



## Short communication

# Thermodynamic evaluation of hydrogen production for fuel cells by using bio-ethanol steam reforming: Effect of carrier gas addition

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## ABSTRACT

Omitting the influence of the addition of carrier gas to the reaction system for hydrogen production by bio-ethanol steam reforming can lead to wrong conclusions, especially when it is going to be made to scale. The effect of carrier gas addition to produce hydrogen using bio-ethanol steam reforming to feed fuel cells was evaluated. Thermodynamic calculations in equilibrium conditions were made, however the analysis derived from them can also be applied to kinetic conditions. These calculations were made by using the Aspen-HYSYS software at atmospheric pressure and different values of temperature, water/ethanol molar ratios, and inert (argon)/(water/ethanol) molar ratios. The addition of inert carrier gas modifies the concentrations of the reaction products in comparison to those obtained without its presence. This behavior occurs because most of the reactions which take place in bio-ethanol steam reforming have a positive difference of moles. This fact enhances the system sensitivity to inert concentration at low and moderated temperatures (<700 °C). At high values of temperature, the inert addition does not influence the composition of the reaction products because of the predominant effect of inverse WGS reaction.

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## 1. Introduction

Hydrogen is a clean and efficient fuel from an energetic point of view, but its handling has some technological problems which still have not been solved appropriately. The ethanol produced from biomass (energetic crops and harvest wastes) is a renewable fuel of easy handling, transport and storage. These characteristics make bio-ethanol an environmentally friendly alternative compared to fossil fuels, whose usage for many years has caused several environmental problems. In addition to this, bio-ethanol can be used as a hydrogen chemical storage [1,2]. The hydrogen can be released from bio-ethanol by chemical reaction, for example by catalytic reforming. Most of the research on hydrogen production for to feed fuel cells using bio-ethanol steam reforming has been focused on the development of different catalysts based on non-noble metals, Ni, Mn, Fe, Zn, Co, Zr and La [3–8] or noble metals [9].

The objective of bio-ethanol steam reforming is to produce a hydrogen-rich gas which will be able to feed fuel cells, especially PEFCs (polymer electrolyte fuel cells) [10]. For this fuel cell type, the fuel must have a low quantity of carbon monoxide (CO) because this gas causes platinum electrode poisoning. Hence, it is desirable that a smaller quantity of CO will be produced in the reforming

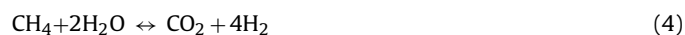
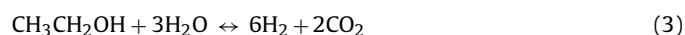
process. Otherwise, it would be necessary to include some hydrogen purification stages.

Another reaction product that is of interest for this process is the methane, because this molecule contains hydrogen atoms in its structure and their presence in the reaction products reduces the hydrogen yield in the process. However, the methane content in the feeding of fuel cells is not an operating drawback for high temperature fuel cells like SOFCs (solid oxide fuel cells), which can process this substance electrochemically.

Because of the technological importance of the composition of the reaction products in ethanol steam reforming in fuel cells applications, an analysis of inert carrier gas addition (whose usage is very frequent in catalysts evaluation) was made in this study.

