A Proposal of a Highly-efficient Purification System for Hydrogen Production to Achieve a Lower LCCO₂ Level

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This study aims at proposing a new and highly-efficient H₂ purification system that is able to achieve a low carbon emission level. In general, the conversion of pure hydrogen fuel from syngas requires pressure within a range of 1.0 to 2.0 MPaG. However, the auxiliary power of a compression is quite high, and hence produces a greater eco-burden. In this study, an experimental apparatus is fabricated to observe the performance of a variety of adsorbents in different operating conditions. Based on the results of these tests, this study attempts to propose the design of an optimal system. Next, the observations reveal that a pressure as low as 0.4 MPaG has a high refining efficiency, while the operating temperature is similar to room temperature. Besides, the fabricated apparatus is able to produce a H₂ concentration at 97.0 vol.% with a refining efficiency at approximately 55%. In fact, it is close to that of a conventional system. In parallel, CO₂ gas can be extracted separately through the system, thus the gas will be available for the cultivation of agricultural products as a growth agent. Then, a further discussion is taken over the experimental results to consider the environmental effects on the basis of life-cycle assessment methodology.

Key Words

Biomass gasification, Pressure Swing Adsorption (PSA), HAS-Clay, LCCO₂

1. Introduction

Hydrogen has been argued as being the most versatile, efficient and environmentally friendly fuel, while also acts as the cheapest and safest form of transportation energy. H₂, however, has not been a primary energy source but a carrier, in which its real costs associated with related activities, including production, distribution and utilization, must be quantified to address some issues, including environmental cleanliness and sustainability. Furthermore, life cycle assessment (LCA) has been widely taken as an effective analytical tool to investigate the total environmental impacts in all phases of an industrial activity, from raw materials acquisition to the final disposal.

In recent researches related to the LCA of H₂ fuel, the eco-burden of H₂ fuel is compared to those of resources from other origins, e.g. the lowest specific greenhouse gas emissions of H₂ fuel from renewable resources are produced by wind. In particular, emission from biomass has been
known at approximately 25% of those of conventional H2 production systems from natural gas origins [9]. Besides, the H2 supply from biomass feedstock has some advantages, including a steady supply that is not influenced by weather condition besides CO2 mitigation.

In one prior studies, the specific CO2 emission has been revealed for H2 produced from biomass resources. Through a gasification process and pressure swing adsorption (PSA), pure H2 fuel has been assumed to be produced. In the case, which uses a "Well-to-Tank" basis, CO2 emission of auxiliary power in an energy plant mainly occupied by PSA operation would be around 60% of total emissions. As long as H2 production system is considered as contributing to global warming protection, it is hence necessary to reduce eco-burden in the production system in addition to the application of H2 fuel.

Therefore, this study aims at proposing an improvement of PSA system so as to purify H2 fuel for polyelectrolyte fuel cell (FC) equipment with a lower life-cycle CO2 (LCCO2) emission. The current study is conducted as follows: (1) reduce the operating pressure of PSA, (2) select suitable adsorbents to achieve a higher refining efficiency, and (3) gather sequestered CO2 for being supplied to agricultural facilities as a growth agent. Considering the stages, this study is expected to decrease the LCCO2 emission of the entire system.

2. Experiments

2.1 Experimental apparatuses

In this study, a refining process of pure H2 fuel and an extraction of CO2 as a by-product based on an improved Blue Tower (BT) process including two furnaces of coupling zones for reforming and pyrolysis and a pre-heater were designed. Practically, two sets of apparatus were prepared to measure the gaseous yields through a gasification process, and the performances of CO2 adsorption and H2 purification. Fig. 1 shows the experimental apparatuses taken to conduct biomass gasification based on the improved BT process and a two-step gas cleaning.

2.2 Experimental conditions

First, the gaseous yields were investigated through the modified BT process by using the equipment. Besides, waste woody biomass was taken as the feedstock. The samples included incense cedar from California, USA, which was provided by Kita-Boshi Pencil Co., Ltd.

Table 1 and 2 show the results of proximate and ultimate analyses, respectively. Based on gaseous yields at pyrolysis and reforming stages, the flow rate and concentrations of syngas from the performance simulator were observed. Note that the plant scale in this study is assumed to be 20 t/d.

