Gasification and Reduction Behavior of Plastics and Iron Ore Mixtures by Microwave Heating

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Effective utilization of waste materials is a key issue for environmental protection. In this work, fundamental research on co-generation of H₂ and metallic iron from plastics and iron ore powder mixtures by microwave heating was carried out. Thermal decomposition behaviors of plastics powders, the effects of plastics type and their blending composition on the H₂, CH₄, CO, CO₂ generation from the samples were studied.

As the results, about 57–88 % of hydrogen contained in the samples were recovered in forms of H₂ and CH₄. Concentration of generated gas was able to control by changing the blending composition of plastics and iron ore powders mixtures. Under the condition of C/O=2, about 88 % of hydrogen in the sample was recovered in forms of H₂ and CH₄, and hydrogen did not contribute to the reduction of iron ore, apparently.

KEY WORDS: microwave heating; waste materials; waste plastics; polyethylene; polypropylene; hydrogen; metallic iron; co-generation.

1. Introduction

Effective utilization of waste materials is a key issue for environmental protection. Major component of organic waste materials are waste plastics and waste papers. Major components of waste plastics are polyethylene (PE) and polypropylene (PP). Refuse Derived Fuel (RDF) was made from waste plastics; however, most of RDF is just burnt or partly used for electrical power generation.

On the other hand, Japanese iron and steelmaking industry has to reduce CO₂ emission by 10.5% in 2010 relative to the level of emissions in 1990. Thus, Japanese iron and steelmaking industry has to develop alternative reducing agent to reduce CO₂ emission. Waste plastics and waste papers contain carbon and hydrogen. Therefore, if reduction of iron ore by waste plastics is possible, co-generation of H₂ and metallic iron will be achieved. However, highly concentrated CO₂ and H₂O are problems when we use conventional processes to obtain H₂ from waste plastics.

Microwave processing has been widely investigated and developed by many researchers. Advantages of microwave heating are; (1) small amount of waste gas due to burner-less process, (2) high energy efficiency due to internal heat generation of the samples. Moreover, microwave heating has the following potential; (1) rapid and selective heating of materials, (2) reactions can be catalyzed because the heating occurs on a molecular or atomic level, (3) the gas volume is reduced and the atmosphere can be controlled, (4) the materials is heated internally; and (5) the temperature of the refractory can be minimized. Microwave is able to heat various kinds of oxides including iron oxide, selectively.

Therefore, fundamental research on co-generation of H₂ and metallic iron from plastics and iron ore powder mixtures by microwave heating was carried out. Thermal decomposition behaviors of plastics powders, the effects of plastics type and their blending composition on the H₂, CH₄, CO, CO₂ generation from the samples were studied in this work.

2. Experiments

2.1. Availability of Microwave Heating

Iron ore and plastics powders were individually irradiated by microwave. Chemical composition of the iron ore powder is shown in Table 1. In this experiment, reagent grade polyethylene (-(CH₂-CH₂)ₙ) and polypropylene (-(CH₃-CH(CH₃)₋)ₙ) powders, and RDF powder were used as plastic powders. Particle diameters of polyethylene and polypropylene powders were ~425 μm. RDF powder was prepared by crushing RDF pellets with a high velocity revolution type blender to minimize the effect of particle diam-

<table>
<thead>
<tr>
<th>Fe₂O₃</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>CaO</th>
<th>MnO</th>
<th>MgO</th>
<th>P</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>96.6</td>
<td>1.36</td>
<td>0.62</td>
<td>0.28</td>
<td>0.13</td>
<td>0.06</td>
<td>0.03</td>
<td>0.004</td>
</tr>
</tbody>
</table>

Particle size: 45-75 μm
eter difference between polyethylene, polypropylene and RDF powders. Chemical composition of RDF powder is shown in Table 2. 4 g of iron ore, polyethylene, polypropylene and RDF powders were used for the experiments.

Figure 1 shows schematic diagram of the microwave heating apparatus. Experiments were conducted with an industrial microwave oven whose power output was variable from 0 to 1.6 kW at 2.45 GHz. The samples were placed in an alumina crucible, which was covered with fine ceramic fiber to prevent heat loss to the surroundings, and located in a chamber. The alumina crucible was placed in a silica glass chamber with inlet and outlet ports. The chamber was placed on the center of the microwave oven. An infrared thermometer was used to monitor samples temperature during microwave heating. When the samples temperature did not reach the measurable temperature range of the infrared thermometer, thermo-couples were used to measure the samples temperature just after microwave irradiation was terminated. The argon gas was introduced at a flow rate of 0.4 NL/min to the chamber as a carrier gas. The sample was irradiated with a 1.6 kW of microwave for 0.5–2 min.

