# Thermodynamic analysis of hydrogen production from ethanol using CaO as a $CO_2$ sorbent

Jose Comas*, Miguel Laborde, Norma Amadeo

*Laboratorio de Procesos Catalíticos, Depto. Ingeniería Química, Facultad de Ingeniería Pabellón de Industrias, Ciudad Universitaria, 1428 Buenos Aires, Argentina*

## Abstract

Ethanol steam reforming with and without the presence of CaO as a $CO_2$ sorbent is modeled. Potential advantages of the presence of CaO as $CO_2$ sorbent include higher energy efficiency, higher hydrogen production and lower CO content in the reformer gas exit. The presence of CaO eliminates the need of a WGS reactor for PEMFC application. Favorable operation conditions in the presence of CaO are (1) atmospheric pressure, (2) reactor temperatures around 700 °C, and (3) water/ethanol molar ratio of 4.
© 2004 Elsevier B.V. All rights reserved.

*Keywords:* Ethanol reforming; Hydrogen production; Fuel cell

## 1. Introduction

Fuel cell powered vehicles using hydrogen as a fuel are currently being developed in an effort to mitigate the emissions of green house gases such as $CO_2$, $NO_x$ and hydrocarbons.

The fast development of fuel cell technologies and particularly of the solid polymer fuel cell (SPFC) [1] involves the storage of a liquid fuel free from sulfur and metals, which would be transformable into hydrogen without polluting emissions. There exist several routes for hydrogen production from the primary fuels. A promising route involves the steam reforming of alcohols, primarily methanol and ethanol. The possibility of using alcohol steam reformer to generate hydrogen for a fuel cell engine has resulted in an increased interest in the study of the alcohol-steam reforming process [2–4].

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 bioethanol-to-hydrogen system has the significant advantage of being nearly $CO_2$ neutral, since the produced carbon dioxide is consumed for biomass growth, thus offering a nearly closed carbon loop.

In conclusion, among the various processes and primary fuels that have been proposed in the production of hydrogen for fuel cell applications, steam reforming of ethanol is very attractive.

Thermodynamic studies [5,6] have shown that the steam reforming of ethanol is feasible for temperature higher than 500 K, the main products being methane, CO and $H_2$. Experimental studies over Ni and Rh catalysts have corroborated these results [7,8].

Inspite of the apparent simplicity of the stoichiometry reaction for maximum hydrogen production:

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2$$
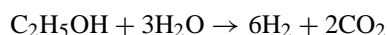
the steam reforming of ethanol for hydrogen production involves a complex reaction system, therefore the selectivity for hydrogen is affected by many undesirable side reactions and its production is limited by the thermodynamic equilibrium. To obtain maximum hydrogen production this reaction has to be carried in two steps, an endothermic step that involves the reforming of ethanol into $CH_4$, CO, $CO_2$ and $H_2$, followed by a lower temperature step where the CO is

* Corresponding author. Tel.: +54-11-457-63240;
fax: +54-11-457-63241.
*E-mail address:* comasjose@di.fcen.uba.ar (J. Comas).

converted into $CO_2$ and $H_2$ by the water gas shift (WGS) reaction. As the shift reaction is limited by the equilibrium and the fuel cells must be feed by a stream containing only trace amounts of CO (lower than 20 ppm) to avoid poisoning, an additional step must be carried out to further convert the CO. This is generally done by preferential CO oxidation. Ioannides [9] has carried out a thermodynamic analysis of this system considering a steam reformer and a partial oxidation reactor. He concluded that the most important parameter that affects the efficiency is the $H_2O$/ethanol molar feed ratio, because of the large enthalpy requirements for water evaporation.

This paper describes an alternative route for the steam reforming of ethanol combining reaction and separation in a single unit operation. It is considered that the reactor not only contains the catalyst needed for the reforming process but also a $CO_2$ sorbent (calcium oxide) for the removal of $CO_2$ from the gas mixture. Reaction and separation occur simultaneously and it is expected that the removal of $CO_2$ from the gas phase will displace the equilibrium to higher $H_2$ production.

