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Energy Self-Sufficiency Conditions of Ethanol Autothermal Reforming: a Simulation Study

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HIGHLIGHTS

- Pressure is not statistically significant for ethanol autothermal reforming.
- Temperature and steam/ethanol ratio have a positive effect on hydrogen production.
- Autothermal Reactor can achieve energy self-sufficiency.

Abstract: Natural gas steam reforming is commonly used for hydrogen production. However, research has shown that ethanol autothermal reforming can produce cleaner hydrogen gas efficiently. Despite this, there is a lack of studies on the energy self-sufficiency conditions of the ethanol autothermal reform. In this paper, we use simulations and the Response Surface Methodology (RSM) for the multivariate analysis of the energy self-sufficiency conditions in this process. First, we constructed and validated an industrial flowchart. After that, RSM allowed us to assess the process variables effects. The process variables studied were temperature (0 to 1000 ºC), pressure (20 to 30 bar), steam/ethanol ratio (2 to 5 mol/mol) and O_2/ethanol ratio (0 to 1.5 mol/mol). We observe that the temperature and steam/ethanol ratio increase have a positive effect on hydrogen production. On the contrary, the O_2/ethanol ratio increase has a negative effect, and the pressure increase is not statistically significant on hydrogen production. Therefore, the pressure was used at its minimum level (20 bar) while the temperature and the steam/ethanol ratio at its maximum levels (1000 ºC and 5 mol/mol). We also evaluated the energy consumption for the Autothermal Reactor (ATR). The reactor consumed 477.92 kJ/mol ethanol to produce 5.12 mol H_2/mol ethanol when we use 1000 ºC, 20 bar, steam/ethanol 5 mol/mol, and O_2/ethanol 0 mol/mol. ATR's energy self-sufficiency is achieved by using 1000 ºC, 20 bar, steam/ethanol 5 mol/mol, and O_2/ethanol 0.86 mol/mol. In these conditions, 3.95 mol H_2/mol ethanol is produced with 0 kJ/mol ethanol.

Keywords: Hydrogen gas production; modeling and simulation; renewable energy generation.

INTRODUCTION

Energy is a resource closely linked to the excellent performance of contemporary socioeconomic activities. Nevertheless, it is estimated that more than 80% of the global energy matrix is supplied by fossil fuels, like for example, oil, natural gas, and mineral coal [1,2,3]. Despite the practical and energetic advantages of fossil fuels, their excessive consumption brings problems, such as the generation of gases intensifying the greenhouse effect and air pollution. Besides that, due to its scarcity over the years, a probable energy crisis might be another problem [1,4,5]. The disadvantages of fossil resources and the growth of environmental awareness drive the development of clean and efficient technologies and fuels [6,7]. In this context, gas hydrogen is an alternative to traditional fuels due to five characteristics [1,5]:

a. It has the highest energy density among the known substances (120 MJ/kg);
b. It can be produced from different sources (including renewable sources as water and biomass);
c. It is sustainable;
d. It is not toxic;
e. It has clean burning (releases only water).

The five characteristics mentioned have attracted the attention of scientists. Since 1970, the “Hydrogen Economics” studies relate the production, use, transportation, and storage of hydrogen to the construction of a scenario in which this fuel is a primary source of energy. This scenario can promote high energy efficiency and reductions in environmental impacts and CO_2 emissions [1, 5]. The hydrogen production to contribute to the global energy matrix decarbonization can be done from various methodologies. Some methodologies are natural gas steam reforming, coal gasification, water electrolysis, photocatalysis, and alcohol reform [4]. Regardless of the methods, the key to large-scale hydrogen production is to cheapen raw materials and the process as a whole [1,2,4].

Hydrogen is the most abundant element in the universe. Despite this, it is little found on Earth in its gaseous form because it is usually associated with water and hydrocarbons [8]. Although there are many ways to produce hydrogen gas, 90% of production uses non-renewable raw materials, with natural gas being the primary raw material [9-11]. It is estimated that the natural gas steam reform, due to its high concentration of methane, exceeds 500,000 kg H_2/day [9,12]. Steam reform consists of a highly reactive endothermic reaction of natural gas with steam. High temperatures favor this reaction. The increase in the amount of steam also favors the reaction. However, increasing the temperature and the steam amount require higher costs in reactor operation and steam production, respectively. Therefore, a ratio of around 2.5-5.5 steam/methane is commonly used in refineries [9,12,13].

Ethanol as well as methane can be used to produce hydrogen. Inside a reforming reactor, ethanol is decomposed into methane, carbon monoxide and hydrogen, according to Equation 1. The combination of ethanol partial oxidation, Equation 2, which is extremely exothermic, and the ethanol reforming, Equations 3 and 4, produces the ethanol autothermal reforming, Equation 5. This is an alternative technology to achieve sustainable hydrogen production. Therefore, this methodology has a lower environmental impact and can achieve energy self-sufficiency [9,14,15]. Most studies on ethanol autothermal reform were concerned with the structural part of the reactors [16,17] and the development of cheap and efficient catalysts for the process [18-20]. Few studies in the scientific literature evaluate the ethanol autothermal reform based on modeling and simulation [21]. However, the modeling and simulation processes are useful tools for decision making, since they allow us to study the behavior of the process, as well as to evaluate and compare the impacts of operational conditions [22]. Also, it is essential to multivariate analysis, based on statistics, to determine which independent variables most affect the process, as well as to generate mathematical models to assess operational conditions [23]. In this work, multivariate statistical analysis was used to determine the energy self-sufficiency conditions of the ethanol autothermal reform. There is no knowledge in the literature of the energy self-sufficiency conditions in this process.

