Fuel 89 (2010) 1647–1653

Contents lists available at ScienceDirect

Fuel

journal homepage: www.elsevier.com/locate/fuel

Comparison of the associative structure of two different types of rich coals and their coking properties

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ARTICLE INFO

Article history:
Received 22 May 2009
Received in revised form 5 August 2009
Accepted 7 August 2009
Available online 26 August 2009

Keywords:
Rich coal
Solvent extraction
Hydro-thermal treatment
Coking property

ABSTRACT

Solvent extractions of two different types of Chinese rich coals i.e. Aiweiergou coal (AG) and Zaozhuang coal (ZZ) using the mixed solvent of carbon disulfide/*N*-methyl-2-pyrrolidinone (CS_2/NMP) with different mixing ratios were carried out and the caking indexes of the extracted residues were measured. It was found that the extracted residues from the two types of coals showed different changing tendencies of the caking indexes with the extraction yield. When the extraction yield attained about 50% for ZZ coal, the extracted residue had no caking property. However for AG coal, when the extraction yield reached the maximum of 63.5%, the corresponding extracted residue still had considerable caking property with the caking index of 25. This difference indicated the different associative structure of the two coals although they are of the same coalification. Hydro-thermal treatment of the two rich coals gave different extract fractionation distributions for the treated coals compared to those of raw coals respectively. The coking property evaluations of the two coals and their hydro-thermally treated ones were carried out in a crucible coking determination. The results showed that the hydro-thermal treatment could greatly improve the micro-strengths of the resulting coke from the two coals, and the improvement was more significant for the more aggregated AG coal. The reactivities of hydro-thermally treated AG coal blends were almost the same as those of raw coal blends. The higher coke reactivities of AG raw coal and its hydro-thermally treated ones than those of ZZ coal might be attributed to its special ash composition.

1. Introduction

With the rapid development of iron and steel industry, many new technologies to reduce greenhouse gas emission and improve energy intensity have been applied in blast furnace operation, such as carbon-lean fuel injection, lower-temperature operation, and operation in the absence of nitrogen [1]. As one and the only "high temperature filling" in cohesive zone of blast furnace, coke plays a very important role in the gas permeability and the drainage of molten metal and slag. As the coke usage rate decreases, the coke-to-ore volume ratio decreases, resulting in a lower thickness of the coke layer in the cohesive zone of the blast furnace [2]. Therefore, coke suffers a longer period of mechanical, thermal and chemical stresses, which leads to increased degradation and hence increased fines generation. Thus, there are increasing requirements for the quality of coke. The physical and chemical properties of coals used in the coking blends would determine the quality (reactivity and strength) of the finished cokes. When a coal is heated to 350–400° C, it begins to soften and form a coherent porous plastic mass, which can swell to fill into the gaps of the coal particles. On further heating and subsequent cooling, the mass contracts and quite large strong lumps of coke can remain [3]. The quality of the coke formed is dominated by the plastic mass. The hydrogen donor vehicles within the products of thermal decomposition of coals are important for the generation of the plastic state [4,5]. The formation of plastic masses depends on the release of some low melting-point species as hydrogen donors that are already present within the coal structure. These low melting-point species serve as the mobile hydrogen donors being able to stabilize the radical fragments split from the coal macrostructure, and to convert them into plastic species [6].

The amount and the compositions of the solvent soluble constituents in coal would affect the caking property of the coal. We have found that the amount of extractible constituents in the mixed solvent of carbon disulfide/*N*-methyl-2-pyrrolidinone (CS_2/NMP) has a great effect on the caking property of coal. With the increase of the extraction yield in the mixed solvent, the caking index of coal increased [7]. It is also known that chloroform soluble constituents of coal have a greater effect on the caking property of coal compared to pyridine soluble constituents. The soluble constituents of coal extracted by the CS_2/NMP mixed solvents with NMP less than 50% were found to be beneficial for improving the caking property of the coal [7]. There is a reasonable correlation between

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doi:10.1016/j.fuel.2009.08.011

the fluidity level of the plastic mass of coal and the amount of its solvent soluble constituents. The solvent soluble constituents also have a higher hydrogen donating ability. They can supply active hydrogen to stabilize the radical fragments formed in the plastic state thus to extend the plastic temperature range.

The hydro-thermal treatment is one of the most important pretreatments of coal. It can improve the solvent extraction and modify the caking properties of coal. Iino et al. [8] found that water treatments of three Argonne Premium coals at 600 K increased their extraction yields greatly. We have also found that hydro-thermal treatment at proper conditions could increase the extraction yields of bituminous coals, especially for coals of a higher rank [9]. The decreases of total oxygen and hydroxyl oxygen in the hydro-thermal treatment might be responsible for the enhancement of the solubility of the treated coals [9,10].

