

# Development of Waste Plastics Recycling Process Using Coke Oven

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## Abstract

*At the advent of the 21st century, mankind is facing global environmental problems, and the industrial sector is required to take initiatives in the establishment of a recycling society for efficient utilization of natural resources. The Containers and Packaging Recycling Law was enforced in 2000. The Japan Iron & Steel Federation (JISF) as its voluntary energy-saving action plan, proposed a 10% energy reduction by 2010 compared with 1990 as the basis. Further, it has put forward an additional 1.5% energy savings by the use of waste plastics as a metallurgical raw material. To solve these problems, Nippon Steel developed waste plastics recycling process using coke ovens. This paper describes the technology for waste plastics recycling process into chemical raw materials using coke ovens.*

## 1. Introduction

In recent years, the volume of hard-to-recycle waste plastic which is simply incinerated for disposal has seen a sharp increase, posing a serious social problem. From the standpoint of effective utilization of resources, developing technology for recycling waste plastic is an important task. In the 21st century, utilizing resources effectively and building a sustainable recycling-oriented society is strongly called for. In 1999, in Japan, 9,760,000 tons of waste plastic were incinerated. Of that total, municipal waste plastic accounted for as much as 4,900,000 tons<sup>1)</sup>. Containers and packaging materials accounted for about 70% of such municipal waste plastic. In the past, waste plastic had been disposed of as municipal waste by incineration or as landfill. Once the Containers and Packaging Recycling Law came into full force in April 2000, the recycling of municipal waste plastic, in particular waste plastic containers and packaging, began in earnest.

Looking at the recent movement of the Japanese iron and steel industry, in its voluntary action plan to save energy as a measure to curb global warming, the Japan Iron & Steel Federation has set a goal of reducing the industry's energy consumption to 90% of the 1990 level by the year 2010 and achieving energy saving of 1.5% by

recycling one million tons of waste plastic annually as a raw material for steelmaking.

Under that condition, Nippon Steel Corporation developed a new technology for waste plastic recycling process using coke ovens in order to enable a reduction in the consumption of energy in the iron and steel industry and thereby help build a sustainable recycling-oriented society. In 2000, the process was put into practice for the first time in the world<sup>2-5)</sup>.

This paper describes the waste plastic recycling process using coke ovens – a typical high-temperature process in the infrastructure of the iron and steel industry.

## 2. Outline of Coke Production Process

**Fig. 1** shows a schematic of the cokemaking process. The cokemaking process is one in which coal is put into a coke oven chamber and carbonized in a superheated reducing atmosphere free of oxygen (about 1,100 to 1,200°C) to produce coke (solid) and by-products – coke oven gas (COG: gas), tar and light oil (liquid). COG is rapidly cooled from about 700 to 800°C to about 80°C or lower as it is flushed with ammonia liquor from the ascension pipe at the coke

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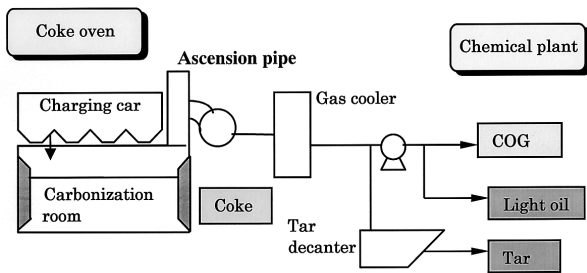


Fig. 1 Cokemaking process flow

oven top. It is then further cooled down to about 35°C by the gas cooler. The COG condensate is separated by the tar decanter into tar and ammonia liquor and recovered.

As described above, the cokemaking process not only produces coke by carbonizing solid coal in a superheated reducing atmosphere but also refines the by-products – COG, tar and light oil. Thus, as a process, it is well suited to the thermal decomposition of waste plastic<sup>2-4</sup>.