2.2. Microwave Heating Experiments

Weighed plastics and iron ore powders mixtures were prepared for microwave reduction experiments. Properties of samples are shown in Table 3. Experiments were conducted with the apparatus shown in Fig. 1. The argon gas was introduced at a flow rate of 1.5 NL/min to the chamber as a carrier gas. The sample was irradiated with a 1.6 kW of microwave for 2–3 min. H₂, CH₄, CO and CO₂ concentrations of generated gas were measured continuously by a quad-pole mass spectrometer. Flow rates of H₂, CH₄, CO and CO₂ were calculated based on the flow rate of the carrier gas.

2.3. Thermal Decomposition Experiments

The properties of the samples for the measurements of thermal decomposition behavior of the plastics at the temperature range of 1 273–1 573 K were shown in Table 4. It is very difficult to understand what sort of reactions proceed in the sample, because thermal decomposition of plastic and reduction reaction of iron oxide will proceed simultaneously when iron ore and plastic mixture samples were irradiated with microwave. Thermal decomposition behavior of plastics green body should be different from that of the plastics in iron ore and plastic mixture samples, because thermal decomposition behavior of plastic will strongly depend on properties of the samples, such as thermal conductivity, porosity and size of the samples. Therefore, the samples for thermal decomposition experiments should have the same properties as the samples for microwave heating experiments as far as possible. Then, the samples were prepared by blending weighed plastics and alumina powders which was used instead of iron ore powder in the microwave heating experiments, and compacting into briquettes with an oil hydraulic press. The average diameter and height of the polyethylene/polypropylene containing samples is 15 mm and 7 mm, respectively. The average diameter and height of the RDF containing samples is 15 mm and 12 mm, respectively.

A schematic drawing of the apparatus for the experiments is shown in Fig. 2. The sample was placed in a Pt basket, and the basket was suspended by a Pt wire. The electric resistance furnace was maintained at 1 273, 1 373, 1 473 and 1 573 K. When the furnace reached the operating temperatures, the basket was held in a proper region of the

Table 2. Composition of RDF (mass%).

<table>
<thead>
<tr>
<th>Particle size: 650 μm</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
</tr>
<tr>
<td>-----</td>
</tr>
<tr>
<td>41.65</td>
</tr>
</tbody>
</table>

Table 3. Properties of plastics and iron ore mixture samples for microwave heating experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Iron ore (g)</th>
<th>PE (g)</th>
<th>PP (g)</th>
<th>RDF (g)</th>
<th>C/O</th>
<th>C/Fe</th>
<th>H/Fe</th>
<th>O/Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>M-PE1</td>
<td>1.55</td>
<td>0.39</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>1.5</td>
<td>3.0</td>
<td>1.5</td>
</tr>
<tr>
<td>M-PE2</td>
<td>3.19</td>
<td>0.81</td>
<td>-</td>
<td>-</td>
<td>1.0</td>
<td>1.5</td>
<td>3.0</td>
<td>1.5</td>
</tr>
<tr>
<td>M-PE3</td>
<td>1.55</td>
<td>0.76</td>
<td>-</td>
<td>-</td>
<td>2.0</td>
<td>3.0</td>
<td>6.0</td>
<td>1.5</td>
</tr>
<tr>
<td>M-PP1</td>
<td>1.55</td>
<td>-</td>
<td>0.39</td>
<td>-</td>
<td>1.0</td>
<td>1.5</td>
<td>3.0</td>
<td>1.5</td>
</tr>
<tr>
<td>M-RDF1</td>
<td>1.55</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
<td>0.82</td>
<td>2.75</td>
<td>4.52</td>
<td>3.38</td>
</tr>
</tbody>
</table>

Table 4. Properties of plastics and alumina mixture samples for thermal decomposition experiments.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Al₂O₃ (g)</th>
<th>PE (g)</th>
<th>PP (g)</th>
<th>RDF (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-PE</td>
<td>1.05</td>
<td>0.39</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>D-PP</td>
<td>1.05</td>
<td>-</td>
<td>0.39</td>
<td>-</td>
</tr>
<tr>
<td>D-RDF1</td>
<td>1.05</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
</tr>
</tbody>
</table>
furnace at the operating temperatures. The argon gas was introduced at a flow rate of 2 NL/min to the chamber as a carrier gas. H₂, CH₄, CO and CO₂ concentrations of generated gas were measured continuously by the quad-pole mass spectrometer. Weight losses of the samples were measured continuously by a strain gauge located top of the furnace.

