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Article

Concentration Analysis of Catalytic Conversion of Carbon Gas into Natural Gas (Hydrogen)

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Abstract: The annual energy matrix has been changing in the last years because of the necessity of less dependence on fossil fuels, which are running out on the planet. Therefore, a study was started to simulate the most efficient production of H_2 through COMSOL Multiphysics®, as it is a gas that in the future will be essential to supply the world's energy necessities, due to its easy to get and insert in piped gas pipes. From this study, we were able to present an optimization of parameters that presents good indications of how to obtain efficient hydrogen production in an idealized reactor.

Keywords: production of H_2; numerical simulation; optimization

1. Introduction

The Since the beginning, humanity has been using different sources of energy for survival. In recent years, because of the high demand for petroleum-derived raw materials, the world has been concerned about the enormous amounts of pollutants released into the atmosphere by burning fossil fuels and the dependence on an energy source that may run out in the future.

Despite this enormous necessity to reduce the release of carbon gas into the atmosphere, the global energy matrix is still predominantly based on non-renewable sources. In order to fulfill the objectives of COP 21 (an agreement between 195 nations of the world to reduce the emissions of gases responsible for the greenhouse effect, with the aim of reducing global warming), the market for the use of natural gas, emerged as a competitive solution in the generation of less polluting energy for the planet [1].

Natural gas (NG) is a mixture of light hydrocarbons, that remains in the gaseous state at normal temperature and pressure, and today generates more efficiency in the reduction of pollutants. In addition, it's growing by about 38% per year in the amount of use, composing the matrix world energy. It is predominantly composed of CH_4 and H_2, mostly obtained from oil excavations [2].

As it is a fossil fuel, is estimated that in 40 or 50 years from now, NG reserves will have reached critical levels, and in Brazil since 2019, annual reductions of 10% of our reserves have been observed. Thinking about highly efficient alternatives, countries in Europe and Brazil are studying the possibility of generating H_2, to contribute to the natural gas originating from excavations, due to being more efficient in the energetic matrix [3].

H_2 can be obtained through numerous reactions, due to the easy connection with various chemical elements. In this project, we will simulate through the COMSOL Multiphysics® software the most efficient way of producing this gas in a cylindrical reactor and pre-established conditions through the chemical equation:

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$$CO + H_2O \rightleftharpoons H_2 + CO_2 \quad (1)$$

that from readings in scientific texts and previous numerical simulations it was noted the reverse reaction can be considered negligible in our analysis that mainly aims to present a case study that analyzes the optimization, or the best composition of three variables of the proposed case, inlet velocity, inlet concentration (H_2O) and reactor geometry.

2. Chemistry Kinetic

Chemical kinetics studies the behavior of chemical reactions according to the time and rate (speed) at which they occur, with the objective of understanding their evolution at a macroscopic and microscopic level [4].

According to [4], there are many factors that interfere with the rate of a reaction, but we can mention four main ones: the physical state of the reactants, inlet concentrations, the temperature of the medium, and the presence or absence of a catalyst. Therefore, the rate of a general reaction can be given by:

$$rate = k[reagent\ 1]^m[reagent\ 2]^m \quad (2)$$

Where:

- m and n make up the overall reaction order and are determined empirically;
- k is the speed constant.

The reaction rate constant depends on the collision energy of the molecules, their orientation, and the temperature of the medium. This relationship can be defined using the Arrhenius equation [5]:

$$k = Ae^{\frac{-Ea}{RT}} \quad (3)$$

where: k is the reaction rate constant; E_a is the activation energy of the reaction; R is the gas constant (R = 8.314 J/K.mol); T is the temperature in K; A is the frequency of collisions that happen with correct geometry.

The activation energy is the minimum energy for the chemical reaction to occur, that is, for the bonds between the reactants to be broken and the new bonds between the products to be formed, as exemplified in Figure 1.

