Addition Effect of Model Compounds of Coal Extract on Coke Strength

Koji KOYANO,¹ Kenta UEOKA,¹ Toshimasa TAKANOHASHI,¹ Kiyoshi FUKADA² and Kohei OTA³

¹) Advanced Fuel Group, Energy Technology Research Institute, National Institute of Advanced Industrial Science and Technology, 16-1 Onogawa, Tsukuba, 305-8569 Japan. E-mail: toshi-takanohashi@aist.go.jp
²) Steel Research Laboratory, JFE Steel Corporation, 1 Kokan-cho, Fukuyama, 721-8510 Japan.

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Eight polyaromatic hydrocarbons that are model compounds of coal extract were added to coal blends to clarify the mechanism of the effects of coal extract (HyperCoal) on coke strength. Addition of large aromatic-ring compounds (coronene, perylene, naphtho[2,3-al]pyrene) greatly enhanced coke strength, whereas three-ring aromatics (anthracene, phenanthrene) had no significant effect on coke strength. Because large polyaromatic compounds have greater affinity for coal molecules, they co-fused with the coal particles. As a result, formation of large pores during coking was suppressed, leading to increased coke strength.

KEY WORDS: HyperCoal (coal extract); coke strength; polyaromatic hydrocarbon; co-fuse; anisotropy.

1. Introduction

Though coal is widely distributed around the world, half of it consists of sub-bituminous coal and lignite, and the amount of caking-coal suitable for coke making is limited. Also, the price of imported coal has increased since 2005, and the price of caking-coal doubled in 2008.¹) The tight supply and rising price of caking-coal is an inevitable problem in Japan, so use of slightly and non-caking coals is required.

There are two ways to use slightly and non-caking coals. One is to replace coking plants with a new coke-making process, such as the “super coke oven for productivity and environmental enhancement toward the 21st century” (SCOPE21), developed by the Japan Iron and Steel Federation and the Center for Coal Utilization, Japan. In this process, the coking property of coal is increased by rapid heating; as a result, the blending ratio of slightly caking coals is increased from 20% to more than 50%.

The second way to use slightly and non-caking coals is to add a caking agent. This method is applicable to existing plants and has a lower initial cost. We have proposed an ash-free coal extract, called “HyperCoal” (HPC), as an additive or alternative for caking coal.³) HPC can be produced from a wide range of coal types, including slightly and non-caking coals.⁴,⁵) When HPC was added to a coal blend containing 50% slightly caking coal, the strength of the coke was markedly enhanced.⁶) Although the effect of HPC was attributed to its higher fluidity,⁷) it was unclear which fraction(s) in HPC was responsible for the enhanced strength and what the mechanism was. Understanding the mechanism may make possible further enhancement of coke strength.

In this paper, we used polyaromatic hydrocarbons as model compounds of coal extract to be added to coal. We investigated the effects of these compounds on coke strength and their mechanism of action.

2. Experimental Section

2.1. Samples

Two caking coals, K-9 (K9) and Goonyella (GO), and one slightly caking coal, Koryusho (KRS), were used. Ultimate and proximate analyses of these coals are shown in Table 1. The coals were ground to a particle size less than 1.0 mm for coke preparation, and less than 0.15 mm for thermal analyses.

Coal extract was prepared following a published procedure.⁸) Briefly, Upper Freeport coal (Argonne Premium Coal Sample) was extracted using CS₂/NMP mixed solvent at room temperature, and then the extract was fractionated with pyridine. After recovering the solvent, the pyridine-soluble (PS) fraction was prepared and used as an additive. The average molecular structure of PS is shown in Fig. 1.

As model compounds, anthracene, pyrene, naphtho[2,3-
apyrene, and coronene (TOKYO CHEMICAL INDUSTRY CO., LTD.), phenanthrene, pentacene, and perylene (Sigma-Aldrich Corporation), and benz[a]anthracene (KANTO CHEMICAL CO., INC.) were used. Additionally, a C-36 alkane, n-hexatriacontane (TOKYO CHEMICAL INDUSTRY CO., LTD.) was used for comparison.

