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HYDROGEN PRODUCTION FROM BIOGAS: COMPUTATIONAL THERMODYNAMICS APPLIED TO OPTIMIZATION OF REFORMING CONDITIONS AND DEVELOPMENT OF CATALYSTS[1]

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Abstract

The aim of this research is to determine the optimized conditions for H_2 production by biogas/methane reforming technologies for fuel cells use. The effect of controllable operating parameters on H_2 production is evaluated through thermodynamic equilibrium calculations using the Gibbs energy minimization approach. The heat needed for each reforming process is also analyzed. As one can see from the results, high selectivity towards H_2 formation can be achieved under thermo-neutral operating conditions. A new reforming process involving the in situ CO_2 capture – known as Sorption Enhanced Reforming (SER) – is also studied. It is found that high purity H_2 (>90mol%, on dry basis) can be obtained in a single step process, with no need of water-gas shift reactors, which simplifies enormously the hydrogen plant. Thermodynamic modeling of SER process using CaO, Li_2ZrO_3 and Li_4SiO_4 is carried out, and the best material to be used as sorbent is indicated. Theoretical results are validated against experimental values from literature. In this way, the relevance of computational thermodynamics to the development of new processes and materials for H_2 generation is shown.

Key words: Computational thermodynamics; Biogas; Hydrogen; Catalyst; Reforming.

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1 INTRODUCTION

Recently, much attention has been focused on methane/biogas reforming for the production of pure H_2 or synthesis gas – *syngas* – which is a mixture composed essentially of H_2 and CO. The usual temperature for Solid Oxide Fuel Cells (SOFCs) is over 800ºC, at which ion-conducting ceramic electrolyte becomes a conductor of oxygen ion.(1) Due to their high operating temperatures and the ability to use CO as fuel, SOFCs can be run on *syngas* produced by biogas/methane reforming technologies. However, low temperature fuel cells such as PEMFC (Proton Exchange Membrane Fuel Cells) run on pure H_2, since CO poisons Pt catalyst. In this way, for PEMFC use, besides the reformer, the hydrogen plant must include water-gas shift (WGS) and preferential CO oxidation (COPROX) reactors.

Biogas is one of the most potential renewable sources for *syngas*/hydrogen production. Biogas refers to a gas produced by anaerobic digestion or fermentation of any biodegradable organic matter, including municipal solid waste, sewage sludge, agricultural wastes, animal dung and energy crops.(2) The main components of biogas are methane and carbon dioxide. Biogas reforming is essentially CO_2 reforming of CH_4 (dry reforming of methane). However, the huge energy required and carbon deposition formation on catalyst surface at high temperatures are the main disadvantages of this process.(3) In this way, other processes can be employed, such as combined CO_2 reforming and partial oxidation of methane (feedstock composed of CH_4+CO_2+O_2).(4) Another possibility of *syngas* production is a new process known as methane tri-reforming (feedstock composed of CH_4+CO_2+H_2O+O_2).(3,4) These latter technologies could lead to an auto-thermal operation, besides of high selectivity towards H_2 formation, while minimizing (or inhibiting) carbon deposition.

The present work is aimed at investigating, from a thermodynamic point of view, the following methane reforming technologies for *syngas* production:

- dry Reforming (DR);
- combined carbon dioxide reforming and partial oxidation (oxy-CO_2 reforming);
- tri-reforming (TR);

The effect of controllable operating parameters – inlet temperature and feedstock composition (CH_4/CO_2 molar ratio, concentration of O_2 and H_2O) – on the selectivity of H_2 and CO, CH_4 and CO_2 conversions and the heat needed for reforming process is analyzed, and theoretical results are compared with experimental values from literature.

In this research, a new reforming process involving the in situ CO_2 capture – known as Sorption Enhanced Reforming (SER) – is also studied. The possibility of producing high purity H_2 (>90mol%, on dry basis) in a single step process, with no need of water-gas shift reactors, is investigated. This is particularly interesting for H_2 use in PEMFCs. Thermodynamic modeling of SER process using CaO, Li_2ZrO_3 and Li_4SiO_4 is carried out, and the best material to be used as sorbent is indicated.

