Evaluation of an integrated methane autothermal reforming and high-temperature proton exchange membrane fuel cell system

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Abstract

The aim of this study was to investigate the performance and efficiency of an integrated autothermal reforming and HT-PEMFC (high-temperature proton exchange membrane fuel cell) system fueled by methane. Effect of the inclusion of a CO (carbon monoxide) removal process on the integrated HT-PEMFC system was considered. An increase in the S/C (steam-to-carbon) ratio and the reformer temperature can enhance the hydrogen fraction while the CO formation reduces with increasing S/C ratio. The fuel processor efficiency of the methane autothermal reformer with a WGS (water gas shift reactor) reactor, as the CO removal process, is higher than that without a WGS reactor. A higher fuel processor efficiency can be obtained when the feed of the autothermal reformer is preheated to the reformer temperature. Regarding the cell performance, the reformate gas from the methane reformer operated at \( T_{\text{in}} = T_{\text{R}} \) and with a high S/C ratio is suitable for the HT-PEMFC system without a WGS reactor. When considering the HT-PEMFC system with a WGS reactor, the CO poisoning has less significant impact on the cell performance and the system can be operated over a broader range to minimize the required total active area. A WGS reactor is necessary for the methane autothermal reforming and HT-PEMFC integrated system with regard to the system efficiency.

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1. Introduction

Due to environmental problems and the energy crisis, many studies have aimed to develop both effective and clean technologies. Fuel cells are one of the most attractive power generation technologies that do not release pollution. Compared to other types of fuel cells, the PEMFC (proton exchange membrane fuel cell) is suitable for portable and automotive application as well as small scale power generation, such as residential application, due to its low weight, volume and operating temperature, which provide for the shortest start-up time [1]. On-site and on-board hydrogen productions are the best choices during the development of hydrogen infrastructure and storage.

Currently, natural gas is the most common fuel employed for hydrogen production because of its cost effectiveness for industrial hydrogen. Natural gas primarily consists of methane, as well as nitrogen, CO\(_2\), ethane, propane, butane, pentane and traces of other components. The high hydrogen-to-carbon ratio of methane results in a product with a high hydrogen concentration. The steam reforming of methane reportedly yields the highest hydrogen content of 75–78 vol.% [2]. When synthesis gas with a higher hydrogen concentration is fed to fuel cells, the efficiency of the fuel cell system is improved because the hydrogen fraction directly affects the performance of the fuel cell.

Many studies have focused on fuel processors integrated with PEMFC systems [2–5]. Eszos et al. [6] concluded that steam reforming and autothermal reforming are the most competitive fuel processing options in terms of fuel processing efficiencies and heat integration within the PEMFC systems to provide a high PEMFC system efficiency. Ouzounidou et al. [7] studied a combined methanol autothermal steam reforming and PEM fuel cell system in order to develop a model for exploring the interactions of the integrated system. In addition, Salemme et al. [8] investigated a steam reforming and autothermal reforming integrated with PEMFC system.
with various types of fuel. The methane steam reforming-based system achieved the highest efficiency. Furthermore, Specchia et al. [9] revealed that the efficiency of a steam reforming integrated with a PEMFC system was higher than that of an autothermal integrated system. However, steam reforming systems are more complex in term of heat integration, which impacts the system start-up time. The very good dynamic response of the autothermal reforming process makes it suitable for mobile applications [10,11]. Given the required fast start up and size and weight limitation for automobiles, the ATR (autothermal reforming) has an initially higher reaction rate than the steam reforming and can be operated without an external heat-supplying unit.

