Production of Metallurgical Coke Utilizing Low Rank Coal Depolymerized by Wet Oxidation

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The authors have previously proposed to pretreat low rank coals with aqueous oxidant such as hydrogen peroxide in order to convert them by oxidative degradation reactions into thermoplastic coals suitable for coke making. The treatment with hydrogen peroxide aqueous solution at 60°C improved a brown coal's thermoplasticity and high-strength cokes were successfully prepared from the dried treated coal. In this study effect of water content of the treated coal on its thermoplastic behavior was investigated. The water-containing treated coal melted and re-solidified at less than 200°C whereas the dried treated coal only softened at around this temperature. Apparent viscosity of the wet treated coal was dependent only on temperature and water content and could be lowered to as low as 2.5 × 10³ Pa s. The apparent viscosity of the treated coal containing a certain amount of water decreased with increasing temperature. The apparent viscosity at a certain temperature decreased with the increase of water content, reached a minimum value at around 40 wt% of water content on dry basis, and increased with the further increase of water content. As expected from the low apparent viscosity of the wet treated coal, the possibility was shown to utilize the treated coal as a binder for producing cokes from slightly- or non-coking coals.

KEY WORDS: brown coal; wet oxidation; metallurgical coke.

1. Introduction

Japanese steel industries, which are importing all coal resources required, are facing the necessity of increasing usable coal resources due to the recent rapid decrease of high-grade coking coal reserve and increase of its price. Coking coals show thermoplasticity between around 400°C and 550°C, which is required for producing a coke with high mechanical strength using conventional coke ovens. The thermoplasticity of the coking coals are believed to be related to 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) On the other hand, abundant and cost-effective low-rank coals such as brown coals generally have no thermoplasticity due to lack of the low-molecular-weight compounds. In order to utilize such low-rank coals as a raw material for coke making, it is necessary to develop a method to increase low-molecular-weight compounds in the coals to enhance thermoplasticity of the coals.

The authors have proposed to pretreat low rank coals with aqueous oxidant such as hydrogen peroxide in order to convert them by oxidative degradation reactions into thermoplastic coals suitable for coke making.7) The pretreatment with hydrogen peroxide aqueous solution at 60°C was found to be effective in increasing low-molecular-weight compounds in a brown coal and enhancing thermoplasticity of the coal. The coke strong enough to be used in a blast furnace was successfully prepared from the dried pretreated coal with the aid of pelletization at room temperature. Since the oxidized coal became more hydrophilic than the original brown coal, interaction between the coal and water needs to be clarified in order to utilize the oxidized coal more effectively. In this study effect of water existing in the treated coal on its thermoplastic behaviors and a possibility of utilizing the wet treated coal as a binder for producing cokes from low-rank coals were investigated.

2. Experimental

2.1. Samples

Australian Loy Yang coal (C: 65.5%, daf, water content: 55 wt% on wet basis) was used as a brown coal sample. The brown coal which was ground into fine particles of less than 1 mm was treated with 30% hydrogen peroxide aqueous solution at 60°C for 2 h.7) The treated coal was separated from the solution by vacuum filtration, and then dried under ambient condition for different times to obtain treated coals containing different amounts of water.

A coal (C: 82.9%, daf, maximum fluidity in Geisler Plastometer test: 6 ddpm) and KPC coal (C: 73.6%, daf, maximum fluidity in Geisler Plastometer test: 1 ddpm) were used for investigating the possibility of the treated coal as a
2. binder for producing coke. Each coal was pulverized to less than 1 mm in diameter.

2.2. Thermal Analyses

Thermal analyses of the raw coals, the treated brown coal with different water contents, or their mixture were performed using a thermogravimetric analyzer (Shimadzu, TGA-50) and a thermomechanical analyzer (Shimadzu, TMA-50). In both analyses, the sample was heated up to 900°C in a nitrogen stream at the rate of 10°C/min. In the thermomechanical analysis, the raw or treated coal sample was placed in a pan (5.2 mm I.D. and 6.0 mm high) at the height of 1 mm. The rod of 4.3 mm in diameter was loaded with a constant load of 0.098 N for the measurement. The thermomechanical analyzer continuously monitored a displacement depth of a descending rod into a sample bed in order to examine a thermoplastic behavior of the sample.

2.3. Coke Preparation and Evaluation

Figure 1 shows a schematic of the mold used for coke preparation. 1 g of the sample was 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 10°C/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.

