

THERMODYNAMIC ANALYSIS OF HYDROGEN PRODUCTION FROM ETHANOL FOR FUEL CELL APPLICATIONS

Eveline De Robertis

Combustion and Propulsion Laboratory, National Institute for Space Research
Rod. Presidente Dutra, km 40, SP/RJ, Cachoeira Paulista, SP, 12.630-000
erobertis@yahoo.com.br

Elisângela Martins Leal

Combustion and Propulsion Laboratory, National Institute for Space Research
Rod. Presidente Dutra, km 40, SP/RJ, Cachoeira Paulista, SP, 12.630-000
elisangela@lcp.inpe.br

Rodrigo de Santis Neves

Combustion and Propulsion Laboratory, National Institute for Space Research
Rod. Presidente Dutra, km 40, SP/RJ, Cachoeira Paulista, SP, 12.630-000
rodrigo_santis_neves@yahoo.com.br

Amauri Menezes Leal Junior

Combustion and Propulsion Laboratory, National Institute for Space Research
Rod. Presidente Dutra, km 40, SP/RJ, Cachoeira Paulista, SP, 12.630-000
amaurileal@yahoo.com.br

Abstract. *The emerging of a new economy based on hydrogen will basically change our social, politics and economic institutions in the same way that the coal and vapor engine did in the beginning of the Industrial Age. Hydrogen is mainly produced by steam reforming, partial oxidation, coal gasification and electrolysis. An interesting option for Brazil is the production of hydrogen from ethanol of sugarcane with consolidated logistic of distribution and supplying infrastructure. Etanol (C₂H₅OH) has greater volumetric energy density if compared with hydrogen and advantages compared to methanol. Methanol has a favorable H:C ratio of 4 and can be transported and reformed more easily than natural gas. However, its main drawback is its high toxicity. Ethanol is more promising since it is less toxic and can be more easily stored and safely handled. Most importantly, it can be produced in large amounts from biomass hence is a renewable resource, as against methanol and gasoline. However, its main drawback is its bond C-C. The breakage of such bond can form several unwanted by-products and catalyst coking. This paper presents a methodology for the study of hydrogen production from ethanol reforming. The methodology is based on detailed thermodynamic and electrochemical analyses of the system. The plant performance has been evaluated on the basis of fuel utilization efficiency and each component of the plant has been evaluated on the basis of Second Law efficiency.*

Keywords: Ethanol reforming, hydrogen production, energy analysis, exergy analysis, fuel cell.

1. Introduction

In recent years, hydrogen has been playing an important role as an energy source which could contribute to both the reduction of atmospheric pollution and greenhouse gas emissions, and the reduction of global dependency on fossil fuels. Hydrogen generation is expected to be accomplished on-site by gaseous or liquid fuels reformation until all technical problems related to its storage and transportation are solved.

The steam reforming of alcohols for hydrogen production involves a complex multiple reaction system, the purity of a hydrogen product being affected by many undesirable side reactions. Therefore, the yield of hydrogen depends in a complex manner on the process variables such as pressure, temperature, reactants ratio, etc. In order to maximize the yield of hydrogen, it is necessary to know the effect of these variables on the product composition. Usually, the first step in such investigations is to perform a thermodynamic analysis of the process (Fishtik *et al.*, 2000).

Among liquid fuels, ethanol is a very interesting option for Brazil because of its available annual quantities and potential of production growing. Ethanol presents several advantages related to natural availability, storage and handling safety, ethanol can be produced renewably from several biomass sources, including energy plants, waste materials from agro industries or forestry residue materials, organic fraction of municipal solid waste, etc. Besides the ethanol-to-hydrogen system has the significant advantage of being nearly CO₂ neutral, since the produced carbon dioxide is consumed for biomass growth, thus offering a nearly closed carbon loop. Furthermore, the energy benefits of hydrate ethanol storage are about 11.5 times related to hydrogen storage at 20 MPa (Vaidya and Rodrigues, 2006).

Recently, the thermodynamic analysis of the steam reforming of ethanol has been examined by some investigators. Fishtik *et al.* (2000) found that for temperatures at or above 700–800K and for high water/ethanol ratios the desired reaction of ethanol steam reforming is predominant and the amount of undesired products is minimized. Ioannides (2001) concluded that an H₂O/EtOH molar ratio higher than stoichiometry results in reduced efficiency in hydrogen production, because of increased enthalpy needs for water evaporation. Mas *et al.* (2006) suggested that high temperatures and high water-to-ethanol ratios favor hydrogen production and low water-to-ethanol ratios are suitable to minimize CO formation. At a water-to-ethanol molar ratio of 3, temperatures higher than 500K are required to avoid coke formation. Vasudeva *et al.* (1996) and Garcia and Laborde (1991) have shown that an increase in temperature leads to an increase in the H₂ and CO concentration and decrease in CH₄ concentration at equilibrium. The thermodynamics of ethanol reforming have been also examined by other investigators (Freni *et al.*, 1996, Cavallaro and Freni, 1996, Maggio *et al.*, 1998) in relation to applications in molten carbonate fuel cells. It has been found that the only gaseous products at equilibrium are hydrogen, carbon monoxide, carbon dioxide and methane. Formation of elemental carbon is predicted only at low H₂O/EtOH ratios and temperatures lower than 900 K.

2. Technical aspects

The use of ethanol for the production of hydrogen shows some problems such as the bond C-C, which needs a catalytic surface for the ethanol oxidation. The breakage of such bond can form several unwanted by-products and catalyst coking. The ethanol reforming is a strongly endothermic reaction and produces only H₂ and CO₂ in the most desirable way. The global reaction is as follow:



This reaction is represented by two other partial reactions, one endothermic and one exothermic:



Other reactions that can also occur are: ethanol dehydrogenation to acetaldehyde (4), ethanol dehydration to ethylene (5), ethanol decomposition to CO₂ and CH₄ or CO, CH₄ and H₂.



Figure 1 shows a reaction mechanism for ethanol steam reforming. In the scheme, the avoided path is the one that pass in the dehydration of ethanol. The greatest concern in ethanol steam reforming is the development of an active catalyst that avoids coke formation and CO production mainly when using PEM fuel cells.