Because the CO (carbon monoxide) tolerance of the PEMFC is low, sophisticated CO removal units are needed to reduce the amount of CO (carbon monoxide) to less than 10 ppm. Recently, a HT-PEMFC (high-temperature proton exchange membrane fuel cell) was developed as a promising technology to handle the CO poisoning problem found in a conventional PEMFC [12,13]. When operating at a high temperature, the quantity of CO that adsorbs to the Pt catalyst in the HT-PEMFC decreases, and thus, the CO removal units of the HT-PEMFC system are less complex than those of a conventional PEMFC system [14]. Presently, the HT-PEMFC integrated with reforming processes has been widely reported. Garde- mann et al. [15] studied the compact ethanol autothermal processor integrated with the HT-PEMFC system for small scale power generation. The advantages of such system are its compactness and startup reliability. It was found that heating of the shift reactor to remove CO in the fuel processor is the most time-consuming step. Wichert et al. [16] developed the LPG fuel processor integrated with an HT-PEMFC system. The results showed that main reactors of the systems can be operated with stable performance and were easy to control during long-term experiments. Arsalis et al. [17] investigated a 1 kWc HT-PEMFC integrated with a fuel processor consisting of a methane steam reformer and a water gas shift reactor for Danish single-family households. The waste heat was applied for space heating and producing hot water. The obtained electrical efficiency of the partial (25%) and full loads was 45.4% and 38.8%, respectively. As the CO removal unit is related to the fuel processing process and the HT-PEMFC performance, the effect of its inclusion on the HT-PEMFC system efficiency should be clearly analyzed.

The aim of this study was to analyze and design an integrated autothermal reforming and HT-PEMFC system fueled by methane. To investigate the effect of a CO removal unit, two HT-PEMFC systems are considered in this study. The first system consists of the HT-PEMFC and methane autothermal reformer without the CO removal process. The second involves a HT-PEMFC whose fuel processor consists of a methane autothermal reformer and a WGS (water gas shift reactor) to remove CO. The mathematical models of the HT-PEMFC are based on the electrochemical model and the diffusion model of the gas diffusion layer and electrolyte film layer. The effects of the operating parameters, such as the reformer temperature, inlet temperature and S/C (steam-to-carbon) ratio on the reformer efficiency, hydrogen yield and CO content are analyzed. The operating parameters considerably affect not only the system efficiency but also the complexity of the system. The optimal operating conditions of the autothermal reformer that provide a suitable product gas for HT-PEMFC are given. The efficiency and performance of the HT-PEMFC systems were analyzed by considering the required total active area of the HT-PEMFC of each designed HT-PEMFC system.

2. System description

The autothermal reforming was selected as a hydrogen production process because of its advantageous fast start up and low energy requirement. In addition, the autothermal reforming process can be operated without an external heat supply, and this condition is referred to as “the adiabatic condition”. Two HT-PEMFC systems are considered here. The first involves a HT-PEMFC and a methane autothermal reformer without a CO removal process, as shown in Fig. 1. To enhance the hydrogen concentration and improve the overall system efficiency, water gas shift reactors were added to an integrated HT-PEMFC system, as presented in Fig. 2. The methane and oxidants, which are air and water, are fed to the methane autothermal reformer when the air feed content is controlled to supply the required heat of reforming via an oxidation reaction. Therefore, a burner for supplying heat to the reforming process was not added to this system. The inlet temperature of the autothermal reformer feed stream was set at the reaction temperature and standard temperature (298 K). The recovery heat from the HT-PEMFC is used to preheat the reactant of the autothermal reformer when the inlet temperature of the autothermal reformer feed stream is equal to the reaction temperature, as shown in Figs. 1(b) and 2(b). In contrast, the recovery heat from HT-PEMFC is not necessary when the inlet temperature is specified at 298 K, as shown in Figs. 1(a) and 2(a). The target power output of the HT-PEMFC systems is 50 kW for a small vehicle.

