A METHODOLOGY FOR THERMODYNAMIC SIMULATION OF HYDROGEN PRODUCTION FROM REFORMING OF BIOMASS GAS

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Abstract. The purpose of this work is to present a methodology for thermodynamic simulation of hydrogen production from reforming and purification of biomass gas. Hydrogen can be produced from the conversion of methane and carbon monoxide molar fractions in the gaseous mixture. The proposed methodology consists of the modelling of a reaction system for conversion of methane and carbon monoxide, as well as the gaseous flow purification in PSA (Pressure Swing Adsorption). The simulation of the reforming reactions is made for obtaining the equilibrium molar fractions at the reactor exit, and is used with several types of gasification gases in the study. Energy and exergy analyses are done to evaluate the performance of the system model. The simulation demonstrates that hydrogen production has a better performance when reforming a gaseous mixture from the IFB (Indirect Fluidized Bed) system, since the total system irreversibility is 50% lower than that of a system reforming a gaseous mixture produced by gasification with air.

Keywords: Hydrogen, biomass gas, steam reforming, thermodynamics

1. INTRODUCTION

The use of hydrogen to drive vehicles or stationary equipment is becoming a reality. Advancements in technologies to convert hydrogen into electricity -- the fuel cells -- have become a reality in recent years. Development of fuel cells combined with oil scarcity can make hydrogen a viable proposition as an alternative fuel. Hydrogen is considered an energy vector, as it can be extracted from various sources (water, alcohol, biogas, natural gas, etc.) by processes using renewable or non-renewable energy sources.

One of the raw materials for hydrogen is the biomass gasification gas (GGAS), a mixture of H_2, CO, CH_4, C_xH_y, CO_2 and N_2. The molar fractions of these gaseous species in the composition of GGAS depend on the type of gasification process, and the potential of GGAS to produce hydrogen depends, in turn, on its composition, mainly on its CH4 and CO contents.

This work presents a methodology for the thermodynamic simulation of hydrogen production by GGAS reforming. Gas mixtures produced by different gasification processes were used in order to find which had the highest potential for hydrogen production. The "highest potential" is understood as the one in which GGAS reforming and purification results in the minimum irreversibility for the total system.

2. SYSTEM OF HYDROGEN PRODUCTION FROM GGAS

Figure 1 illustrates the model of the system for hydrogen production from GGAS. GGAS at 850°C and atmospheric pressure enters the reforming reactor at Point 1, and leaves it at Point 2 at a temperature that depends on its composition at the entrance. Reform gas (REF_{GAS}) must be cooled before passing through the shift reactor for the reaction of carbon monoxide with steam. After the shift reactor, the $SHIFT_{GAS}$ must be cooled and compressed. The final part of the system is hydrogen purification by a PSA cycle (pressure swing adsorption). Point 7 represents the flow of pure hydrogen, and Point 8 represents the flow of the OFF_{GAS} gas mixture at the PSA exit.
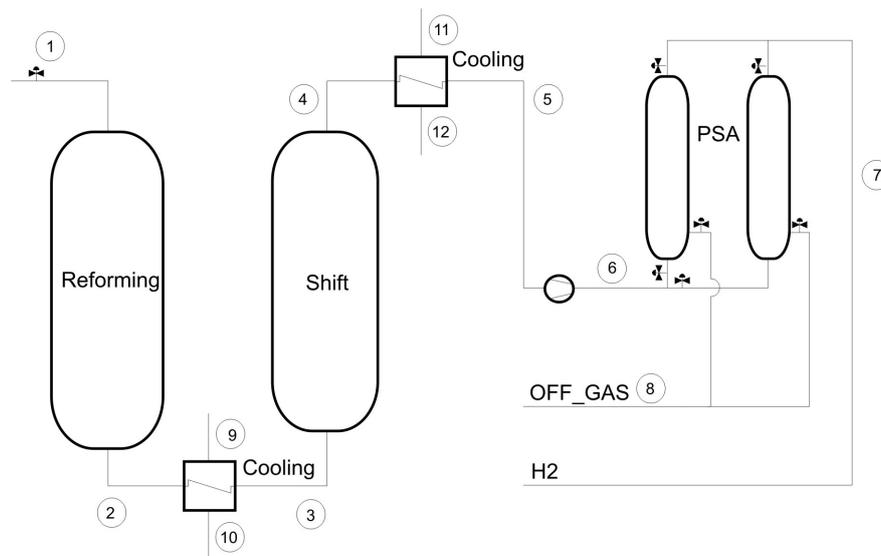
Figure 1. System for the production and purification of hydrogen from GGAS