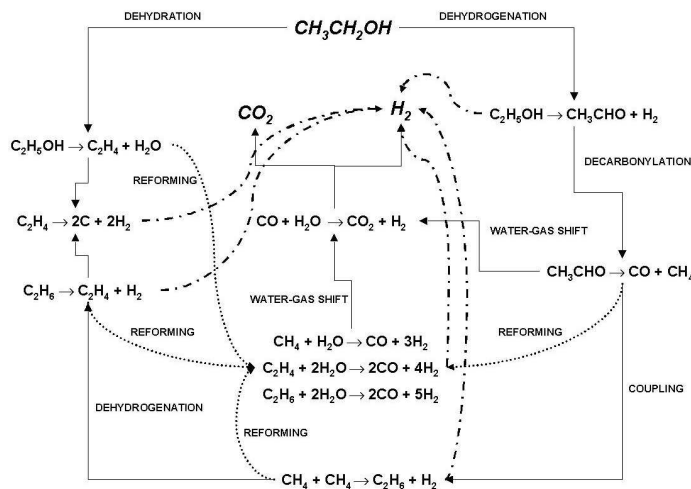


Figure 1. Reaction mechanism for steam reforming of ethanol (Adapted from Benito, 2005).

3. Catalyst review

Recently, catalysts for the steam reforming of ethanol have been extensively studied. The performance of the supported metal catalyst depends on several factors that are: reaction conditions, type of metal precursor and support, method of catalyst preparation, metal content, and presence of additives (Vaidya, 2006, Haryanto, 2005).

As in Figure 1, several reactions can occur in ethanol steam reforming process, which depends on the behavior of the metal or metals employed. To understand the process is important to know ethanol-catalyst interaction type. Studies of ethanol reaction over several metal surfaces indicated that ethanol is adsorbed as ethoxide species. On Rh and Ni metals, the ethoxide specie forms an oxametallacycle intermediate, which favors the C-C bond breaking. Rh is effective in oxametallacycle formation to decompose the ethoxy species by C-C and C-H bond cleavage, however its activity towards water-gas shift (WGS) reaction is limited and has a high cost (Vesselli, 2005, Aupretre, 2004). Pt presents higher activity to WGS reaction than Rh and is thermally stable. Ru has good activity to hydrocarbons steam reforming and is less expensive than Pd, Rh and Pt. Ru is active to ethanol dehydration reaction, leading to ethylene formation and carbon deposition suppression when combined to some additives (Liguras, 2003, Breen, 2002).

Due to its low cost and high activity towards hydrogenation reaction, Ni is the most utilized in steam reforming. Pure Ni causes ethanol bond breaking in the following order: O-H, -CH₂-, C-C and CH₃. However Ni has low activity for WGS reaction, but some additives can improve its performance by enhancing the interaction between adsorbed intermediates and metal phase (Bergamaschi, 2005, Kugai, 2005), and avoiding coke formation (Trimm, 1999). Cu has limited steam reforming activity however it is a good dehydrogenation catalyst and has high activity for WGS reaction, therefore can be used as additive (Bergamaschi, 2005). Co has a good performance in H₂ production, however cannot be used at high temperatures because it is easily sintered and oxidized (Vargas, 2005, Frusteri, 2004, Haga, 1997).

Despite their properties, metals cannot be used alone to produce hydrogen, so their performance is enhanced using supports. The adequate support choice can improve thermal and mechanical stability of the supported metals preventing catalyst sintering and helping to achieve the desired reaction pathway, according to its chemical properties, in order to avoid coke deposition and consequently catalyst deactivation (Llorca, 2001).

Among the supports, Al₂O₃ is the most commonly used for steam reforming reaction, although its acidic character promotes dehydration of ethanol to ethylene and forms coke in catalyst surface (Vaidya, 2006, Haryanto, 2005, Liguras, 2003, Llorca, 2001). Differently, MgO (Frusteri, 2004, Batista 2004) and ZnO (Llorca, 2003) have alkaline character, and can avoid the dehydration reaction of ethanol to ethylene since they promote ethanol dehydrogenation to acetaldehyde. CeO₂ (Kugai, 2005) also has alkaline characteristics and redox properties. It has oxygen storage capacity and its presence improves resistance to coke deposition and avoids precious metals sintering. Another support frequently used is ZrO₂, which has acidic and alkaline properties and when is used with CeO₂ increases the oxygen storage capacity, redox properties, and thermal stability (Breen, 2002, Srinivas, 2003).

Ethanol steam reforming process is complex with several products formation. Some care should be taken not only in the choice of the catalyst and support employed but also in operational conditions such as temperature, pressure and water-to-ethanol ratio. The right choice of these parameters can imply in higher performance and longer life to the catalyst.

4. Reactor Design

The design of the reactor volume is based on the ethanol steam reforming reaction, and Ni is used as a catalyst in the design calculation. The volume of a reactor obtained from the material balance is given by (Fogler, 1992):

$$V = \frac{\dot{q}_{\text{EtOH}}}{\rho(1-\varepsilon)} \int_0^{X_{\text{EtOH}}} \frac{dx}{r_{\text{REF}}} \quad (8)$$

Where \dot{q}_{EtOH} is the mass flow rate of ethanol, ρ the catalyst density, ε the voidage of catalyst and r_{REF} is the reaction rate for ethanol steam reforming. This parameter can be calculated as:

$$-r_{\text{REF}} = k_0 \exp\left(\frac{-E_a}{RT}\right) C_{\text{EtOH}}^n C_{\text{H}_2\text{O}}^m \quad (9)$$

The various kinetic studies over Ni-based catalysts are listed in Table 1.

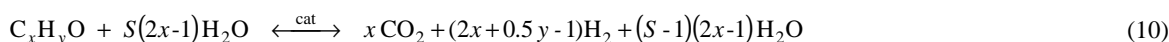
Table 1. Kinetics of steam reforming of ethanol over Ni-based catalysts (Vaidya and Rodrigues, 2006).