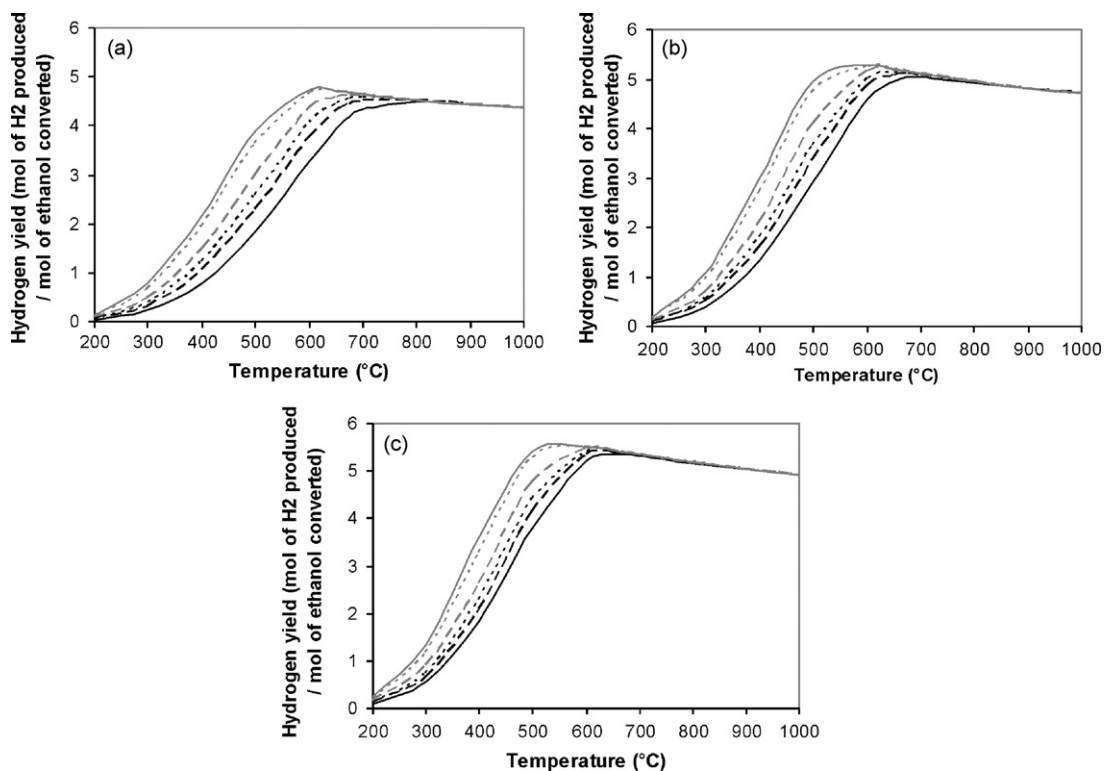
## 2. Thermodynamic considerations

The following reactions can take place in the water-ethanol reaction system in equilibrium conditions:



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**Fig. 1.** Hydrogen yield for different water/ethanol molar ratios: (a) 3, (b) 6 and (c) 9. Inert (argon)/(water/ethanol) molar ratios: (—) 0, (---) 5, (---) 10, (— — —) 20, (— · — · —) 50 and (— · — · — · —) 70.

The final distribution of reaction products will be determined by favoring some reactions against others as a consequence of different changes in temperature, pressure, amount of water and inert carrier gas addition. Several thermodynamic studies have reported that for both high and low temperatures, the predominant reactions are the thermal decomposition of ethanol (Eqs. (1) and (2)) [11]. For high temperatures the predominant reaction is the inverse WGS reaction (inverse equation of (5)) [12] and for high amounts of water they are the reforming reactions (Eqs. (3) and (4)) [11,13]. The changes observed in the equilibrium composition caused by the inert carrier gas addition depend on the temperature as well as on the amount of water present. For this reason, that effect is mainly observed at low temperatures and water–ethanol molar ratios.

In general, for chemical reactions in the gaseous phase, the effect caused by the inert carrier gas addition is similar to that obtained with a decreasing in pressure. For a reaction whose difference of moles is positive, a decrease in the reactants partial pressure (at constant temperature, as in the case of inert carrier gas addition) produces a shift toward products formation because they can take up more volume. This occurs because of the inverse ratio between pressure and volume and it is an expected behavior according to the Le Chatelier's principle.

The situation described previously can be formulated mathematically by means of the existing equations to calculate the equilibrium constant. To illustrate this, Eq. (3) was used. This chem-

ical reaction takes place in gaseous phase and its difference of moles is

$$\Delta n = n_{\text{products}} - n_{\text{reactants}} = 4 > 0,$$

where  $n$  is the number of moles.

