UTILIZATION OF WASTE PLASTIC MATERIAL AS REDUCING AGENT AND GASEOUS SOURCE DURING IRON REDUCTION PROCESS[1]

Ko-ichiro Ohno [2]
Yasuaki Ueki [3]
Takayuki Maeda [2]
Koki Nishioka [4]
Masakata Shimizu [5]

Abstract

Reduction of CO_2 emissions in the ironmaking process is one of emergency countermeasures against global warming. An effective use of waste plastic materials in the ironmaking process is regarded as a particularly advantageous solution. Waste materials contain huge amount of hydrogen, and the hydrogen is expected to contribute toward the reduction of iron oxide in iron ore. In this work, we conducted fundamental research on co-production of metallic iron and H_2 gas from mixtures of iron oxide and waste plastic materials as follows: polyethylene, polypropylene and RDF (Refuse Derived Fuel). Mixture samples of waste plastic materials and iron oxide were heated up to 1000~1300°C in argon gas flow. Multi-component measurement of generated gases from samples and variation measurement in sample weight were carried out using the quad-pole mass spectrometer and thermo balance, respectively. The results were summarized as follows: The final fractional reductions of sample containing Refuse Derived Fuel at 1200°C were 100%. The conversion ratio of H_2 by reduction of mixture samples was almost the same ratio by thermal decomposition of waste plastic materials alone. From the same figure, it was found that the conversion ratio of H_2 by reduction of mixture samples reached 55~65% at 1200°C. In conclusion, the metallic iron and H_2 gas were obtained by heating the mixture of waste plastic materials and iron oxide.

Key words: Waste plastic materials; Ironmaking process; Co-production of metallic iron and H_2 gas; quad-pole mass spectrometer

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[2] *Graduate Student, Materials Science and Engineering, Kyushu University, Fukuoka, Japan*

[3] *Associate Professor, Materials Science and Engineering, Kyushu University, Fukuoka, Japan*

[4] *Professor, Materials Science and Engineering, Kyushu University, Fukuoka, Japan*

1 INTRODUCTION

CO_2 emissions in the steel industry make up for about 15% of total emissions in Japan.[1] Especially, CO_2 emissions in ironmaking process account for about 70% of CO_2 emissions in the steel industry. Therefore, reduction of CO_2 emissions from the ironmaking process is a pressing issue to avoid global warming.One of the promising solutions is an effective use of organic waste materials including waste plastic materials in the ironmaking process. Waste plastic materials contain a huge amount of hydrogen. The utilization of waste plastic materials enables the process to reduce CO_2 emissions due to substitution of hydrogen for the conventional fossil fuels. As practicable examples,[2-4] a partial alternative of coal by coke ovens and injections of waste plastics into blast furnaces from tuyeres are mentioned.

From the viewpoint of reaction rate enhancement, the carbon composite method,[5-10] which uses a briquetted mixture of iron ores and coals, has also received the limelight recently. Therefore, utilization of waste plastic materials as reducing agent in the carbon composite method is hoped to contribute to deterrence of global warming. This hopeful technology is also expected to help both suppression of CO_2 emissions and recovery of H_2 and CO gases from waste plastic materials. However, there are few researches[11-13] on this trial technology in combination of waste plastic materials usage and the carbon composite method. In this work, in order to enable efficient use of waste plastic materials in the carbon composite method, we carried out investigations of the thermal decomposition of waste plastic materials and reaction of waste plastic materials and iron oxide mixture samples.

2 MATERIALS AND METHODS

2.1 Waste Plastic Materials

In this work, polyethylene (hereafter PE) reagent and Refuse Derived Fuel (hereafter RDF) were used as typical waste plastic materials. The particle diameters of PE powders were -425µm. RDF was crushed and screened to obtain samples having -600µm in diameter. Table 1 shows properties of the PE and RDF powders. PE consists entirely of hydrogen and carbon. On the other hand, RDF includes oxygen, fixed carbon and ash.