### 3. Study of Waste Plastic Recycling Technology Utilizing Functions of Coke Oven

#### 3.1 Study of thermal decomposition behavior of waste plastic in coke oven and estimation of yields of products of carbonization

With the aim of studying the thermal decomposition behavior of waste plastic in a coke oven, thermal decomposition behaviors of plastic and coal were studied<sup>2,3</sup>. Fig. 2 shows the losses in weight due to thermal decomposition of various types of plastics – polyethylene (PE), polystyrene (PS), polypropylene (PP), polyethylene terephthalate (PET), and polyvinyl chloride (PVC) – and coal (Goonyella coal), measured by a thermo-balance after they were heated in a nitrogen atmosphere at a heat-up rate of 10°C/min<sup>3</sup>.

PE, PS, PET and PP begin to be thermally decomposed at a temperature of around 300°C, and their thermal decomposition completes in the temperature range 420 to 470°C. In the case of PVC, a marked thermal decomposition reaction initially begins to take place at a temperature of around 250°C. Then, at a temperature of around 400°C, a second thermal decomposition reaction, that is, thermal decomposition of the principal chains of the plastic begins to take place. From these facts, it can be seen that ordinary plastics begin to thermally decompose at a lower temperature than the coal (Goonyella coal), that they become gaseous in a temperature range of between

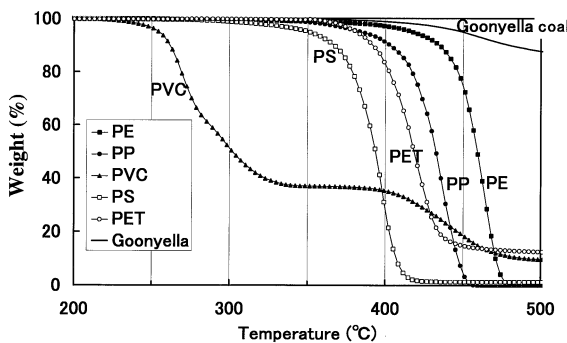


Fig. 2 Thermal decomposition curve of various plastic and coal

200 and 450°C, and that they produce carbides as their residues at about 500°C and over<sup>2</sup>. Since the coke oven carbonizes coal in a reducing atmosphere and is heated to a very high temperature (about 1,100 to 1,200°C), waste plastic is readily thermally decomposed in a coke oven.

First, a basic study was conducted of the conversion ratios of waste plastics by subjecting them to thermal decomposition in an experimental coke oven. Then, using general waste plastic (containers and packaging) (Tables 1 and 2), the ratios of conversion were made of those waste plastics into different products by carbonizing them, together with coal, in an actual coke oven<sup>2,3</sup>.

Municipal waste plastic containers and packaging were agglomerated by using pretreatment equipment<sup>6,7</sup>, whose process flow is shown in Fig. 3. In the pretreatment process, waste plastic was first crushed into pieces about 100 mm in size by a primary crusher and then any metals, heavy objects and other foreign matter was removed using a combination of magnetic and pneumatic separators. They were then crushed into pieces of less than 20 mm in size by a secondary crusher. In order to make it easier to transport crushed waste plastics to a coke oven and charge them into the coke oven, together with the coal, they were agglomerated into balls of about 25 mm in diameter. In the test using an actual coke oven, coal to which 1 to 2% by mass of agglomerated waste plastic was added was charged into the coke oven for carbonization. After that, the conversion ratios of the waste plastic into different products were measured.

As a result, it was found that when general waste plastic is carbonized in a coke oven, together with coal, it is converted into tar/light oil (about 40%), coke (about 20%) and coke oven gas (about 40%) as shown in Fig. 4. Thus, it was confirmed that almost the entire amount of waste plastic could be utilized effectively<sup>2,3</sup>.