2.2. Strength Measurements

Figure 2 is a schematic of the procedure used for the preparation of coke samples and their indirect strength tests. Approximately 5-g samples, composed of a KRS-GO-K9 (50/20/30 wt%) coal blend or KRS coal alone with and without 0.15 g of the additive (3 wt%), were prepared. Samples were carbonized under a weight load of 6.24 kPa at 1 273 K for 30 min and the coke yield determined by weight loss. Each sample was then cut into two pieces horizontally, and the tensile strength was measured using an Auto Graph AG-IS-5kN (SHIMADZU). Details of the procedure have been reported elsewhere.6) The strength data were distributed on a Weibull plot, and the value corresponding to the scale parameter was defined as the representing strength. Each experiment was carried out in triplicate.

2.3. Thermal Analysis

Approximately 10 mg of sample was tested by thermogravimetric (TG) analysis using a TGA-51 (SHIMADZU) at a heating rate of 3 K/min under a nitrogen flow of 50 mL/min. A dynamic shear rheometer (DSR) test was carried out using an ARES-2KSTD-FC (TA Instruments) on 0.4 g of sample at a heating rate of 3 K/min under a nitrogen flow of 80 L/min. Details of this procedure were described elsewhere.7)

2.4. Optical Texture Observation

The distribution of coke texture was counted at 200 points in each picture of coke samples using a polarizing microscope (Leica Microsystems model DM2500P) at 500-fold magnification. The textures were classified into five groups, according to shape and size: isotropic, fine mosaic, coarse mosaic, fibrous, and leaflet.

2.5. Pore Structure Analysis

A schematic of the image analysis procedure is shown in Fig. 2. The coke samples were prepared as described in Section 2.2 for strength measurement. Each sample was cut into two pieces vertically, embedded in epoxy resin and polished. The exposed inner portion of each piece was photographed with a digital microscope (KEYENCE, model VHX-600) having a field of view of 9.3 mm × 7.0 mm (approximately one quarter of the sample section) and a resolution of 5.8 μm/pixel. The area, maximum length, and roundness of each pore were determined using software developed in-house, and the histogram for each parameter was integrated from 20 images.

3. Results and Discussion

3.1. Strength Change by Adding Model Compounds

The coke strength prepared from a coal blend, with and without addition of the model compounds, is shown in Fig. 3. The value for the coal blend alone was 3.67 MPa. The effects of the polyaromatics on coke strength were classified into three groups. First, naphtho[2,3-a]pyrene, perylene, and coronene (5–7 rings) enhanced the strength markedly. Second, pyrene and benz[a]anthracene (4 rings) enhanced the strength moderately. Pentacene, consisting of 5 rings but
having a cata-condensed structure, had less effect on coke strength than did peri-condensed 5-ring compounds. Third, phenanthrene and anthracene (3 rings) decreased the strength slightly. In contrast, a straight-chain hydrocarbon, \( n \)-hexatriacontane, greatly decreased the strength.

Figure 4 shows the relationship between coke strength and the boiling points and melting points of the compounds. The melting point did not correlate with the strength. However, there was a strong correlation between boiling point and strength \((r = 0.96)\), except in the case of \( n \)-hexatriacontane and pentacene, both of which decreased coke strength. The molecular structure of these two compounds is quite different from coal molecular structure (Fig. 1), so they may have lower affinity with coal. A detailed mechanism is described below.

Figure 5 shows the relationship between coke yield and the boiling points of the compounds. There was a strong correlation \((r = 0.98)\), except in the case of \( n \)-hexatriacontane. We hypothesize that the compounds with higher boiling points remained in the coal blend at higher temperatures and consequently may have been better at co-fusing with the coal. Although the melting point of \( n \)-hexatriacontane is approximately 343 K, it is unstable thermally and has a lower affinity with coal; thus, it probably decomposed and was volatilized below the coal softening temperature (around 673 K) and did not co-fuse with the coal. On the other hand, three-ring compounds such as phenanthrene and anthracene were volatilized almost all, resulting in the coke yield to 70.3 wt%, which corresponds to 97% of that obtained from the coal blend (72.4%).

The relationship between coke yield and coke strength is shown in Fig. 6. The correlation was excellent \((r = 0.997)\), except for \( n \)-hexatriacontane and pentacene. Peri-condensed polycyclic aromatics may have co-fused with the coal particles and undergone condensation reactions with each other. The larger-ring compounds showed a stronger interaction and had higher boiling points, so the increase in coke yield correlated with the strength enhancement. On the other hand, \( n \)-hexatriacontane and pentacene decreased the coke strength despite increasing the coke yield. We suggest they remained in the coke but did not contribute to the co-fusing interaction because of their lower affinity for the coal molecules.