Table 1. Properties of samples. (Dry base, mass %)[15]

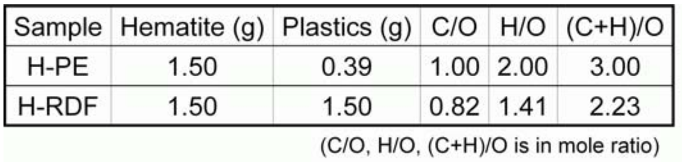
Sample	Ultimate analysis				Proximate analysis		
	C	H	N	O	FC	VM	Ash
PE	85.63	14.37	-	-	-	100	-
RDF	41.65	5.75	1.23	38.00	11.46	75.17	13.37

2.2 Experimental Samples

In thermal decomposition experiments, 0.39g of PE powders was directly used as experimental samples. 1.5g of RDF powders was pressed into tablet shape using a die of 15mm in inner diameter because the density of RDF powder was too low to set enough amounts of samples in a sample holder for the experiments.

In reduction experiments, weighted PE or RDF powders and hematite reagent powders were well mixed and used as shown in Table 2. In the case of H-PE sample, the hematite and PE reagent powders were mixed to become an equal mole ratio of carbon and oxygen. H-RDF sample was mixture of equal weight ratio of the hematite and RDF powders. H-PE and H-RDF samples were pressed into tablet shape using the die.

Table 2. Properties of waste and iron ore mixtures.[15]



Sample	Hematite (g)	Plastics (g)	C/O	H/O	(C+H)/O
H-PE	1.50	0.39	1.00	2.00	3.00
H-RDF	1.50	1.50	0.82	1.41	2.23

(C/O, H/O, (C+H)/O is in mole ratio)

2.3 Experimental Method

Figure 1 shows a schematic diagram of the experimental system. The sample was placed in a Pt basket, and the basket was suspended by a Pt wire connecting with the thermo balance. The electric resistance furnace was maintained at experimental temperatures of 1000, 1100, 1200 and 1300°C by a PID temperature controller. When the furnace reached the experimental temperatures, the basket was inserted into isothermal zone. This timing was defined as heating start time in this experiment. The Ar gas was introduced at a flow rate of $3.33\times10^{-5}m^3/s$ to the reaction tube (ID: 35mm) as a carried gas by the mass flow controller. The generated gases from samples were introduced into the quad-pole mass spectrometer via the filter and cold trap. Fine particles and agglomerations in generated gas, such as soot, tar and water, were removed by the filter and the cold trap, respectively.

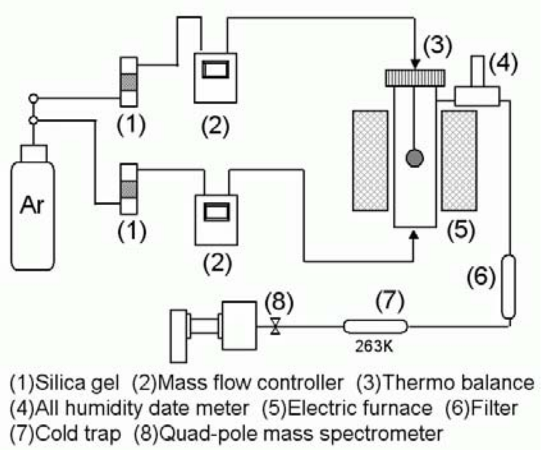


Figure 1. Schematic diagram of experimental system.[15]

H_2, CO, CO_2, CH_4, C_2H_2 and C_2H_4 concentrations of generated gases were measured continuously by the quad-pole mass spectrometer. H_2O concentration of generated gases and weight changes of the samples were measured continuously by the humidity meter and thermo balance, respectively. When the weight changes of the samples reached stagnant period, the samples were rapidly cooled in Ar gas flow. After reduction experiments, the fractional reduction of samples were determined by chemical analysis (JIS M8212, M8213, M8713).

2.4 Definition of Conversion Ratio

This study adopted a conversion ratio to evaluate recovery amount of gases from the waste plastic materials. A value of the conversion ratio shows how much hydrogen and carbon were decomposed into utilizable gas from waste plastic materials during the thermal decomposition and reduction reaction.

