DRY GAS CLEANING SYSTEM FOR BIOMASS GASIFICATION POWER GENERATION
(PERFORMANCE VERIFICATION BY TESTS WITH PILOT PLANT AND FEASIBILITY EVALUATION)

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ABSTRACT Gasification power generation plant has significant potential for highly efficient utilization of biomass and refuse derived materials. This work evaluates the performance of the dry gas cleaning system for the power generation plant and to examine its feasibility in commercial scale. Sorbents for impurity removal was prepared as copper based mercury sorbent, glass fiber reinforced halide sorbent and zinc oxide sulfur sorbent. Performance evaluation in the demonstration plant showed sufficient performance for various impurities. Power generation test with the molten carbonate fuel cell (MCFC) was also successful in accomplishing stable power generation with the MCFC. The commercial scale plant of dry and wet system was designed and compared, which showed large advantage of the dry system. These results confirmed that the dry gas cleaning system is sufficiently feasible to establish the biomass gasification based power generation system.

Keywords: Dry Gas Cleaning, Gasification, Sorbents, Fixed Bed, High Temperature Fuel Cell

1. INTRODUCTION
Environmental protection is exhibiting an imperative necessity according to the global climate change and its recognizable effect on our daily life. Efficient energy conversion from various renewable fuel as well as fossil fuel is growing concern for the electric enterprise and other energy suppliers. To improve thermal efficiency of the power generation systems, integrated gasification combined cycle power generation and gasification combined with high temperature fuel cell power generation are developed by various projects. Attempt to produce liquefied fuel from biomass or wastes are matters of great expectation these days, because the convenience for transportation and preservation will expand the application of the renewable energy to the transport sector and general purposes. Those applications of efficient energy conversion are confronted with common technical tasks to be solved; contaminant control during the energy conversion processes is essential for protecting equipments in the power generation system and for inhibiting the degradation of the catalysts in the conversion processes.

This work tries to provide feasible gas cleaning system that has wide range of applicability to the various energy conversion processes. We selected a power generation plant with high temperature fuel cell that is operated on gasification fuel derived from biomass, waste, and other unused energy as design criteria for determining target performance of the gas cleaning system [1]. The plant is expected to have high efficiency of power generation and flexibility in fuel selection to establish practical use of energy conversion system of biomass and waste. The required system should be equipped with an advanced dry gas purifier for removing various impurities contained in the raw fuel gas. The expected impurities are dust, mercury, halides, and sulfur compounds. The removal procedure, however, has concatenation of processes to capture the series of impurities; the appropriate sorbents are necessary for each process to attain sufficient performance.

This work thoroughly describes the development of the gas cleaning system, includes the development of suitable sorbents for the impurities, pilot plant operation of the gas cleaning system equipped with the obtained sorbents, and feasibility study of the system in comparison to the wet system.

2. DESIGN CRITERIA OF GAS CLEANING SYSTEM
Operation condition of the power generation plant is deeply related to the strategy for designing the gas cleaning system. Thus, we determined the outline of the power plant and issues related to the development of the gas cleaning system. The power plant is combination of biomass/waste gasification (BG) and high temperature fuel cells (MCFC or SOFC). Installed capacity of the unit plant is assumed to be several MW or less, because the accumulation of the fuel is limited by the density of biomass and the distributed source of waste. Practical and simple gas purification system is required for the relatively smaller capacity of the power plant. The minimum requirement for the system is removal of various impurities that are harmful to fuel cells and environment, which includes dust, tar, halides, sulfur compounds and heavy metals. Dust and tar are to be removed by physical processes, such as pre-coat type bag filter. Thus, we concentrated on the development of chemical processes for the mercury, halides, and sulfur compounds, and to demonstrate their performance in the pilot plant with actual and simulated gasified gas.