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2 METHODOLOGY

Thermodynamic equilibrium calculations using the Gibbs energy minimization approach was carried out using the commercial software FactSage 6.3. The selected databases were SGPS and FactPS, which include thermodynamic data for compounds only. The species considered for describing the ideal gas phase were: H_2, H_2O, CO, CO_2, CH_4 and O_2. The solid phase graphite was considered to predict carbon deposition over the catalyst. For the SER analysis, the following solid phases were included:

- CaO, $Ca(OH)_2$ and $CaCO_3$ (CaO sorbent);
- Li_2ZrO_3, $(Li_2O)(ZrO_2)$, Li_2CO_3, ZrO_2 (monoclinic, tetragonal and cubic phases were considered) (Li_2ZrO_3 sorbent);
- Li_4SiO_4, Li_2CO_3, Li_2SiO_3 (Li_4SiO_4 sorbent).

In this study, CH_4 conversion (XCH_4), CO_2 conversion (XCO_2), selectivity of H_2 and CO (SH_2 and SCO, respectively), H_2 and CO yields (YH_2 and YCO, respectively) were defined as follows:(2,4)

$$XCH4 = \frac{F_{CH4,in} - F_{CH4,out}}{F_{CH4,in}} \times 100\% \qquad (1)$$

$$XCO2 = \frac{F_{CO2,in} - F_{CO2,out}}{F_{CO2,in}} \times 100\% \qquad (2)$$

$$SH2 = \frac{F_{H2}}{2 \times (F_{CH4,in} - F_{CH4,out})} \times 100\% \qquad (3)$$

$$SCO = \frac{F_{CO}}{(F_{CH4,in} - F_{CH4,out}) + (F_{CO2,in} - F_{CO2,out})} \times 100\% \qquad (4)$$

$$YH2 = \frac{F_{H2,out}}{2F_{CH4,in} + F_{H2O,in}} \times 100\% \qquad (5)$$

$$YCO = \frac{F_{CO,out}}{F_{CH4,in} + F_{CO2,in}} \times 100\% \qquad (6)$$

Where *F* is the molar flow rate of gas flow.

3 RESULTS AND DISCUSSION

3.1 Dry Reforming

Fig.1 shows the effect of inlet CH_4/CO_2 ratio in clean model biogas (sulfur compounds are not included) on conversion (CH_4 and CO_2), selectivity (H_2 and CO), carbon deposition and energy demand for dry reforming. The theoretical results from the present work are validated against experimental values from Xu et al.(2)

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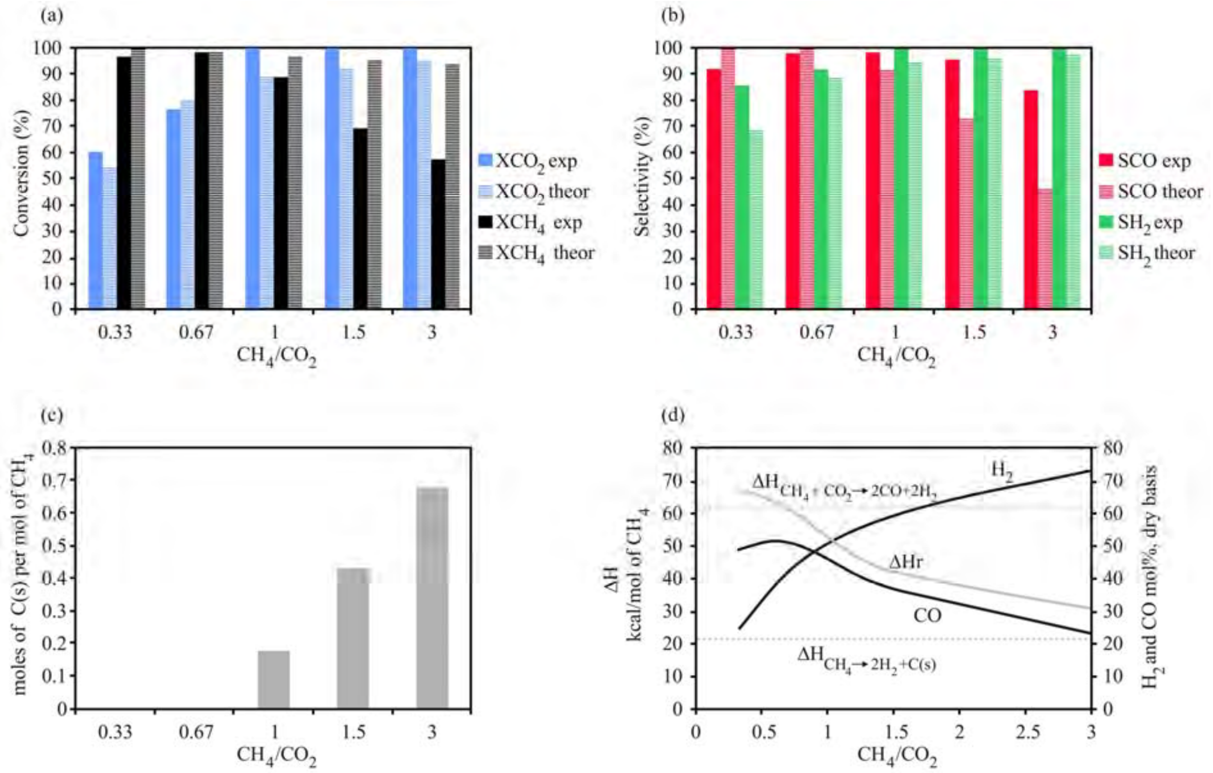

