EVALUATING THE CRUCIAL FACTORS AFFECTING HYDROGEN GAS GENERATION FROM MUNICIPAL SOLID WASTE INCINERATION BOTTOM ASH (MSWIBA)

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ABSTRACT

In this study, we examined the factors influencing hydrogen gas generation from municipal solid waste incineration bottom ash and methods to improve this process. A series of mixing and stirring experiments using bottom ash and water were conducted. The reaction temperature, liquid-solid ratio, stirring rate, and presence or absence of a grinding treatment were set as the experimental parameters. According to the results obtained in the present study, the optimum temperature for efficient recovery of hydrogen gas was 50°C. When the liquid-solid ratio was 5, or exceeded 3, more hydrogen gas was generated. When the stirring rate was 600 rpm, or exceeded 400 rpm, more hydrogen gas was produced. When bottom ash was crushed, the initial gradient of hydrogen gas generation dramatically increased.

1. INTRODUCTION

Approximately 44.0 million tons of municipal solid waste (MSW) was generated in Japan in 2015, 80% of which was incinerated. This resulted in the generation of approximately 3.2 million tons of MSW incineration residue, which was disposed of mainly in sanitary landfills (Ministry of the Environment of Japan, 2017). MSW incineration bottom ash (MSWIBA) contains an appreciable amount of metal aluminum that is distributed throughout various particle fractions of bottom ash. (Saffarzadeh et al., 2016; Arumugam, 2016). Hydrogen gas is generated by an aluminum-assisted water splitting reaction, which can be given by the following equation (Armstrong and Braham, 1996; Takatsuki, 1994; Toyofuku, 1989):

$$2Al + 6H_2O \rightarrow 2Al\,(OH)_3 + 3H_2 \uparrow \qquad (1)$$

Bottom ash imparts alkalinity to the reacting solution because it contains a large amount of Ca compounds. Hydrogen gas is generated through the reaction between water and essentially the metal aluminum in the bottom ash. When the hydration reaction proceeds in MSWIBA, a layer of hydrate is formed on the surface of the metal aluminum (Saffarzadeh et al., 2016), which prevents the aluminum from coming into further contact with the water. This is one of the reasons why hydrogen gas generation decreases over time.

Hydrogen gas is the only carbon-free energy source and its energy potential is higher than that of other known fuels, such as methane, ethane, and gasoline (Marbán & Valdés-Solís, 2006; Marbán et al., 2006; Shinnar, 2003; Granovskii et al, 2006). A newly developed energy source can replace fossil fuels. When hydrogen in fuel cells is subject to direct combustion, it is possible to generate energy without the production of CO_2, because water is the only by-product formed (DeLuchi, 1989; Momirlan & Veziroglu, 2002; Momirlan & Veziroglu, 2005).

If the generated hydrogen gas can be efficiently recovered, MSWIBA may be considered a source of hydrogen for energy production. To make the system of hydrogen gas generation from bottom ash and water practically feasible, it is necessary to reduce the production unit cost. Additionally, it is necessary to understand the most suitable conditions for efficient collection of the hydrogen gas. The most critical parameters are reaction temperature, stirring rate, and liquid-solid ratio. If the amount of water (l/s) required for hydrogen gas generation is reduced, it would be possible to reduce the amount of waste liquid after collection

of the hydrogen gas. Equipment for mixing and stirring of bottom ash with water is also necessary. The size of the equipment depends on the amount of bottom ash and the time until completion of hydrogen gas generation with mixing and stirring. For these reasons, a shorter mixing and stirring time is important, and it is also necessary to consider accelerating the hydrogen gas generation process.

The purpose of this study was to elucidate the factors influencing the hydrogen gas generation from MSWIBA and to determine whether hydrogen gas generation can be promoted by crushing the bottom ash. A series of mixing and stirring experiments using bottom ash and water were conducted by regulating the reaction temperature, liquid-solid ratio, stirring rate, and the presence or absence of grinding treatment as the experimental parameters.

