

VOL 57, 2017



DOI: 10.3303/CET1757017

Guest Editors: Sauro Pierucci, Jiří Jaromír Klemeš, Laura Piazza, Serafim Bakalis Copyright © 2017, AIDIC Servizi S.r.l. **ISBN** 978-88-95608- 48-8; **ISSN** 2283-9216

Design and Evaluation of the Sorption Enhanced Steam Reforming and Solid Oxide Fuel Cell Integrated System with Anode Exhaust Gas Recirculation for Combined Heat and Power Generation

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Solid oxide fuel cell (SOFC) is an electrochemical device for power generation with high efficiency and low environmental impact. Due to a high-temperature operation of SOFC, useful heat can be recovered to enhance its system efficiency. Regarding the environmental concern, bio-oil, the renewable liquid fuel, can be applied to SOFC system. In this study, the SOFC integrated with a steam reforming of bio-oil is considered. A sorption enhanced reforming process is studied for the production of high purity hydrogen for SOFC, and the anode gas recirculation in the SOFC system is proposed for the system improvement. Modeling of such an integrated process is performed using Aspen Plus simulator. As heat and power are generated from the SOFC system, the effect of key design parameters; fuel utilization and recirculation ratio of the anode gas, on a heat-to-power ratio is analyzed. The system performance regarding to the electrical and thermal efficiencies is also evaluated. The results show that increasing the anode recirculation ratio increases the combined heat and power (CHP) performance, but increasing the fuel utilization decreases the thermal efficiency. It is also found that the appropriate range of heat-to-power ratio of the system varies from 0.24 to 0.89.

1. Introduction

At present, the development of power generation technologies with high efficiency and low environmental impact is required. Solid oxide fuel cell (SOFC) is a highly efficient energy conversion which directly converts fuel to electricity via electrochemical reactions. Also, it is the quite technology with low CO₂ emissions (Huang and Goodenough, 2009). Due to its high-temperature operation, SOFC is the type of fuel cell that is suitable for combined heat and power and trigeneration applications. Useful thermal energy production can be used in cogeneration purposes, such as steam and domestic hot water production. However, heat and power consumption are unstable, which usually changes in demand. Consequently, a parameter design of the SOFC system to response in variable heat and power ratio is interesting (Chutichai and Arpornwichanop, 2015).

Typically, fossil fuel is usually used as a feedstock to produce hydrogen for SOFC. It is non-renewable fuel and the use of this fuel type causes high CO₂ emission. Using the renewable fuel can mitigate the environmental issues. Bio-oil aqueous fraction is the renewable liquid fuel from a biomass fast pyrolysis process. Because of the low hydrogen to carbon ratio of bio-oil, steam reforming of bio-oil produces low purity hydrogen, reducing the SOFC efficiency (Trane et al., 2012). A sorption enhanced steam reforming process can be applied to the SOFC system to produce high purity hydrogen supplied to the SOFC. However, the sorption enhanced steam reforming process requires a sorbent generator, the endothermic reactor which requires high energy consumption (Wess et al., 2015). As the high-temperature waste heat is generated by SOFC, this useful energy can be supplied to the regenerator. In addition, since bio-oil aqueous fraction is a

liquid fuel which needs high energy to vaporize and preheat the bio-oil feed at the required operating temperature, the recirculation of an anode exhaust gas from SOFC to the reformer can decrease a demand of fresh steam and energy requirement (Saebea et al., 2012).

Previous researchers studied the effect of changes in process parameters on the heat-to-power ratio of the power systems applying for the residential sector. Most of the studies focused on the conventional steam reforming process and SOFC integrated system and provided the operating range of heat-to-power ratio (Lamas et al., 2013; De Arespacochaga et al., 2015). However, the heat-to-power ratio is varied with the studied process and fuel sources. Thus, the objective of this study is to investigate the effect of key operating parameters, i.e., fuel utilization and anode exhaust gas recirculation, on the heat-to-power ratio of the sorption enhanced steam reforming and SOFC integrated system using bio-oil fuel. The performance of the proposed SOFC process regarding to the electrical and thermal efficiencies and the combined heat and power efficiency is also considered.

