Non-stationary and LCA analysis of impurity adsorption using Kanuma clay and HAS-Clay in a Bio-H\textsubscript{2} production system

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Abstract. In recent years, fuel cell (FC) applications have shown potential in the reduction of greenhouse gas (GHG) emissions, leading to an increase in demand for hydrogen fuel. The current source of hydrogen is generally fossil fuel origin. Therefore, for mitigating GHG emissions in the hydrogen production stage, we focused on the biomass-derived hydrogen (Bio-H\textsubscript{2}) production process. In this study, we discuss the environmental impacts of Bio-H\textsubscript{2} through the biomass pyrolysis process of Blue Tower (BT) biomass gasification. The bio-syngas contains H\textsubscript{2}S, HCl, and NH\textsubscript{3} as impurities, which can reduce the performance of FCs. In our previous experimental studies, we used hydroxyl aluminum silicate clay (HAS-Clay) as an adsorbent for removing impurities. However, based on the life cycle assessment methodology, it was found that the impact of HAS-Clay was higher, indicating that the environmental contribution of the one through operation using HAS-Clay would be lower. Thus, in this study, using Kanuma clay, which is a natural resource and lower impact adsorbent, we used the desulfurization test and designed an optimal process to mitigate its eco-burden and maintain removal performance. Finally, using the dynamic process simulator of ANSYS fluent (2020 R1), we compared the proposed process to the conventional process in terms of plant performance and evaluated the environmental impacts. The results showed that there was a 12.3% reduction in GWP due to the replacement of Kanuma clay and HAS-Clay as compared to ZnO, a chemical adsorbent.

1. Introduction
Recently, fuel cell (FC) applications have shown potential in contributing to the reduction of greenhouse gases (GHGs). Thus, the demand for hydrogen fuel would increase. Hydrogen is a sustainable and clean energy source. However, the current source of hydrogen is generally of fossil fuel origin, and according to its life cycle assessment (LCA), is a major source of GHG emissions. Therefore, producing hydrogen from renewable energy sources is necessary. As biomass is carbon-neutral, biomass-derived hydrogen (Bio-H\textsubscript{2}) is considered to be effective in combating global warming. In particular, sewage sludge is easily available in large quantities to produce Bio-H\textsubscript{2} in a large city with a large population. Therefore, in this study, we discuss the environmental impacts of Bio-H\textsubscript{2} production from sewage sludge using the Blue Tower (BT) gasification process.

The gasified biomass (bio-syngas) contains the following impurities: HCl, NH\textsubscript{3}, and H\textsubscript{2}S, which can reduce the performance of FCs. Thus, it is necessary to remove these factors. It is known that H\textsubscript{2}S
decreases the catalytic activity of FC even at low concentrations. Therefore, this study focused on the desulfurization process of hydrogen production. Desulfurization is often conducted at a high temperature (400 °C) [1] by using adsorbent. Usually, high-temperature dry desulfurization process is more energy efficient than wet desulfurization using a scrubber although sulfur removal ratio of the high-temperature dry desulfurization is not so high as low temperature wet desulfurization. However, increasing the temperature is energy-intensive, and this could increase the eco-burden. Thus, we propose a desulfurization system at low temperature.

Various adsorbents have been used in the dry desulfurization process. Conventionally, desulfurization has been performed by the chemisorption of ZnO. However, as chemisorption is difficult to desorb, ZnO is used only once. Using a large amount of ZnO increases the associated environmental impacts. Therefore, in our previous research, we proposed the use of hydroxyl aluminum silicate clay (HAS-Clay) for physical adsorption [2]. The HAS-Clay can adsorb H₂S and can be used multiple times due to its easy desorption. However, LCAs have shown that the environmental impact of HAS-Clay is substantial. In other words, it is necessary to reduce the amount of HAS-Clay used, thereby reducing the eco-burden.

Thus, in this study, we used Kanuma clay before HAS-Clay to reduce the amount of HAS-Clay used. Kanuma clay is a pumice stone found in Kanuma City, Tochigi Prefecture, Japan, and is considered to have a small environmental impact during its life cycle. Kako et al. found that Kanuma clay can adsorb NH₃ [3], but an experimental study on the separation of H₂S by Kanuma clay has not been conducted. In addition, an adsorption column using Kanuma clay and HAS-Clay has not been designed yet. Therefore, the purpose of this study was to experimentally examine if Kanuma clay can adsorb H₂S, design a desulfurization system using Kanuma clay and HAS-Clay as adsorbents, and compare environmental impacts between the conventional and the proposed systems.