2. MATERIAL AND METHODS

2.1 Sampling

Bottom ash sample was collected from the incineration facilities S (Stoker-type, 750 t/day) and R (Stoker-type, 900 t/day) located in the F. city in Japan. Bottom ash from the S plant is hereinafter referred to as S-BA and that from the R plant as R-BA. The S-BA was sieved to less than 9.5 mm in diameter. Ferrous metals were manually removed from R-BA by a magnet and subsequently sieved to less than 30 mm in diameter. The R-BA was only used to evaluate the promotion of hydrogen gas generation. The samples were air-dried and then oven-dried at 65°C for 24 hours to remove moisture and minimize the effect of weathering. The samples were dried at 105°C, crushed to less than 0.5 mm, boiled in HCl (1 mol/l) for 30 min and then metal aluminum contents in the samples were measured by an atomic absorption spectrophotometer (UV-1230, Japan, SHIMADZU CORPORATION). The S-BA and R-BA contained 3.9 and 3.8% of metal aluminum by mass percentage, respectively.

To enhance hydrogen gas generation, S-BA was crushed to less than 45 μm by a vibration mill and R-BA was crushed to 4.2 μm in average particle size by a cutting mill and a jet mill. A cutting mill that was a crusher using blades, was used to reduce sample particle size to be suitable for the jet mill. The jet mill was a crusher using a high speed jet of compressed air. Sample particles were crushed by mutual contact. Particles that could not be crushed during the milling process were excluded from the experiments because it was presumed that the crushed and non-crushed bottom ash samples had the same metal aluminum contents.

2.2 Stirring and mixing experiment using bottom ash and water

Figure 1 shows a schematic diagram of the experimental setup, which included a reactor, liquid collection bottles, hydrogen gas concentration sensor, and flowmeter, all of which were connected by the PVC tubes. The bottom ash and water were mixed and stirred in the reactor, which could maintain a constant temperature and change the stirring rate. Hydrogen gas, generated in the reactor, flowed through the tube and passed through a liquid collection bottle to cool it and condense water vapor. The gas passed
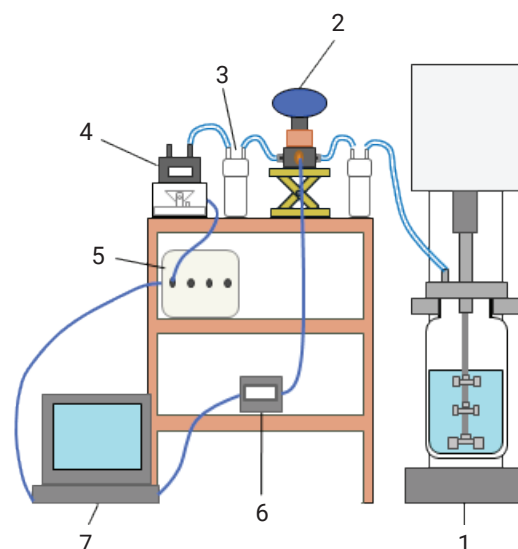

FIGURE 1: Schematic diagram of the experimental setup. 1) Reactor, 2) Sensor of hydrogen gas concentration, 3) Liquid collection bottle, 4) Flowmeter, 5) Data logger, 6) Display of hydrogen gas concentration, 7) PC.

through the sensor, followed by the liquid collection bottle, which prevented the breakdown of the sensor from the backflow of the flowmeter oil, and finally the flowmeter. Hydrogen gas concentration was measured at intervals of 1 minute during the experiment. The amount of gas generated was measured every 3.24 mL which was the collection capacity of the flowmeter. In the experiments, 500 g of the samples were used. Before the experiment began, the gas in the entire setup was substituted with nitrogen by purging 1 L/min of nitrogen gas for 5 min. Table 1 shows the experimental conditions.

