Effect of Recirculation on Carbon Deposition for Direct Internal Reforming Solid Oxide Fuel Cells

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Abstract

In this paper, a direct internal reforming solid oxide fuel cell (SOFC) operating with a gas mixture is analyzed in terms of carbon deposition. Using Gibbs’ equilibrium thermodynamics, exit and inlet gas composition of the fuel cell is calculated by taking into account the recirculation of the exit gas stream of the anode side. The results are interpreted through C-H-O triangular diagrams. In these diagrams, carbon deposition boundary; hence safe operating conditions for preventing the deposition of carbon are shown. Effects of different fuel, temperature and fuel utilization ratio on the carbon deposition are also investigated. The results show that the minimum recirculation ratio needed, at a global fuel utilization of 0.85, is 0.68, 0.51 and 0.4 for LT-SOFC, IT-SOFC and HT-SOFC, respectively, for a SOFC operating with methane; and 0.62, 0.3, and 0.07 for LT-SOFC, IT-SOFC and HT-SOFC, respectively, for a SOFC operating with a typical cleaned gas produced from pyrolysis.

Keywords: SOFC, carbon deposition, recirculation, thermodynamics, C-H-O triangular diagrams.

1 Introduction

Fuel cells are considered electrochemical devices that convert the energy in the fuel into electricity with high efficiency and low environmental impact. There are different types of fuel cells which differ from each other according to the type of electrolyte and fuel used. Hence, the electrochemical reactions that occur at the electrode/electrolyte interface and ion conducting at the electrolyte differ for each fuel cell type. Among them, SOFC has the highest operating temperature range, i.e. 500-1000ºC, which provides several advantages for its usage; such as: reforming inside the fuel cell, fuel flexibility and efficient thermal integration with bottoming cycles. However, there are some challenges for construction and durability, and carbon may be deposited due to using fuels containing carbon; such as carbon monoxide, methane, methanol, ethanol, etc.

There are basic three types of reforming in SOFCs; which are external reforming (ER), direct internal reforming (DIR) and indirect internal reforming (IIR). The current trend is to develop intermediate temperature DIR-SOFCs. In this type of SOFCs, the overall electrochemical reaction, Eq. (1), occur simultaneously with the steam reforming reaction, Eq. (2), and water-gas shift reaction, Eq. (3). It should be noted that although carbon monoxide can be electrochemically oxidized in SOFCs, the water-gas shift reaction may be assumed to represent the conversion of this gas into carbon dioxide and hydrogen.

\[
\begin{align*}
\text{H}_2 + \frac{1}{2} \text{O}_2 & \rightarrow \text{H}_2\text{O} \\
\text{CH}_4 + \text{H}_2\text{O} & \rightleftharpoons \text{CO} + 3\text{H}_2 \\
\text{CO} + \text{H}_2\text{O} & \rightleftharpoons \text{CO}_2 + \text{H}_2 
\end{align*}
\]  

(1)

(2)

(3)

During the past decade SOFCs, which are known as high temperature fuel cells, particularly for power generation, have received significant attention from researchers and industry due to their advantages such as internal reforming and fuel flexibility. However, it has the disadvantage of having the possibility of carbon deposition which will cause degradation in the performance of the fuel cell and eventually its breakdown. So, the carbon deposition problem should be prevented because it results in the growth of carbon filaments that are
attached to anode crystallites, which generate massive forces within the electrode structure and, thereby, result in its rapid breakdown [1, 2]. Depending on the fuel, there might be different mechanisms causing carbon deposition. For example, if we take methane and carbon monoxide as the fuel, the following three reactions are the most possible ones for the formation of carbon:

\[
\begin{align*}
\text{CH}_4 & \rightleftharpoons C(s) + 2\text{H}_2 \\
2\text{CO} & \rightleftharpoons \text{CO}_2 + C(s) \\
\text{CO} + \text{H}_2 & \rightleftharpoons C(s) + \text{H}_2\text{O}
\end{align*}
\]

