A LCA on the H$_2$S and HCl Removal Procedures Using in HAS-Clays

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The environmental performance of hydrogen production by steam-based gasification processes for fuel cell (FC) applications was evaluated using a Life Cycle Assessment (LCA) approach because the use of metal oxides as adsorbents or catalysts has a significant impact on the LCAs of FC applications.

In this paper investigating systems for the removal of impurities from syngas, the process design of a Bio-H$_2$ system was discussed in terms of the eco-burden of the impurity adsorbent. The HAS-Clay (a synthetic substance composed of hydroxyl aluminum silicate and clay) has particular potential as an adsorbent. This composite adsorbent can sequester H$_2$S and/or HCl, though it is generally used in desiccant heat pumps to adsorb CO$_2$ and H$_2$O. By comparing two different removal systems, the role of HAS-Clay as an adsorbent was investigated via the eco-indexes of global warming potential (GWP) and abiotic depletion potential (ADP). Consequently, it was found that HAS-Clay had a direct or indirect capture capacity of H$_2$S and HCl as well as CO$_2$ and H$_2$O. Compared to the conventional case in which a metal oxide is used as an adsorbent, a greater environmental benefit was obtained in the case of H$_2$S removal. In this case, the GWPs of the two-step pressure swing adsorption (2-step PSA) +ZnO or Fe$_2$O$_3$ were 3.18 and 1.43 g-CO$_2$/Nm$^3$-Bio-H$_2$ respectively compared to 19.4 g-CO$_2$/Nm$^3$-Bio-H$_2$ for the conventional system. Furthermore, the ADPs of 2-step PSA+ZnO or Fe$_2$O$_3$ were 763×10$^{-6}$ and 342×10$^{-6}$ g-Sb eq./Nm$^3$-Bio-H$_2$, as opposed to 2.75×10$^{-2}$ g-Sb eq./Nm$^3$-Bio-H$_2$ for the conventional system. On the other hand, in the case of HCl removal, a blend of HAS-Clay and CaCO$_3$ cannot obtain any environmental benefit without either the regeneration of HAS-Clay or the substitution of clay (a natural resource). Our results may imply that HAS-Clay is an extremely important adsorbent in terms of reducing the eco-burden.

Key Words
HAS-Clay (a synthetic substance composed of hydroxyl aluminum silicate and clay), 2-step PSA (pressure swing adsorption), GWP (global warming potential), ADP (abiotic depletion potential)

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1. Introduction

Biomass feedstock is a promising material from which several renewable fuels can be produced. However, from the viewpoint of eco-burden analysis, especially life cycle assessment (LCA), environmental analysis of the entire system is important, as this eco-friendly material cannot always contribute to environmental protection. In our previous studies, the LCA of bio-hydrogen (Bio-H₂) through the steam-based Blue-Tower (BT) gasification process was analyzed. Based on the operating profiles of the process design and considering our basic experimental results, an inventory analysis of the Bio-H₂ fuel was performed. Consequently, specific CO₂ emissions of 38.40 to 92.03 g-CO₂/MJ-H₂ were obtained \(^1\). It was essentially found that the sub-process of fuel production (e.g., the auxiliary power) had a significant impact on the emissions. In order to reduce emissions, and especially to reduce the auxiliary power necessary to refine pure H₂, a two step pressure swing adsorption (2-step PSA) was developed by our group.

In general, the conversion of pure H₂ requires a compression power with pressures of 1.0 to 2.0 MPaG. However, our observations revealed that a pressure as low as 0.4 MPaG can have a high conversion efficiency. Note that the inlet temperature of the 2-step PSA is 40 °C, which corresponds to the design temperature of the BT process \(^2\).

There are currently several types of biomass feedstock gasifiers in use. Using these systems, the composition of outlet gas obtained depends on the gasifying agents (air, steam, or O₂) and/or various operating parameters, which are unique for each installation. The highest H₂ and CO concentrations are obtained under a steam atmosphere. Gasification with air, the most common gasifying agent for fixed-bed reactors, leads to low CO and H₂ concentrations. While in a steam-based gasification process, the following gaseous components would be obtained: H₂ of 38-56 vol.%, CO of 17-32 vol.%, CO₂ of 13-17 vol.%, CH₄ of 7-12 vol.%, and H₂O of 52-60 vol.% \(^3\). Our targeted gasification processes are therefore steam-based gasifiers. It seems probable that the production of Bio-H₂ is the most advantageous, as the H₂ concentration is higher than in other gaseous components.