The use of CaO for the separation of $CO_2$ in reforming processes is not new. Chun et al. [10], by experimental study, analyzed the effect of adding CaO on a water gas shift reactor and Balasubramanian et al. [11] studied its effect over the steam methane reforming. In both processes, the hydrogen production obtained was higher than those obtained from the reformer process without CaO as $CO_2$ sorbent. Sato et al. [12] presented the effects of calcium oxide over the hydrogen production from heavy oil and Lin et al. [13] analyzed its effect over coal gasification.

A process simulation was done by Kinoshita and Turn [14] studying the steam reforming of bio-oil considering a system containing a adsorbing (reforming)/desorbing (regeneration) reactor and a pressure-swing adsorption (PSA) unit for final product purification. They found that, although, the hydrogen yield was comparable to the predicted for steam reforming of bio-oil without the use of sorbents, the $H_2$ content in the outlet stream was higher.

In this work, a thermodynamic analysis of ethanol steam reforming with and without CaO as $CO_2$ sorbent is carried out to determine thermodynamically favorable operating conditions to produce $H_2$ for a PEM fuel cell. In this sense, first the influence of water/ethanol feed molar ratio, reaction temperature and pressure is analyzed for two cases. Next, material and energy balances are performed for two possible processes for producing hydrogen with CO concentrations lower than 20 ppm. The first one involves an ethanol steam reformer, a water gas shift reactor and a preferential CO oxidation reactor. The second one considers the ethanol steam reforming in presence of CaO plus a partial CO oxidation reactor. Evaluation of the thermal energy efficiency is also analyzed.

As equilibrium is assumed the results may vary in a practical situation, nevertheless they provide a valuable indication of the starting point for experimental research.

## 2. Simulation methods

The equilibrium of chemical reactions is generally solved by two methods. One is based on the equilibrium constants, while the other one is by minimization of the Gibbs free energy of the system. The former approach needs the knowledge of the chemical reactions involved and makes it difficult to analyze the carbon formation during the reforming process. As no exact knowledge of the reactions involved in the steam reforming of ethanol process and as carbon formation is expected, the latter method was preferred for this study. The operating parameters used were the following: (a) temperature, (b) $H_2O$/ethanol molar feed ratio, and (c) pressure. For a given operating condition the equilibrium compositions have been calculated. In order to determine the thermal efficient the material and energy balances are solved for each system.

## 3. Simulation results and discussion

### 3.1. Ethanol steam reforming without CaO

The general reforming reaction can be written in the following way:

$$C_2H_5OH + H_2O \rightarrow products$$
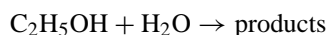
The products considered where $CH_4$, $H_2O$, $CO_2$, CO, $H_2$, C(s), acetaldehyde and ethylene. All this products appeared during the experimental testing of the ethanol steam reforming over a Ni catalyst [8]. In the simulations, the concentration of products with two carbon atoms is found to be negligible compared with the other products and the ethanol conversion was total in agreement with previous simulations [5,6]. The water to ethanol molar feed ratio was varied between 2 and 10, the temperature between 500 and 900 °C and the pressure between 1 and 25 atm.

The temperature has a significant effect on the equilibrium concentrations of the products (Fig. 1). As the reaction temperature is increased the hydrogen molar flow increases and reaches a maximum at 725 °C which coincides with the total disappearance of methane. After that the hydrogen molar flow decreases. Water, $CO_2$ and methane molar flows decrease with temperature while CO increases.

The effect of the water to ethanol ratio over the molar flows of the products is illustrated in Fig. 2 for reformer reactor operating under atmospheric pressure and 700 °C. Clearly, it can be seen that the addition of water increases the hydrogen production while reducing the methane and CO molar flows. Although high water to ethanol molar ratios are favorable from the thermodynamic point of view, the maximum water to ethanol ratio will be limited by the energy cost of the system. A higher ratio will represent a higher energy cost because of the extra steam generated.

