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Performance Evaluation of Biogas-fed Solid Oxide Fuel Cell System Coupling with CO_2-selective Membrane Separator

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Biogas is an interesting fuel for hydrogen production in solid oxide fuel cell (SOFC). However, CO_2 is a main composition of biogas, resulting in the dilution of hydrogen in syngas and low electrical efficiency of SOFC. To increase the hydrogen concentration, the power plant of biogas-fuelled SOFC requires the installation of carbon dioxide-selective membrane separator. The aim of this work is the performance analysis of the power plant of SOFC system utilizing biogas as fuel with and without installing the CO_2-selective membrane separator. The simulation results showed that the membrane area has direct effect on the amount of permeated CO_2 and the system performance. The increase of membrane area of separator enhances the SOFC and thermal efficiencies. However, the hydrogen loss in the retentate side increases and resulting in the decrement of system electrical efficiency. When considering performance of both systems, the SOFC efficiency of the SOFC system with CO_2-selective membrane separator is superior to the conventional system about 7.54%. Also, its thermal efficiency is higher, compared to the conventional system.

1. Introduction

The environmental issues and limitation of fossil resource have been considerably concerned. Fuel cell is considered as promising device for power generation due to its low emissions, high efficiency, and silent operation. There are different types of fuel cell. Solid oxide fuel cell (SOFC) is interesting for power station. It is operated at high temperature; hence, the various advantages compared to low-temperature fuel cell, i.e., high reaction rate, high efficiency, and fuel flexibility. Moreover, it can be integrated with engine cycles to improve the system efficiency (Jienkulsawad et al., 2015).

SOFC needs hydrogen to generate the electricity. Hydrogen can be produced from hydrocarbon. Generally, natural gas is used for hydrogen production. However, the natural gas as fossil fuel has been depleted. Thus, the sustainable energy sources and environment-friendly fuels have been seeking to substitute for fossil resources. Biogas has been considerably received attention because it is renewable fuel (Authayanun et al., 2016). It can be produced from various biomasses, i.e., anaerobic digestion of urban, industrial, and agricultural wastes (Manenti et al., 2015). SOFC can use biogas as fuel due to its high tolerance on impurity. Shiratori et al. (2008) investigated the real biogas fed directly on the anode of SOFC. Their results showed that SOFC obtains cell voltage above 0.9 over 50 h. Although biogas can directly reformed to hydrogen-rich gas on SOFC, a major problem of SOFC with direct feeding biogas is the occurrence of high temperature gradient from the temperature drop of inlet temperature due to highly endothermic of reforming reaction (Meusinger et al., 1998). Moreover, the direct reforming SOFC is lower electrical efficiency and shorter durability compared with external reforming mode. To avoid these problems, the biogas-fueled SOFC installs with a fuel processor.

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The biogas is composed of high CO_2 content about 35-40 %vol. Therefore, there is low hydrogen concentration in the product gas obtained from the reformer. The hydrogen concentration of syngas is main parameter for the electricity efficiency of SOFC. This results in low performance of SOFC (Saebea et al., 2013).
To improve the SOFC performance and the system efficiency, the power plant of biogas-fueled SOFC requires the installation of CO_2 separator to reduce the amount of CO_2 fed to the SOFC. The various technologies of CO_2 separation are available in the present, such as solvent absorption, calcium oxide adsorption, and membrane. Membrane separation technology for CO_2 separation has been considerable attention because of its low energy consumption (Hamidreza et al., 2018). Polydimethylsiloxane as CO_2-selective membrane is interesting. It can operate at room temperature and high selectivity of CO_2.
The operating parameters of SOFC, reformer, and CO_2-selective membrane separator have a direct relationship with the performance of each unit. The suitable condition of the integrated system should be studied. The aim of this work is the performance analysis of the power plant of biogas-fueled SOFC with/without integrating the CO_2-selective membrane separator. The inlet steam to carbon ratio for the reformer on the performance of biogas-fueled SOFC system without CO_2-selective membrane separator is firstly investigated. Then, the effect of area membrane is studied to find the proper for performance the biogas-fueled SOFC system with CO_2-selective membrane separator.

