RECOVERY BRIQUETTING TECHNOLOGIES OF WASTE BIOMASS AND PYROLYZED WASTE CHAR PRODUCED FROM SOLID INDUSTRIAL AND AGRICULTURAL ORGANIC WASTES

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ABSTRACT
In this study, several experiments were performed to decrease volume or weight and detoxification of solid organic wastes produced from various agricultural activities and industries in Japan using the pyrolyzing and/or carbonizing process. Additionally, these solid organic wastes were also transformed into the stable materials of char (so-called 'pyrolyzed waste char'). The objective of this study was to develop an effective utilization system of the waste char pyrolyzed and carbonized from the solid industrial organic wastes using the pyrolysis equipment with overheated steam or fluidized bed pyrolysis equipment. From the feasibility study, it was suggested that waste char-biomass briquettes that are produced from the pyrolyzed waste chars of waste tires, cow manure and poultry manure are used instead of the fossil solid fuel (e.g. coal) based on their burning characteristics and analytical results of exhaust gases.
Keywords: Biomass, carbonizing processes, solid industrial and agricultural organic waste, waste char, waste char-biomass briquettes.

1 INTRODUCTION

In Japan, many kinds of solid industrial and agricultural organic wastes are discharged due to various industrial activities. Especially, if livestock waste and thinning woody material are left in the environment, they will be decomposed and may cause the bad smell and the public health problems. Therefore, the processes for the volume or weight reduction and detoxification of solid organic wastes have become very important day by day. In addition, the waste tires are needed to be processed because of the air pollution due to its spontaneous combustion and a noxious insect. Moreover, a shortage of the last disposal place is also a well-known economical problem. As for many organic natural wastes, defusing toxicity and volume (or weight) reduction have been carried out by incineration processing till today. However, incineration processing is regarded as questionable, noting that toxic substances, such as dioxin, are generated and discharged during unsuitable combustion of processing. Since all possible organic matters of useful resources are discharged as greenhouse gases, e.g. carbon dioxide (CO_2), the waste processing technology replaced with the same problem like CO_2 emission of the fossil energy utilization. Here, the attention has been attracted toward the organic waste carbonizing technology (i.e. carbonization). This organic waste carbonizing technology is a waste processing technology that is based on pyrolytic decomposition and used for defusing toxicity and volume reduction by heating the organic wastes under oxygen-less condition or others. Due to the oxygen-less conditions, there is no generation of dioxin, and the pyrolyzed waste char with a high utility value are expected. Some studies were focused on the production and characterization of synthetic woody chars for using as surrogates for natural sorbents [1], and others were performed based on the conditions of the char yield from pyrolysis [2]. However, since the carbonization conditions in processing technology are indefinite and stabilization evaluation of char wastes is not enough, the present conditions do not help in the spread of the technology. Furthermore, there are less researches on char obtained from the carbonization processing for energy recovery

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e.g. biomass steam gasification [3] and carbon resources such as preservation of fossil energy, although the CO_2 emission will be effectively reduced comparing with the decomposable original organic wastes.

It has been reported that the coal-biomass briquette (referred to as BB) technology for the reduction of sulfur dioxide (SO_2), particulate matters [4–6] and greenhouse gas emitted from BB combustion compared with the original coal combustion. BB is produced from pulverized raw coal, biomass (such as straw), various woody wastes and agricultural wastes (e.g. barks, sawdust, bagasse, beet pulp, rice husk) and slaked lime was used as a sulfur-fixing agent under high pressure. In this study, it was attempted to apply the BB technology to develop a method for waste char-biomass briquetting.

In the previous study, the possible utilization system to process intermediates carbonized from solid industrial organic wastes was investigated [7–9]. The objective of this study is to establish an effective utilization system of the carbonization wastes, so-called 'waste char,' that are pyrolyzed and carbonized from the solid industrial organic wastes (e.g. scrap tire, cow manure and poultry manure) using the pyrolysis equipment. This feasibility study suggested that waste char-biomass briquettes (WCBBs) produced from the pyrolyzed chars of waste tires, cow manure and poultry manure are used instead of the solid fossil fuel (e.g. coal) based on their burning characteristics and analytical results of exhaust gases.