The simulation results in terms of reactor pressure are represented in Fig. 3. It can be seen that the pressure
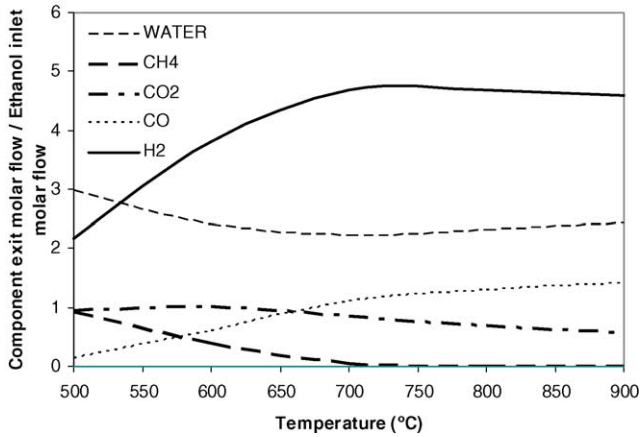
Fig. 1. Effect of reactor temperature on equilibrium component molar flows for the steam reforming of ethanol (water/ethanol molar ratio, 4; pressure, 1 atm).
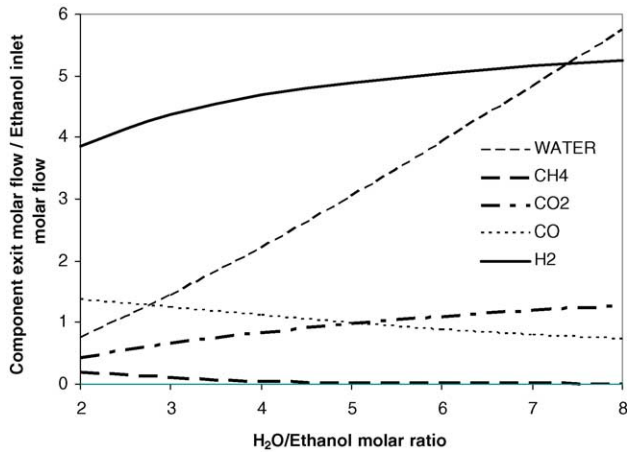


Fig. 2. Effect of water/ethanol ratio on the equilibrium component molar flows. Pressure, 1 atm; temperature, 700 °C.
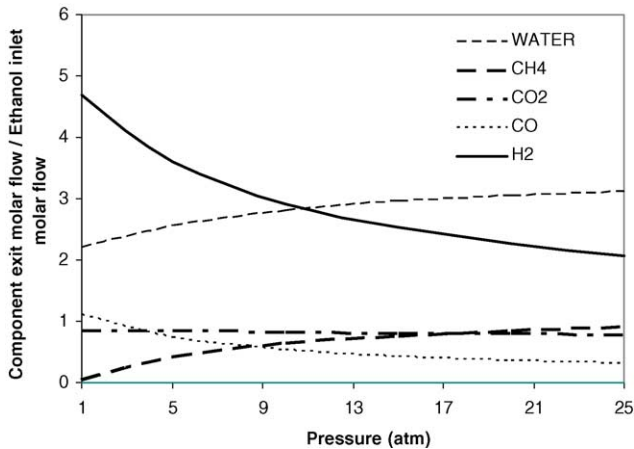


Fig. 3. Effect of reactor pressure on equilibrium component molar flows. Water/ethanol molar ratio, 4; temperature, 700 °C.
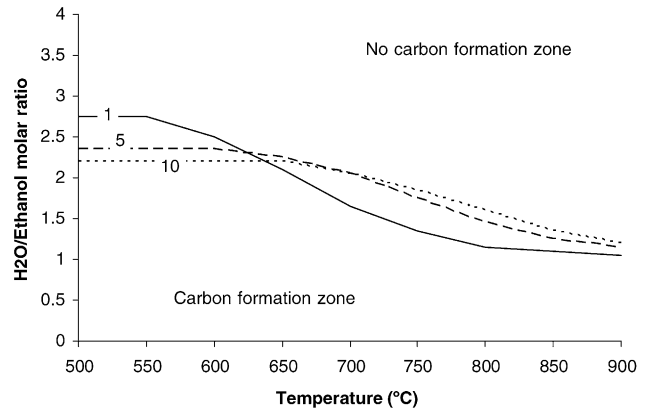


