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SOFC Running on Steam Reforming of Biogas: External and Internal Reforming

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In this work, two approaches of SOFC operation fuelled by biogas are considered: one where the endothermic steam reforming and electrochemical reaction are operated in different units (external reforming SOFC) and another where biogas is introduced to the SOFC stack and directing reformed on the anode side (internal reforming SOFC). The model of SOFC system is designed and developed using Aspen Plus simulator software. Equilibrium gas composition obtained from steam reforming reaction can be calculated based on Gibbs free energy minimization method. Electrochemical equations taking into account all voltage losses (activation, ohmic and concentration lo sses) are written in a calculator block by Fortran code. Effect of operating conditions, i.e. temperature, pressure and steam to carbon molar ratio on SOFC performances is examined. From the simulation results, it was found that under the same operation conditions (steam to carbon molar ratio of 0.5, SOFC temperature of 1,173 K and SOFC pressure of 3 atm), the internal reforming SOFC has higher electrical efficiency (24 %) than external reforming SOFC (85.67 %). However, when the carbon dixide emission is considered, the simulation result reveals that the anode exhuast gas of the internal reforming SOFC has higher amount of carbon dioxide (7.4 %) compared with that of the external reforming SOFC (1.4 %(.

1. Introduction

Solid oxide fuel cell (SOFC) has attracted considerable interest for distributed power sources due to its high efficiency. The main advantage of SOFC over a low temperature fuel cell is a tolerance to impurities and the flexibility of using various fuel types, e.g., methane, methanol, ethanol and biogas. This implies that not only pure hydrogen but also any hydrocarbon fuels can be used as fuel for an SOFC. Among various types of fuels, biogas is considered as an alternative and environmental-friendly fuel. Biogas is a renewable fuel which can be produced through from the anaerobic digestion process of the residual biomass, such as municipal sewage, forestry residues, animal waste and organic matter (Saebea et al., 2014) and further in (Santos et al., 2016). However, biogas is needed to be reformed into hydrogen-rich gas required for the electrochemical reaction on the anode side. In general, there are two main approaches to incorporate a fuel processor in the SOFC operation: external reforming and internal reforming. The former approach uses an external reformer to convert biogas into hydrogen which is then fed to the SOFC at the anode side. For the latter approach, biogas is directly fed and reformed on the anode side of SOFC. In the internal reforming operation, because the reforming and electrochemical reaction can be carried out within a single unit, this operation has more benefit in terms of energy consumption. The direct conversion of fuel into electricity results in an improved overall efficiency. However, the carbon may be formed on the anode material due to the complete internal reforming of fuel in SOFC (Liso et al., 2016), resulting in the loss of cell performance and poor durability. Moreover, the

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unbalance between endothermic and exothermic reactions should be concerned because the large thermal gradient causes the mechanical failure of the SOFC stack (Chatrattanawet et al., 2014). Although an integrated system of an external reformer and SOFC has lower system efficiency, this approach presents some attractive features. Firstly, the SOFC always provides a high temperature exhaust gas which can be used for other heat-requiring units in the SOFC system, leading to a decrease in the external energy demand and this can improve the overall efficiency. Secondly, the integrated system offers an opportunity for heat integration and control design.

Recently, the investigation of direct internal reforming of biogas in SOFC has been found in the literature. Lanzini and Leone (2010) investigated the behaviour of planar SOFC fed by a biogas. When a biogas is fed to the cell directly without the addition of a reforming agent, it was found that a biogas CH_4/CO_2 in a 60/40 volumetric proportion generates carbon-deposition over the whole temperature range of SOFC operating conditions. In addition, they tested the addition of air, steam and carbon dioxide to produce a direct internal reforming of methane onto the anode surface. The result showed that the air addition can prevent carbon-deposition. However, since this approach is still facing aforementioned problems, there are a few studies proposed the power system consisting of an external reformer of biogas and SOFC. Piroonlerkgul et al. (2008) investigated the performance of biogas-fed SOFC systems with different reforming agents (steam, air and combined air/steam) based on thermodynamic analysis. Their results revealed that steam is the most suitable reforming agent in this study as the steam-fed SOFC has much higher power density than the air-fed SOFC although its electrical efficiency is slightly lower. To improve the electrical efficiency of the steam-fed SOFC, the biogas split option was proposed. It was found that a higher electrical efficiency can be achieved.

Because these two approaches have noticeable different advantages and disadvantages, this work aims to compare two approaches in terms of system efficiency and environmental effect. The favourable operating condition of SOFC incorporating with different approaches of reforming is identified.

