An LCA and energy analysis of a biomass integrated-pyrolysis gasification/SOFC system with H₂S removal

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Abstract. Fuel cell power systems are considered attractive for their potential for mitigating climate change. Here, the fuel is assumed to be synthesized through an indirect pyrolysis gasification process, and the integrated gasification SOFC system is considered in this study. In the performance of SOFC, the impurities (e.g., H₂S) in a fuel affect the system, i.e., the voltage of a cell drops. Regarding the removal of impurities, conditions besides the species of adsorbent, like temperature and pressure, must be considered. Therefore, we compared the following two adsorbents in terms of the operational and environmental performances: non-recyclable CeO₂ (high temperature) and recyclable Hydroxyl Aluminum Silicate Clay (HAS-Clay) (low temperature). Moreover, we estimated energy and exergy efficiencies, and life cycle assessment impacts on both adsorbents. The total exergy efficiencies were 35.6 % for CeO₂ and 33.0 % for HAS-Clay. This implies that 19 recycling cycles with the use of HAS-Clay are necessary to obtain the advantage for the CeO₂ case in terms of abiotic depletion potential which is one of the impact categories.

1. Introduction

In recent years, fuel cell technologies have been considered a countermeasure against climate change. In this context, solid oxide fuel cells (SOFC) are attractive because they can utilize various species of hydrocarbon fuels and operate efficiently. In Japan, for instance, an operating test of SOFC fueled by bio-syngas from organic waste has been implemented at Kyushu University [1].

A previous study performed a life cycle assessment (LCA) of a SOFC power generation system using natural gas. It was observed that the environmental impacts of fuel production during the operation of a SOFC power generation system were substantial [2]. In addition, environmental impacts from the manufacturing stage of a SOFC stack were also significant [3]. Therefore, environmentally-friendly fuels that can replace natural gas are required. However, few studies investigate SOFC power generation systems that use bio-syngas as fuel.

This study focuses on a SOFC power generation system using bio-syngas as fuel. The syngas is derived from the gasification of woody biomass. However, due to the diversity of biomass feedstocks, the generated syngas contains approximately 20 to 50 ppmv of H₂S [4]. Therefore, there is a risk of electrode poisoning by H₂S, which can cause drops in voltage [5].

In a previous study of a biomass integrated-pyrolysis gasification/SOFC system, the system design, performance, and environmental impact were evaluated considering the deterioration by H₂S. The results indicated that the environmental impacts from the production of the adsorbent used to remove
S components were considerable. However, no study has been conducted on the adsorption and operating conditions (e.g., temperature and SOFC life) during the removal of S components.

Kuroda et al. examined the use of Hydroxyl Aluminum Silicate Clay (HAS-Clay) as an adsorbent of S content [6]. The results indicated that HAS-Clay has a similar level of adsorption performance compared with other adsorbents. It can also be recycled; therefore, its environmental impacts are less substantial. However, it is important to consider that changing the adsorbent also changes the operating conditions of the SOFC.

Therefore, in this study, we evaluated the performance and environmental impact under different adsorption and operating conditions (e.g., temperature and SOFC life) of the biomass integrated-pyrolysis gasification/SOFC system. For the energy performance analysis, the process design of each sample was simulated using the process simulator Aspen Plus Ver. 9. The exergy efficiency was also analyzed. To evaluate the environmental aspects, the eco-indexes were based on the LCA methodology, which was implemented using the software SimaPro Ver. 8.5.0.0.

2. Simulation method

2.1. Simulation condition

In this study, woody biomass is gasified, and the generated synthesis gas is used as fuel to drive the SOFC to generate electricity and heat. The generated heat was reused as gasifier heat. The simulation was performed in a static state, and the plant conditions are presented in Table 1. The performance and environmental impacts of a biogas SOFC power generation system using different adsorbents were compared. HAS-Clay and metal oxide (conventional adsorbent) were used [7]. A high-temperature adsorbent, CeO$_2$, was chosen as the metal oxide for this experiment. The detailed performance of both adsorbents is shown in Table 2. The schematic design of the studied system is shown in Figure 1-1 and 1-2.