#### 3.2 Evaluation of influence of waste plastic addition to coal on coke strength

The Japanese iron and steel industry consumes some 60 million tons of coal annually for production of coke. If 1% by mass of waste plastic on average could be added to coal for coke production in coke ovens, it would become possible to recycle some 600,000 tons of waste plastic a year. This amount corresponds to about 60% of the amount of waste plastic the Japan Iron & Steel Federation aims to recycle every year in order to save energy. Therefore, we carried out a test using an actual coke oven to evaluate the influence of waste plastic addition to coal on the strength of the resultant coke. As indices of coke strength, drum strength (DI<sup>150</sup><sub>15</sub>), which indicates coke strength at normal temperature, and coke strength in reduction (CSR) were measured. As a result, it was found that even when 1% by mass of waste plastic was added to coal, it did not affect the coke strength at all (Figs. 5 and 6)<sup>2,3</sup>.

Table 1 Component of waste plastics

Component (%)						
PE	PS	PP	PVC	PVDC	PET	Others
21.4	24.8	13.7	5.2	0.4	15.5	19.0

Table 2 Ultimate analysis and ash content of waste plastics

Ultimate analysis (mass%, dry)						Ash (mass%)
C	H	N	Cl	S	O (diff.)	
71.1	9.0	0.4	3.0	0.02	10.8	5.7