3. GGAS REFORMING AND PURIFICATION

GGAS has a hydrogen molar fraction that can be maximized by the reformation of the molar fractions of methane (CH_4), hydrocarbons (CxHy), and carbon monoxide (CO). For maximum conversion of these gaseous species into hydrogen there should be two reactors: one for hydrocarbon reforming and another for CO processing.

The process of reforming is defined as a thermochemical and catalytic conversion of a liquid, solid or gaseous fuel into a hydrogen-rich mixture. According to Silva (1991), most processes use light hydrocarbons for extracting hydrogen. Light hydrocarbons are those with molecular mass between methane and naphtha, and a boiling point below 250°C. These compounds can react with water at temperatures of 800-900°C. In the case of methane, a nickel-alumina catalyst is used.

The best known reforming methods are: steam reforming, partial oxidation, and autothermal reforming. In this work, steam reforming was considered. The global GGAS reforming reactions are described by Eqs. (1), (2) and (3).

$$CH_4 + aH_2O \rightarrow bCO + cCO_2 + dH_2 + eH_2O \tag{1}$$

$$C_2H_4 + aH_2O \rightarrow bCO + cCO_2 + dH_2 + eH_2O \tag{2}$$

$$CO + aH_2O \rightarrow bCO_2 + cH_2 \tag{3}$$

The maximum carbon monoxide conversion is generally carried out in two fixed-bed reactors connected in series, and with intermediate cooling. The first reactor operates between 300 and 500°C and uses an iron/chrome catalyst. The second reactor operates at lower temperatures (180-300°C) and uses a copper/zinc/alumina catalyst (GIUNTA et al. 2005). The present work considered a reactor operating at 300°C, in which the global reaction is that of Eq.(3).

Hydrogen purification can be done by a PSA (Pressure Swing Adsorption) system, which is widely used for gas purification. PSA is generally employed for oxygen or nitrogen from air, and for hydrogen generated by processes such as hydrocarbon reforming. This technology has been in commercial use for hydrogen purification since 1966, and is currently widely used (MYERS et al., 2002).

Basically, PSAs function by the action of an adsorbent bed selective for certain gaseous species. A gaseous mixture is introduced into the bed under high pressure, and the adsorbing solid selectively adsorbs certain components, allowing the non-adsorbed component to pass through the bed as a purified gas. According to Myers et al. (2002), there are two basic principles to separate components of a gaseous mixture using a solid material. In the first one, there is a surface adsorption: gas molecules adhere due to their preferential chemical interaction. In the second, selectivity is by size; the adsorber is a porous solid with pores of a sufficient size to allow certain molecules into the pellet, whereas larger or smaller molecules go through the pellet. The energy required for this separation of gaseous species is obtained from the mechanical work of compressing the gaseous mixture. Energy expended in this mechanical work is a significant component of the operational cost of a PSA system.