Fig. 4. Contour diagram of C(s) formation with regard to reactor temperature and water/ethanol ratio for different operating pressures.

impacts significantly over the equilibrium molar fractions of the system. As the pressure is increased the molar fractions of hydrogen decrease which is not desirable for the operation of the reactor, this is due to the expansive reactions involved in the steam reforming. These means that operating the steam ethanol reformer at atmospheric pressure is desirable. On the other hand high pressures diminish the CO concentration in the reformer exit.

Carbon (as graphite) formation in the steam reforming of ethanol has shown to be significant in the experimental studies. It is interesting to define the conditions that will not favor this formation. Fig. 4 shows the carbon formation boundaries for the steam ethanol reformer which is studied taking into account the temperature, the water to ethanol ratio and the pressure. It can be seen that it decreases when the water to ethanol ratio and temperature increase, while the pressure effect depends on the operating temperature. Favorable operating conditions for ethanol steam reforming can ensure no carbon formation at atmospheric pressures when water/ethanol ratios are higher than 3.

### 3.2. Ethanol steam reforming in the presence of CaO

The advantage of adding CaO to the steam reforming of ethanol can be analyzed by considering the following exothermic reaction:

$$CaO(s) + CO_2(g) \rightarrow CaCO_3(s)$$
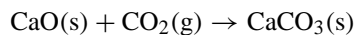
The separation of the $CO_2$ from the gaseous phase will displace the equilibrium of the gas mixture to a higher production of hydrogen and a lower concentration of CO. The products considered for the simulation are the same as in the previous case plus CaO and $CaCO_3$.

The temperature effect over the product molar flows is shown in Fig. 5. At temperatures lower than 750 °C the hydrogen production is greatly enhanced by the separation of $CO_2$, above this temperature the molar flows are similar to the ones without the addition of CaO, meaning that the $CO_2$
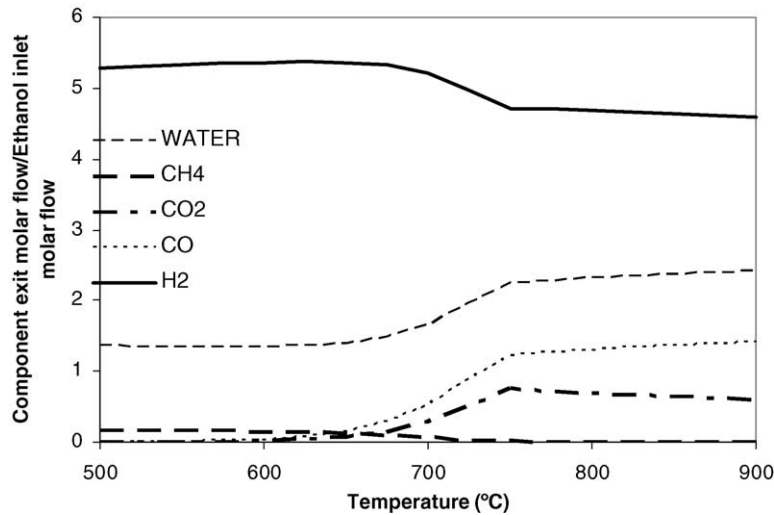
Fig. 5. Effect of temperature on molar flows in the presence of CaO, Pressure 1 atm. Water/ethanol molar ratio, 4.

separation reaction is no longer effective, this is because the separation of $CO_2$ is an exothermic reaction and at high temperatures it is displaced. The hydrogen content on a dry basis is over 95% (mol/mol) at all temperatures below 700 °C. At low temperatures (500–650 °C) all carbon oxides are practically removed (less than 5000 ppm), $CH_4$ being the major impurity. At 650 °C the hydrogen molar flow is 5.36 mol of hydrogen per mol of ethanol feed, compared to a maximum yield of 6 considering complete steam reforming of ethanol, and 4.2 (Fig. 1) in the case of the equilibrium conditions with no CaO addition under the same conditions.