In the literature some theoretical and experimental studies have been carried out to investigate the carbon deposition problem. In theoretical studies, equilibrium thermodynamics is generally taken into account and possibility of carbon deposition for different input parameters is studied. There are also very few studies that take into account the chemical kinetics. For example, Assabumrungrat et. al. [3] analyzed the carbon formation in a DIR-SOFC fueled by methanol. In their study, equilibrium calculations are performed to find the range of inlet steam methanol ratio where carbon formation is thermodynamically unfavourable in the temperature range of 500 to 1200 K. Sangtongkitcharoen et al. [4] compared the different reforming types, namely external reforming, direct internal reforming and indirect internal reforming, on carbon formation. They also considered hydrogen-conducting electrolytes as well as oxygen-conducting electrolytes. Their study shows that DIR-SOFC with the oxygen-conducting electrolyte is the most promising choice for operation. Singh et al. [5] studied the risk of carbon deposition due to the tars present in the feed stream and the effect various parameters like current density, steam, and temperature on carbon deposition. A total of 32 species are considered for the thermodynamic analysis, which is done by the Gibbs energy minimization technique. The results show that the carbon deposition decreases with an increase in current density and becomes zero after a critical current density. Steam in the feed stream also decreases the amount of the deposited carbon. A similar study to Singh et al.’s is done by Koh et al. [6]. The rate of carbon deposition and the composition of an anode gas mixture in equilibrium are predicted as a function of current density by minimizing the total Gibbs free energy of a system with 21 chemical species, including a condensed phase for carbon deposition. Sasaki and Teraoka [7] calculated the amounts of equilibrium products calculated for various fuel cell fuels including alkanes, alkenes, alicyclic hydrocarbons, and dimethyl ether, as well as for other hydrocarbon-containing fuels such as biogas and coke oven gas, in the temperature range between 100 and 1000°C. They concluded that, with increasing carbon number of hydrocarbon-related species and with decreasing temperature, a higher S/C is required to prevent carbon deposition. Addition of CO_2 or O_2 is also useful to prevent carbon deposition.

In experimental works, the effect of different anode materials and input parameters are observed. For example, Takeguchi et al. [8] showed that CaO-modified Ni-YSZ cermet is effective in suppressing carbon deposition without deteriorating the reforming activity. Finnerty et al. [9] studied two different nickel/zirconia anode formulations and a molybdenum-doped nickel/zirconia anode. The effects of adding steam to the methane, the operating temperature, and doping the nickel/zirconia anode with a small quantity of molybdenum, on the methane reforming activity of the anode, the surface chemistry and the nature and level of carbon deposition, were investigated. The most conspicuous conclusion of this study is that doping the anode with small quantities of molybdenum (<1%) is found to lead to a substantial reduction in the level of carbon deposited on the anode. Koh et al. [10] tested a single cell of an anode supported planar SOFC operating with hydrogen and methane to investigate the carbon deposition effects. They suggested two different carbon formation mechanisms; which are reversible carbon formation at which deposited carbon may be oxidized electrochemically; and irreversible carbon formation where carbon particulate are formed. They concluded that irreversible carbon particulate is the main reason for cell performance degradation. In the study by Macek et al. [11], Ni–YSZ cermet materials prepared by different processes (sol–gel and combustion synthesis) with variations in composition and presence of dopants were tested by exposing these materials to methane at elevated temperatures. The effects of anode composition, its microstructure, and some dopants on carbon deposition were studied; and the amount of the carbon deposited was determined. Their results showed that the sample CS–50–Ag–Cu doped with silver and copper and prepared by the combustion synthesis, gives less carbon deposits than other tested samples. In the paper by Horita et al. [12], the effect of applied voltages on surface catalytic activities was compared at the Ni-mesh/YSZ interfaces for CH_4 decomposition and elimination of carbon deposition by SIMS imaging analysis. They observed a significant carbon deposition at the Ni-mesh under zero-voltage condition. However, they found that the applied voltages can eliminate the deposited carbon on the Ni-mesh effectively. Additionally, they concluded that oxygen spill-over around the Ni/YSZ interfaces can eliminate the deposited carbon.