| Table 1. Plant conditions |
|---------------------------|
| Plant scale               | 5 t/day |
| Generation scale          | 300 kW  |
| S/C                       | 1.0     |
| Uf                        | 75%     |
| Operating voltage         | 0.85 V  |
| SOFC temperature          | 800°C   |
| Plant life                | 10 years|
| Converter efficiency      | 95%     |
| Pyrolysis temperature     | 550°C   |
| Reformer temperature      | 950°C   |
| Plant pressure            | 0.11 MPa|
**Figure 1-1.** Schematic designs of biomass integrated-pyrolysis gasification/SOFC system structure (CeO$_2$)

**Figure 1-2.** Schematic designs of biomass integrated-pyrolysis gasification/SOFC system structure (HAS-Clay)
Table 2. Adsorbent performance [6][7]

| Adsorbent | Temperature (K) | Performance (mol/kg) |
|-----------|-----------------|-----------------------|
| HAS-Clay  | 363.15          | 0.021                 |
| CeO₂      | 973.15          | 0.672                 |

The biomass material used in this study was cedar. Table 3 shows the measured chemical properties of the biomass feedstock. Ammonia and chlorine contaminants are also present in the biomass feedstock; however, they were not considered in this study. Further research should consider the environmental impact of such pollutants.

Table 3. Chemical properties of Cedar

| Property                | Value [wt.%] |
|-------------------------|--------------|
| Carbon                  | 46.66        |
| Hydrogen                | 5.48         |
| Nitrogen                | 0.12         |
| Oxygen                  | 47.351       |
| Ash                     | 0.389        |
| Volatiles               | 86.21        |
| Higher Heating value   | 18.348       |

One kilogram of biomass in Table 3 is reformed and gasified by adding steam. Table 5 shows the composition of the syngas after reforming.

Table 4. Syngas components after reforming

| Component | Value [mol/h] |
|-----------|---------------|
| H₂        | 28.9          |
| CO        | 16.2          |
| CH₄       | 2.69E-01      |
| CO₂       | 7.49          |
| NH₃       | 1.02E-03      |
| H₂O       | 23.5          |
| N₂        | 2.94E-02      |
| H₂S       | 2.65E-03      |
| C₂H₅      | 4.92E-10      |
| C₂H₆      | 2.29E-11      |

2.2. \(H₂S\) poisoning simulation

In the degradation mechanism of SOFC, the S component from \(H₂S\) attaches to the Ni portion of the SOFC anode, and degradation occurs due to the reduction of the three-phase interface, which is a power generation site.

Assuming that the chemical reaction below occurs during the degradation process, \(H₂S\) accumulation can be calculated by determining the reaction rate and the SOFC voltage drop over time.
The adsorption reaction formula is as follows:

\[ H_2S + Ni \rightarrow NiS + H_2 \]  \hspace{1cm} (1)

The reaction rate can be calculated according to:

\[
\frac{\mathrm{d}[H_2S]}{\mathrm{dt}} = -k[H_2S]
\]  \hspace{1cm} (2)

The Arrhenius formula is given in Equation 3.

\[ k = A \exp \left( \frac{-E}{RT} \right) \]  \hspace{1cm} (3)

where \( k \) is reaction rate constant, \( A \) is frequency factor, \( R \) is gas constant, \( T \) is temperature, \( E \) is activation energy.

The length of the SOFC cell stack was 13.4 m, the flow rate of \( H_2 \) was 52.4 mol/h, and the flow path was \( 25 \times 25 \text{ cm}^2 \). \( H_2S \) was the only impurity contained in the syngas. The concentration of \( H_2S \) at the inlet of the SOFC, after desulfurization, was 2 ppm for the CeO\(_2\) sample and 2 ppm for the HAS-Clay sample. The SOFC was replaced at a 10% voltage drop from the initial operating voltage. Moreover, the rate constant \( k \) was calculated based on the deterioration simulated in the literature [8].

3. Evaluation methodology

3.1. Energy and Exergy analysis

In this study, power generation efficiency and exergy analyses were used for performance evaluation. Power generation and its efficiency were calculated through Equation (4) and (5), respectively.

\[ P_{SOFC} = -\Delta G \times \frac{V}{V_0} \times n_{H_2} \]  \hspace{1cm} (4)

\[ \eta_{SOFC} = \frac{P_{SOFC}}{n_{H_2} \text{LHV}} \times 100 \]  \hspace{1cm} (5)

where \( \Delta G \) is the Gibbs free energy \([\text{kJ/mol}]\), \( V \) is the operating voltage \([\text{V}]\), \( V_0 \) is the theoretical voltage \([\text{V}]\), \( n_{H_2} \) is the amount of reacted hydrogen \([\text{mol/h}]\), and \( n_{H_2} \text{LHV} \) is the hydrogen lower heating value \([\text{kJ/mol}]\).