3. Modeling of HT-PEMFC system

3.1. Fuel processor

The equilibrium composition of the reformate gas obtained from the methane autothermal reforming was calculated by directly minimizing the Gibbs free energy, as shown in Eq. (1). For the methane autothermal reforming process, the gaseous components in the system are CH4, H2, CO, CO2, O2, N2 and H2O.

\[
\min \left(G^f\right)_{TP} = \sum_{i=1}^{C} n_i C_i = \sum_{i=1}^{C} n_i \left( G_i + R T \ln \frac{T}{T_i} \right) \tag{1}
\]

where C is the total number of components in the reaction system, and \( n_i \) is the moles of each gaseous component. Regarding the

![Fig. 1. Autothermal reforming integrated with HT-PEMFC system without a water gas shift reactor (case 1): (a) \( T_m = 298 \text{ K} \) and (b) \( T_m = T_r \).](image-url)
conservation of atomic species, \( n_i \) must satisfy the element balance in Eq. (2).

\[
\sum_i n_i d_{ik} - A_k = 0 \quad (k = 1, 2, ..., w)
\]  

(2)

where \( a_k \) is the number of atoms of element \( k \) in component \( i \), \( A_k \) is the total number of atoms of element \( k \) in the reaction mixture, and \( w \) is the total number of elements.

Lagrange’s undetermined method was used to solve the optimization problem mentioned above and find the amounts of gaseous components (in moles) in the system at equilibrium [18]. In addition, the WGS reactor was also modeled as an equilibrium reactor, and its operating temperature was specified at 473.15 K. Only a water gas shift reaction occurs in this reactor. The fuel processor efficiency that accounts for the methane autothermal reformer and WGS reactor (in the case of HT-PEMFC system with WGS reactor) can be calculated from Eq. (3) when the heat from high temperature reformate gases is recovered to the preheated reactant with a heat exchanger.

\[
\eta_{FP} = \frac{n_{H_2} \cdot \text{LHV}_{H_2}}{n_{CH_4} \cdot \text{LHV}_{CH_4} + Q_R + Q_p}
\]  

(3)

where \( n_{H_2} \) and \( n_{CH_4} \) are the molar flow rates of produced hydrogen and used methane, respectively. \( \text{LHV}_{H_2} \) and \( \text{LHV}_{CH_4} \) are the lower heating value of hydrogen and methane, respectively. \( Q_p \) is the heat requirement of the reforming process that accounts for the heat to preheat the reactant (no external heat input to maintain autothermal reformer because it is operated at the adiabatic condition, and the required heat is supplied by the oxidation reaction that occurs within the reactor). \( Q_R \) is the heat recovery from the hot reformate gas.

### 3.2. HT-PEMFC

Based on the electrochemical model, the operating cell voltage \( (E_{\text{cell}}) \) can be calculated by subtracting the reversible cell potential \( (E_r) \), the maximum voltage that can be achieved by a fuel cell at specific operating conditions, from various voltage losses.

\[
E_{\text{cell}} = E_r - \eta_{\text{act.a}} - \eta_{\text{act.c}} - \eta_{\text{ohmic}}
\]  

(4)

where \( \eta_{\text{act.a}} \) is the activation loss at the anode, \( \eta_{\text{act.c}} \) is the activation loss at the cathode and \( \eta_{\text{ohmic}} \) is the Ohmic loss. The model describing the reversible cell potential and voltage losses of the HT-PEMFC based on a phosphoric acid doped polybenzimidazole membrane is given in Table 1 in detail.

To reach the catalyst active surface, the gaseous reactants need to transport from the gas diffusion and the electrolyte film covering the catalyst agglomerates [19]. The concentration of hydrogen and oxygen can be obtained from Stefan Maxwell equation (Eq. (5) and Fick’s law (Eqs. (6)–(7))). It is noted that the validation of the HT-PEMFC model used in this study can be seen in our previous work [20].

\[
dX_i = \frac{RT}{P} \sum \frac{X_i N_j - X_j N_i}{D_i^{ij}}
\]  

(5)

where \( N \) is the molar flux of each component at the anode and cathode sides of HT-PEMFC and LT-PEMFC, \( X \) is the mole fraction of each component, and \( D_i^{ij} \) is the diffusion coefficient calculated with the Slattery–Bird correlation [21]. The parameters used to calculate the diffusion coefficient are shown in Table 2.