Figure 1. Effect of inlet CH_4/CO_2 ratio on (a) CH_4 and CO_2 conversion (b) CO and H_2 selectivity (c) amount of solid carbon and (d) enthalpy of dry reforming reaction and concentration of H_2 and CO. The experimental (exp) results in (a) and (b) were obtained from Xu et al.(2) and the theoretical (theor) ones were calculated in the present work. T=1073K.

As can be seen from Figures 1a and 1b, when CH_4/CO_2 ratio is in the range of 0.33-1, theoretical results for conversion and selectivity are very close to experimental ones. For higher values of CH_4/CO_2, however, there is a relevant difference between simulated and experimental values, especially for the values of CH_4 conversion and CO selectivity. According to Xu et al.,(2) a high CH_4 concentration in the reactants facilitates CH_4 cracking and carbon deposition, resulting in destabilization of the catalyst. In fact, thermodynamic analysis predicts an increasing amount of solid carbon as CH_4/CO_2 ratio also increases (Figure 1c). Figure 1d shows that al low CH_4/CO_2 ratios the enthalpy of the overall reaction (ΔHr) approaches the value of enthalpy of methane dry reforming reaction (R1), while that at high CH_4/CO_2 ratios ΔHr approaches the value of enthalpy of methane cracking reaction (R2), which is consistent with the fact that higher CH_4 concentrations in feedstock results in methane decomposition and, consequently, in greater amounts of solid carbon being deposited over the catalyst.

$$CH_4 + CO_2 \rightarrow 2CO + 2H_2 \qquad \Delta H^0_{298K} = 60 \text{ kcal mol } CH_4^{-1} \qquad (R1)$$

$$CH_4 \rightarrow 2H_2 + C(s) \qquad \Delta H^0_{298K} = 20 \text{ kcal mol } CH_4^{-1} \qquad (R2)$$

Thus, in dry reforming process, reformate becomes richer in H_2 as CH_4/CO_2 ratio in feedstock increases, that is, for biogas compositions richer in CH_4. However, under these conditions, there is an increasing trend for carbon deposition. If the catalyst is deactivated during experiments, the H_2/CO ratio experimentally obtained is inferior to the predicted one, as shown in Table 1. It should be noted that, similarly to the

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conversion of CH_4 and CO selectivity, experimental and theoretical results for H_2/CO ratio are in agreement for inlet CH_4/CO_2 ratios in the range of 0.33-1.