$CR_H = H_G/H_{Waste} \times 100$ (1)
$CR_C = C_G/C_{Waste} \times 100$ (2)

Where, CR_H(%) and CR_C(%) are the conversion ratios of hydrogen and carbon, respectively. H_G(mol) and C_G(mol) are the number of moles of hydrogen atom and carbon atom in the recovered gases, respectively. H_{Waste}(mol) and C_{Waste}(mol) are the number of moles of hydrogen atom and carbon atom in the initial waste plastic materials, respectively.

3 RESULTS AND DISCUSSION

3.1 Thermal Decomposition of Waste Plastic Materials

Figure 2 shows gas generation behaviors in the thermal decomposition experiment of PE sample at 1000°C and 1200°C. In the case of the thermal decomposition at 1000°C, flow rates of each generated gas reached the maximum value in about 30 s, and gas generation finished in about 100 s. The volumes of H_2 and CH_4 were quite larger than those of the other gaseous species. The thermal decomposition finished in a shorter period of time by increasing temperature from 1000°C to 1200°C. Furthermore, generation volume of H_2 became about twice by increasing temperature. After experiment, decomposed carbon did not remain in the Pt basket, and the carbon adhered to the reaction tube and the filter.

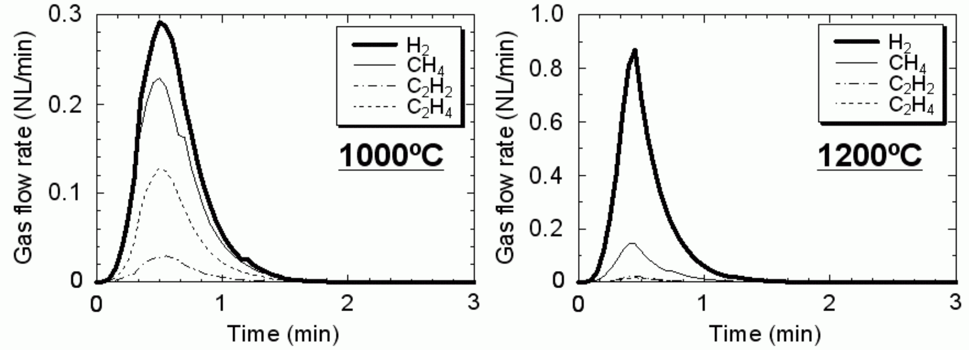


Figure 2. Thermal decomposition behaviors of PE sample at 1000ºC and 1200ºC.[15]

Figure 3 shows gas generation behaviors in the thermal decomposition experiment of RDF sample at 1000°C and 1200°C. In the case of the thermal decomposition at 1000°C, flow rate of each generated gas reached the maximum values in around 30~50s and gas generation did not finish even in 180s. The reason is that the RDF contains thermally persistent components such as small pieces of paper.[14] The volume of generated H_2 was the largest in the detected gases. CO, CO_2 and H_2O were detected because RDF contains oxygen itself differ from PE. The decomposition of RDF also finished in a shorter period of time by increasing temperature as PE did. Additionally, generation volumes of H_2 and CO became about twice by increasing temperature from 1000°C to 1200°C. After experiment, residual carbon existed as not only adhesion soot at the reaction tube and the filter but also char in the Pt basket. This char is fixed carbon of RDF.

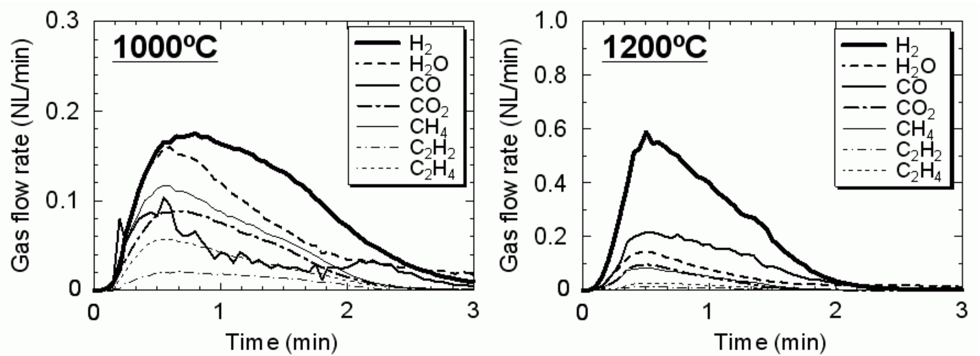


Figure 3. Thermal decomposition behaviors of RDF sample at 1000ºC and 1200ºC.[15]