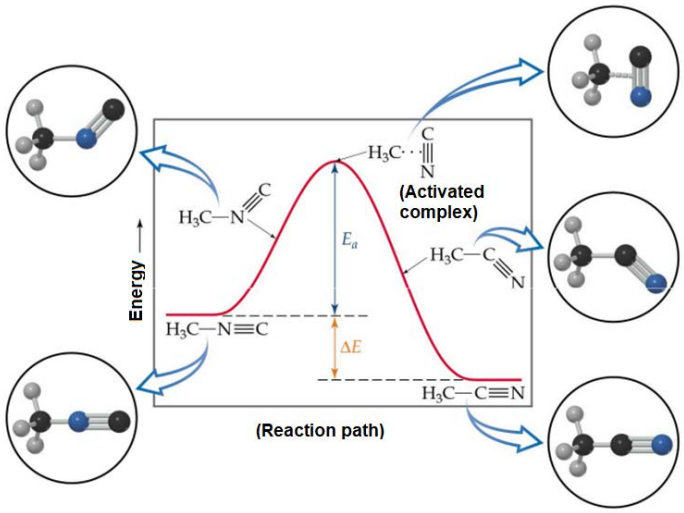

Figure 1. Exemplification of Activation Energy [6].

To increase the speed of the chemical reaction, we can use a catalyst, which is a substance capable of accelerating the process without undergoing changes, that is, it is not consumed and regenerates itself at the end of the reaction. The catalytic agent acts to reduce the activation energy of the reaction, as we can see in Figure 2 [7].

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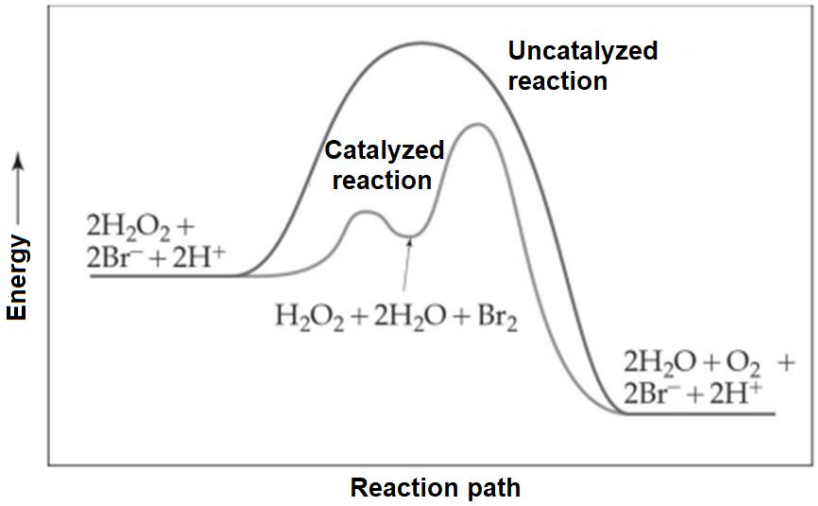

Figure 2. Reaction without and with the presence of catalyst [6].

Therefore, the lower the activation energy, the faster the reaction takes place, and vice versa.

Finally, the last important topic to describe in this process is the concept of chemical equilibrium, which represents a dynamic state between two or more processes occurring at the same time and at the same speed [8].

Still according to [8], for the chemical equilibrium to be reached, it is necessary that the pressure and temperature of the reactor remain constant, in addition to the system being closed. With this, the concentrations remain constant over time, not changing while the environment is not changed, as we can see in Figure 3.

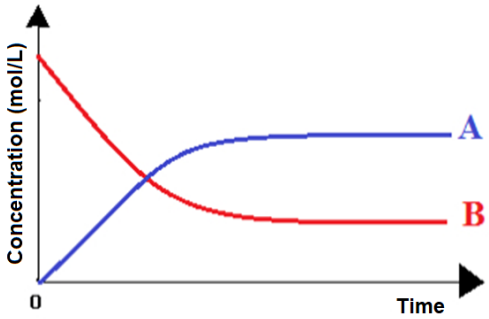

Figure 3. Chemical Equilibrium [5].

3. Methodology

3.1. Parameters

In order to analyze the influence and/or importance of the three parameters proposed here (inlet speed, reactor geometry, and inlet concentration), the reactor geometry is initially presented, as shown in Figure 4.

