



**PRODUCTION OF HYDROGEN BY SYNERGY OF SOFCS AND
MICROREFORMERS, PART 1: THEORETICAL STUDY OF MICROREFORMER
PARAMETERS**

**PRODUCCIÓN DE HIDRÓGENO POR SINERGI A DE SOFCS Y
MICROREFORMADORES, PARTE 1: ESTUDIO TEÓRICO DE LOS PARÁMETROS
DEL MICROREFORMADOR**

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Abstract

In this work it was determined the necessary anodic recirculation ratio that maximizes the hydrogen production for a process integrated by a solid oxide fuel cell (SOFC) and a micro-reformer fed with biogas. For this purpose, a thermodynamic study was made of the recirculation effects over: a) the ratio of reforming agents/methane, b) the outlet/inlet atomic hydrogen ratio (ψ), c) the reactor relative size, and d) the normalized electric energy output. The results show that in order to avoid coking, a steam-to-carbon ratio (S/C) higher than 2 is unnecessary, for a combined reforming with steam and CO₂. Moreover, it was found that ψ is maximized at a recirculation ratio of 0.22; and that an increase of recirculation caused a decrease in the electrical energy produced, and an increase in the relative reactor volume. Finally, it was found that a recirculation ratio of 0.22 was the best option for an operating temperature of 850°C. If the recirculation ratio is exceeded to achieve S/C= 2, the hydrogen fraction produced will decrease 50% and the reactor volume will increase 118% for the same amount of biogas fed.

Keywords: biogas, reforming, fuel cells, SOFC, anodic recirculation.

Resumen

En este trabajo se determina la recirculación anódica necesaria para maximizar la producción de hidrógeno en un proceso integrado por una celda de combustible de óxido sólido (SOFC) y un micro-reformador, alimentado con biogás. Para esto, se realizó un estudio termodinámico de los efectos de la cantidad recirculada sobre: a) las relaciones de agentes de reformación/metano, b) la proporción de hidrógeno atómico salida/entrada (ψ), c) el tamaño relativo del reactor y d) la producción de energía eléctrica normalizada. Los resultados revelaron que para evitar la coquización, es innecesario tener una proporción de agua a carbón (S/C) mayor a 2, para una reformación combinada de agua y CO₂. Además, se encontró que se maximiza ψ para una proporción de recirculación de 0.22; y que un incremento de la recirculación causa un decremento en la energía eléctrica producida y un aumento relativo en el volumen del reactor. En suma, una relación de recirculación de 0.22 fue la mejor opción para la temperatura de operación de 850°C. Si ésta es sobrepasada para tener S/C=2, la fracción de hidrógeno producido disminuirá en 50% y el volumen del reactor aumentará en un 118% con la misma alimentación de biogás.

Palabras clave: biogás, reformación, celdas de combustible, SOFC, recirculación anódica.

1 Introduction

The growth in the demand for electricity could surpass the central power generation capacity. Because fossil fuels are limited, a distributed generation approach could be an option, using local

renewable energy sources (Domínguez-Maldonado *et al.*, 2014). For instance, at countryside locations the synergy between microreformers and solid oxide fuel cells (SOFCs) could provide a sustainable source of

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electricity by using renewable biogas produced from manure. This integrated system could be a feasible alternative because of the following features: a) high efficiency, since experimental efficiencies for SOFCs have been reported between 75%-85% for a combined heat power (CHP) system; b) thermal integration of the exothermic and endothermic reactions c) safety, as the microchannel reformer avoids explosions and combustion flames; d) good performance, as the residence time could be in the microseconds range; e) hydrogen storage not required, as the production and consumption are in situ; f) possible use of methane from renewable biogas; and g) purification stage unnecessary for carbon monoxide, as SOFCs resist CO. Given all these features, integration looks promising.

Internal and external reforming (InR and ExR) are of great interest for thermal integration (Georgis *et al.*, 2011), because on one hand reforming reactions provide a heat sink, and on the other hand hydrogen is the most reactive of the several kinds of feeds that SOFCs can use (Lo Faro *et al.*, 2012). Nevertheless, complete InR could result in coke formation in the anode of the SOFC and in large temperature gradients, so an ExR could be useful. For instance, Peters *et al.* (2000) built a SOFC with an ExR, fed with natural gas (NG), steam, and recirculated gases from the anode. They found that without additional steam, the anodic recirculation was enough to reform the NG. However, excess CO₂ could compete for the active catalyst sites in the reformer. Those results indicate that some level of anodic recirculation could be useful for improving the efficiency. Other authors studied recirculation using a simulation approach. For example, Farhad *et al.* (2010a and 2010b) compared partial oxidation, steam reforming, and anodic recirculation for a SOFC-ExR, and found that gas recirculation has the highest electrical efficiency: 42.4% and 45.1% for residential and industrial applications, respectively. Kazempoor *et al.* (2009) proposed several configurations considering chemical equilibrium and using recirculation from anode and cathode, and concluded that pre-heaters and recirculation improve the electrical and CHP efficiencies.