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3. EXPERIMENTAL AND EVALUATION METHOD

3.1 Sorbent Development and Preparation

Impregnated activated carbon is generally used for removal of mercury from flue gas, natural gas or other application. Their effectiveness in biomass derived gas was revealed by extensive screening test for eight candidates of activated carbon sorbents, which includes deodorants, acid gas removal, and organochloride removal as well as mercury specific sorbents. Only one candidate (denote as AC) was confirmed to have considerable capacity for the mercury removal under coexistence of H₂S and HCl at 160 °C [2]. Because the mercury capacity of the AC showed considerable decrease by increasing concentration of coexisting hydrogen sulfide, other candidates were sought to obtain higher durability to the sulfur compounds. We investigated to the copper based sorbent that has potential to remove mercury in the specific application. The sorbent (Cu*) mainly consists of copper(II) oxide that was prepared a coprecipitation method from copper(II) nitrate, sodium hydroxide and silica sol. The obtained precipitate was extruded in pellet sorbent of a cylindrical shape of 3 mm diameter using an inorganic binder. The pellets were air-dried at 60 °C and were calcined at 400 °C for 4 hours.

Sodium based sorbent is potential candidate material for the halide removal, because it has the favorable chemical equilibrium for the reaction with HCl and HF. Consequently, we developed preparation procedure to obtain reactive sodium aluminate from sodium carbonate and colloidal alumina [4]. We endeavored to establish molding procedure for the sodium aluminate sorbent by introducing various additives and supporting materials to prepare porous structure or to act as aggregates of the pellet. Extrusion method was principally applied to pelletize the raw materials, so that the mass production of the developed sorbent is possible with minimum improvement of the procedure. Preproduction of the halide sorbents provided the pellet in various shape and structure. The products were screened by the comparable evaluation of the strength of the pellet and halide removal performance. We adopted practical crush test of free falling from height of two meters to compare the strength of those pellets [5] instead of the established compression test.

While regenerable desulfurization sorbents such as zinc ferrite, zinc titanate, and other zinc-based sorbent are available for high temperature desulfurization, single-use sorbents are suitable to establish simplicity of the system by eliminating side stream for regeneration procedure. Zinc oxide sorbent is primary candidate for the sulfur removal process. It is known that the zinc oxide has lower reactivity toward organic sulfur compounds, typically COS. Thus, commercial plant usually adopts COS conversion process in the upstream of the zinc oxide bed. Thus, we considered the performance for COS removal and necessity of the conversion catalyst in the screening test.

3.2 Impurity Removal Performance Tests

Performance tests of all sorbents were carried out in the fixed bed reactor at the condition summarized in the Table 1. The main gas composition simulated gasified gas of cedar chip. The fuel was selected because the simulated gas contains considerable amount of moisture, which represents the most difficult condition to remove halides and sulfur compounds. Moisture is considered to act negatively for halide removal and desulfurization according to the chemical equilibrium of the reactions for those contaminants with the reactive species in the sorbent, as shown in the Eqs. (1) and (2).

\[ \text{NaAlO}_2 + \text{HCl} \rightarrow \text{NaCl} + 0.5\text{Al}_2\text{O}_3 + 0.5\text{H}_2\text{O} \]  \hspace{1cm} (1)

\[ \text{ZnO} + \text{H}_2\text{S} \rightarrow \text{ZnS} + \text{H}_2\text{O} \]  \hspace{1cm} (2)

The condition also brings difficulty in avoiding condensation of moisture during operation of actual plant. The gas condition was achieved in the laboratory by introducing component gases from gas cylinder through mass flow controllers to the reactor, while only steam was injected through the evaporator from micro plunger pump. The impurities were also introduced from gas cylinder, while mercury was carried by nitrogen from a vessel filled with desired vapor pressure of the contaminant. Condition concerning to the residence time in the sorbent bed was set by the purpose of the tests, namely acceleration test or practical condition test. Concentration of the contaminants and their species to the simulated gas was determined individually in each test. Breakthrough curves were measured at the reactor outlet by monitoring the impurity concentration. Mercury concentration was monitored by Hg⁰/Hg²⁺ analyzer (NIC, MS-D1 and DM-6B). Hydrogen chloride was measured by ionic electrode analyzer (Toa DKK, GNC-224) to determine the breakthrough. The sulfur compounds at reactor exit were determined by gas chromatograph equipped with flame photometric detector (Round Science Inc., AG-1 FPD).