The water to ethanol ratio greatly enhances the steam reforming of ethanol in the presence of CaO. Fig. 6 shows the results of varying this ratio between 3 and 8 at 600 °C and 1 atm. At a ratio of 8, the $H_2$ molar flow per mol of ethanol is 5.9 and the CO concentration is lower than 3000 ppm on a dry basis.

The effect of pressure on the product molar flows is shown in Fig. 7. As in the previous case operating the reactor at
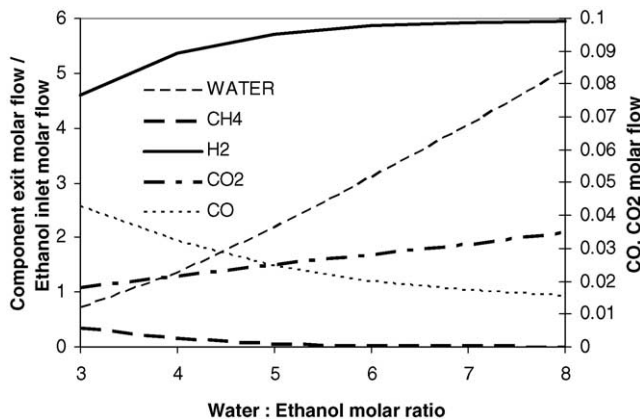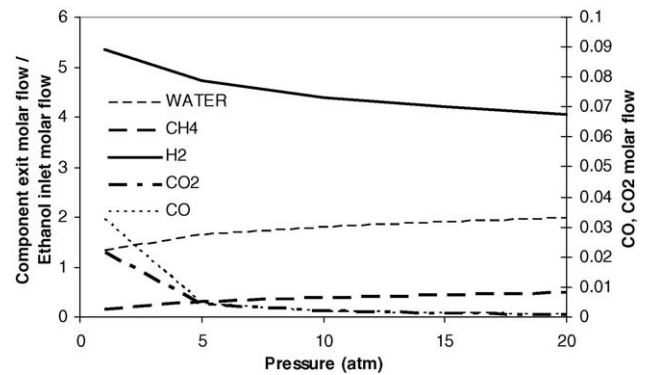


Fig. 7. Effect of pressure on product molar flows for ethanol steam reforming in the presence of CaO. Temperature, 600 °C; pressure, 1 atm.

higher pressures is not desirable because of the decrease in hydrogen production. The molar flow of CO is greatly diminished because of the enhancement of $CO_2$ separation at higher pressures.

Carbon formation was negligible for the analyzed operation conditions when working with CaO. Favorable operation conditions of the ethanol steam reforming in presence of CaO to obtain high production of $H_2$ with a low concentration of CO are temperatures between 500 and 650 °C, atmospheric pressure and a water to ethanol ratio higher than 3.

Table 1 shows the exit composition of the reformer for the two cases. It can be seen that incorporating CaO to the



Fig. 6. Effect of water/ethanol ratio on the equilibrium molar flow for the steam reforming of ethanol in the presence of CaO. Temperature, 600 °C; pressure, 1 atm.

Table 1
Reformer exit composition

| Component | Without CaO | With CaO |
|---|---|---|
| $CH_4$ | 0.049 | 0.022 |
| $CO_2$ | 0.122 | 0.0031 |
| CO | 0.07 | 0.0047 |
| $H_2$ | 0.46 | 0.777 |
| Water | 0.29 | 0.194 |