Table 1. Experimental values for H_2/CO ratio in syngas obtained from (2) and theoretical ones

Inlet CH_4/CO_2	H_2/CO molar ratio	
	theoretical	experimental
0.33	0.51	0.65
0.67	0.80	0.86
1	1.08	0.99
1.5	1.61	1.07
3	3.17	1.37

3.2 Combined CO_2 Reforming and Partial Oxidation

In the previous section, it was seen that dry reforming is a highly endothermic process besides of being very prone to carbon deposition for inlet CH_4/CO_2 ratios greater than 1. Since the typical biogas composition corresponds to inlet CH_4/CO_2 ratios >1,(5) such drawbacks should be overcome. In this way, oxy-CO_2 reforming could be an alternative route for *syngas* generation from biogas.

Figure 2 shows the effect of O_2 addition on conversion (CH_4 and CO_2), selectivity (H_2 and CO), carbon deposition and energy demand. O_2 is added to a clean model biogas whose inlet CH_4/CO_2 ratio is 2:1. From Figure 2a, one can see that the experimental results reported by Sun et al.(4) for CH_4 conversion and H_2/CO ratio approach the theoretical ones as molar ratio of O_2 increases (for O_2/CO_2 ratios≥0.6). This behavior could be related to the reduction of solid carbon deposition as molar ratio of O_2 increases, as depicted in Figure 2c, preventing catalyst poisoning. In fact, solid carbon is oxidized by O_2, producing CO and CO_2. Interestingly, theoretical and experimental values of CO_2 conversion are in agreement over the whole range of molar ratio of additional O_2. It should be noted that, for O_2/CO_2 ratios≥0.6, CO_2 conversion decreases. CH_4 could be oxidized to CO_2 and the product CO could also be oxidized to CO_2 when there is much more oxygen, and thus the apparent conversion of CO_2 is suppressed.(4) As O_2 is added to the feedstock, the enthalpy of the overall reaction (ΔHr) becomes more exothermic due to partial oxidation of methane (R3), as can be seen in Figure 2b.

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \qquad \Delta H^0_{298K} = -8.6\ \text{kcal mol}^{-1} \qquad \text{(R3)}$$

At a molar ratio of O_2/CO_2 equal to 0.91, a thermo-neutral (TN) condition can be reached, at which ΔHr=0. Under this condition, no external heat is necessary, the process runs auto-thermally, and H_2/CO ratio in *syngas* is 1.3.

Figure 3 shows the effect of temperature on H_2 selectivity and energy demand in the oxy-CO_2 reforming. With increasing temperature, both H_2 selectivity and enthalpy of the overall reaction (ΔHr) increase. From Figure 3a, one can see that experimental results obtained for gas hourly space velocities (GHSV) of $10000 cm^3 g^{-1} h^{-1}$ are closer to the theoretical ones. Figure 3b shows that at 1.137K auto-thermal operation can be theoretically achieved; this value is between the experimental values of 1.101K and 1.173K.