<table>
<thead>
<tr>
<th>Table 1: Evaluation condition of contaminant removal agents</th>
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<tr>
<td>Temperature [°C]</td>
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<tr>
<td>Pressure [MPa]</td>
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<tr>
<td>Gas composition [vol%]</td>
</tr>
<tr>
<td>CO</td>
</tr>
<tr>
<td>CO₂</td>
</tr>
<tr>
<td>H₂</td>
</tr>
<tr>
<td>H₂O</td>
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<tr>
<td>N₂</td>
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</table>

While screening of the sorbent, accelerated reaction condition was applied to emphasize the difference in the performance of candidates. The inlet concentrations of the target impurities were ten times as high as those expected in the raw gasified gas. Residence time in the sorbent bed was reduced to one-third or a tenth of actual reactor operation. These conditions enable us to evaluate more candidates in shorter period and to select the superior sorbent.

3.3 Demonstration Plant Test

Biomass carbonizing gasifier. The configuration of the biomass gasification plant consists of four units of fuel carbonizer and entrained-flow type gasifier that is operated at ambient pressure [6]. Fuel processing capacity of the plant is 5t/d, which is appropriate size for the demonstration plant. Raw fuel is partly pyrolyzed at around 400 °C to produce volatile component and carbonized portion in the carbonizer. The carbonized portion of fuel is injected to the
combustor which is located at the bottom of gasifier to produce required heat for gasification in the reductor. The volatile component together with the steam contained in the raw fuel is carried to the reductor. The mixture is converted to combustible gas through the water gas shift reaction and char gasification reactions. Because the mean gasification temperature at around 1500 °C is achieved at the combustor, the tar formation is retarded to considerably low level even with raw fuel of high moisture content.

Dry gas purification demonstration plant. The demonstration plant of the dry gas purification system is shown in Fig. 1. The order of the processes for each contaminant and their operating conditions are optimized according to the specific sorbents and filter elements that are adapted to the system. The system consists of dry processes throughout the gas stream; the configuration successfully avoids the waste water treatment from the system. At the first process of the system eliminates dust and injected hydrated lime. The removal processes for mercury, halides, and sulfur compounds are all fixed bed reactor of specific sorbents that remove each contaminant by chemical reactions. The reactor design is important to reconcile the persistence of removal-performance of the sorbents and extended period for the replacement of the sorbents. The copper based mercury sorbent was installed in the mercury reactor to attain its appropriate temperature. The halide sorbent and desulfurization sorbent, zinc oxide, are placed in the combined reactor as their operation temperatures are in the same range.

![Schematic flow diagram of the demonstration plant of the dry gas purification system.](image)

**Figure 1**: Schematic flow diagram of the demonstration plant of the dry gas purification system.

Molten carbonate fuel cell test apparatus. The unit cell of MCFC was used to demonstrate the biomass gasification power generation system, because the evaluation of unit cell is suitable for reproducible test and comparative tests. The warming up of the cell was performed by supplying simulated reforming fuel of natural gas to anode and mixture of carbon dioxide and oxygen to cathode. The fuel gas at anode was then replaced with the purified biomass derived gas (syngas) through the heated tube to eliminate condensation of steam and to avoid adsorption of contaminants in the purified syngas. The cell performance was measured during the cell operation with the sole purified syngas.

### 3.4 Power Generation Test with MCFC

The pelleted cedar chip with moisture of 10 wt % was used as gasifier fuel. Warming up of the gasifier takes half a day with gas fuel, then the fuel is switched to the carbonized biomass. The fuel switching to the biomass takes another six hours. After the gasification of sole biomass was established, the raw syngas was separated to the gas purification system at required flow rate, typically 100 m³/h. The rest of the syngas was incinerated at combustor furnace. The raw syngas is purified sequentially through the gas purification system at ambient pressure and at elevated temperature between 130 and 300 °C. The syngas composition and content of hydrocarbons were determined with gas chromatograph (Round Science, Co. Ltd., AG-1 TTFH) equipped with dual TCDs and FID. Sampling was taken between the bag filter and the blower.