3.2 Reduction of Waste Plastic Materials and Iron Oxide Mixtures

Gas generation behaviors in the reduction experiments of H-PE sample at 1000°C and 1200°C are shown in Figure 4. The final fractional reductions at 1000°C and 1200°C were 40% and 63%, respectively. It was found that major component of the generated gases were H_2 and CH_4 from this figure. The occurrence of iron oxide reduction by H_2 was confirmed by a detection of H_2O. In the case of the reduction at 1000°C, flow rates of generated gases became the maximum values in around 30~60s except CO. CO was not detected in the first period of the reaction, and CO was detected in the middle and last periods (about 90~240s). Flow rate of CO became the maximum value in about 160 s. Increase of the reaction temperature from 1000°C to 1200°C caused increases of H_2 and CO gas volumes. Particularly, CO was already detected in the first period of the reaction at 1200°C differ from the reaction at 1000°C. I

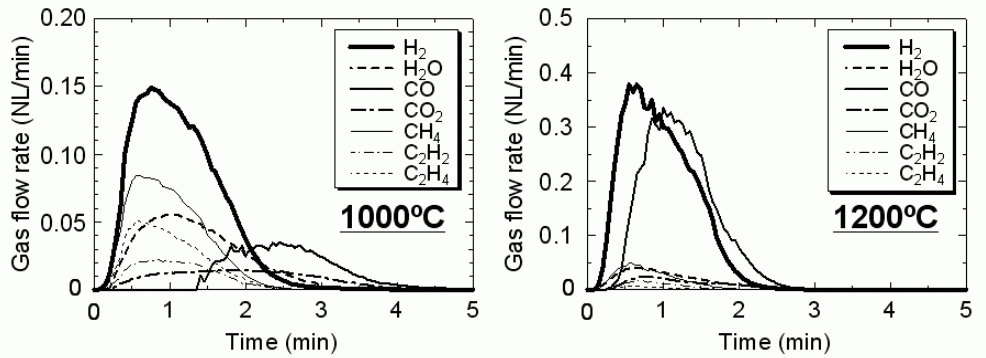


Figure 4. Reduction behaviors of H-PE sample at 1000ºC and 1200ºC.[15]

Gas generation behaviors in the reduction experiments of H-RDF sample at 1000°C and 1200°C are shown in Figure 5. The final fractional reduction of H-RDF sample at 1000°C and 1200°C were 93% and 100%, respectively. In the case of the reduction at 1000°C, flow rates of generated gases became the maximum values in around 20~50s except CO. CO was detected in the first period of the reaction differ from the case of H-PE sample. The flow rate of CO had another peak in about 170 s besides earlier one. It was indicated that the former and latter peaks correspond to the thermal decomposition of RDF and the reduction of iron oxide, respectively. Increase of the reaction temperature from 1000°C to 1200°C also caused increases of H_2 and CO gas volumes in all samples as H-PE. The flow rate of CO had only one peak at the temperature of 1200°C, though the flow rate of CO had two peaks at 1000°C. An increase of the reduction rate of iron oxide with increasing temperature supposed to cause the result that the two peaks of thermal decomposition and reduction overlapped each other.