Some authors [24,25] have presented studies on the thermodynamic behavior of hydrogen production concerning temperature, steam/ethanol ratio, and O_2/ethanol ratio. These studies use Equations of State and univariate analyzes of the operational conditions of the process [24,25]. Both Graschinsky and coauthors. [24] and Rabenstein and Hacker [25] performed simulations varying the temperature, the steam/ethanol ratio, and the O_2/ethanol ratio to study the behavior of hydrogen production. However, to the best of our knowledge,

the simulations performed did not rely on multivariate analysis, limiting the understanding of the process, since the univariate analysis does not allow us to assess whether the process variables interact with each other. Besides, these studies did not take into account the process pressure variations, which is also one of its operational conditions. As the global reaction of the ethanol autothermal reforming does not have the same number of moles on the side of reagents and products, according to Le Chatelier's principle, it is expected that pressure variations affect the reaction equilibrium [26].

In this paper, we use simulations and the Response Surface Methodology (RSM) to assess the influence of temperature, pressure, steam/ethanol ratio, and O_2/ethanol ratio on the ethanol autothermal reforming. RSM is a collection of statistical and mathematical techniques that can be applied in the optimization and approximation of first- and second-order response surface models. The independent variables (control factors) are the input, and the outputs are the dependent variables (or response variable). In this work, RSM allowed us to determine the statistical significance of the controlled variables. Also, it was used to study the interaction effects of the parameters and to obtain a mathematical relationship between control variables (temperature, pressure, steam/ethanol ratio, and O_2/ethanol ratio) and responses (hydrogen production and energy consumption).

MATERIAL AND METHODS

Choice of Software and Thermodynamic Package

The construction of the flowcharts of the ethanol autothermal reform plant, as well as their simulations, were performed using the Aspen HYSYS V9 software, which is widely used in research and the industrial field for the study of chemical processes. Regarding the thermodynamic package, UNIQUAC was chosen, due to the polarity presented by the ethanol molecule.

Determination of reagents

In the simulations of the reforming plant, pure streams of ethanol, steam, and oxygen were used. The flow rate of ethanol used in each simulation was 100 kmol/h. The steam flow rate used was 200 kmol/h, and for the oxygen, the flow rate was 100 kmol/h. All reagent streams were initially simulated under pressure and temperature conditions equal to 20 bar and 300 ºC, respectively.

Construction of the flowchart of the ethanol autothermal reforming

The ethanol autothermal reforming is not yet used in the industry for the production of hydrogen. Therefore, its process flowchart was built based on the existing steps for the steam reform of natural gas [13] and suggested by Vita and coauthors [9] considering only the stages of reform and the water displacement reaction. The simulations of the ethanol autothermal reform were carried out according to the flowchart shown in Figure 1.

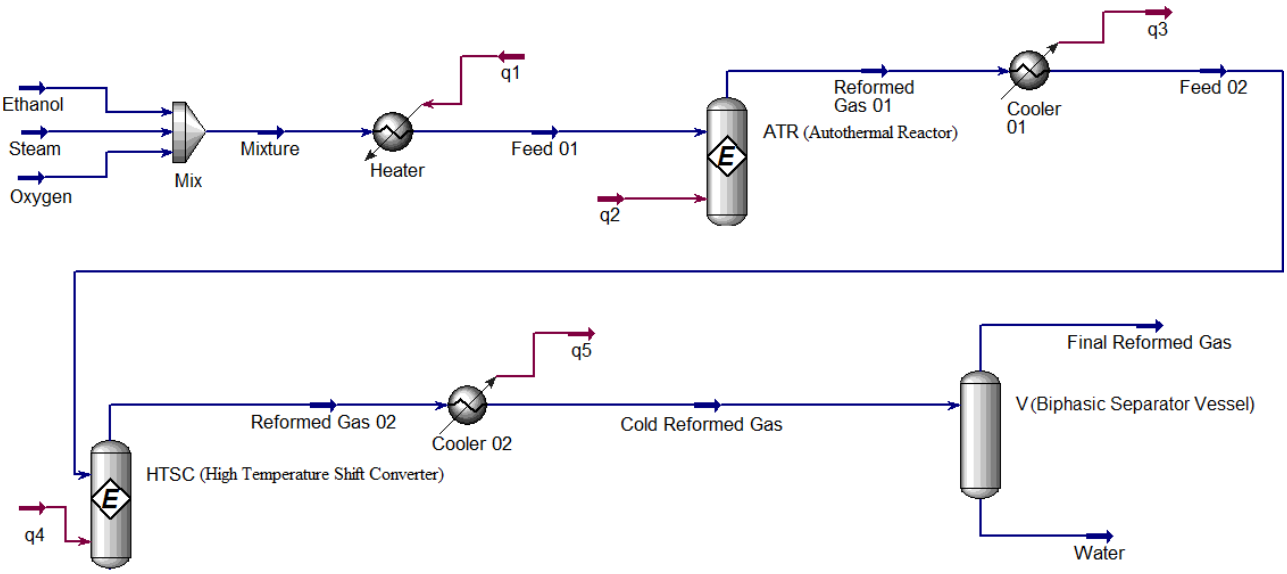

Figure 1. Flowchart for the ethanol autothermal reform plan built on Aspen HYSYS. The currents q1 to q5 represent the energy flows involved in the heating and cooling processes of the material currents in the process.