When designing the desulfurization process, it is necessary to measure the H₂S concentration at the outlet of the adsorption column in order to assess whether H₂S has been adsorbed. In addition, it is necessary to determine the exact amount of adsorbent used to compare the environmental impacts. If H₂S is adsorbed on Kanuma clay by chemisorption, it is predicted that the amount adsorbed would change between the first and second adsorption. This change would affect the calculation of the amount of Kanuma clay used. To obtain an accurate amount of Kanuma clay, it is necessary to examine the concentration distribution in the adsorption column and to determine the distribution of the decline in adsorption when the adsorbent is used multiple times. Therefore, in this study, we simulated H₂S adsorption from experimental results using the dynamic process simulator of the ANSYS Fluent (2020 R1). Therefore, the concentration distribution in the adsorption column was investigated.

2. Design of Adsorption Model

2.1 Removal Experiment of H₂S

The removal experiments of H₂S were conducted using the following apparatus (Figure 1). The reactor size was φ15.8mm×82mm. In the experiment, Kanuma soil was sifted, the size was unified to 4-4.75 mm, and the reactor was filled. Then, after evacuating for 1 h to remove air, Ar was flowed at 50 ml/min for 1 h to raise the temperature to the operating temperature, and then sample gas was flowed at 90 ml/min. The sampling gas composition is shown in Table 1, and the details of the experimental conditions are shown in Table 2. The H₂S concentration was measured using a gas chromatograph (GC-8A, Shimadzu Corp.). In this experiment, we examined the variation in sulfur capture capacity of Kanuma clay by changing the operating temperature. The space velocity (SV), based on the packed bed volume of the adsorbent, was approximately 234 h⁻¹. In addition, we also examined the variation of its sulfur capture capacity when adsorbing H₂S multiple times. Thus, after finishing the H₂S adsorption experiment, we vacuumed the adsorption column for 1 h by filling Ar and conducted an experiment on H₂S adsorption again. The major components of the Kanuma clay are shown in Table 3.
As Kanuma clay includes Fe$_2$O$_3$, the reaction of Fe$_2$O$_3$ + H$_2$S → Fe$_2$S$_3$ + 3H$_2$O was expected to occur. Therefore, it was presumed that chemisorption would occur between Kanuma clay and H$_2$S, and the adsorption of H$_2$S by Kanuma clay would increase with increasing temperatures.

2.2 Modeling

A numerical model was used for designing the desulfurization system and comparing the environmental impacts. In order to determine whether the model in this study could accurately express the adsorption of HAS-Clay and Kanuma clay, it was necessary to compare the values in the model with those from the experiment. Thus, we simulated the model under the experimental conditions and validated that the results of the model corresponded to those of the experiments.

The model was developed and simulated using ANSYS Fluent (2020 R1). The details of the adsorption column and the conditions are shown in Table 2. The fluid was assumed to be incompressible, Newtonian, and in a laminar flow regime. The feed gas composition under standard conditions in the HAS-Clay simulation was Ar-H$_2$S (99.95–0.05% by volume) [2], and the feed gas composition under standard conditions in the Kanuma clay simulation is shown in Table 1. The porous medium approach was used in simulating the fluid flow in the packed bed as the adsorbent inside the packed bed can be treated as a porous medium. The porous medium was assumed to be isotropic. The approach uses an additional mass source term to the standard fluid flow equations to account for the flow resistance due to the porous medium. The following assumptions were made in the model.

| Table 1. Sample gas composition |
|---------------------------------|
| N$_2$ | 4.61 vol% |
| CH$_4$ | 57.70 vol% |
| H$_2$S | 0.0197 vol% |
| CO$_2$ | 37.7 vol% |
| Ar | balance vol% |

| Table 2. Parameters in the experiment |
|-------------------------------------|
| Operating pressure, bar | 1 |
| Operating temperature, °C | 40, 80, 120 |
| Operating flowrate, ml/min | 90 |
| Adsorbent | Kanuma clay |
| Particle diameter, mm | 4–4.75 |
| Bulk density, kg/m$^3$ | 314 |

Figure 1. Experimental apparatuses.
(i) Ideal gas law was applicable.
(ii) Plug flow was assumed; that is, there was no axial or radial dispersion.
(iii) The mass transfer rate was given by the linear driving force (LDF) model.