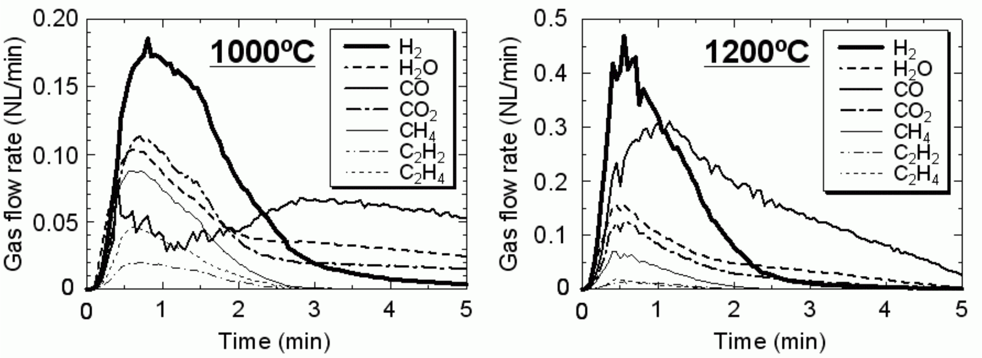


Figure 5. Reduction behaviors of H-RDF sample at 1000ºC and 1200ºC.[15]

3.3 Comparison of Conversion Ratios between Thermal Decomposition and Reduction

Figure 6 shows CR_H by thermal decomposition of PE and reduction of H-PE. ‘Others’ in the figure means higher order of hydrocarbons which were not measured in this work, char and tar. CR_H by thermal decomposition was larger than that by reduction.

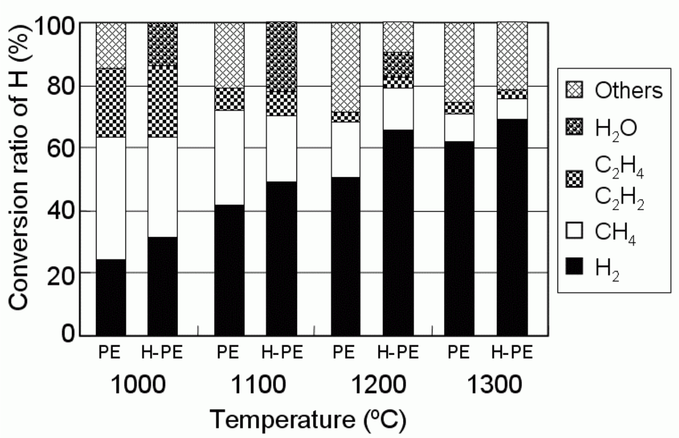


Figure 6. Conversion ratio of H by thermal decomposition of PE sample and reduction of H-PE sample.[15]

Figure 7 shows CR_H by thermal decomposition of RDF and reduction of H-RDF. In the case of RDF, the CR_H by thermal decomposition and that by reduction were almost the same. The occurrence of iron oxide reduction by H_2 was confirmed because the conversion ratio into H_2O by reduction was 3~10% larger than that by thermal decomposition.

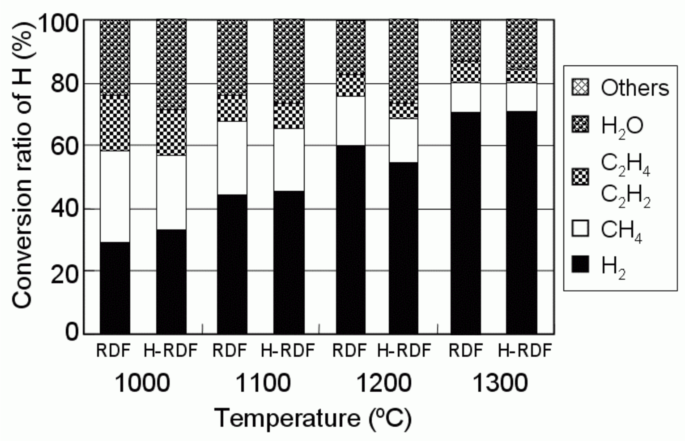


Figure 7. Conversion ratio of H by thermal decomposition of RDF sample and reduction of H-RDF sample.[15]

The final fractional reductions increased with increasing temperature, nevertheless the conversion rates into H_2O of H-PE and that of H-RDF decreased by 6% and 2% with increasing temperature from 1000°C to 1200°C, respectively. These results indicated that reduction of H_2O to H_2 by the water gas reaction (Eq. (3)) was enhanced with increasing temperature.

