Mining Science and Technology (China) 21 (2011) 401–405

Contents lists available at ScienceDirect

Mining Science and Technology (China)

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

Upgrading of Yi'an gas coal by low temperature pyrolysis under different atmospheres

Wei Xiaomei [a], Zhou Min [a,*], Zhang Chun [b], Lei Jiali [a], Song Liqiang [a]

[a] Key Laboratory of Coal Processing & Efficient Utilization, School of Chemical Engineering & Technology, China University of Mining & Technology, Xuzhou 221008, China
[b] Institute of Process Engineering, Chinese Academy of Sciences, Beijing 100190, China

ARTICLE INFO

Article history:
Received 15 October 2010
Received in revised form 13 November 2010
Accepted 10 December 2010
Available online 12 June 2011

Keywords:
Yi'an gas coal
Atmosphere
Upgrading
Coke quality

ABSTRACT

The quality of Yi'an gas coal before and after low temperature upgrading under either a N_2 or H_2 atmosphere was examined by thermogravimetric and infrared analyses. The effect of upgrading on the prepared coke quality was analyzed. The results show that the carboxyl and phenolic hydroxyls in the coal molecular structure are removed after upgrading by low temperature pyrolysis under either N_2 or H_2 atmospheres. This improves coal caking properties to a certain extent. The upgrading effect under a H_2 atmosphere is remarkably better than the effect observed after upgrading under N_2. Compared to coke obtained from raw coal, the compressive- and micro-strength of the cokes obtained from upgraded coal are greatly improved. The effect on coke reactivity with CO_2 is not significant. The best upgrading temperature for Yi'an gas coal under either a N_2 or H_2 atmosphere is 250 or 275 °C respectively.

1. Introduction

The modification and upgrading of coal by low temperature pyrolysis is of great practical importance because it creates new opportunities for enlarging coal resources usable for coking. The technology functions by controlling the carbonization process to obtain coke having desirable properties. During the modification and upgrading process most oxygen-containing groups of the coal are removed, which improves the coking and caking property [1–3]. The authors have studied the modification of thermoplastic properties of coals, and the coke quality obtained, by pyrolysis in an inert atmosphere [4–7].

Blending some gas coals for a conventional coking oven is restricted by the high volatiles and weak caking properties of these coals. In this paper we discuss the coal quality of Yi'an gas coals before and after upgrading under N_2 or H_2 atmospheres. Thermogravimetric and infrared analyses are used to analyze the coals. The effect on the individual indexes of coke quality after the upgrading is examined by a carbonization test.

2. Experimental

2.1. Coal samples

Yi'an Gas Coal from the Huanyu Coking Plant, Co., Ltd., located in Xuzhou, and anthracite from Taixi in Ningxia were used for this study. The anthracite was used as an inert component to estimate the coke quality by the carbonization test. All these samples were air-dried prior to use: their properties are listed in Table 1.

2.2. Coal upgrading at different temperatures

Yi'an gas coal was pyrolyzed at different temperatures, all lower than the softening temperature. The chosen upgrading temperatures are listed in Table 2. In this test the electric tube furnace was heated to the assigned temperature and then N_2, or H_2, were passed into the tube at a rate of 0.5 L/min. After that a 25 g sample in a steel vessel was quickly pushed into the constant temperature zone of the tube and a rubber stopper was tightly screwed onto the tube portal. The coal samples were cooled to room temperature, under an inert atmosphere, after being pyrolyzed for a fixed time. They were then crushed mechanically to –0.2 mm and the remains were devoted to the carbonization test. Table 2 also lists the corresponding coke names for the samples obtained from upgrading samples by carbonization.

The upgrading time was determined by the change in oxygen containing functional groups. Samples were pyrolyzed for different times at a heat treatment temperature of 250 °C. Chemical methods were used to measure the oxygen containing functional groups [8]. The total acidic and carboxylic content was, respectively, measured by the exchange method using barium ion and calcium acetate. The difference between these was taken as the content of phenolic hydroxyl. Fig. 1 shows the results.

As shown in Fig. 1 the carboxylic oxygen and phenolic hydroxylic oxygen contents both decreased rapidly under either a

* Corresponding author. Tel.: +86 13852138866.
E-mail address: zm@cumt.edu.cn (M. Zhou).

1674-5264/$ - see front matter © 2011 Published by Elsevier B.V. on behalf of China University of Mining & Technology.
doi:10.1016/j.mstc.2011.05.027

Table 1
Proximate and ultimate analyses of the coals (%).

Sample	Proximate analysis				Ultimate analysis				
	M_{ad}	A_d	V_{daf}	FC_{daf}	C_{daf}	H_{daf}	O_{daf}	N_{daf}	$S_{t,daf}$
Yi'an gas coal	1.49	6.68	37.31	62.69	84.19	5.59	8.26	1.31	0.65
Taixi anthracite	1.28	1.69	7.25	92.75	94.11	3.99	1.16	0.68	0.06

Table 2
Upgrading temperatures and corresponding coke names.