The supply of the ATR (Autothermal Reactor) is a mixture of ethanol, steam, and oxygen that was heated by the Heater to 500 ºC. When ethanol enters the ATR, it can be decomposed according to the reaction of Equation 1. In contrast, reactions showed in Equations 2, 3, and 4 occur in parallel, and correspond to partial oxidation of ethanol, the reform of methane, and the conversion of carbon monoxide to carbon dioxide that is known as Water-Gas Shift (WGS), respectively. Equation 5 represents the global balance of ethanol autothermal reforming.

$$C_2H_5OH(g) \leftrightarrow CH_4(g) + CO(g) + H_2(g), \quad (1)$$

$$C_2H_5OH(g) + 3/2O_2(g) \rightarrow 3H_2(g) + 2CO_2(g), \quad \Delta H = -549\ kJ/mol, \quad (2)$$

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g), \quad \Delta H = +206\ kJ/mol, \quad (3)$$

$$CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g), \quad \Delta H = -41\ kJ/mol, \quad (4)$$

$$C_2H_5OH(g) + xO_2 + (3 - 2x)H_2O \rightleftharpoons (6 - 2x)H_2 + 2CO_2 \quad (5)$$

From the analysis of Equation 5, it is clear that the amount of oxygen used in the process has a direct impact on the production of hydrogen. Since Equation 4 is exothermic, the ATR product passes through Cooler 01 to be cooled to 500 ºC, going to the HTSC (High-Temperature Shift Converter), whose function is to react methane and carbon monoxide with steam to produce more hydrogen. The HTSC was operated at a fixed temperature of 500 ºC. After this step, Reformed Gas 02 passes through Cooler 02, to be cooled to room temperature. Water is separated in a Biphasic Separator Vessel (V), from which Water and the Final Reformed Gas come out. The Final Reformed Gas has a high concentration of hydrogen and carbon dioxide. The equilibrium constants of the reactions performed in the flowchart of Figure 1 were calculated from the minimization of Gibbs Free Energy.

Validation of the flowchart of the ethanol autothermal reforming

In order to validate the proposed flowchart for the ethanol autothermal reforming, as shown in Figure 1, we carried out simulations, varying the reforming temperature and the flow rates of the reagents. These simulations were performed according to the work of Rabenstein and Hacker [25].

Statistical analysis of operational conditions

We investigated the statistical significance of four factors (temperature, pressure, steam/ethanol ratio, and O2/ethanol ratio) of the ethanol autothermal reforming, as shown in Table 1.

Table 1. Factorial Design - Coded and real values for the variables of the ethanol autothermal reforming.

Factors/Codes	-1	0	+1
Temperature (ºC)	600.00	800.00	1000.00
Pressure (bar)	20.00	25.00	30.00
Steam/ethanol (mol/mol)	2.00	3.50	5.00
O_2/ethanol (mol/mol)	0.00	0.75	1.50

Our factorial design was complete for two levels of each factor. In total, 17 simulations (with one central point) were performed. The values of the indicators were defined based on the operating conditions of an industrial reforming process [13,16].

In this paper, the statistical analyses were made from the assessment of the estimated effect tables and Pareto graphs. We use a confidence level of 95% to assess the significance of the operational conditions studied in the production of hydrogen and energy consumption. Besides that, we also obtain mathematical models for hydrogen consumption and energy consumption in ATR. Based on the ANOVA of these models, we performed the F test to prove the significance of the models and thus evaluate the point of better hydrogen production and the energy self-sufficiency of the ATR.

RESULTS AND DISCUSSION

Validation of the flowchart of the ethanol autothermal reforming

Rabenstein and Hacker [25] carried out a thermodynamic study that evaluated the production of hydrogen as a function of the operational conditions of the ethanol autothermal reforming (temperature, steam/ethanol ratio, and O2/ethanol ratio). The results were obtained from the Peng-Robinson and Gibbs Free Energy Minimization equations. The calculations were performed at Aspen-Tech. The variables were studied in the ranges of 200 ºC to 1000 ºC; 0 to 10 (mol/mol) and 0 to 0.75 (mol/mol), for temperature, steam/ethanol ratio, and O2/ethanol ratio, respectively, at atmospheric pressure. These same conditions were reproduced in this study with the Aspen HYSYS software using the UNIQUAC thermodynamic package. Figure 2 shows the results obtained in this study.