Its equilibrium constant can be calculated as a function of the temperature by Eq. (6) and as a function of the composition by Eq. (7):

$$\frac{d \ln K}{dT} = \frac{\Delta H^0}{RT^2} \quad (6)$$

where  $K$  is the equilibrium constant,  $\Delta H^0$  the reaction heat,  $R$  the gas constant and  $T$  is the temperature.

$$\prod_i (y_i \hat{\phi}_i)^{\nu_i} = \left(\frac{P}{P^0}\right)^{-\nu} K, \quad (7)$$

with

$$\nu \equiv \sum_i \nu_i$$

and

$$y_i = \frac{n_i}{\sum_i n_i}, \quad i = \text{CH}_3\text{CH}_2\text{OH}, \text{H}_2\text{O}, \text{H}_2, \text{CO}_2 \text{ and inert}$$

where  $K$  is the equilibrium constant,  $P$  the pressure,  $P^0$  the pressure in standard conditions (101.325 kPa),  $y_i$  the mole fraction of the  $i$ th species,  $\hat{\phi}_i$  the fugacity coefficient of the  $i$ th species and  $\nu_i$  is the stoichiometric coefficient of the  $i$ th species.

Eq. (7) was used to evaluate the influence of composition in the calculation of equilibrium constant. Considering that the behavior of equilibrium mixture is ideal  $\hat{\phi}_i = 1$ , atmospheric pressure and

**Table 1**

Operating conditions used for thermodynamic calculations.

Variable	Values
Temperature (°C)	200–1000
Pressure (kPa)	101.325
Water/ethanol molar ratio	3–9
Inert (argon)/(water/ethanol) molar ratio	0–70