Regarding the estimation of refinery performance, an experimental apparatus for the 2-step PSA was fabricated. The experimental apparatus had two species of adsorbents: HAS-Clay (a synthetic substance composed of hydroxyl aluminum silicate and clay, Toda Kogyo Corp.) as the 1st stage, and a 2nd stage of Zeolite A-5 (Wako Pure Chemical Industries, Ltd., Particle size: 2.36-4.75 mm). According to our experimental results, it was found that a pure H₂ concentration of 97.0 vol.% with a refining efficiency of approximately 55% could be achieved at 0.4 MPaG and 30 °C. This efficiency is close to that of a conventional system \(^4\). The concentration of H₂ could be purified to 99.99 vol.% by an optimal arrangement of HAS-Clay and Zeolite A-5. Although the original use of HAS-Clay is as a desiccant in heat pumps, this composite material features CO₂ adsorption as well as acting as a drying agent at low temperatures and atmospheric pressures \(^5\). Upon investigating this advantageous characteristic in previous experiments, it was confirmed that the main syngas components other than CO₂ gas passed through the HAS-Clay. That is, the permeability of CO₂ was low, although those of H₂, CO and CH₄ were relatively high. Thus, 2-step PSA can refine pure H₂ while requiring lower auxiliary power, as the compression power can be reduced by using the decreased volume of syngas without CO₂. The reduction rate of auxiliary power in the Bio-H₂ purification process was approximately 20%, implying that further environmental benefit could be obtained \(^6\).

The refined Bio-H₂ is now available for fuel cell (FC) applications. However, impurities such as H₂S and/or HCl contaminate the Bio-H₂ fuel. Several types of contaminants in the syngas are generated during the gasification process. Various components of these contaminants can cause technical or environmental problems. For instance, H₂S is a major problem since it can cause corrosion of piping and cause acid rain if emitted into the atmosphere. This is also applicable to other elements such as alkali metals or chlorine \(^7\). The contaminants present depend on the species of biomass, and can cause a performance drop in FC applications. It is well-known that a H₂S-containing fuel gas can induce a power loss. Shi et al. describe that the rate of H₂S poisoning is a strong function of the H₂S concentration. During exposure to 5, 10, 20 and 50 ppm H₂S/H₂, it took 72, 29, 20, and 1.5 h for a cell voltage to fall to 0.3 Volts. Regarding the effect of the current density on the cell performance, the poisoning rate has a close relationship with the current density. After exposure to 20 ppm H₂S/H₂ for 1.0 h, the performance decreased by 2% at 200 mA/cm² as compared to a 17% decrease at 500 mA/cm² and a 35% decrease at 800 mA/cm²\(^8\). Similarly, there is damage due to the influence of HCl contamination. Although there are few examples on H₂ fuel stream in the anode side of polymer electrolyte fuel cells, Yadav \textit{et al.} found that a chloride ion concentration as low as 10 ppm could induce Pt dissolution as chloride complexes. That is, the mass of Pt catalyst was reduced, strongly affecting performance \(^9\).

The removal of H₂S is supposed to be carried out during 2-step PSA, in which a HAS-Clay can be used as an adsorbent as it can adsorb polar substances besides H₂O.
and CO₂⁻. It is therefore expected that H₂S will be adsorbed by the HAS-Clay 2-step PSA. Furthermore, to achieve HCl elimination, since HAS-Clay can sequester CO₂ the reaction CaCO₃+2HCl → CaCl₂+H₂O+CO₂ could be promoted by the packed HAS-Clay and CaCO₃ in the removal reactor. Accordingly, the load amount of metal oxide for H₂S or HCl elimination in conventional processes can be reduced by using HAS-Clay. The removal performances were evaluated by basic experiments, the results of which were used to propose impurity removal systems.