2. Process description

The flowsheet of an integrated system of an external reformer and SOFC is design in Aspen Plus simulator, as shown in Figure 1. The biogas feed (FEED), consisting of 60 % methane and 40 % carbon dioxide, and water stream (WATER) is separately fed through compressor (COMP) and heater (HEATER) to reach the specified operating condition. In the reformer (REFORMER), biogas reacts with steam through steam reforming reaction in which the hydrogen and carbon monoxide can be generated. The obtained carbon monoxide is further reacted with the residual steam through water gas-shift reaction and thus, the production of carbon dioxide and hydrogen can be observed. In this work, RGibbs reactor is used to calculate the product composition under the conditions that minimize of Gibbs free energy. The components consisting of CH_4, CO_2, H_2O, CO, and H_2 are considered as the possible species in steam reforming of methane. Then, the synthesis gas (SYNGAS), which is composed of mainly hydrogen, is introduced into the anode side of SOFC (ANODE) as modelled by RGibbs reactor. At the anode side, the remaining methane can be reformed via steam reforming, carbon monoxide can be shifted via water gas-shift reaction and hydrogen is oxidized via electrochemical reaction. While the stream ‘SYNGAS’ is fed to the anode, the stream ‘AIR’ which is compressed (COMPR3) and preheated (HEATER3) is simultaneously fed to the cathode side (CATHODE). For the cathode side, it is modeled as Sep to separate out the oxygen required for the electrochemical reaction. Hydrogen produced from the steam reforming and water gas-shift reactions and in the synthesis gas reacts with oxygen to generate the electrical power and steam via electrochemical reaction. It is noted that since the ions transfer cannot be modelled in Aspen Plus and thus, the overall electrochemical reaction (H_2 + 0.5 O_2 (H_2O) is used instead of the cell half reactions (Doherty et al., 2010).

In case of SOFC operated with internal reforming, as seen in Figure 2, the preheated biogas and water stream are directly fed into the anode side of SOFC. When the air stream is fed in to the cathode side, the steam reforming, water gas-shift and electrochemical reactions are simultaneously carried out. The possible reactions in the SOFC operation are shown in Table 1.

3. SOFC model

The SOFC model is based on the main following assumptions: (1) model is zero-dimensional; (2) isothermal and steady state operation are considered; (3) pressure drops are neglected; (4) reforming and shift reactions reach chemical equilibrium; and (5) only H_2 is electrochemically oxidized. Electrochemical model described the relationship of fuel conversion to electricity is used to predict the performance of SOFC. The open-circuit voltage which is the maximum voltage of SOFC can be determined by the Nernst equation. However, the operating cell voltage is always lower than open-circuit voltage since there are three main voltage losses occurred in real operation: activation loss, ohmic loss and concentration loss. The electrochemical equations of SOFC used in this study were reported in our previous work (Patcharavorachot et al., 2008).

Table 1: Possible reactions in the SOFC operation

Steam methane reforming	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	(1)
Water-gas shift	$CO + H_2O \leftrightarrow CO_2 + H_2$	(2)
Electrochemical	$H_2 + 0.5O_2 \leftrightarrow H_2O$	(3)