Name	Upgrading temperature (°C)							
	Raw coal	200	225	250	275	300	325	350
Coal sample	YQ	YQ-200	YQ-225	YQ-250	YQ-275	YQ-300	YQ-325	YQ-350
Coke	JK	JK-200	JK-225	JK-250	JK-275	JK-300	JK-325	JK-350

nitrogen or hydrogen atmosphere. After 20 min the loss in oxygen became relatively slower so the upgrading time chosen for the following work was 20 min.

2.3. Thermogravimetric analysis

Thermogravimetric analysis was carried out using a STA409C thermogravimetric analyzer. Samples weighing 10 ± 0.1 mg were heated to 900 °C at a 3 °C/min rate under a nitrogen flow of 100 mL/min.

2.4. FTIR spectroscopy

All Fourier Transform Infrared (FTIR) experiments were conducted using a Nicolet 380 spectrometer. The dried samples were milled with potassium bromide in the proportion of 1:200 (by weight) to enable quantitative analyses. Each sample was scanned 32 times and the scans averaged to give the final spectrum.

2.5. Carbonization tests

The 50 g co-carbonization tests of Yi'an gas coal and Taixi anthracite were carried out in an electric resistance furnace. Because of the high volatility of the Yi'an coal samples, the anthracite was used to provide an inert component during carbonization. This caused the fluidity and swelling of the resulting plastic mass to decrease. Samples before and after upgrading were mixed uniformly with the anthracite in the proportion of 1:1 and then charged to a steel cup (height 70 mm and Φ57 × 4 mm) and carbonized by heating at 3 °C/min from 200 °C up to 900 °C. Several 5 mm diameter holes were punched in the bottom of the cup so that gas released during carbonization could pass freely from the sample. The cokes obtained were allowed to cool naturally and stored for further use.

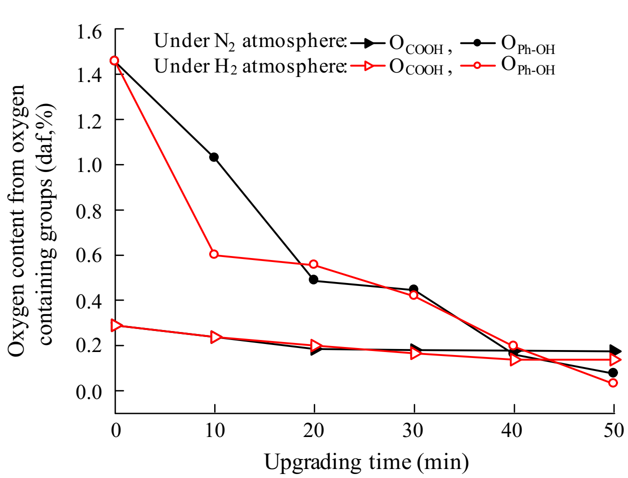

Fig. 1. Effect of upgrading time on O_{COOH} and O_{Ph-OH} of coals.

2.6. Compressive- and micro-strength measurements of the coke

The cokes were analyzed with a TYE-20 compression testing machine to determine the compressive strength index. Then the cokes were broken and 5 g of coke 3–6 mm in size were put into a steel vessel (diameter 64 mm and height 69 mm) with five steel balls (diameter 28 mm). The weight percentage of particles greater than 0.2 mm, compared to the total mass, after 800 rotations in the drum over 3 min was taken as the micro strength index, $MSI^{0.2}$. The data reported are the average of two identical tests.

2.7. Coke reactivity measurements

The cokes were obtained from the carbonization tests. About 20 g of a 3–6 mm particle size coke were placed in a reaction tube and heated from room temperature to 800 °C at a rate of 20–25 °C/min and then kept at 800 °C for 5 min. Then carbon dioxide gas was introduced into the reaction tube for 2.5 min at a flow rate of 500 mL/min. Then the effluent gas was collected with a gas analyzer at 1 min intervals and the CO_2 flow was stopped. This process was repeated at increasingly higher temperatures every 50 °C until the temperature of 1100 °C was reached. The data obtained were the average value of two duplicate tests.

3. Results and discussion

3.1. Coal quality before and after upgrading

The changes in coal quality after upgrading under a N_2 or H_2 atmosphere are shown in Tables 3 and 4. As the upgrading temperature increases, the carbon content rises and the content of hydrogen, nitrogen, and sulfur changes irregularly. In addition, the oxygen content gradually drops, which agreed with changes in the oxygen/carbon ratio that revealed the distribution and variation of oxygen. This proved that the objective of de-oxidation upgrading was realized. The volatiles in the upgraded coal also decrease.

The caking index, G, increases after treatment under a N_2 atmosphere when the upgrading temperature was lower than 275 °C.