A user-defined function was introduced to incorporate the source term in order to include the LDF model. The governing equation for fluid flow in isotropic porous media is given by equation (1). Incorporating the source term, in equation (1) enabled us to define the concentration points of the adsorbed gas. Thus, the mass and momentum conservation equations for the discussed model are given by equations (2) and (3), respectively. The inertial and viscous resistances encountered by the fluid were incorporated in the model by the last two terms. Permeability \((\alpha)\) and viscous resistance \((C_2)\) were calculated using equations (4) and (5), respectively, due to the presence of porous media. The LDF model describing the mass transfer phenomena is given by equations (6) and (7). The governing equations were discretized by the second-order backward difference method.

\[
\begin{align*}
\frac{\partial (\gamma \rho \phi)}{\partial t} + \nabla \cdot (\gamma \rho \nabla \phi) &= \nabla \cdot (\gamma \Gamma \nabla \phi) + \gamma S_b \#(1) \\
\frac{\partial (\gamma \rho \mathbf{V})}{\partial t} + \nabla \cdot (\gamma \rho \mathbf{V} \mathbf{V}) &= \nabla \nabla P + \nabla \cdot (\gamma \tau) \\
&+ \gamma \mathbf{B}_f - \left( \frac{\mu}{\alpha} + \frac{C_2 \rho}{2} |\mathbf{V}| \right) \mathbf{V} \#(3) \\
\alpha &= \frac{d_p^2 \varepsilon^3}{150(1 - \varepsilon)^2} \#(4) \\
C_2 &= \frac{3.5(1 - \varepsilon)}{d_p \varepsilon^3} \#(5) \\
\frac{\partial q_i}{\partial t} &= k(q_i^* - q_i) \#(6)
\end{align*}
\]
\[ k = \frac{15D_p}{d_p^2} \]  

where \( \rho \) is density [kg/m\(^3\)], \( V \) is velocity [m/s], \( \gamma \) and \( \varepsilon \) are porosity [-], \( D_p \) is effective diffusion coefficient [m\(^2\)/s], \( \tau \) is shearing stress [N], \( \mu \) is viscosity [Pa s], and \( d_p \) is particle size [m].

In chemisorption, it is difficult to completely desorb materials adsorbed on adsorbents. Therefore, while separating H\(_2\)S using Kanuma clay, it was expected that the amount of H\(_2\)S adsorbed on Kanuma clay in the second adsorption would be less than that in the first adsorption. Considering this reduction in adsorption, the adsorption phenomenon can be expressed more precisely, and we could calculate the amount of Kanuma clay with more precision. Thus, in this study, we considered the reduction in the amount of adsorption, calculated the amount of Kanuma clay used, and designed the desulfurization process using Kanuma clay and HAS-Clay as adsorbents. The concentrated distribution of H\(_2\)S in the adsorption column was observed by simulating the numerical model. An equation calculating the amount of H\(_2\)S adsorbed on Kanuma clay from this concentration distribution is given by equation (8).

\[ S_{cap,i} = \frac{\int_0^{t_{st}} FR(C_{inlet,i} - C_i(t))dt \times 32.07}{22.4 \times W_{sorbent}} \]  

where \( S_{cap,i} \) [g-H\(_2\)S/kg-adsorbent], \( t_{st} \) [s], \( FR \) [m\(^3\)/s], \( C_{inlet} \) [-], \( C_i(t) \) [-], and \( W_{sorbent} \) [kg] are the amount of adsorption in the \( i \)-th place, breakthrough time, flow rate, inlet concentration of sulfur, sulfur concentration in the \( i \)-th place, and packed amount of adsorbent, respectively. Note that the atomic mass of sulfur is 32.07. We divided the adsorption column into four parts and numbered them from the inlet (see Figure 2). After calculating the adsorbed amount in each place, we explored the amount of degradation adsorbed by calculating the decrease in the saturated adsorption amount for each \( i \)-th place (\( q_i^f \) in equation (6)).