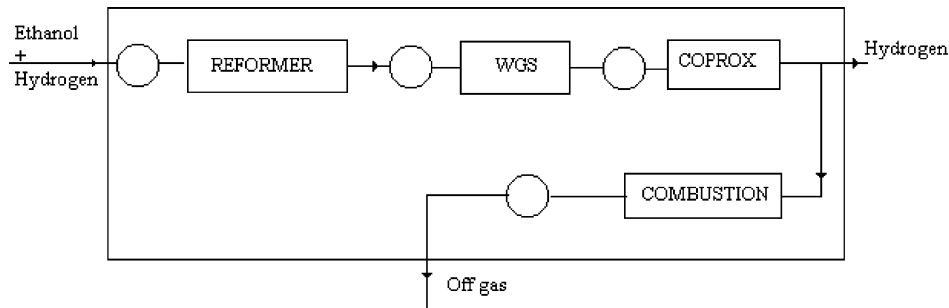At 600 °C, 1 atm and water:ethanol ratio of 4.

Fig. 8. Simplified flow diagram for the steam reforming of ethanol process consisting of an ethanol steam reformer, a water gas shift reactor (WGS), and a preferential CO oxidation reactor (COPROX).

steam reforming greatly diminishes the CO concentration. This will eliminate the water gas shift stage and feed a partial CO oxidation directly with the exit of the steam reformer to achieve a concentration lower than 20 ppm for fuel cells operation, which is not possible in absence of CaO.

### 3.3. Analysis of thermal energy

#### 3.3.1. Ethanol steam reforming without CaO
The CaO-free ethanol steam reforming process is shown in Fig. 8. This involves first, a vaporizer where the ethanol and water mixture is vaporized and heated to the reformer inlet temperature. Then a reformer where the reaction is approximated by minimizing the Gibbs free energy of the system. After cooling, the exit stream from the reformer enters a water gas shift reactor which takes into account only the equilibrium of the WGS reaction:

$$CO + H_2O \leftrightarrow CO_2 + H_2$$
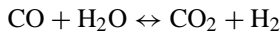
Finally, it enters into a preferential CO oxidation reactor (COPROX), where the remaining CO is totally converted to $CO_2$. The following two reactions occur in this reactor:

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2$$
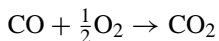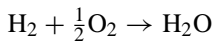
It is considered that the selectivity, defined as the ratio of oxygen consumed for the CO oxidation reaction (to $CO_2$) over the total oxygen consumed, which includes the oxygen loss due to the $H_2$ oxidation (to $H_2O$), is equal to 0.4 as reported in literature for a platinum catalyst [15].

It is considered that the fuel cell does not operate at total hydrogen conversion and part of the hydrogen produced is recycled to supply heat for the system. The combustion of the recycled stream is approximated by mixing it with a stoichiometric amount of air and letting it react to equilibrium compositions as an adiabatic reactor. The hot stream exiting the burner is then cooled down to the specified exhaust temperature (150 °C). Perfect heat exchange is assumed in all the system, which is unrealistic but provides the maximum possible efficiency of the system. This process runs as a closed loop; it is not dependant on any other source of heat.

#### 3.3.2. Ethanol steam reforming with CaO
The ethanol steam reforming process in presence of CaO is shown in Fig. 9. Ethanol and water are mixed, vaporized and heated to the reactor inlet temperature. Then, the mixture is feed into the reactor containing CaO and the catalyst. The hydrogen-rich gas produced is cooled down and feed directly into a COPROX working in the same conditions as the above process. There is no need for a WGS reactor because of the low concentration of CO in the exit gas. Over
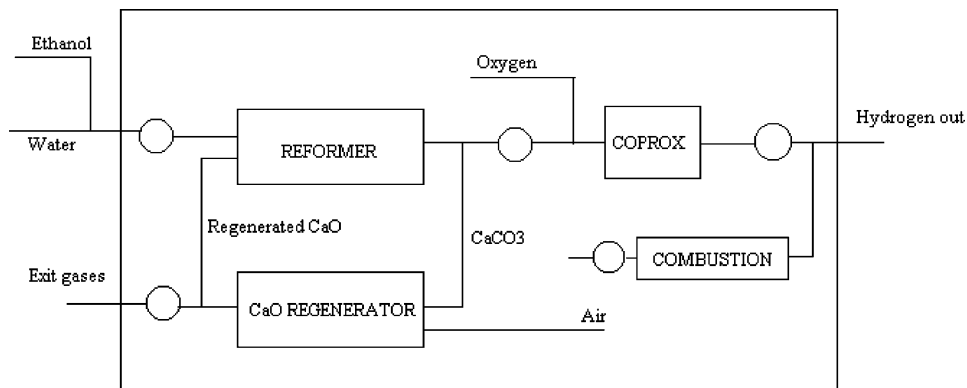


