Production of Metallurgical Coke Utilizing Low-Rank Coals Upgraded by Mild Solvent Treatment

Ryuichi ASHIDA,^{1)*} Kazumi IWASE¹⁾ and Kouichi MIURA²⁾

1) Department of Chemical Engineering, Kyoto University, Kyoto-daigaku Katsura, Nishikyo-ku, Kyoto, 615-8510 Japan.

2) Institute of Advanced Energy, Kyoto University, Gokasho, Uji, Kyoto, 611-0011 Japan.

(Received on May 16, 2016; accepted on September 1, 2016; J-STAGE Advance published date: November 24, 2016)

Steel industries need to increase the use of low-rank coals in coke making since coking coals have been depleting and the price of coking coal has been increasing. In this study we propose to pretreat low-rank coals in non-polar solvent such as 1-methylnaphthalene below 400°C for converting them to a substitute for coking coals. The proposed method was found to be effective in deoxygenating low-rank coals significantly while suppressing cross-linking or polymerization reactions which often accompany deoxygenation reactions. The amount of low-molecular-weight compounds formed in the solvent-treated coals was comparable to that existing in coking coals. Coking tests utilizing the solvent-treated coals suggested that the solvent-treated coals can be substitutes for slightly-coking coals in coke making process.

KEY WORDS: low-rank coals; metallurgical coke; solvent treatment; upgrading.

1. Introduction

Steel industries need to increase the use of low-rank coals in coke making since coking coals have been depleting and the price of coking coal has been increasing. In order to produce cokes with mechanical strength using conventional coke ovens, it is necessary that coals have thermal plasticity. It is believed that the thermal plasticity of coals is associated with the amount of inherent low-molecular-weight compounds, γ compounds,^{1–3)} and the amount of low-molecular-weight compounds formed during pyrolysis, metaplast.^{4–6)} Since coking coals generally have a sufficient amount of such low-molecular-weight compounds, they show thermal plasticity around 400 to 550°C. Low-rank coals such as brown coals and subbituminous coals, on the other hand, have no thermal plasticity upon being heated in inert gas atmosphere, suggesting a lack of the low-molecular-weight compounds. This is partly because so-called cross-linking reactions or polymerization reactions take place below 400°C at hydrogen bondings forming between oxygen-containing functional groups such as hydroxyl groups and carboxyl groups.^{7–9)} The cross-linking reactions are more significant for lower-rank coals such as brown coals.

In this study we propose to pretreat low-rank coals in non-polar solvent below 400°C for converting them to a substitute for coking coals. In the proposed method, it is expected that the solvent breaks the hydrogen bondings which are thermally weakened above 140°C¹⁰⁾ and pulls the molecules apart by dissolving them to suppress the cross-linking reactions while decomposing oxygen-containing

functional groups. Non-polar solvent was chosen in the proposed method because polar solvents which are strongly associated with coal molecules are difficult to be recovered from the product.

We have recently shown that the treatment of low-rank coals or biomass wastes in non-polar solvent such as 1-methylnaphthalene at around 350°C can produce a significant amount of low-molecular-weight compounds whose elemental compositions were comparable to that of bituminous coal.^{11–13)} In this study we first validated the concept of increasing the low-molecular-weight compounds by the proposed method and then examined the possibility of the solvent-treated coal as a raw material in coke making process.

2. Experimental

2.1. Samples

An Australian brown coal, Loy Yang coal, and an Indonesian subbituminous coal, Adaro coal, were used in this study. The properties of the coals used were shown in **Table 1**. 1-methylnaphthalene (Merck) was used as the solvent.

Table 1. Properties of the low-rank coals used in this study.

Sample	Ultimate analysis [wt%, d.a.f.]				Atomic ratio [–]		Ash [wt%, d.b.]
	C	H	N	O+S (diff.)	H/C	O/C	
Loy Yang	69.1	3.8	0.7	26.4	0.66	0.29	1.5
Adaro	70.0	5.2	1.7	23.1	0.89	0.25	2.7

* Corresponding author: E-mail: ashida@cheme.kyoto-u.ac.jp

DOI: <http://dx.doi.org/10.2355/isijinternational.ISIJINT-2016-276>

2.2. Solvent Treatment

The coal and solvent at different mixing ratios were charged in a small autoclave (ca. 12 cm³) made of stainless steel. After purging the inside of the autoclave with nitrogen gas, the autoclave was heated at 5 K/min up to 350°C or 400°C, at which it was kept for 1 h. Final autogenic pressure was 2 to 4 MPa. The solvent was evaporated at 140°C under reduced pressure to obtain solvent-treated coals (STC).