2 EXPERIMENT METHODS

2.1 Sampling of solid industrial and agricultural organic wastes

In this study, the waste char samples of scrap tire, cow manure and poultry manure were obtained from DMX Co., Ltd. (Japan) and UNIREX Co., Ltd. (Japan) with the conventional pyrolysis equipment or the others with overheated steam or fluidized bed pyrolysis equipment, and waste wood chip was used as the biomass. Each char sample from carbonization was ground below 0.25 mm, and the biomass samples wheat straw and waste wood chip were made below 1 mm. The proximate analysis, the ultimate analysis, and the measurement of calorific values of these samples were carried out, and these were considered as basic investigation.

2.2 Briquetting preparations and combustion of waste char-biomasses

To prepare WCBBs, first, waste char and biomass were mixed at the predetermined weight ratios and then sulfur-fixing agent $Ca(OH)_2$ with a Ca/S ratio of 2 (chemical equivalent ratio) was added. Then, the mixtures were pressed under high pressure compression (~4 ton cm^{-2}) using a high-pressure jack (J-15, Iuchi) (Fig. 1) to obtain the WCBB samples such as scrap tire char-biomass briquettes, cow manure char-biomass briquettes and poultry manure char-biomass briquettes. Since the breaking strength of WCBB is important for transportation and handling at the time of combustion, usually the breaking strength is set to >40 kgf. The breaking strength of briquettes was measured under varying mixing ratio of char to biomasses by a uniaxial compression testing machine (S56A; Maruto Testing Machine Corp.) with a steel ball (10 mm in diameter). After that, the WCBB combustion experiment was conducted with the combustion equipment shown in Fig. 2.

The sample was inserted into the tubular electric furnace heated to 600°C and 800°C and was burned at the constant temperature for 1 hour. The burning air was supplied at the flow rate of 1.0 L min^{-1}. The exhaust gas was diluted and cooled by N_2 gas and introduced into SO_2 meter (SOA-7000; Shimadzu, Co. Ltd.) and carbon monoxide (CO) and carbon dioxide (CO_2) meter

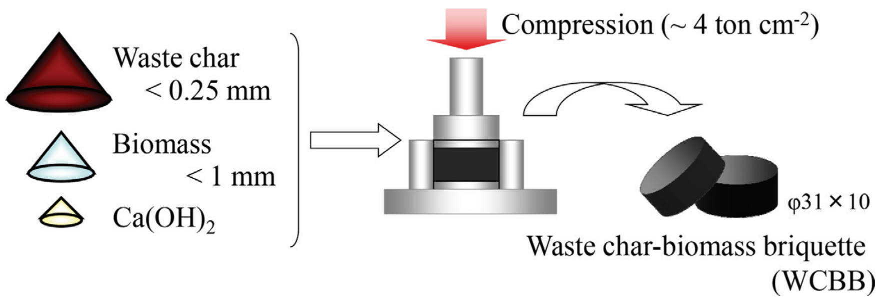

Figure 1: Schematic diagram for preparation of waste char-biomass briquettes.

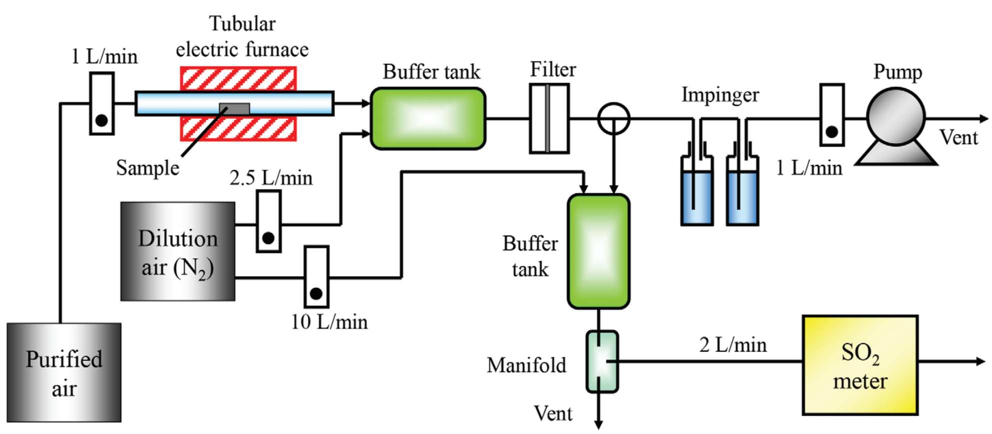

Figure 2: Equipment for combustion experiment of waste char-biomass briquettes.