4. SYSTEM PERFORMANCE ANALYSIS

The methodology for the system performance analysis was the energy and exergy balance. Initially the simulation of GGAS reforming was done, in which the final mixture composition, corresponding to the chemical equilibrium in a given thermodynamic condition, was calculated from the minimization of the total Gibbs free energy of the system. The equilibrium constant of a given reaction is:

$$\ln(k) = \frac{-\Delta \bar{g}_f}{\bar{R} \cdot T}$$ (4)

where:

k = reaction equilibrium constant

$\Delta \bar{g}_f$ = molar-specific total Gibbs free energy variation (J.mol^{-1}.K^{-1})

$\bar{R}$ = universal gas constant (8,314 J.mol^{-1}.K^{-1})

T = absolute temperature (K)

The hydrogen molar fraction in the mixture is a function of the temperature, pressure and the steam/carbon ratio (γ). In the present work, the pressure was 101.325 kPa, and the parameter γ was equal to 2 for CH_4 reforming, 3 for C_2H_4, and 1 for CO reforming. For this, a system of dependent equations is formulated, for which the calculation of the free energy of the species considered as products of the reforming process, as well as of the mass balance of these species from the reactants' entry conditions into the system, should be done.

With regard to input conditions, GGAS can exhibit different compositions depending on the gasification process and biomass type. Table 1 illustrates the molar fractions of some gaseous mixtures produced by different gasification processes reported by Bain (2004). Codes in Table 1 have the following meanings:

CFB : circulating fluidized bed
FB : fluidized bed
IFB : indirect fluidized bed
ICFB : indirect circulating fluidized bed
DRF : downdraft
UPF : updraft

Table 1. GGAS composition for different gasification processes.

Process	CFB	ICFB	FB	IFB	IFB	FB	DRF	UPF
	air	steam	air	steam	steam	air	air	air
Biomass	Bagasse	Wood	Wood	Black liquor	Wood	Wood	Wood	Wood
[%mol.mol^{-1}]	GGAS1	GGAS2	GGAS3	GGAS4	GGAS5	GGAS6	GGAS7	GGAS8
Y_H$_2$	10.0	26.2	21.7	29.4	31.5	11.0	16.0	10.0
Y_CO	12.7	38.2	23.8	39.2	22.7	17.0	21.5	14.8
Y_CO$_2$	16.7	15.1	9.4	13.1	27.4	18.0	14.4	12.8
Y_N$_2$	56.4	1.6	41.6	0.9	3.2	44.0	44.8	57.5
Y_CH$_4$	3.7	14.9	2.9	13.0	11.2	7.0	3.3	4.9
Y_C$_2$H$_4$	0.5	4.0	0.6	4.4	4.0	3.0	0.0	0.0

Once the hydrogen molar fraction in the gaseous mixture in the shift reactor (SHIFT$_{GAS}$) is calculated, the next step is the hydrogen purification by PSA. In the present work, a PSA system was considered with an operation pressure of 650 kPa, and a hydrogen recovery factor of 0.85 of the volumetric flow of the molar fraction of this species in the SHIFT$_{GAS}$. These characteristics were chosen on the basis of research and development at the Hydrogen Laboratory of UNICAMP's IFGW.

Thermodynamic analysis of the system illustrated in Fig. 1 assumed the ideal gas model. Equations (5) and (6) represent the enthalpy and entropy calculations for an ideal gas mixture.

$$\bar{h}_i = \sum_{i=1}^{n} y_i \cdot \left(\bar{h}_i^0 + \int_{T0}^{T} \bar{c}_{p_i} . dT \right)$$ (5)

$$\bar{s}_i = \sum_{i=1}^{n} y_i \cdot \left(\bar{s}^0_i + \int_{T0}^{T} \left(\frac{\bar{c}_{p_i}}{T} \right).dT - \bar{R}.\ln(y_i) \right) \tag{6}$$

where:

$\bar{h}$ = specific molar enthalpy (J.mol⁻¹)

$\bar{s}$ = specific molar entropy (J.mol⁻¹.K⁻¹)

$\bar{c}_p$ = specific molar heat (J.mol⁻¹.K⁻¹)

The mass and energy balances in reactors and heat exchangers are represented by Eqs. (7), (8) and (9).

$$\sum \dot{m}_{in} = \sum \dot{m}_{out} \tag{7}$$

$$\sum_{i=1}^{n} \dot{n}_i \left(\bar{h}_i(T) \right)_P - \sum_{i=1}^{n} \dot{n}_i \left(\bar{h}_i(T) \right)_R = 0 \tag{8}$$

$$\sum_{i=1}^{n} \dot{n}_{in} \cdot \bar{h}_{in} - \sum_{i=1}^{n} \dot{n}_{out} \cdot \bar{h}_{out} = \dot{Q} \tag{9}$$

where:

$\dot{n}$ = molar flow (mol.s⁻¹)

$\dot{m}$ = mass flow (kg.s⁻¹)

First law efficiency of the hydrogen production system is defined as:

$$\eta_I = \frac{\dot{n}\left(LHV(H_2) \right)}{\dot{n}\left(LHV(GGAS) \right)} \tag{10}$$

where:

LHV = lower heating value (J.mol⁻¹)

The exergy balance for a control volume is:

$$\dot{W}_{VC} - \dot{I} = \dot{n}_{out} \left(\bar{ex}_{out} \right) - \dot{n}_{in} \left(\bar{ex}_{in} \right) \tag{11}$$

where:

$\dot{I}$ = irreversibility rate (J.s⁻¹)

$\bar{ex}$ = specific molar exergy (J.mol⁻¹)

The definition of specific physical and chemical exergy, according to Szargut et al. (1988), is represented by Eqs.(12) and (13):

$$\bar{ex}_{ph} = \left(\bar{h} - \bar{h}_0 \right) - T_0 \left(\bar{s} - \bar{s}_0 \right) \tag{12}$$

$$\overline{ex}_{ch} = \sum_{i=1}^{n} y_i . \overline{ex}^0{}_{chi} + \overline{R}.T_0 . \sum_{i=1}^{n} y_i . \ln . y_i \qquad (13)$$

Where the total specific exergy is:

$$\overline{ex} = \overline{ex}_{Ch} + \overline{ex}_{ph} \qquad (14)$$

The reference environment in which physical and chemical exergies are defined consisted in the proposal by Szargut et al. (1988), where standard temperature and pressure (298.15 K and 101.3 kPa) and the standard atmosphere composition can be found.

Exergetic efficiency calculations adopted the input/output criterion defined by Kotas (1995) as ratio efficiency. The ratio efficiencies of the following control volumes were calculated: reforming reactor, PSA, and the system as a whole. Eqs.(15), (16) and (17) respectively represent these efficiencies.

$$\psi_{,RR} = \frac{\dot{n}\left(\overline{ex}_{ch}(REF_{GAS})\right)}{\dot{n}\left(\overline{ex}_{Ch}(H_2O) + \overline{ex}_{ph}(H_2O)\right) + \dot{n}\left(\overline{ex}_{ch}(GGAS) + \overline{ex}_{ph}(GGAS)\right)} \qquad (15)$$

$$\psi_{,PSA} = \frac{\dot{n}\left(\overline{ex}_{ph}(H_2)\right)}{\dot{W}_{PSA}} \qquad (16)$$

The exergetic efficiency of the hydrogen production systems took into account as inputs the chemical exergy, and the compression work of GGAS.

$$\eta_{II} = \frac{\dot{n}\left(\overline{ex}_{ch}(H_2)\right)}{\dot{n}\left(\overline{ex}_{ch}(GGAS)\right) + \dot{W}_{PSA}} \qquad (17)$$

5. RESULTS

Figures 2 and 3 show the molar fractions of the equilibrium composition of GGAS1 and GGAS2 reforming simulations respectively. It is apparent that the potential for hydrogen production is higher from GGAS2, since it has higher CH_4 and CO molar fractions than GGAS1. The temperature at which hydrogen production reaches its peak depends on the amount of CH_4, CO and inert gases such as N_2 and CO_2. The CH_4 reforming reaction is favored by higher temperatures (800-900°C), while the CO reforming reaction is favored by lower temperatures (250-400°C).

Thus, gas cooling is necessary at the reforming reactor exit to allow the conversion of the remaining CO molar fraction in the shift reactor. In order to allow the use of the GGAS physical exergy at the reforming reactor, GGAS pre-cleaning must be done by the hot system. If it were a cold system, the gaseous mixture would have to be heated up to the reforming operation temperature again, increasing the energy consumption of the hydrogen production system.