3. RESULTS AND DISCUSSION

3.1 Consideration of the factors that influence hydrogen gas generation

3.1.1 Influence by reaction temperature

Figure 2 shows the relationship between hydrogen gas generation and time. At 50°C, the highest amount of hydrogen generated was 11.4 m³/t-ash, and the shortest experiment time of 13.0 days was achieved. At 40°C, 10.4 m³/t-ash of hydrogen gas was generated over 21.0 days. At 60°C, the amount of hydrogen gas generated was 10.2 m³/t-ash over 20.5 days. According to the research of Zhao, Z et al., 2011, the chemical reaction rate increases when temperature increase. However, when temperature increase, also the concentration of OH- is decrease lead to the reduce of hydrogen generated. And the chemical reaction is heat dissipation reaction. For these reasons, the same phenomenon occurs in this study, at 50°C the amount of hydrogen generated was the highest, compare to 40°C and 60°C.

3.1.2 Influence of the liquid-solid ratio (l/s)

According to Figure 3, at l/s = 3, 7.9 m³/t-ash of hydrogen gas was generated over 14.6 days. This was about

Case	Sample	Reaction Temperature (°C)	l/s	Stirring rate (rpm)	Crushing process
1	S-BA	40	5	600	Non-crushed
2		50			
3		60			
4		50	3		
5			5	400	
6				800	
7					Crushed
8	R-BA			600	Non-crushed
9					Crushed

3.5 m³/t-ash lower than that produced at l/s = 5. At l/s = 3, the precipitation of bottom ash particles was identified in the reactor. This could be because the mixing of bottom ash with water was insufficient at lower l/s. Therefore, l/s should be greater than 3.

3.1.3 Influence of stirring rate

As displayed in Figure 4, the highest amount of hydrogen gas generated was 11.4 m³/t-ash at 600 rpm. The second highest amount of hydrogen gas generated was 11.0 m³/t-ash at 800 rpm. The lowest amount of hydrogen gas generated was 6.8 m³/t-ash at 400 rpm. At 400 rpm, bottom ash and water were not sufficiently stirred and mixed in the reactor, as was the case when l/s = 3 (50°C, 600 rpm). The amount of bottom ash precipitated in the solution increased, which is why hydrogen gas generation decreased. The stirring rate should, therefore, be greater than 400 rpm. It is possible to achieve a practical hydrogen gas generation volume and speed even at 400 rpm or less if the stirring efficiency of bottom ash and water increases by optimizing the shapes of the stirring blades and reactor.

3.2 Promotion of hydrogen gas generation by crushing

In the case of S-BA, 6.6 m³/t-ash of hydrogen gas was generated from crushed S-BA and water. This was approximately 4.8 m³/t-ash lower than that for the non-crushed bottom ash (Figure 5). In the case of R-BA, 5.1 m³/t-ash of hydrogen gas was generated from crushed R-BA and water. This was approximately 7.6 m³/t-ash less than for the non-crushed bottom ash (Figure 6).

Conversely, the initial gradient of hydrogen gas generation (i.e. from 0 to 20%) increased. In the case of S-BA, this was from 3.8 m³/t-ash/day when non-crushed S-BA was used to 274.5 m³/t-ash/day when crushed S-BA was used. In the case of R-BA, this decreased from 8.2 m³/t-ash/day for non-crushed R-BA to 135.1 m³/t-ash/day for crushed R-BA. The initial gradient of hydrogen gas generation increased significantly by crushing; however, the cumulative amount of hydrogen gas generation decreased. Because of the rigorous crushing of BA, metal aluminum that is presumed to trigger hydrogen generation has turned to very fine particulates with significantly large surface areas. As a
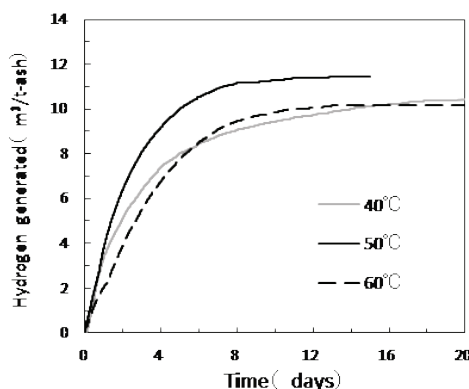