2.3 Life Cycle Assessment

In order to compare the eco-burdens between the conventional desulfurization system (adsorbent: ZnO or HAS-Clay) and the proposed system, we conducted environmental impact assessment using the LCA approach. Sima Pro v.8.3.0.0 was used to build the life-cycle models. The functional unit was 1 Nm\(^3\) of bio-syngas, and the bio-syngas composition is shown in Table 5. The assessment scope using the Well to Tank approach consists of the production and use of adsorbents. The system boundary is shown in Figure 3. The inventory data of HAS-Clay and Kanuma clay were obtained from Seo et al. [5] (See Table 6 and Table 7).
3 Results and Discussion

3.1 Experimental Result

The results for the sulfur capture capacity of Kanuma clay at 40, 80, and 120 °C are shown in Table 8. These experiments were conducted 20 minutes 25 seconds (40 °C, 80 °C) and 60 minutes 25 (120 °C). As shown in Table 8, the sulfur capture capacity increased with increasing temperature. In addition, the sulfur capture capacity when adsorbing H₂S multiple times is shown in Figure 4, which shows that the sulfur capture capacity decreased with increasing number of adsorption cycles. These results indicate
that the Kanuma clay adsorbed H_2S by chemisorption. It was assumed that Fe_2O_3 reacts with H_2S.

3.2 Simulation Result

3.2.1 Simulation Result of HAS-Clay and Kanuma clay

The simulation results of HAS-Clay are shown in Figure 5. At 30 °C, the simulation results did not match the experimental results. However, at 60 and 90 °C, the simulation results matched the experimental results. In this study, the operational temperature of HAS-Clay in the proposed system was assumed to be high (60–90 °C). Thus, this numerical model can be used for designing the desulfurization process.

The simulation result of the Kanuma clay at 120 °C is shown in Figure 6. It was found that the breakthrough time of the simulation was the same as that of the experiment. In addition, the sulfur capture capacity of regenerated Kanuma clay at 120 °C, shown in Figure 7, shows that the simulation result is in accordance with the experimental result. These results proved that the numerical model in this study accurately expresses the adsorption phenomenon.

3.2.2 Design Desulfurization System

To decrease the eco-burden of the impurity removal system, we proposed a desulfurization system using HAS-Clay and Kanuma clay. When designing this system, we need to consider three factors.

| Temp [°C] | Kanuma clay |
|-----------|-------------|
| 40        | 9.67×10^{-4} |
| 80        | 3.89×10^{-3} |
| 120       | 1.65×10^{-2} |

*Unit g-S/100 g-sorbent

Figure 4. Change in Kanuma clay’s sulfur capture capacity with temperature and the number of adsorption cycles.

Figure 5. Breakthrough curve of HAS-Clay.

Figure 6. Breakthrough curve of Kanuma clay.
These are the size of the adsorption column, SV, and operating temperature. First, the size of the adsorption column should be small as we assumed that hydrogen is prepared from sewage sludge in a small factory near a large populated city. We designed the adsorption column based on an experimental adsorption column. Next, SV is related to throughput per unit time. If SV varies, the sulfur capture capacity might also change. Thus, it is necessary to adjust the proposed system’s SV to the experimental SV. As the experimental SV of HAS-Clay and Kanuma clay were 219.2 and 234 h⁻¹, respectively, the proposed system’s SV was designed to be in the range of 150–300 h⁻¹. With respect to the adsorption properties of HAS-Clay and Kanuma clay, it was found that the adsorption temperature was significantly affected. The sulfur capture capacity of the Kanuma clay increased at higher temperatures. Inversely, the value of HAS-Clay increased at low temperatures. Therefore, an air cooler was installed between the Kanuma clay of the foregoing part and the HAS-Clay of the latter part. The cooling method used an air blower with the air temperature set at 25 °C. The proposed desulfurization system accounted for these problems, and is shown in Figure 8. The quantities of Kanuma clay and HAS-Clay were 16.85 and 6.98 g, and SV values were 150 and 300 h⁻¹, respectively. The flow rate was 66.4 mL/min. The temperature distribution in the adsorption column is shown in Figure 9, and it was found that the temperature in the column of Kanuma clay was 120 °C and that in the HAS-Clay column was 60 °C.