Fig. 9. Simplified flow diagram of the ethanol steam reforming in presence of CaO.
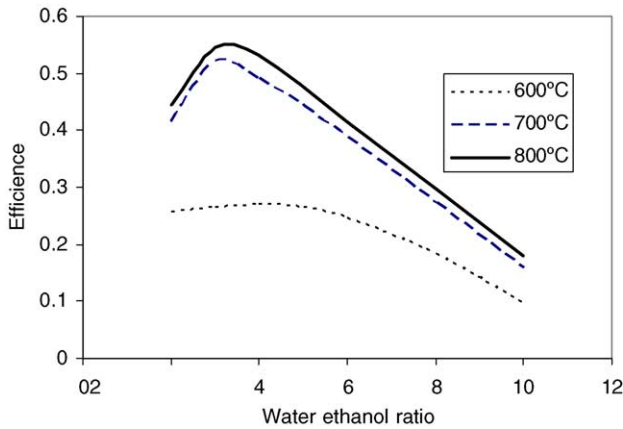
Fig. 10. Thermal efficiency of the ethanol steam reforming system without CaO.

time most of the CaO is converted into $CaCO_3$ and must be regenerated. This is done by heating the reactor and passing air through it. The regenerator is also modeled as a Gibbs reactor operating at 850 °C for complete regeneration of the CaO. As in the previous case it is considered that the fuel cell does not operate at total hydrogen conversion and part of the produced hydrogen is recycled and burned to generate the energy needed by the system. Again, the process is not dependant of any other heat source.

To compare the two systems a thermal efficiency of the process is evaluated using the expression:

$$\eta = n_{H_2} LHV_{H_2} / n_{Ethanol} LHV_{Ethanol}$$

where $\eta$ is the thermal efficiency, $n_{H_2}$ the outlet hydrogen molar flow, $n_{Ethanol}$ the inlet molar flow of ethanol, and $LHV_{H_2}$ and $LHV_{Ethanol}$ the low heating values of hydrogen and ethanol, respectively.

Figs. 10 and 11 show the effect of temperature and water to ethanol ratio on the thermal efficiency for the two cases. In both processes as the temperature of the reformer increases
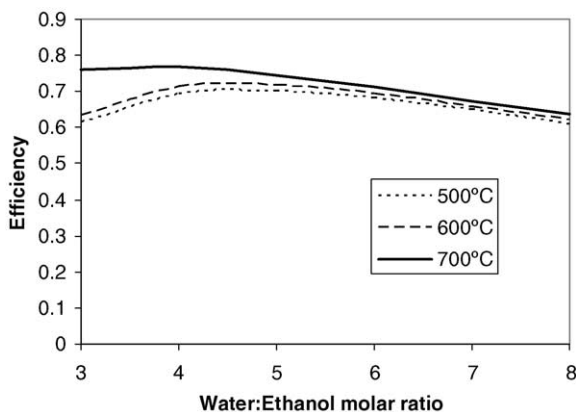


Fig. 11. Thermal efficiency for the ethanol steam reforming in the presence of CaO.

Table 2
Outlet dry gas composition

| Component | Without CaO | With CaO |
|---|---|---|
| $H_2$ | 0.54 | 0.96 |
| $CO_2$ | 0.27 | 0.03 |
| $CH_4$ | 0.19 | 0.01 |

Temperature, 600 °C; 1 atm; water to ethanol ratio, 4.

and a higher efficiency is obtained meaning a higher hydrogen flow at the exit of the system. The effect of the water to ethanol variation presents a maximum. In the case of the steam reforming of ethanol without CaO this maximum is at the stoichometric relation of 3, while in the case with CaO the maximum is around 4. The efficiency of the process with CaO is always higher than without CaO showing that the addition of a $CO_2$ sorbent into the system greatly increases the hydrogen production. Another advantage of using CaO is that the exit composition of the process has a $H_2$ composition higher than 95% (Table 2) which is better for the operation of the fuel cells.