Several authors have suggested the use of anodic recirculation with a steam to carbon ratio (S/C = water moles / carbon moles excluding CO₂) higher than two to avoid coking (Barelli *et al.*, 2011; Liso *et al.*, 2011b), which is the recommended ratio for methane steam reforming (SR). However, this ratio could be disproportionate for the combined stream made from

the methane and anodic recirculation gases. For example, Yi *et al.* (2005) found that biogas needs a lower recirculation ratio than NG for a tubular SOFC, and therefore a lower S/C because in order to obtain a S/C > 2, CO₂ is recirculated with the steam, which decreases the methane concentration and the CO₂ may also block the active catalyst sites (Peters *et al.*, 2000). The net effect would decrease the production rate of hydrogen, requiring a larger reformer apparatus, which becomes important for portable applications where size is an issue.

Yi *et al.* (2005) and Liu *et al.* (2013) showed that the optimum recirculation ratio changes with the type of feed. This is relevant for a SOFC-ExR fed with biogas because its composition (CH₄/CO₂ ratio) could vary from day to day in a conventional bio-reactor due to changes in reactor temperature, pH, or the type of feed used (Sánchez-Hernández *et al.*, 2013; Teniza-García *et al.*, 2015). By the analysis of the effects of the anodic recirculation over the reformer agents/methane ratios, the variations in biogas composition can be compensated. Therefore, the analysis of the recirculation over the composition and the system performance becomes useful.

This work focuses on the effects of the recirculation ratio over: a) the ratios of reformer agents to methane (from biogas), b) the microreformer relative dimensions, and c) efficiencies. In order to do so, a deeper analysis of the thermodynamics of SR, DR (dry reforming) and combined SR-DR is conducted. An additional process analysis considers the kinetic model of the reforming reactions, by taking into account the amount of catalyst and the reactor volume required. Finally, the performance was evaluated using these analyses.

2 Methodology

2.1 Variables definition

To compare the performance of the system, the following variables are defined:

- Water/methane ratio (WMR)

$$WMR = \frac{F_{in.H_2O}}{F_{in.CH_4}} \quad (1)$$

- Carbon dioxide/methane ratio (DMR)

$$DMR = \frac{F_{in.CO_2}}{F_{in.CH_4}} \quad (2)$$

- Conversion (X) of species “ i ”

$$X_i = \frac{F_{in,i} - F_{out,i}}{F_{in,i}} \quad (3)$$

- Hydrogen production to methane fed (ϕ)

$$\phi = \frac{F_{out,H_2} - F_{in,H_2}}{F_{in,CH_4}} \quad (4)$$

- Outlet/inlet atomic hydrogen ratio is the fraction of molecular hydrogen at the outlet, divided by the hydrogen content in methane, water, and the hydrogen fed (ψ)

$$\psi = \frac{F_{out,H_2}}{2F_{in,CH_4} + F_{in,H_2O} + F_{in,H_2}} \quad (5)$$

Since ϕ does not consider other sources of hydrogen besides methane, ψ could be a better parameter for normalized hydrogen yield.

- Finally, the fraction of coke formation (C_{frac})

$$C_{frac} = \frac{F_{out,Cs}}{F_{in,CH_4}} \quad (6)$$

which represents the fraction of coke formed divided by the methane fed.

2.2 Thermodynamic analysis

In order to understand the performance of the system, the thermodynamic analysis was divided into three parts: SR, DR, and a combination of both. By minimizing the free Gibbs energy, the molar composition of each component in each phase at the equilibrium is determined, as a function of temperature and pressure. This minimization could be done with the Lagrange multipliers:

$$\sum F_{out,i}(\Delta G_{f_i}^0 + RT \ln(\frac{\hat{f}_i}{f_i^0}) + \sum \lambda_i a_{ik}) + F_{out,Cs} \Delta G_{fC(s)} = 0 \quad (7)$$

The following species were considered: H_2 , H_2O , $C(s)$, CO , CO_2 , CH_4 . The software Aspen Plus 11.0 was used to solve Eq. (7), with a Gibbs Reactor model and the properties calculation method set to SRK.

2.2.1 Steam reforming (SR)

For this analysis, it was assumed that only water and methane enter the system. The parameters analyzed were: methane conversion (X_{CH_4}), water conversion (X_{H_2O}), ϕ , ψ , and C_{frac} . The function of water to methane ratio (WMR) from 0.5 to 2.5 was evaluated for several temperatures (700-950°C).