Finally, in order to evaluate the eco-burden, our proposed and conventional cases were compared using a LCA approach. If metal oxides for a chemical adsorbent were assumed to be used in the conventional case, the amount of metal required could be reduced using our proposed scheme. In this research, the estimation of life-cycle inventories (the load amounts of metal oxides) was implemented using SimaPro 8.2. In the impact analysis of the LCA, global warming potential (GWP) and abiotic depletion potential (ADP) were among the environmental impacts evaluated using the CML method. Both are widely used for the characterization of energy systems. In particular, the energy system in which rare metals are used makes significant contributions to ADP. Using the eco-indexes of ADP and GWP, the necessary design policy to meet more environmentally conscious conditions will be proposed. Based on the promotion of 2-step PSA for purifying H₂, our aim was to estimate the removal effects of impurities by considering the LCA approach.

2. Estimation of impurities removal
2.1 Summary of the entire process

In this study, eco-indexes were analyzed in the following two cases (See Fig. 1). The common characteristics of these comparative cases were assumed to be as follows: (1) the synthesis of raw gas (syngas) was generated through a steam-based gasification process, and (2) pure Bio-H₂ in a 2-step operation with an operating pressure of 0.4 MPaG. Here, ZnO can absorb H₂S in the relatively low temperature range of 300 to 550 °C. Thus, it is suitable to put the ZnO reactor in the fore position of a conventional PSA (see Fig. 1 (a)). Note that the adsorbents used were Zeolite Molecular Sieves (ZMS), and that CO₂ was not removed in this process.

Subsequently, to remove HCl Na₂CO₃ was chosen as the adsorbent. This reason for this is as follows. In general, calcium base substances are often adopted, since HCl can be neutralized by the reaction with calcium-based sorbents, such as solid lime (Ca(OH)₂), limestone (CaCO₃), and calcium oxide (CaO). In the case of CaO, which is obtained from CaCO₃ at high temperature, the HCl binding capacity of CaO reaches a maximum at 650 °C, where CaO can also adsorb H₂S. The purpose of this study was to evaluate the eco-index which is attributed to a metal carbonate and/or a metal oxide for impurity removal from syngas. If CaCO₃ or CaO, which are well-known absorbents of H₂S at high temperature ranges (e.g. >700 °C), were adopted in the conventional case, H₂S would be adsorbed prior to HCl. Hence, in order to differentiate the effect of a metal carbonate on only HCl, it was determined that neither CaCO₃ nor CaO but instead Na₂CO₃ was most suitable in terms of equitability.

It is necessary to discuss the position of HCl in the removal reactor. In the Bio-H₂ production system, the water gas-shift reactor (WGS) is often equipped to increase H₂ concentration in the syngas. The purpose of this is to improve the refining efficiency in the purification process. It is known that common WGS catalysts, such as copper and/or nickel, have considerable affinity for HCl, which inhibits the catalyst through the formation of a chloride surface barrier. It is therefore desirable to reduce the gaseous chloride content to < 1 ppmv. Considering this situation, the conventional HCl removal system should be put at the fore position of the WGS reactor. Conversely, in our proposed system, WGS cannot be equipped at this position, if HCl concentration in the syngas is 1.0 ppmv or more. That is, the installation of the WGS reactor was affected by the removal temperature. Note that it is not necessary to compensate for the additional thermal energy due to the selection of a suitable position, which is in common with the case of H₂S. The concept of estimation of eco-burden of the adsorbent was as follows: the metal oxide or metal carbonate used as a chemical adsorption is non-recyclable. This means that the desorption process, i.e. the recovery
process, was not considered. In addition, the recycling of used materials is beyond the scope of this study.

On the other hand, in the proposed system, the eco-burden was evaluated using the following procedure (see Fig. 1 (b)) [19]. In the H2S removal system, the adsorption and desorption procedures were assumed to be executed during 2-step PSA because H2 and other gases, including impurities, could be separated by controlling the pressure and flow under the same operating conditions. H2S elimination would probably be almost completely achieved. However, according to the performance experiments, the metal oxides ZnO and Fe2O3, which are non-recyclable, might be a necessary addition to achieve complete elimination. Thus, the load amount of metal oxide was also considered.

During HCl elimination, our purpose was to reduce the amount of metal carbonate used as the adsorbent. In our previous studies, as previously explained, we showed that HAS-Clay can capture CO2 at ambient temperatures. Due to its specific character, a blend of CaCO3 and HAS-Clay was expected to reduce the amount of CaCO3 necessary to achieve the elimination of HCl. Thus, the blended adsorbent of HAS-Clay and CaCO3 was analyzed. Note that HAS-Clay can be regenerated, although the blended adsorbent would be non-recyclable. The issue of the regeneration of HAS-Clay, including in the used CaCO3, will be the subject of future research. When considering the position of the removal system, it seemed better to prefix the 2-step PSA with a condenser due to the property of
the adsorbent (see Fig. 1 (b)). The capture capacity in this situation at temperatures between 40 °C and 200 °C was discussed.