\[
\frac{N_{O_2}}{S_{\text{Pt-cathode}}} = \frac{-D_{O_2}(C_{O_2}\text{pt} - C_{O_2\text{dissolve}})}{\delta_{\text{cathode}}}
\]  

(6)

### Table 1: Electrochemical model of HT-PEMFC.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Model equations</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reversible cell potential</td>
<td>( E_r = \frac{RT}{F} \ln \left( \frac{P_{H_2}^a}{P_{H_2}^c} \cdot \frac{P_{CO}^c}{P_{CO}^a} \right) )</td>
<td>[19]</td>
</tr>
<tr>
<td>Anode activation loss</td>
<td>( \eta_{\text{act.a}} = \frac{RT}{2F} \ln \left( \frac{n_{H_2} + n_{CO}<em>r}{n</em>{H_2} + n_{CO}_p} \right) )</td>
<td>[20]</td>
</tr>
<tr>
<td>Anode activation energy, ( \alpha_{act,a} )</td>
<td>( \alpha_{act,a} = a + b \ln(T_{\text{ref,a}}) + c )</td>
<td>[19]</td>
</tr>
<tr>
<td>Cathode activation loss</td>
<td>( \eta_{\text{act.c}} = \frac{RT}{2F} \ln \left( \frac{n_{H_2} + n_{CO}<em>p}{n</em>{H_2} + n_{CO}_r} \right) )</td>
<td>[19]</td>
</tr>
<tr>
<td>Cathode activation energy, ( \alpha_{act,c} )</td>
<td>( \alpha_{act,c} = a + b \ln(T_{\text{ref,c}}) + c )</td>
<td>[19]</td>
</tr>
<tr>
<td>Ohmic loss</td>
<td>( \eta_{\text{ohmic}} = \frac{R_0}{A_m} )</td>
<td></td>
</tr>
</tbody>
</table>
\[
\frac{N_{\text{H}_2}}{S_{\text{Pt-anode}}} = \frac{-D_{\text{H}_2} \left( C_{\text{H}_2-\text{pt}} - C_{\text{H}_2-\text{dissolve}} \right)}{\delta_{\text{anode}}} \tag{7}
\]

where \(N\) is the molar flux, \(C_{\text{pt}}\) is the reactant concentration on the catalyst surface, \(C_{\text{dissolve}}\) is the equilibrium reactant concentration in the electrolyte film at the studied temperature, \(S_{\text{Pt}}\) is the real platinum surface area and \(\delta\) is the film thickness. \(C_{\text{Pt}}\) is used to calculate the theoretical voltage and activation loss in the electrochemical model.

To evaluate the performance of the HT-PEMFC, the power density \((P_{\text{FC}})\) and the thermal efficiency as given in Eqs. (8)-(9) are determined.

\[
P_{\text{FC}} = iE_{\text{cell}} \tag{8}
\]

\[
\eta_{\text{FC}} = \frac{P_{\text{FC}} \cdot U_f}{m_{\text{H}_2} \cdot \text{LHV}_{\text{H}_2}} \tag{9}
\]

where \(m_{\text{H}_2}\) is the hydrogen molar flow rate that is used in electrochemical reaction, and \(U_f\) is the fuel utilization, which is defined by the ratio of consumed hydrogen to supplied hydrogen.

The system efficiency can be defined as follows:

\[
\eta_{\text{sys}} = \eta_{\text{PP}} \cdot \eta_{\text{FC}} \tag{10}
\]

4. Numerical solution

In this work, the mathematical models of the fuel processor and HT-PEMFC were coded in Matlab. A flow chart of the simulation

Fig. 3. A flow chart of the simulation approach of the integrated autothermal reforming process and HT-PEMFC system.

Table 3 Required oxygen molar flow rate to sustain the heat requirement of autothermal reforming at the adiabatic condition.