Figure 7 shows the coke strength as a function of the amount of additive. The strength of coke prepared from KRS coal without and with coronene or PS was plotted. The
strength was increased by the addition of coronene up to 7 wt%. At 10 wt%, the strength decreased greatly and the coke sample broke while cutting. A similar tendency was observed in the case of PS addition; the strength showed a maximum value at 7 wt% and decreased at 10 wt%. Figure 8 shows the increase of coke yield by the addition of coronene or PS, compared with the yield from KRS coal alone. The increase in yield was proportional to the amount of additive, indicating that approximately 60 wt% of coronene or 70 wt% of PS remained in the coke. Thus, the additives increased coke yield, presumably by co-fusing and co-carbonizing with the coal; however, excessive amounts decreased the coke strength, probably because of excessive dilatation of the additive.

3.2. Behavior during Co-fusing of Coal with Additive.

TG analysis was carried out to measure the co-fusing property of anthracene (3 ring) and coronene (7 ring). Figure 9 shows TG curves of KRS coal with and without 3 wt% anthracene. Each curve showed basically the same shape at temperatures greater than 473 K; below 473 K the anthracene apparently volatilized completely. The data for coronene is shown in Fig. 10. Weight loss for both KRS coal and
coronene began around 643 K; the two curves then diverge dramatically. A hypothetical curve, derived from the arithmetic average of the curves for KRS coal and coronene, is shown in Fig. 10. This hypothetical curve is very different from the actual curve obtained for KRS coal with coronene as an additive; in particular, the weight loss at 873 K is much smaller in the experimental curve than in the hypothetical curve. This result indicates that a significant portion of the coronene remained in the KRS coal and increased the coke yield.

Figure 11 shows DSR curves of KRS coal with and without coronene. The softening of KRS coal occurred at 643 K, which is approximately the temperature at which weight loss began. Coronene softened at around 525 K, indicating greater fluidity. The fluidity of KRS coal with 7% coronene was enhanced over a wide temperature range.

Figure 12 shows the distribution of coke texture in coal blends with and without naphtho[2,3-a]pyrene, perylene and coronene, all of which significantly enhanced the coke strength. A 3 wt% addition of each compound increased the relative percentage of anisotropic texture at the expense of the isotropic texture. Furthermore, as shown in Fig. 13(a), in coke without any compounds, isolated particles derived from coal were observed, whereas when naphtho[2,3-a]pyrene was added (Fig. 13(b)), the particle boundaries became less well defined and the anisotropic texture became widely dispersed. These results suggest that the polynuclear aromatic compounds co-fused with the coal particles and

![Image of diagram showing coke texture distribution](image1)

**Fig. 12.** Results of optical texture analysis for cokes.

![Image of polarized microscopic images](image2)

**Fig. 13.** Polarized microscopic images of cokes prepared from coal blend with/without naphtho[2,3-a] pyrene.

![Image of images of cokes](image3)

**Fig. 14.** Images of cokes prepared from KRS with/without coronene.
made the coal more caking.

Figure 14 shows images of coke samples prepared from KRS coal with and without 7 wt% coronene. In the case of KRS coal alone (Fig. 14(a)), there were many isolated particles and large pores derived from inter-particle spaces. However, with the addition of coronene (Fig. 14(b)) the coke matrices were linked together. The distributions of pore structure in these images are shown in Fig. 15. The pores of larger maximum length and lower roundness, which can be the origin of fracture, were relatively decreased by coronene addition. As a result, the coke strength was enhanced markedly.

Finally, as shown in Fig. 7, PS had a greater enhancement effect on coke strength than did coronene, which had the highest effect of the model compounds tested. This difference between PS and coronene can be explained by the fluidities of the coal blends, shown in Fig. 16. PS greatly enhanced the fluidity around the softening temperature range of KRS coal, whereas coronene enhanced fluidity in a relatively lower temperature range. PS has a higher molecular weight than coronene and a higher polarity. Thus, PS most likely fused at a higher temperature range than coronene, resulting in a greater effect on coke strength.

4. Conclusions

Addition of large peri-condensed aromatic-ring compounds, such as coronene, perylene, and naphtho[2,3-a]pyrene, to a coal blend markedly enhanced the resulting coke strength. In contrast, 3-ring compounds with lower boiling points, as well as a straight chain compound, did not enhance the strength.

The large peri-condensed aromatic-ring compounds co-fused and co-coked with the coal particles and inhibited formation of large pores from inter-particle spaces. As a result, the strength was enhanced significantly.

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