As mentioned above, steam-to-carbon ratio is one of the major factors influencing the carbon deposition possibility. This is mostly adjusted by sending sufficient amount of water vapor to prevent carbon deposition from an external source. Another way of adjusting the molar composition of the inlet is recirculating the depleted fuel at the fuel channel exit, which has high water vapor content, to the fuel channel inlet; which is shown in
Figure 1. The objective of this paper is to investigate the effect of recirculation ratio on the carbon deposition possibility in DIR-SOFCs for different input parameters such as fuel, operating temperature and global fuel utilization ratio.

2 ANALYSIS

2.1 Carbon Deposition Boundary

Considering equilibrium thermodynamics, carbon deposition possibility at a certain temperature and pressure may be determined for all possible variations of C-H-O systems. In the determination of the carbon deposition boundary, C-H-O triangular diagrams are generally used, which is first introduced by Cairns and Tevebaugh [13]. In their study, they considered six species to be in chemical equilibrium which are \( \text{H}_2\text{O}, \text{CO}_2, \text{H}_2, \text{CO}, \text{C}, \) and \( \text{CH}_4 \). According to the phase rule, \( F=(C+P-2) \), six degree of freedom are needed. These are selected as temperature, pressure, one material balance constraint and three equilibrium constant equations. The material constraint is selected as one mole of total reactants containing a fixed O/H ratio. In the study by Broers and Treijtel [14], instead of O/H ratio as the constraint parameter, the partial pressure of one of the gas species is used. Based on these two papers, the carbon deposition boundary is determined with a more current thermodynamic data and a different solution method as described below.

Three reactions needed to represent the equilibrium between gases are chosen as steam-reforming reaction, water-gas shift reaction and cracking of methane reaction.

Using the JANAF thermochemical tables [15], change of Gibbs free energy of formation of the chemical species are obtained for different temperature; and using Eq.(7), equilibrium constants for reactions (2-6) are calculated as shown in Table 1.

\[
K(T) = \exp \left( \frac{-\Delta G^o_{\text{rxn}}}{RT} \right) \tag{7}
\]

Let’s assume the partial pressures of the gases at the equilibrium as: \( P_{\text{CH}_4} = \alpha \), \( P_{\text{CO}_2} = \beta \), \( P_{\text{CO}} = \delta \), \( P_{\text{H}_2\text{O}} = \epsilon \) and \( P_{\text{H}_2} = \zeta \) in atm. If we fix the partial pressure of methane and solve Eqs. (8-11) simultaneously, we may calculate the partial pressure of the gases at equilibrium for a fixed partial pressure of methane.

\[
K_2 = \frac{\delta \cdot \zeta^3}{\alpha \cdot \epsilon} \tag{8}
\]

\[
K_3 = \frac{\beta \cdot \zeta}{\delta \cdot \epsilon} \tag{9}
\]

\[
K_4 = \frac{\zeta^2}{\alpha} \tag{10}
\]
\[ \alpha + \beta + \delta + \epsilon + \zeta = P \]  \hspace{1cm} (11)