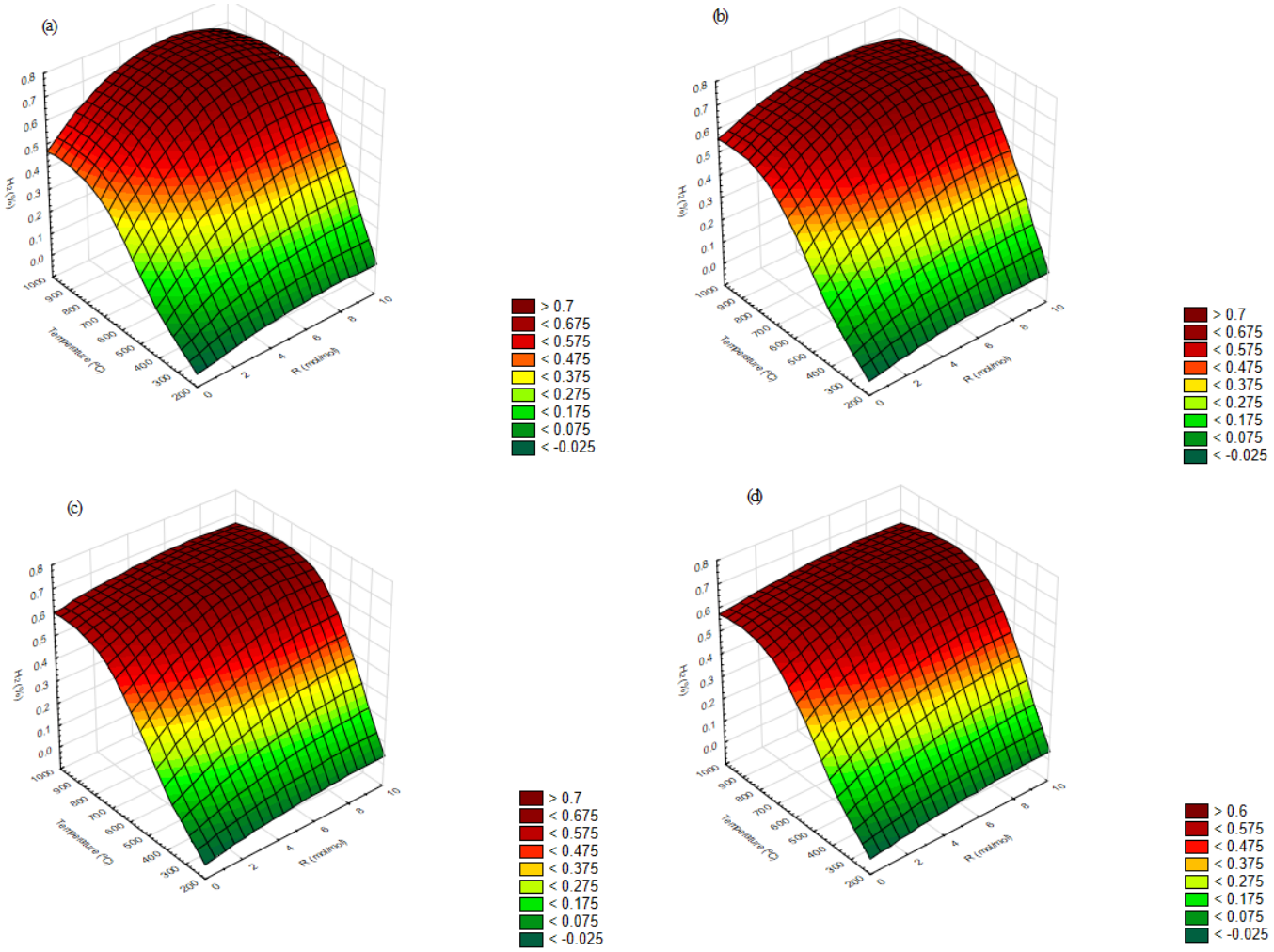

Figure 2. Results of the simulations for the molar fraction of H_2 as a function of temperature and steam/ethanol ratio (R), obtained in Aspen HYSYS. (a) (O_2/ethanol) = 0; (b) (O_2/ethanol) = 0.25; (c) (O_2/ethanol) = 0.50; (d) (O_2/ethanol) = 0.75.

The results found in this study (Figure 2) were similar to those obtained by Rabenstein and Hacker [25]. Therefore, we concluded that the flowchart presented in Figure 1 is valid and can be used to study the ethanol autothermal reform. The behaviors obtained in Figure 2 are following Eqs. 3 and 4. The increase of temperature and the steam/ethanol ratio favors hydrogen production. This occurs because Equation 3 (methane reforming) is an endothermic reaction. Therefore, high temperatures favor it. Also, Equation 4 shows that excess water steam contributes to the conversion of CO to H2. In contrast, increasing O2/ethanol ratio reduces hydrogen production according to Equation 5. This decrease in hydrogen production occurs because higher amounts of oxygen favor more the partial oxidation of ethanol than the reform reaction. It is perceived in Equation 2 that the ethanol partial oxidation produces 3 hydrogen mols while its reforming can produce 6 hydrogen mols, according to Equation 5 in absence of oxygen.

Statistical analysis of the influence of the operational parameters of the ethanol autothermal reforming

We use a complete factorial design (temperature, pressure, steam/ethanol ratio, and O2/ethanol ratio) to determine which variables are statistically significant for ethanol autothermal reforming. The simulated conditions are shown in Table 2, together with the results of hydrogen production and energy consumption.

Table 2. Matrix of planning of 4 factors and results of the simulations - Ethanol Reforming

Simulations	T (°C)	P (bar)	R* (mol/mol)	Ro** (mol/mol)	molH_2/mol *ethanol*	E(kJ/mol ethanol)
1	600	20.00	2.00	0.00	0.84	-8.19
2	1000	20.00	2.00	0.00	4.30	357.12
3	600	30.00	2.00	0.00	0.70	-15.85
4	1000	30.00	2.00	0.00	4.08	337.82
5	600	20.00	5.00	0.00	1.58	38.12
6	1000	20.00	5.00	0.00	5.37	430.92
7	600	30.00	5.00	0.00	1.33	25.62
8	1000	30.00	5.00	0.00	5.29	426.96
9	600	20.00	2.00	1.50	0.89	-600.48
10	1000	20.00	2.00	1.50	2.64	-362.16
11	600	30.00	2.00	1.50	0.74	-609.12
12	1000	30.00	2.00	1.50	2.63	-362.52
13	600	20.00	5.00	1.50	1.35	-567.72
14	1000	20.00	5.00	1.50	2.81	-307.15
15	600	30.00	5.00	1.50	1.15	-578.52
16	1000	30.00	5.00	1.50	2.81	-306.54
17	800	25.00	3.50	0.75	3.30	208.01

*Steam/ethanol ratio; **Oxygen/ethanol ratio

From the statistical analyzes, we generated the Pareto graphs for hydrogen production and energy consumption in the ATR, as shown in Figure 3.

