this case, the difference between the two reactors was even more significant. Considering the membrane reactor, it is possible to observe that methane conversion increases with the increase in reaction pressure. On the other hand, the effect in the conventional reactor was the opposite, with increasing the pressure leading to a decrease in methane conversion. This is one of the main reasons

of using a membrane. In membrane reactors, increasing the reaction pressure leads to an increase in the difference between the partial pressure of hydrogen in the reaction side and in the permeate side. This represents an increase in the driving force and consequently a higher hydrogen permeation, which also enhances the conversion [5,9].

Fig. 5 shows the effects of steam to methane ratio in the feedstock on the methane conversion considering the membrane reactor (MR) and PBR.

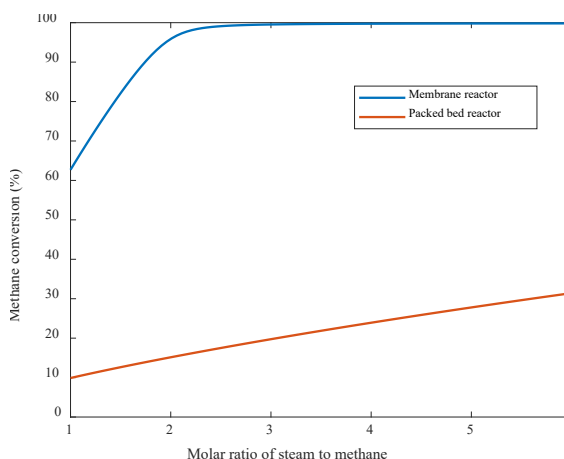


Fig. 5: Comparison of the CH<sub>4</sub> conversion with the variation of the steam to methane ratio in the feedstock (T = 800 K; P = 10 bar; F<sub>CH<sub>4</sub></sub><sup>0</sup> = 1 kmol h<sup>-1</sup>).

For both reactors, the conversion increased with higher values of steam to methane molar ratio in the feed, indicating that an excess of steam was desirable to achieve higher conversions. However the membrane reactor presented a much higher conversion under the same operating conditions than PBR, allowing a ratio of approximately 3 and avoiding the excessive dilution of hydrogen.

The optimization results for the membrane reactor are shown in Table 4.

TABLE IV: OPTIMIZATION ROUTINE RESULTS.

Variable	Value
Temperature (K)	784.3
Reaction pressure (bar)	10.0
H <sub>2</sub> O/CH <sub>4</sub> ratio	2.81
CH <sub>4</sub> flow rate (kmol h <sup>-1</sup> )	1.00
Permeate pressure (bar)	0.50
Objective function (F <sub>obj</sub> )	4.9543
<b>Methane conversion (X<sub>CH<sub>4</sub></sub>)</b>	<b>0.9994</b>
<b>Hydrogen recovery (Y<sub>H<sub>2</sub></sub>)</b>	<b>3.9550</b>

Considering the optimal operating conditions, the maximum methane conversion obtained was 99.94% while the maximum value of hydrogen recovery

obtained, that was 3.9550, equals 98.87% according to stoichiometry. A total hydrogen recovery (100%) for the model proposed is physically unfeasible due to the concurrent flux. In this reactor configuration, the hydrogen pressure at the end of the reactor was the same in the reaction side and in permeate due to the chemical equilibrium. Therefore, permeation no longer occurs [5].

An optimum temperature value of 784 K was obtained, which is much lower than the normally used in conventional reformers (approximately 1123 K). This confirms that, in fact, it is possible to obtain higher conversions at much lower temperatures and, consequently, lower energy expenses in reformers with membranes [5].

The optimum pressure obtained for both the reaction side (10 bar) and permeate (0.5 bar) were also coherent since hydrogen permeation was based on the difference between hydrogen partial pressure at both sides of the membrane. Therefore, it was expected that the optimum points would be close to the maximum pressure on the reaction side and the minimum pressure on the permeate, allowing a maximum difference in pressure, which is a great driving force and results in an efficient hydrogen permeation by the membrane [7-9].

Regarding the steam to methane molar ratio in the feedstock, an intermediate value (2.81) was obtained regarding the established limits. This happened because as H<sub>2</sub>O/CH<sub>4</sub> ratio increased, the methane conversion also increased. However, a decrease in hydrogen recovery was observed due to the dilution of hydrogen in the reaction medium, which reduces its partial pressure and, thus, permeation. Therefore, the optimal value obtained for this ratio is ideal, as values lower than 2.5 may lead to coke formation in practice, which has a devastating effect for both the membrane and catalyst [5,9].

The methane molar flow rate in the feed is directly related to the contact time of reactants with catalyst. In general, an increase in methane flow results in a decrease of both methane conversion and hydrogen recovery [9]. Thus, it was expected that the optimum value obtained for this parameter, which was 1.00 kmol h<sup>-1</sup>, would be equal to the value of its constraint lower limit.

## V. CONCLUSIONS

The optimization of the hydrogen production by steam methane reforming in a membrane reactor was performed, aiming to maximize the sum of methane conversion and hydrogen recovery. Both variables are strongly influenced by the reaction temperature, reaction pressure in the reaction side and permeate; steam to methane molar ratio in the feedstock, and methane flow rate in the feed. Therefore, these

operational conditions were chosen as decision variables.

The methodology used to maximize the objective function was able to reach optimum values close to the maximum conversion of methane and hydrogen recovery, X<sub>CH<sub>4</sub></sub> = 99.94% and Y<sub>H<sub>2</sub></sub> = 98.87%. The operating conditions applied were consistent with what was expected for this process and what is usually described in literature.

It was shown that the membrane reactor has the potential to be efficient alternative when compared to the conventional reactor (PBR), since it was able to reach higher conversion at lower temperature. Moreover, to reach the same conversion as the membrane reactor, the conventional reactor should be operated at higher temperature. Therefore, the use of membrane reactor for steam methane reforming could contribute to decrease process costs due to a reduction in energy demand.

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