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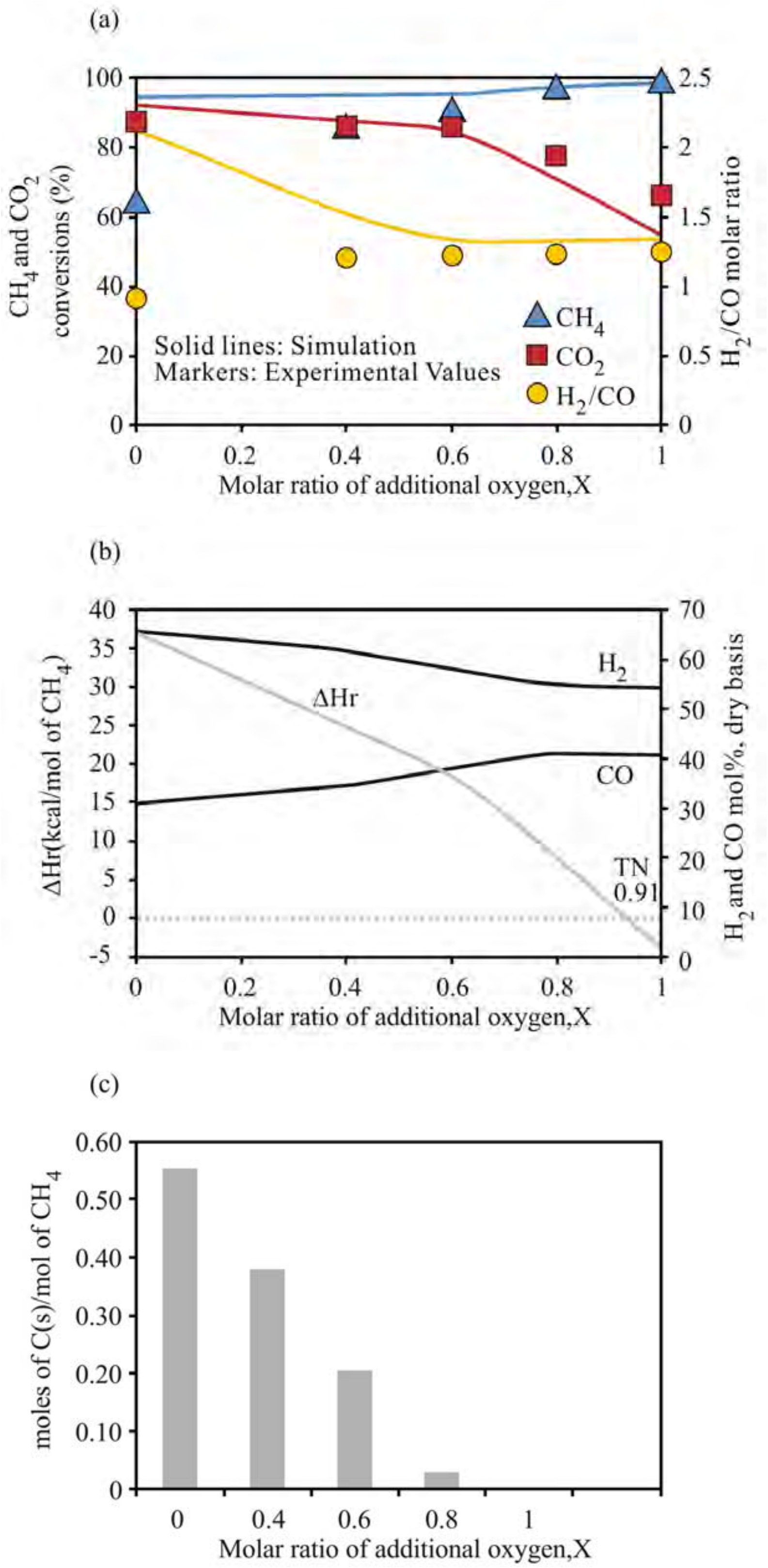

Figure 2. Effect of additional oxygen on (a) CH_4 and CO_2 conversions and H_2/CO ratio, (b) enthalpy of oxy-CO_2 reforming reaction and H_2 and CO concentrations, (c) amount of solid carbon. 1073K. CH_4:CO_2:O_2=2:1:X. Experimental results from (4).

