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Characteristics of coal upgraded with heavy oils

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Abstract−We investigated the ability of an oil coating to upgrade Indonesian low-rank coal, which has a low ash content and a moisture content of approximately 30%. Proximate and ultimate analyses of the characteristics of coal samples containing different amounts of asphalt (ASP) and palm fatty acid distillate (PFAD) were studied, including the samples' calorific values, crossing-point temperatures (CPT), specific surface areas, pore sizes, structural changes, and moisture readsorption. The results showed that the 0.5% PFAD-coated coal was the highest quality. This coal showed few physical and chemical changes, and it had a low surface area and a high CPT value.

Keywords: Low-rank Coal, Upgrading, Heavy Oil, Spontaneous Combustion, Moisture Readsorption

INTRODUCTION

Indonesian brown coal, which is a low-rank coal, has a low ash content, ranging from 2% to 5%, and a high moisture content of between 30% and 50%. Due to its high moisture content, Indonesian brown coal has a low calorific value, exhibits poor combustibility, and contains large amounts of useless moisture, which has knock-on effects on transport costs. The quality of Indonesian brown coal can be increased to a level similar to that of high-rank coal with the addition of only a simple drying technology. Diverse drying technologies aimed at upgrading low-rank coal have been developed [1]. However, after drying, low-rank coal displays many pores, resulting in a high risk of moisture readsorption and spontaneous combustion [2]. To overcome these problems, low-rank coal should not only be dried but also further stabilized after being treated. The use of heavy oil to upgrade brown coal is well known in Japan [3-5]. In this process, raw coal is mixed with kerosene and a low-sulfur waxy residue to prepare coal slurry. The slurry undergoes dewatering at a range of 130-160 °C and 400-450 kPa.

Although many technologies have been developed to upgrade low-rank coal, the resulting calorific values of the coal are not high enough, and the coal is not stable enough to prevent spontaneous combustion. In addition, the technologies are not economically feasible. In the present study, to address the aforementioned problems, an oil coating was applied to Indonesian brown coal in an attempt to upgrade this low-rank coal. Asphalt (ASP) derived from petroleum, and palm fatty acid distillate (PFAD), which is a plant extract, were used for the heavy oil.

EXPERIMENTAL MATERIALS AND METHOD

1. Sample Preparation

Indonesian low-rank coal was used in this study. The raw coal was sieved to 0.425-1 mm sizes. To ascertain the properties of the raw coal, a proximate analysis was conducted of the as-received coal, and an ultimate analysis was conducted of the dried coal. The calorific values of the coal were also determined (Table 1).

The asphalt solution used in the oil coating was produced by dis-

Table 1. Analysis data of the coal samples

Sample name	Proximate analysis (%)				Ultimate analysis (%)					Calorific value (kcal/kg)
	Moisture	Volatile	Ash	Fixed carbon	C	H	N	O	S	
Raw coal	28.84	42.86	2.26	26.04	-	-	-	-	-	4552
Dried raw coal	1.61	56.78	3.14	38.49	66.05	5.03	0.79	24.92	0.07	6472
ASP 0%	0.40	56.99	3.07	39.54	-	-	-	-	-	6450
ASP 0.5%	0.77	55.84	2.80	40.60	65.75	5.52	0.84	25.00	0.09	6453
ASP 1.0%	1.29	55.26	3.01	40.46	66.60	5.68	0.45	24.10	0.16	6522
PFAD 0.5%	0.32	55.11	3.08	41.51	67.40	5.23	0.98	23.25	0.06	6500

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solving the asphalt in kerosene. The PFAD solution (PT, Megasurya Mas, Indonesia) was produced by dissolving the PFAD in kerosene. The physical and chemical characteristics of the PFAD were as follows: melting point 42-60 °C, flash point at least 200 °C, density 0.85-0.90 kg/m^3 (at 87.8 °C), moisture content 0.1%, and calorific value 9250 kcal/kg.

The raw coal and the solution were mixed at a ratio of 1 : 1, and the mixture was left to stand for approximately 5 minutes. The solution was then extracted with a vacuum pump so that the residual solution content was 3-6%. To remove the moisture and the kerosene, the processed sample was dried for 12 hours at 107 °C in a nitrogen atmosphere (flow rate 1.5 L/min) in a normal pressure vessel.