<table>
<thead>
<tr>
<th>(T_{\text{R}}) (K)</th>
<th>Required oxygen molar flow rate (mole/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(T_{\text{in}} = 298) K</td>
<td>(S/C = 2)</td>
</tr>
<tr>
<td>673</td>
<td>0.0684</td>
</tr>
<tr>
<td>773</td>
<td>0.1681</td>
</tr>
<tr>
<td>873</td>
<td>0.3370</td>
</tr>
<tr>
<td>973</td>
<td>0.4145</td>
</tr>
<tr>
<td>1073</td>
<td>0.4258</td>
</tr>
</tbody>
</table>

Fig. 4. (a) \(\text{H}_2\) and (b) \(\text{CO}\) fraction of methane autothermal reformer at different operating condition: \(T_{\text{R}} = 298\) K (Black line) and \(T_{\text{in}} = T_{\text{R}}\) (Red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)
approach of the integrated reforming process and HT-PEMFC system is shown in Fig. 3. First, the methane molar flow rate and oxygen molar flow rate are initially guessed, and the equilibrium composition and enthalpy balance of the autothermal reformer are then calculated. The oxygen molar flow rate changes until the enthalpy balance between the inlet and outlet stream of the autothermal reformer is equal to zero. For the HT-PEMFC system without the WGS reactor (case 1), the obtained H2 and CO fraction is applied to calculate the voltage loss, cell voltage, and power output directly, whereas the product composition of the autothermal reformer is used to calculate the H2 and CO fractions from the WGS reactor for the HT-PEMFC system with the WGS reactor (case 2). The voltage loss, cell voltage, and power output are subsequently calculated. The calculation is repeated until the calculated voltage is equal to the specified voltage.

5. Results and discussion

Integrated methane autothermal reforming and HT-PEMFC systems with and without a water gas shift reactor were considered. First, the effects of the reformer temperature, inlet reformer temperature and S/C on the H2 fraction, CO fraction and fuel processor efficiency were studied. The required oxygen flow rate to sustain the heat requirement of autothermal reforming at the adiabatic condition (external heat input is not needed because the heat required for the autothermal reformer is supplied by the oxidation reaction that occurs within the reactor) is shown in Table 3. The required oxygen flow rate increases when the autothermal process is operated at high temperatures, and the excess steam is fed to the process. However, this flow rate decreases as the inlet reformer temperature increases. This trend is similar to that reported in the other studies on the autothermal reformer [22,23]. In addition, the performances of the HT-PEMFC fueled by reformate gas from the methane autothermal reformer with and without WGS reactor at different operating conditions were investigated. The optimal conditions and required total active area of the HT-PEMFC that provide the target power output of all designed system are also reported.

5.1. Fuel processor

Methane autothermal reformers without and with a WGS reactor were studied to observe the effect of the reformer operating conditions on the H2 fraction, CO fraction and fuel processor efficiency, which significantly affect the HT-PEMFC performance and overall system efficiency. The H2 and CO fraction of methane autothermal reformers without and with a WGS reactor at different reformer temperatures and S/C ratios are shown in Figs. 4 and 5, respectively. Two inlet reformer temperatures \( T_{\text{in}} = T_R \) and \( T_{\text{in}} = 298 \) K were investigated in this work. For the autothermal reformer without a WGS reactor in Fig. 4, the

![Fig. 5. (a) H2 and (b) CO fraction of methane autothermal reformer with WGS reactor at different operating condition: \( T_{\text{in}} = 298 \) K (Black line) and \( T_{\text{in}} = T_R \) (Red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image1)