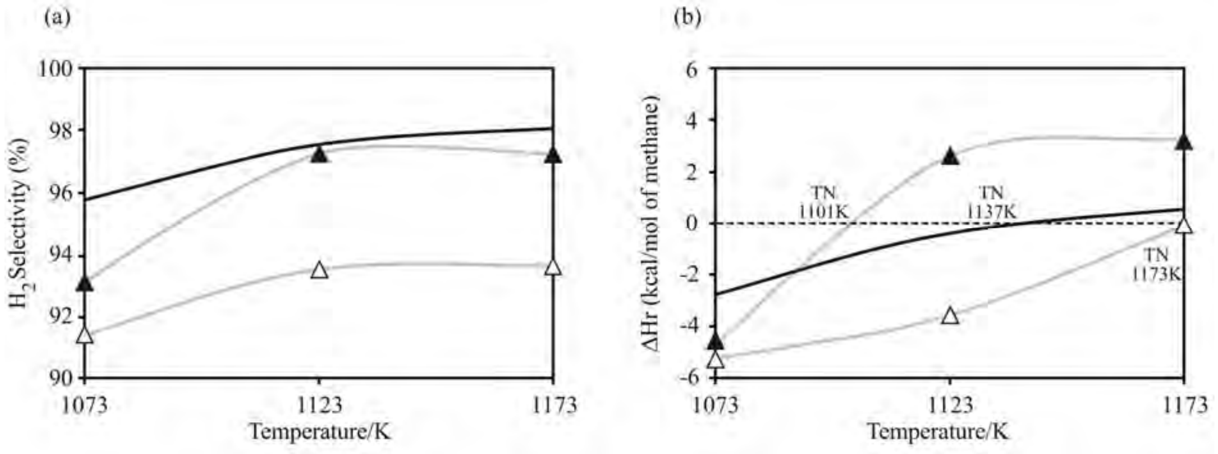

Figure 3. Effect of temperature on (a) H_2 selectivity and (b) enthalpy of oxy-CO_2 reforming reaction. Reaction conditions: $O_2/CH_4=0.45$ and $CO_2/CH_4=0.14$. ——theoretical result, experimental results from (6) for a GHSV, in $cm^3g^{-1}h^{-1}$, of ▲ 10000 and △46000.

3.3 Tri-Reforming

In the case of tri-reforming process, steam and oxygen are fed into the system. The most important reactions, including (R1) and (R3), are the following:

$$CH_4 + H_2O \rightarrow CO + 3H_2 \quad \Delta H^0_{298K} = 49.3 \text{ kcal mol}^{-1} \qquad \text{(R4)}$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad \Delta H^0_{298K} = -9.8 \text{ kcal mol}^{-1} \qquad \text{(R5)}$$

Figures 4a to 4c shows the effect of H_2O addition on conversion (CH_4 and CO_2), H_2/CO ratio, carbon deposition and energy demand. H_2O is added to a clean model biogas whose inlet CH_4/CO_2 ratio is 2:1. Figure 4a shows that CH_4 conversion increases and CO_2 decreases when steam is added to the feedstock. Steam favors reaction (R4) instead of reaction (R1). In fact, (R1) would be depressed by increasing inlet steam molar ratio. In addition, steam enhances the water-gas shift reaction (R5), resulting in an increasing H_2/CO molar ratio. The amount of solid carbon is greatly reduced (Figure 4c). The experimental results from Sun et al.(4) are in reasonable agreement with theoretical ones for inlet molar ratio of additional steam in the range of 0-1. Note that for the experimental conditions adopted by Sun et al.,(4) the enthalpy of the overall reaction was positive (endothermic), and external heat would be necessary. However, the tri-reforming process can be adjusted to result in auto-thermal or even exothermic, as shown in Table 2. For a same H_2/CO ratio, dry reforming would result in highly endothermic, with the undesirable formation of solid carbon. On the other hand, tri-reforming process is slightly exothermic, with no carbon deposition.