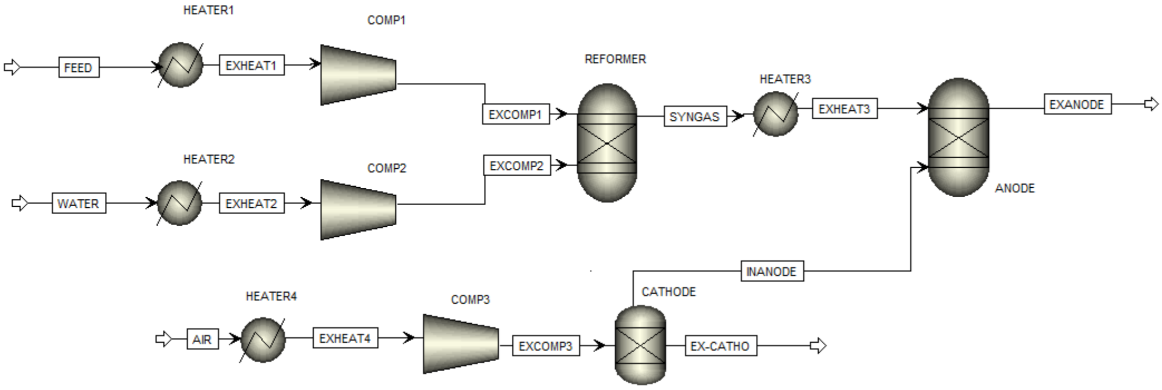

Figure 1: Flowsheet of the external reforming SOFC

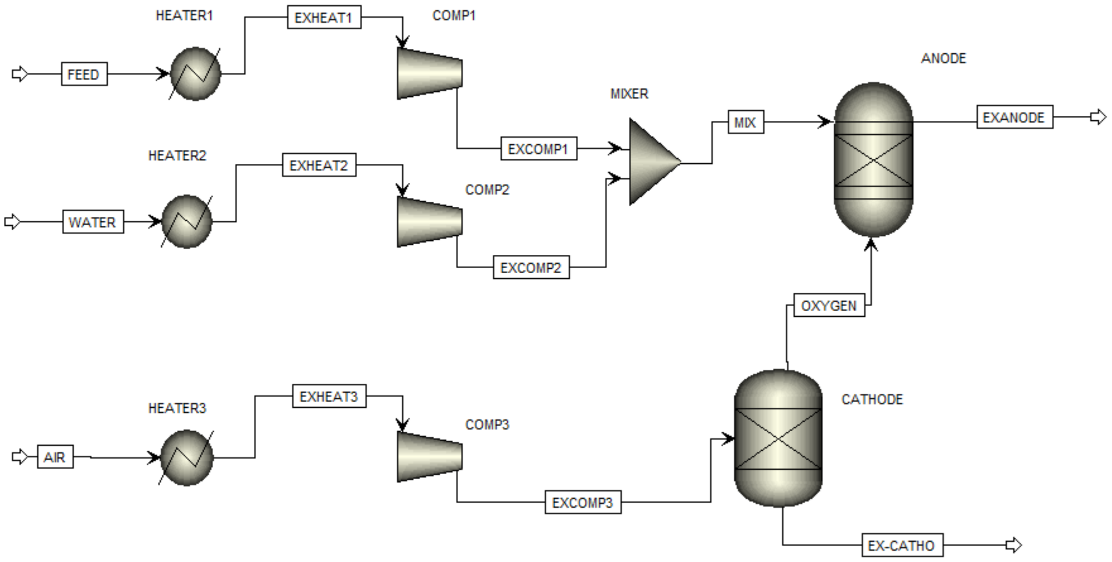

Figure 2: Flowsheet of the internal reforming SOFC

4. Methodology

In this work, the thermodynamic calculation is performed by using AspenPlus^{TM}. For the external reforming SOFC, the calculation consists of two steps. Firstly, for a given operating conditions of reformer (temperature (T_{Ref}), pressure (P_{Ref}) and steam-to-carbon molar ratio (S/C)), the equilibrium compositions in the reforming process can be determined by using Gibbs free energy minimization method. The molar flow rate of CH_4 (n_{CH4}), CO (n_{CO}) and H_2 (n_{H2}) obtained from reforming process is further used as the input parameters for the SOFC calculation. The electrochemical equations is performed by a calculator block in the Aspen Plus flowsheet. Finally, when the operating conditions of SOFC (temperature (T_{SOFC}), pressure (P_{SOFC}) and current density (i_{SOFC})) and physical parameters of cell components are specified, the cell voltage (V), power density (P_W) and SOFC electrical efficiency (ε_{SOFC}) are determined as Eqs(4) and (5):

$$P_w = i_{SOFC}V \tag{4}$$

$$\varepsilon_{EX\text{-}SOFC} = \frac{P_w}{n_{CH_4}LHV_{CH_4} + n_{H_2}LHV_{H_2} + n_{CO}LHV_{CO}} \times 100\% \tag{5}$$

$$\varepsilon_{IN\text{-}SOFC} = \frac{P_w}{n_{CH_4}LHV_{CH_4}} \times 100\% \tag{6}$$

where A is area of SOFC and LHV_{CH_4} LHV_{H_2} and LHV_{CO} represent the lower heating value of methane, hydrogen and carbon monoxide, respectively.

Because the reforming reaction is occurred within the SOFC stack for the internal reforming operation, there is only calculation in the SOFC. In this case, the operating conditions of SOFC and physical parameters of cell components are used to compute the cell voltage and power density (Eq(4)). In the internal reforming operation, SOFC electrical efficiency can be calculated from Eq(6). The anode exhaust gas can be determined based on Gibbs free energy minimization method.

5. Results and discussion

Under the nominal operating condition, the reformer is operated at T_{Ref} = 973 K, P_{Ref} = 1 atm and S/C = 0.5 whereas the SOFC is set the operating conditions as T_{SOFC} = 1,073 K, P_{SOFC} = 1 atm and i_{SOFC} = 5,000 A/m^2. It is noted that values of material property parameters for the SOFC are the values reported in the literature our previous work (Patcharavorachot et al., 2008). In this work, the thickness of anode, electrolyte and cathode are 500, 20 and 50, respectively.