2. Analysis of the Characteristics of the Coal

The proximate analyses were conducted based on ASTM D7582 using a TGA 701 Thermogravimeter (LECO Co., St. Joseph, MI, USA). The ultimate analyses were conducted by using a TruSPec elemental analyzer (LECO Co.), and the sulfur analyses were completed with an SC-432DR sulfur analyzer (LECO Co.). The calorific values were measured with a Parr 1261 calorimeter (LECO Co.). The functional groups were analyzed with a Nicolet 6700 FT-IR spectrometer (Thermo Fisher Scientific, Madison, WI, USA). The adsorption-desorption isotherms of N_2 were measured with an ASAP 2420 Surface Area and Porosimetry System (Micromeritics, Norcross, GA, USA). The pore volume values were measured in the range of p/p_o 0.05 to 0.990.

The crossing-point temperature (CPT) was used to analyze the tendency of the coal to spontaneously combust [6-8]. The CPT is an important measure to assess spontaneous combustion characteristics [6]. The experimental apparatus used in the CPT analysis is shown in Fig. 1. In each experiment, 35 g each of the coal samples was put into each of two vessels, and the temperature of the oven was fixed at 40 °C while nitrogen gas was injected. When the oven temperature and the temperature in the vessels achieved equilibrium, the oven temperature was increased at a rate of 0.5 °C/min. The two vessels were continuously injected with oxygen and nitrogen gases, respectively, at a flow rate of 30 ml/min. The temperature of the vessel injected with the nitrogen was used as the reference data [7,8].

To assess the moisture readsorption characteristics of the upgraded coal, changes in the mass of 5 g of the upgraded coal were measured for 48 hours at 30 °C and 95% relative humidity.

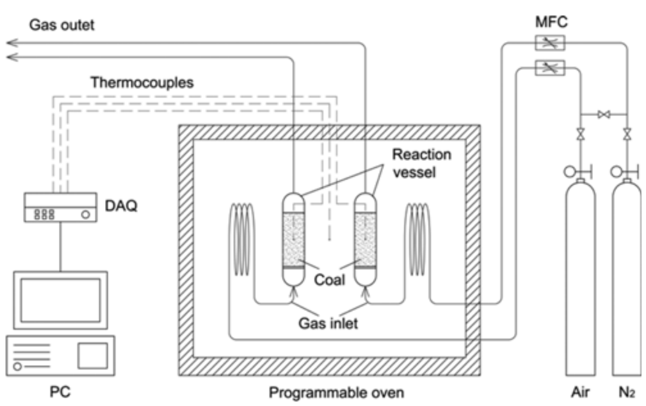

Fig. 1. Experimental apparatus used in the crossing-point temperature (CPT) analysis.

RESULTS AND DISCUSSION

1. Results of Physical and Chemical Analyses

The results of the analysis of the physical and chemical characteristics of the upgraded coal are shown in Table 1. From the proximate analyses, the composition of the upgraded coal did not change greatly, except for a decrease in the moisture content, compared to that of the dried raw coal. Thus, drying the coal for 12 hours at 107 °C in a nitrogen atmosphere does not greatly affect the composition of the raw coal. Ultimate analyses were conducted on the dried raw coal, 0% ASP, 0.5% ASP, 1.0% ASP, and 0.5% PFAD samples. The sulfur content of the coal changed during the upgrading process, increasing more in the samples treated with the asphalt and the kerosene than in the samples treated with the PFAD and the kerosene. Thus, as the amount of asphalt residue increases, more sulfide gas (SO_2) might be generated during the combustion of the upgraded coal. The sulfur content of the PFAD upgraded coal was not vastly different from that of the raw coal. Upgrading the coal with PFAD is more environmentally friendly than upgrading it using asphalt. The results of the calorific value analyses showed that the calorific value of the raw coal increased from 4,552 kcal/kg to 6,500 kcal/kg as a result of drying. However, the calorific values of the upgraded coals were not significantly increased.