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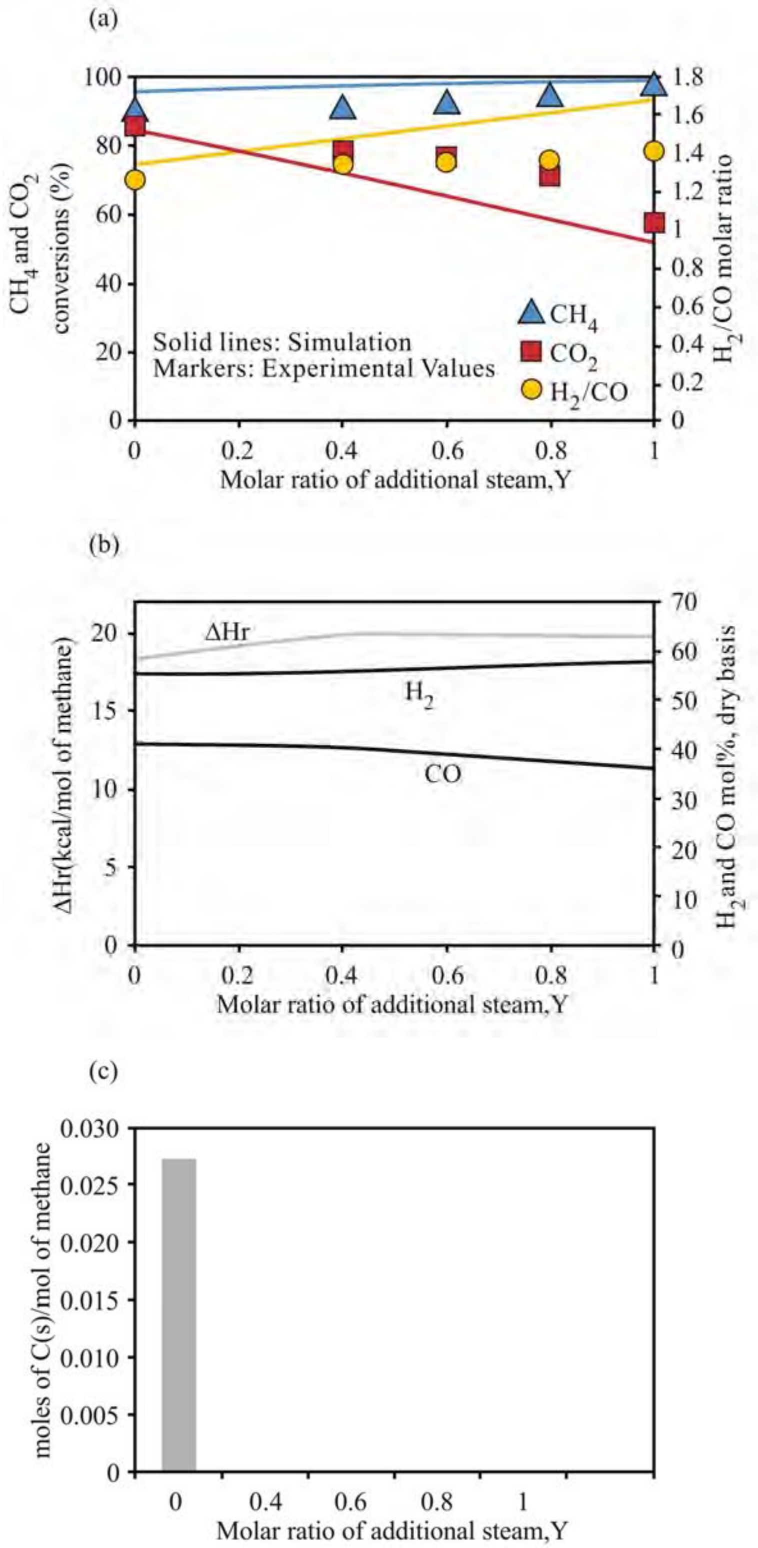

Figure 4. Effect of additional steam on (a) CH_4 and CO_2 conversions and H_2/CO ratio, (b) enthalpy of tri- reforming reaction and H_2 and CO concentrations, (c) amount of solid carbon. 1073K. CH_4:CO_2:O_2:H_2O=2:1:0.6:Y. Experimental results from Sun et al.(4)

Table 2. Equilibrium data for tri-reforming (CH_4:CO_2:O_2:H_2O=2:1:1:2.2) and dry reforming (CH_4:CO_2 =2:1), at T=1.073K

Route	XCH_4	XCO_2	SH_2	SCO	H_2/CO	C(s)	ΔHr
	(%)	(%)	(%)	(%)	Molar ratio	mol/mol of CH_4	kcal/mol CH_4
DR	94.5	92.6	96.2	60.6	2.1	0.55	36.7
TR	99.8	−8.1	100	100	2.1	-	−5.9