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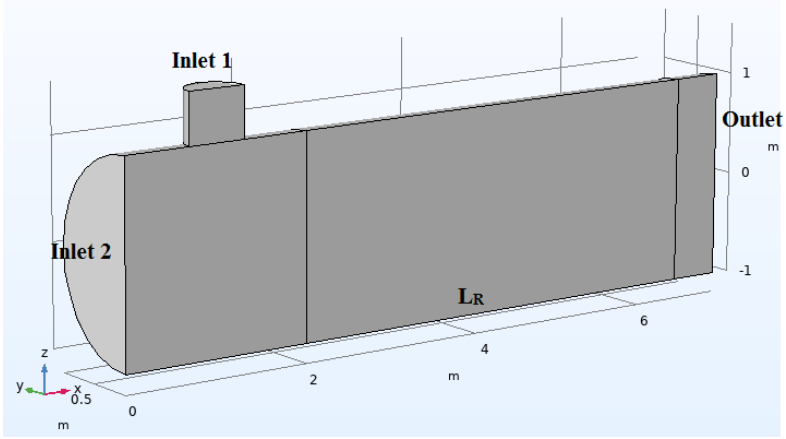

Figure 4. Reactor geometry.

Here, the following simplifications or considerations will be adopted:

1- Due to the geometry of the reactor, symmetry in the $y = 0$ plane will be considered;

2- CO inlet concentration is equal to 10 mol/m^3 (Inlet 1) in all numerical simulations;

3- Reactor diameter is equal to 1 m;

4- The domain is entirely composed of air;

5- The speeds at inputs 1 and 2 are the same;

6- Isothermal analysis (T = 675 K);

7- Porosity equal to 0.5 and permeability 10^{-9} m^2;

8- The formula used to calculate the diffusivity between gases (D_{AB}), according to [9] is the following:

$$D_{AB} = 1{,}053 \times 10^{-3} \frac{T^{3/2}}{Pd^2{}_{AB}} \left[\frac{1}{M_A} + \frac{1}{M_B}\right]^{1/2} \quad (4)$$

where, T is the temperature [K], P is the pressure [atm], M_A is the molar mass of element A (CO, H_2O, CO_2 or H_2), M_B is the molar mass of element B (Air) and d_{AB}, is defined by

$$d_{AB} = \left(\sum \mathrm{v}\right)_A^{1/3} + \left(\sum \mathrm{v}\right)_B^{1/3} \quad (5)$$

In this work will be considered the values presented in Table 1.

Table 1. Diffusion molecular volumes [9].

Molecule	$\left(\sum \mathbf{v}\right)$	Molar Mass
Air	16.2	28.96
CO	18.0	28.01
H_2O	13.1	18.01
CO_2	26.9	44.01
H_2	6.12	2.016

9 - As we mentioned in the introduction, in this work the chemical reaction will be adopted as irreversible, and with that, we can use the simplified equation, it would be:

$$[H_2] = k[CO][H_2O] \quad (6)$$

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$$[CO_2] = k[CO][H_2O] \tag{7}$$

where k is defined by Equation (3) and using as reference Xu and Froment [10], yield that

$$k = 5.43 \times 10^5 e^{-\left(\frac{67100}{8{,}31 \times 675}\right)} \tag{8}$$

3.2. Governing Equations

In order to study the conservation of motion, Brinkman's equations were used in the form:

$$\nabla \cdot [-p\boldsymbol{I} + \boldsymbol{K}] - \left(\mu\kappa^{-1} + \beta\epsilon_p|\boldsymbol{u}| + \frac{Q_m}{\epsilon_p^2}\right)\boldsymbol{u} + \boldsymbol{F} \tag{9}$$

$$\rho\nabla \cdot \boldsymbol{u} = Q_m \tag{10}$$

More details about the terms of Equations (9) and (10) can be found in [11]. While for the study of conservation of mass, the equation given by:

$$\nabla \cdot \mathbf{J}_i + \boldsymbol{u} \cdot \boldsymbol{\nabla} c_i = R_i + S_i \tag{11}$$

$$\mathbf{J}_i = -D_{e,j}\nabla c_i \tag{12}$$

$$\theta = \epsilon_p \tag{13}$$

More details about the terms of Equations (11)-(12) can be found in [12].