2.3. Fractionation of the Treated Coals

In order to quantify the amount of low-molecular-weight compounds in STCs, the STCs were extracted by 1-methylnaphthalene at 350°C using a flow-type extractor.^{14,15} The extraction separated the STC into residue (Residue), the solid extract that precipitated from the extract at room temperature (Deposit), and the extract soluble in solvent even at room temperature (Soluble). Molecular weight of the Soluble should be the lowest and that of the Residue should be the highest among the three fractions.

2.4. Analyses of the Treated Coals

Ultimate analyses of the STCs were performed using a CHN analyzer (Yanaco, MT-6). Melting and plastic behaviors of the Solubles were examined using a thermomechanical analyzer (Shimadzu; TMA50) in which the displacement depth of a rod into a solid sample bed was continuously monitored while heating the sample at 10 K/min in a nitrogen flow. In the thermomechanical analysis, a sample was placed in a pan (5.2 mm I.D. and 6.0 mm high) at the height of 1 mm and the rod of 4.3 mm in diameter was loaded with a constant load of 0.098 N.

2.5. Coke Preparation and Evaluation

Four coking coals shown in **Table 2** were used for coke preparation. A, B, C coals are strongly-coking coals whereas D coal is a slightly-coking coal. Each coal was pulverized to less than 1 mm in diameter. **Table 3** shows the mixing ratios of the coals for preparing cokes. The coking coals were

mixed with the raw low-rank coals, the N₂-treated low-rank coals (solvent-to-coal ratio = 0), or STCs.

Figure 1 shows a schematic of the mold used for coke preparation. 2 g of the mixed coals were placed in a stainless steel tube (I.D.: 17.0 mm) between two stainless steel cylinders (Diameter: 16.8 mm, Height: 20.0 mm). The mold was heated in a nitrogen atmosphere at a rate of 3 K/min up to 900°C where it was kept for 30 min. The evolved gas can get out of the mold through a small gap between the tube and cylinders.

Prepared cokes were served to a compressive strength test as well as observation under crossed nicols using a polarization microscope.

3. Results and Discussion

3.1. Upgrading Behavior in Solvent Treatment

Figure 2 shows the effect of solvent-to-coal ratio on the yields of gaseous products and fractions constituting STC (or N₂-treated coal for solvent-to-coal ratio = 0) for Loy Yang coal. The yield of STC is a sum of the Residue, Deposit, and Soluble yields and is shown with thick lines in

Fig. 1. A schematic of the mold used for coke preparation.

Fig. 2. Effect of solvent-to-coal ratio on the yields of gaseous products and fractions constituting STC (or N₂-treated coal for solvent-to-coal ratio = 0) for Loy Yang coal.

Table 3. Mixing ratios of the coals for preparing cokes (wt%-d.b.).

Abbreviation	A	B	C	D	Loy Yang or Adaro		
					Raw	N ₂	STC
Base	40	5	5	50	0	0	0
Raw	40	5	5	45	5	0	0
N ₂	40	5	5	45	0	5	0
STC	40	5	5	45	0	0	5

Table 2. Properties of the coking coals used in this study.

Sample	Ultimate analysis [wt%, d.a.f.]					Atomic ratio [-]		Proximate analysis [wt%, d.b.]		log MF [-]
	C	H	N	S	O (diff.)	H/C	O/C	Ash	VM	
A	90.5	4.6	1.4	0.4	3.1	0.61	0.03	9.6	23.0	1.50
B	90.2	4.6	2.0	0.6	2.6	0.62	0.02	10.3	21.2	2.02
C	89.6	4.7	1.6	0.3	3.8	0.63	0.03	10.5	21.8	1.82
D	83.4	5.5	2.0	0.5	8.6	0.79	0.08	7.5	35.9	1.11

the figure. The yield of STC ranged from 0.80 to 0.88 kg/kg-dry raw coal. CO_2 and H_2O were formed at any solvent-to-coal ratio, suggesting that deoxygenation reactions took place during the treatment. A larger amount of low-molecular weight compounds or the Soluble formed in the presence of the solvent than in the absence of the solvent, suggesting the validity of the proposed method. The STC became more abundant in the Soluble with increasing the solvent-to-coal ratio, reaching as large as 0.38 kg/kg-STC (0.34 kg/kg-dry raw coal). It can be expected that the abundance of the Soluble should contribute to improving caking property of the low-rank coals.