Catalyst	Temp. [K]	Rate constant (k_0)	Ethanol order (n)	Water order (m)	E_a (kJ/mol)
Ni/Al ₂ O ₃	673	77.8 kmol/kg _{cat} s atm	2.52	7	N.A.
Ni/Y ₂ O ₃	403	2.95x10 ⁻³ m ³ /kg _{cat} .s	1	N.A.	7.04
Ni/Al ₂ O ₃	N.A.	2.32x10 ⁻³ m ³ /kg _{cat} .s	1	N.A.	16.88
Ni/La ₂ O ₃	N.A.	19.1x10 ⁻³ m ³ /kg _{cat} .s	1	N.A.	1.87
Ni/Al ₂ O ₃	593-793	N.A.	0.43	0.57	4.41
Cu/Raney Ni	523-573	N.A.	1	N.A.	149

5. Thermodynamic analyses methods

5.1. Steam Reforming

A very common method of hydrogen production is the steam reforming process. Normally, steam reforming consists of the reaction of the fuel and steam over a catalyst to produce a mixture of H₂, CO, CO₂ and CH₄. First, a global reaction mechanism is required to analyze the thermodynamics of steam reforming of a fuel at a basic level:



S is the steam-to-carbon ratio. The term “global reaction” recognizes that the above reaction is actually the net result of a series of elementary reactions, some of which include catalytic interactions with surfaces. These are of no consequence to the overall thermodynamic analyses, but they are important to understand for reactor design and efficient operation and control of reformer systems. Using Eq. (10), the formation enthalpies of the species can be added to determine the net enthalpy change as follows:

$$\Delta H_R = xh_{CO_2}^f + (S-1)(2x-1)h_{H_2O(g)}^f - [h_{C_xH_yO}^f + S(2x-1)h_{H_2O(l)}^f] \quad (11)$$

ΔH_R is the net enthalpy change in the reaction [kJ], h_k^f is the formation enthalpy per mole of species k at standard temperature and pressure [kJ/mol]. Table 2 shows the net enthalpy change using a steam-to-carbon ratio from 2 to 5 for some alcohols.

Table 2. Net enthalpy change for some alcohols.

Comp.	x	y	h_{fuel}^f [kJ/mol]	ΔH_R^* [kJ/mol] ($S = 2$)	ΔH_R^* [kJ/mol] ($S = 3$)	ΔH_R^* [kJ/mol] ($S = 4$)	ΔH_R^* [kJ/mol] ($S = 5$)
CH ₄ O	1	4	-201.0	137.32	181.32	225.32	269.32
C ₂ H ₆ O	2	6	-235.3	437.77	569.77	701.77	833.77
C ₃ H ₈ O	3	8	-255.6	724.22	944.22	1164.22	1384.22
C ₄ H ₁₀ O	4	10	-275.3	1010.05	1318.05	1626.05	1934.05

* The positive value means the process is endothermic.

5.2. Chemical Equilibrium Analysis

There are two common methods used to express chemical equilibrium. One method is based on the use of equilibrium constants, while the other is based on minimization of the free energy. One of the disadvantages of using equilibrium constants is that it is more difficult to test for the presence of condensed species in the reaction products. However, it is anticipated that solid carbon may be produced during the fuel reforming process, which can deactivate the catalytic reactions. Therefore, a method based on minimization of free energy is normally used in fuel reforming analysis. Summarizing, for a given temperature (T) and pressure (P), the equations for species conservation, atoms conservation, and condensed species are, respectively (Gordon and McBride, 1994):

$$N = \sum_{k=1}^m N_k \quad k = 1, \dots, m \quad (12)$$

$$b_l^0 = \sum_{k=1}^m a_{lk} N_k = b_l \quad l = 1, \dots, l \quad (13)$$

$$\frac{\mu_k^0}{R_u T} + \sum_{l=1}^i \left(\frac{\lambda_l}{R_u T} \right) a_{lk} = 0 \quad k = m + 1, \dots, n \quad (14)$$

Where: N is the molar flow [kmol/s], b_l^0 is the number of atoms of element l in the reactants [kmol], a_{lk} is the number of atoms of element l in species k in the products [kmol], μ is the molar chemical potential of species k [kJ/kmol], λ_l is a Lagrange multiplier, and R_u is the universal gas constant [8.314 kJ/kmol K]. Equations (12) to (14) form a set of $n + 1$ equations that can be simultaneously solved for the unknowns N_k , λ_l , and N . The thermodynamic function is then solved by the Newton-Raphson method for the unknowns.

6. Results and Discussion

Figure 2 shows an example for the solution of the chemical equilibrium equations for ethanol as a function of temperature for steam-to-carbon (S) of 2.0 and pressure of 1 atm. As can be seen in Fig. 2, the best temperature to run a reformer is between 600°C and 800°C, a temperature condition for which production of hydrogen is maximized. The thermodynamically predicted molar fraction of methane decreases with increase of temperature (after 200°C) and becomes lower than 500 ppm after 900°C. The curve for carbon dioxide shows an increase before 500°C and a decrease after this temperature. It is observed that carbon dioxide molar fraction decreases at a lower rate than methane after 900°C. It is not interesting to run an ethanol reformer for temperatures superior to 600°C due to the increase in the molar fraction of carbon monoxide mainly if a PEM fuel cell is used. Even in these conditions it may be necessary the use of a WGS reactor coupled to the steam reformer and a purifying system, in order to decrease the CO levels to adequate values for PEMFC applications.