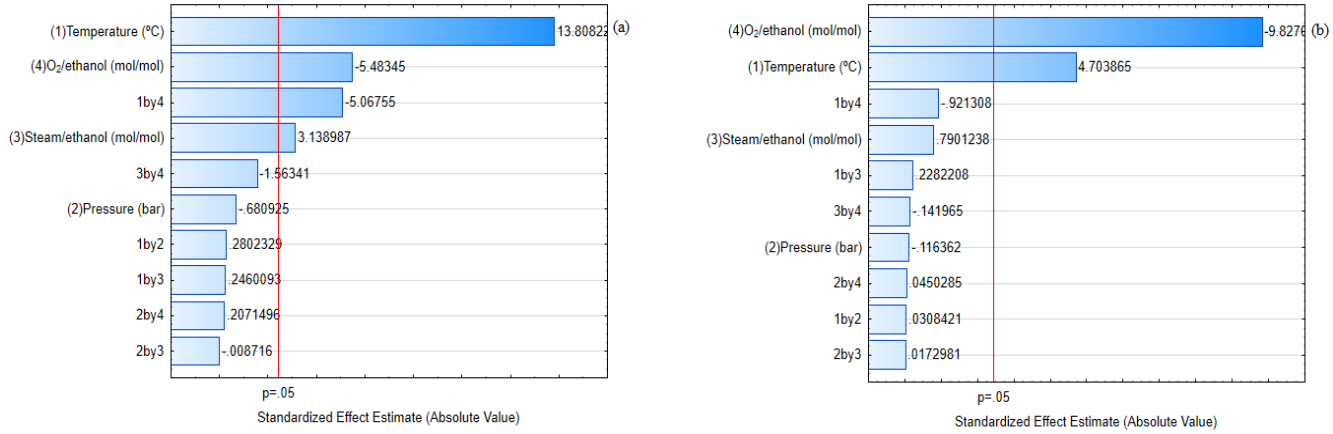

Figure 3. Pareto graph for the factorial design of four factors. (a) H_2 production; (b) Energy consumption in the ATR.

We noticed that the increasing temperature and the steam/ethanol ratio favor hydrogen production (Figure 3.a) and increase the ATR energy consumption (Figure 3.b). In contrast, increasing the pressure and O2/ethanol ratio decreases the ATR energy consumption (Figure 3.b) and the production of hydrogen (Figure 3.a). Still, based on Figure 3, we noticed that the pressure was not statistically significant for the production of hydrogen or the consumption of energy in the ATR. Therefore, it can be set at its minimum level (20 bar), without impairing the production of hydrogen. Besides, lower pressure values are safer in industrial operations. The temperature, steam/ethanol ratio, and O2/ethanol ratio were statistically significant for the production of hydrogen (Figure 3.a). There was also a negative interaction between temperature and the O2/ethanol ratio. This result means that different levels of these variables (+1 and -1 or -1 and +1, respectively) can be used to increase hydrogen production. For the ATR energy consumption, only the temperature and O2/ethanol ratio were statistically significant. Based on the statistical analysis, we generate the estimated effects of the factors on hydrogen production, according to Table 3.

Table 3. Estimated effects for hydrogen production

Factor	Effect	Std.Err.	p	-95%	+95%
(1) Temperature (ºC)	2.668	0.193	0.000	2.196	3.141
(2) Pressure (bar)	-0.132	0.193	0.521	-0.604	0.341
(3) Steam/ethanol (mol/mol)	0.607	0.193	0.020	0.134	1.079
(4) O_2/ethanol (mol/mol)	-1.060	0.193	0.002	-1.532	-0.587
1 by 2	0.054	0.193	0.789	-0.419	0.527
1 by 3	0.048	0.193	0.814	-0.425	0.520
1 by 4	-0.979	0.193	0.002	-1.452	-0.506
2 by 3	-0.002	0.193	0.993	-0.474	0.471
2 by 4	0.040	0.193	0.843	-0.432	0.513
3 by 4	-0.302	0.193	0.169	-0.775	0.171

Std.Err. (Standard Error), p (p-values).

The evaluation of the estimated effects for hydrogen production indicates that the steam/ethanol ratio has a positive effect on it. Thus, the use of this operational condition at its maximum level (5 mol/mol) will favor production. However, the temperature and the O2/ethanol ratio showed a significant negative interaction. The negative interaction means that the temperature and the O2/ethanol ratio must not be analyzed separately. Therefore, using temperature and oxygen/ethanol ratio at different levels (+1 and -1 or -1 and +1) favor hydrogen production. The pressure was not statistically significant, and it can be used at its minimum level (20 bar). Table 4 shows the estimated effects of ATR energy consumption.

Table 4. Estimated effects for energy consumption on ATR

Factor	Effect	Std.Err.	p	-95%	+95%
(1) Temperature (ºC)	316.323	67.248	0.003	151.775	480.872
(2) Pressure (bar)	-7.825	67.248	0.911	-172.374	156.724
(3) Steam/ethanol (mol/mol)	53.134	67.248	0.460	-111.415	217.683
(4) O_2/ethanol (mol/mol)	-660.845	67.248	0.000	-825.394	-496.296
1 by 2	2.074	67.248	0.976	-162.475	166.623
1 by 3	15.347	67.248	0.827	-149.202	179.896
1 by 4	-61.956	67.248	0.392	-226.505	102.593
2 by 3	1.163	67.248	0.987	-163.386	165.712
2 by 4	3.028	67.248	0.966	-161.521	167.577
3 by 4	-9.547	67.248	0.892	-174.096	155.002

Std.Err (Standard Error), p (p-values).