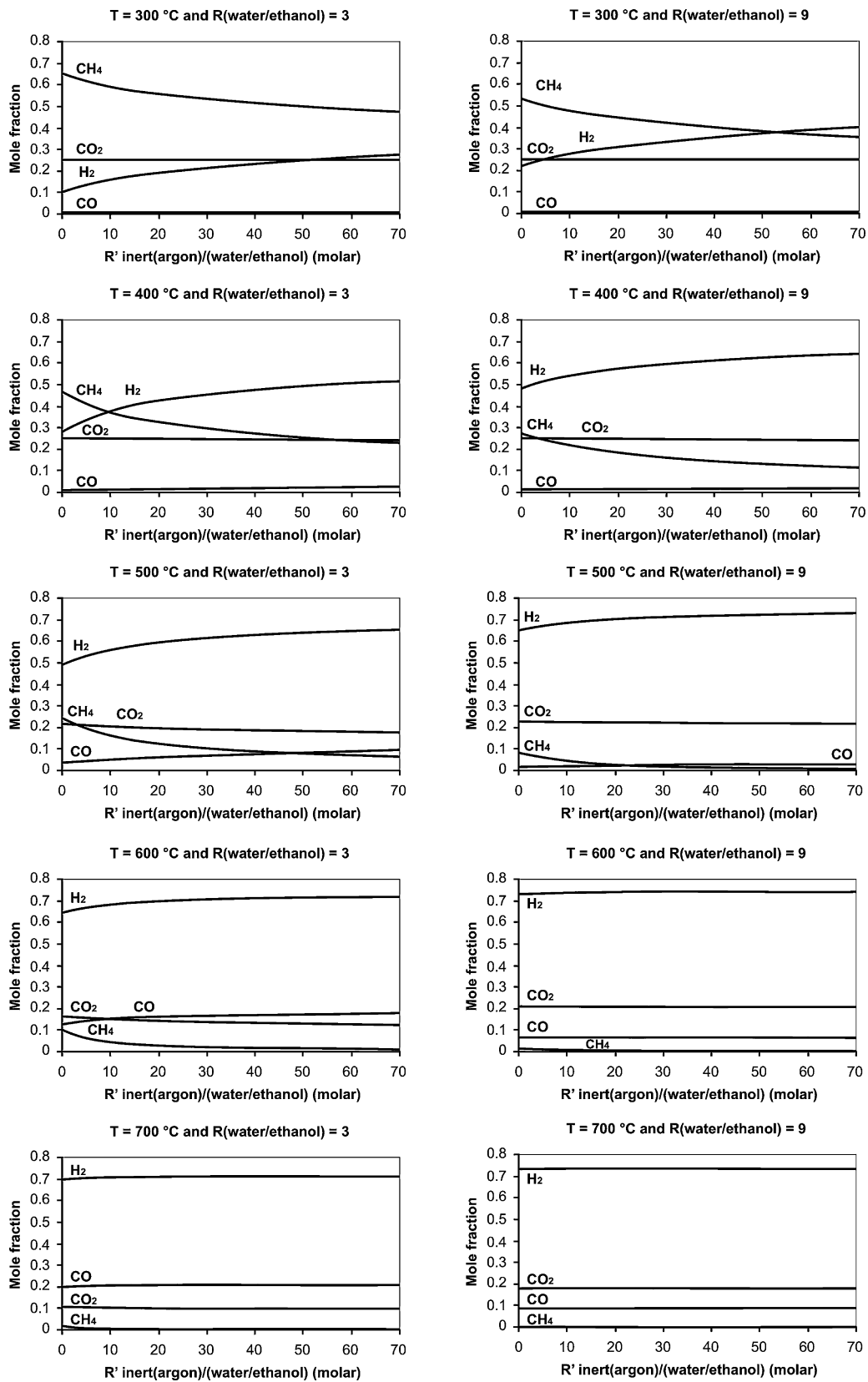


Fig. 2. Effect of inert carrier gas addition in the concentration of reaction products for bio-ethanol steam reforming.

simplifying, Eq. (8) was obtained:

$$K = \frac{n_{\text{CO}_2}^2 n_{\text{H}_2}^6}{n_{\text{CH}_3\text{CH}_2\text{OH}} n_{\text{H}_2\text{O}}^3 (\sum_i n_i)^4} \quad (8)$$

In the denominator of Eq. (8) the term  $(\sum_i n_i)^4$  is found and inside it, the number of moles of the inert gas added to the system. Then, a change in the number of moles of inert gas modifies the total number of moles (at constant temperature and pressure) and if the number of moles of the reaction products ( $\text{H}_2$  and  $\text{CO}_2$  (carbon dioxide)) remains equal, the value of  $K$  would be changed numerically, which is not possible because of the value of the equilibrium constant for each temperature is only one (according to Eq. (6)). Therefore, a change in the system to equilibrate this fact must take place. Such change involves an increment in the numeric value of the numerator of Eq. (8), which leads to increase the number of moles of reaction products ( $\text{H}_2$  and  $\text{CO}_2$ ) shifting the reaction toward the right side.

Taking into account the above thermodynamic considerations, the inert gas addition will favor the reactions described in Eqs. (1)–(4) at atmospheric pressure and at temperatures and water/ethanol molar ratios where they predominate instead of the reaction described in Eq. (5).

### 3. Results and discussion

With the aim of making a more detailed analysis about the effect of inert gas addition to the reaction system for bio-ethanol steam reforming, some thermodynamic calculations were made by using the Aspen-HYSYS software with the operating conditions showed in Table 1. In this simulation a Gibbs reactor was used. This reactor calculates the distribution of reaction products by minimizing the Gibbs free energy of each one of the existing species in the reaction system. The state equation of Peng–Robinson Stryjek Vera was used as thermodynamic model [14].

#### 3.1. Hydrogen production

The hydrogen yield (moles of hydrogen produced/moles of ethanol converted) for three water/ethanol molar ratios: 3, 6 and 9, and several inert (argon)/(water/ethanol) molar ratios is shown in Fig. 1. A systematic increase of hydrogen production is illustrated because of a complementary effect between the inert addition (which favors the reactions described in Eqs. (3)–(5)) and the water addition (which favors the reactions described in the Eqs. (1)–(4)).

The variation of hydrogen yield versus temperature has a maximum value because the favoring of inverse WGS reaction at high temperatures consumes the hydrogen produced by the reactions shown in Eqs. (2)–(4). On the other hand, the inert gas addition at high temperatures does not increase the hydrogen production; due to this factor it does not influence the inverse WGS reaction because its difference of moles is zero.