2.2.2 Dry reforming (DR)

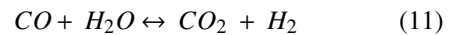
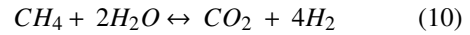
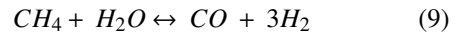
For this analysis, it was assumed that only carbon dioxide and methane are present at the inlet. The parameters analyzed were: X_{CH_4} , X_{CO_2} , ψ (since $\phi = 2$, ψ , is not plotted), and C_{frac} . The function of carbon dioxide to methane ratio (DMR) from 0.5 to 1.5 was evaluated for several temperatures (700-1000°C).

2.2.3 SR-DR combined

Two cases were analyzed; the first case has a WMR of 0.44 and a DMR of 1.03, and the second case has a WMR of 0.5 and a DMR of 1.08. The temperature necessary to avoid coking, the optimum operational temperature, ψ , and ϕ are estimated.

2.3 Anodic recirculation analysis

Since many reactions take place simultaneously, it would be impractical to consider all of them. Thus, in order to simplify the analysis, only the reforming reactions are considered:



This is valid when no oxygen enters the reactor and no coking takes place outside of the equilibrium. The kinetics of reaction 8 were taken from Olsbye *et al.* (1997), and those for reactions 9-11 were taken from Hou and Hughes (2001). These kinetics rate models have been used extensively for Ni/Al₂O₃, which is a catalyst commonly used in methane reforming.

Even with these simplifications, a complex network of reactions is formed. Fig. 1 shows the interaction of the chemical compounds in the reactions. The dotted lines indicate consumption and the solid ones indicate production. For example, methane and water are consumed by the SR reaction to produce hydrogen and carbon monoxide. Carbon dioxide interacts in both the production and consumption of hydrogen. It reforms methane by the DR reaction, but it also consumes hydrogen by the reverse water gas shift (RWGS) reaction. So its concentration must be fixed appropriately.

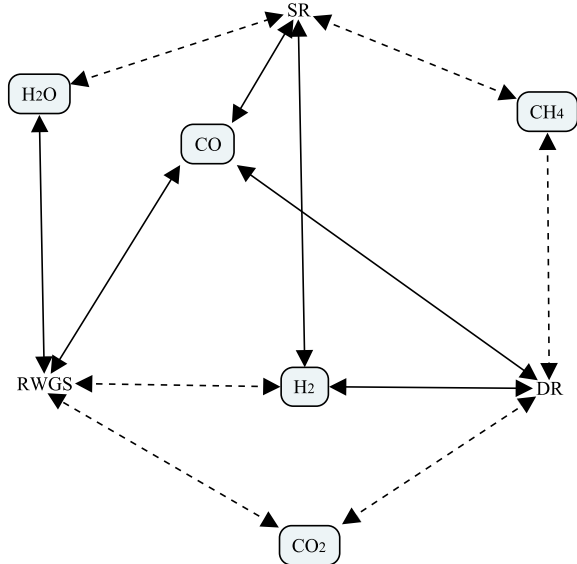


Fig. 1. Scheme of H₂, H₂O, CO, CO₂ and CH₄ interactions with the reforming reactions (SR, DR and RWGS).

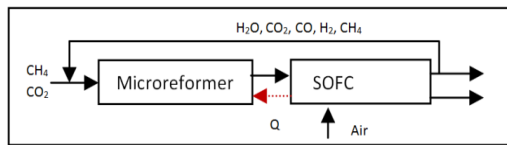


Fig. 2. Scheme of a simplified system, composed of a micro-reactor and a SOFC with anodic recirculation and a coupling heat flow.

Comsol 3.5a was the software used to estimate the conversion in the reactor. The process diagram is shown in Fig. 2, and operates at a temperature of 850°C. It was considered that the biogas has a composition of 60% methane and 40% carbon dioxide, and that the pressure loss is negligible. The fuel utilization of the SOFC is assumed to be 80% with an efficiency of 60%.

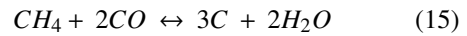
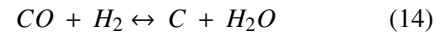
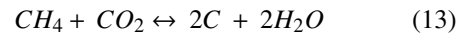
With the purpose of analyzing the effect of the recirculation ratio over the initial hydrogen production rate, an estimation was made using the same reaction rate models mentioned above and considering 100% combustion in the SOFC. With these considerations, the initial y_{H_2} and y_{CO} are zero, so the initial production rate from reactions (8-9) will have the form of equation (12).

$$r_{0,H_2} = \frac{k_1[CH_4]_0^a[CO_2]_0^b}{f_x(CH_4, CO_2, H_2O)} + \frac{k_2[CH_4]_0^c[H_2O]_0^d}{f_x(CH_4, CO_2, H_2O)} \quad (12)$$