The gaseous mixture composition has an important effect on system performance. For the gaseous mixtures in Table 1, Figure 4 shows the variation on reformer exergetic efficiency as a function of the nitrogen molar fraction in GGAS. The higher the amount of this inert gas, the lower the reformer efficiency. In practice, the presence of inert gases has a negative influence on reaction kinetics.
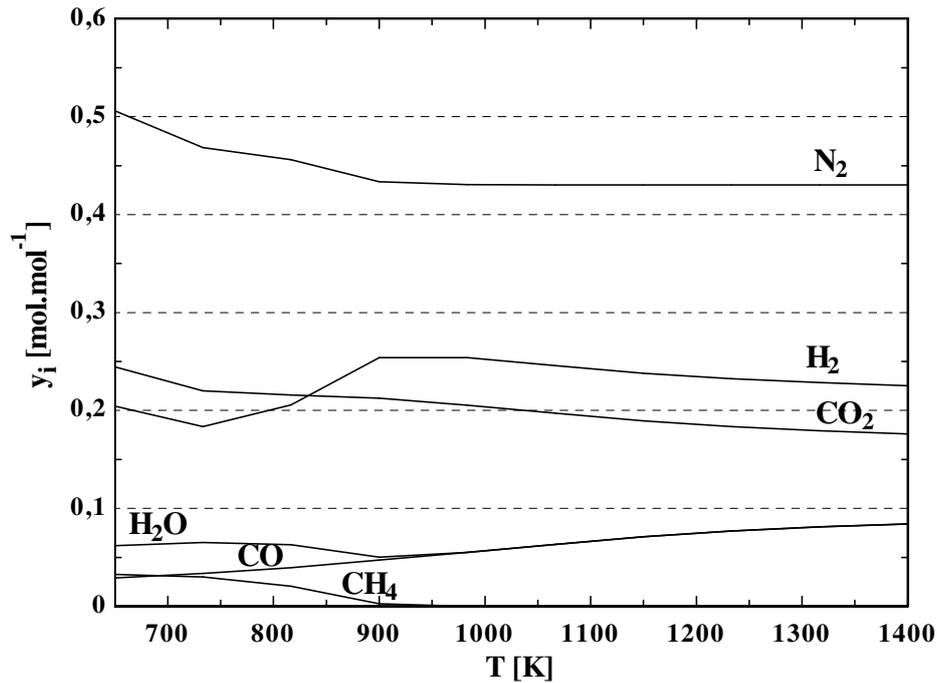
Figure 2. Molar fractions from GGAS1 reforming simulation.
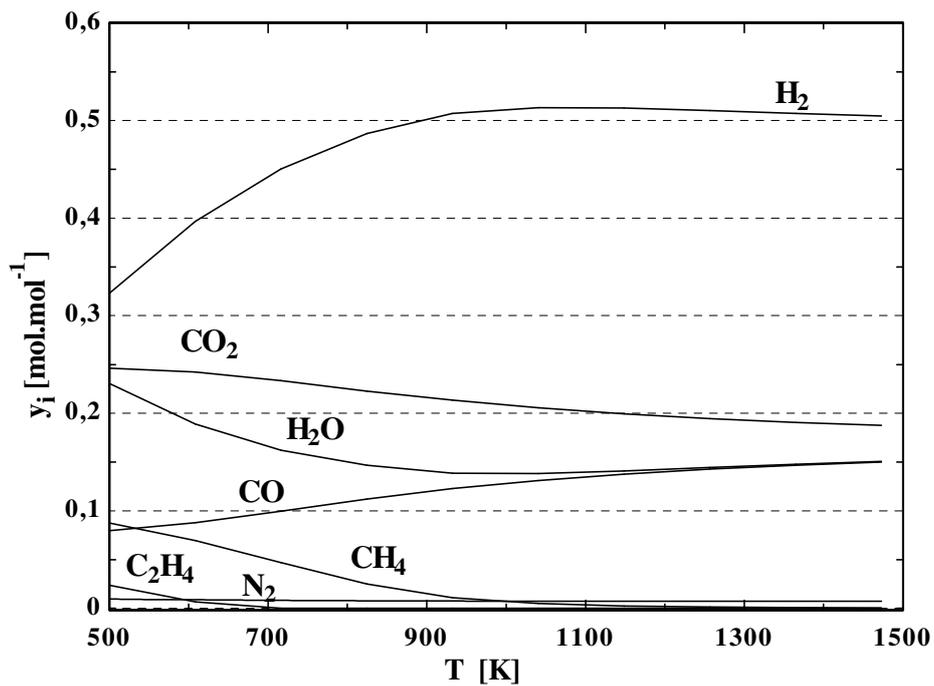
Figure 3. Molar fractions from GGAS2 reforming simulation