2. Process description

In this study, a sorption enhanced steam reforming (SESR) and solid oxide fuel cell (SOFC) integrated process with anode exhaust gas recirculation for a combined heat and power (CHP) generation is studied. A bio-oil aqueous fraction, a carbohydrate-derived fraction of bio-oil which produces from the biomass fast pyrolysis process, is a feedstock for the CHP system. The bio-oil aqueous fraction consists of a mixture of oxygenated compounds, such as carboxylic acids, aldehydes, ketones, alcohols, and phenols (Yao et al., 2014). Because of the complex components of bio-oil, the major compositions of the mixture are selected as a model compounds of the bio-oil aqueous fraction feedstock. The bio-oil from wheat stalk biomass, which has a high heating value of 19.3 MW/kg is used in this work (Liu et al., 2013). The highest component of the bio-oil aqueous fraction is acetic acid by 55.6 % (Table 1). Under standard conditions of the combined heat and power system, bio-oil is fixed at 1 kmol/h, 80 % of bio-oil feedstock is fed into the reformer, and the rest is directly fed into an afterburner to generate useful heat. In this study, the SESR and SOFC integrated system with an anode exhaust gas recirculation is simulated by the process simulation program (Aspen Plus) and the Peng-Robinson method is selected to predict thermodynamic properties. The minimization of the Gibb's free energy is used to calculate the equilibrium compositions of the product stream. Figure 1 shows the simulation model of the SESR and SOFC integrated system with anode exhaust gas recirculation. The process consists of a fuel processor (sorption enhanced steam reformer and regenerator), a solid oxide fuel cell, and an afterburner.

The process starts with a fuel processing section. Steam and bio-oil are vaporized before they are fed into the sorption enhanced steam reformer which is the fuel processor to produce hydrogen. In this work, the steam to fuel (S/F) ratio is fixed at 6, and excess of CaO are used. The operating conditions of the SESR are 600 °C and 1 bar. Steam reforming, water-gas shift, and carbonation reactions occur within this reactor. Gaseous products are fed into SOFC, while the solid of CaCO₃, the product of the carbonation reaction, is fed into the regenerator and regenerated to CaO. To simulate the SESR and the regenerator, two equilibrium reactors (RGibbs reactor model in Aspen Plus) are used to represent the solid $CaCO_3$ from gas products (CYCLONE1) and solid CaO from

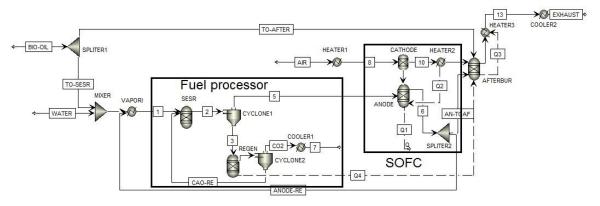


Figure 1: Schematic of the sorption enhanced steam reforming and SOFC integrated system with anode exhaust gas recirculation

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Table 1: Bio-oil model compounds (Yao et al., 2014)

Model compounds	wt. (%)
Acetic acid	55.6
Hydroxy acetaldehyde	18.0
Furfural	8.0
Acetaldehyde	4.0
Hydroxy acetone	8.0
Guaiacol	4.0
Dextrose	2.4

Table 2: Design parameter and operating conditions of the CHP system

Parameters	Value
Bio-oil (kmol/h)	1
S/F ratio (-)	6
SESR temperature (°C)	600
Regenerator temperature (°C)	900
SOFC temperature (°C)	800
Fuel utilization	0.85
Cell length (m)	0.4
Cell width (m)	0.1
Number of cell	2500
Anode recirculation ratio (-)	0.4
SOFC thermal losses (%)	2
Afterburner temperature (°C)	1000

CO₂ (CYCLONE2).The operating temperature of the regenerator is fixed at 900 °C. Some useful heat from SOFC and afterburner are supplied to this reactor for an endothermic calcination reaction as an indirect heat. Table 2 presents the operating parameters of the SESR and SOFC integrated system with anode exhaust gas recirculation.