(CGT-7000, Shimadzu, Co. Ltd.). The particulate matter collected in quartz filter was extracted with an absorption solution (2.7 mm Na_2CO_3/0.3 mm $NaHCO_3$), and the concentrations of SO_3^{2-}, SO_4^{2-} and Cl^- in the extract were analyzed with an ion chromatograph (DX-100; Dionex, Co. Ltd.). The amount of sulfur emitted was calculated as the sum of gaseous and particulate sulfur.

3 RESULTS AND DISCUSSION

3.1 Basic investigation of waste chars of carbonization

The results of ultimate analysis and the calorific value measurement of pyrolyzed materials, which are so-called waste chars of scrap tire, cow manure and poultry manure, are shown in Tables 1 and 2, respectively.

Since calorific value of 4,000 kcal kg^{-1} is required for a material to be considered as a fuel, it was suggested that all waste chars could be used as the solid fuel. Particularly, the calorific value of scrap tire char was very high about 7,400 kcal kg^{-1}. However, the content of sulfur in scrap tire char was approximately 2%; if scrap tire char was used as WCBB and burnt, the environmental pollution caused by the discharge of sulfur oxides would be high.

Table 1: Proximate analysis of testing core samples.

Sample	Proximate analysis (wt%, dry base)				Calorific value (kcal kg^{-1}) (wet base)
	MS	Ash	VM	FC	
Scrap tire char	2.0	8.8	3.1	86.1	7,400
Cow manure char	7.4	36.6	21.2	34.8	4,000
Wood char	4.1	4.6	35.1	56.2	6,200
Poultry manure char	9.8	34.3	16.0	39.9	4,100

Table 2: Ultimate analysis of tested char samples.

Sample	Ultimate analysis (wt%, dry base)				
	C	H	N	S	O
Scrap tire char	87.5	0.6	0.2	1.7	1.1
Cow manure char	40.9	2.8	2.1	0.4	14.6
Wood char	67.8	4.1	1.5	0.1	21.9
Poultry manure char	44.0	2.0	2.5	0.8	13.1

3.2 Measurement of the breaking strength of WCBBs

In order to investigate whether WCBB has the breaking strength, which solid fuels require for transportation and handling, the mixing ratio of the biomass (wheat straw) was changed and WCBBs were created. WCBBs were produced from pyrolyzed chars and biomass such as sawdust and waste straw and slaked lime ($Ca(OH)_2$) was used as a sulfur-fixing agent under high pressure (~4 ton cm^{-2}).

The relationships between the breaking strength of different WCBBs and additional amounts of different biomasses are presented in Figs 3 and 4. It was found that the breaking strength of WCBBs was increased with the increment of the additive amount of biomass as the general trend.

It is thought that this increment in the breaking strength of char-biomass briquettes was due to the presence of lignin contents in the biomass. The lignin contents show cohesion under high pressure and then it will be softened. Therefore, the char particles are glued, and it is thought that the breaking strength increased. Generally, the breaking strength required for transportation and handling is set to >40 kgf. As shown in Figs 3 and 4, the breaking strengths of scrap tire char-biomass briquettes and poultry manure char-biomass briquettes were more than 40 kgf by the addition of 20% or more biomass. However, in the case of cow manure char-biomass briquettes, additional biomass had not been added because it showed hardness more than 40 kgf. Since cow manure char-biomass briquettes had inadequate carbonization of the biomass in cow dung or the biomass mixed on the occasion of sample extraction, it can be conjectured to have the estimated breaking strength. These might be due to the existence of lignin in the biomass. Lignin has adhesiveness under high pressure. As mentioned above, since each WCBB was found to have sufficient breaking strength and density by the addition of the biomass, the suitable breaking strength (>40 kgf) for the substitution of fossil solid fuel was obtained.

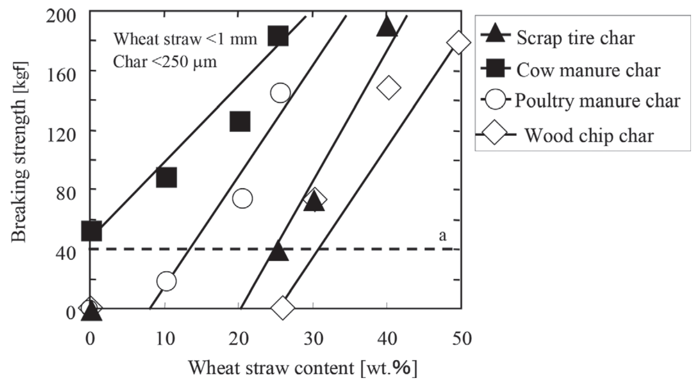

Figure 3: Relationship between the breaking strength of different WCBBs and the wheat straw content. Broken line at 40 kgf represents adequate strength for 100 km transportation.