![Fig. 6. The fuel processor efficiency of methane autothermal reformer at S/C = 3 and different reformer temperatures and inlet reformer temperatures: (a) without WGS reactor and (b) with WGS reactor.](image2)
hydrogen production and CO formation were lower when the inlet reformer temperature was equal to 298 K because some of the fuel was used to sustain the adiabatic autothermal reformer, and the energy needed for the reformer at low inlet reformer temperatures exceeds that at high inlet reformer temperatures. At $T_{\text{in}} = T_R$ (Red line), an increase in the operating temperature and S/C ratio enhanced the hydrogen fraction, whereas the CO fraction decreased at low temperatures and high S/C ratios. At $T_{\text{in}} = 298$ K (Black line), increasing the S/C ratio increases the hydrogen fraction at low reformer temperatures, but the hydrogen fraction decreases in response to increasing S/C ratios at high temperatures. This relationship arises because the heat required to maintain the autothermal reactor at $T_{\text{in}} = 298$ K is higher than that at $T_{\text{in}} = T_R$, and thus the high amount of methane is consumed by the oxidation reaction instead of producing hydrogen via the reforming reaction. The hydrogen production from the methane autothermal reformer with the WGS reactor shows the same trend as the other system, as shown in Fig. 5. However, the CO fraction seems to decrease at high reformer temperatures when the inlet reformer temperature is 298 K. Compared to methane autothermal reforming without a WGS reactor, the addition of a WGS reactor to the fuel processor improves the quality of the product gas for HT-PEMFC by means of increasing the hydrogen fraction and reducing the CO concentration. The optimal reformer temperature of both the autothermal reactor without and with a WGS reactor that provides the maximum hydrogen yield is in the range of 773–873 K.

The fuel processor efficiencies of the methane fuel processors without and with WGS reactor at different operating condition designs are shown in Fig. 6(a) and (b), respectively. Heat is not needed to preheat reactant at $T_{\text{in}} = T_R$ for $T_{\text{in}} = 298$ K. However, heat is required to preheat the reactant at $T_{\text{in}} = T_R$, and thus the fuel processor efficiency is calculated by considering heat recovery from the hot reformate gases and without considering the heat recovery (external heat is required). The simulation results indicate that the fuel processor efficiency is higher for the autothermal reformer with a WGS reactor because of the high hydrogen production of this process. At high reformer temperatures ($T_R \geq 973$ K), the methane autothermal reformer operated at $T_{\text{in}} = T_R$ with heat recovery shows the highest fuel processor efficiency. However, the methane autothermal reformer should be operated at $T_R = 873$ to achieve the highest fuel processor efficiency when the inlet temperature is set to 298 K for both methane autothermal reformers with and without a WGS reactor. The heat recovery can enhance the fuel processor efficiency, especially for high reformer temperature operation.

5.2. HT-PEMFC system

The product gases obtained from the hydrogen production unit at different operating conditions are fed to the HT-PEMFC, and the performance of the HT-PEMFC was investigated while considering the CO poisoning effect. The polarization curve of the HT-PEMFC fueled by hydrogen from the methane autothermal reformer without a WGS reactor is presented in Fig. 7. The simulation results show that the performance of the HT-PEMFC is higher at 773 K and a high S/C ratio due to the low CO concentration obtained from the methane reformer at this condition. Compared to the reformate gas from the methane reformer operated at $T_{\text{in}} = 298$ K, the reformate gas from the methane reformer operated at $T_{\text{in}} = T_R$ is more suitable for a HT-PEMFC run at a voltage exceeding 0.3 V. However, the performance of the HT-PEMFC operated on reformate gas from a methane reformer with $T_{\text{in}} = T_R$ was lower than that of the other system at low voltage operation (high current density) and reformer temperature of 873 K due to the higher CO concentration, which significantly affects the cell performance, especially at a high current density. Conversely, the HT-PEMFC system with a WGS reactor showed similar performances when the methane reformer was operated at all studied reformer temperatures and S/C ratios (see Fig. 8). This similarity arises because the CO concentration in
the reformate gas from the methane reformer with a WGS reactor is low and insignificantly impacts the HT-PEMFC. However, the system performed better at $T_{\text{in}} = T_R$ than at an inlet reformer temperature of 298 K.