3.4 Sorption Enhanced Reforming (SER)

SER provides a promising alternative for single-step production of hydrogen with high purity, which is desirable for PEMFCs application. The concept of SER is based on *Le Chatelier's* principle in which the reaction equilibrium will be shifted to favor hydrogen production upon in situ CO_2 removal. So, if CO_2 generated from reforming reaction is separated from the gas phase using a solid acceptor such as CaO, H_2 production can be enhanced towards completion. In this case, the reformer contains both the catalyst needed for the reforming process and the sorbent for the removal of carbon dioxide.(7) The carbonation reactions for the different sorbents are shown as follows:

$$CaO(s)+CO_2 \rightarrow CaCO_3(s) \quad \Delta H^0_{298K} = -43 \text{ kcal mol}^{-1} \qquad \text{(R6)}$$

$$Li_2ZrO_3 + CO_2 \rightarrow Li_2CO_3 + ZrO_2 \quad \Delta H^0_{298K} = -38.9 \text{ kcal mol}^{-1} \qquad \text{(R7)}$$

$$Li_4SiO_4 + CO_2 \rightarrow Li_2CO_3 + Li_2SiO_3 \quad \Delta H^0_{298K} = -34 \text{ kcal mol}^{-1} \qquad \text{(R8)}$$

As can be seen from Table 3, when CaO sorbent is employed, both concentration and yield of H_2 are greatly enhanced, achieving values as high as 93 mol% and 77%, respectively. It should be noted that these results are much greater than those obtained for the process without a sorbent (51.9 mol% and 52.3%, respectively). With respect to CO, its concentration in SER is lower than that in tri-reforming process (no sorbent) – the concentration is decreased from 15 to only 0.7 mol% in the case of CaO sorbent. This fact allows simplifying the hydrogen plant, eliminating unnecessary purification reactors. The enhanced water-gas shift reaction (R5) due to CO_2 adsorption results in a decrease of CO production, accompanied by an increase in H_2 concentration. In this way, Ni/CaO multifunctional catalysts could be used for methane/biogas conversion.

Calcium-based sorbents are typically employed in SER technology. However, it is reported that CaO sorbent loses more than half of their absorption capacity after several absorption/regeneration cycles. A suitable absorbent should combine relatively low regeneration temperatures and good multi-cycle performance. In this context, synthetic Li-based sorbents have been developed recently,(8) which can withstand several absorption/regeneration cycles without important loss of CO_2 absorption capacity. According to thermodynamic results from Table 3, the order from higher to lower hydrogen concentration and yield is as follows: CaO>Li_2ZrO_3>Li_4SiO_4. In fact, CaO is able to form a greater amount of carbonate than the other sorbents. It should also be noted that in the presence of a sorbent the process becomes more exothermic, due to reactions (R6)-(R8).

Table 3. Equilibrium data for sorption enhanced reforming with different sorbents (CaO, Li_2ZrO_3 or Li_4SiO_4) and tri-reforming. Reaction conditions: 873K, CH_4:CO_2:O_2:H_2O:sorbent=2:1:1:2.2:2.7

Sorbent	H_2	CO	carbonate	YH_2	YCO	ΔHr
	Mol%, dry	Mol%, dry	Mol per mol of CH_4	(%)	(%)	kcal/mol CH_4
CaO	93.4	0.7	1.33	77.7	1.2	−75.1
Li_2ZrO_3	71.5	8.2	0.8	57.3	13.5	−51.9
Li_4SiO_4	54.3	14.4	0.13	52.7	28.9	−24.2
Tri-reforming	51.9	15.2	-	52.3	31.6	−20.2

4 CONCLUSION

The present work was aimed at investigating, from a thermodynamic point of view, different reforming technologies for *syngas* production from biogas and methane. The following conclusions can be drawn from the present study:

- DR technology: Higher H_2 selectivity can be obtained with increasing inlet CH_4/CO_2 molar ratios. However, under these conditions, there is an increasing trend for carbon deposition. Besides, the overall process is highly endothermic;
- Oxy-CO_2 reforming: H_2/CO ratio and process exothermicity can be controlled by manipulating the temperature and the concentration of O_2 in feedstock;
- Tri-reforming: By manipulating both O_2 and H_2O it is possible to achieve an auto-thermal/exothermic process with high H_2 selectivity, without carbon deposition;
- SER: High purity H_2 can be produced at lower temperatures by using CaO sorbent along with the catalyst in the reformer. The order from higher to lower hydrogen concentration and yield is as follows: CaO>Li_2ZrO_3>Li_4SiO_4.

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