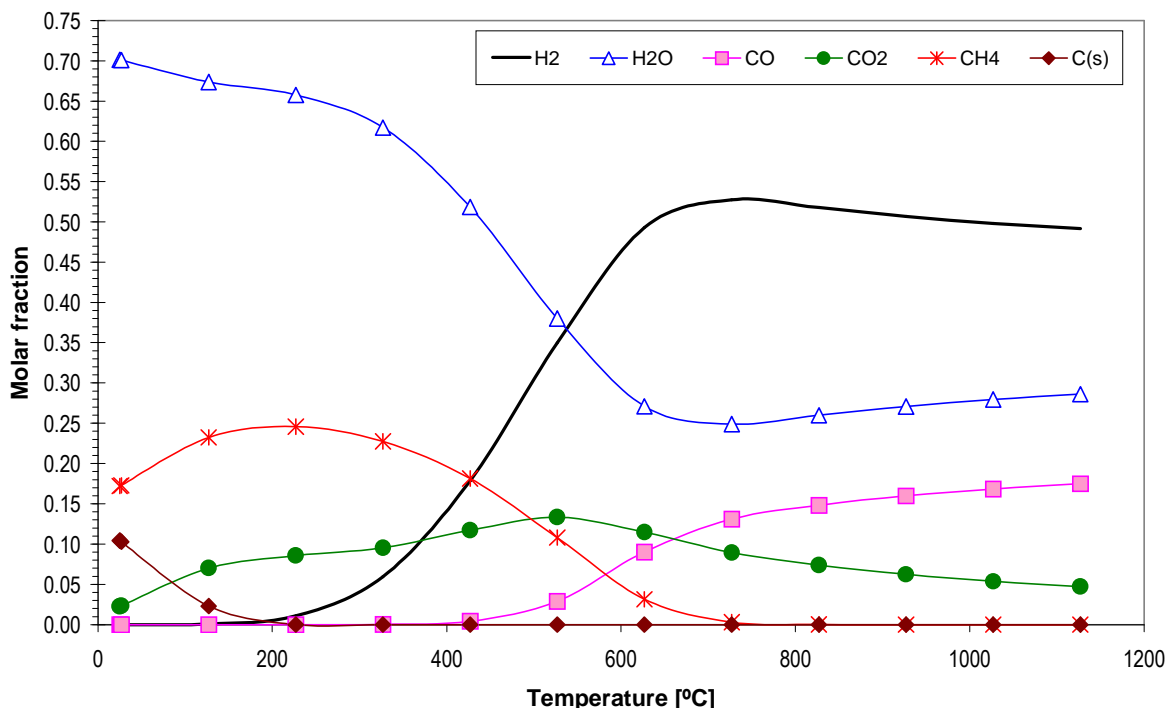


Figure 2. Results of molar fraction for the ethanol steam reforming process as a function of temperature ($S = 2$).

The main operating parameters of the system are steam-to-carbon ratio (S), temperature of the reformer, and pressure. The effect of reformer operating temperature on hydrogen yield (Y_{H_2}) for various steam-to-carbon ratios are presented in Fig. 3. It can be observed that Y_{H_2} increases and tends to the stoichiometric value for about $550^\circ\text{C} < T < 650^\circ\text{C}$ and $S \geq 5$. It is expected that hydrogen yield increases with the increase of steam-to-carbon ratio because the equilibrium reactions (Eqs. 2 and 3). It is not interesting to increase S values higher than 5 because it does not result in any significant gain in hydrogen yield and besides processing of feeds with high S requires larger reactor sizes (Eqs. 8 and 9) and more heat to evaporate the feed (as can be seen in Table 2). It is worth to note that these results do not include the effect of a catalyst. If a catalyst is added, the production of hydrogen would be higher.

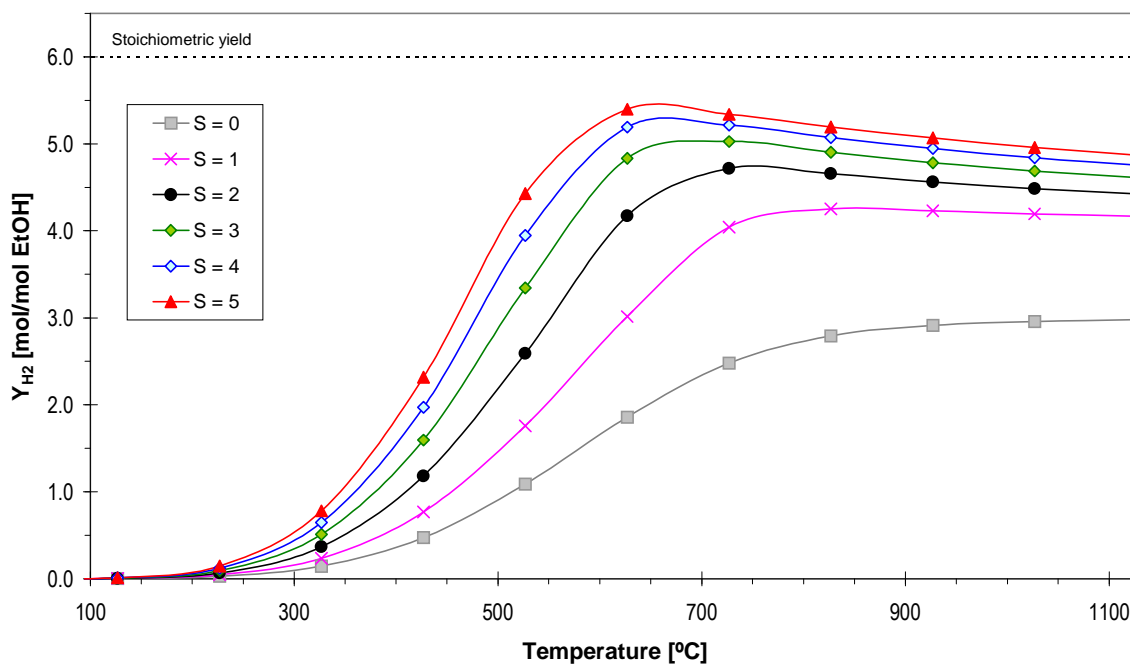


Figure 3. Effect of reformer operating temperature on hydrogen yield ($P = 1\text{atm}$).

Figure 4 displays the effect of operating pressure on hydrogen yield in the range of 1 to 5 atm, temperatures of about 730°C (dashed line) and 530°C (solid line), and steam-to-carbon ratio from 1.0 to 5.0. This figure exhibits the decrease of hydrogen yield due to the increase of pressure because pressure shifts the equilibrium reactions (Eqs. 2 and 3) to the right side. It is interesting to note that for 730°C hydrogen yield decreases linearly with increasing pressure while for 530°C this dependence is exponential. This can be explained by the dependence of the activation energy and temperature in the reaction rate equation (Eq. 9). The higher the temperature, the lower is the Gibbs free energy (which means higher hydrogen yield) and consequently the lower is the activation energy. Also, the production of hydrogen is high at higher steam-to-carbon ratio and temperature. The strongest effect of pressure occurs at low values of S and low temperatures. Therefore, the combination of factors such as pressure, temperature and steam-to-carbon ratio must be carefully chosen when designing an ethanol steam reformer.