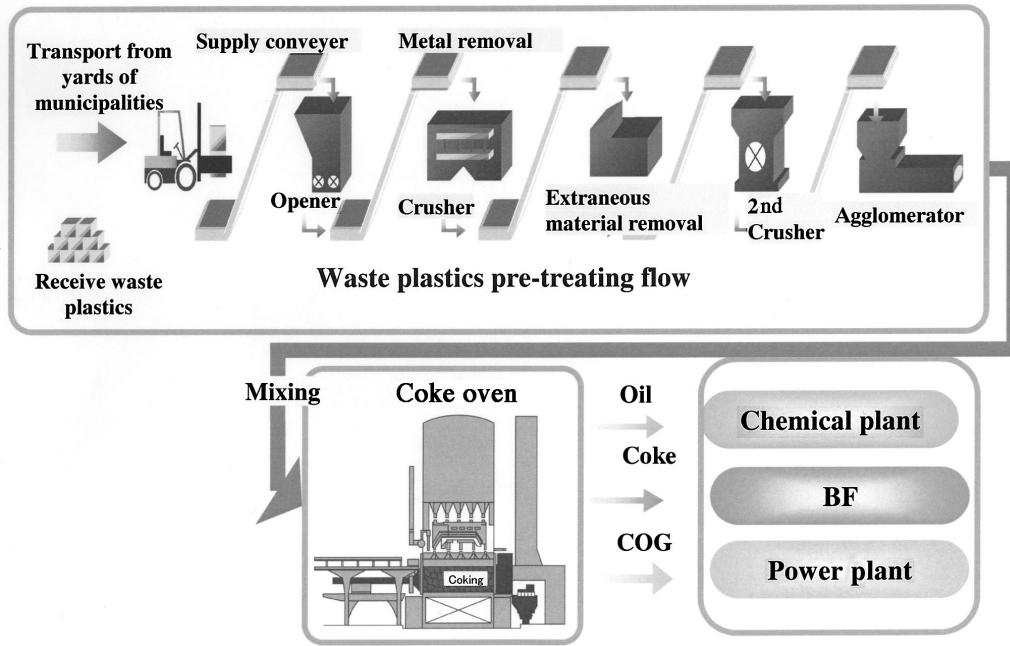


Fig. 3 Waste plastics pre-treating and recycling process

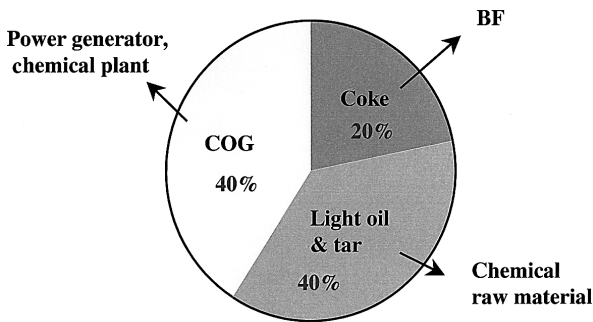


Fig. 4 Waste plastics conversion ratio

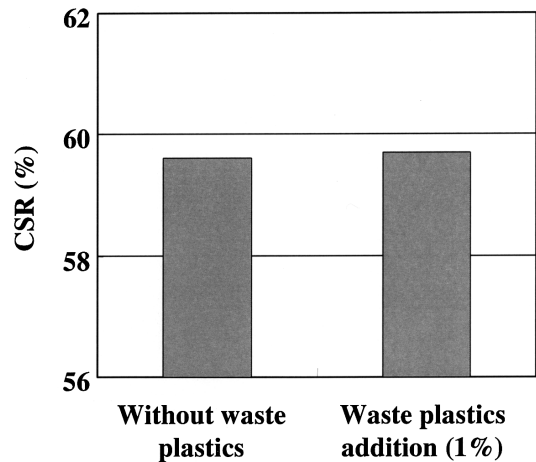


Fig. 6 Influence of waste plastics addition on CSR

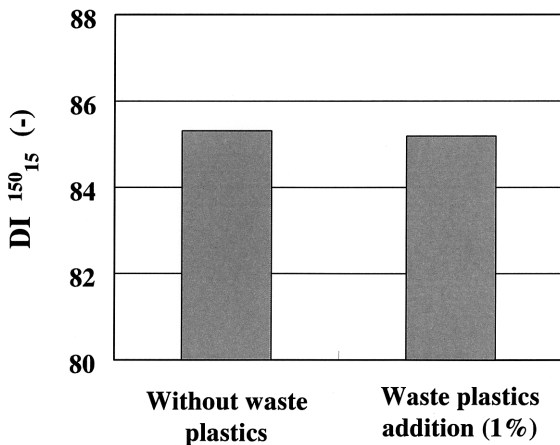


Fig. 5 Influence of waste plastics addition on DI<sup>150</sup><sub>15</sub>

As shown in Fig. 2, plastics are thermally decomposed at temperatures below the coal softening temperature (about 400°C). Therefore, when coal to which waste plastic has been added is carbonized in a coke oven, voids are formed by the thermal decomposition of the waste plastic before the coal softens and melts. As a result, the coal around the waste plastic demonstrates free expansion toward those voids<sup>6,7)</sup>. Because of this, a brittle coke structure which is made up of free-expanded foamed coal and residue of thermally decomposed plastic is formed in the voids that occur after the thermal decomposition of the plastic. Furthermore, since the plastic is subjected to thermal decomposition at lower temperatures than the coal and generates pyrolytic gases in the temperature range at which the coal softens and melts (about 400 to 500°C), some types of plastics can adversely affect the coking property of coal<sup>6,8,11)</sup>. Thus, if the propor-

tion of waste plastic added to coal is increased beyond 1% by mass, there are concerns that the coke strength would decline<sup>6,7,12</sup>).

In order to increase the proportion of waste plastic that can be added to coal without causing the coke strength to decline in the waste plastic recycling process, it is considered effective to reduce the area of contact between the coal and waste plastic by adjusting the grain size, bulk density, etc. of the waste plastic in the volume reduction process<sup>7,8,15</sup>. More detailed study is required in the future concerning any technology that permits an increase in the proportion of waste plastic that can be added to coal, including waste plastic pretreatment technology and coke oven operating technology.

### 3.3 Waste plastics recycling process using coke oven

The waste plastic recycling process using coke ovens is presented schematically in Fig. 7. Waste plastic which is collected and baled in accordance with the Waste Plastic Containers and Packaging Recycling System is then transported to a steelworks yard, where it is crushed, removed of foreign matter and agglomerated by the pretreatment process shown in Fig. 3. The waste plastic that has been agglomerated by the pretreatment process is, together with the coal, charged into a coke oven, in which they are carbonized in an oxygen-free reducing atmosphere at about 1,100 to 1,200°C. As a result, the waste plastic is thermally decomposed into coke (about 20%), tar/light oil (about 40%) and coke oven gas (about 40%). These products obtained by the carbonization of waste plastic have their own uses: the coke is used as an iron ore reducing material in a blast furnace, the tar and light oil are used as raw materials for various plastics, etc. and the coke oven gas (COG) is used as clean energy at thermal power stations, etc. (Fig. 7)<sup>13</sup>.