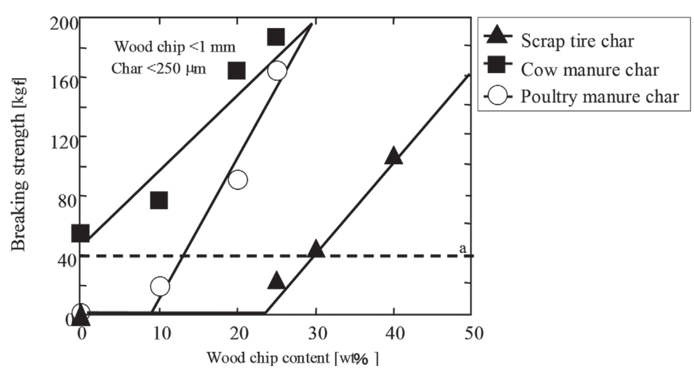

Figure 4: Relationship between the breaking strength of different WCBBs and the waste woody chip content. Broken line at 40 kgf represents adequate strength for 100 km transportation).

3.3 Combustion experiment and measurement of exhaust gases

The combustion experiment was conducted with tubular electric furnace combustion equipment. The sample was placed in the tubular electric furnace which was preheated to 500°C, and temperature rate was 800°C; the combustion time of the sample was 20 min. The exhaust gases produced due to combustion were diluted and then cooled by N_2 gas and introduced into the CO-CO_2 meter as well as to the SO_2 meter, and the concentration of each gas in exhaust gases was measured. The SO_2 concentration during combustion of scrap tire char-biomass briquettes is shown in Fig. 5. Just after starting combustion, SO_2 concentration has increased rapidly (175 ppm) but SO_2 emission was no longer observed within several minutes. It was considered that the sulfur contents contained in original waste char might be fixed effectively by $Ca(OH)_2$ during the combustion.

The CO and CO_2 concentrations in exhaust gases produced due to combustion of scrap tire char-biomass briquettes are given in Fig. 6. There was a little CO concentration immediately after combustion starts, and the direction of CO_2 concentration went up highly and showed the tendency which descended gradually after several minutes. This showed that perfect oxidation reaction during combustion continued for about 20 minutes.

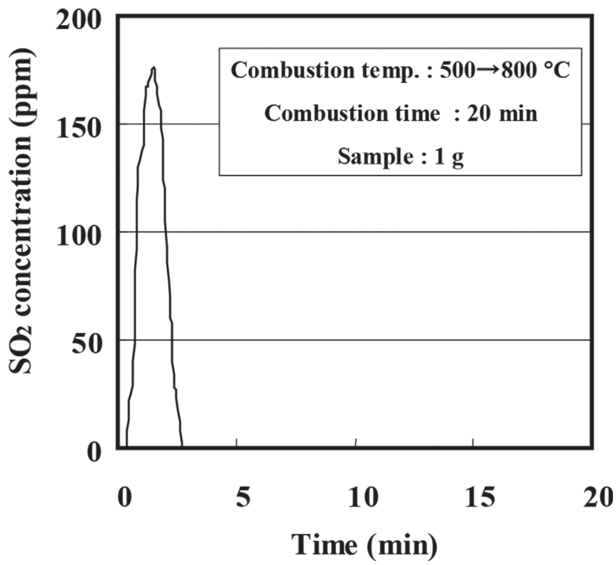

Figure 5: Variation in SO_2 concentrations in exhaust gases produced due to combustion of scrap tire char-biomass briquettes.

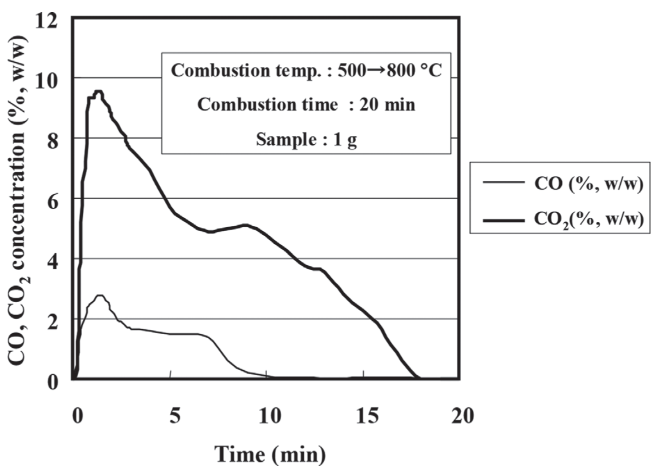

Figure 6: Variation in CO and CO_2 concentrations in exhaust gases produced due to combustion of scrap tire char-biomass briquettes.