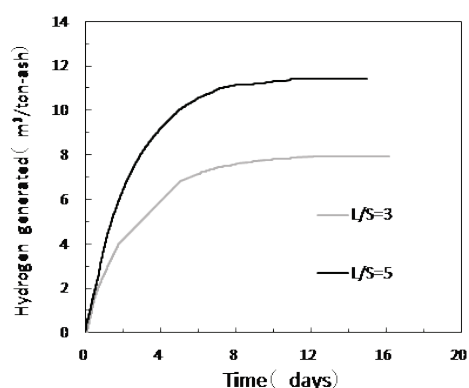**FIGURE 2:** Influence of reaction temperature.
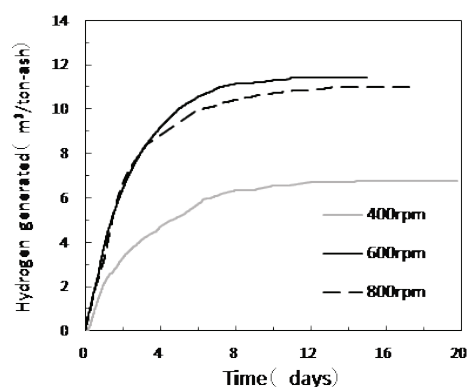

FIGURE 3: Influence of liquid solid ratio.

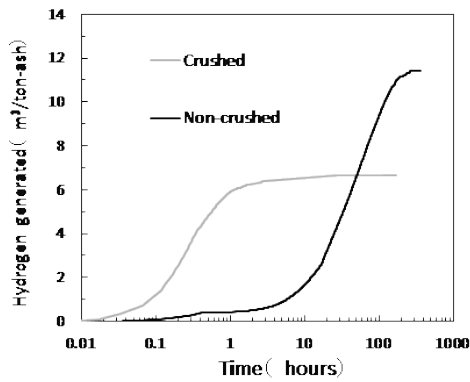**FIGURE 4:** Influence of stirring rate.

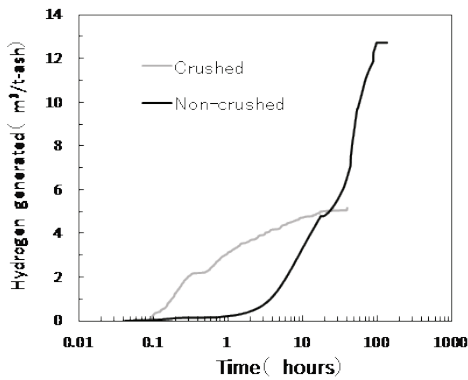**FIGURE 5:** Promotion effect by crushing process (S-BA).

FIGURE 6: Promotion effect by crushing process (R-BA).

result, the corrosion rate of such fine metallic particulates has considerably accelerated and they rapidly consumed at the beginning of the reactions. Therefore, almost no or little reactive metal aluminum remained for the advanced steps of the experiment that resulted in lower cumulative hydrogen in the crushed BA.

3.3 Relationship between hydrogen gas generation and pH

Table 2 shows the volume of hydrogen gas generated and the pH of the liquid phase when the experiment completed. At the end of the experiment, the pH was within 10.9–12.0 when S-BA and R-BA were used. There is no no-

ticeable relationship with reaction temperature or stirring rate. Mixing and stirring were insufficient for cases 4 and 5, which had comparatively low pH values of 11.5 and 11.4. When S-BA was crushed, the pH was 12.0, which is comparatively high. Because S-BA had a higher pH compared with R-BA, hydrogen generation was strongly influenced by factors other than pH.