3 Results

3.1 Steam reforming (SR) thermodynamic analysis

The methane conversion estimated for several WMR values (using a Gibbs Reactor model) is plotted in Fig. 3-a; the conversion of methane tends to lower values until reaching a minimum when WMR values less than 1 were evaluated. This is due mainly because water prevents the carbon formation from methane and carbon monoxide by displacing the thermodynamic equilibrium to the reactants according the following reactions:



For WMR values greater than 1, the conversion of methane increases because the higher concentrations of water promote methane reforming (reaction 9-10) and CO reaction by water gas shift reaction (WGS). This feature is observed at all temperatures evaluated here but the lowest conversion was observed from slightly lower WMR values for higher temperatures (>750°C). This could be explained with the effect of the temperature on exothermic and endothermic reactions, i.e. exothermic reactions displace from products to reactants when the temperature increases. The estimated conversion of methane was a result of the equilibria between exothermic and endothermic reactions. On the other hand, the behavior of $X_{H_2O}^{eq}$ (Fig.3-b) is inverse to the behavior of $X_{CH_4}^{eq}$; lower values of WMR tend toward higher values of $X_{H_2O}^{eq}$ until the maximum is reached, and later at higher WMR values, the $X_{H_2O}^{eq}$ tends to lower values due to the water excess.

The variables ϕ (Fig. 3-c) and ψ (Fig. 3-d) were used to measure the performance of the system. The variable ϕ is enhanced by higher values of WMR, because the excess water reacts with methane or carbon monoxide so more hydrogen is produced (reactions 9 to 11). However, ϕ does not consider that hydrogen is also available from water, which will have an energy cost and will decrease both the methane concentration and the hydrogen fraction, leading to a larger reformer to maintain production. Therefore, a high ϕ does not necessarily imply high efficiency, thus the system performance cannot be evaluated just with this parameter.