In recent years, exergy analysis has gained considerable interest in the thermodynamic analysis of thermal processes and plant systems. This concept is especially useful because First Law analysis is insufficient from an energy performance point of view [9]. The aim of the exergy analysis is to identify the magnitudes and locations of exergy losses, to improve existing systems and develop new processes or systems [10].

Exergy can be defined by the sum of the chemical exergy \( Ex_{ch} \) and the physical exergy \( Ex_{ph} \) [11].

\[ Ex = Ex_{ch} + Ex_{ph} \]  \hspace{1cm} (6)

where the chemical and physical exergy can be written, respectively, as:

\[ Ex_{ch} = \sum_i n_i \left( e_{0_i} + RT_0 \ln \frac{n_i}{\sum n_i} \right) \]  \hspace{1cm} (7)
6

\[ E_{x_{ph}} = \sum n_i \left[ (h_i - h_0) - T_0 (s_i - s_0) \right] \]

where \( n_i \) is the molar yield of the gas component \( i \) [mol/kg]; \( R \) is the gas constant [J/molK]; \( \epsilon_i \) is the standard chemical exergy of a pure chemical compound \( i \) [kJ/mol]; \( h_i \) and \( s_i \) are, respectively, enthalpy [kJ/mol] and entropy [J/molK] at the designed temperature and pressure; and \( h_0 \) and \( s_0 \) are enthalpy and entropy at standard conditions, respectively.

To calculate the exergy of biomass with less complexity, the correlation developed by Szargut and Styrylska was used (Equation 9) [11][12].

\[ E_{x_{biomass}} = \eta \beta LHV_{biomass} \]

The correlation factor \( \beta \) is given by:

\[
\beta = \frac{1.0412 + 0.2160 \left( \frac{H}{C} \right) - 0.2499 \left( \frac{O}{C} \right) + 0.0450 \left( \frac{N}{C} \right) + 0.3035 \left( \frac{C}{O} \right)}{1 - 0.3035 \left( \frac{O}{C} \right)}
\]

where O, C, H, and N are the weight fractions of oxygen, carbon, hydrogen, and nitrogen in the biomass, respectively. The exergy efficiency expresses all exergy input as used exergy and all exergy output as utilized exergy [13].

\[ \varepsilon = \frac{E_{x_{out}}}{E_{x_{in}}} = \frac{P_{sofc}}{E_{x_{biomass}} + E_{x_{water}} + E_{x_{air}}} \]

where \( E_{x_{in}} \) and \( E_{x_{out}} \) are the total input and output exergies [kJ/mol], respectively.

3.2. Life Cycle Assessment
The LCA method analyses the environmental performance of a product during its life cycle: from raw material extraction, through manufacturing and transportation, to disposal [14]. In this study, the “cradle-to-gate” approach covers the process from biomass chipping to power production. The system boundary is illustrated in Figure 2. Six subsystems were defined: chipping (SS1), transportation (SS2), drying (SS3), syngas production (SS4), desulfurization (SS5), and SOFC (SS6). In addition, the functional unit for our estimation is 1 kWh electricity.
Background data was acquired from the Ecoinvent 3.2 database using SimaPro (ver. 8.5.0.0) and from the CML database. In this research, global warming potential (GWP 100 years), acidification potential (AP), abiotic depletion (ADP), and eutrophication potential (EP) were calculated based on the analysis subject in the FC-Guide [15]. For the chipping process, electric power and diesel consumption were set to 0.0136 kWh/kg-feedstock and 1.033 g/kg-feedstock [16]. Based on the assumed plant scale, the collection area of biomass feedstock is estimated to cover from 5 to 50 km [17]. An average transportation distance of 27.5 km was used. The energy consumption of the drying, syngas production, and hydrogen purification steps was estimated based on the Aspen Plus simulation results.

The inventory data at the SOFC manufacturing stage was based on the literature [2][18][19]. The rated output value in the literature and the one defined in this research were different; therefore, a 0.6 power law was performed to meet specifications. The recycling scheme on used materials is outside the scope of this study because the SOFC system is still not promoted and has uncertainties in its inventory data. The consideration of precious metals for SOFC will be considered in our future work. Inventory data appear in Table 5. Note that all emission factors of secondary energy are those used in Japan.