### 3.4 Evaluation of chlorine behavior in waste plastic recycling process using coke oven

Municipal waste plastic includes polyvinyl chloride, polyvinylidene chloride and other chlorinated plastics. At present, various types of technologies for recycling waste plastic, such as the technology for converting waste plastic into materials for use in blast furnaces<sup>14-16</sup> or into oils<sup>1</sup>, are being developed. However, in any case, it is indispensable to develop technology to remove chlorine from waste plastic, since the chlorine contained in waste plastic can corrode equipment during

the plastic combustion or thermal decomposition process and, depending on the method of treatment, can generate harmful byproducts<sup>16</sup>. When it comes to treating waste plastic which contains chlorine, it is important to evaluate the behavior of the chlorine. Therefore, the behavior of chlorine was studied when chlorinated plastics were carbonized in a coke oven by the waste plastic recycling process<sup>17,18</sup>.

In the experiment, municipal waste plastic, whose composition and chemical properties are shown in Tables 1 and 2, and a coking coal (see Table 3) were used. Using apparatus for laboratory experiments and an actual coke oven, the conversion ratios were measured of the individual samples of chlorinated products when the samples were carbonized. Described below are the details of the experiment carried out by using an actual coke oven<sup>17</sup>.

Using a coke oven (height: 6.5 m, width: 430 mm, coal charging rate: 30 tons/oven) at Nippon Steel Chemical's Kimitsu Works, a study was made of the behavior of chlorine when coal mixed with municipal waste plastic was carbonized at 1,100°C for 21 hours. First, waste plastic containers and packaging were crushed and agglomerated into balls about 25 mm in diameter by the pretreatment equipment (see Fig. 3) using the procedure described in 3.1. In the experiment using an actual coke oven, coal samples to which were added either 1 or 2% by mass of agglomerates were separately carbonized in the coke oven to measure their conversion ratios into different products.

The chlorine concentrations of the plastic samples and coal samples used in the experiment and the chlorine concentrations of the products of carbonization of the samples were measured using the combustion tube oxygen combustion – ion chromatography method in which each sample is incinerated at 1,350°C in a combustion tube and its combustion gases are absorbed by liquid absorbent

Table 3 Ultimate analysis and ash content of raw coal

Ultimate analysis (mass%, dry)						Ash (mass%)
C	H	N	Cl	S	O (diff.)	
87.36	4.59	1.59	0.045	1.02	5.40	8.9