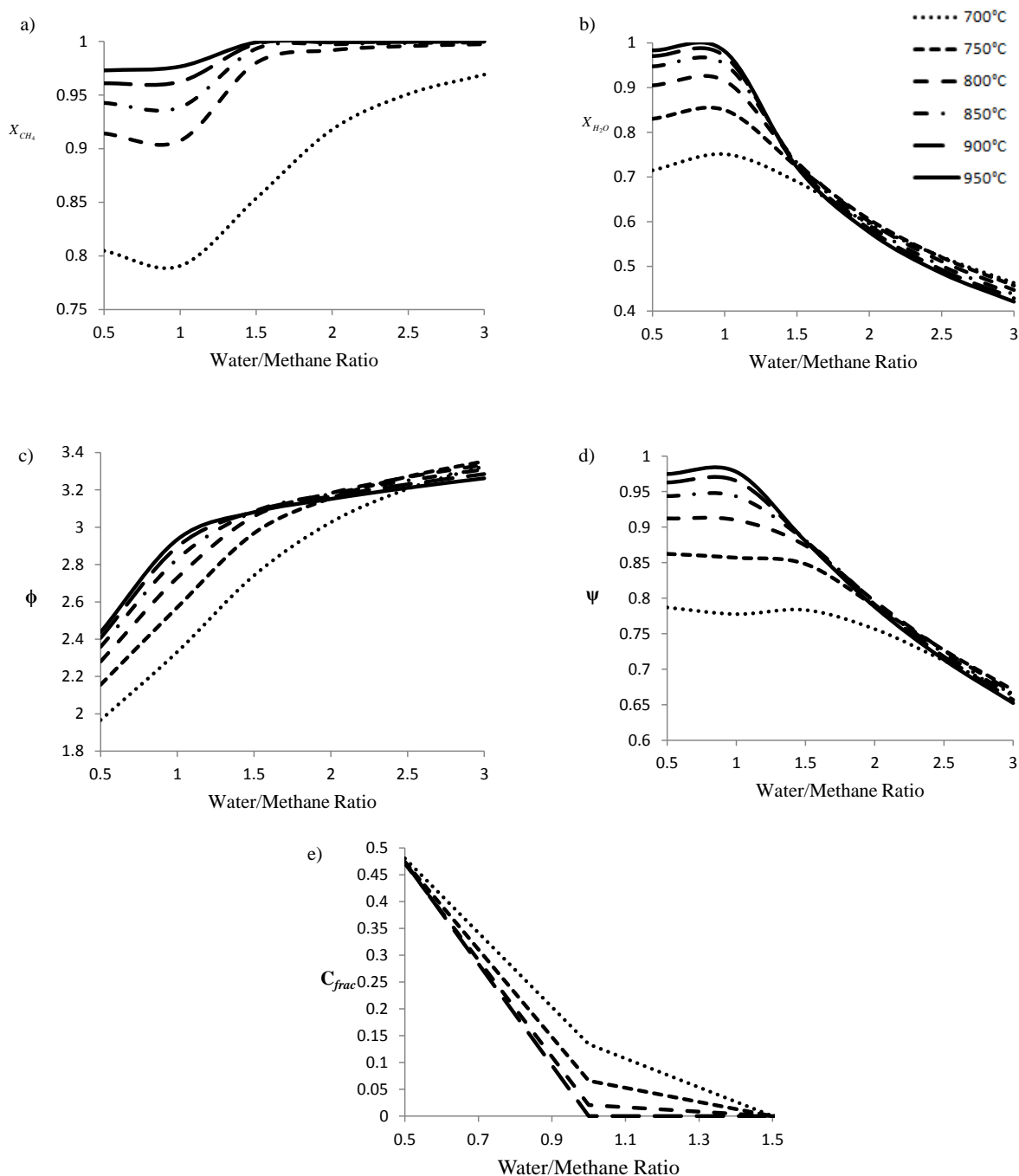


Fig. 3. Diagrams of thermodynamic study for steam reforming vs. water/methane ratio for several temperatures.

The variable ψ was used to complement the analysis of ϕ , which decreases when higher WMR values were tested, because more hydrogen is produced but also higher concentrations of hydrogen precursors are present. This causes a net decrement of γ_{H_2}

(hydrogen molar fraction) that would increase the Nernst overpotential in the SOFC, so the efficiency will be lower (Kazempoor *et al.*, 2009; Barelli *et al.*, 2011; Georgis *et al.*, 2011; Liso *et al.*, 2011a; Liso *et al.*, 2011b). Finally, regarding coke formation

(Fig. 3-e), increasing either the WMR values or the temperature will decrease the coke formation, and when the WMR is larger than 1.5, almost no coke is formed for the temperature range studied. The typical value reported for coking inhibition is $WMR > 2$ for pure methane SR (Kazempoor *et al.*, 2009; Barelli *et al.*, 2011; Georgis *et al.*, 2011; Liso *et al.*, 2011b). In conclusion, considering ϕ , ψ , and coke formation, it seems that the operating conditions of WMR values between 1.5 and 2 should be used. Moreover, ψ and ϕ are significantly affected by the temperature, as they present maximums at $\sim 875^\circ\text{C}$ for $WMR=1.5$ and at $\sim 800^\circ\text{C}$ for $WMR=2$. In order to avoid coke formation and to maintain high hydrogen yields, a $WMR=2$ at 800°C seem adequate as operating conditions.

3.2 Dry reforming (DR) thermodynamic analysis

Fig. 4-a shows that $X_{CH_4^{eq}}$ increases with higher values DMR and temperature. As the DR reaction is endothermic and CO_2 is used to reform the methane, these conditions favor the equilibrium displacement to the consumption of methane. In Fig. 4-b, it is shown that $X_{CO_2^{eq}}$ increases similarly with temperature but decreases with higher values of DMR, since DR and RWGS are endothermic and there is more CO_2 with the increase of DMR. Since an increase of DMR and temperature promotes both production and consumption of hydrogen by DR and RWGS reactions, ψ (Fig. 4-c) has a maximum, which is reached at a DMR near 1 and a temperature of 1000°C .