2. Changes in the Surface Characteristics of the Upgraded Coal

The results of the Fourier transform infra-red (FT-IR) analyses of the dried raw coal and the upgraded coal samples are shown in Fig. 2. In the range of 2,750-3,000 cm^{-1}, -CH_2 asymmetric dilation liberation (2,920 cm^{-1}) and -CH_2 symmetric dilation liberation (2,850 cm^{-1}) peaks were observed [8,9]. In the range of 1,400-1,850 cm^{-1}, C=C dilation liberation in aromatic or condensed rings (1,605 cm^{-1}) and -CH_3 asymmetric dilation liberation (1,440 cm^{-1}) peaks were identified [9-13]. The peak intensity of the dried raw coal was strong in all ranges in the FT-IR analyses. Thus, diverse functional groups were activated during the drying process.

Among the upgraded coals, the peak intensity of the ASP 1.0%

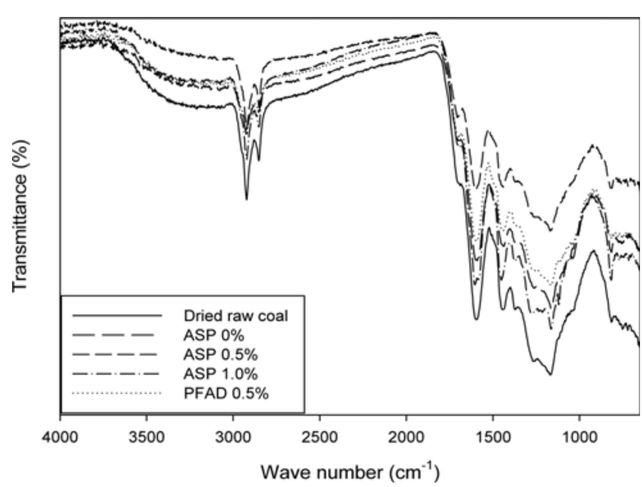

Fig. 2. Fourier transform infra-red (FT-IR) spectra of dried raw coal and upgraded coal.

Table 2. BET surface area, pore volume, and average pore size from adsorption/desorption isotherm data (N_2)

Sample name	BET surface area (m^2/g)	Pore volume (cm^3/g)	Average pore size (nm)
Dried raw coal	10.515	0.031	11.759
ASP 0%	8.019	0.027	13.671
ASP 0.5%	5.226	0.021	16.379
ASP 1.0%	5.788	0.022	15.517
PFAD 0.5%	3.267	0.015	18.853

sample was the lowest, followed by the 0% ASP, 0.5% PFAD, and 0.5% ASP upgraded coals. The peak intensities of the aliphatic hydrocarbon structure functional groups were decreased in all the upgraded coals. Therefore, the upgrading process was able not only to coat the surface of the coal, but also to deactivate the active functional groups on the surface.

The results of the Brunauer-Emmett-Teller (BET) [14] analyses are shown in Table 2. The upgraded coal treated with the solution containing 0.5% PFAD with a surface area of 3.267 m^2/g showed the largest change in surface area. The pore volumes showed a tendency similar to that of the surface areas. The pore sizes were smallest in the dried raw coal and largest in the 0.5% PFAD sample. Fig. 3 shows the distribution of the Barrett-Joyner-Halenda (BJH) [15] pore sizes. In the raw coal, which had the largest BET surface area, micropores in the range of 2-10 nm were identified most frequently. When the raw coal was treated with only kerosene, the number of

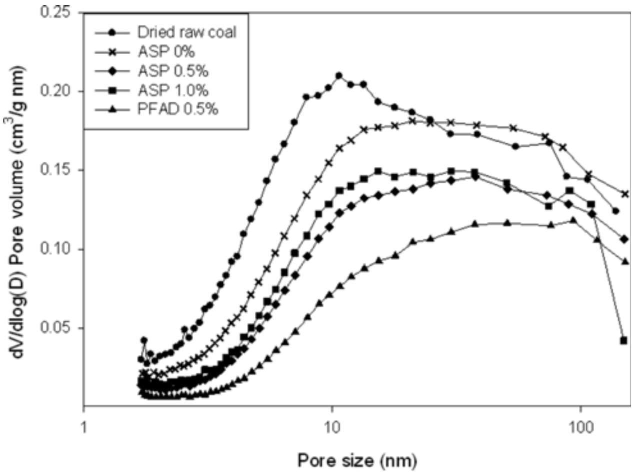

Fig. 3. Pore size distribution from the BJH adsorption.