**Table 1. Chemical equilibrium constants of reactions (2-6)**

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>(K_2)</th>
<th>(K_3)</th>
<th>(K_4)</th>
<th>(K_5)</th>
<th>(K_6)</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>0.03096</td>
<td>4.23010</td>
<td>0.72762</td>
<td>99.40913</td>
<td>23.50044</td>
</tr>
<tr>
<td>900</td>
<td>1.29752</td>
<td>2.30504</td>
<td>3.16266</td>
<td>5.61843</td>
<td>2.43746</td>
</tr>
<tr>
<td>1000</td>
<td>26.27617</td>
<td>1.43813</td>
<td>10.42663</td>
<td>0.570664</td>
<td>0.39681</td>
</tr>
<tr>
<td>1100</td>
<td>311.63685</td>
<td>0.98837</td>
<td>27.98823</td>
<td>0.088766</td>
<td>0.08981</td>
</tr>
<tr>
<td>1200</td>
<td>2463.98168</td>
<td>0.72956</td>
<td>64.19021</td>
<td>0.019006</td>
<td>0.026051</td>
</tr>
<tr>
<td>1300</td>
<td>14224.63263</td>
<td>0.56841</td>
<td>130.16993</td>
<td>0.005202</td>
<td>0.009151</td>
</tr>
<tr>
<td>1400</td>
<td>64018.71788</td>
<td>0.46162</td>
<td>239.28786</td>
<td>0.001725</td>
<td>0.003738</td>
</tr>
<tr>
<td>1500</td>
<td>235779.25236</td>
<td>0.38736</td>
<td>406.29556</td>
<td>0.000668</td>
<td>0.001723</td>
</tr>
</tbody>
</table>

For the solution, Mathcad’s ‘Given-Find block’, which can solve a set of nonlinear equations effectively, is used. First, the initial guesses for the partial pressures of CO\(_2\), CO, H\(_2\)O and H\(_2\) are made. The program solves the equations for a given partial pressure of CH\(_4\) and finds the partial pressure of the gases. Then, the partial pressure of CH\(_4\) is changed between the values for which H ratio and O ratio become approximately zero. The atom ratios of C, H and O are shown in Eqs. (12-14).

\[
C = \frac{\alpha + \beta + \delta}{5\alpha + 3\beta + 2\delta + 3\epsilon + 2\zeta} 
\]  \hspace{1cm} (12)

\[
O = \frac{2\beta + \delta + \epsilon}{5\alpha + 3\beta + 2\delta + 3\epsilon + 2\zeta} 
\]  \hspace{1cm} (13)

\[
H = 1 - C - O 
\]  \hspace{1cm} (14)

Using the set of data obtained by solving the equations shown above with changing the partial pressure of methane, carbon deposition boundary may be formed and shown in a C-H-O triangular diagram. If a given composition is above the boundary (towards the C vertex), then there is carbon deposition in the system; if the composition is below the boundary, then it may be interpreted that there is no risk of carbon deposition from the viewpoint of thermodynamics.

### 2.2 Effect of Recirculation on Carbon Deposition

In a previous paper by the authors [16], the performance of a planar DIR-SOFC has been assessed for different recirculation and fuel utilization ratios in detail. They have showed that equilibrium gas composition of the fuel channel exit for a SOFC operated with CH\(_4\), CO\(_2\), CO, H\(_2\), H\(_2\)O and N\(_2\) may be shown as follows.

\[
x_{CH_4}^{eq} = \frac{\dot{N}_{CH_4}^{eq}}{\dot{N}_{CH_4^{eq}}} - \frac{a}{N_{CH_4} + 2a} \]  \hspace{1cm} (15)

\[
x_{H_2}^{eq} = \frac{\dot{N}_{H_2}^{eq}}{\dot{N}_{H_2} + 3a + b} \left( \frac{1 - r}{1 - r + U_F} \right) \]  \hspace{1cm} (16)

\[
x_{CO}^{eq} = \frac{\dot{N}_{CO}^{eq} + a - b}{N_{CO} + 2a} \]  \hspace{1cm} (17)

\[
x_{CO_2}^{eq} = \frac{\dot{N}_{CO_2}^{eq} + b}{N_{CO_2} + 2a} \]  \hspace{1cm} (18)

\[
x_{H_2O}^{eq} = \frac{-a - b + \frac{(\dot{N}_{H_2O} + 3a + b) \cdot U_F}{1 - r + U_F}}{N_{H_2O} + 2a} \]  \hspace{1cm} (19)

\[
x_{N_2}^{eq} = \frac{\dot{N}_{N_2}^{eq}}{N_{N_2} + 2a} \]  \hspace{1cm} (20)

where the states ‘f1’ and ‘f4’ are shown in Figure 2. The recirculation ratio, \(r\), is defined as...
For determining the composition of the exit gas, chemical equilibrium equations for steam-reforming and water-gas shift reaction are solved together via Eq.(22).