2.2 Removal experiments of H₂S and HCl

The removal experiments of H₂S and HCl were executed using the following apparatus (see Fig. 2).

For the H₂S removal experiment, HAS-Clay (Toda Kogyo Corp.) which consists of amorphous aluminum hydroxide silicates, and zinc oxide (ZnO, Alfa Aesar HiFUEL A310) or iron oxide (Fe₂O₃, Toda Kogyo Corp.) was chosen (see Table 1). HAS-Clay possesses the functions of physical adsorption and sequestration of CO₂. The metal oxide (e.g. ZnO) has the function of chemical adsorption, and displays better performance at lower temperatures. In a conventional H₂S removal system, the elimination of H₂S and other sulfide compounds is usually done in the temperature range 150-300 °C by the adsorption

(a) H₂S removal test

(b) HCl removal test

| Specification                  | HAS-Clay       | Zinc oxide | Iron oxide | Calcium carbonate |
|-------------------------------|----------------|------------|------------|-------------------|
| Target Impurities             | H₂S/HCl        | H₂S        | H₂S        | HCl               |
| Chemical composition          | SiO₂·Al₂O₃·H₂O | ZnO        | Fe₂O₃      | CaCO₃             |
| Particle size [mm]             | 2.2–3.35 (H₂S) | 2.2–3.35   | 2.2–3.35   | 12 × 10⁻¹⁵—15 × 10⁻³ |
| Pore diameter [nm]             | <0.02          | -          | -          | -                 |

Fig. 2 Experimental apparatuses
of a specific metal oxide (e.g., ZnO) doped ceramic filter. Furthermore, H$_2$S concentration in the syngas produced through a biomass gasification process would be between 20 and 200 ppmv. Based on this situation, HAS-Clay was used in the 2-step PSA. That is, the removal system would be better placed before or in the first stage of 2-step PSA (see Fig. 1 (b)).

In this case, physical adsorption by the HAS-Clay was expected. Also, the operating temperature of HAS-Clay corresponds with the temperature profile of a plant at around 40 °C. However, complete removal might not be achieved. Hence, chemical adsorption would be required to satisfy the fuel specifications of FC applications (cf. below 0.004 ppmv of ISO14687-2).

According to Novochinskii et.al, the metals V, Zn, Co and Fe are used between 300 and 550 °C, and increasing the CO$_2$ concentration in the feed up to 12 vol% decreases the capacity of ZnO to capture H$_2$S. That is, the chemical removal system seems to be better placed downstream of 2-step PSA. However, the different operating temperatures from the optimum conditions of adsorbent could be disadvantageous. Considering the process conditions, two candidates which can operate at lower temperature were selected for this study (see Table 1). In the case of H$_2$S removal, the following two types of performance experiments were carried out: (1) the physical adsorption of HAS-Clay and (2) the chemical adsorption by the metal oxide ZnO or Fe$_2$O$_3$. In (1), it was assumed that the removal system of H$_2$S was placed in the 1st stage of the 2-step PSA reactor (see Fig. 1 (b)), whose inner temperature and pressure were respectively 40 °C and 0.4 MPaG. These performance tests were executed in our previous study using a feed gas of 50 Nml/min, which consisted of 9.0 vol%CH$_4$, 17.6 vol% CO$_2$, 30 ppmv H$_2$S and H$_2$ balance. These gaseous components are almost the same as those of syngas from a steam gasification process. 4.0 g of coarse particles of HAS-Clay was inserted in the reactor as an adsorbent (see Fig. 2 (a)). The space velocity (SV) on the basis of a packed bed volume of adsorbent was 199 h$^{-1}$). Note that the packed bed height (α) was 168 mm. The Zeolite A-5, which was packed in the 2nd stage of 2-step PSA, can also adsorb H$_2$S. However, the reaction of H$_2$S+CO$_2$ ↔ COS+H$_2$O was also observed. It is known that the reaction of CO$_2$ and H$_2$S forming COS in the presence of Zeolite with a high concentration of CO$_2$ gas occurs. Note that this result was obtained by experiment under the conditions of 3.0 g of Zeolite A-5 and a SV of 741 h$^{-1}$ with a bed height (α) of 45 mm. HAS-Clay can sequester CO$_2$ and remove some H$_2$S, but cannot eliminate H$_2$S entirely. Due to the Zeolite A-5, it is unknown whether the H$_2$ standard can be met or not. Thus, a compensating system for H$_2$S removal should be positioned after the 2-step PSA. However, due to the combination of HAS-Clay and Zeolite A-5 in the 2-step PSA, H$_2$S was not observed in our experiments. So far, there is not enough proof to satisfy the fuel specification due to the limitations of our detector, a gas-chromatograph. Therefore, in this study, it was assumed that the metal oxide eliminates H$_2$S by chemical adsorption to a concentration below the detection limit of 1.0 ppmv.