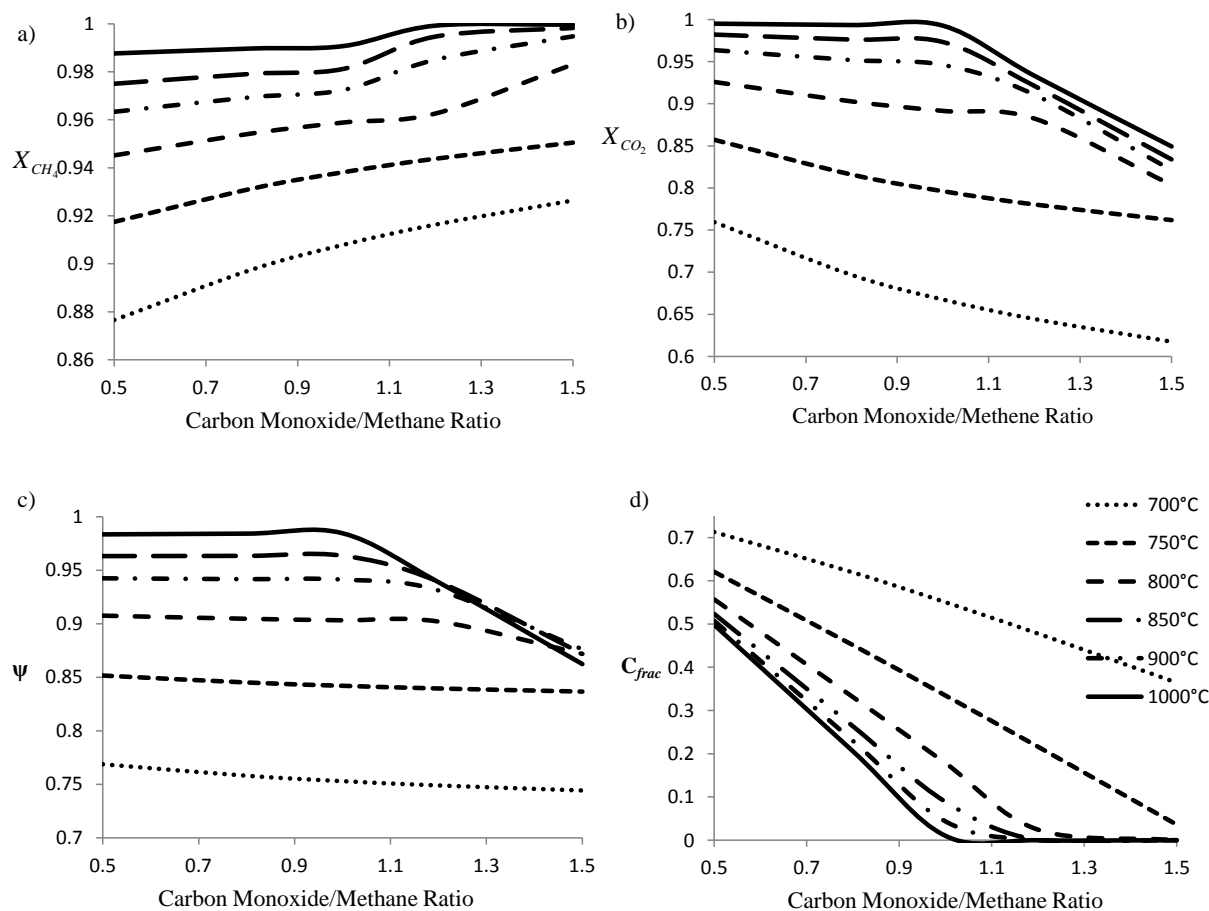


Fig. 4. Diagrams of thermodynamic study for dry reforming vs. water/methane ratio for several temperatures.

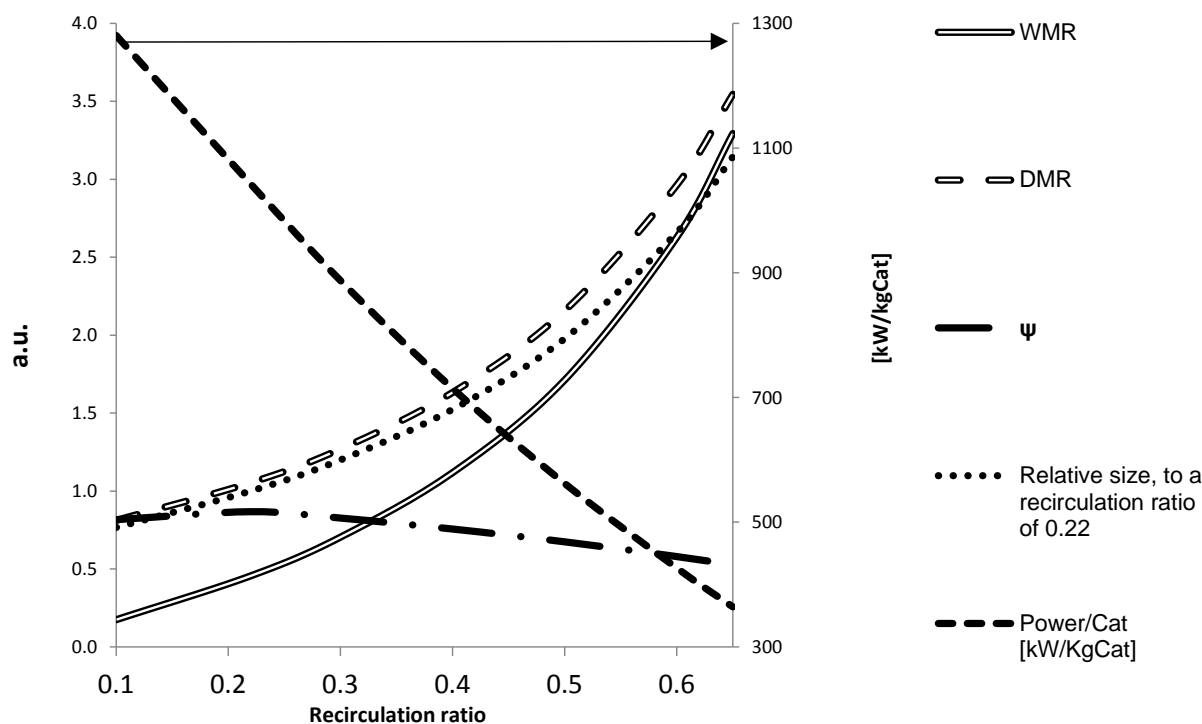


Fig. 5. Performance of a system composed of a micro-reactor and a SOFC vs. anodic recirculation ratio.