In SOFC section, hydrogen-rich gas from the fuel processing section is fed into the anode side of the SOFC, while air is preheated and fed into the cathode side. At the cathode, oxygen ion is produced from the reduction reaction and transferred to the anode side through the electrolyte. Hydrogen fuel at the anode is reacted with oxygen ion via an oxidation reaction to generate steam and electrons. Steam and unreacted fuel are left from the anode side whereas electrons are transferred to the cathode via an external circuit for the reduction reaction resulting in electrical generation. In the simulation, a separator (CATHODE) is used to simulate the cathode. The certain amount of oxygen determined from the electrochemical reaction and fuel utilization is separated in the CATHODE, and moves to the anode, which is represented by the RGibbs reactor model (ANODE). The oxidation of H₂, water-gas shift of CO, and steam reforming of CH₄ are occurred at the anode. In this work, air flow rate is varied to keep the SOFC temperature constant at 800 °C. In addition, it is assumed that SOFC has an energy loss of 2 %. The fuel utilization is varied from 0.6 to 0.9 to investigate its effect on the CHP system performance. To calculate the electricity, the electrochemical model equations are employed as follows (Aguiar et al., 2004):

$$E^{ocv} = E^{0} - \frac{RT}{2F} \ln \left(\frac{p_{H_2O,f}}{P_{H_2} P_{O_2,a}^{0.5}} \right)$$
(1)

$$V = E^{ocv} - (\eta_{ohm} + \eta_{act} + \eta_{conc})$$
⁽²⁾

 $\eta_{ohm} = j \times R_{ohm} \tag{3}$

$$\eta_{act,electrode} = \frac{RT}{F} \sinh^{-1} \left(\frac{j}{j_0} \right)$$
(4)

$$\eta_{conc} = \frac{RT}{2F} \ln \left(\frac{p_{H_2O,TPB} p_{H_2,f}}{p_{H_2O,f} p_{H_2,TPB}} \right) + \frac{RT}{4F} \ln \left(\frac{p_{O_2,a}}{p_{O_2,TPB}} \right)$$
(5)

Eq(1) is the Nernst equation used to determine the theoretical open-circuit voltage (E^{ocv}). However, the actual cell voltage (V) is lower than the theoretical open-circuit voltage because of ohmic losses (η_{ohm}), activation

overpotentials (η_{act}), and concentration overpotentials (η_{conc}) (Eq(2)). The ohmic losses are loss due to the electrode and electrolyte resistances which can be calculated by Eq(3). The activation overpotentials are caused by the part of the energy used for chemical reaction (Eq(4)). Eq(5) is used to calculate the concentration overpotentials which are the voltage losses due to the mass transfer of the products and reactants.

The anode exhaust gas consisting mainly of steam and unreacted fuel is divided into two streams; ones are fed into an afterburner, and the others are recycled into the fuel processor. The anode recirculation ratio is varied to study its effect on the CHP system. To simulate the afterburner, the RGibbs reactor model (AFTERBUR) is used to represent the combustor which is operated at a temperature of 1000 °C and 1 bar, and the complete combustion is assumed (Table 2).

The model of the SESR and SOFC integrated system was validated with the experimental results. The model prediction and experimental data of the sorption enhanced steam reforming reactor and SOFC are in good agreement (Wiranarongkorn and Arpornwichanop, 2017).

3. CHP performance indicator

In order to evaluate the performance of SOFC and the overall process, the following parameters are used to analyze the simulation results.

$$Heat-to-power \ ratio = \frac{Useful \ heat \ produced}{Electric \ produced}$$
(6)

$$Electrical \ Efficiency \ (\%) = \frac{Electric \ produced}{Bio-oil \ flow \ rate \times HHV} \times 100$$
(7)

Thermal Efficiency (%) =
$$\frac{Useful heat produced}{Bio-oil flow rate \times HHV} \times 100$$
 (8)

$$CHP \ Efficiency \ (\%) = \frac{Electric \ produced + Useful \ heat \ produced}{Bio-oil \ flow \ rate \times HHV} \times 100$$
(9)