Total carbon emission tendency during combustion of cow manure char, scrap tire char and their WCBBs are indicated in Figs 7 and 8, respectively. The sulfur equivalent of the SOx discharged at the combustion temperature of 800°C for each waste char and its WCBB is summarized in Fig. 9, and the chlorine equivalent of hydrogen chloride is also shown in Fig. 10.

Figures 9 and 10 show about 91% reduction in sulfur discharge during combustion of scrap tire char-biomass compared with that during combustion of BBs. However, the reduction of the amount of sulfur emission was not obvious for both cow manure char-biomass briquette and poultry manure

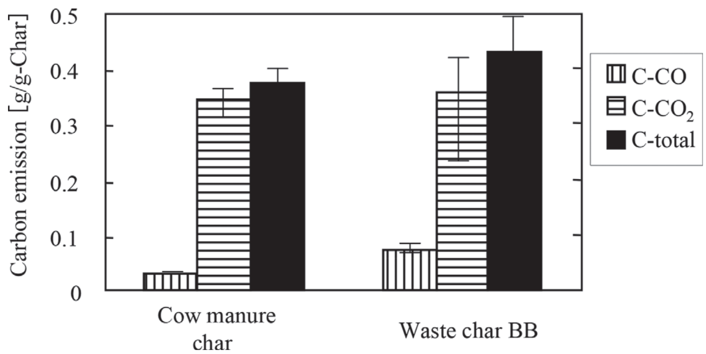

Figure 7: Carbon emission during combustion of cow manure char and its waste char-biomass briquettes.

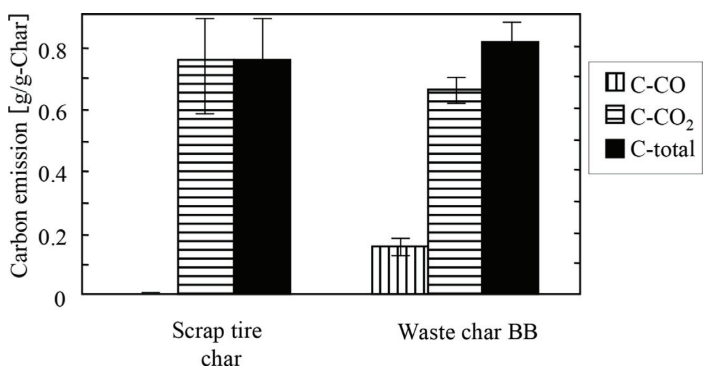

Figure 8: Carbon emission during combustion of scrap tire char and its waste char-biomass briquettes.

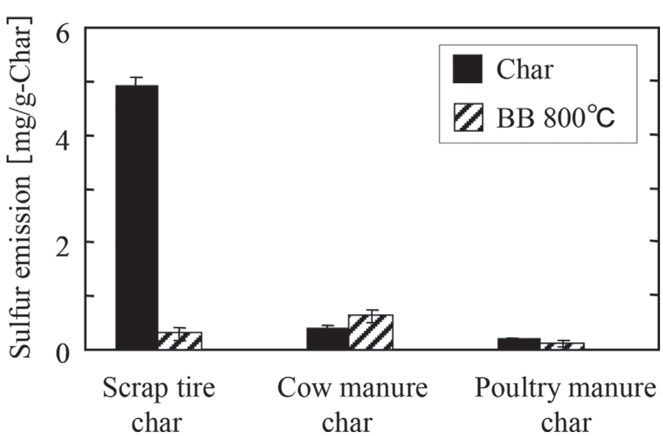

Figure 9: Sulfur emission during combustion of char and its briquettes.