3.4 Comparison with theoretical hydrogen gas generation and utility value by engineering

The S-BA and R-BA contained 3.9% and 3.8% of metal aluminum by mass percentage, respectively – if all of the aluminum in the bottom ash reacted then this would correspondingly result in 48.5 and 47.3 m^3/t-ash of hydrogen gas. However, the highest volume of hydrogen gas generated in this study was 12.7 m^3/t-ash (Case 8). Comparing the experimental values with theoretical values, hydrogen gas yield of about 26% was achieved. According to Macanas et al. (2011), an $NaBO_2$ solution is more effective for hydrogen gas generation than other solutions. If a small amount of 0.01 M NaF, MgCl, or $Fe_2(SO_4)_3$ is added to metal aluminum and water, the amount of hydrogen gas generated increases. Thus, an increase in hydrogen gas generation is expected from those additives.

By crushing S-BA, 6.6 m^3/t-ash of hydrogen gas was generated from S-BA and water within 1 day. Approximately 15,600 tons of bottom and fly ash is generated annually from the S Incineration plant of F city, i.e., we could obtain about 25 kg (282 m^3) of hydrogen gas in a day. Assuming the mileage of a fuel-cell car is 83 km/kg-H_2, a fuel-cell car could travel for over 2000 km using the recovered hydrogen gas. This distance is sufficient for fueling a garbage truck, for example. Owing to these reasons, a hydrogen gas recovery system using crushed bottom ash and water is valuable from an engineering standpoint.

4. CONCLUSIONS

1) In these experiments, the highest volume of hydrogen generated was 12.7 m^3/t-ash at case 8 (a reaction temperature of 50°C, liquid-solid ratio of 5, stirring rate of 600 rpm, and with non-crushed R-BA).
2) The optimum temperature for hydrogen generation from MSWIBA exists. In this study, the highest volume

TABLE 2: Amount of hydrogen gas generated and pH after the experiment completed. Cases1-7 represent S-BA and 8-9 represent R-BA.

Case	Hydrogen gas generation time (days)	Hydrogen gas generation amount (m³/t)	pH after experiment
1	21.0	10.4	11.4
2	13.0	11.4	11.8
3	20.5	10.2	11.7
4	13.1	7.9	11.5
5	15.0	6.8	11.4
6	15.1	11.0	11.4
7	1.1	6.6	12.0
8	4.1	12.7	11.0
9	1.8	5.1	10.9

of hydrogen gas was generated at 50°C.

3) When l/s = 5 more hydrogen gas was generated than when l/s = 3 scenario. The reason for the lower amount of hydrogen gas generated could have been that mixing between bottom ash and water was insufficient due to a water shortage at l/s = 3.

4) At stirring rates of 600 and 800 rpm more hydrogen gas was generated than at a stirring rate of 400 rpm. This could be because bottom ash and water were not well mixed at 400 rpm.

5) By crushing bottom ash, the initial gradient of hydrogen gas generation dramatically increased, but the cumulative volume produced did not increase. In this study, the initial gradient of hydrogen gas generation increased from 3.8 to 274.5 m^3/t-ash/day in the case of S-BA, and from 8.2 to 135.1 m^3/t-ash/day in the case of R-BA.

6) In this study, the maximum amount of hydrogen gas yield was about 26% of the theoretical hydrogen gas generation amount.

From the above, to generate a large volume of hydrogen gas within a short period of time by mixing and stirring bottom ash with water, it is desirable to set the reaction temperature to at least 50°C, and the minimum stirring rate of 600 rpm. If the shape of the stirring blade and the reactor are optimized, however, even if the liquid-solid ratio is reduced to less than 5, or the stirring rate is reduced to less than 600 rpm, the amount of hydrogen gas generation would not decrease as it did in this study.

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