For the mixture of KPC coal and the treated coal containing water, water was removed at 100°C or 120°C under a mechanical load (5 MPa) using the same mold as that shown in Fig. 1. Then, the sample as in the mold was heated in a nitrogen atmosphere without any mechanical load at a rate of 10°C/min up to 900°C where it was kept for 30 min.

Tensile strength of the resulting cokes was measured by a tensile testing machine (Shimadzu, AGS-J) at room temperature.

3. Results and Discussion

3.1. Effect of Water Content on Thermoplastic Behavior of the Treated Coal

We have shown that cokes of high strength can be produced from ‘dried’ treated coal if pelletization at room temperature before carbonization was employed.7) In other words, the ‘dried’ treated coal doesn’t have enough thermoplasticity to be hard coke without the aid of pelletization at room temperature. Then, we examined the possibility of utilizing ‘wet’ treated coals. Figure 2 shows microscopic images of cross sections of the coke prepared from the treated coal with 7.8 wt% water (left) or 15.4 wt% water (right) on wet basis. For the coke prepared from the treated coal with 7.8 wt% water, original coal particle shape still remained after coking. For the treated coal with 15.4 wt% water, however, no border of original particles was observed in the coke, suggesting the coal underwent melting in the presence of water.

Figure 3 shows results of thermogravimetric and thermomechanical analyses for the treated coals having different initial water contents. Weight decrease observed in this temperature range, around 100°C, was mainly due to water vaporization. When the initial water content was over 27.8 wt% on wet basis, the normalized displacement of thermomechanical analysis started to decrease at less than 100°C and sharply dropped to less than 0.2, meaning that the rod finally reached the vicinity of the bottom of the sample cell. These sharp drop of normalized displacement occurred during vaporization of water, prior to complete water vaporization. These results suggest that the treated coal containing a certain amount of water melted. When the initial water content was as low as 2.8 wt%, on the other hand, notable melting behavior was not observed. The sharp peaks which appeared for the thermomechanical analysis curves of the treated coals having initially 27.8 and 33.5 wt% of water were due to dilatation caused by release of water vapor, which was confirmed visually.

Figure 4 shows thermogravimetric and thermomechanical analysis curves for the raw brown coal containing 56.8 wt% water on wet basis initially. The change of normalized displacement for the raw coal was much less than that for the treated coal having a similar water content (54.9 wt%,...
The raw coal was judged not to melt even with high water content. This means that a mixture of solid coal and around 55 wt% liquid water cannot behave like a slurry. The thermoplastic property of the wet treated coal cannot be explained by a slurry behavior. As the microscopic observation result (Fig. 2) suggests as well, the wet treated coal did not remain a mixture of solid and liquid upon heating, but turned to a liquid mono phase, which gave the notable thermoplasticity to the coal. This phenomenon indicates that the treated coal and water are miscible at a molecular level to be a single liquid phase. Presumably, such molecular level contacts with easily mobile water molecules could release the interaction among the molecules of treated coal and enhance the mobility of the treated coal molecules. Although the raw brown coal is known to interact with water at a molecular level as well, the size of the raw coal molecules is not small enough to be mobile or to become a liquid phase at temperatures where water still co-exists. The reduction of the coal molecule size by the treatment was thus necessary for the coal to have such thermoplastic property.

Apparent viscosity of the wet treated coal was estimated from the thermomechanical analysis curves shown in Fig. 3 by assuming that the samples behave as a Newtonian fluid. Figure 5 shows the apparent viscosity of the treated coals having different initial water content. The apparent viscosity of all the samples generally decreased upon heating and then increased when the water content became less at higher temperature. The treated coal having higher initial water content tends to have lower minimum apparent viscosity at higher temperature. For the treated coal with 54.9 wt% initial water content, the minimum viscosity was reached at 108°C. The minimum viscosity was $2.5 \times 10^3$ Pa s, which is much lower than the minimum viscosity of coking coals, $10^4 - 10^5$ Pa s, although temperature ranges where minimum viscosity is reached are different. This result indicates the possibility to use the wet treated coal as a binder for coke making.

Since the amount of water remaining in the treated coal apparently affected its thermoplastic behavior, nitrogen containing water vapor (partial pressure of H$_2$O, $p_{H2O} = 7$ kPa) was supplied to the thermomechanical analyzer in order to suppress and delay water vaporization from the treated coal. Figure 6 shows apparent viscosity estimated from thermomechanical analysis curves measured in the absence (left) or in the presence (right) of water vapor in gas phase for the wet treated coal. As a result of water vaporization delay, the minimum viscosity was a little lowered and the low viscosity level lasted for longer time. The temperature where the viscosity started to rise was 115°C for the analy-
sis without water vapor while it was 120°C for the analysis with water vapor.