Next, the performance of CO2 adsorption and H2 purification affected by the syngas were examined. In this case, the gaseous sample of the test includes an artificially-synthesized gas (simulant gas, Sumitomo Seika Chemicals Co., Ltd.) based on the gasification tests. Besides, the synthesized gas was not fed into the apparatus for preserving measurement devices. The components of simulant gas were mainly taken for the optimization of pressure and temperature. In details, the gaseous components of simulated gas are set at 55.9 vol.% H2, 19.7 vol.% CO, 16.4 vol.% CO2, and 8.0 vol.% CH4. The gaseous concentrations were measured by a gas chromatograph (GC-8A, Shimadzu Corp.) and/or a benchtop mass spectrometer (MicrotracBEL Corp.).

Next, using the developed two-step gas-cleaning equipment (see Fig. 1), the adsorption performance was measured. Tables 3 and 4 show the measurement conditions and the adsorbent candidates in experiments, respectively. In particular, the adsorbent candidates include HAS-Clay (synthetic substances of hydroxyl aluminum silicate and clay, Toda Kogyo Corp.), zeolite (Wako Pure Chemical Industries, Ltd.), and activated carbon (Kuraray Co., Ltd. and Japan Enviro Chemicals, Ltd.).

3. Results and Discussion

3.1 Results of the gasification test

Using the gasification apparatus, gaseous yields at reforming temperatures of 900°C and 950°C were obtained (see Fig. 2). Note that the gaseous concentrations are dry basis. In this study, H2 concentration in syngas was over 55 vol.% and that of CO2 reached approximately 17 vol.% at 950 °C. In fact, CO, CH4, and C2H4 were discovered, while H2O and sulfur compounds were also synthesized. However, H2S and COS are not shown in Fig. 2 for too small concentrations.

3.2 Results of the adsorption test

Next, a performance test to determine the most suitable combination during the change to different adsorbents was executed. The test was conducted by using the simulant gas based on the gaseous yields of syngas.

Fig. 3 shows the gaseous concentrations in the refining process after varying the adsorbent candidates. In the first process, it is critical to separate CO2 from other gases, including H2 under a lower compression circumstance. However, the volume of H2 that passes through the reactor in addition to its concentration must in fact be considered. Fig. 3 indicates that all gaseous components can pass
In the case of 2 steps, this single step PSA system is equipped in series.

Fig. 1 Experimental equipment

| Table 1  | Proximate analysis |
|---------|--------------------|
| Moisture [wt.%] | 6.02 |
| Ash [wt.%]        | 0.35 |
| Volatiles [wt.%]  | 82.92 |
| Fixed carbon [wt.%] | 10.71 |

| Table 2  | Ultimate analysis |
|---------|-------------------|
| Carbon [wt.%] | 50.9 |
| Hydrogen [wt.%] | 7.3 |
| Nitrogen [wt.%]  | 0.13 |
| Oxygen [wt.%]*   | 41.27 |
| Chlorine [wt.%]  | 0.01 |
| Sulfur [wt.%]    | 0.02 |
| Ash [wt.%]       | 0.37 |

*Oxygen by difference
### Table 3 Measurement conditions

| Conditions          | 1st step | 2nd step |
|---------------------|----------|----------|
| Volume of adsorbents [mL] | 200      | 200      |
| Temperature [°C]   | 30       | 30       |
| Adsorption pressure [MPaG] | 0.4      | 0.4      |
| Purified gas [MPaG] | 0.4-0.2  | 0.4-0.2  |
| Off gas [MPaG]     | 0.2-atmospheric Pressure | 0.2-atmospheric Pressure |

### Table 4 Adsorbent candidates

| Specification | HAS-Clay | ZeoliteA-3 | ZeoliteA-4 | ZeoliteA-5 | ZeoliteF-9 | Activated carbon (Kuraray) | Activated carbon (JE Chem.) |
|---------------|----------|------------|------------|------------|------------|---------------------------|-----------------------------|
| Chemical composition | SiO₂·Al₂O₃·H₂O | MeO·Al₂O₃·mSiO₂·nH₂O (Me: Cation) | Carbon | Carbon |
| Particle size [mm] | >2.0 | 2.36-4.75 | 2.36-4.75 | 2.36-4.75 | 2.39-4.75 | 4-5.5 | 2.36-4.75 |
| Pore diameter [nm] | <0.02 | 0.3 | 0.4 | 0.5 | 0.9 | 0.5-10 | 0.5 |

Fig. 2 Results of the gasification test

(a) Concentration of percolated syngas

(b) Permeability in each adsorbent

Note: HAS-Clay (Hydroxyl Aluminum Silicate+Clay)