Rich coal is one of the most important coke-making coals to provide the main caking constituents in a coal blend. Its solvent extraction property has a great effect on the coke quality. It was found that one of Chinese rich coals produced more than 74% extraction yield in the CS_2/NMP mixed solvents (1:1 by volume) [9], and this was consistent with its higher caking index value. In this study, two different types of Chinese rich coals with different associative structure were hydro-thermally treated, and the relations between the solvent extraction yields for these two rich coals including their hydro-thermally treated residues and their caking properties were investigated. The caking mechanism during the coal carbonization was discussed by crucible coking experiments of the two coals and their hydro-thermally treated ones.

2. Experimental

2.1. Coal sample

Two Chinese rich coals as the coke-making coals, i.e. Aiweiergou coal (AG) and Zaozhuang coal (ZZ), were used in this study. The properties of the two coals are shown in Table 1. The coal samples were ground and sieved to particles of a size less than 100 μm, stored under a nitrogen atmosphere and dried for 12 h under vacuum at 80 °C before use.

2.2. Coal extraction and fractionation

Coal extraction with the mixed solvent of CS_2/NMP was carried out at room temperature, as described in details elsewhere [11]. Coal (1.5 g) and about 40 ml CS_2/NMP mixed solvent were charged into a centrifuge tube shaken for 30 min under ultrasonic (38 Hz) irradiation at room temperature. The mixture was filtered after centrifugation for 50 min at 14,000 rpm. The residue was thoroughly extracted with the fresh mixed solvent repeatedly for about 6 times in the same way until the filtrate became colorless. The residue was washed with acetone three times, and dried for 12 h under vacuum at 80 °C. The extraction yield was then determined from the weight of the residue:

$$\text{Extractionyield} = \frac{1 - M_r/M_{\text{coal}}}{(100 - A_d)/100} \times 100\%$$

where, M_r is the weight of dried residue (g), M_{coal} is the weight of dried coal (g), and A_d is the ash content of coal (db, %).

The extract was fractionated with pyridine to produce pyridine insolubles (PI) and pyridine solubles (PS). PS was subsequent fractionated with acetone into acetone insolubles (AI) and solubles (AS).

2.3. Hydro-thermal treatment

The hydro-thermal treatment of coal was performed using 0.25 L autoclave. In each run, 20 g of dried coal sample and 40 g of water were loaded into the autoclave, purged with nitrogen gas for three times to displace the residual air in the reactor, and finally the autoclave reactor was pressurized with nitrogen to 0.1 MPa at room temperature. The autoclave was then heated to the desired temperature with stirring. This temperature was maintained for 1 h under autogenous pressure. The autoclave was then allowed to cool down to room temperature in 2–3 h. Before opening the autoclave, the accumulated gas was carefully released into a fume hood and the reactor was equilibrated with atmosphere. The treated coal was filtered to remove excess water, and then dried under vacuum at 80 °C for 12 h.

2.4. Caking index measurement

The caking index (G) was used to characterize the caking property of coal. The measurement was carried out according to GB5447-85 (national standard of China). The measurement method of G index is based on Roga index, which is known worldwide. Briefly, 1 g of coal was mixed with 5 g of standard anthracite (Ruqigou). The mixture was carbonized in an inert atmosphere at 850 °C for 15 min. The coke obtained was subject to the drum tests for twice, which is slightly different from the Roga index testing requiring drum tests for three times. The coal sample preparation, stirring, carbonization and drum test are all the same as those of the Roga index measurement, and the caking index G was calculated as:

$$G = 10 + \frac{30m_1 + 70m_2}{m}$$

where m is the weight of coal sample (g), m_1 is the weight (g) of the coke fraction (>1 mm) after the coke abrasion test (the first drum test), and m_2 is the weight (g) of the coke fraction (>1 mm) after the second drum test.

2.5. Crucible coking determination

The carbonization experiments were carried out in an electrically-heated oven using a 300 ml crucible. 300 g coal blends (gas coal 35 wt.%, coking coal 35 wt.%, lean coal 10 wt.% and rich coal 20 wt.%) with a particle size less than 1.25 mm were loaded into the crucible. An iron cake of 500 g was put on the coal sample to maintain the bulk density of coal feed. The filled crucible with a cover was placed in the oven in an inert atmosphere and heated at the rate of 5–7 °C/min to 400 °C, at 3 °C/min to 950 °C, and held

Table 1
Ultimate and proximate analyses of coals.

Coal	Ultimate analysis (%, daf)					Proximate analysis (%)			G
	C	H	N	S	O*	Moisture (air dried)	Ash (dry)	VM (daf)	
AG coal	87.97	5.17	1.54	0.52	4.80	10.6	9.1	29.2	102
ZZ coal	86.12	5.26	1.52	1.88	5.22	11.4	10.0	31.5	92

* By difference.