Although the effectiveness of the reforming process is very important for the performance of the system, PSA has the most striking influence on energy consumption. Hydrogen purification is the main determinant of energy consumption, due to the need to compress the gaseous mixture, and due to the use of part of the purified hydrogen for adsorption bed regeneration. Figure 5 shows that purification performance is proportionally better for higher molar fractions of hydrogen in the $SHIFT_{GAS}$.

This favorable condition is obtained in the reforming of GGAS2, GGAS4 and GGAS5. These gaseous mixtures are produced by the gasification process with steam injection and indirect heating, which yields gases of a higher quality. For a pilot plant, steam production should be provided for the gasification process; part of the required heat can be obtained by burning poor gas rejected by the PSA (OFF_{GAS}).
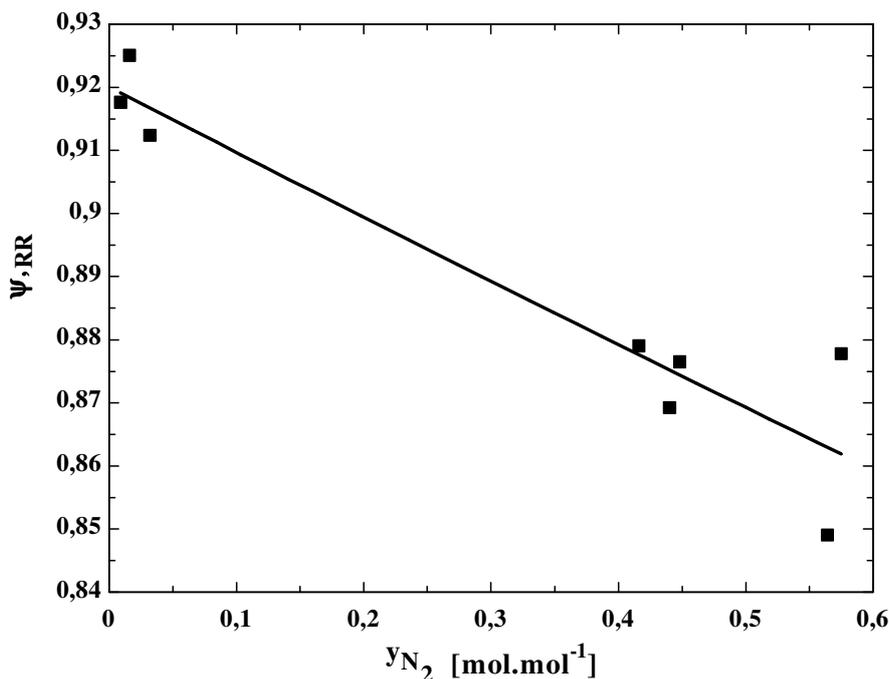
Figure 4. Exergetic efficiency of the reforming reactor as a function of nitrogen molar function
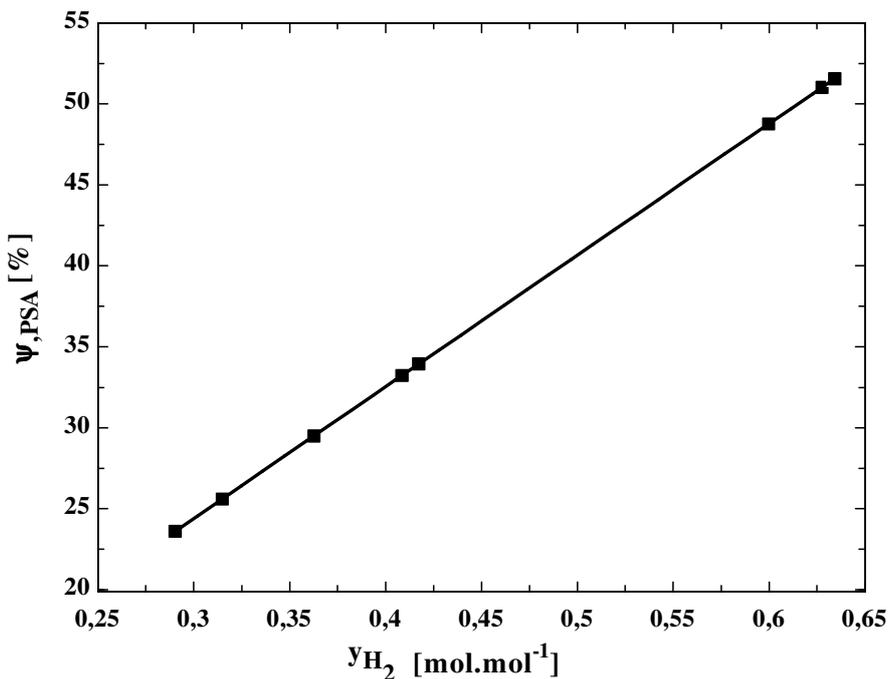
Figure 5. Exergetic efficiency of PSA as a function of hydrogen molar fraction in the $SHIFT_{GAS}$

