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Thermoplasticity and strength improvement of coking coal by addition of coal extracts

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HIGHLIGHTS

- A cost-effective thermal extraction was at an applicable temperature and pressure.
- It is workable and effective for industry application with creosote oil.
- Extracted from slight-caking coals instead of the more expensive high-caking coals.
- Thermoplasticity and strength of coals were improved by addition of coal extracts.

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ABSTRACT

Thermoplasticity and coke strength of individual coals and coal blends were improved by addition of coal extracts. Thus, this process caused the coals to bind better. Additionally, the strength of coke increased after the addition of 0–10 wt% of extracts from various caking coals. This result fully demonstrates that the extracts are a useful binder for coals.

1. Introduction

All coal extracts exhibit high thermal plasticity and can also be used as additives for coke production because coal extract can enhance the fluidity and extend the plastic range of other slightly caking coals, which usually exhibit low thermoplasticity at low temperatures [1,2]. The production of coal extracts from other low-quality coals, such as high-ash, high-sulfur, or high-nitrogen coals, may be important from the perspectives of cost-effectiveness and the variety of available coal resources [3,4]. Furthermore, because the high-caking coals are more expensive than the slight-caking coals, in this study, the thermal extraction of such inexpensive low-rank coals by using industrial solvents has been used to produce coal extracts to reduce the use of high-caking coals in coke production was investigated [5–7]. Those coal extracts could also have a variety of uses, including as additives to improve thermoplasticity and coke strength.

In previous work, extractions have been performed using a flowing-solvent extractor with an aprotic solvent (light cycle oil) and in relatively high-pressure systems [8–10]. Instead, in this study, the extraction was performed at an applicable temperature and under normal atmospheric pressure, and this method may be workable and effective for industrial applications. The creosote oil, distillate of coal tar, was used as the coal extraction solvent in this study. Furthermore, it contains numerous polar compounds with functional groups that are expected to provide a strong extractive effect [5].

Based on the chemical and physical tests performed during this investigation, a positive correlation was established between the caking coals, thermoplasticity and coke strength by addition of coal extracts. Research into how coal blends work after being merged with different types of coal extracts is useful for further improvement of thermoplasticity and coke strength.

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2. Experimental section

2.1. Coal samples

The coals are classified to different ranks according to their volatile materials and the content of carbon. There were four kinds of metallurgical coals directly extracted involving high volatile bituminous caking Coal-A, medium volatile bituminous caking Coal-B, low volatile bituminous caking Coal-C and a high volatile bituminous slightly-caking Coal-D all of which were supplied by CSC (China Steel Corporation). The coals were ground to a powdery particle size less than 100 mesh and dried under vacuum at 80 °C for 12 h [11]. A standard mixed coal composed of Coal-A (35 wt%), Coal-C (40 wt%) and Coal-D (25 wt%) was prepared for thermoplastic measurements and Roga test [15].

2.2. Solvent

The creosote oil supplied by CSC was industrial grade and was generally obtained from the fraction of the coal-tar distillation. It is a yellowish to greenish-brown oily liquid that contains primarily naphthalene (21.5 wt%), phenanthrene (13.0 wt%), acenaphthene (7.3 wt%), fluoranthene (6.1 wt%), pyrene (4.6 wt%), fluorene (4.3 wt%), and anthracene (3.6 wt%), and among other substances. The creosote oil was fractional distillated at the temperature of 360 °C, the boiling point of solvent under 360 °C was collected for further extraction experiment.

2.3. Thermal extraction of coals

A sample of 50 g of coal was loaded into a round-bottom flask that was fitted with a condenser and placed onto a heating mantle. Thermal extraction was performed by supplying fresh creosote oil under nitrogen atmosphere and extracting at temperatures of 360 °C [12,13]. An excess of *n*-hexane was added to the extract solution to precipitate the coal organic components [14], and the mixture was filtered and washed with dichloromethane. The solvent was subsequently recycled using the vacuum distillation method by transferring the rest of samples into a vacuum oven at 200 °C for 6 h until the pitch-like sample was dry; the sample was then scraped and gathered as a the solid glass-like sample for further tests. A procedure for extraction yield determination was indicated in Eq. (1), extraction yield (wt%, daf) [14]

$$\varepsilon = \frac{1 - \text{residue (g)}/\text{feed coal (g)}}{1 - \text{ash (wt\%, db)}/100} \times 100 \quad (1)$$