The coke formation (Fig. 4-d) is reduced with the increase of temperature and the ratio of reforming agents, such as in the SR (where steam was the reforming agent). In this sense, the DR needs to operate at a high temperature ($T > 1000^{\circ}\text{C}$) or a $\text{DMR} > 1$ to avoid coke formation. This agrees with several theoretical calculations; for example, Bradford and Vannice (1999) concluded that to avoid coking, a high operation temperature is needed ($T > 1000\text{ K}$) with a DMR far above unity. Considering ψ and coke formation, it seems that a DMR near 1 is the better option, in agreement with Blesa *et al.* (2002) who experimentally found that the production has a maximum at $\text{DMR}=1$.

3.3 Combined reforming thermodynamic analysis

In section 3.2, it was shown that for a $\text{DMR} \approx 1$, ψ reached a maximum and that for a $\text{DMR} < 1$ the system would produce coke (for $T < 1000^{\circ}\text{C}$). For these reasons, in this section a DMR near 1 was used for the two cases, the results are shown in Table 1. The two cases were very similar; the main differences are the optimal temperatures for the highest ψ values and the necessary ones to avoid coking. The optimal temperature for the first case was 850°C , whereas

for the second case was 825°C . Because case 2 has more CO_2 , and this reacts in the RWGS reaction, a decrease of 25°C was observed compared to case 1. Using the minimal temperatures to avoid coking (740 and 750°C) and the optimal temperatures for ψ , an operational range can be established. Because the differences of the temperatures are small, either condition could work.

Table 1. Combined Steam and Dry reforming. Case 1 $\text{WMR} = 0.44$ and $\text{DMR} = 1.03$. Case 2 $\text{WMR} = 0.5$ and $\text{DMR} = 1.08$.

	Case 1	Case 2
Minimum Temperature [$^{\circ}\text{C}$]	750	740
Optimum Temperature [$^{\circ}\text{C}$]	850	825
Max ψ @	0.88	0.86
Optimum Temperature Max ϕ @	2.15	2.15

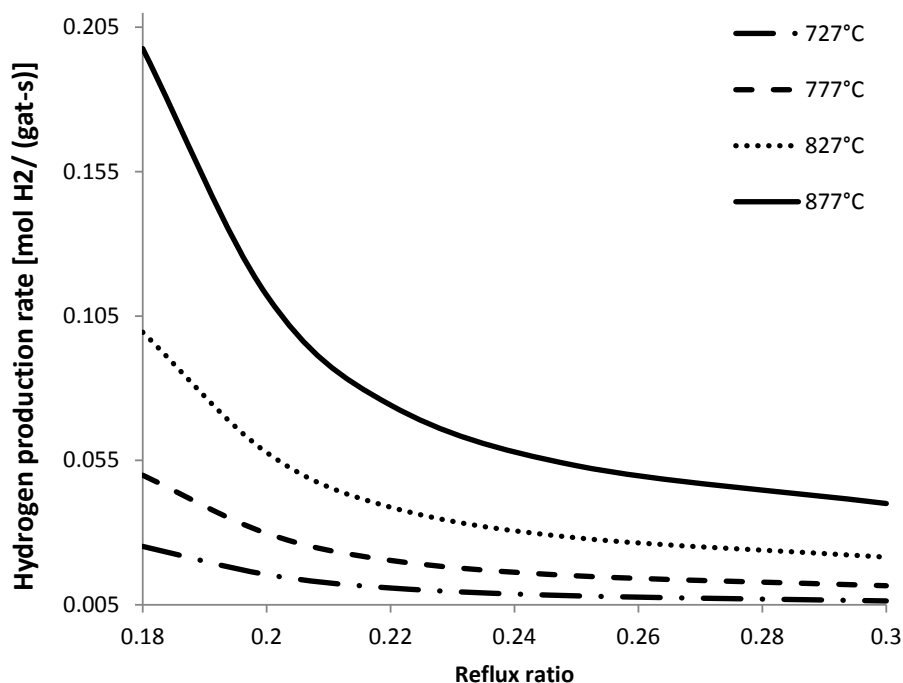


Fig. 6. Initial rate of hydrogen production vs anodic recirculation ratio for several temperatures.

3.4 Anodic recirculation analysis

The comsol results were analyzed and the Fig. 5 shows the behavior of WMR, DMR, ψ , the relative reactor size (in comparison to the reactor with a recirculation ratio of 0.22) and the power generated per kilogram of catalyst with respect to the recirculation ratio. As expected, the WMR and DMR increases with the recirculation ratio, then the molar fraction of water and carbon dioxide are increased, while the methane concentration is diluted. Instead, ψ shows a maximum of 0.87 at a recirculation ratio of 0.22, close to the thermodynamic maximum of 0.88, meaning that 99% of the thermodynamic equilibrium is achieved. This maximum indicates that there would be insufficient reformer agents when the recirculation ratio is lower than 0.22 or an excess of them if it is higher, lowering ψ in both cases. In addition, y_{H_2} has a value of 48.7 which represents 99.4% of its maximum obtained at a recirculation ratio of 0.1 and a DMR close to 1, in agreement with the thermodynamic analysis.