Table 4 shows elemental compositions of STCs or N_2 -treated coals prepared from Loy Yang coal at different solvent-to-coal ratios and temperatures. Carbon contents of the STCs were all over 79%-d.a.f., which was comparable to those of bituminous coals. **Figure 3** shows elemental compositions of STCs, N_2 -treated coals, and raw coal on H/C vs O/C diagram for Loy Yang coal. The O/C values of STCs were reduced to less than half of that for the raw coal. The O/C values of STCs prepared at 400°C were reduced down to smaller than 0.10, which was comparable to that of the slightly-coking coal, D. The STCs had a little smaller O/C values than N_2 -treated coals (solvent-to-coal ratio = 0). Although the H/C value did not change significantly through the treatment, the H/C values of STCs prepared at 400°C were a little smaller than that of STCs prepared at 350°C.

These results indicate that the treatment in 1-methylnaphthalene solvent can deoxygenate low-rank coals significantly while suppressing cross-linking or polymerization reactions which often accompany deoxygenation reactions. Instead of the cross-linking reactions, deoxygenation reactions within a single molecule should take place such as dehydration reactions of alcoholic hydroxyl groups within a molecule to form C=C bonds.

3.2. Possibility of STC as a Raw Material for Coke

Figure 4 compares relative abundance of the Soluble, Deposit, and Residue for N_2 -treated coal (solvent-to-coal ratio = 0), and STC (solvent-to-coal ratio = 50) prepared from Loy Yang coal at 400°C as well as for the four coking coals. The lower-molecular-weight fractions, Soluble and Deposit, accounted for 0.32 – 0.36 kg/kg-d.b. of the coking coals. On the other hand, the N_2 -treated coal had as small as 0.20 kg/kg-d.b. of Soluble and Deposit. The STC had as large as 0.32 kg/kg-d.b. of Soluble and Deposit although its Deposit fraction was less than those of the coking coals.

Figure 5 shows thermomechanical analysis curves for

Solubles of the STCs prepared from Loy Yang coal and the coking coals. When the sample melts completely in this analysis, the rod displaces the sample and reaches the bottom of the sample pan, which corresponds to the normalized displacement value, -1.0. All the Solubles can be judged to have melted completely. The Solubles of the STCs melted at around 100°C, a little lower temperature than those of the coking coals.

It was thus shown that the solvent treatment can increase the ratio of low-molecular-weight compounds, whose softening and melting behavior are similar to those of coking coals, up to the ratio of low-molecular-weight compounds

Fig. 3. Elemental compositions of STCs, N_2 -treated coals, and raw coal on H/C vs O/C diagram for Loy Yang coal.

Fig. 4. Relative abundance of the Soluble, Deposit, and Residue for N_2 -treated coal, STC (solvent-to-coal ratio = 50) prepared from Loy Yang coal at 400°C, and the coking coals.

Table 4. Elemental compositions of STCs or N_2 -treated coals prepared from Loy Yang coal.

Solvent-to-coal ratio [-]	Treatment temperature	Ultimate analysis [wt%, d.a.f.]				Atomic ratio [-]		Ash [wt%, d.b.]
		C	H	N	O+S (diff.)	H/C	O/C	
0 (N_2)	350	78.8	4.7	0.9	15.6	0.72	0.15	2.1
1	350	80.6	5.0	0.9	13.5	0.74	0.13	2.6
4	350	79.9	5.1	0.8	14.2	0.77	0.13	2.0
50	350	79.1	5.0	0.9	15.0	0.76	0.14	2.3
0 (N_2)	400	84.3	4.6	1.0	10.1	0.65	0.09	2.1
4	400	85.7	4.7	1.0	8.6	0.66	0.08	2.4

Fig. 5. Thermomechanical analysis curves for Solubles of the STCs prepared from Loy Yang coal and the coking coals.