2. Process description

The integrated systems between SOFC and reformer without or with coupling to CO_2-selective membrane separator are shown in Figure 1. Figure 1(a) shows the conventional system. Biogas is composed of 60 %CH_4 and 40 %CO_2 (Rasi et al., 2007). Biogas and steam are heated at the reforming temperature of 1,073 K before introducing to the reformer. The syngas from the reformer is heated and sent to SOFC at the fuel channel. At the air channel, preheated air is fed. The electrochemical reaction occurs in the SOFC. The exhaust gas of both sides from SOFC is introduced to the afterburner in order to combust unreacted H_2 and CO and increase quality of exhaust gas. The outlet gas from the afterburner can be used in preheater and units required the heat input. For the retrofitted system, the CO_2-selective membrane separator is added between the reformer and SOFC, as shown in Figure 1(b). After reformer, the syngas is reduced the temperature and compressed at the operating condition of membrane separator. Then, it is sent to the membrane separator. The syngas separated CO_2 at retentate is increased temperature and fed to the SOFC. The permeate gas is combusted at afterburner.

2.1 SOFC model

The electricity is produced from SOFC via electrochemical reactions. Oxygen at the cathode is reduced to oxygen ions that pass through electrolyze to the anode side. Hydrogen at anode side reacts with oxygen ion, which occurs oxidation reaction. The steam and electron are produced at anode/electrolyte interface. The electron flows to external circuit that generates the electricity. The power generation from SOFC can be evaluated from operating voltage (V) and current density (I), which can be written as:

$$P_{\mathrm{sofc}} = V \times I \tag{1}$$

The electrochemical equations are concluded in Table 1. The operating voltage can be calculated from reversible cell voltage (E^{OCV}) deducted by internal voltage loss. There are three major internal voltage losses that are activation overpotentials (η_{act}), ohmic overpotential (η_{ohmic}), and concentration overpotentials (η_{conc}).

Table 1: Electrochemical equations of SOFC model

Parameters	Equation	
Operative cell voltage	$V = E^{\mathrm{OCV}} - (\eta_{\mathrm{act}} + \eta_{\mathrm{ohm}} + \eta_{\mathrm{conc}})$	(2)
Reversible cell voltage	$E^{\mathrm{OCV}} = E^0 - \frac{RT}{2F}\ln(\frac{P_{\mathrm{H_2O}}}{P_{\mathrm{H_2}} P_{\mathrm{O_2}}^{0.5}})$	(3)
Activation overpotentials	$\eta_{\mathrm{act}} = \frac{RT}{F}\sinh^{-1}\left(\frac{i}{2i_{0,\mathrm{a}}}\right) + \frac{RT}{F}\sinh^{-1}\left(\frac{i}{2i_{0,\mathrm{c}}}\right)$	(4)
Ohmic overpotential	$\eta_{\mathrm{ohm}} = iR_{\mathrm{ohm}}$	(5)
Concentration overpotentials	$\eta_{\mathrm{conc,anode}} = \frac{RT}{2F}\ln\left(\frac{p_{\mathrm{H_2O,TPB}}\, p_{\mathrm{H_2,f}}}{p_{\mathrm{H_2O,f}}\, p_{\mathrm{H_2,TPB}}}\right) + \frac{RT}{4F}\ln\left(\frac{p_{\mathrm{O_2,a}}}{p_{\mathrm{O_2,TPB}}}\right)$	(6)

Ohmic overpotentials arise from the flow resistance of electron though the current collectors and ionic through the electrolyte. Activation overpotentials are related to the sluggishness of the electrochemical reaction.
Concentration overpotentials are the resistance to mass transport due to the decrease in the substance concentration. From Table 1, R_{ohm} is the internal electrical resistance; $i_{0,a}$ and $i_{0,c}$ are the exchange current density pre-exponential factors of the anode and cathode respectively; and $p_{i,TPB}$ is the partial pressure of H_2, H_2O and O_2 at the electrode/electrolyte interfaces (Saebea et al., 2013).

2.2 2.2 CO_2-selective membrane separator model

Polydimethylsiloxane (PDMS) is used as CO_2-selective membrane in separator. In the membrane separator, CO_2 from syngas fed at the retentate side permeates polymer membrane to the permeation side. Gas flux of species i diffuses through membrane can be expressed following equation.

$$J_i = Pi \cdot \frac{A}{L} \cdot \left(\left(P_r \cdot X_{i,r(ave)} \right) - \left(P_p \cdot X_{i,p} \right) \right) \tag{7}$$

Gas flux is function of the membrane permeability (Pi), the membrane thickness (L), and the gas concentration. P_r and P_p are pressure at retentate side and permeate side, respectively. $X_{i,r(ave)}$ is average mole fraction of species i at the feed side. $X_{i,p}$ is mole fraction of species i at the permeate side.
Average molar flow rate of species i at feed side is calculated by Eq(8).