Fig. 5 also shows that the relative volume (number of the micro-reformers necessary to process the same amount of biogas, with the same residence time, and hydrodynamic conditions with respect to a recirculation ratio of 0.22) increases with the recirculation ratio. This causes a decrease in the

power generation (per kilogram of catalyst). For instance, at a recirculation ratio of 0.53 (needed to have a WMR=2) the relative volume is 2.18 and the power generation (per kilogram of catalyst) drops by 50% in comparison with a recirculation ratio of 0.22 (WMR=0.53). However, the power generated per mole of CH_4 is 7% higher at a recirculation ratio of 0.53, but this study does not take into account the dilution effect of y_{H_2} and y_{CO} over the Nernst overpotentials, although from some models (Kazempoor *et al.*, 2009; Barelli *et al.*, 2011; Georgis *et al.*, 2011; Liso *et al.*, 2011a; Liso *et al.*, 2011b) a decrease in the power output can be expected with the decrease in y_{H_2} and y_{CO} . Therefore, a recirculation ratio of 0.22 seems to be the best option, because a smaller or a larger ratio will be inefficient. Also, with this recirculation ratio coke formation is avoided.

For quick analysis of the anodic recirculation tendency for other operational temperatures, the initial rate was studied using Eq. (12). Fig. 6 shows a decrease of the initial rate with the recirculation ratio over the whole range of temperatures. This is because the recirculation will enhance the WMR and DMR, but the y_{CH_4} will decrease and the net effect is a decrease in the hydrogen production. Therefore, it would be unwise to recirculate indiscriminately for any temperature of the range studied.

Conclusions

Thermodynamic analysis and process simulation were made, for a system integrating a solid oxide fuel cell (SOFC) and a microreformer. From this study, we can conclude the following:

- An increase of the recirculation ratio caused in an increase over DMR and WMR, but decreased the methane concentration, which decreases the hydrogen production rate. Tuning the recirculation ratio is needed to compensate for small variations in the biogas composition feed, to avoid both coke formation and over dilution of methane.
- Coking is inhibited simultaneously by water and carbon dioxide; therefore, a WMR > 2 is unnecessary. Although recirculation is necessary to avoid coking, an excess will cause an increase in the residence time, reactor volume, catalyst needed, and more important, a dilution of fuel concentration (y_{H_2} and y_{CO}) at the inlet of SOFC, leading to a larger Nernst overpotential and lowering SOFC efficiency.
- From the process analysis, a system operating at 850°C with a recirculation ratio of 0.22 seems the best option. If the inlet temperature of the microreformer is below 750°C, coking could happen.
- Because the outlet/inlet atomic hydrogen ratio (ψ) considers more sources of hydrogen than the hydrogen production to methane fed (ϕ), both should be considered jointly, as well as the coke formation, to determine the operating conditions.

Nomenclature

a_{ik}	stoichiometric number of the jth component in the kth constituent, dimensionless
C_{frac}	fraction of coke deposition, dimensionless
DMR	carbon dioxide methane ratio, dimensionless
$F_{in,i}$	inlet mol flow of specie i, mols^{-1}
$F_{out,i}$	outlet mol flow of specie i, mols^{-1}
\hat{f}_i	fugacity, bar
f_i^0	fugacity at standard conditions, bar
f_x	catalytic free, dimensionless

k	kinetic constant, $\text{molms}^{-1}\text{gcat}^{-1}$
r_{0,H_2}	initial rate of hydrogen production, $\text{mols}^{-1}\text{gcat}^{-1}$
R	ideal gas constant, $\text{Jmol}^{-1}\text{K}^{-1}$
S/C	stream to carbon ratio, dimensionless
T	temperature, K
X_i	conversion, dimensionless
X_i^{eq}	conversion at equilibrium, dimensionless
y_{CO}	carbon monoxide molar fraction
y_{H_2}	hydrogen molar fraction
WMR	water methane ratio, dimensionless
<i>Greek symbols</i>	
ΔG_{fi}^o	Gibbs free energy of formation, Jmol^{-1}
$\Delta G_{fc(s)}$	Gibbs free energy of formation of coal, Jmol^{-1}
Θ	kinetic function, $\text{mol}^n\text{s}^{-1}\text{gcat}^{-1}$
λ	Lagrange multiplier
ϕ	yield of hydrogen per mol of methane fed
ψ	fraction of hydrogen in form of molecular hydrogen at the output

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