Each process with the sorbent, that was placed at downstream of the blower, was evaluated from the performance data of contaminant removal through the fixed bed reactor. The contaminant concentration was determined by the specific analyzer instruments listed in Table II. Detection limit of halide measurements are approximately 0.4 ppm for the each compounds. Mercury analyzer is able to determine concentration above 0.1 μg/m³. Two types of sulfur analyzer were applied to the performance evaluation of the desulfurization sorbent. Sulfur concentration up to 1000ppm was measured with FPD-GC. Purified gas at outlet of sorbent bed was detected by the SCD-GC, whose detection limit is 0.02 ppm.

**Table II**: Analyzer instruments to determine contaminant removal performance of the purification processes.

<table>
<thead>
<tr>
<th>Target imp.</th>
<th>Instruments</th>
<th>Principle</th>
<th>Supplier</th>
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<tr>
<td>Hg</td>
<td>AM-4</td>
<td>CVAAS</td>
<td>NIC, Ltd.</td>
</tr>
<tr>
<td>HCl</td>
<td>GNC-224</td>
<td>IE</td>
<td>DKK-TOA</td>
</tr>
<tr>
<td>HF</td>
<td>LC-10A</td>
<td>ISE</td>
<td>Shimadzu</td>
</tr>
<tr>
<td>Sulfur comp.</td>
<td>AG-1(FPD)</td>
<td>FPD-GC</td>
<td>Round Science</td>
</tr>
<tr>
<td>Low sulfur</td>
<td>Antek 7090S</td>
<td>SCD-GC</td>
<td>Shimadzu</td>
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CVAAS: cold vapor atomic absorption spectroscopy
IE: ion electrode
ISE: ion selective electrode
FPD: flame photometric detector
SCD: sulfur chemiluminescence detector
GC: gas chromatography

The purified biomass gas was then introduced to the MCFC test apparatus at anode inlet through the heated flow meter. Mixture gas containing 67 vol% of carbon dioxide, and 33 vol% of oxygen was supplied to the cathode. Current density of the cell was fixed at 100 mA/cm². During the warming up operation, the flow rate of the simulated fuel was 170 ml/min, and cell voltage was 895 mV. Flow rate of the purified syngas was increased according to the low calorific value of the syngas. Stability of generated power of the unit cell was evaluated under the operation with the purified fuel.

### 3.5 Feasibility Evaluation of the Gas Cleaning System

Based on the test results with the pilot plant of dry gas cleaning system, we tentatively designed the scale upped plant with gas processing capacity of 2,430 m³/h that is able to supply purified syngas to the MCFC with generation capacity of 1,000 kW. The results compared with the wet gas purification system of same scale that was configured by conventional process.
4. EVALUATION OF DEVELOPED SORBENTS

4.1 Regenerable Mercury Sorbent

Copper based sorbent (Cu*) showed remarkable performance for Hg removal and high durability to H2S. The existence of H2S is required for Hg removal with the sorbent. Although the effect of COS or NH3 was examined under existence of 500 ppm of H2S, the overlay effect was not recognized. Hg capacity of AC and Cu* was compared under coexistence of both H2S (500 ppm) and HCl (100 ppm). Cu* exhibited superior Hg capacity at 160 °C, which is more than ten times larger than that of AC at 120 °C. To summarize the results for mercury removal, the copper based sorbent has advantages of high durability to H2S and Hg capacity at higher temperature over impregnated activated carbon. Thus, it is possible to place the mercury removal process with the copper based sorbent at upper stream of the gas purification system.

The Cu* sorbent has another advantage of regenerable at moderate condition. The breakthrough curves shown in Figure 2 indicate the mercury removal characteristics of the Cu* sorbent pellets over the first five regeneration cycles. In these cycles, spent sorbent was subjected to regeneration step that was carried out in 1-2 vol% of oxygen mixed with nitrogen at 250 °C. Mercury capacity gradually increased during the five cycles, and then the capacity reached stable value up to 20 cycles.