\[ I = i \cdot A = 2 \cdot F \cdot c = 2 \cdot F \cdot \frac{(N_{H2}^{i} + 3a + b) \cdot U_F}{1 - r + r \cdot U_F} \]  

(22)

This approach may be regarded as zero-dimensional since only the thermodynamic considerations at the inlet and exit of the fuel cell are considered. In such an approach, carbon deposition possibility should be investigated at the exit and a point at a thermodynamic equilibrium which is very close to the inlet. This point is labeled as ‘f6’ in Figure 2.

Fig. 2. 2-D representation of a SOFC with anode recirculation

If we assume that local fuel utilization ratio is approximately zero at state ‘f6’, only steam reforming and water-gas shift reactions occur at this point. The gas composition at this point may be calculated as follows:

\[ x_{CH4}^{f6,eq} = \frac{N_{CH4}^{f6} - e}{N_{f3} + 2e} \]  

(23)

\[ x_{H_2}^{f6,eq} = \frac{N_{H2}^{f6} + 3e + f}{N_{f3} + 2e} \]  

(24)

\[ x_{CO}^{f6,eq} = \frac{N_{CO}^{f6} + e - f}{N_{f3} + 2e} \]  

(25)

\[ x_{CO_2}^{f6,eq} = \frac{N_{CO_2}^{f6} + f}{N_{f3} + 2e} \]  

(26)

\[ x_{H_2O}^{f6,eq} = \frac{N_{H2O}^{f6} - e - f}{N_{f3} + 2e} \]  

(27)

\[ x_{N_2}^{f6,eq} = \frac{N_{N2}^{f6}}{N_{f3} + 2e} \]  

(28)

where

\[ N_{f3}^i = N_{f1}^i + x_{eq}^i \cdot (N_{f1} + 2a) \frac{r}{1 - r} \]  

(29)

The extents of the reactions, e and f, may be found by solving the equilibrium reactions for steam reforming and water-gas shift reaction simultaneously. Hence, the composition at state ‘f6’ may be found.

The equations given in this section are valid when there is no carbon deposition at the inlet and exit of the fuel channel. Hence, if the carbon activities at the inlet and exit are both less than 1, these equations may be used to estimate the gas composition and there is no carbon deposition risk in the viewpoint of equilibrium thermodynamics. The carbon activity may be found from one of the following equations since they give the same results for the equilibrium at state ‘f6’.
\[ a_{c4} = \frac{K_4 \cdot x_{eq}^{CH_4}}{(x_{eq}^{H_2})^2} \]  
(30)

\[ a_{c5} = \frac{K_5 \cdot (x_{eq}^{CO})^2}{x_{eq}^{CO_2}} \]  
(31)

\[ a_{c6} = \frac{K_6 \cdot x_{eq}^{CO} \cdot x_{eq}^{H_2}}{x_{eq}^{H_2O}} \]  
(32)

3 Results and Discussion

3.1 Carbon Deposition Boundary

C, H and O atom ratios are calculated at 1 atm for the temperature range between 800 K-1400 K using the method described above and its results are shown in Figure 3. As it can be interpreted from Figure 3, for higher temperature carbon deposition region becomes smaller which means the number of C-H-O systems that may cause carbon deposition reduce. At 800 K, at C-O axis where H ratio is zero, C and O ratios become 34.5% and 65.5%; at C-H axis where O ratio is zero, C and H ratios become 13.3% and 86.7%, respectively. At 1400 K, at C-O axis where H ratio is zero, C and O ratios become 50% and 50%; at C-H axis where O ratio is zero, C and H ratios become 1.5% and 98.5%; respectively.