The system exhibits a lower exergy destruction, i.e., a lower irreversibility is generated when a better quality gaseous mixture is used for hydrogen production. Figure 6 shows the total system irreversibility as a function of the hydrogen molar fraction in the $SHIFT_{GAS}$.

The graph in Figure 7 shows the first law and second law efficiency variations of the hydrogen production system as a function of the hydrogen molar fraction in the $SHIFT_{GAS}$. The first law efficiency is not an adequate parameter to measure system performance since the GGAS lower calorific value does not reflect the quality of the gaseous mixture for hydrogen production. The second law efficiency, on the other hand, is indicative of GGAS quality in the sense that the smaller the gas flow required to produce a given amount of hydrogen, the higher the system performance will be. For the construction of a pilot plant, the higher exergetic efficiency illustrated in Figure 7 translates into components of

a smaller volume. Figure 6 also indicates that the system will be smaller due to the lower irreversibility. A pilot plant with components of a smaller volume will have a correspondingly lower capital cost. The produced hydrogen can be used in a fuel cell either for stationary electricity generation or for mobile generation aboard an electric vehicle.
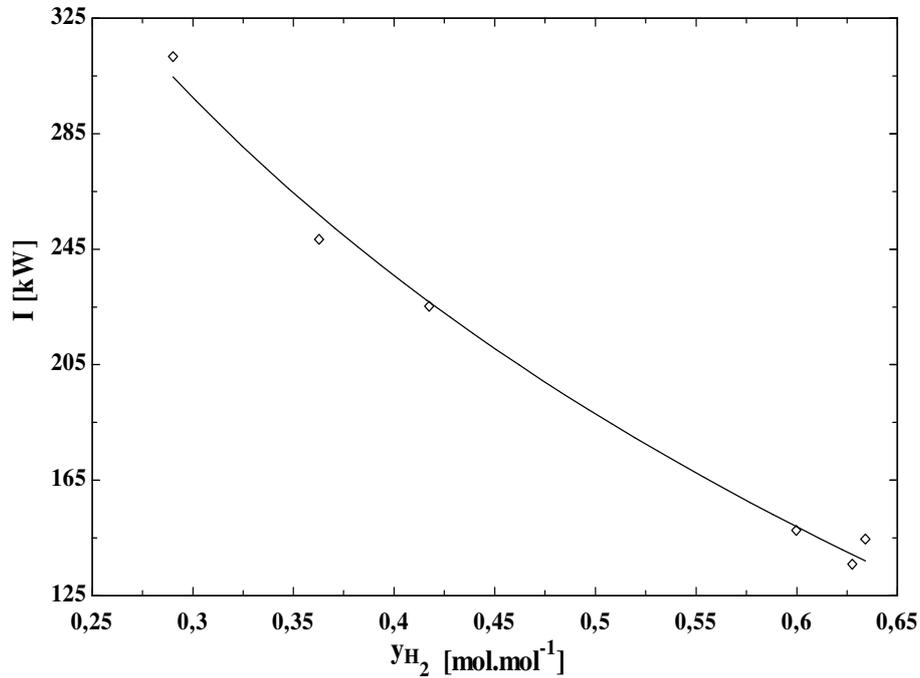
Figure 6. Total system irreversibility as a function of the hydrogen molar fraction in the SHIFT$_{GAS}$
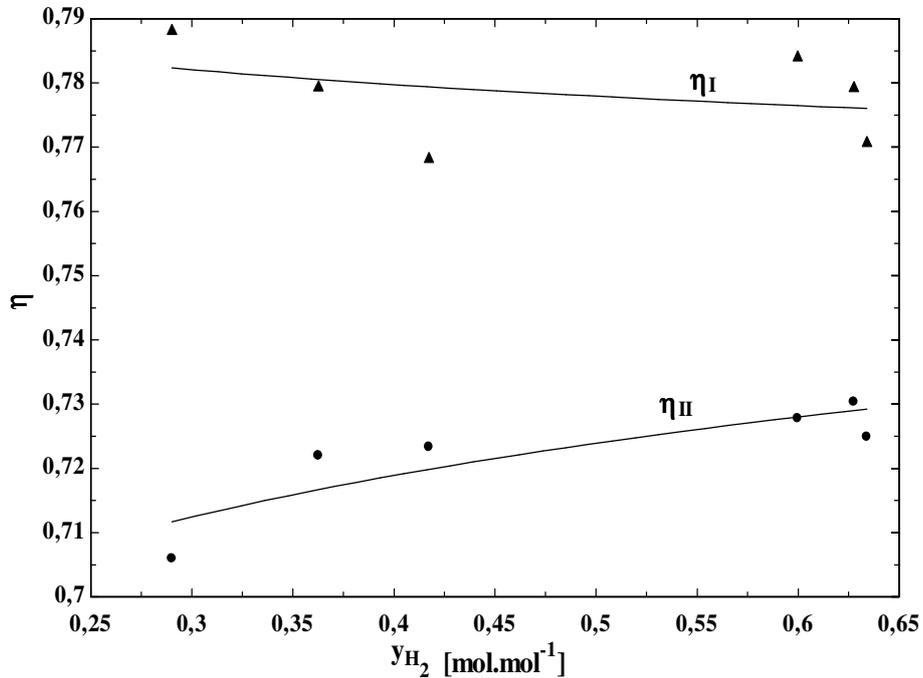
Figure 7. First and second law efficiencies as a function of the hydrogen molar fraction

6. CONCLUSION

The thermodynamic simulation methodology presented here constitutes an useful way of measuring the performance of a system for the production of hydrogen by the reforming and purification of GGAS. The simulation showed that the gaseous mixtures with the highest potential to produce hydrogen are those produced by the IFB gasification processes.

These use steam for the thermochemical gasification reactions, which has an indirect heating effect; the flow of processed gases for obtaining hydrogen is smaller than for air gasification processes, and the total generated irreversibility is about 50% smaller. A hydrogen production plant using GGAS 2 would have components with a smaller volume than a plant using GGAS 1, resulting in lower capital and operational costs, mainly in hydrogen purification.

7. ACKNOWLEDGEMENTS

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