Based on this result, the adsorption capability of H$_2$S due to the metal oxide ZnO or Fe$_2$O$_3$ was evaluated using a sample gas of H$_2$S (100 ppmv) / N$_2$ balance and the same apparatus (see Fig. 2 (a)). The experimental conditions were a flow rate of 250 Nml/min, and either 1.3 g of ZnO or 0.95 g of Fe$_2$O$_3$. Note that the packed bed height of each metal oxide (α) was the same, namely 19 mm. That is, the space velocities (SV) of ZnO and Fe$_2$O$_3$ had the same value of 8,780 h$^{-1}$. These chemical adsorption tests were carried out at constant atmospheric pressure and a temperature of 40, 80 or 120 °C. In this experiment, the reaction of MeO+H$_2$S → MeS+H$_2$O (Me: metal element) was expected, even if the suitable reaction temperature was low. It was absolutely necessary to consider the pressure control in this removal procedure. The operating pressure was significantly attributed to the filling condition of the Bio-H$_2$ storage tank. However, the pressure of the chemical adsorption procedure was assumed to have been carried out under atmospheric conditions in this study. The effects of varying pressure condition will be investigated at a time when the practical design of a Bio-H$_2$ production system can be implemented.

The H$_2$S concentration was measured using a gas-chromatograph (GC-8A, Shimadzu Corp.). The measurement intervals were 20 min and 30 min. Based on the results of the outputted gas concentrations, the breakthrough curves were analyzed. Note that the detection limit of gaseous concentration was 1.0 ppmv for all trials.

Next, in the HCl removal experiment, CaCO$_3$ (Kanto Chemical Co., Inc.) and HAS-Clay were used. HCl concentrations in biomass (such as demolition wood and Cacao shell etc.) derived syngas are between 1 and 200 ppmv. Our aim was to reduce the amount of adsorbent needed, and to indicate the environmental benefit in comparison to the conventional system. This implies that some environmental benefit would be obtained by decreasing the adsorbent amount. Performances were estimated considering the blended HAS-Clay and CaCO$_3$ adsorbent. According to the adsorbent characteristics, HAS-Clay can work effectively at lower temperatures, while the effective working temperature of CaCO$_3$ is higher. It is therefore necessary
to seek an optimal operating temperature. Based on the plant operating conditions, a temperature between 100 and 200 °C could be a suitable candidate. This is appropriate in terms of the temperature profiles present in the plant. In order to evaluate the adsorption performance, the following experiments were executed using the apparatus depicted in Fig. 2 (b). The combination of the effects of CaCO3 and HAS-Clay were investigated. Sample combinations of mono 1.0 g CaCO3, mono 0.1 g HAS-Clay and blended-CaCO3 (1.0g) + HAS-Clay (0.1g) were prepared. For each sample, the feed gas, which consisted of 1,160 ppmv HCl and N2 balance, was fed into the apparatus at a flow rate of 200 Nml/min. Note that the flow rate was kept at a constant rate through use of a pressure control valve. That is, the inner pressure of the reactor was altered in accordance with the set temperature. Set temperatures of 100, 150 and 200 °C were chosen for this experiment. However, in general, the operating temperature of HAS-Clay was between 60 and 80 °C. It was necessary to seek a temperature which maximized the capture capacity. The unreacted gas (output), which passed through the reactor, flowed into a beaker containing 400 ml of distilled water. After this, the dynamic pH values were measured using a portable pH/ORP meter (D-72, HORIBA, Ltd.). The measurement interval was 30 s, and the pH resolution was 0.01 pH. The combinations of sample weight, and its SV including the bed height (β) of each specimen are shown in Table 2.