A generic porous catalyst will be used for the H_2 production reaction, with porosity equivalent to 0.5 and with the domain defined only in the L_R region. The COMSOL Multiphysics® defined equation of the diffusivity in the catalyst is defined by:

$$D_{e,j} = \frac{\epsilon_p}{{\epsilon_p}^{-1/2}} D_{f,j} \tag{14}$$

where: $D_{\mathrm{e,j}}$ is the diffusivity of the catalyst; ϵ_{p} is the porosity of the catalyst; and, $D_{\mathrm{f,j}}$ is the diffusivity of the reaction element in the porous medium of the catalyst.

This section may be divided by subheadings. It should provide a concise and precise description of the experimental results, their interpretation, as well as the experimental conclusions that can be drawn.

4. Results and Discussions

Conform cited in the introduction, there will be presented the analysis of the efficiency of a generic idealized reactor from the variation of three parameters: H_2O Concentration (Case 1), Geometry reactor (Case 2), and Inlet Velocity (Case 3). Finally, a proposed optimization for three parameters will be presented. To carry out this optimization, the average concentrations of H_2 and CO_2 in the outlet were analyzed as an output parameter. In the three cases proposed below, the input concentration of CO at 10 mol/m^3 will be simulated as fixed.

4.1. Case 1: Varying H_2O

In the first case the H_2O was varied in the values 1, 2, 5, 10, 20, 50, and 75 mol/m^3 (H_2O inlet), conform presented in Figures 5 and 6. Note that in this case was varied L_R in the values 2.5 and 5 meters.

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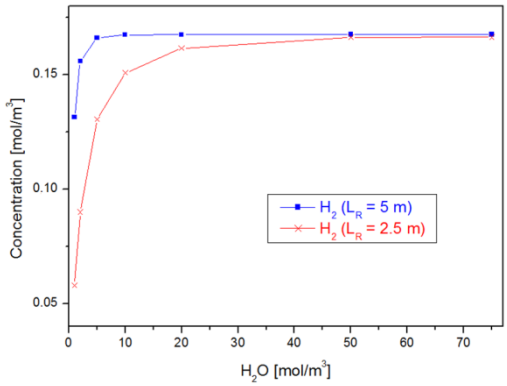

Figure 5. Medium concentration values H_2 varying H_2O.

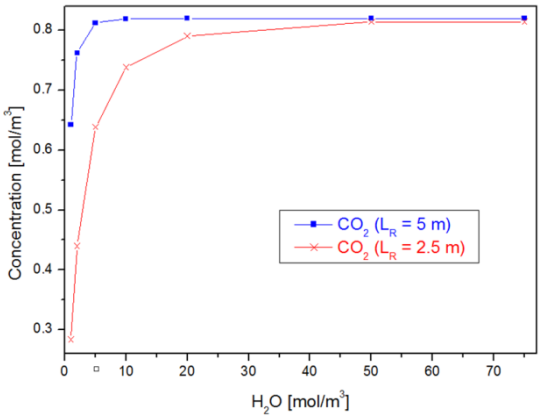

Figure 6. Medium concentration values CO_2 varying H_2O.

In Figures 5 and 6, some interesting information can be seen: both the production of H_2 and CO_2 reached their maximum points close to 50 mol/m^3 of input H_2O, highlighting that it occurs for both L_R equal 2.5 and 5 meters. It's easy to note that the production of CO_2 is most that H_2 (in turn of 5 times).

4.2. Case 2: Varying the reactor geometry (L_R)

As in Case 1 the H_2O inlet concentration equal to 10 mol/m^3 was found to be a highlight, in this case, the inlet concentration was fixed (H_2O = 10 mol/m^3).