## 4. Conclusions

A thermodynamic analysis of ethanol steam reforming with and without CaO as a $CO_2$ sorbent was carried out by minimizing the Gibbs free energy of the system. Both processes show the same behavior with pressure and water to ethanol ratio, atmospheric pressure and water to ethanol relations higher than 3 are favorable conditions for higher hydrogen productions without carbon formation. The addition of CaO to the reactor greatly enhances the hydrogen production while reducing the CO concentration at the outlet of the reformer.

The temperature effect is different for both processes, while the ethanol steam reforming without CaO has a higher hydrogen production at temperatures between 700 and 900 °C and has a maximum at a temperature near 700 °C, the reforming in presence of CaO has the highest hydrogen production at lower temperatures between 500 and 700 °C.

In addition, the efficiency of two possible processes for hydrogen production that include a WGS reactor and a preferential CO oxidation reactor has been analyzed. The efficiency of the process with CaO was higher than without CaO showing that the addition of a $CO_2$ sorbent in the process increases the $H_2$ production. Favorable operation conditions in the presence of CaO are (1) atmospheric pressure, (2) reactor temperatures around 700 °C, and (3) water/ethanol molar ratio of 4.

In conclusion, potential advantages of the combination of ethanol steam reforming and separation of $CO_2$ using CaO for a PEM fuel cell application are higher hydrogen production, elimination of the need of a WGS reactor and higher thermal efficiency.

## Acknowledgements

## References

[1] V. Klouz, V. Fierro, P. Denton, H. Katz, J.P. Lisse, S. Bouvot-Mauduit, C. Mirodatos, J. Power Sources 105 (2002) 26–34.

[2] B.A. Peppley, J.C. Amhlett, L.M. Kearns, R.F. Mann, Appl. Catal. A: Gen. 179 (1999) 21–29.

[3] B.A. Peppley, J.C. Amhlett, L.M. Kearns, R.F. Mann, Appl. Catal. A: Gen. 179 (1999) 31–49.

[4] B. Lindstrom, L.J. Pettersson, Int. J. Hydrogen Energy 26 (2001) 923–933.

[5] E.Y. García, M.A. Laborde, Int. J. Hydrogen Energy 16 (1991) 307–312.

[6] K. Vasudeva, N. Mitra, P. Umansankar, S.C. Dhingra, Int. J. Hydrogen Energy 2 (1996) 13–18.

[7] S. Cavallaro, V. Chiodo, S. Freni, N. Mondello, F. Frusteri, Appl. Catal. A: Gen. 249 (2003) 119–128.

[8] J. Comas, F. Mariño, M. Laborde, N. Amadeo, Chem. Eng. J. 98 (2004) 61–68.

[9] T. Ioannides, J. Power Sources 92 (2001) 17–25.

[10] C. Han, D.P. Harrison, Chem. Eng. Sci. 49 (1994) 5875–5883.

[11] B. Balasubramanian, A. Lopez Ortiz, S. Kaytakoglu, D.P. Harrison, Chem. Eng. Sci. 54 (1999) 3543–3552.

[12] S. Sato, S.-Y. Lin, Y. Suzuki, H. Hatano, Fuel 82 (2003) 561–567.

[13] S. Lin, M. Harada, Y. Suzuki, H. Hatano, Fuel 81 (2002) 2079–2085.

[14] C.M. Kinoshita, S.Q. Turn, Int. J. Hydrogen Energy 28 (2003) 1065–1071.

[15] M.J. Kahlich, H.A. Gasteiger, R.J. Behm, J. Catal. 171 (1997) 93–105.