2.4. Thermogravimetric analyses

Thermogravimetric analyses of four raw coals and their extracts produced under various extraction conditions was performed using a thermogravimetric apparatus (TGA, TA Instruments Q500). A sample of 5 mg was placed on a platinum plate and was preserved in a nitrogen atmosphere. The measurements were executed over the temperatures range of 40–800 °C at a heating rate of 3 °C/min and under a nitrogen flow of 40 ml/min balance gas and 60 ml/min sample gas.

2.5. Thermoplasticity

Thermoplasticity measurements were performed using a viscoelastic machine (Plast &2000). Tin and lead were combined to form a stable heating bath. A coal sample woth a mass of 5.0 g was pressed by 10 kg of plummet to prepare a cylinder shape with a diameter of 18 mm and a height of 20 mm. The measurements were performed at temperatures from 300 to 550 °C at a heating rate of 3 °C/min and was recorded in dial divisions per minute (ddpm), which is the unit of Giesler fluidity.

2.6. Roga index – determination of caking power

The purpose of the Roga test [15], which provides one of the parameters adopted for the "International Classification of Hard Coal by Type" by the United Nations Economic Commission for Europe, is to assess the caking power of a coal under standard conditions. The detailed procedures for the Roga test are described below. The Roga index (R.I.) is given by Eq. (2).

$$\text{Roga index (R.I.)} = \frac{100}{3m_1}\left(\frac{m_2 + m_5}{2} + m_3 + m_4\right) \quad (2)$$

To a weighted clean, dry crucible, 1 g of the coal and 5.0 g of the standard anthracite were loaded and weighed to an accuracy of 0.01 g. Each sample was mixed for 2 min with stirring, the surface was leveled off and the steel cylinder weight was places on the sample. The cylinder was pressed for at least 30 s under a weight with a mass of 6 kg, and the crucible was subsequently removed from the press. The temperature of the furnace was increased to 850 °C at a heating rate of 30 °C/min, and the crucible was immediately inserted into the furnace. After the crucible was heated 7 min, the crucible was removed from the furnace. After being allowed to cool, the weight was removed from the crucible. Any particles of coke adhered to the weight were brushed back into the crucible, and the larger pieces of coke were also transferred back into the crucible. The remaining coke was carefully sieved, and the oversized portions were transferred back to the crucible. The contents of the crucible were subsequently transferred to the drum, which was fit with a cover. The drum was connected to the axle, and rotated for 5 min at a speed of 50 rpm. The coke was subsequently removed from the drum and sieved again. The coke that remained on the sieve was transferred back to the crucible and reweighed. The coke was then transferred from the crucible to the drum, and the abrasion procedure was repeated, with the sieving and reweighing of the oversized particles performed exactly as previously described. A third abrasion test was performed under the same conditions.

3. Results and discussion

3.1. Fundamental analysis of the coals and extracts

Four raw caking coals and their extracts were analyzed. As shown in Table 1, the atomic ratio of carbon hydrogen, C/H, directly depended on the pyrolysis temperature and the remaining materials in the columns but inversely depended on the volatile material contents. The thermogravimetric analysis results not only corroborate the data discussed in Table 1 but also reveal a correlation between the pyrolysis temperature and the final remaining materials of different caking coals, as shown in Fig. 1(a), the pyrolysis temperature is the samples begin to pyrolyze and the remaining materials were ash left after the thermogravimetric analysis, it was found that the higher the volatile materials, the lower the remaining materials of coals. Therefore, this information is useful in discriminating different sources of coals.

The elemental analysis results of the four extracts from different caking coals exhibited no significant differences. Fig. 1(b) illustrates the thermogravimetric characteristics of the four extracts and reveals that the amount of final remaining materials from Coal-C is relatively high compared with those of Coal-A and Coal-D. A comparison of the amount of materials that remains from ex-