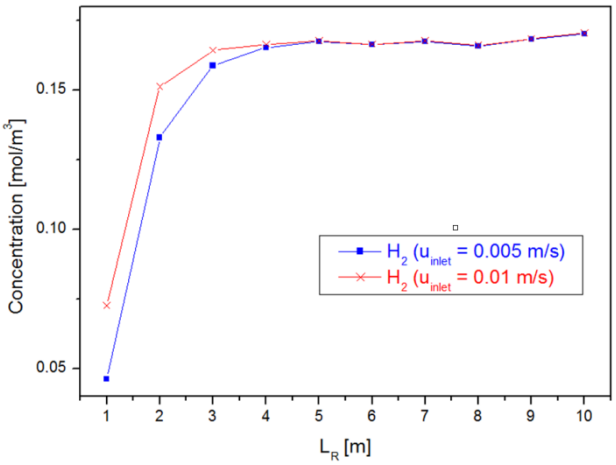

Figure 7. Medium concentration values H_2 varying L_R.

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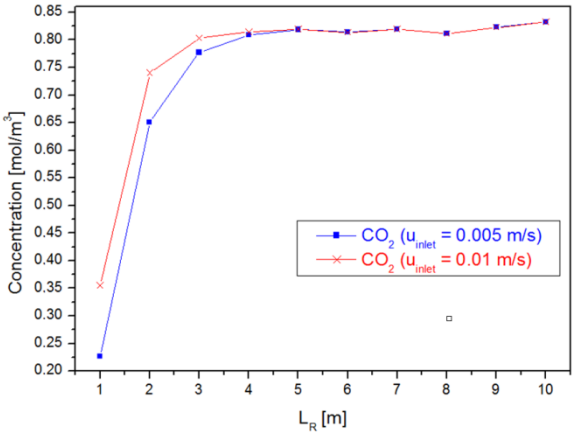

Figure 8. Medium concentration values CO_2 varying L_R.

Figures 7 and 8 present the average concentration at the reactor outlet for different reactor sizes for two different inlets (u_{inlet}) velocities. As in Case 1, both H_2 and CO_2 reach a stabilization at the average concentration of outlet of the reactor around a reactor of length 5 m for two evaluated velocities.

4.3. Case 3: Varying the Inlet Velocity (u_{inlet})

Finally, in this last case, the speed variation will be presented for, again, an H_2O inlet concentration of 10 mol/$m^3$and for two L_R values, 5 (highlighted value in Case 2) and 10 m.

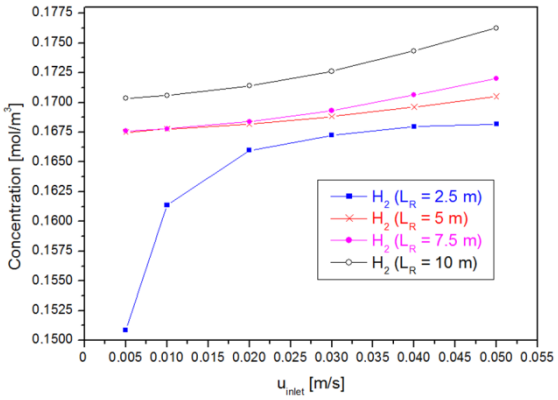

Figure 9. Medium concentration values H_2 varying Inlet velocity.

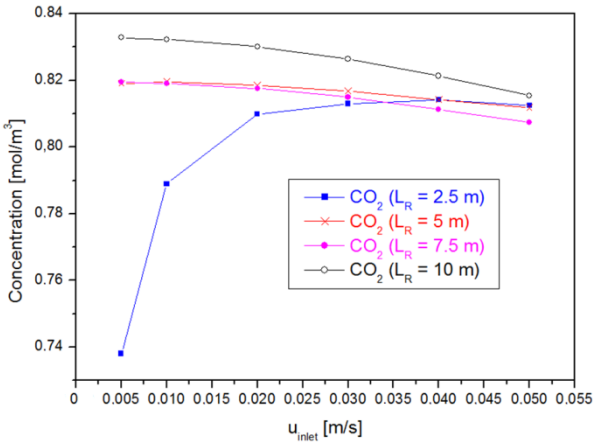

Figure 10. Medium concentration values CO_2 varying Inlet speed.