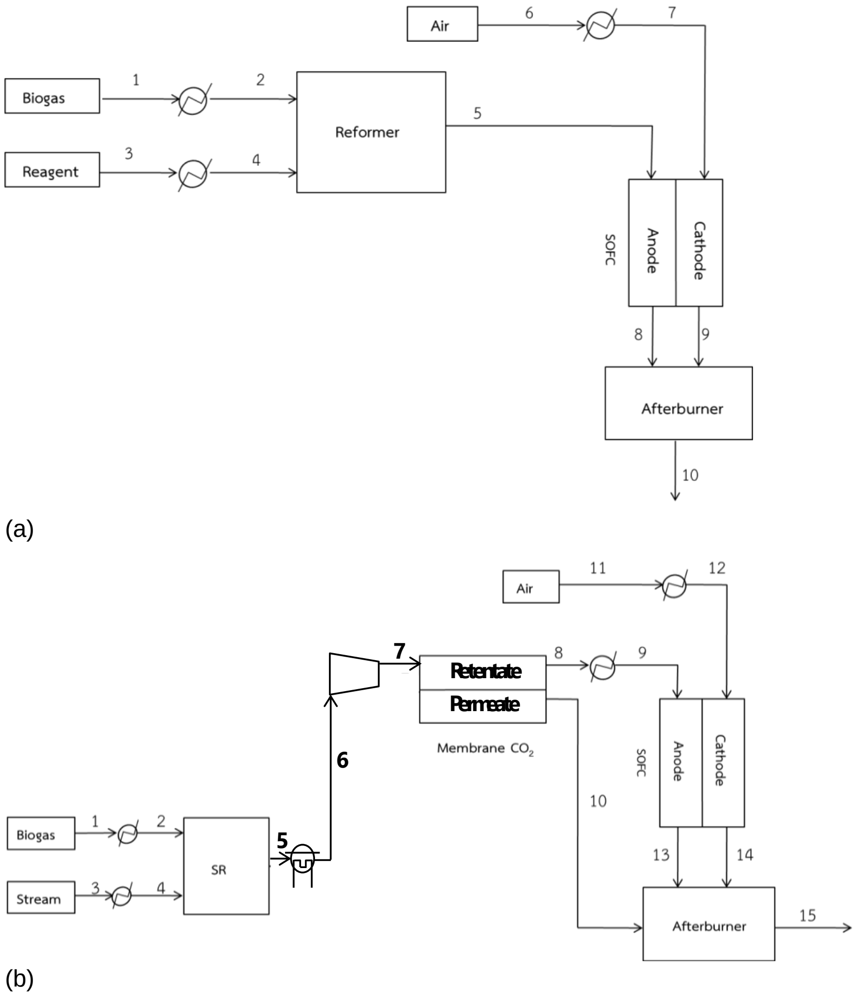

Figure 1: Schematic diagram of the integrated system between SOFC and reformer (a) system without coupling to CO_2-selective membrane separator (b) system with coupling to CO_2-selective membrane separator.

$$X_{\mathrm{i,r(ave)}} = \frac{X_{\mathrm{i,p}} - X_{\mathrm{i,r}}}{\ln\left(X_{\mathrm{i,p}} / X_{\mathrm{i,r}}\right)} \quad (8)$$

The system performance is indicated by the SOFC efficiency ($\eta_{\mathrm{el,sofc}}$), the system electrical efficiency (η_{el}), and the thermal efficiency (η_{th}), which are calculated by using the following expression;

$$\eta_{\mathrm{el,sofc}} = \frac{P_{\mathrm{sofc}}}{\dot{n}_{\mathrm{H_2}} LHV_{\mathrm{H_2}} + \dot{n}_{\mathrm{CO}} LHV_{\mathrm{CO}} + \dot{n}_{\mathrm{CH_4}} LHV_{\mathrm{CH_4}}} \quad (9)$$

$$\eta_{el} = \frac{P_{\mathrm{sofc}}}{\dot{n}_{\mathrm{i}} LHV_{\mathrm{i}}} \quad (10)$$

$$\eta_{th} = \frac{Q_{\mathrm{rec}} - Q_{\mathrm{use}}}{\dot{n}_{\mathrm{i}} LHV_{\mathrm{i}}} \quad (11)$$

where LHV_i is the lower heating value; $\dot{n}_{\mathrm{i}}$ is the molar flow rate of species i at inlet; Q_{use} is the overall thermal energy consumption in the system; and Q_{rec} is the thermal energy obtained from the combustion referring to 100 °C.