The apparent viscosity estimated from all the thermomechanical analysis data performed was plotted against water content on dry basis and temperature in Fig. 7. The data when dilatation was observed were omitted. Generally, the apparent viscosity of the treated coal containing a certain water amount decreased with increasing temperature as shown in Fig. 8 (water content: 70 wt% on dry basis) as an example. At a certain temperature, the apparent viscosity of the treated coal decreased with the increase of water content up to around 40 wt% of water content on dry basis, and increased at over 40 wt% as shown in Fig. 9 (50°C) as an example. The dependency on the water content may be related to the types of water on coal.10,11) At lower water contents, water on the coal surface and in the pore, which is strongly associated with the coal, is the majority. When the water content increased, more bulk water exists on the coal. Too much bulk water seems to have a negative effect on fluidity. It was found that the apparent viscosity was dependent only on temperature and water content in the treated coal regardless of $p_{H_2O}$, suggesting that desired viscosity profiles can be realized by controlling temperature and water content. The water content can reasonably be controlled by controlling the vapor pressure of H$_2$O in the atmosphere.
3.2. Possibility to Utilize the Wet Treated Coal as a Binder

Since the viscosity of the treated coal can be lowered to less than $10^4$ Pa s, the possibility of utilizing the treated coal as a binder for making coke from low-grade coals was examined. The treated coal having 43.1 wt% of initial water content was added to the A coal by 12% on dry basis and the coke was prepared from the mixture. The tensile strength of the coke was significantly increased from 0.18 MPa to 0.90 MPa by adding the wet treated coal. The wet treated coal melts and re-solidifies at less than 200°C, where it can act as a binder. The remaining solid of the treated coal may reduce the A coal fluidity at higher temperature. In order to examine the effect of addition of the treated coal on the thermoplastic behavior of the A coal, thermomechanical analyses were performed. Figure 10 compares apparent viscosity estimated from the thermomechanical analysis results for the A coal with that for A coal mixed with 14% wet treated coal on dry basis.

Next, a much lower grade coal, KPC coal, was mixed with the wet treated coal (water content: 69.1 wt%) by 28.5% on dry basis and the coke was prepared. When only the KPC coal was carbonized, the coal remained in the original particle shape. On the other hand, the KPC coal mixed with the wet treated coal was turned into one lump when heated, although the strength was not enough to be measured. Since the wet treated coal melts simultaneously with the vaporization of water, the volume of the wet treated coal decreases during melting, which may reduce the performance of the treated coal as a binder. In order to minimize the effect of the shrinking of the binder caused by water vaporization, mechanical compression was applied to the sample at 100°C or 120°C using the mold shown in Fig. 1 prior to carbonization under no mechanical compression. Figure 11 shows a relationship between a degree of water removal under mechanical compression and strength of the resulting cokes. The coke strength increased with increasing the degree of water removal. When the mixed coal was compressed at 120°C for 20 min, most of water in the treated coal was removed and the coke strength reached 0.5 MPa.
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KPC coal alone remained in its particle shape even under the same mechanical compression and coking conditions. These results show that the mechanical compression during vaporization of water in the treated coal is effective in enhancing the performance of the treated coal as a binder. In addition to the effect of compensating the shrinkage of the binder, mechanical compression could facilitate the transfer of melting binder into spaces among KPC coal particles and possibly enlarge the bonding area. Further investigation will be necessary to distinguish these effects of mechanical compression.

4. Conclusions

We have previously shown that a pretreatment with hydrogen peroxide aqueous solution at 60°C effectively increased low-molecular-weight compounds in a brown coal and enhanced thermoplasticity of the coal. Effect of amount of water remaining in the treated coal on its thermoplastic behavior was investigated. It was shown that the wet treated coal softened, melted, and re-solidified at less than 200°C. Apparent viscosity of the coal solely depended on temperature and the remaining water content in the coal, suggesting the possibility to control the thermoplastic behavior of the treated coal by controlling temperature and atmosphere. It was also shown that addition of the wet treated coal to a slightly- or non-coking coal was effective in producing coke of high strength from only such low-grade coals.

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