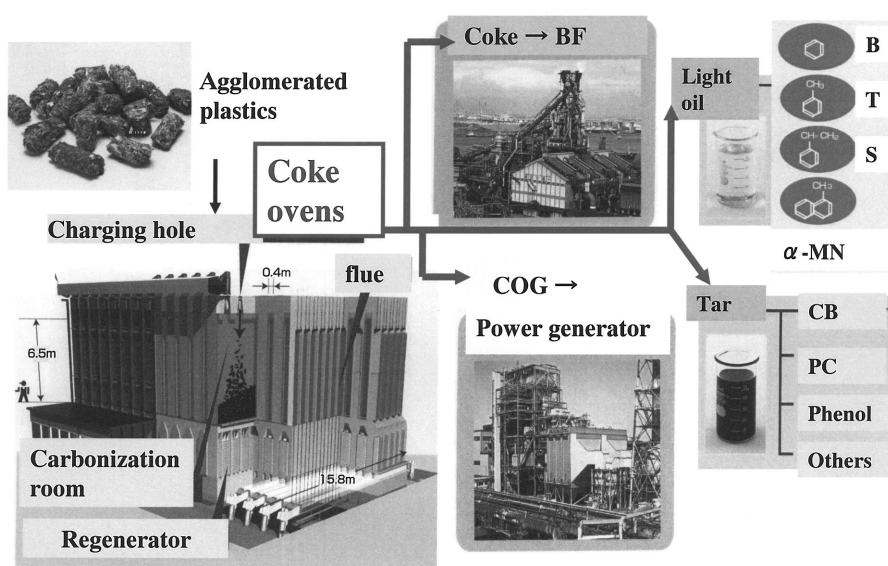


Fig. 7 Waste plastics recycling process using coke ovens



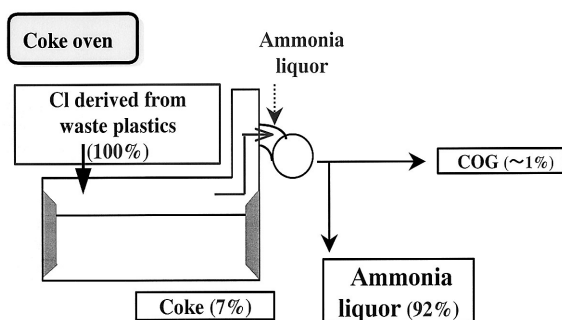


Fig. 8 Material balance of Cl derived from waste plastics

so that its chlorine concentration can be measured by iron chromatography. In the combustion tube, 0.2 grams of each sample was incinerated at 1,350°C in an oxygen stream in accordance with JIS M 8813 (Total Sulfur Combustion Volumetric Method). The combustion gases were absorbed by 80 ml of NaOH solution of 1/500 standard, from which a suitable amount of sample was taken and subjected to iron-exchange chromatography (DIONEX 2000 i/sp Chromatograph of Japan Dionex Inc.) to measure its chlorine concentration. The chlorine concentration tolerance of the ion-exchange chromatograph is 0.1 to 10 ppm.

Adding 1% (2%) by mass of waste plastic, whose composition and properties are shown in Tables 1 and 2, to the coking coal, whose properties are shown in Table 3, increased the chlorine concentration of the coking coal – 450 ppm – to 750 ppm (1,050 ppm). Fig. 8 shows the conversion ratios for chlorine contained in waste plastic into different products, measured from the difference between the addition of 2% by mass of chlorinated waste plastics and no addition of waste plastic<sup>21</sup>. It was determined experimentally that the chlorine derived from the waste plastic was converted into ammonia liquor (92%), coke (7%) and coke oven gas (1%). Many studies have been undertaken on the types of chlorine contained in coal. It is considered that the chlorine contained in coal is mostly inorganic chlorine derived largely from NaCl<sup>19,25</sup>.

Even when the chlorine concentration of the raw material for coke increases as a result of addition of 1 to 2% by mass of chlorinated general waste plastics to coking coal, the chlorine concentrations of coke and coke oven gas – products of carbonization in a coke oven – only increase slightly, since most of the chlorine (organic chlorine) contained in general waste plastics reacts with ammonia liquor when it is thermally decomposed, and is converted into ammonium chloride and absorbed by ammonia liquor<sup>20</sup>.

#### 4. Development of Waste Plastics Recycling Process into Commercial Equipment and Current Operating Condition of Equipment

As the Containers and Packaging Recycling Law came into full force in 2000, Nippon Steel's first waste plastic treatment equipment (capacity: 50,000 tons/year) was put into operation at its Nagoya Works and Kimitsu Works, respectively, in that year. Then, in 2002, more waste plastic treatment equipment (capacity: 25,000 tons/year) became operational at the Yawata and Muroran Works, respectively<sup>6,7</sup>.

The salient characteristic of the waste plastics recycling process is that it utilizes the coke oven – a large-scale, high-temperature reducing process in the infrastructure of the iron and steel industry – to thermally decompose waste plastics efficiently and produce coke, tar, light oil and coke oven gas for refinement by existing equipment, thereby allowing for nearly 100% recycling of waste plastic as a raw material for chemicals. The waste plastic recycling process using coke ovens has been certified as a chemical resources recycling technology by the Containers and Packaging Recycling Law.