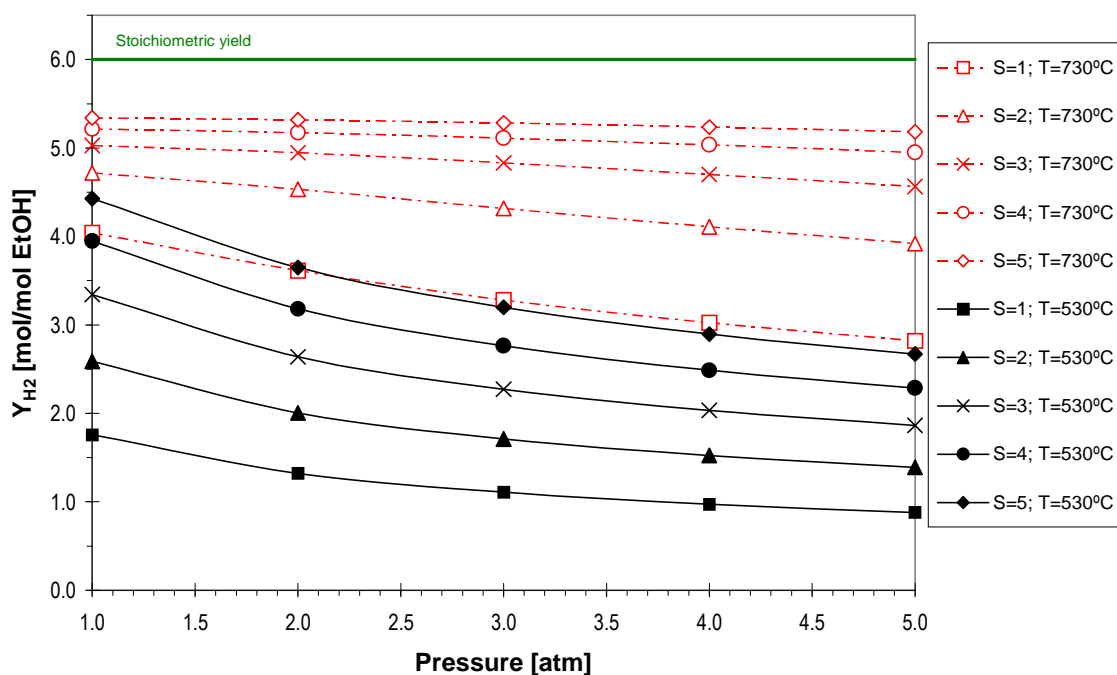


Figure 4. Effect of reformer operating pressure on hydrogen yield.

Finally, a comparison among three different cycle configurations was proposed. The specific cycle configurations include a reformer, a WGS reactor, a purifying system (which can be PSA-based or a membrane reactor) and a proton exchange membrane fuel cell (PEMFC). PEMFCs works on temperatures lower than 100°C, with Pt-based catalysts. The use of Pt-based catalysts gives to a PEMFC characteristics of being low tolerant to CO. Therefore, the operational conditions of the reformer should result in a H₂-rich gas with low CO concentration (less than 100 ppm) in the operating temperature. Figure 5 presents three different cycle configurations comprised mainly of ethanol steam reformer and proton exchange membrane fuel cell. These generic cycle configurations were developed to examine the general impacts of system design on the thermodynamic performance of an ethanol reformer for hydrogen production.

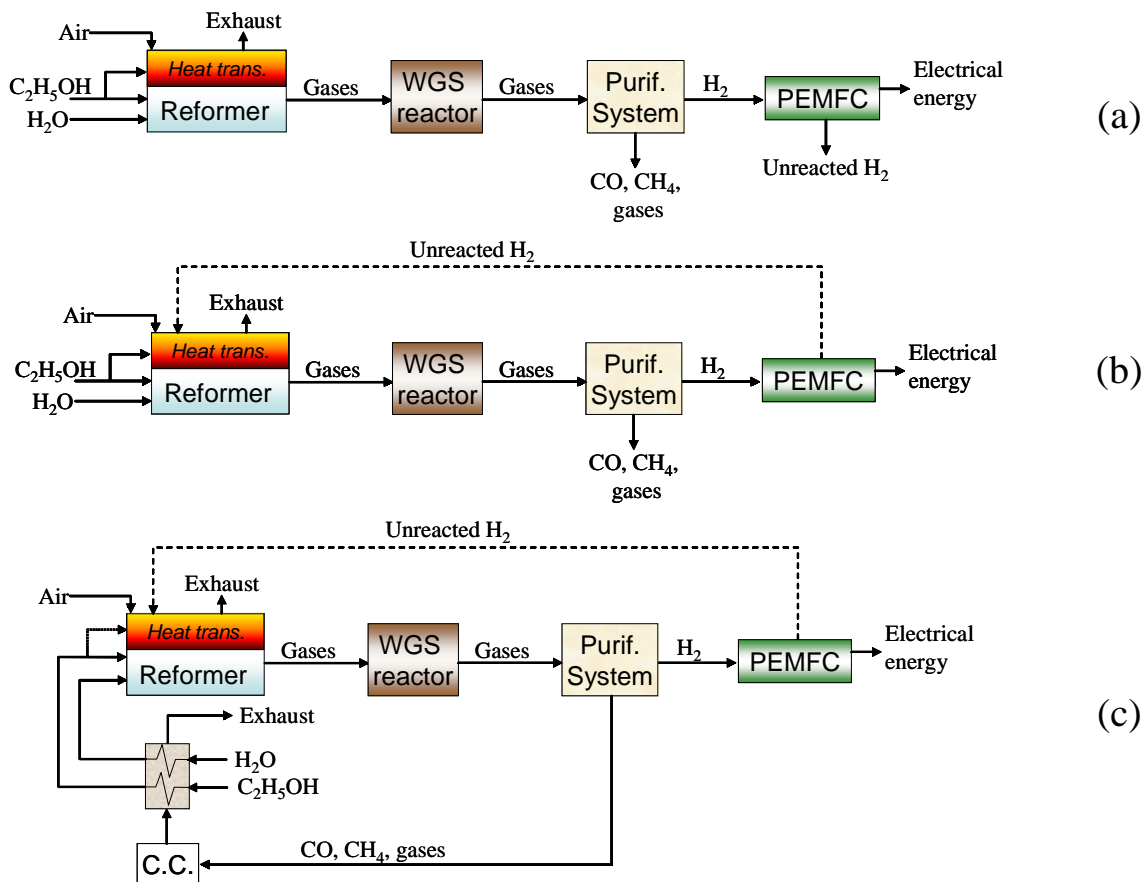


Figure 5. Cycle configurations: (a) first configuration with no gases recycling; (b) second configuration with H₂ recycling; and (c) third configuration with all gases recycling.