Figs. 9 and 10 show the required total active area of the HT-PEMFC system without and with a WGS reactor at different reformer operating conditions to achieve the target power output (50 kW) when the cell is operated at a voltage of 0.6. Fig. 9 shows that the studied HT-PEMFC system without a WGS reactor requires a higher total active area to reach the target power output when the inlet reformer temperature is 298 K. In addition, the minimum total active area requirement is approximately 70 m$^2$ for a HT-PEMFC system operated at $T_R = 773$–873 K, $S/C = 3$–4 and $T_{\text{in}} = T_R$. Operating the methane autothermal reformer at temperatures of 673 and 973 K results in a large total active area requirement due to the low hydrogen and high CO concentration of the reformate gas from the methane autothermal reformer run at these temperatures.

For the HT-PEMFC system with a WGS reactor, Fig. 10 shows that the required total active area is in a similar range (70–85 m$^2$) at all studied reformer operating conditions because of the similar cell performance obtained from the HT-PEMFC system with a WGS reactor. Furthermore, the minimum total active area requirement of the HT-PEMFC system with a WGS reactor is approximately 70 m$^2$ for a system operated at $T_R = 773$–973 K, $S/C = 2$–4 and $T_{\text{in}} = T_R$. The simulation results indicate that the HT-PEMFC systems with and without a WGS reactor require the same minimum total active area to reach the target power output, but the HT-PEMFC system with a WGS reactor can be operated over a broader range.

At the desired power output, the system efficiencies of the HT-PEMFC system without and with a WGS reactor at various reformer operating conditions are shown in Figs. 11 and 12, respectively. For the HT-PEMFC system without a WGS reactor, the system efficiency increases with the reformer temperature until it reaches an optimal level, and it then decreases with the reformer temperature.

For the HT-PEMFC system with a WGS reactor, Fig. 10 shows that the required total active area is in a similar range (70–85 m$^2$) at all studied reformer operating conditions because of the similar cell performance obtained from the HT-PEMFC system with a WGS reactor. Furthermore, the minimum total active area requirement of the HT-PEMFC system with a WGS reactor is approximately 70 m$^2$ for a system operated at $T_R = 773$–973 K, $S/C = 2$–4 and $T_{\text{in}} = T_R$. The simulation results indicate that the HT-PEMFC systems with and without a WGS reactor require the same minimum total active area to reach the target power output, but the HT-PEMFC system with a WGS reactor can be operated over a broader range.

At the desired power output, the system efficiencies of the HT-PEMFC system without and with a WGS reactor at various reformer operating conditions are shown in Figs. 11 and 12, respectively. For the HT-PEMFC system without a WGS reactor, the system efficiency increases with the reformer temperature until it reaches an optimal level, and it then decreases with the reformer temperature.
temperature for \( T_{\text{in}} = 298 \) K and remains constant for \( T_{\text{in}} = T_R \). In addition, the S/C ratio positively affects the system efficiency when the reformer temperature is lower than the optimal point. When the temperature exceeds this point, the effect of the S/C ratio on the system efficiency is insignificant. The optimal efficiency is near 24\% and can be obtained at a temperature of 873 K and all studied S/C ratios for \( T_{\text{in}} = 298 \) K (see Fig. 11). For \( T_{\text{in}} = T_R \), the optimal efficiency is near 25\% and can be obtained at temperatures at or above 873 K.

A similar trend was observed for the HT-PEMFC system with a WGS reactor, and the optimal operational range that yields the preferable system efficiency is a temperature of 873 K and above in the absence of a preheating reaction before it is fed to adiabatic autothermal reformer (\( T_{\text{in}} = 298 \) K). However, a temperature of 973 K and S/C ratio of 2 are preferred when the reactant of the autothermal reformer is preheated to the reformer temperature. In addition, the system efficiency of the HT-PEMFC system with a WGS reactor at both \( T_{\text{in}} = T_R \) and \( T_{\text{in}} = 298 \) K is maximized near 30\%.