4. Results and discussion

4.1 Fuel utilization

To study the variation of heat-to-power ratio of the SESR and SOFC integrated system with anode exhaust gas recirculation, the fuel utilization with different anode gas recirculation ratio is varied. Figure 2 shows the effect of a variation of fuel utilization on the performance of SESR and SOFC integrated system when the system operates with anode recirculation ratio of 0.4. The results show that increasing the fuel utilization increases the electrical efficiency; on the other hand, it decreases the thermal efficiency. This is because higher hydrogen is reacted to generate electricity and heat. However, air is highly needed to keep the SOFC temperature constant at 800 °C, leading to the need of higher energy for air preheating (Figure 3). Consequently, the CHP efficiency slightly decreases with fuel utilization from 70 to 68 % when the fuel utilization increases from 0.6 to 0.9. Regarding the heat-to-power ratio as shown in Figure 4, the variation of fuel utilization highly impacts the heat-to-power ratio drops from 0.73 to 0.34 because of the electricity production increases, but useful heat decreases at the higher fuel utilization as mentioned above.

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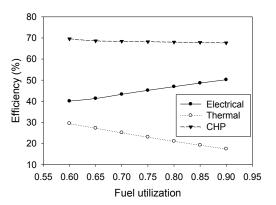
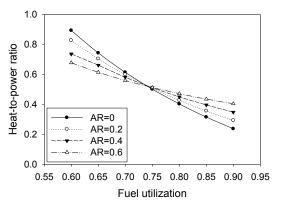


Figure 2: Effect of the variation of fuel utilization on the electrical and thermal efficiencies, and the CHP efficiency



4.0 3.8 Excess air ratio 3.6 3.4 AR=0 AR=0.2 3.2 AR=0.4 AR=0.6 3.0 0.60 0.65 0.70 0.75 0.80 0.55 0.85 0.90 0.95 Fuel utilization

Figure 3: Effect of the variation of fuel utilization in different anode recirculation ratio (AR) on excess air ratio

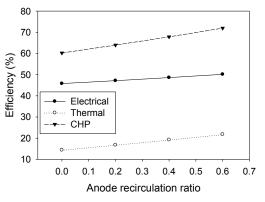


Figure 4: Effect of the variation of fuel utilization in different anode recirculation ratio (AR) on heat-to-power ratio

Figure 5: Effect of the variation of anode recirculation ratio on the electrical and thermal efficiencies, and the CHP efficiency

4.2 The variation of anode recirculation ratio

Figure 5 presents the effect of a variation of anode recirculation ratio on the performance of SESR and SOFC integrated system when the system operates at fuel utilization of 0.85. The results indicate that an increase in the anode recirculation ratio slightly increases the electrical efficiency because higher unreacted fuel is recirculated for the electrochemical reaction within the SOFC. When considering the thermal efficiency of the CHP system, it is found that the thermal efficiency sharply increases with anode recirculation ratio. This is because the higher amount of heat and steam is recirculated into fuel processor, so the energy consumption for feed steam preheating dramatically decrease at higher anode recirculation ratio. From the electrical and thermal trend, CHP efficiency sharply increases from 60 % without anode exhaust gas recirculation to 72 % with anode exhaust gas recirculation of 0.6. When regard the effect of a variation of anode recirculation ratio on heat-to-power ratio (Figure 4), the simulation results show that the ratio of heat-to-power steady increases from 0.31 to 0.43 with anode exhaust gas recirculation ratio at fuel utilization of 0.85 because increasing of anode exhaust gas recirculation more beneficially affect heat generation than the electrical production. However, at fuel utilization lower than 0.75, increasing of anode exhaust gas recirculation decreases heat-topower ratio. At fuel utilization of 0.6, heat-to-power ratio decreases from 0.89 to 0.68. This is because the amount of unreacted fuel in the anode exhaust gas is higher than the amount of hot steam resulting in the higher fuel concentration in the inlet stream of SOFC to produce higher electric production. Consequently, it is concluded that higher anode recirculation ratio increases the CHP efficiency, but to achieve the variable heatto-power ratio depends on the composition of the anode exhaust gas recycling. In addition, because high energy consumption is required for the regeneration and liquid bio-oil vaporization of the SESR and SOFC integrated system, the range of the variation of heat-to-power ratio of this system is lower than that of the conventional CHP system (De Arespacochaga et al., 2015; Liso et al., 2011)