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As in the first two cases, it is noted that the four L_R variations together with the u_{inlet} variations suggest stability of H_2 production (Figures 9 and 10), with the caveat that except in the case $L_R = 2.5$ m, the other curves are slightly decreasing.

4.4. Optimization

In order to understand how the control variables influence the generation of hydrogen, from the highest production, $H_2 = 0.175$, found in the condition: $L_R = 10$ m, u_{inlet}= 0.04 m/s, and $H_2O = 10$ mol/m^3, for L_R ranging between 1 and 10 m, u_{inlet} between 0.005 and 0.04 m/s, H_2O between 1 and 10 mol/m^3, in the data set analyzed in the previous sections, a new data set was generated in the simulations, varying p% for more and/or for less the values of the input variables. In this way, the process was repeated, always starting from the highest value found, until obtaining a new set of data with sufficient size to test regression models with 3 independent variables and their combinations 2 by 2. What, in this case, were 4 iterations using: p = 0.2, p = 0.1, p = 0.05, and p = 0.05 forming a new dataset with 32 points.

For this new set of data, using the K-fold cross-validation with 10 folds, the best model adjustment was obtained as shown in Equation (15).

$$H_2 = 0.14429 + 0.004254L_R - 0.151u_{inlet} - 0.000196H_2O - 0.000207L_R^2 + 0.0381L_Ru_{inlet} \quad (15)$$

The statistics regarding the quality of adjustment of the model (Equation 15) are shown in Table 2, in which it is possible to observe that the model fits very well to the simulated data, showing high adjusted R2 and cross-validation values, indicating that the model has good generalization capacity with a test for normal residuals (Aderson Darling), P-Value = 0.164.

Table 2. Summary of the quality model fit (Equation 15).

S	R2	R2(aj)	R2(pred)	10-fold S	10-fold R2
0.0007019	98.16%	97.81%	97.40%	0.0007624	97.33%

The analysis of the variance of the model (Equation 15) is shown in Table (3). In this table, it is evident from the analysis of the P-Value and the F-distribution that the variable that most influences the generation of H_2 is L_R followed by u_{inlet}. In the region studied, H_2O has a threshold significance.

Table 3. Analysis of variance for proposed model (Equation 15).

	GL	SQ (Aj.)	QM (Aj.)	F-Value	P-Value
Regression	5	0.000684	0.000137	277.67	0.000
L_R	1	0.000018	0.000018	35.64	0.000
u_{inlet}	1	0.000001	0.000001	1.53	0.227
H_2O	1	0.000002	0.000002	3.99	0.056
L_R^2	1	0.000013	0.000013	25.40	0.000
$L_R \times u_{inlet}$	1	0.000006	0.000006	12.95	0.001
Error	26	0.000013	0.000000		
Total	31	0.000697			

The quality of the adjustment can be observed in Figure 11. It is interesting to observe in this figure that the strategy of prospecting for new data with the objective of obtaining a greater production of H_2 appears to be successful because it presents several combinations of L_R, u_{inlet}, and H_2O with H_2 greater than 0.175 than in the initial dataset.

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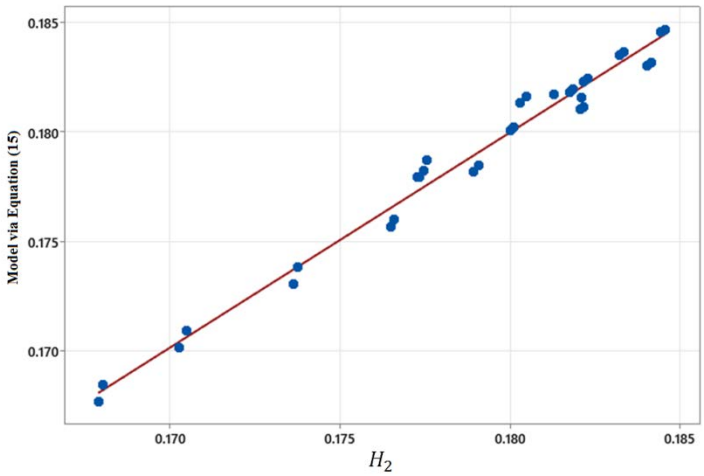

Figure 11. Quality of fit of the model (Equation 15) with respect to simulated H_2 production data.