The considerations and assumptions made for the energy and exergy analysis presented herein are: (i) fuel cell overall efficiency of 35% (Hoogers, 2002); (ii) fuel cell operating temperature of 80°C (EG&G Technical Services, 2002); (iii) heat exchanger is 85% efficient (Iwahashi et al., 1998), (iv) all gas stream pressures are atmospheric (Dunbar et al., 1991).

In this work, it was chosen the fuel utilization efficiency (or the First Law efficiency) and the Second Law efficiency to compare each cycle configuration. Here, the fuel utilization efficiency (ϵ_F) is defined as the ratio of all useful energy extracted from the system (which in the case of a reformer, the hydrogen produced by it) to the thermal energy of the input fuel (E_F). Thus (Utgikar *et al.*, 1995):

$$\epsilon_F = \frac{Q_{H_2}}{E_F} \quad (15)$$

The electrical energy of the fuel cell is a useful energy that could be extracted from the system and could be accounted for in Eq. (15). However, this work is proposed to simulate and evaluate an ethanol reformer in different cycle configurations on system performance.

The Second Law efficiency (ϵ_{II}) may be defined as the ratio of the amount of products exergy (hydrogen produced) to the amount of exergy supplied (Ex_S). This parameter is a more accurate measure of the thermodynamic performance of the system. Thus (Utgikar *et al.*, 1995):

$$\epsilon_{II} = \frac{Ex_P}{Ex_S} \tag{16}$$

Figures 6 and 7 show the results of the overall energy analysis and of the overall exergy analyses, respectively, for all three cycle configurations.

Figure 6 shows that the fuel utilization efficiency of the cycles is between 21% and 78%. These values are for the steam-to-carbon ratio of 1 and 2 for different cycle configurations and temperatures. When comparing the energy analyses amongst cycle configurations, Fig. 6 indicates that for the same amount of hydrogen produced by the reformer, configuration 3 ($T = 730^\circ\text{C}$ and steam-to-carbon of 2) shows the highest First Law efficiency, achieving a remarkable overall efficiency of nearly 80%. One of the reasons for this high efficiency is the synergy associated with both the use of the hydrogen not consumed by the fuel cell and the use of the steam reforming by-products (mainly methane and carbon monoxide). This results in a significant increase in the heat consumed by both the reforming reaction and vaporization and heating of the reactants (ethanol and water). Figure 6 also exhibits that configuration 1 ($T = 530^\circ\text{C}$) is the worst cycle configuration with the highest thermal losses on an energy basis. This is because most of the gases produced in the system are thrown out.

When comparing between temperatures (530°C versus 730°C), Fig. 6 indicates that the best results for 730°C occurs at low steam-to-carbon ratio (1 and 2) while the best results for 530°C occurs at high steam-to-carbon ratio (3 to 5). These results indicate an important parameter for designing an ethanol steam reformer. If the designer chooses low temperatures, the volume of the reactor would be bigger than for higher temperatures. On the other hand, if the temperature of the reformer is high, the construction material could be the limiting factor.

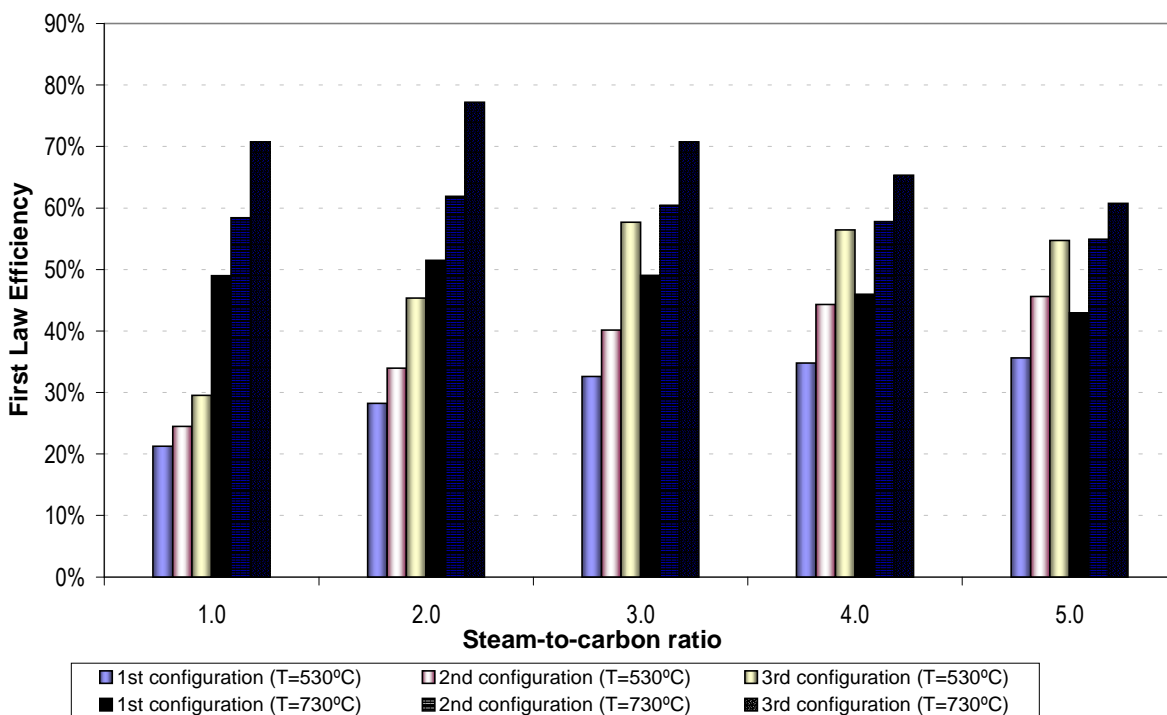


Figure 6. Results of energy performance analysis.