\[ SV = \frac{\text{feed gas volume at standard temperature and pressure [m}^3/\text{h]} }{\text{volume of packed bed adsorbent [m}^3] } \]

3. Experimental Results and Discussion

3.1 H2S Removal Test

As explained in our previous studies, the performance of H2S removal due to HAS-Clay has been confirmed. This result implies that H2S as well as CO2 can be simultaneously adsorbed by HAS-Clay. However, in order to meet the strict fuel specification for FC application, a complementary chemical adsorption would also be necessary. Considering this situation, the result of breakthrough time due to chemical adsorption was estimated. Here, breakthrough time is defined as the time taken from the start of operation to the time when H2S concentration reached 1.0 ppmv. Fig. 3 shows the results of chemical adsorption using ZnO and Fe2O3. From these results, the values of sulfur capture capacity Scap [g-S/100 g-sorbent] of ZnO and Fe2O3 adsorbents were estimated (see Table 3). Scap [g-S/100 g-sorbent] is defined by Eq. (1).

\[ S_{\text{cap}} = 100 \times \frac{t_{\text{BT}} \times V \times C_{\text{PG}} \times A_{\text{tot}}}{V_a \times W_{\text{sorbent}}} \] (1)

where, \( t_{\text{BT}} \), \( V \), \( C_{\text{PG}} \), \( A_{\text{tot}} \), \( V_a \) and \( W_{\text{sorbent}} \) are the breakthrough time [min], flow rate [L/min], concentration

| Temp. [°C] | ZnO | Fe2O3 |
|-----------|-----|-------|
| 40        | 0.24| 0.54  |
| 80        | 0.31| 1.65  |
| 120       | 0.28| 1.69  |

Unit: g/S/100 g-sorbent

![Fig. 3 Breakthrough curves of ZnO and Fe2O3](image-url)
of pollutant gas [ppmv], atomic weight of absorbed material [-] (=32.07), molar volume [L/mol] (=22.413) and adsorbent weight [g], respectively 13).

3.2 HCl Removal Test

The performances of mono-adsorbent CaCO3 or HAS-Clay and blended CaCO3 and HAS-Clay were estimated (see Fig. 4). The aim of this experiment was to prove that the blended adsorbent possessed a more advantageous capacity than that of either mono-substance. In Fig. 4, the breakthrough time for each adsorbent was shown. Note that this value is the time from the start of operation to the time when HCl concentration reached 30 ppmv. The reason why the concentration of 30 ppmv was adopted is due to the detection limit of a blank test. Using these results, the chlorine capture capacity (Cl-ct) [g-Cl/100 g-sorbent] was estimated using Eq. (1). Note that the atomic weight of Cl is 35.45.

The performance effect of blended adsorbent was next investigated. The weight ratio of CaCO3 to HAS-Clay is 0.91:0.09, corresponding to a total weight of 1.1 g. Note that this weight ratio can be changed, and that this trial is only one example. Experiments tested in use of the blended adsorbent at temperatures of 100, 150 and 200 °C. Based on the resulting capture capacities, the mono-substance of CaCO3 or HAS-Clay and the blended adsorbent are compared in Table 4. Consequently, we can state that a more advantageous effect can be obtained by using the blended adsorbent rather than either mono-adsorbent. Furthermore, the performance at 200 °C was better, although HAS-Clay can effectively be used at lower temperatures. This advantage is probably due to the adsorption effect of HAS-Clay H2O and CO2 formed by the following reaction: CaCO3+2HCl → CaCl2+H2O↓+CO2↓ 24).

3.3 Impact Analysis

As this paper describes, HAS-Clay including blended HAS-Clay would significantly contribute to improving the adsorption of impurities in syngas. Here, the following conditions are assumed in the LCA study: (1) as the system boundary, the consumption amount of adsorbent to eliminate H2S and/or HCl completely is estimated. (2) In the case of H2S removal, using a metal oxide for chemical adsorption

| Temp. [°C] | CaCO3 | HAS-Clay | Blend |
|-----------|-------|----------|-------|
| 100       | 0.06  | 0.38     | 0.52  |
| 150       | 0.07  | 0.30     | 0.52  |
| 200       | 0.10  | 0.16     | 0.70  |