micropores decreased, but the number of mesopores (pore size 10-10^2 nm) did not change significantly. The numbers of micropores also decreased in the 0.5% ASP and 1.0% ASP samples. In the 0.5% PFAD sample, the numbers of micropores and the numbers of mesopores greatly decreased. Thus, the coal solution containing PFAD was very well infiltrated at the the micropore scale.

Fig. 4 shows the results of the N_2 adsorption/desorption isotherm at a low temperature (77 K). The isothermal characteristics of four samples were analyzed: dried raw coal, 0%, ASP, 0.5% ASP, and

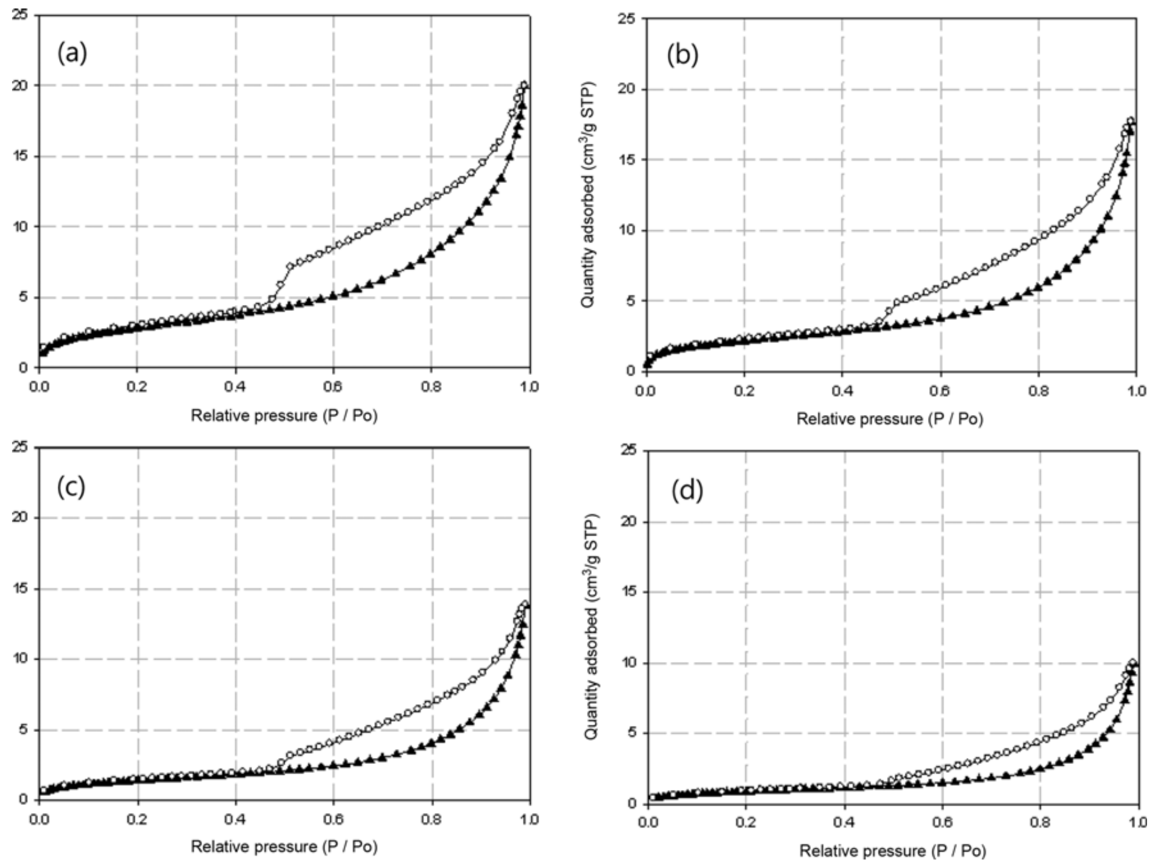

Fig. 4. N_2 adsorption/desorption at low temperature (77 K).