3. Results and Discussions

3.1. Availability of Microwave Heating

The heating curves of the samples are shown in Fig. 3. Iron ore powder showed very good sensitivity for microwave heating. The temperature of the iron ore powder reached 1 273 K in 30 s, and then the temperature was over 1 573 K in about 40 s, which was the upper limit measurable temperature of the infrared thermometer. Therefore, iron ore will act as heat resource of microwave heating. The polyethylene/polypropylene/RDF and iron ore mixtures will reach high enough temperature for reactions.

The temperatures of the polyethylene and polypropylene powders did not reach even 323 K in 60 s of microwave heating. On the contrary, the temperature of the RDF powder reached around 773 K in about 40 s, after that, the RDF powder started to melt and decompose. The power absorbed per unit volume \( P \) [W/m³], is given by the following equation.

\[
P = 2\pi f E^2 \varepsilon \tan \delta \quad \text{(1)}
\]

where, \( f \) is the frequency of the microwave [Hz], \( E \) is the magnitude of the electrical field [V/m], \( \varepsilon \) is the dielectric constant [−], \( \tan \delta \) is the dielectric loss [−]. The RDF powder contains certain amount of waste paper and wood. The dielectric loss (\( \varepsilon \tan \delta \)) of paper is about 0.16 and that of wood is about 0.1 which are much larger than that of plastics (for example, the dielectric loss of polyethylene is about 5.2 × 10⁻⁴).

3.2. Thermal Decomposition Behavior

Thermal decomposition behaviors of D-PE sample at 1 273, 1 373, 1 773 and 1 573 K are shown in Fig. 4. CO and CO₂ were not detected in the experiments because oxygen was not contained in polyethylene at all. Thermal decomposition of the samples started in about 15–30 s, and the reaction times were about 90–120 s in all cases. There is no obvious relation between the reaction times and the reaction temperatures. The maximum flow rate of CH₄ in generated gas is slight larger than that of H₂ at 1 273 K. An increase of the reaction temperature results in increases of the maximum flow rate and total amount of H₂ in generated gas, and decreases of those of CH₄. Total recovery percentage of hydrogen at 1 273 K is only 36.76%. Probably 63.24% of hydrogen in the sample vaporized as carbureted hydrogen because no residual was detected except alumina powder in the sample after experiment. Total recovery percentage of the hydrogen increased as increasing the reaction temperature, and the total recovery percentage of the hydrogen is about 98% at 1 573 K. Therefore, if plastic and iron ore mixture samples temperature reaches 1 573 K in short time by microwave heating, corresponding quantities of hydrogen in the sample will be recovered from plastics and iron ore mixtures.

Thermal decomposition behaviors of D-PP and D-RDF
samples at 1473 K are shown in Fig. 5. Temperature dependence of D-PP sample’s thermal decomposition behavior showed almost the same pattern as that of D-PE sample’s one. Polyethylene powder decomposed in shorter time than polypropylene powder. D-PP sample’s total recovery percentages of hydrogen were almost the same as D-PE sample’s ones. Thermal decomposition behavior of D-RDF sample differed from those of D-PE and D-PP samples. CO and CO₂ were detected in generated gas because RDF contains oxygen itself as waste paper and wood. The decomposition time of D-RDF sample is longer than those of D-PE and D-PP samples. Probably, decomposition of waste paper and wood require longer time than that of plastics. Decomposition of polyethylene, polypropylene and RDF produced H₂ and CO. Therefore, co-generation of hydrogen and metallic iron will be highly expected by microwave heating of these plastics and iron ore mixtures.