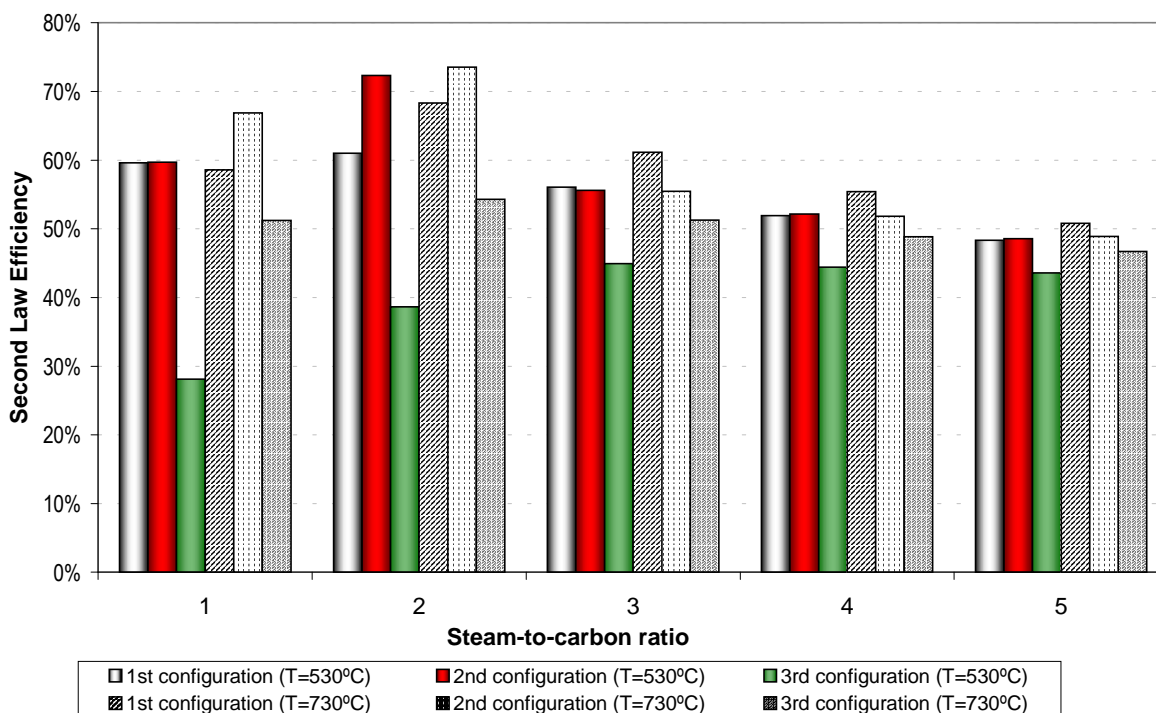


Figure 7. Results of exergy performance analysis.

Figure 7 presents the exergy analyses for all of the configurations, indicating the components that contribute most significantly to irreversibilities within each configuration. Components with high irreversibilities or low Second Law efficiency and the manner in which they are implemented in the cycle are those that designers should focus upon to improve system performance.

A general analysis of Fig. 7 shows that the highest overall Second Law efficiency occurs for $S = 2$ in the same configuration (second) for both temperatures and configuration 3 exhibits the lowest Second Law efficiency among all cycle configurations considered. The Second Law efficiency of configuration 2 is high due to cumulative better exergy performance of the components. This is primarily manifested in lower irreversibilities in the components (not shown here). In the case of configuration 3, it can be observed that there are two combustion chambers in this configuration, which contributes to the major destruction of exergy. The combustion chamber is associated with the maximum temperature of the products related to the dead state. However, this result indicates that there is the potential for significant performance improvements for this option. These potential improvements will be addressed in future studies.

When comparing the efficiency between configurations 1 and 2 (except for $S = 2$) the second law efficiency is similar for 530°C, indicating that the hydrogen recycling does not improve the efficiency, while for 730°C the hydrogen recycling and burning gives to the second configuration higher irreversibilities than the first configuration, for $S \geq 3$.

Further research is justified using the insight gained through the present investigation. This research should focus on those subprocesses having large exergy losses and should include, for example, process integration, design and optimization, temperature profile changes, etc.

7. Summary and Conclusions

Hydrogen production is expected to be accomplished on-site by gaseous or liquid fuels reformation until all technical problems related to its storage and transportation are solved. In this case, the steam reforming of ethanol for hydrogen production is a very interesting option for Brazil because of its available annual quantities and potential of production growing. However, the ethanol steam reforming involves a complex multiple reaction system, and the yield of hydrogen depends in a complex manner on the process variables such as pressure, temperature, reactants ratio, etc.

This paper presents thermodynamic and electrochemical analyses for the study of hydrogen production from ethanol reforming. Three generic cycle configurations are presented. The energy analyses of these cycles show that configuration 3 exhibits the best cycle efficiency. However, the exergy analysis of this same configuration shows that much effort should be invested to further improve this cycle configuration. The overall energy efficiency, which is the ratio of the hydrogen produced by the reformer to the ethanol thermal energy, ranges from 21% to 78%. The lowest overall energy efficiency was for a case that the gases produced in the system are thrown out (configuration 1). Also, the best exergy performance was for configuration 2 due to cumulative better exergy performance of the components.

The concept presented in this paper is clearly worthy of further investigation, development, and demonstration. Thermodynamic analyses suggest a clear advantage of fuel savings for the hydrogen production, which is only augmented by the avoidance of transport energy and emissions benefits. Fuel cell technology is advancing with several commercial products emerging into the market. But significant challenges remain, including integration with small-scale hydrogen separation, compression and storage technology, and cost reduction.

8. Acknowledgements

The second author would like to acknowledge FAPESP (Fundação de Amparo à Pesquisa do Estado de São Paulo, process number 2005/55375-2) for the financial support in this project.