![Figure 2: Multi-cycle absorbing test results of the regenerable mercury sorbent at 160 °C, 0.1 MPa.](image)

4.2 Halide Sorbent for Sub ppm Level Removal

Various preproduction halide-sorbents were prepared and subjected to the test on practical strength and halide removal capacity at 1 ppm breakthrough. Their results are summarized in Fig. 3. The conventional procedures were improved with two different methods; supporting material and pore building material was introduced to increase strength and reactivity, respectively. The former provided stronger pellet as circled by broken line. The latter had definitive effect on the reactivity, while strength improved as indicated by dotted line. Further modification of the two methods were proceeded to increase the HCl capacity by enriching sodium content, which had sufficient effect. Thus, mass production of the improved sorbent was carried out by applying the procedures of the best results in the three methods. The final was the sorbent reinforced by supporting material with increased sodium content (M1). The M1 sorbent reconcile the reactivity and the strength of the pelletized sodium aluminate at higher level.

The most advanced halide sorbent was examined by the breakthrough test at the condition representing the operation of reactor in actual gas purification plant. The result was expressed as HCl concentration at reactor outlet versus halogenation ratio of the sorbent bed. The parameter on the abscissas was calculated as a ratio of absorbed mole of HCl to the mole of sodium contained in the bed. The value designates the effectiveness of utilization of the sorbent. Concentration of HCl at reactor outlet was sufficiently low during pre-breakthrough. Halogenation ratio attained 70% at 1 ppm breakthrough, and the ratio exceeded 75% at 20 ppm breakthrough. This result demonstrated the applicability of the improved halide sorbent to the gas cleaning system.

![Figure 3: Effect of Na content and true density of the halide sorbent prepared by various methods. Marker size denotes the HCl capacity at 1 ppm breakthrough.](image)

4.3 Sulfur Sorbent Omitting COS Conversion Catalyst

Zinc oxide sorbent is available in several forms according to the operation temperature [2]. The low temperature type has advantage in sulfur uptake below 250°C. Three types of zinc oxide sorbents were evaluated in screening test for the application to biomass derived gas. Their operating condition recommended by supplier is summarized in Table III. Although The reaction temperature varies from 190 to 350 °C, breakthrough tests were consistently operated at 300 °C.

<table>
<thead>
<tr>
<th>Table III: Specification of ZnO desulfurization sorbents</th>
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<tr>
<td>Material</td>
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<tr>
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</tr>
<tr>
<td>Shape</td>
</tr>
<tr>
<td>Temp. [°C]</td>
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</table>

Figure 4 summarizes the screening test results of the sorbents. It shows amount of sulfur captured at 15 ppm breakthrough at various H2O concentration. The sorbent B exhibited stable performance at higher moisture concentration regardless of the hydrogenation catalyst. The low temperature type zinc oxide sorbent B was selected for further breakthrough test at practical condition.
5. DEMONSTRATION OF GAS CLEANING PLANT

5.1 System Performance with Simulated Gas Stream

The raw syngas contains considerably small amount of impurities according to the low impurity content in the raw fuel, cedar chip. The low contaminant level could not verify the sufficient performance of impurity removal for the developed sorbents. Thus, simulated gas experiments with higher contaminant concentration are required to evaluate the actual performance of each process that has chemical reactors filled with the sorbents. The contaminant level in the raw gas was increased to the range where the unexpected contribution of reactor materials in the plant is eliminated.

The key processes to be verified in the simulated gas are mercury removal, halide removal, and sulfur removal. The summary of the performance test is shown in Fig. 5. Each result is shown as a trend of impurity concentration measured at the upstream and the downstream of the sorbent bed. In all results, the impurity was added to the simulated gas stream at the operation time of one hour. Then, the impurity concentration increased at upstream of the sorbent to specific level. The impurity concentration at downstream remained below the detection limit of each analyzer instrument in all results. Sulfur removal performance of zinc oxide should be confirmed for both hydrogen sulfide, H$_2$S and carbonyl sulfide, COS. Although the reaction rate of COS with zinc oxide is generally inferior to that of H$_2$S, the selected zinc oxide sorbent exhibited the suitable performance to both of the sulfur compounds. This confirmed that the sorbent could be used in the desulfurization process without COS conversion catalyst. The simulated syngas tests revealed the applicability of the key processes to the purification system.