Fig. 3 Results of the adsorption test

Through HAS-Clay. The permeability of CO₂ was lower, although those of H₂, CO and CH₄ were relatively higher compared to other adsorbent cases. In fact, HAS-Clay was found as being able to accumulate more CO₂ while H₂, CO and CH₄ can pass to some extent. Besides, H₂ permeability in this case was relatively higher in comparison to those of other gaseous components. In the next step, more H₂ may thus recover if H₂ can selectively separate from mixed gaseous components. Because Fig. 3 also indicates that Zeolite A-5 can adsorb syngas components except H₂ and CH₄.

According to these results, a combination of HAS-Clay at the first step with Zeolite A-5 at the second step is likely to be the most appropriate setting. To this extent, pure H₂ at 99 vol.% or higher concentration can be refined with a 55% refining efficiency. In order to increase refining efficiency, therefore, some optimizations are required over several settings, i.e. the operating pressure and temperature, the combination of adsorbents, and the breakthrough time of each component in syngas.

Next, the CO₂ gas extraction was investigated. Based on the discovered refining strategy, CO₂ sequestration has to be achieved with a high efficiency at the first step of PSA. Fig. 4 shows the breakthrough curve of each gas.
In this test, the syngas and carrier gas (Ar) were fed continuously into the apparatus at 13.1 NL/min. The loaded amount of HAS-Clay was 200 cc. The test was executed at an atmospheric temperature and at 0.4 MPaG operating pressure. In the end, CO₂ was found to be completely sequestered at around 3.5 to 4.0 NL of accumulated feed gas as a result of gas flow control and/or operating time.

Looking at the result, H₂ and CO₂ are likely to be separated individually by the combination of HAS-Clay at the first step with Zeolite A-5 at the second step, while gas flow control is taken by considering CO₂ retention time.

3.3 Life-cycle assessment

From the viewpoint of operation energy consumption, previous studies have found that residual CO₂ has a negative effect on the auxiliary power of PSA for purification of H₂ fuel. Hence, the operation of the modified BT process, including the PSA, was simulated based on the experimental results by using Aspen Plus. The energy consumption of a H₂ fuel production plant through a gasification process is estimated by referring to the design data (calculation) of a real plant. Practically, the energy consumption is primarily based on the auxiliary power. In this plant, electricity consumption covers blowers, instrumentation devices, PSA, bucket conveyors and pumps. In particular, the PSA system run by electricity is operated through successive adsorption (compression) and desorption (decompression) cycles. In a previous study, total auxiliary power has been estimated, e.g. the total power consumption is at around 280 kW in a 20 t/day case. The consumption is based on the result of a process simulation, which includes a bucket conveyor, blowers, pumps, PSA, induced draft fans and instrumentation devices. In fact, the electricity consumption of PSA occupies 60% of the total plant electricity consumption. In general, the total energy input originated from fossil fuel would be significantly affected by the energy input of auxiliary power within the renewable energy path of a biomass energy production plant. In terms of environmental benefit, some countermeasures for reducing energy consumption from fossil resources should hence be necessary. To gain more environmental benefits, this study considers these following approaches: (1) purifying H₂ with a low pressure in PSA; (2) reducing working fluid, i.e. CO₂ in syngas; and (3) utilizing sequestered CO₂ in agricultural products. Simultaneously, a strong attention is required to refining H₂ fuel with a higher efficiency. Thus, an LCA concept is taken to investigate the performance in terms of environmental burden.

Referring to the experimental results in conjunction with the designed plan, the optimal conditions are observed from LCA viewpoint. In the current study, the critical point is to propose a H₂ production system for mitigating specific CO₂ emission, which is equivalent to life-cycle CO₂ emission. In particular, this study focuses on the H₂ production system through the improved BT gasification process. The next step hence needs to refer to an energy management that considers the relationship between energy input and output to continuously and steadily operate the plant. Thus, an index is necessary, by which the eco-footprint of H₂ fuel is expressed and defined as Eqs. (1) and (2). Assuming that \( \eta_{\text{energy}} \) and \( FCO_2 \) are the H₂ fuel production efficiency [%] and the specific CO₂ emission of H₂ fuel [g-CO₂/MJ-H₂],

\[
\eta_{\text{energy}} = \frac{Q_{H_2}}{W_1 + W_2 + H_2(T_1) + H_2(T_2) + Q_{\text{syngas}} - Q_{\text{aux}}}
\]