Fig. 6. Compressive strengths of the cokes prepared.

Fig. 7. Polarization microscope images of cokes prepared (anisotropic textures are seen inside the broken lines). (Online version in color.)

in coking coals.

Then, the possibility of STC as a raw material for metallurgical coke was examined. The STC itself did not have distinct thermal plasticity, which may be due to the lack of Deposit fraction. So, the possibility of STC as a substitute for a slightly-coking coal was examined. Coke prepared from a mixture of 50 wt% strongly-coking coals (A, B, and C coals) and 50 wt% slightly-coking coal (D coal), abbreviated to Base, was compared with the coke prepared from a mixture of 50 wt% of the same strongly-coking coals, 45 wt% of the same slightly-coking coal, and 5 wt% of STC (prepared at 400°C) as the mixing ratios of the coals are shown in Table 3. Raw low-rank coals or the N₂-treated coals were also used in the same way by substituting for 5 wt% of the slightly-coking coal. Compressive strengths of the cokes were compared in Fig. 6. When using raw coals or N₂-treated coals even by 5 wt%, the strength decreased dramatically from that of the Base coke. When using STC, however, much stronger cokes than the Base cokes as well as the cokes prepared using raw coals or N₂-treated coals were obtained, suggesting the possibility of STC as a raw material for coke making.

Figure 7 compares polarization microscope images of the cokes prepared. A large amount of anisotropic texture was observed in the Base coke and the coke prepared using STC whereas much less anisotropic texture was found in the cokes prepared using raw coal or N₂-treated coal. This result shows that STC did not prevent anisotropic texture of coking coals from developing, which should be one of the reasons why the coke prepared using STC was of high strength.

4. Conclusions

Treatment in non-polar solvent at 350°C to 400°C was found to be effective in converting low-rank coals such as brown coals and subbituminous coals into upgraded coals having a large carbon content and a large amount of low-molecular-weight compounds. The possibility of the solvent treated coal (STC) as a raw material for coke making was shown.

REFERENCES

- 1) T. Shimmura: *Fuel*, **12** (1933), 204.
- 2) H. R. Brown and P. L. Waters: *Fuel*, **45** (1966), 17.
- 3) K. Ouchi, K. Tanimoto, M. Makabe and H. Itoh: *Fuel*, **62** (1983), 1227.
- 4) D. W. van Krevelen, F. J. Huntjens and H. N. M. Dormans: *Fuel*, **35** (1956), 462.
- 5) H. A. G. Chermin and D. W. van Krevelen: *Fuel*, **36** (1957), 85.
- 6) I. G. C. Dryden and W. K. Joy: *Fuel*, **40** (1961), 473.
- 7) E. M. Suuberg, D. Lee and J. W. Larsen: *Fuel*, **64** (1985), 1668.
- 8) P. R. Solomon, M. A. Serio, G. V. Deshpande and E. Kroo: *Energy Fuel*, **4** (1990), 42.
- 9) J. V. Ibarra, I. Cervero, M. Garcia and R. Moliner: *Fuel Process. Technol.*, **24** (1990), 19.
- 10) K. Miura, K. Mae, W. Li, T. Kusakawa, F. Morozumi and A. Kumano: *Energy Fuel*, **15** (2001), 599.
- 11) R. Ashida, S. Umemoto, Y. Hasegawa, K. Miura, K. Kato, K. Saito and S. Nomura: Proc. 26th Annual Int. Pittsburgh Coal Conf., University of Pittsburgh, Pittsburgh, PA, (2009), Paper No. 5-1.
- 12) J. Wannapeera, X. Li, N. Worasuwannarak, R. Ashida and K. Miura: *Energy Fuel*, **26** (2012), 4521.
- 13) X. Li, R. Ashida and K. Miura: *Energy Fuel*, **26** (2012), 6897.
- 14) K. Miura, K. Mae, H. Shindo, R. Ashida and T. Ihara: *J. Chem. Eng. Jpn.*, **36** (2003), 742.
- 15) R. Ashida, K. Nakagawa, M. Oga, H. Nakagawa and K. Miura: *Fuel*, **87** (2008), 576.