### 6. Conclusions

A methane autothermal reformer integrated with a HT-PEMFC was designed and analyzed in this work. Effect of the inclusion of a CO removal unit in the HT-PEMFC system was studied. The simulation results showed that the inlet reformer temperature strongly affects the efficiency because it is a key factor for controlling the energy use of the autothermal reformer. The hydrogen production and CO formation are lower at an inlet reformer temperature of 298 K for the autothermal reformer without a WGS reactor. The S/C ratio has a positive effect by both increasing the hydrogen fraction and decreasing the CO formation, while an increase in the operating temperature can enhance the hydrogen concentration. An almost identical trend was also observed for the methane autothermal reformer with a WGS reactor, but CO the fraction decreased at high reformer temperatures when the inlet reformer temperature was 298 K. The fuel processor efficiency of the methane autothermal reformer with a WGS reactor was higher than that for the system without a WGS reactor, and reformer operation at \( T_{\text{in}} = T_R \) is preferable to achieve a high fuel processor efficiency. Considering the cell performance, the reformate gas from the methane reformer operated at \( T_{\text{in}} = T_R \) and a high S/C ratio is suitable for HT-PEMFC. The minimum total active area required to reach the target power output is similar for both HT-PEMFC systems with and without a WGS reactor, but the HT-PEMFC system with a WGS reactor can be operated over a broader range. The highest efficiencies of the HT-PEMFC systems without and with a WGS reactor are 25\% and 30\%, respectively. Considering the system efficiency, it is found that a WGS reactor is necessary for the methane autothermal reforming and HT-PEMFC integrated system.
Acknowledgments

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Nomenclatures

- $C_{\text{dissolve}}$: equilibrium concentration, mole cm$^{-3}$
- $C_{\text{Pt}}$: concentration on the catalyst surface, mole cm$^{-3}$
- $C_{\text{Pt}}^{\text{ref}}$: reference concentration on the catalyst surface, mole cm$^{-3}$
- $D_{\text{eff}}$: binary diffusion coefficient, m$^2$ s$^{-1}$
- $E_{\text{cell}}$: cell voltage, V
- $E_r$: reversible cell potential, V
- $F$: Faraday constant, 96,485 C mol$^{-1}$
- $G$: Gibbs free energy, J mol$^{-1}$
- $H$: enthalpy, J mol$^{-1}$
- $i$: current density, A m$^{-2}$
- $i_0$: exchange current density, A m$^{-2}$
- $L_c$: catalyst loading, mg cm$^{-2}$
- $L_{\text{HV}}$: lower heating value, kJ mol$^{-1}$
- $m$: membrane thickness, m
- $m$: molar flow rate, mol s$^{-1}$
- $N$: molar flux, mol s$^{-1}$ m$^{-2}$
- $P$: pressure, atm
- $P_{\text{FC}}$: power output of fuel cell, W
- $Q_e$: heat required for the steam reforming process, J s$^{-1}$
- $Q_f$: heat recovery for the hot reformate gas, J s$^{-1}$
- $R$: gas constant (=8.314), J mol$^{-1}$ K$^{-1}$
- $S_{\text{Pt}}$: real platinum surface area
- $T$: cell temperature, K
- $T_{\text{in}}$: inlet reformer temperature, K
- $T_{\text{R}}$: reformer temperature, K
- $X$: mole fraction

Greek letters

- $\alpha$: transfer coefficient
- $\gamma$: reaction order
- $\theta_{\text{CO}}$: CO coverage
- $\theta_{\text{H}_2}$: H$_2$ coverage
- $\sigma_m$: proton conductivity, S cm$^{-1}$
- $\eta_{\text{ohmic}}$: ohmic loss, V
- $\eta_{\text{act}}$: activation loss, V
- $\eta_{\text{sys}}$: system efficiency

Subscripts and superscripts

- $a$: anode
- $c$: cathode
- $m$: membrane
- $ij$: components “i” and “j”
- $\text{in}$: inlet stream
- $\text{out}$: outlet stream

References