$$H_2O\ (g) + C\ (s) = H_2\ (g) + CO\ (g) \qquad (3)$$

Figure 8 shows CR_C by thermal decomposition of PE and reduction of H-PE. In the case of PE thermal decomposition, the conversion ratio into 'Others' increased and the ratios into hydrocarbon gases decreased with increasing temperature. The reason for the decrease of hydrocarbon gases is that decomposition of hydrocarbon gases into H_2 and carbon was promoted by increasing temperature. In the case of H-PE reduction, the conversion ratio into 'Others' decreased, and the conversion ratio into CO increased with increasing temperature. These results indicated that deposited carbon was consumed by the water gas reaction (Eq. (3)), the Boudouard reaction, as written in Eq. (4) and the reduction of iron oxide as written in Eq. (5).

$$CO_2\ (g) + C\ (s) = 2CO\ (g) \quad (4)$$
$$FeO_n\ (s) + C\ (s) = FeO_{n-1}\ (s) + CO\ (g) \quad (5)$$

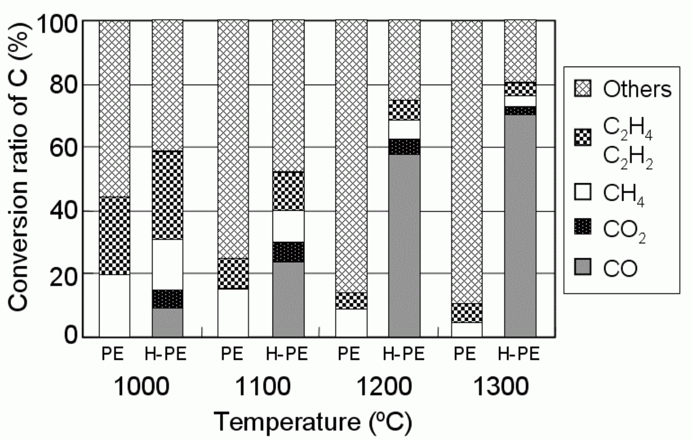


Figure 8. Conversion ratio of C by thermal decomposition of PE sample and reduction of H-PE sample.[15]

Figure 9 shows CR_C by thermal decomposition of RDF and reduction of H-RDF. The conversion ratio into CO and CO_2 by reduction of H-RDF sample is 2~4 times and about twice of the ratio by thermal decomposition of RDF sample, respectively.

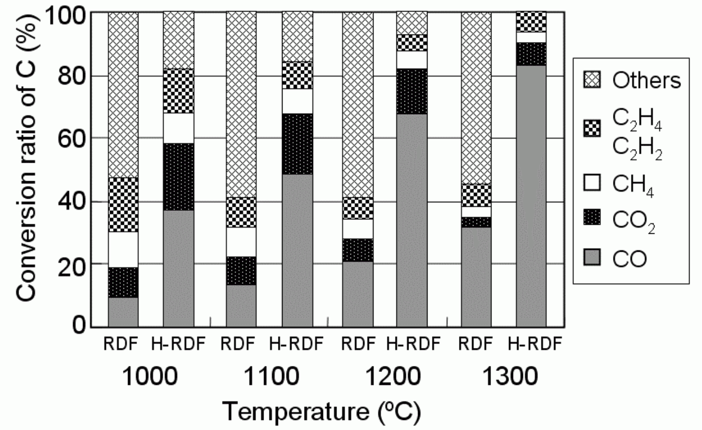


Figure 9. Conversion ratio of C by thermal decomposition of RDF sample and reduction of H-RDF sample.[15]

3.4 Effect of Kind of Waste Plastic Materials on Reaction Behavior of Iron Oxide Mixtures

The final fractional reductions of H-PE and H-RDF were 63% and 100%, respectively. This difference indicates that reaction behavior of waste plastic materials and iron oxide mixtures depends on kinds of waste plastic materials.