3.3. Microwave Heating

3.3.1. Effect of Plastic Type

Time dependence of flow rates of H₂, CH₄, CO and CO₂ in generated gas from M-PE sample (Sample weight: 1.94 g, C/O: 1.0) is shown in Fig. 6. The greater part of the generated gas from the mixture sample consisted of H₂ and CO as reported by Takekawa et al.⁹ H₂, CH₄, CO and CO₂ were appeared in about 30 s and their flow rate reached peak values in about 45–50 s. CH₄ and CO₂ disappeared in about 90 s. Thermal decomposition of polyethylene and reduction of iron ore finished within about 3.5–4 min because H₂ and CO were not almost detected. Thermal decomposition of polyethylene and reduction of iron ore started simultaneously because H₂, CH₄, CO and CO₂ appeared at the same time in about 30 s. After experiment, round shaped metallic iron as shown in Fig. 7 was obtained. Final reduction degree of the iron ore powder by carbon, which was calculated by the total volume of CO and CO₂ in exhaust gas, was about 57%. Considering the facts that reduction of iron oxides by H₂ is much faster than that by C or CO, and that flow rate of H₂ is larger than that of CO in the early and middle stage of the reaction, the reduction reaction mainly proceeded by the reaction shown in Eq. (2). There was no free C in the plastics and alumina mixture samples after thermal decomposition experiments; there were some free C in the plastics and iron ore mixture samples after microwave heating experiments, because metallic iron acted as a catalyst for the decomposition of carbureted hydrogen in the samples.¹⁰–¹² H₂O generated by the reduction reaction reacted with C (Eq. (3)) generated by the thermal decomposition of carbureted hydrogen, and H₂ was re-generated by the reaction. Of course, reduction of iron oxides by C or CO also could proceed. However, the effect of the reduction reactions by C or CO was emphasized by the reactions shown in Eqs. (2) and (3), apparently.

$$\text{FeO}_n(s) + \text{H}_2(g) \rightarrow \text{FeO}_{n-1}(s) + \text{H}_2\text{O}(g) \quad \text{........(2)}$$

$$\text{H}_2\text{O}(g) + \text{C}(s) \rightarrow \text{H}_2(g) + \text{CO}(g) \quad \text{........(3)}$$

Time dependence of flow rates of H₂, CH₄, CO and CO₂ in generated gas from M-PP1 sample (Sample weight: 1.94 g, C/O: 1.0) is shown in Fig. 8. The flow rates showed almost the same trend as in the case of M-PE sample except the peak value of H₂ flow rate is slight lower than that in the case of M-PE1. This is the same behavior as the thermal decomposition of D-PE and D-PP mixture samples. There is a broad peak in the CO flow rate in about 2.5 min. This peak would correspond to the direct reduction reaction by free carbon generated by the thermal decompo-
sition of polyethylene (Eq. (4)) or coupling reaction of the in-direct reduction reaction by CO and gasification of carbon shown in Eqs. (5) and (6) because CO\(_2\) was not detected in the generated gas.

\[
\text{FeO}_n(s) + C(s) \rightarrow \text{FeO}_{n-1}(s) + CO(g) \quad \text{...........(4)}
\]

\[
\text{FeO}_n(s) + CO(g) \rightarrow \text{FeO}_{n-1}(s) + CO_2(g) \quad \text{...........(5)}
\]

\[
\text{CO}_2(g) + C(s) \rightarrow 2CO(g) \quad \text{.................(6)}
\]

### 3.3.2. Effect of Sample Weight

Time dependence of flow rates of H\(_2\), CH\(_4\), CO and CO\(_2\) in generated gas from M-PE2 sample (Sample weight: 4.0 g, C/O: 1.0) is shown in Fig. 9. Comparison of Figs. 6 and 9 provides us that H\(_2\), CH\(_4\), CO and CO\(_2\) were generated from M-PE2 sample in a shorter time than that from M-PE1 sample slightly even though total weight of M-PE2 sample is about twice of that of M-PE1 sample. The reason is Fe\(_2\)O\(_3\) in iron ore powder was a heat resource for microwave heating.

Flow rate of CO in the case of M-PE2 sample shows peak value in about 50 s, and shows almost constant value in 60–140 s. An increase of sample weight means an increase of sample volume and residence time of H\(_2\)O generated by the reaction shown by Eq. (2). As the result, the reforming reaction (Eq. (3)) proceeded more, adequately. Decrease rate of H\(_2\) flow rate slows down in about 60–120 s also indicates occurrence of the reaction.