##### 3.1.1. Distribution of reaction products

The variation of the concentration of the reaction products with the inert gas addition (in dry basis) for bio-ethanol steam reforming at some temperatures and water/ethanol molar ratios is shown in Fig. 2. The inert gas addition modifies the composition of hydrogen, methane and carbon monoxide at temperatures lower than 700 °C. This is expected because most of the reactions involved have a positive difference of moles. When inert gas is added the total number of moles involved in the reaction decreases and the reaction shifts to the side with a greater number of moles. In this case the shifting is done toward reaction products because the number of moles of the products is greater than the reactants. But, for carbon dioxide composition this effect does not happen. This is altered only by changes

in temperature and/or water/ethanol molar ratio, because the number of  $\text{CO}_2$  moles produced in each reaction is lower than other products, even though this substance is produced by the majority of the reactions (Eqs. (1) and (3)–(5)). This fact added to the high influence of the WGS reaction (Eq. (5)), which is not affected by the inert gas addition, causes that the  $\text{CO}_2$  concentration will not be affected by the carrier gas addition.

The carbon monoxide concentration is enhanced by the increase of temperature and inert gas addition but it is reduced with the increase of the amount of water. This behavior is the result of the competition between the reactions described in Eqs. (2) and (5). At low temperatures, the inert gas addition favors the reaction of thermal decomposition (Eq. (2)) because its difference of moles is positive, but it does not affect the WGS reaction (Eq. (5)). When the temperature is increased, the inverse WGS reaction prevails (inverse of Eq. (5)) which increases the CO concentration. Then, the best conditions for low production of CO are low temperatures and high water/ethanol molar ratios, but with a consequent reduction in the hydrogen concentration. These conditions are congruent with those reported by several authors who have obtained low concentrations of CO (lower than 2%) at low temperatures (300–450 °C) and high amounts of inert carrier gas [15–23].

On the other hand, if the desired effect is the methane reduction in reaction products, the best conditions are high temperatures (>700 °C) and water/ethanol molar ratios, but without the addition of inert carrier gas. Although to reduce the methane composition at moderated temperatures, it is feasible to increase the amount of inert carrier gas (at 500 °C, values lower than 10% are obtained).

The modifications in the composition of reaction products for bio-ethanol steam reforming caused by inert carrier gas addition obtained in equilibrium conditions can take place under kinetic conditions too, because of the thermodynamic considerations mentioned before are applicable evenly. Experimental evidence of this fact can be found on Llorca et al. [24].

The inclusion of thermodynamic analysis in the catalytic studies for ethanol steam reforming, taking into account the addition of an inert carrier gas, is considered very important to make appropriate comparisons between equilibrium conditions and experimental results.

### 4. Conclusions

The thermodynamic analysis carried out to study the influence of the addition of inert gas to hydrogen production using bio-ethanol steam reforming, at atmospheric pressure and in equilibrium conditions, demonstrates that this factor modifies the products distribution significantly compared to conditions without its addition. This effect is not isolated; on the contrary, it appears combined with the influence of other operating variables like temperature and water/ethanol molar ratio. These changes were evidenced mainly in hydrogen, methane and carbon monoxide concentrations because most of the reactions have a positive difference of moles. This fact makes the reaction system very sensitive to inert carrier gas addition at low and moderated temperatures (<700 °C). So the omission of the influence of carrier gas addition in the reaction system to produce hydrogen for bio-ethanol steam reforming can lead to inappropriate conclusions, especially when it is made to scale. However, for high temperatures (>700 °C), the predominant effect of inverse WGS reaction permits that the inert addition does not modify the concentration of the reaction products. These observations are applicable to kinetic conditions because the thermodynamic considerations that support them are valid in this case too. Therefore for both, to carry out experimentation and elaboration of comparisons under equilibrium conditions, it is necessary to take into account the influence of inert carrier

gas addition because its presence modifies substantially the distribution of reaction products, which can affect the conversion and selectivity calculations.

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