In the case of H-PE, H_2 and hydrocarbon gases were generated by the thermal decomposition of PE in the first period of the reaction. The thermal decomposition of waste plastic materials is an endothermic reaction. At this time, the reduction reaction of iron oxide by H_2, written in Eq. (6), progressed mainly near the surface of the sample, because the temperature at the sample surface is higher than that at the inside of the sample.

$$FeO_n (s) + H_2 (g) = FeO_{n-1} (s) + H_2O (g) \qquad (6)$$

When metallic iron formed near the surface of the sample, it would be a catalyst for the thermal decomposition of a hydrocarbon gases. At low temperature such as 1000°C, a small amount of carbon was deposited near the surface. The direct reduction (Eq. (5)) could occur by this deposited carbon. As a result, these reduction reactions generated H_2O and CO. However, as shown in Figure 4, CO was not able to detect in the first period of reaction. CO was supposed to be consumed by the water gas shift reaction, as written in Eq. (7), and the reduction of iron oxide as written in Eq. (8).

$H_2O\ (g) + CO\ (g) = H_2\ (g) + CO_2\ (g)$ (7)
$FeO_n\ (s) + CO\ (g) = FeO_{n-1}\ (s) + CO_2\ (g)$ (8)

CO was detected since the middle period of reaction when thermal decomposition of PE has nearly finished. This behavior indicated that a small amount of carbon deposited near the surface of the sample was oxidized to CO by the water gas reaction (Eq. (3)) and Boudouard reaction (Eq. (4)). The reduction of iron oxide, as written in Eq. (8), progressed mainly by this CO near the surface since the middle period of reaction. However, at the inside of the sample, enough amount of carbon necessary for generation of reducing gases such as H_2 and CO (Eq. (3),(4)) was not deposited because there was not metallic iron which would be a catalyst for the thermal decomposition of a hydrocarbon gases.

On the other hand, at high temperatures such as 1200°C, the amount of carbon deposited near the surface was larger than that at 1000°C. These increases of the amount of carbon and temperature promote the water gas reaction (Eq. (3)) and Boudouard reaction (Eq. (4)). As a result, CO also existed in the first period of reaction. However, the reduction reaction at the inside of the sample stagnated because an amount of carbon was not enough.

In the case of H-RDF, CO was detected in the first period of reaction. The CO was generated by the thermal decomposition of RDF as shown in Figure 3. In the middle period of reaction, a large amount of char which was fixed carbon remained in the sample differ from the case of H-PE. Therefore, the water gas reaction (Eq. (3)) and the Boudouard reaction (Eq. (4)) could progress more actively and larger volume of CO was generated than H-PE. This CO gas reduces iron oxide. Consequently, in the H-RDF, the reduction reaction at the inside of the sample did not stagnate and higher fractional reduction was obtained than H-PE even at the same temperatures.

From these results, when waste plastic materials are used as a reducing agent, plastics which contains large amount of fixed carbon is suitable to obtain a high fractional reduction.

4 CONCLUSIONS

The possibility of efficient using of waste plastic materials in the carbon composite method was investigated by examining the reaction behavior of the waste plastic materials and iron oxide mixtures. Following results were obtained.

(1) H_2 and CH_4 were mainly obtained by thermal decomposition of PE at 1000~1300°C. H_2 was mainly obtained with a small amount of CO by thermal decomposition of

RDF. 60~70% of hydrogen atom in waste plastic materials was converted to H_2 at 1300°C.

(2) Reduced iron was obtained by heating the PE/RDF and iron oxide mixture samples, and a higher fractional reduction was obtained with increasing temperature. In particular, the fractional reductions of the mixtures containing RDF at and above 1200°C were 100%.

(3) In the case of PE, the reduction reaction of iron oxide stagnated because a small amount of carbon deposited in the sample. On the other hand, in the case of RDF, the reduction reaction of iron oxide progressed well because a large amount of carbon generated by thermal decomposition of RDF remained inside of the sample.

(4) Almost the same conversion ratio of H_2 between thermal decomposition of waste plastic materials and reduction of waste plastic materials and iron oxide mixtures was obtained. In addition, the conversion ratio of CO by reduction increased rather as compared with that by thermal decomposition.

(5) When waste plastic materials are used as a reducing agent, plastic which contains large amount of fixed carbon is suitable to obtain a high fractional reduction.

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