5. Conclusions

In this study, a sorption enhanced steam reforming (SESR) and solid oxide fuel cell (SOFC) integrated system with anode exhaust gas recirculation using bio-oil feed stock is investigated. The key operating parameters of the SOFC system such as fuel utilization and anode recirculation ratio, are varied to examine the performance of the combine heat and power (CHP) generation and the variation of heat-to-power ratio. The results reveal that increase of the fuel utilization enhances the electrical efficiency but reduces the thermal efficiency. However, the CHP efficiency slightly decreases with fuel utilization. The anode recirculation ratio affects the system electrical, thermal efficiency as well as the CHP efficiency. When SOFC is run at low fuel utilization, an increase in the anode recirculation reduces the heat-to-power ratio, whereas an opposite trend is observed when it is operated at high fuel utilization. In this study, the heat-to-power ratio of the SESR and SOFC integrated system with anode exhaust gas recirculation is in a range of 0.24 to 0.89.

Acknowledgments

Support from The Asahi Glass Foundation and The Chulalongkorn Academic Advancement into Its 2nd Century Project is gratefully acknowledged. K. Wiranarongkorn would like to thank The Royal Golden Jubilee Ph.D. Program (The Thailand Research Fund).

Reference

- Aguiar P., Adjiman C.S., Brandon N.P., 2004, Anode-supported intermediate temperature direct internal reforming solid oxide fuel cell. I: model-based steady-state performance. Journal of Power Sources. 138,120-136.
- Chutichai B., Arpornwichanop A., 2015, Performance improvement of biomass gasification and PEMFC integrated system–design consideration for achieving high overall energy efficiency and power-to-heat ratio variation Chemical Engineering Transactions. 43, 1501-1506.
- De Arespacochaga N., Valderrama C., Peregrina C., Mesa C., Bouchy L., Cortina J.L., 2015, Evaluation of a pilot-scale sewage biogas powered 2.8 kWe solid oxide fuel cell: Assessment of heat-to-power ratio and influence of oxygen content. Journal of Power Sources. 300, 325-335.
- Huang K., Goodenough J.B., 2009, Solid Oxide Fuel Cell Technology: Principles, Performance and Operations .Woodhead Publishing Limited, Cambridge
- Lamas J., Shimizu H., Matsumura J., Senda J., 2013, Fuel consumption analysis of a residential cogeneration system using a solid oxide fuel cell with regulation of heat to power ratio. International Journal of Hydrogen Energy. 38, 16338-16343.]
- Liso V., Zhao Y., Brandon N., Nielsen M.P., Kær S.K., 2011, Analysis of the impact of heat-to-power ratio for a SOFC-based mCHP system for residential application under different climate regions in Europe. International Journal of Hydrogen Energy. 36, 13715-13726
- Liu S., Chen M., Hu Q., Wang J., Kong L., 2013, The kinetics model and pyrolysis behaviour of the aqueous fraction of bio-oil. Bioresource Technology. 129, 381-386.
- Saebea D., Patcharavorachot Y., Arpornwichanop A., 2012, Analysis of an ethanol-fuelled solid oxide fuel cell system using partial anode exhaust gas recirculation. Journal of Power Sources. 208, 120-130.
- Trane R., Dahl S., Skjøth-Rasmussen M.S., Jensen A.D. 2012, Catalytic steam reforming of bio-oil. International Journal of Hydrogen Energy. 37, 6447-6472.
- Wess R., Nores-Pondal F., Laborde M., Giunta P., 2015, Single stage H2 production, purification and heat supply by means of sorption-enhanced steam reforming of glycerol. A thermodynamic analysis. Chemical Engineering Science. 134, 86-95.
- Wirananrongkorn K., Arpornwichanop A., 2017, Analysis of the Ca-looping sorption-enhanced steam reforming and solid oxide fuel cell integrated process using bio-oil. Energy Conversion and Management. 134, 156-166.
- Yao D., Wu C., Yang H., Hu Q., Nahil M.A., Chen H., Williams P.T., 2014, Hydrogen production from catalytic reforming of the aqueous fraction of pyrolysis bio-oil with modified Ni-Al catalysts. International Journal of Hydrogen Energy. 39, 14642-14652.

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