3. Results and discussion

The integrated system of SOFC and membrane separator was simulated in Aspen Plus. Input and operating parameters of SOFC and CO_2-selective membrane separator are concluded in Table 2. The parameter relation of reformer and SOFC on the performance of system without CO_2 selective membrane separator was firstly investigated. Consequently, the effect of membrane area in separator on the system efficiency was investigated. Finally, the performance of SOFC systems without and with coupling to CO_2 selective membrane separator was compared.

3.1 Conventional system

In the integrated system between the reformer and SOFC, the effect of operating condition of reformer has direct effect on the SOFC performance. The effect of steam to carbon ratio on SOFC efficiency, system electrical efficiency, and thermal efficiency presents in Figure 2. From Figure 2, the increase in the steam to carbon ratio decreases the SOFC efficiency. This is because the reduction of H_2 concentration with increasing steam to the reformer results in the increase of concentration overpotential and the decline of cell voltage. The SOFC efficiency is relatively sensitive to the system efficiency, as shown in Figure 2. The system efficiency reduces with increasing the steam to carbon ratio. Moreover, the increase of the steam to carbon ratio has influence on the reduction of thermal efficiency. It can be explained that the increment of input energy for preheating steam and steam reforming reaction.

Table 2: Input and operating parameters for the integrated system of SOFC and CO_2-selective membrane separator.

Parameters	Value	Parameters	Value
SOFC model		Temperature (K)	1,073
Operating temperature (K)	1,073	Membrane separator	
Air composition	21 %O_2, 79 %N_2	Pressure of permeate side (bar)	1
Air ratio	8.5	Pressure of retentate side (bar)	10
Fuel utilization	70 %	Operating temperature (K)	298
Anode thickness (µm)	500	Membrane thickness (µm)	1.6
Electrolyte thickness (µm)	20	Permeability (barrer)	
Cathode thickness (µm)	50	CH_4	940
Activation energy of anode (J mol^{-1})	140,000	CO_2	3,200
Activation energy of cathode (J mol^{-1})	137,000	CO	400
Reformer		H_2O	10
Pressure (bar)	1	H_2	500
Steam to carbon (-)	1		

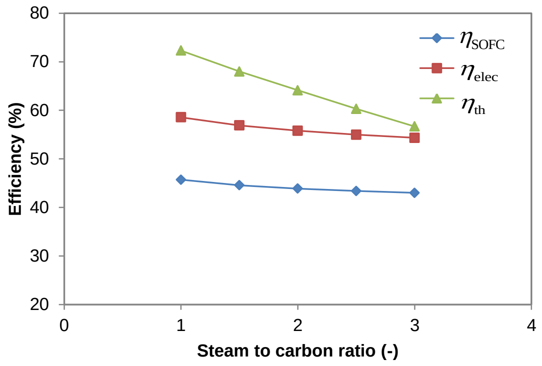

Figure 2: Effect of steam to carbon ratio on efficiencies of the conventional system.

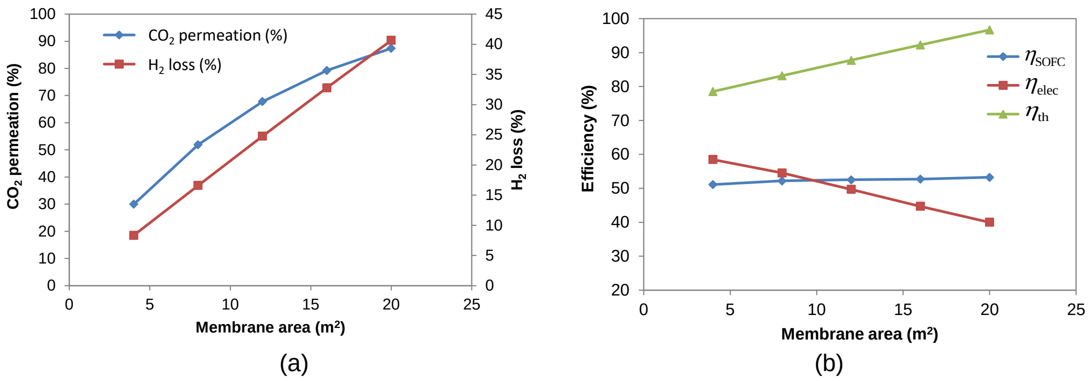

Figure 3: Effect of membrane area of separator in the SOFC system with coupling to CO_2-selectivity membrane separator on (a) carbon dioxide permeation and hydrogen loss (%) and (b) efficiencies.