**Table 5. Inventory data**

|                      | CeO₂       | HAS-Clay  |
|----------------------|------------|-----------|
| **SS.1 Chipping**    |            |           |
| Electric energy      | 4.10.E-03  | 4.10.E-03 |
| Diesel               | 3.00.E-04  | 3.00.E-04 |
| **SS.2 Transportation** |          |           |
| Diesel               | 1.00.E-02  | 1.00.E-02 |
| **SS3. Drying**      |            |           |
| Electric energy      | 1.62.E-01  | 1.62.E-01 |

Figure 2. System Boundary
SS4. Syngas production

|    | kg/kWh-product |
|----|----------------|
| Air | 4.22           |
| Water | 2.10.E-01     |

SS.5 Desulfurization

|    | kg/kWh-product |
|----|----------------|
| CeO₂ /HAS-Clay | 1.01.E-04 |

SS6. SOFC

|    | kg/kWh-product |
|----|----------------|
| Anode | 6.30.E-05 |
| Cathode | 3.50.E-06 |
| Electolyte | 1.10.E-06 |
| Insulation material | 1.48.E-05 |
| Stainless steel | 6.44.E-05 |
| Electric energy | 6.98.E-03 |

4. Results and Discussion

4.1 Results of SOFC performance

The SOFC voltage drop with time is shown in Figure 3, and the change in output power with time (based on the results from Figure 3) is shown in Figure 4. These show that in a period of approximately 1.1 years, the power generation output reduces by 10% of the initial value.

![Figure 3. Cell voltage curve](image1)

![Figure 4. Plant life](image2)

4.2 Results of energy and exergy analysis

Exergy diagrams of the bio-syngas SOFC power generation system are shown in Figure 7, 8. Energy efficiency was also calculated from Equation (5). When CeO₂ is used, the energy and exergy efficiencies are 39.1% and 35.6%, respectively. When HAS-Clay is used, these values drop to 36.7% and 33.0%, respectively (Figure 7 and 8). Therefore, the efficiency of the bio-syngas SOFC power generation system is lower when HAS-Clay is used.

This result can be attributed to the low H₂S adsorption temperature (90 °C) in HAS-Clay, which leads to a loss during the reheating step before the syngas is introduced into the SOFC and some of the syngas is sent to the combustor.
4.3 Results of LCA

Figures 9, 10, 11, and 12 show the results of the LCA, according to the adsorbent used. These make apparent that when HAS-Clay is not recycled, the environmental impacts can be approximately 2 to 4 times that of CeO₂.

In addition, when HAS-Clay is recycled 19 times, its environmental impacts are smaller than those of CeO₂ in ADP. When recycled 27 times, HAS-Clay’s environmental impacts are less than those of CeO₂ in EP. After being recycled 33 times, HAS-Clay’s environmental impacts are less than those of CeO₂ in AP. Furthermore, when 36 recycling cycles are considered, the environmental impacts of HAS-Class are low for all impact categories. Therefore, the biomass integrated-pyrolysis gasification/SOFC system using HAS-Clay requires 36 recycling cycles.

If HAS-Clay is not recycled, all impact categories present high values. However, these environmental impacts gradually decrease with recycling. Moreover, the environmental impacts of SOFC related to ADP and AP are large, which is likely caused by the use of several rare metals in SOFC production.
5. Conclusion
In this study, the performance of a biomass integrated-pyrolysis gasification/SOFC system using two different adsorbents (HAS-Clay and CeO$_2$) was evaluated for energy and exergy efficiencies. The environmental impacts were also evaluated through an LCA.

The following findings were obtained:

- H$_2$S degraded 10% of the SOFC initial voltage in approximately 1.1 years when the H$_2$S concentration of syngas is 2 ppm. Therefore, an adsorbent to remove H$_2$S is necessary.

- The energy efficiency was 36.7% and the exergy efficiency was 33.0% when HAS-Clay was used. These values were smaller than when CeO$_2$ was used.

- In the LCA of the biomass integrated-pyrolysis gasification/SOFC system, the use of HAS-Clay allowed for 19 cycle recycling, indicating that HAS-Clay has superior ADP. In addition, the adoption of 36 recycling cycles with HAS-Clay can improve the performance in all impact categories considered.

6. References
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