\[
FCO_2 = \frac{C_1 + C_2 + A_{\text{aux}} - \alpha C_2}{Q_{H_2}}
\]

where \( Q_{H_2} \), \( Q_{\text{syngas}} \), \( W_1 \), \( W_2 \), \( H_2(T_1) \), and \( H_2(T_2) \) are the lower heating value of H₂ [MJ/h], lower heating value of syngas [MJ/h], lower heating value of off-gas from the first and second steps of PSA [MJ/h], compression power of the first reactor [MJ/h], compression power of the second reactor [MJ/h], sensible heat of the first reactor at T₁ in °C [MJ/h], and sensible heat of the second reactor at T₂ in °C [MJ/h], respectively. In Eq. (1), however, the sensible heat of inlet syngas, \( H_2(T_1) \) and \( H_2(T_2) \) would be very small because operating temperatures in the system being proposed are close to the atmospheric temperature. Thus, these sensible heats would be negligible. In general, required thermal energy in the plant operation is determined by its scale. The balances between product energy and off-gas energy are extremely significant; and the indexes of Eqs. (1) and (2) then have critical meanings. In details, the thermal energy for chemical reaction heat in the BT process has been compensated by partial syngas and char, the heat exchange of sensible heat from each piece of equipment, and the energy supply of off-gas from PSA. These energy resources are supplied to the reactors by a cascade circulation process. Besides, both energy factors are in a trade-off relationship, and should be balanced. Thus, it is necessary to reduce the input energy of \( W_1 \) and \( W_2 \) to maximize \( \eta_{\text{energy}} \). During a cycle of pressurization and depressurization in PSA, the gauge pressure of raw gas (syngas) is increased from 0.0 to 0.4 MPaG in the first step. Since the pressure drop due to adsorbed gases in the first step occurs, that increases to 0.4 MPaG again at the second step, while the fluid passing through the reactor of Zeolite A-5 gas is the purified H₂.

Furthermore, \( C_1 \), \( C_2 \), \( C_{\text{aux}} \), and \( C_{\beta} \) in Eq. (2) are the CO₂ emission of compressor at the first reactor due to electricity consumption [g-CO₂/h], CO₂ emission of compressor at the second reactor from electricity consumption [g-CO₂/h], auxiliary CO₂ emission other than
that of the compressor of PSA but including the portion of feedstock pre-treatment [g-CO₂/h] and CO₂ emission of the feedstock [g-CO₂/h], respectively. In detail, Cₛ is the sequestrated CO₂ emission. The coefficient α (0.0 ≤ α ≤ 1.0) is the percentage of adsorbed CO₂ gas that is potential for being taken as a growth agent in the cultivation of agricultural products and is affected by CO₂ adsorption performance. In case of α > 0, FCO₂ would be a negative emission. In other words, it is necessary to increase α as a means to achieve a more effective CO₂ sequestration to mitigating FCO₂. The coefficient α is possible to determine by a CO₂ assimilation test using a model plant (e.g., Arabidopsis thaliana). In the current study, α is assumed to be 1.0.

As an example of calculation, η_energy and FCO₂ in the case of a combination between HAS-Clay with Zeolite A-5 are at 82.8% and -47.6 g-CO₂/MJ-H₂, which imposes a negative emission. In a conventional case, η_energy and FCO₂ are at 79.0% and 57.4 g-CO₂/MJ-H₂. The auxiliary power is reduced by 112 kW in comparison to 164 kW of a conventional PSA. It implies that the proposed PSA has a significant advantage from an environmental viewpoint.

Referring to the results, H₂ is likely to be produced without a drop in terms of refining efficiency. Besides, with a negative CO₂ emission it can greatly contribute to global warming protection. Within this year, a further study has measured the growth effect and change of nutrients by using several model vegetables for the intake of CO₂ gas. In the end, the completion of the entire system is expected to produce a substantial contribution to the global warming protection.

4. Conclusions

The current study discussed the production of hydrogen fuel from biomass feedstock. By conducting an improved Blue Tower gasification process, the production of pure H₂ was found to have a lower LCCO₂ emission. Besides, a higher refining efficiency and the adsorption of CO₂ are able to be achieved as the results of observations involving the performance tests. In the future, the sequestered CO₂ is expected to be available and utilized as a growth agent in a variety of agricultural facilities.

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