9. References

- Aupretre, F., Descorme, C., Duprez, D., 2004, "Hydrogen production for fuel cells from the catalytic ethanol steam reforming", *Topics in Catalysis*, 30/31, pp. 487.
- Batista, M.S., Santos, R.K., Assaf, E.M., Assaf, J.M., Ticianelli, E.A., 2004, "High efficiency steam reforming of ethanol by cobalt-based catalysts", *Journal of Power Sources*, 134, pp. 27-32.
- Benito, M., Sanz, J.L., Isabel, R., Padilla, R., Arjona, R., Dazaet, L., 2005, "Bio-ethanol steam reforming: Insights on the mechanism for hydrogen production", *Journal of Power Sources*, 151, pp. 11–17.
- Bergamaschi, V.S., Carvalho, F.M.S., Rodrigues, C., Fernandes, D.B., 2005, "Preparation and evaluation of zirconia microspheres as inorganic exchanger in adsorption of copper and nickel ions and as catalyst in hydrogen production from bioethanol", *Chemical Engineering Journal*, 112, pp. 153–158.
- Breen, J.P., Burch, R., Coleman, H.M., 2002, "Metal-catalysed steam reforming of ethanol in the production of hydrogen for fuel cell applications", *Applied Catalysis B: Environmental*, 39, 65–74.
- Cavallaro, S., Freni, S., 1996, "Ethanol steam reforming in a molten carbonate fuel cell. A preliminary kinetic investigation", *International Journal of Hydrogen Energy*, 21, pp. 465 – 469.
- Dunbar, W.R., Lior, N., Gaggioli, R.A., 1991, "Combining fuel cells with fuel-fired power plants for improved exergy efficiency. *Energy*", Vol. 16 (10), 1259-1274.
- EG&G Technical Services, Inc., 2002. *Fuel Cell Handbook* (6th edition), U.S. Department of Energy, Office of Fossil Energy, National Energy Technology Laboratory.
- Fishtik, I., Alexander, A., Datta, R., Geana, D., 2000, "A thermodynamic analysis of hydrogen production by steam reforming of ethanol via response reactions", *International Journal of Hydrogen Energy*, 25, pp. 31 – 45.
- Fogler, H.S., 1992, "Element of Chemical Engineering", Prentice Hall International, The University of Michigan.
- Freni, S., Maggio, G., Cavallaro, S., 1996, "Ethanol steam reforming in a molten carbonate fuel cell: a thermodynamic approach", *Journal of Power Sources*, 62(1), pp. 67 – 73.
- Frusteri, F., Freni, S., Spadaro, L., Chiodo, V., Bonura, G., Donato, S., Cavallaro, S., 2004, "H₂ production for MC fuel cell by steam reforming of ethanol over MgO supported Pd, Rh, Ni and Co catalysts", *Catalysis Communications*, 5, pp. 611–615.
- Garcia, E.Y., Laborde, M.A., 1991, "Hydrogen production by the steam reforming of ethanol: Thermodynamic analysis", *International Journal of Hydrogen Energy*, 16(5), pp. 307 – 312.
- Haga, F., Nakajima, T., et al., 1997, "Catalytic properties of supported cobalt catalysts for steam reforming of ethanol", *Catalysis Letters*, 48, pp. 223-227.
- Haryanto, A., Fernando, S. et al., 2005, "Current Status of Hydrogen Production Techniques by Steam Reforming of Ethanol: A Review", *Energy & Fuels*, 19, pp. 2098-2106.
- Hoogers, G. (ed), 2002, "Fuel cell technology handbook", New York: CRC press, 327p.
- Iwahashi, T., Yoshida, N., Kosaka, H., 1998, "High efficiency power generation from coal and wastes utilizing high temperature air combustion technology: Thermal performance of compact high temperature air preheater and MEET boiler". In: *Proceedings of the International Symposium on Advanced Energy Technology*. Sapporo, Japan: Hokkaido University; 455 – 462.
- Kugai, J., Velu, S., Song, C., 2005, "Low-temperature reforming of ethanol over CeO₂-supported Ni-Rh bimetallic catalysts for hydrogen production", *Catalysis Letters*, 101, pp. 255.

- Liguras, D. K., Kondarides, D. I. Verykios, X. E., 2003, "Production of hydrogen for fuel cells by steam reforming of ethanol over supported noble metal catalysts", *Applied Catalysis B: Environmental*, 43, pp. 345–354.
- Llorca, J., De La Piscina, P. R., et al., 2003, "CO-free hydrogen from steam-reforming of bioethanol over ZnO-supported cobalt catalysts Effect of the metallic precursor", *Applied Catalysis B: Environmental*, 43, pp. 355–369.
- Llorca, J., De La Piscina, P. R., et al., 2001, "Direct production of hydrogen from ethanolic aqueous solutions over oxide catalysts", *Chemical Communications*, 641–642.
- Lutz, A.E., Bradshawa, R. W., Kellera, J.O., Witmerb, D.E., 2003, "Thermodynamic analysis of hydrogen production by steam reforming", *International Journal of Hydrogen Energy*, 28, pp. 159 – 167.
- Maggio, G., Freni, S., Cavallaro, S., 1998, "Light alcohols/methane fuelled molten carbonate fuel cells: a comparative study", *Journal of Power Sources*, 74(1), pp. 17 – 23.
- Srinivas, D., Satyanarayana, C.V.V., et al., 2003, "Structural studies on NiO-CeO₂-ZrO₂ catalysts for steam reforming of ethanol", *Applied Catalysis A: General*, 246, pp. 323–334.
- Trimm, D.L., 1999, "Catalysts for the control of coking during steam reforming", *Catalysis Today*, 49, pp. 3-10.
- Utgikar, P. S., Dubey, S.P., Prasada Rao, P.J., 1995, "Thermoeconomic Analysis of Gas Turbine Cogeneration Plant - A Case Study". *J.Power and Energy*, Vol. 209, 45-54.
- Vaidya, P. D., Rodrigues, A.E., 2006, "Insight into steam reforming of ethanol to produce hydrogen for fuel cells", *Chemical Engineering Journal*, 117, pp. 39–49.
- Vargas, J. C., Libs, S. et al., 2005, "Study of Ce-Zr-Co fluorite-type oxide as catalysts for hydrogen production by steam reforming of bioethanol", *Catalysis Today*, 107–108, pp. 417–42.
- Vasudeva, K., Mitra, N., Umasankar, P., Dhingra, S.C., 1996, "Steam reforming of ethanol for hydrogen production: Thermodynamic analysis", *International Journal of Hydrogen Energy*, 21(1), pp. 13 – 18.
- Vesselli, E., Comelli, G. et al., 2005, "Ethanol auto-thermal reforming on rhodium catalysts and initial steps simulation on single crystals under UHV conditions", *Applied Catalysis A: General*, 281, pp. 139–147.

10. Copyright Notice

The authors are the responsible for the printed material included in this paper.