Table 4 indicated that the temperature and the oxygen/ethanol ratio were statistically significant in the energy consumption of the ATR. The use of the temperature at its maximum level (1000 ºC) increases the energy expenditure by the ATR, while the oxygen/ethanol ratio at its maximum level (1.5 mol/mol) reduces energy consumption. We did not observe a statistically significant interaction effect between temperature and the oxygen/ethanol ratio for ATR energy consumption. The steam/ethanol ratio and the pressure were not statistically significant. With parameters of Tables 3 and 4, we perform a regression of statistically significant factors. The mathematical models obtained for hydrogen production and ATR energy consumption are shown in Eqs. 6 and 7, respectively.

$$Hydrogen\ Production = 2.462 + 1.334T + 0.303R - 0.530Ro - 0.489TRo\ , \quad (6)$$

$$Energy\ Consumption = -111.393 + 158.162T - 330.423Ro\ , \quad (7)$$

Where:
T: temperature coded;
R: Steam/ethanol ratio coded;
Ro: Oxygen/ethanol ratio coded.

Table 5 shows ANOVA for hydrogen production and ATR energy consumption.

Table 5. ANOVA for the model of hydrogen production by ethanol autothermal reform

Factor: Hydrogen Producion	**SS**	**df**	**MS**	**F**	**p**
Temperature (ºC)	28.483	1	28.483	251.706	0.000
Steam/ethanol (mol/mol)	1.471	1	1.471	13.007	0.003
O_2/ethanol	4.491	1	4.491	39.694	0.000
1 by 4	3.836	1	3.836	33.901	0.000
Error	1.357	12	0.113		
Total SS	39.641	16			
Factor: ATR Energy Consumption	**SS**	**df**	**MS**	**F**	**p**
Temperature (ºC)	400242	1	400242	40.963	0.000
O_2/ethanol (mol/mol)	1746866	1	1746866	178.784	0.000
Error	136791	14	9771		
Total SS	2283900	16			

SS (sum-of-squares); df (degrees of freedom); MS (mean squares); F (f ratio); p (p values).

For hydrogen production, the $F_{calculated}$ (84.58)/$F_{tabulated}$ (3.26) ratio was 25.94. Therefore, the model is statistically significant since this ratio was greater than 1 [27]. For the ATR energy consumption model, the $F_{calculated}$ (109.87)/$F_{tabulated}$ (3.74) ratio was 29.40. Thus, this model was also statistically significant. The R^2 for the Eqs. 6 and 7 were 0.966 and 0.940, respectively. Figure 4 graphically confirm the quality of the models obtained when comparing their predicted values with those obtained in the Aspen HYSYS simulations.

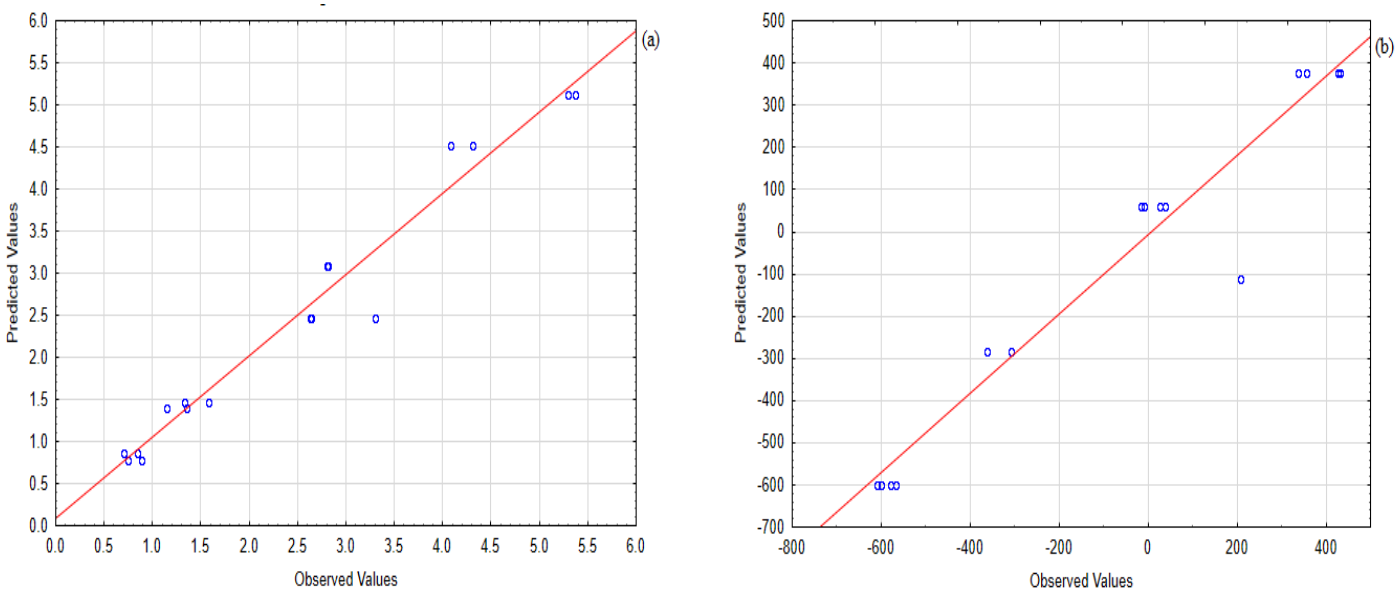

Figure 4. Comparison between the values predicted by the model with those obtained in the Aspen HYSYS simulations. (a) Hydrogen production from the ethanol autothermal reforming; (b) Energy consumption in the ATR from the ethanol autothermal reforming.