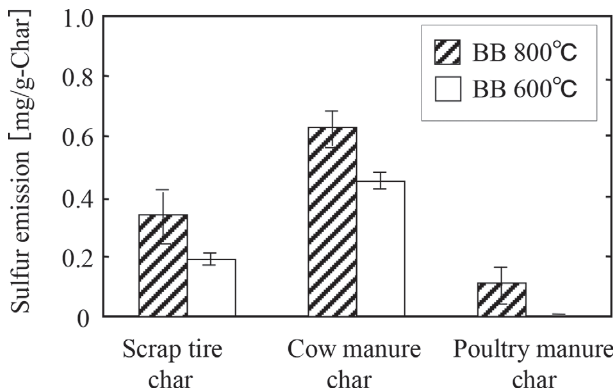

Figure 10: Sulfur emission during combustion of char briquettes at 800°C and 600°C.

char-biomass briquette because the amount of sulfur content was low in the original chars. Moreover, for all WCBBs, reduction of the discharged chlorine was not found.

The improvement in efficiency of combustion and the sulfur reduction could be considered as a cause of sulfur-fixed reaction during WCBB combustion. However, the chlorine reduction was not extremely found by the chlorine-fixed reaction.

$$Ca(OH)_2 + SO_2 + 1/2O_2 \longrightarrow CaSO_4 + H_2O \quad (1)$$

$$Ca(OH)_2 \longrightarrow CaO + H_2O \quad (2)$$

$$CaO + SO_2 + 1/2O_2 \longrightarrow CaSO_4 \quad (3)$$

$$CaO + SO_2 \longrightarrow CaSO_3 \quad (4)$$

$$CaSO_3 + 1/2O_2 \longrightarrow CaSO_4 \quad (5)$$

A sulfur-fixed reaction should pass the course in which $Ca(OH)_2$ and SO_2 directly react (reaction (1)), the decomposition reaction (it decomposes above 400°C) (reaction (2)), and then the sulfur-fixed reactions of SO_2 (reactions (3) to (5)). Since the combustion temperatures were 800°C and 600°C, it has been considered that both direct sulfur-fixed reaction and indirect sulfur-fixed reactions had occurred.

Next, the following reactions are considered as the chlorine-fixed reactions of $Ca(OH)_2$.

$$Ca(OH)_2 + 2HCl \longrightarrow CaCl_2 \cdot 2H_2O \quad (6)$$

$$Ca(OH)_2 \longrightarrow CaO + H_2O \quad (2)$$

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O \quad (7)$$

For the chlorine-fixed reaction, $Ca(OH)_2$ and HCl react directly (reaction (6)) and then decomposition reaction of $Ca(OH)_2$ occurred (reaction (2)). Here, since reaction (6) was a reaction that progresses below the temperature 400°C, it was thought that chlorine was fixed by an indirect reaction. Since the fusing point of crystal $CaCl_2$ is 772°C, it can be considerable that chlorine will be discharged by partially decomposing from the crystal chlorine with the reverse reaction (7) at the combustion temperature of 800°C.

As mentioned above, the mechanism of discharge for the sulfur part fixation by scrap tire char-biomass briquettes and chlorine can be explained. On the other hand, it was found that the phenomena of sulfur fixation of cow manure char-biomass briquettes and poultry manure char-biomass briquettes were not completed; it was suggested that the coexistence reaction system of SO_2 and HCl was needed to take into consideration.

3.4 Improvement on combustion experiment for fixation of sulfur and chlorine

It is considerable that the reactions with the coexistence of SO_2 and HCl are shown in the following reactions.

$$4HCl + O_2 \longrightarrow 2Cl_2 + 2H_2O \text{ (Deacon reaction)} \tag{8}$$

$$Cl_2 + SO_2 + H_2O \longrightarrow 2HCl + SO_3 \tag{9}$$

$$Ca(OH)_2 \longrightarrow CaO + H_2O \tag{2}$$

$$CaO + SO_3 \longrightarrow CaSO_4 \tag{10}$$

$$CaO + 2HCl \longrightarrow CaCl_2 + H_2O \tag{7}$$

$$CaCl_2 + CaSO_4 \longrightarrow CaCl_2 - CaSO_4 \tag{11}$$

It is thought that these reactions also occur under the coexistence of SO_2 and HCl, and the process in which formation of $CaSO_4$ is promoted by HCl. However, the mechanism by which the compounds fixed by $Ca(OH)_2$ in the reaction (11) generated a eutectic can be suggested. This tactic melting point becomes lower than its original fusing point of $CaCl_2$. Therefore, at the combustion temperature of 800°C, the eutectic melts and the reverse reactions of reaction (1), reaction (3) and reaction (7) will be easy to be progressed and then SO_2 and HCl were emitted.