* Unit: g-Cl 100 g-sorbent
and HAS-Clay for physical adsorption are compared. Note that the metal oxide is used once and then discarded. HAS-Clay is assumed to be regenerable, because the regeneration can be carried out iteratively and secondarily in 2-step PSA. This means that the eco-burden of HAS-Clay for H 2S elimination is negligible. (3) Next, in the HCl case, a metal carbonate and the blended HAS-Clay with a metal carbonate are compared. Although the blended adsorbent might be regenerable, the used metal carbonate (e.g. CaCO 3) which HCl binds to has to be separated. Therefore, the GWP and ADP in this case are evaluated including the HAS-Clay.

The eco-burden was assessed using a LCA approach. A LCA is a technique assessing the environmental aspects associated with a system during its entire life cycle. According to both Lee et al. and Zucaro et al., the impact categories of abiotic metal depletion potential (ADP) and/or global warming potential (GWP) in a fuel cell application are highly affected 27) 28). That is, the consumption of a metal which is attributed to the system performance would significantly impact the eco-burden. Thus, the impact indexes of ADP and GWP were estimated by identifying the role of HAS-Clay.

First, the functional unit for our estimation is 1 Nm 3-Bio-H 2. Based on our previous study, the syngas components (dry basis concentrations) were assumed to be 55.96 vol.% H 2, 27.11 vol.% CO, 0.48 vol.% CH 4, 16.39 vol.% CO 2, 0.05 vol.% N 2, 1 ppmv NH 3, 30 ppmv H 2S and 100 ppmv HCl. Based on the process design (see Fig. 1 (a) and (b)), the process syngas volumes were estimated as follows: 2.65 Nm 3-dry/Nm 3-Bio-H 2 in the conventional case and 3.25 Nm 3-dry/Nm 3-Bio-H 2 in the proposed case. Furthermore, in each case, the common cold gas efficiency was 87.3 %-LHV. The recovery efficiencies of Bio-H 2 in each case were 67.5%-LHV and 55.0 %-LHV. The production efficiencies of Bio-H 2, i.e. the ratios between the Bio-H 2 production [MJ/h] and biomass feedstock supply [MJ/h], for the conventional case and proposed case were 39.1 %-LHV and 38.7 %-LHV, respectively 3). This is mainly due to the different operating conditions in the H 2 refinery process including the reduction of off-gas volume. Thus, the amounts of H 2S and HCl removed were 0.11 g-S/Nm 3-Bio-H 2 and 0.42 g-Cl/Nm 3-Bio-H 2 in the conventional case. The corresponding amounts in the proposed case were evaluated as 0.14 g-S/Nm 3-Bio-H 2 and 0.51 g-Cl/Nm 3-Bio-H 2.

Using the above data, the load amount of metal oxide used as an adsorbent (inventory) was next evaluated. In a conventional case, ZnO for H 2S and Na 2CO 3 for HCl were assumed to be used. The capture capacity of ZnO operated at 300 °C is 2.81 g-S/100 g-sorbent (SV=2,660 h -1) 13).那 of Na 2CO 3 is 5.35 g-Cl/100 g-sorbent (SV=24,000 h -1) 20). From these specific data, the required amounts were 4.05 g/ Nm 3-Bio-H 2 of ZnO at 300 °C and 7.84 g/ Nm 3-Bio-H 2 of Na 2CO 3 at 400 °C. Due to mono-Na 2CO 3 in a conventional case, HCl is expected to be removed by the reaction Na 2CO 3+2HCl → 2NaCl+H 2O+CO 2. Nunokawa et al. describes that Na 2CO 3 does not react with Sulphur 26).

In the proposed case, the amount (inventory) was evaluated under the following conditions. (1) As evidenced by our previous studies, almost the entire amount of H 2S can be eliminated through 2-step PSA (HAS-Clay and Zeolite A-5). This fact was confirmed in previous work 20). Due to the detection limit of the measurement apparatus, the purified gas would be residual H 2S of 1 ppmv. Therefore, the residue of H 2S (1 ppmv) is assumed to be completely removed by the metal oxide ZnO or Fe 2O 3 at 40 °C, and (2) HAS-Clay is a regenerable adsorbent because this material is used for a physical adsorption 26). Therefore, the eco-burden of HAS-Clay does not need to be accounted for. Consequently, the required metal oxide ZnO or Fe 2O 3 for H 2S removal at 40 °C was 1.94 g/ Nm 3-Bio-H 2 or 0.869 g/Nm 3-Bio-H 2 considering the experimental results.