Figure 5 (a; b and c) shows the response surfaces for hydrogen production, based on a combination of independent factors, Temperature x Steam/ethanol, Temperature x O_2/ethanol, and Steam/ethanol x O_2/ethanol, respectively. Figure 5 (d) shows the response surface for ATR energy consumption from the combination of Temperature x O_2/ethanol.

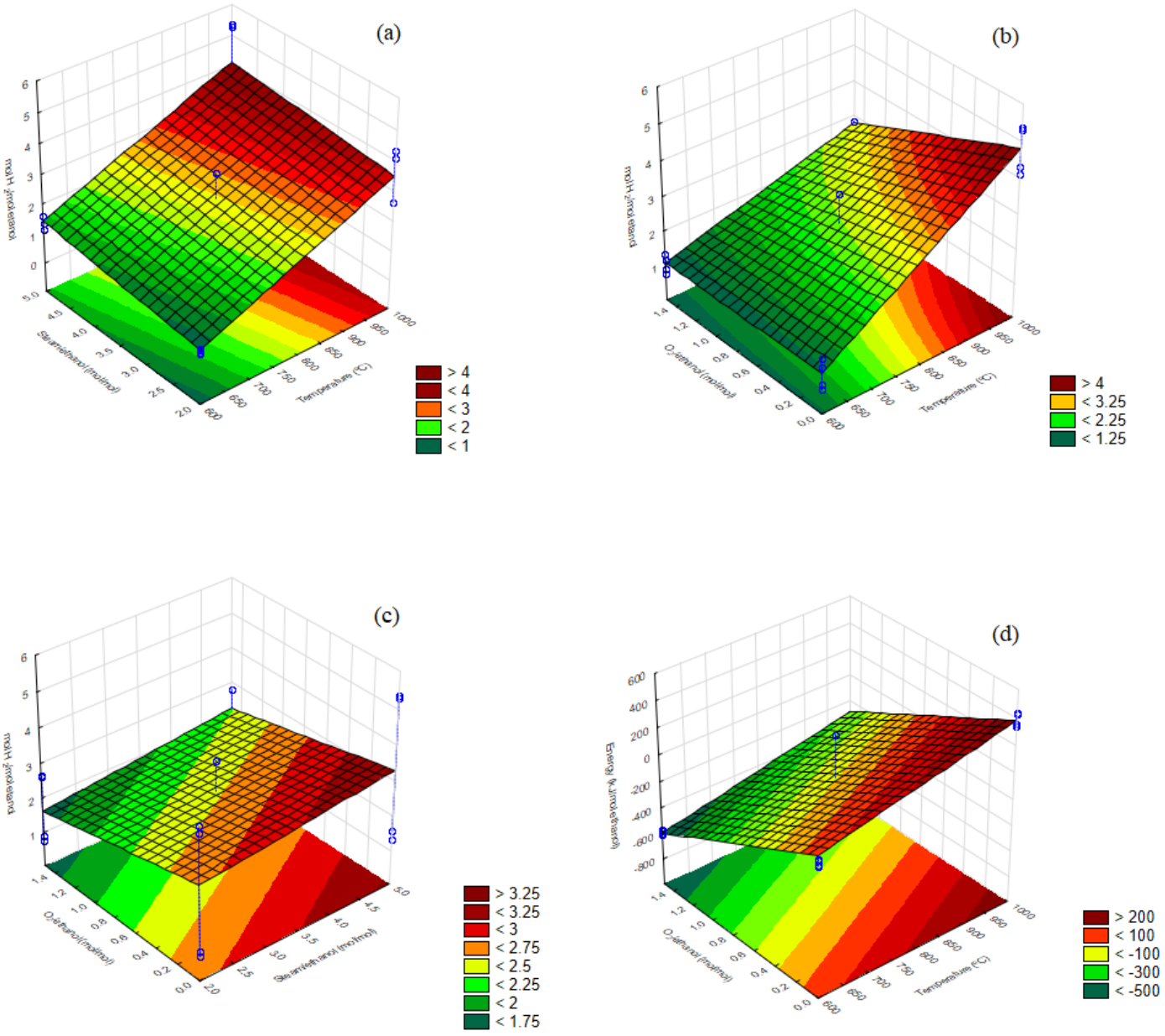

Figure 5. Response surfaces for the hydrogen production and for ATR energy consumption by the ethanol autothermal reforming. (a) H_2 production: Temperature versus Steam/ethanol; (b) H_2 production: Temperature versus O_2/ethanol; (c) H_2 production: Steam/ethanol versus O_2/ethanol; (d) ATR energy consumption: Temperature versus O_2/ethanol.

The analysis of the response surfaces reinforces the idea that the maximum hydrogen production occurs at the maximum levels of temperature and steam/ethanol ratio (1000 ºC and 5 mol/mol) and the minimum level of the O_2/ethanol ratio (0 mol/mol). This result occurs because the hydrogen production decreases with the O_2/ethanol ratio increase and increases at higher temperatures. As the pressure was not statistically significant for the hydrogen production, it was fixed at its minimum value (20 bar).