3.2 Effect of recirculation on carbon deposition

In a previous study by the authors [16], it was shown that as the recirculation ratio increases, power output and electrical efficiency decreases. So, we have to take the recirculation ratio as low as possible if only thermodynamic performance considerations are taken into account. However, degradation of the fuel cell due to carbon deposition and economic considerations should also be considered. Hence, we have studied the effect of recirculation on carbon deposition and investigated the change in the composition of the gas mixture at the inlet and exit, and the carbon activity with recirculation. It is found that the carbon activity at the exit is always lower than the inlet for the operating data that we have considered in this study. Since the possibility of carbon deposition is more severe at the inlet than the exit, we have shown the results that we have obtained for the inlet condition in this section.

In calculations, we have considered three temperature levels to represent different types of SOFCs. These are 800 K (inlet) – 900 K, 950 K (inlet) – 1050 K (exit), 1100 K (inlet) – 1200 K (exit); which represent LT-SOFCs, IT-SOFCs, and HT-SOFCs, respectively. A temperature difference of 100 K is assumed in each case considering the cooling necessity and thermomechanical considerations of the fuel cell. The fuel is taken as methane; and then a cleaned syngas which is assumed to be produced from a pyrolysis process. In all calculations, the pressure of the cell is taken as 1 atm; and the active surface area is taken as 100 cm².
3.2.1 Case-Study I: Fuel as Methane

When pure methane is used as a fuel in a DIR-SOFC, we need water to initiate and continue the steam reforming reaction. If we do not want to use any external water source, some part of the depleted fuel at the exit should be recirculated since the water content at the exit is high due to the electrochemical reaction. However, it should be noted that we still need some external water for start-up operation for a short time for this case. The results in this section reflect the steady state case and consider only the thermodynamic equilibrium conditions.

The effect of recirculation for LT-SOFC, IT-SOFC and HT-SOFC are shown in Figures 4 through 6. These figures show how the composition of a gas at equilibrium approaches the carbon deposition boundary as the recirculation ratio increases. As it may be seen from these figures, less recirculation is needed as the temperature level increases. Approximately, a recirculation ratio of 0.7, 0.5 and 0.4 are needed for LT-SOFC, IT-SOFC and HT-SOFC, respectively, at a fuel utilization ratio of 0.85, to prevent carbon deposition.

At the carbon deposition boundary, the gas mixture is at equilibrium with solid carbon. In equilibrium, the activity of pure solids is approximately equal to one. Above the boundary, the carbon activity is greater than one; and below the boundary, the carbon activity is less than one. We have checked the carbon activity for LT-SOFC, IT-SOFC and HT-SOFC at different global fuel utilization ratios; and the results are shown in Figures 7-9. In these figures, the dashed line shows the carbon deposition boundary. It may be interpreted from these figures that as the global fuel utilization ratio increases, carbon activity decreases. Additionally, although the carbon activity is the highest for HT-SOFCs at low recirculation ratios, the change of carbon activity with recirculation ratio is more than others; hence, less recirculation is needed to obtain the no-carbon deposition conditions.

![Fig. 4. C-H-O diagram of a LT-SOFC operating with methane](image)

![Fig. 5. C-H-O diagram of an IT-SOFC operating with methane](image)
We have mentioned before that we have to take a recirculation ratio which is sufficiently low enough to prevent carbon deposition to have the maximum thermodynamic performance. Due to this fact, we have calculated the minimum recirculation ratio for different temperature levels and global fuel utilization ratios as shown in Figure 10. It can be seen in this figure that as the global fuel utilization ratio changes between 0.5 and 0.85, minimum recirculation ratio changes between 0.78 and 0.68, 0.65 and 0.51 and 0.55 and 0.4 for LT-SOFC, IT-SOFC and HT-SOFC, respectively.