### 3.3.3. Effect of Blending Composition

Time dependence of flow rates of H\(_2\), CH\(_4\), CO and CO\(_2\) in generated gas from M-PE3 sample (Sample weight: 2.33 g, C/O: 2.0) is shown in Fig. 10. Volume of CO generated from M-PE3 sample increased compared to that from M-PE1 sample (C/O = 1) shown in Fig. 6. This increase mainly corresponds to the increase of CO flow rate in about 90–180 s. An increase of polyethylene will result in an increase of free carbon generated by the decomposition of the polyethylene in the sample. As the result, direct reduction of iron oxide (Eq. (4)) or coupling reaction (Eqs. (5) and (6)) contributes to the increase of the CO flow rate. The CO flow rate reached the peak value in about 60 s, and decreased once, and increased again in about 90 s. The temperature of the sample measured by the infrared thermometer during microwave heating did not show monotone increase. The temperature of the sample decreased once in about 90 s. This behavior of the temperature was only seen in the case of M-PE3 sample. Therefore, there are some relations between the CO flow rate and the sample temperature. Detail of the relations between the flow rate and the temperature is under examination.

The amount of iron ore powder in the M-PE3 sample (C/O = 2) was enough for microwave heating. Reduction degree of iron ore by carbon, which was calculated by CO and CO\(_2\) in the generated gas, was 100%. Apparently, hydrogen did not contribute to the reduction of iron ore. Concentration of generated gas is able to control by changing the blending composition of plastics and iron ore powders mixtures. About 88% of hydrogen in the sample was recovered in forms of H\(_2\) and CH\(_4\). There will be an optimum C/O ratio when H\(_2\) and CO are recovered from plastics and iron ore mixtures.

### 3.3.4. RDF and Iron Ore Powder Mixture

Time dependence of flow rates of H\(_2\), CH\(_4\), CO and CO\(_2\) in generated gas from M-RDF1 sample (Sample weight: 3.05 g, C/O: 0.82) is shown in Fig. 11. C/O of the sample (0.82) is smaller than that of M-PE1 and M-PP1 samples because the RDF powder contains oxygen itself. After experiment, round shaped metallic iron was also obtained even C/O of the sample is smaller than 1.0.

Volumes of H\(_2\), CO and CO\(_2\) generated from M-RDF1 samples by microwave heating are about 1.5–2.0 times...
compared to those from M-PE1 and M-PP1 samples. The amount of Fe (Fe₂O₃) in the samples was fixed in this work as shown in Table 3. Values of C/Fe, H/Fe and O/Fe in the M-PE1 and M-PP1 samples are C/Fe = 1.5, H/Fe = 3.0, O/Fe = 1.5, respectively. On the contrary, those values in the M-RDF1 sample are C/Fe = 2.746, H/Fe = 4.52, O/Fe = 3.38, respectively. Thus, M-RDF1 sample contains more C, H and O than M-PE1 and M-PP1 samples, the volumes of generated gas were relatively large.

The recovery percentage of hydrogen in forms of H₂ and CH₄ from M-RDF1 sample was 57% which was smaller value than that from M-PE1 and M-PP1 samples. The reason is tar and C₂ or higher orders of carbureted hydrogen were generated from the M-RDF1 sample because there were many brownish cruds on the filter. In the case of M-RDF1 sample, flow rate of CO has very sharp peak compared to M-PE1 and M-PP1 samples. The RDF sample contains waste paper and wood. Therefore, it is believed that the peak consists of not only CO generated by reduction of iron oxides but also CO generated by decomposition of paper and wood.

4. Conclusions

Fundamental research on co-generation of H₂ and metallic iron from PE/PP/RDF and iron ore powder mixtures by microwave heating was carried out. Following results were obtained.

(1) H₂, CO and metallic iron were produced from PE/PP/RDF and iron ore mixtures by microwave heating at a same time. In this work, about 57–88% of hydrogen contained in the samples were recovered in forms of H₂ and CH₄. Concentration of generated gas was able to control by changing the blending composition of plastics and iron ore powders mixtures.

(2) Iron powder in the plastics and iron ore mixture acts as heat resource to keep enough high temperature for microwave heating.

(3) In the case of polyethylene/polypropylene and iron ore powder mixtures, iron oxide was reduced mainly by hydrogen. H₂ was re-generated by the reforming reaction of H₂O.

(4) About 88% of hydrogen in the polyethylene and iron ore powder mixture sample (C/O₁:O = 2) was recovered in forms of H₂ and CO₂ was recovered in forms of H₂ and CO₂. Reduction degree of iron ore by carbon, which was calculated by CO and CO₂ in the generated gas, was 100%. Apparently, hydrogen did not contribute to the reduction of iron ore.

Acknowledgement

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REFERENCES