For 1000 ºC, 5 mol/mol steam/ethanol ratio, and 0 mol/mol O_2/ethanol ratio, we used Equation 6 and found 5.12 mol H_2/mol ethanol. These conditions were simulated in Aspen Hysys, and we found the production of 5.37 mol H_2/mol ethanol. Therefore, the error between the model and the simulated value is 4.66%. Besides that, we used the same operational conditions in Equation 7 and found an energy consumption of 477.92 kJ/mol ethanol. These operating conditions were simulated in Aspen HYSYS, and we obtained 430.92 kJ/mol ethanol. Thus, the error between the value obtained with the model and the simulated is 10.91%. These results are in agreement with the literature. Nimmas and coauthors [28] and Xue and coauthors [18] also found high conversion of ethanol and high hydrogen production efficiency (above 60% at

the dry output current) from ethanol autothermal reform. In addition, we used our flowchart shown in Figure 1 to simulate some experimental conditions provided by other authors. For this, we used one case from [19] at 540 ºC and 1 atm with steam/ethanol and O_2/ethanol ratios of (9 mol/mol) and (0.9 mol/mol), respectively. Besides, we simulated a second case from [20] at 540 ºC and 1 atm with steam/ethanol and O2/ethanol ratios of (9 mol/mol) and (0.7 mol/mol), respectively. The obtained errors were less than 3.90%, proving that our assumptions are satisfactory.

In order to find the O_2/ethanol ratio that allows the ATR to operate in energy self-sufficiency, we apply the best conditions for the hydrogen production (1000 ºC and 5 mol/mol steam/ethanol ratio) in Equation 7 and equal it to 0. Therefore, we find 0.86 for the mol O_2/mol ethanol ratio. The value obtained in Aspen HYSYS was 0.88 mol O_2/mol ethanol for the ATR to operate in energy self-sufficiency, that is, without requiring external energy. For the O_2/ethanol ratio, the error between the model and the simulated value is 2.27%.

In this work, the errors found between values predicted by the models and those obtained by simulations are acceptable. For the conditions (1000 ºC, 20 bar, 0.86 mol O_2/mol ethanol ratio, and 5 mol/mol steam/ethanol ratio) of ATR energy self-sufficiency, the hydrogen production was 3.95 mol H_2/mol ethanol. The comparison between the points of maximum hydrogen production (1000 ºC, 20 bar, 0 mol O_2/mol ethanol ratio and 5 mol/mol steam/ethanol ratio) and ATR energy self-sufficiency indicates that hydrogen production is reduced from 5.12 to 3.95 H_2/mol ethanol, that is, a drop of 22.85%. In contrast, ATR energy consumption is reduced by 100%.

From the analysis carried out, we observe that the pressure was not statistically significant for the hydrogen production for ethanol autothermal reforming. To the best of our knowledge, the scientific literature does not present data that included pressure in the studies. Therefore, we demonstrate that pressure is not statistically significant for the production of hydrogen in the range studied (20-30 bar). Thus, the pressure does not require precise control in industrial operations and can be fixed at its minimum value (20 bar) in order to guarantee greater operational safety to the process. Both for studies and industrial operations, temperature, steam/ethanol ratio, and O_2/ethanol ratio should be treated with greater importance concerning the process pressure.

To the best of our knowledge, the scientific literature does not present studies that identified negative interaction between temperature and O_2/ethanol ratio for hydrogen production, nor studies that found polynomial mathematical models for hydrogen production and ATR energy consumption for the ethanol autothermal reforming. In this paper, we identify the negative interaction effect between temperature and O_2/ethanol ratio that was taken into account in the polynomial models found for hydrogen production. Finally, we observe that with the obtained models it is possible to evaluate hydrogen production and ATR energy consumption in a precise and straightforward way, thus complementing the knowledge about the thermodynamics of the ethanol autothermal reforming.

CONCLUSION

In this paper, we simulated the ethanol autothermal reforming for hydrogen production. We carried out a complete factorial design for four variables (temperature, pressure, steam/ethanol ratio, and O_2/ethanol ratio) and simulations to assess significant factors, interactions between variables, and for obtaining polynomial mathematical models for hydrogen production and ATR energy consumption.

The industrial flowchart proposed in this study was validated from the similarity found between the behaviors of the response surfaces obtained with the behaviors presented by Rabenstein and Hacker [25]. From the analysis of the Pareto chart, we observed that there was a negative interaction between temperature and the O_2/ethanol ratio and that the steam/ethanol ratio was also statistically significant for hydrogen production. However, the pressure of the process was not statistically significant. In ATR energy consumption, we identified that only the temperature and the O_2/ethanol ratio were statistically significant. Thus, the pressure can be disregarded in statistical analysis for the development of mathematical models for hydrogen production and ATR energy consumption. Furthermore, in industrial cases, it is not necessary to strictly control the process pressure since moderate variations in pressure will not have a significant effect on the final production of hydrogen gas. More considerable attention should be paid to the study and control of temperature, steam/ethanol ratio, and O_2/ethanol ratio since these variables were statistically significant. Our analysis also allowed to obtaining of mathematical models for hydrogen production and ATR energy consumption. After verifying that the models are statistically significant, we used their equations and obtained a production of 5.12 mol H_2/mol ethanol (1000 ºC, 20 bar, 5 mol/mol steam/ethanol ratio, and 0 mol/mol O_2/ethanol ratio). We also found an O_2/ethanol ratio of 0.86 mol/mol for the ATR to achieve energy self-

sufficiency. In these conditions, we found a production of 3.95 mol H_2/mol ethanol at 1000 ºC, 20 bar, 5 mol/mol steam/ethanol ratio. The comparison between these two situations showed that for ATR energy self-sufficiency, the process loses 22.85% of the hydrogen production. However, it reduced ATR energy consumption by 100%.

In summary, we have demonstrated that the addition of oxygen in the ethanol steam reforming process can decrease energy consumption in the reforming reactor. However, this reduction in energy means a loss in the production of H_2. Therefore, in order to decide between maximum H_2 production or less costly conditions from an energy point of view, it is necessary to evaluate other issues (not included in the paper), such as the plant's production goals, the value of the H_2 on the market, among others.

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