5.1 External reforming SOFC

5.1.1. Reformer operating conditions

Figure 3(a) presents the performance of SOFC in terms of the power density and SOFC efficiency at different reformer temperature. The simulation results indicate that higher reformer temperature operation can improve power density while the SOFC efficiency decreases. Increase of reformer temperature leads to an increase in hydrogen product. This is because reforming reaction, as a reversible and endothermic reaction, can be shifted to the product side (right hand side of reaction) at higher temperature. When hydrogen is more fed into the SOFC, the open-circuit voltage increases and thus, higher cell voltage is expected. As a result, the power density can be enhanced. However, the increment of reformer temperature results in a decrease in SOFC efficiency. Although the total molar flow rate of fuel (methane + carbon monoxide + hydrogen) is higher with increasing reformer temperature, the current density is fixed as a constant. This implies that higher amount of fuel is fed into the SOFC whereas the rate of current production is constant and thus, the SOFC efficiency is reduced. In this study, the reformer temperature of 973 K is used in the next study because this operation can provide a good compromise on power density and SOFC efficiency.

Figure 3(b) demonstrates the effect of S/C molar ratio on power density and SOFC efficiency. In general, higher S/C molar ratio can achieve the equilibrium limitation of steam reforming reaction which results in an increase in hydrogen production. From the simulation result, it is found that the mole fraction of hydrogen decreases with increasing S/C molar ratio because the unreacted steam dilutes hydrogen product. When the synthesis gas with the diluted hydrogen concentration is fed to the SOFC stack, the performance of SOFC in terms of cell voltage, power density and SOFC efficiency are reduced. Thus, the S/C molar ratio is selected to use in the next study.

5.1.2. SOFC operating conditions

The effect of SOFC temperature, varied from 1,073 to 1,273 K, on power density and SOFC efficiency is investigated, as shown in Figure 4. As an expectation, SOFC operated at higher temperature has a significant influence on power density and SOFC efficiency. An increase in the SOFC temperature causes a decrease in the ohmic and activation losses. Although the open-circuit voltage and concentration loss increase with increasing SOFC temperature, they have a slight impact compared with decreases of ohmic and activation losses. As a result, the cell voltage is higher. According to Eqs(4) and (5), when the cell voltage is higher, the power density and SOFC efficiency increase.

Figure 4 also demonstrate s the power density and SOFC efficiency as a function of SOFC pressure. The simulation results show that an increase in pressure from 1 to 5 atm can improve both the power density and

SOFC efficiency. When the SOFC pressure is higher, the open-circuit voltage increases. In addition, the reactant is easily diffused into the reaction site at to the interface under high pressure operation and therefore, the concentration loss is lower. This in turn increases in cell voltage, power density and SOFC efficiency.

Although a higher SOFC performance can be obtained when SOFC operated at elevated temperature and pressure, the simulation results indicate that SOFC should be operated at temperature of 1,173 K and pressure of 3 atm to optimize both SOFC performance and capital and operating costs.

5.2 Internal reforming SOFC

In this study, the effect of three operating conditions, i.e., S/C molar ratio, SOFC temperature and SOFC pressure, on the cell performance is examined. Figure 5 presents the power density and SOFC efficiency of internal reforming SOFC as a function of S/C ratio. It can be seen that when an increase in S/C molar ratio, the power density and SOFC efficiency are decreased. The result of power density has the same trend in case of external reforming SOFC because higher amount of steam fed into the SOFC will dilute the hydrogen concentration and thus, the cell voltage as well as power density are reduced. In this case, the inlet molar flow rate of methane is fixed, when the power density is lower and thus, the reduction of SOFC efficiency is presented.

When the impact of SOFC temperature and SOFC pressure on the cell performance is determined, it can be found that the results of internal reforming SOFC have a same trend with external reforming. This means that increasing operating temperature and pressure can improve both power density and SOFC efficiency.

Under the same operating conditions with the external reforming, the SOFC operated with internal reforming can provide the power density of 0.45 W cm^{-2} and SOFC efficiency of 96.24 %. Compared with the external reforming SOFC, it can be seen that the SOFC efficiency of internal reforming SOFC is superior to that of external reforming. This is due to the fact that the there is one step of fuel conversion to electricity in the internal reforming SOFC and thus, the SOFC efficiency is more improved. In order to compare in the environmental effect, the carbon dioxide obtained from the anode exhaust gas of each reforming operation is considered. The result indicates that the anode exhuast gas of the internal reforming SOFC has higher amount of carbon dioxide (7.4 %) compared with that of the external reforming SOFC (1.4 %).