Therefore, it was carried out in the experiment to improve the combustion conditions and to lower the burning temperature to 600°C from 800°C. The results are shown in Figs 11 and 12. According to the results, the amount of sulfur part discharge was in a decreasing trend compared with 800°C combustion.

Moreover, it was confirmed that the amount of chlorine part discharge was decreased remarkably for cow manure char-biomass briquettes and poultry manure char-biomass briquettes at the burning temperature of 600°C compared with 800°C combustion. Therefore, a part of sulfur and chlorine discharge was reduced at the burning temperature of 600°C and the efficiency of combustion was increased when burning the cow manure char-biomass briquettes at 800°C (Figs 11 and 12). The amount of sulfur and chlorine contents from the original cow manure char improved by char-biomass briquetting method. Once the combustion started, it occurred quickly, and it was surmised that a fixed reaction did not meet the deadline.

From the above experiments, it was suggested that the reduction in the emissions of sulfur and chlorine contents [10] the combustion excretions could be achieved by carrying out combustion control with the help of char-biomass briquetting method. Based on the results of this study, more basic experiments have been carried out and different technologies were developed to control air pollutants emitted from biomass fuel, which were also reported in the 4th International Conference on Energy and Sustainability [11, 12].

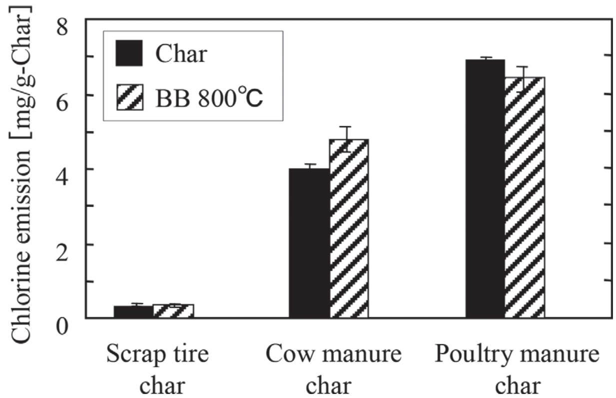

Figure 11: Chlorine emission during combustion of char and its briquettes.

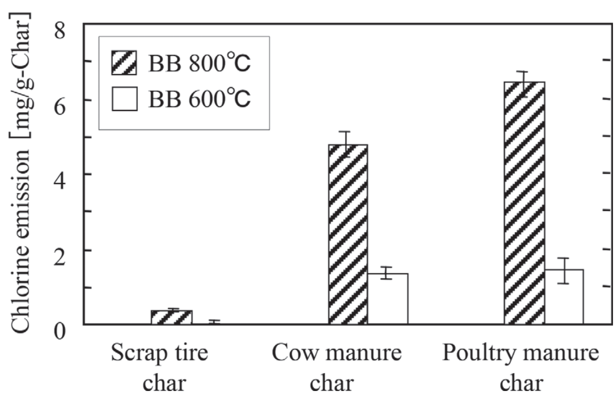

Figure 12: Chlorine emission during combustion of char briquettes at 800°C and 600°C.

4 CONCLUSIONS

From the results of this study, we can suggest that WCBBs can be considered as an alternative to coal fossil solid fuel. Moreover, we also confirmed that the recovery of resources from waste chars, effective use of renewable biomass resources, and the possibility of reduction of exhaustible natural resources can be achieved from the following viewpoints.

1. It was confirmed that carbonized waste chars made from solid industrial and agricultural organic wastes have calorific values more than 4,000 kcal kg^{-1}, which can be used as solid fuel.
2. Even though waste wood chip can be used as biomass, it was confirmed that enough breaking strength is required for transportation and handling. Although cow manure char-biomass briquettes were not added to the biomass, it also showed a hardness exceeding 40 kgf.
3. For these chars containing little amount of chlorine during combustion, when the burning temperature of WCBBs were rated at temperature of 800°C, their usual behavior and the reduction effect of SO_2 were confirmed. However, the controlling effect of HCl was not determined. The necessity for suitable temperature control as post-combustion control of WCBBs was suggested.

4. When the burning temperature of WCBBs was controlled below 600°C, the high reduction effects of both SO_2 and HCl from the analytical results of exhaust gases were also confirmed during the combustion of the cow manure char-biomass briquettes and poultry manure char-biomass briquettes.

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