Finally, for HCl removal, the capture capacity value of the blended adsorbent at 200 °C (0.70 g-Cl/100 g-sorbent) was adopted. Similarly, the load metal carbonate CaCO 3 of the blended adsorbent was 66.9 g/ Nm 3-Bio-H 2. Note that the total amount including HAS-Clay is 73.5 g/ Nm 3-Bio-H 2. As a reference, the amount of mono-CaCO 3 without the H 2S reaction is 381 g/ Nm 3-Bio-H 2.

In general, the result of GWP or ADP was calculated by multiplying the characterization factor of the target material by the amount of target material (inventory data). GWP is the global warming potential for a 100-year time period for each greenhouse gas emitted to the air in kg carbon dioxide equivalent [kg-CO 2 eq]. Furthermore, ADP suggests that the characterization model is a function of the natural reserves of resources combined with their rates of extraction. The natural reserves of these resources are based on the ultimate reserves. This factor is derived from the extraction of elements and fossil fuels and is a relative measure to the depletion of the reference element. In this example, antimony is used as the reference element. The unit of ADP is kg antimony equivalents [kg-Sb eq.] 20). The characterization factors including GWPs in this study are listed in Table 5. Note that these factors were obtained from SimaPro 8.2.

Fig. 5 shows the impact indexes of GWP and ADP in the estimated cases of H 2S and HCl removals. For H 2S removal, the integrated 2-step PSA and Fe 2O 3 adsorbent scheme would be significantly advantageous in terms of...
reducing the eco-burden. According to our previous studies, the role of a metal oxide as complementary chemical adsorption would be enough to entirely eliminate H₂S. Consequently, the eco-indexes of GWP or APD on basis of LCA can be remarkably reduced as opposed to the conventional case. Compared to the conventional case, the GWPs of 2-step PSA+ZnO or Fe₂O₃ were 3.18 and 1.43 g-CO₂/Nm³-Bio-H₂ respectively, as opposed to 19.4 g-CO₂/Nm³-Bio-H₂ for a conventional system. Furthermore, the ADPs of 2-step PSA+ZnO or Fe₂O₃ were 7.63 × 10⁻⁶ and 3.42 × 10⁻⁶ g-Sb eq./Nm³-Bio-H₂ respectively, as opposed to 2.75 × 10⁻² g-Sb eq./Nm³-Bio-H₂ for a conventional system. On the other hand, in the case of HCl removal, the blended HAS-Clay and CaCO₃ cannot yield any environmental benefit without the regeneration of the HAS-Clay or substitution of clay, a natural resource. The variation of syngas components involving its impurities depends on the species of biomass feedstock and/or the process design. Therefore, the selection of adsorbent, blending, and the combination of systems in considering the characterization of adsorbents will be appropriately investigated in future research.

4. Conclusions

This study discussed the eco-burden of the removal procedures using HAS-Clay. In this study, the eco-burdens were analyzed based on experimental results using a LCA approach based on GWP and ADP indicators.

We were able to demonstrate that HAS-Clay can contribute to the reduction of eco-burden in H₂S removal from the syngas used for Bio-H₂ fuel. In this case, the GWPs of 2-step PSA+ZnO or Fe₂O₃ were 3.18 and 1.43 g-CO₂/Nm³-Bio-H₂ respectively, as opposed to 19.4 g-CO₂/Nm³-Bio-H₂ for a conventional system. Furthermore, the ADPs of 2-step PSA+ZnO or Fe₂O₃ were 7.63 × 10⁻⁶ and 3.42 × 10⁻⁶ g-Sb eq./Nm³-Bio-H₂ respectively, as opposed to 2.75 × 10⁻² g-Sb eq./Nm³-Bio-H₂ for a conventional system. On the other hand, in the case of HCl removal, the blended HAS-Clay and CaCO₃ cannot yield any environmental benefit without the regeneration of the HAS-Clay or substitution of clay, a natural resource. The variation of syngas components involving its impurities depends on the species of biomass feedstock and/or the process design. Therefore, the selection of adsorbent, blending, and the combination of systems in considering the characterization of adsorbents will be appropriately investigated in future research.

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