3.3 LCA Result

The comparison between the conventional and proposed systems is shown in Table 9. The amount of Kanuma clay used was calculated using a numerical model, and the eco-burden of ZnO was calculated using the data of Dowaki et al. [6]. It was found that the proposed system showed an approximately 12.3% reduction of GWP as compared to the conventional system (ZnO), and its eco-burden was...
Table 9. The environmental impact comparison using the LCA method

| Impact category                        | ZnO     | HAS-Clay | Proposed system |
|----------------------------------------|---------|----------|-----------------|
| Global warming                         | kg CO2 eq | 4.75     | 4.22            | 4.170            |
| Stratospheric ozone depletion          | kg CFC11 eq | 3.33×10^{-6} | 1.53×10^{-6} | 1.52×10^{-6} |
| Ionizing radiation                     | kBq Co-60 eq | 9.27×10^{-1} | 5.10×10^{-1} | 5.09×10^{-1} |
| Ozone formation, Human health          | kg NOx eq     | 2.60×10^{-2} | 8.15×10^{-3} | 8.03×10^{-3} |
| Fine particulate matter formation      | kg PM2.5 eq  | 1.21×10^{-2} | 1.21×10^{-2} | 1.20×10^{-2} |
| Ozone formation, Terrestrial ecosystems| kg NOx eq     | 2.62×10^{-2} | 8.22×10^{-3} | 8.10×10^{-3} |
| Terrestrial acidification              | kg SO2 eq     | 3.30×10^{-2} | 1.43×10^{-2} | 1.40×10^{-2} |
| Freshwater eutrophication              | kg P eq       | 6.21×10^{-3} | 2.90×10^{-3} | 2.88×10^{-3} |
| Marine eutrophication                  | kg N eq       | 3.56×10^{-4} | 1.89×10^{-4} | 1.88×10^{-4} |
| Terrestrial ecotoxicity                | kg 1,4-DCB   | 2.26×10^{-2} | 4.60            | 4.46            |
| Freshwater ecotoxicity                 | kg 1,4-DCB   | 4.61     | 1.58×10^{-1} | 1.55×10^{-1} |
| Marine ecotoxicity                     | kg 1,4-DCB   | 6.37     | 2.09×10^{-1} | 2.05×10^{-1} |
| Human carcinogenic toxicity            | kg 1,4-DCB   | 2.01     | 2.34×10^{-1} | 2.28×10^{-1} |
| Human non-carcinogenic toxicity        | kg 1,4-DCB   | 1.74×10^{-2} | 4.57          | 4.52            |
| Land use                               | m^2a crop eq | 1.97     | 1.95×10^{-1} | 1.88×10^{-1} |
| Mineral resource scarcity              | kg Cu eq      | 8.83     | 9.02×10^{-3} | 8.55×10^{-3} |
| Fossil resource scarcity               | kg oil eq     | 1.27     | 1.16            | 1.15            |
| Water consumption                      | m^3       | 1.48×10^{-1} | 3.09×10^{-2} | 2.97×10^{-2} |

smaller than that of the conventional system (ZnO and HAS-Clay) under all impact categories. Thus, using Kanuma clay and HAS-Clay simultaneously as adsorbents in desulfurization systems can decrease the eco-burden as compared to that using ZnO or HAS-Clay only as an adsorbent.

4 Conclusion
In this study, we assessed a Bio-H₂ production system from sewage sludge and examined the eco-burden of adsorbents in desulfurization systems. To reduce the amount of HAS-Clay, which has a large eco-burden in its life cycle, we proposed a desulfurization system using Kanuma clay and HAS-Clay simultaneously as adsorbents, and compared the environmental impacts between the conventional and the proposed systems. In addition, to accurately calculate the usage of Kanuma clay in conducting an environmental impact assessment, a simulation including the decrease in sulfur capture capacity was developed. The experimental result of desulfurization showed that the sulfur capture capacity of Kanuma clay was \(1.65 \times 10^{-2}\) g-S/100 g-sorbent. The results of the simulation indicated that the proposed numerical model could accurately express the adsorption phenomenon of HAS-Clay at high temperatures and Kanuma clay at 120 °C. Finally, we designed the proposed desulfurization system and compared the environmental impacts between the conventional and the proposed systems. The result showed that the proposed system had an approximately 12.3% lower GWP than the conventional system.
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