The quantities of waste plastic recycled by the waste plastic recycling process have been steadily increasing year by year<sup>26</sup>. The above four steelworks together recycled 121,000 tons of waste plastic in 2002, 123,000 tons in 2003 and 160,000 tons in 2004. In 2005, waste plastic recycling equipment having a capacity of 25,000 tons/year was newly installed at the Oita Works while the capacity of the Yawata Works' equipment was expanded from 25,000 tons/year to 50,000 tons/year. The total equipment capacity at present is 225,000 tons/year. All the waste plastic recycling processes and coke ovens at the works continue to operate well<sup>8</sup>.

#### 5. Conclusion

More than five years have passed since the waste plastic recycling process was put to practical use in 2000. Both the process and equipment have been working quite satisfactorily. The waste plastic recycling process, which uses the existing infrastructure of large-scale urban steelworks unique to Japan, was developed and put into practice as one of the solutions of Japanese iron and steel industry to help build a sustainable recycling-oriented society. It is expected that in the future this technology will make further contributions to the development of a social system aimed at a recycling-oriented society and to curb global warming.

#### References

- 1) Nifuku, M.: J. Jpn. Inst. Energy. 81 (3), 2002, 154 (2002)
- 2) Kato, K. et al.: Met. Technical. 71 (4), 331 (2001)
- 3) Kato, K. et al.: ISIJ Int. 42 (Supplement), S10 (2002)
- 4) Kato, K.: J. Jpn. Inst. Energy. 81 (3), 174 (2002)
- 5) Kato, K. et al.: J. Mater. Cycles Waste Manag. 5, 98 (2003)
- 6) Nomura, S. et al.: J. Jpn. Inst. Energy. 81 (8), 728 (2002)
- 7) Nomura, S. et al.: J. Jpn. Inst. Energy. 82 (3), 143 (2003)
- 8) Uzumekesici, E.S. et al.: Fuel. 78, 1697 (1999)
- 9) Palmer, S.R. et al.: Prepr. Am. Chme. Soc. Div. Fuel Chem. 40, 1995, p.29
- 10) Amamoto, K. et al.: CAMP-ISIJ. 7 (4), 944 (1994)
- 11) Brzozowska, T.J. et al.: J. Anal. Appl. Pyrolysis. 48, 45 (1998)
- 12) Kato, K.: Bull. Iron Steel Inst. Jpn. 10 (1), 33 (2005)
- 13) Kato, K.: Bull. Iron Steel Inst. Jpn. 8 (12), 890 (2003)
- 14) Asanuma, M. et al.: J. Jpn. Inst. Energy. 77 (5), 423 (1998)
- 15) Asanuma, M. et al.: ISIJ. Int. 40, 244 (2000)
- 16) Asanuma, M. et al.: J. Jpn. Inst. Energy. 79 (3), 210 (2000)
- 17) Kato, K. et al.: Tetsu-to-Hagané. 90 (10), 776 (2004)
- 18) Kato, K. et al.: CAMP-ISIJ. 15 (4), 765 (2002)
- 19) Hodges, N. J. et al.: J. Inst. Energy. 56, 158 (1983)
- 20) Cross, P. et al.: Mine Quarry. 25 (5), 33 (1996)
- 21) Huggins, F. E. et al.: Fuel. 74, 556 (1995)
- 22) Fynes, G. et al.: Fuel. 67, 822 (1988)
- 23) Herod, A.A. et al.: Fuel. 62, 1331 (1983)
- 24) Edgcombe, L.J.: Fuel. 35, 283 (1958)
- 25) Daybell, G.N. et al.: Fuel. 37, 1331 (1983)
- 26) Kato, K. et al.: Resour. Processing. 50 (4), 182 (2003)