0.5% PFAD using methods described elsewhere [16,17]. The dried raw coal and the upgraded coal were classified as isotherm type II according to the reference classification. Isotherm type II is a general form of nonporous or macroporous adsorbent known to show free monolayer-multilayer adsorption. Adsorption hysteresis was clearly identified in the dried raw coal and in the 0% ASP coal (Fig. 4(a), (b)). In the desorption curve, the hysteresis loop type of the pores was H2 type [17]. Thus, the pores were ink-bottle pores [16]. Type H2 loops are generated due to the different mechanisms of condensation and evaporation reactions in the pore structures. They have narrow necks and wide bodies, like ink bottles [17]. In the 0.5% ASP coal sample shown in Fig. 4(c), a weak H2 hysteresis loop type was identified at a relative pressure of 0.470. Unusually, the sample treated with the solution containing PFAD showed H3-type hysteresis loops. H3-type loops appear in aggregates of plate-like particles and have slit-shaped pores [16]. This means that the pore structure of the coal treated with the solution containing PFAD was changed, a finding in accordance with the resulting pore size distribution.

3. Stabilization of the Upgraded Coal

The CPT of each sample is shown in Table 3. In the dried raw coal, the CPT was 141 °C. The CPT value of the 0% ASP upgraded coal sample increased slightly to 143 °C. In the 0.5% ASP, 1.0% ASP, and 0.5% PFAD samples, all the CPT values were at least 150 °C, an increase of approximately 10 °C compared with the dried raw coal. Therefore, the calorific values of the 0% ASP sample were similar to those of the samples treated with the solutions containing asphalt or PFAD, but the former had a high probability of spontaneous combustion.

Table 3. Crossing-point temperature (CPT) of dried raw coal and upgraded coal

Sample name	CPT (°C)
Dried raw coal	141
ASP 0%	143
ASP 0.5%	150
ASP 1.0%	153
PFAD 0.5%	152

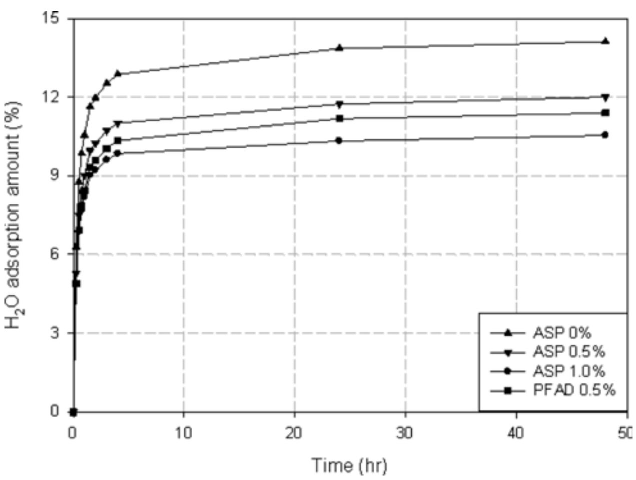

Fig. 5. Moisture readsorption of dried raw coal and upgraded coal.

The moisture readsorption by the upgraded coals varied according to the content of the remaining solutions (Fig. 5). The 0% ASP sample treated with the asphalt or PFAD solutions not containing any heavy oil reabsorbed the largest volume of moisture (14.11%). The samples treated with the 1.0% ASP solution reabsorbed the smallest amount of moisture. Therefore, the moisture readsorption properties were not related to the surface pore size or the pore structure. This may be because the coal surface was coated with asphalt, which is a hydrophobic substance.

CONCLUSION

Low-rank coal containing approximately 30% moisture was upgraded with a kerosene solution to which either asphalt or PFAD was added. Diverse analyses were conducted to determine the changes in the characteristics of the upgraded coal. Based on the results of the low-rank coal upgrade experiments, although high calorific values could be obtained using only simple drying and kerosene treatment, the drawbacks of spontaneous combustion and moisture readsorption were not remedied. The results of the analysis demonstrated that the 0.5% PFAD upgraded coal had the highest quality. It showed few changes in its physical and chemical characteristics, had a small surface area, and high CPT values.

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