5.2 Gas Cleaning of Fuel Gas from Biomass Gasifier

Woody biomass gasification was performed at the fuel supply condition summarized in Table IV. Oxygen ratio of 0.39 was applied to reconcile the syngas higher heat value of 1100 kcal/m$^3$N and the carbon conversion efficiency of 99%.

Table IV: Summary of gasifier operation test for woody biomass.

<table>
<thead>
<tr>
<th>Gasifier test summary</th>
<th>Cedar Chip</th>
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<tr>
<td>Biomass fuel</td>
<td>Fuel supply rate</td>
</tr>
<tr>
<td>Fuel supply rate</td>
<td>Fuel higher heat value</td>
</tr>
<tr>
<td>Oxygen ratio</td>
<td>Syngas higher heat value</td>
</tr>
<tr>
<td>Syngas higher heat value</td>
<td>Flow rate</td>
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</tbody>
</table>

Trend of the syngas composition of the carbonizing biomass gasifier at the test is shown in Fig. 6. The composition is very stable through the duration of gasification. The resulting raw syngas contained CO, 20%; H$_2$, 12%; CO$_2$, 12%; CH$_4$, 1.7%; C$_2$H$_4$, 0.3%; and N$_2$, 54% in vol% for dry gas basis. Tar and higher hydrocarbon are retarded in the raw syngas. Thus, the fuel composition has sufficient potential to operate MCFCs properly. The carbonizing gasifier seems to have advantage in producing syngas from low calorific fuel at relatively small sized plant.

5.3 MCFC Operation with Purified Gas Stream

Power generation test results are summarized in Fig. 7. At the beginning of the syngas test, the fuel was switched from simulated reformer gas to the syngas. The cell voltage showed 50 mV drop due to the difference of fuel component of the both gasses. Then the voltage was stable throughout the test duration, except for the discrete voltage jump at 3.6 hour. The jump is due to the gas dilution by the inert gas in the bag filter that was injected to the process gas stream while the switching of bag filter unit. The defect of the gas composition is improved by applying pulse jet cleaning to the bag filter and establishing the continuous operation of system.
Figure 6: Trend of syngas composition derived from the carbonizing biomass gasifier fueled with cedar chip.

Figure 7: Trend of the MCFC unit cell output.

6. FEASIBILITY OF DRY GAS CLEANING SYSTEM

6.1 Configuration of Compared Systems

The tentative design revealed that the difference in process configuration of both dry and wet gas cleaning systems as shown in Fig. 8. The wet gas purification system with same scale and removal performance could not be configured by conventional process only; the supplemental dry gas purification processes were introduced to achieve suitable performance. Thus the number of main process in the dry system was seven, while wet system requires ten, which affected to the cost and utility of the systems.

6.2 Comparison of Utility Consumption and Plant Size

The utility, plant size, capital cost and operational cost were compared for the both systems. The dry system consume 30% less auxiliary power (internal consumption rate of 14%), which will contribute to the efficiency increase. Plant size of the dry system is 30% smaller than the wet system because of its simple system configuration, thus the plant cost is possibly reduced by 20%. Operational cost for the dry system is significantly low because the absorbing solvent for wet desulfurization, detergents, and waste water treatment can be eliminated.

7. CONCLUSION

Impurity removal sorbents for the dry gas cleaning system were developed. The pilot plant tests exhibited the superior performance of the sorbents. Based on the tests, commercial scale plant of dry and wet system was designed and compared, which showed large advantage of the dry gas cleaning system to the wet system. These results confirmed that the dry gas cleaning system is sufficiently feasible to establish the biomass gasification based power generation system.

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8. REFERENCES