Finally, using Minitab's optimizer it is possible to envision a direction toward greater H_2 production (Figure 12). In these results it is evident that greater production of H_2 can be obtained by increasing L_R and u_{inlet} and decreasing H_2O. And to assess whether these indications are correct, 6 more simulations were performed. The results are shown in Table 4, showing a significant increase in H_2 production.

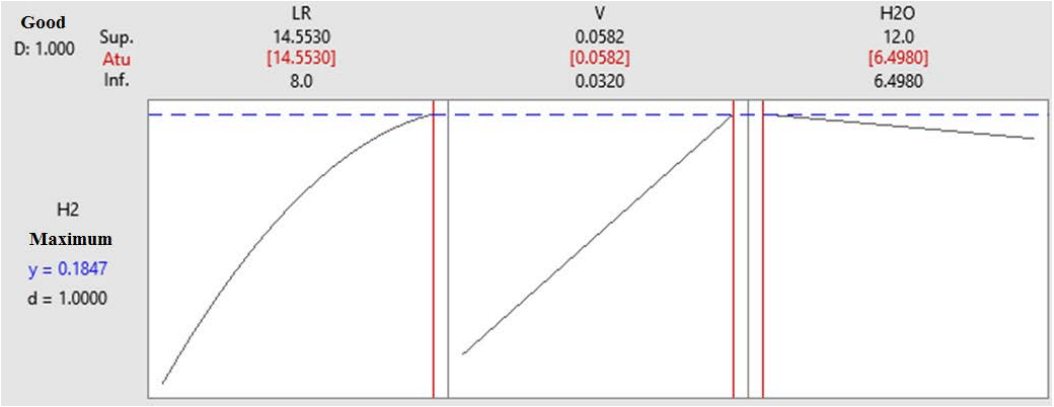

Figure 12. Model optimization (Equation 15) to maximize H_2 production.

In addition, the predictions of the proposed model, even under the extrapolation condition, are close to the simulated values, and several points are within the prediction confidence interval (99%). It is interesting to note that in point 6 there is a large discrepancy between the value of the simulation and the proposed model.

Table 4. Comparison between simulated values and values predicted by the model.

n	L_R [m]	u_{inlet} $[\frac{m}{s}]$	H_2O $[\frac{mol}{m^3}]$	H_2 $[\frac{mol}{m^3}]$	Prediction	LIMP	LISP
1	15	0.065	6	0.190	0.188	0.1854	0.1902
2	15.5	0.07	5.5	0.193	0.190	0.1875	0.1932
3	16	0.08	5	0.201	0.195	0.1912	0.1992
4	18	0.09	4	0.207	0.201	0.1947	0.2080
5	19	0.15	3.5	0.266	0.236	0.2158	0.2559
6	20	0.2	3	0.336	0.268	0.2337	0.3032

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This may be an indication of the use of the proposed model in an excessively extrapolated way or also that there was a change in the flow regime since the data were simulated in the laminar flow condition. In fact, subsequent attempts to simulate the production of hydrogen with higher velocities were not possible due to the numerical divergence presented by COMSOL, possibly due to entering a turbulent flow regime.

5. Conclusions

It can be concluded from this study that considering only three parameters, it is possible to simulate the production of H_2 and CO_2, in order to identify the optimized equation for these defined boundary conditions.

The great influence of the geometry on the concentration of the products is noticed, whereas after L_R greater than 5, the variation in velocity becomes negligible and the production of H_2 is prioritized instead of CO_2. The identified optimization equation has a high accuracy rate, corroborating with the idealization of the project and opening opportunities for the development of other studies considering the different conditions of the proposals in this paper.

After all, it is concluded that this study in addition to its many possible variations, contributes to the theme of sustainability, which has been growing on the world stage and to the development of new technologies for the benefit of society, in addition, to go search for new feasible alternatives for the production of energy more and more efficient.

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Conflicts of Interest: The authors declare no conflict of interest.

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