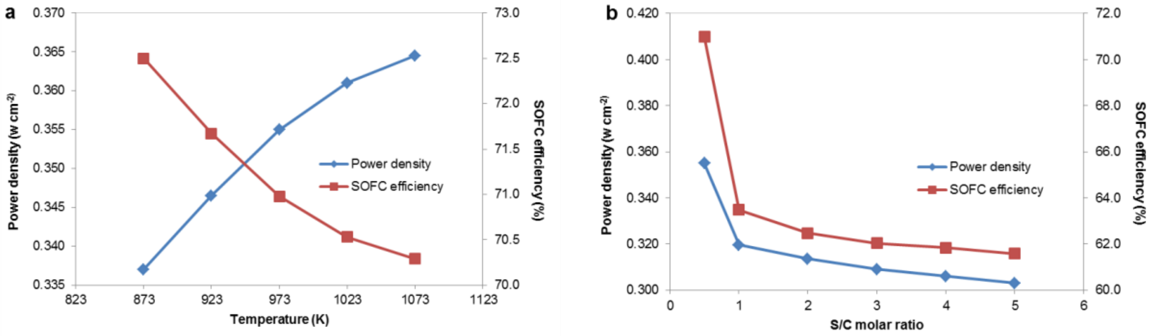

Figure 3: Power density and SOFC efficiency as a function of: (a) reformer temperature and (b) S/C molar ratio

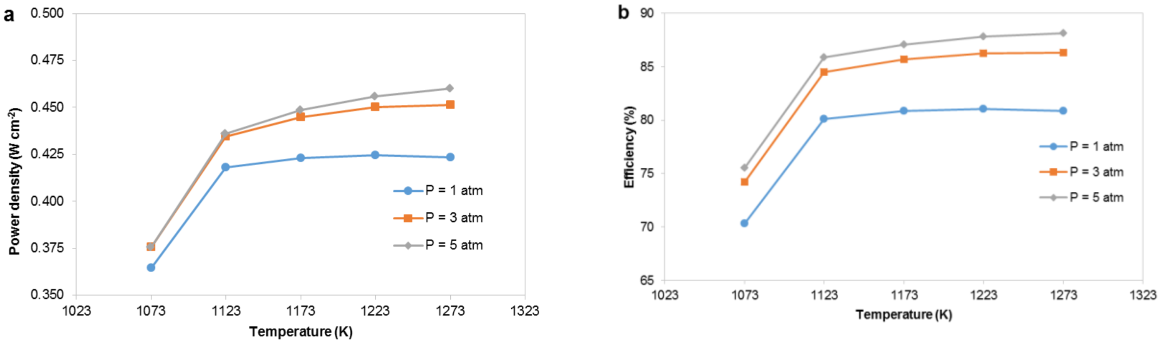

Figure 4: Effect of temperature and pressure of SOFC: (a) power density and (b) SOFC efficiency

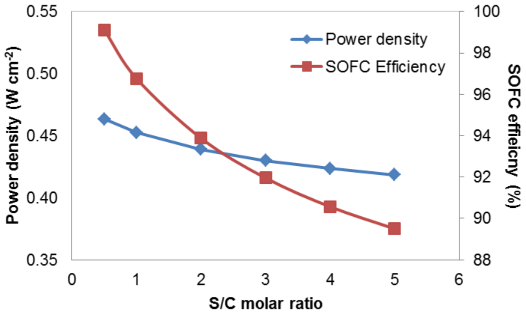

Figure 5: Effect of S/C molar ratio in the internal reforming SOFC on power density and SOFC efficiency

6. Conclusions

The comparative study of different reforming SOFC (external and internal reforming) is presented in this study. Thermodynamic calculation based on the Gibbs free energy minimization is used to compute the equilibrium gas composition. Electrochemical model which includes all voltage losses is implemented in a calculator block by Fortran code. The performance of SOFC in terms of power density and SOFC efficiency is evaluated with respect to changes in operating conditions of reformer (in case of external reforming) and SOFC (both case). It is found that increasing reformer temperature, SOFC temperature and SOFC pressure have significant influence on the power density and SOFC efficiency. As expected, the efficiency of internal reforming operation is higher than that of external one. However, when the carbon dioxide emission is considered, it is found that the internal reforming SOFC relases higher amount of carbon dioxide than the external reforming SOFC

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