Fig. 6. C-H-O diagram of an HT-SOFC operating with methane

Fig. 7. Carbon activity at the inlet for a LT-SOFC operating with methane

Fig. 8. Carbon activity at the inlet for an IT-SOFC operating with methane
Fig. 9. Carbon activity at the inlet for a HT-SOFC operating with methane

Fig. 10. Minimum recirculation ratio for preventing the carbon deposition for a SOFC operating with methane

3.2.2 Case-study II: Fuel as syngas

One of the advantages of SOFCs is their efficient integration with bottoming cycles such as gasification cycles due to their high exit gas temperatures. For this reason, we investigate the carbon deposition possibility of a SOFC operating with syngas produced from a pyrolysis process which has a composition of 21% CH₄, 40% H₂, 20% CO, 18% CO₂ and 1% N₂ in a dry basis [17]. The calculations are repeated with this gas mixture and the results are shown in Figures 11-15 for a LT-SOFC and an IT-SOFC.

Figures 11-14 show similar trends of those for methane. At the fuel utilization ratio of 0.85, it is found that, approximately, a recirculation ratio of 0.6 and 0.3 are needed for LT-SOFC and IT-SOFC, respectively. Additionally, carbon activities and their change with recirculation are found to be lower than those for methane at low recirculation ratios. The results for HT-SOFC are not shown in Figures 11-14 since less than 10% of recirculation is needed to prevent carbon deposition at the global fuel utilization ratios of 0.65 to 0.85. However, the minimum recirculation ratio needed for this type of SOFC is shown together with LT-SOFC and IT-SOFC in Figure 15. The results show that as the global fuel utilization ratio changes between 0.5 and 0.85, minimum recirculation ratio changes between 0.75 and 0.62, 0.46 and 0.3, and 0.13 and 0.07 for LT-SOFC, IT-SOFC and HT-SOFC, respectively.
**Fig. 11. C-H-O diagram of a LT-SOFC operating with syngas**

**Fig. 12. C-H-O diagram of an IT-SOFC operating with syngas**

**Fig. 13. Carbon activity at the inlet for a LT-SOFC operating with syngas**
Conclusions
In this study, the effect of recirculation of the fuel channel exit on the carbon deposition possibility has been investigated. The results are illustrated in C-H-O triangular diagrams. Also, the change of activity and the minimum recirculation ratio with temperature and global fuel utilization ratio are calculated. It can be concluded that in order to operate the SOFC with a minimum recirculation ratio to prevent carbon deposition as required for higher thermodynamic performance, the maximum possible operating temperature level and global fuel utilization ratio should be chosen accordingly. For the range of operating data investigated, such a condition is achieved at the fuel utilization of 0.85 for HT-SOFCs. According to the thermodynamic considerations, the minimum recirculation ratio should be 0.4 and 0.07 for a HT-SOFC operating with methane and a typical cleaned gas produced from pyrolysis, respectively, at a fuel utilization of 0.85. In a future study, chemical kinetics and economical aspects will be taken into account for a better analysis and possible optimization.

NOMENCLATURE
a extent of steam reforming reaction for methane, mole/s
ac carbon activity
A active surface area, cm²
b extent of water gas shift reaction, mole/s
c extent of electrochemical reaction, mole/s
C number of components
e extent of steam reforming reaction for methane, mole/s
f extent of water gas shift reaction, mole/s
F  degree of freedom; Faraday constant
HT  high temperature
i  current density, A/cm²
I  current, A
IT  intermediate temperature
K  equilibrium constant
LT  low temperature
m  mass flow rate, g/s
m  molar flow rate, mole/s
r  recirculation ratio
P  number of phases; pressure, atm
R  universal gas constant, J/mole-K
T  temperature, K
UF  fuel utilization ratio
x  molar concentration
∆G rxn  change of Gibbs free energy of formation, kJ/mole

References