3.2 SOFC system with CO_2 membrane separator

The performance of the integrated system between SOFC and reformer with coupling to CO_2-selectivity membrane separator is shown in this section. The retentate pressure of CO_2-selectivity membrane separator was specified at 10 bar. To more separate the amount of CO_2 from the syngas before feeding to SOFC, the CO_2-selectivity membrane area is increasingly required, as shown in Figure 3a. The hydrogen concentration is higher with the addition of membrane area in separator. This results in a higher cell voltage. Consequently, the electricity efficiency of SOFC improves, as seen in Figure 3b. However, the system efficiency decreases with increasing the membrane area of separator. This can be explained in Figure 3a, which indicates the increase of membrane area raises the amount of hydrogen loss, leading to the reduction of the inlet molar flow rate of hydrogen. When considering the thermal efficiency, the increment of membrane area in separator increases the thermal efficiency. This is because an increasing hydrogen loss at the permeate side fed to the afterburner with increasing the membrane area. The thermal energy of exhaust gas from the afterburner, which can be used for the unit required input energy, is higher. Thus, the thermal efficiency of system increases.

3.3 Comparison of systems without/with membrane separator

Comparison of SOFC system without and with the CO_2-selective membrane separator is demonstrated in Figure 4. In comparison of both systems, the operating parameters of reformer and SOFC were specified at similar condition. SOFC was operated at the fuel utilization of 70 % and air ratio of 8.5. For the system with CO_2 membrane selective membrane separator, the membrane area was fixed at 20 m^2. Figure 4 indicates that the SOFC efficiency of the SOFC system with CO_2-selective membrane separator is higher than that of the conventional system about 7.54 %. However, the system electrical efficiency of SOFC system with the CO_2-selective membrane separator is lower, compared with the conventional system. This can be expressed that the amount of H_2 in the rentetate side decreases and results in the decline of SOFC power output, for the system with CO_2-selective membrane separator. Additionally, the system with CO_2-selective membrane separator needs the power consumption of compressor to increase the pressure of retentate side. Although the electrical efficiency of system instilling the CO_2-selective membrane separator is low, its thermal efficiency is superior to the conventional system.

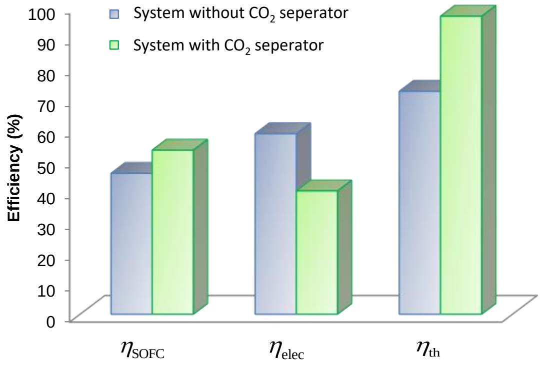

Figure 4: Comparison of systems without/with CO_2 selective membrane separator

4. Conclusions

Performance of biogas-fuelled systems with and without installing CO_2-selective membrane separator was studied in this work. The influence of inlet steam to carbon ratio to the reformer on the performance, for the system without CO_2-selective membrane separator, was firstly. The increase of the steam to carbon ratio decreases SOFC, system electrical, thermal efficiencies. Thus, the steam to carbon ratio of 1 was fixed for analysis of system with CO_2-selective membrane separator. The amount of permeated CO_2 increases with increasing the membrane area. The SOFC and thermal efficiencies are elevated as increasing the membrane area. On the other hand, the system electrical efficiency decreases due to the increment of H_2 loss in the retentate side. When comparing the both systems, the SOFC and thermal efficiencies of the system with CO_2-selective membrane separator are higher, whereas its system electrical efficiency is lower.

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