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Investigation on pyrolysis characteristic of natural coke using thermogravimetric and Fourier-transform infrared method

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Abstract

Natural coke is a kind of fossil fuel with calorific value of 18–28 MJ kg^{-1}. There are abundant natural coke reserves in the world, but at present it is abandoned and needs research and development for its utilization. The morphology comparison between the natural coke from Peicheng Mine, Xuzhou, Jiangsu, China and the bituminous coal from Hanqiao Mine, Xuzhou, Jiangsu, China was made with scanning electron microscopy (SEM). Thermogravimetric analysis (TG) and Fourier-transform ifrared (FT-IR) coupled technology was used to investigate pyrolysis characteristics of the natural coke and the bituminous coal. The pyrolysis products were analyzed with the VECTOR 22 infrared analyzer. The effects of the heating rate, the final pyrolysis temperature, the particle diameter, and the operating pressure on the pyrolysis process of natural coke were examined with the Thermax500 pressurized thermogravimetry. The pyrolysis process of the natural coke can be divided into two different degasification stages, different from that of coal, which includes three stages—drying, semi-char forming and degasification. The results show that TG curve shifts to the higher temperature region as the heating rate increases. The heating rate has almost no effect on the ultimate volatile release. The final pyrolysis temperature has a strong impact on the ultimate volatile release. The higher the final pyrolysis temperature is, the more the ultimate volatile yield is. SEM pictures show that the natural coke at higher temperature has better porous structure, which is beneficial to volatilization, and a better reduction activity. Decrease in the particle size leads to more volatile release. The pressure has less effect on pyrolysis under lower temperature, while the effect becomes stronger when the temperature is higher than a given point.

Keywords: Natural coke; Pyrolysis; Thermogravimetry; Infrared; SEM

1. Introduction

Natural coke is a by-product during the process of coal mining and is also a kind of high metamorphic grade coal. It is a solid combustible fossil fuel and formed from coal by a relatively local elevated heat flow caused by an intrusive igneous rock [1]. The volatile matter is released in short periods when the magma intrudes into coal. Natural coke has pores which are empty or filled with mineral matter. The textural features, such as the size, shape, distribution and orientation of pores are variable. The immediate contact between the igneous intrusive body and the coal may be sharp and planar or it may be diffuse and irregular. It becomes porous and penetrable and it is suitable for gasification. Calorific value of natural coke is about 18–28 MJ kg^{-1}. There are abundant natural coke reserves in the world. For example, it is estimated that there are 6.73 hundred million tonnes natural coke in Huaibei coalfield, 7.3 hundred million tonnes natural coke in Fengcheng, Peicheng, and Tongchuan, Jiangsu Province, 4.1 hundred million tonnes in Zaozhuang and Tengzhou, Shandong Province, 1 hundred million tonnes in Fuxin, Liaoning Province.

Kwiecinska et al. studied the formation temperature of natural coke by SEM-EDX [2]. Sanyal investigated the reason of forming natural coke from coal from the point of geognosy [3]. Khorasani et al. analyzed the molecular structure of natural coke [4]. However, investigations about natural coke are still few in present, which results in the quite limited utilization of natural coke. In most cases, natural coke was discarded in nature or was not exploited in the mine. Natural coke was embedding in the ground with the mine discarded. This is harmful to environment, and is tremendous waste as well.

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Nomenclature

R_m	the maximal weight loss (% °C^{-1})
t	pyrolysis time (min)
T	pyrolysis temperature (°C)
T_b	starting reaction temperature (°C)
T_f	terminal reaction temperature (°C)
T_m	temperature when the maximal weight loss (°C)
w	weight percentage composition of sample at either time (%)
w_f	terminal quantity of weight loss (%)

Natural coke may be used as the gasification fuel for power generation system. It is suitable for the utilization of natural coke resource and lightening the crisis of energy sources. It is also environmental friendly. Coal gasification is the key technology for the integrated gasification chemical-looping combustion (CLC) combined cycle system, Coal fired CLC system may be used to generate electricity with CO_2 separation and it can be zero emission [5–7]. In this paper, the natural coke is selected as the gasification fuel. Natural coke gasification has two stages, i.e., pyrolysis and gasification. The pyrolysis process affects the gasification process. The natural coke pyrolysis was studied on thermogravimetric analyzer, and at the same time, the volatile release was analyzed on-line with Fourier-transform Infrared system, and the results were compared with those of the coal pyrolysis [8–10]. In order to better understand the pyrolysis process of the natural coke, in this paper, pyrolysis experiments were carried out at the condition of slow heating. The effects of the heating rate, the final pyrolysis temperature, the particle diameter, and the operation pressure on the pyrolysis process of Peicheng natural coke were examined with the Thermax500 pressurized thermogravimetric analyzer. The work aims to find the characteristics of natural coke pyrolysis process and to obtain operative parameters on TG.

2. Experimental

2.1. Experimental samples and conditions

Natural coke from Peicheng Mine (Jiangsu, China) and bituminous coal from Hanqiao Mine (Jiangsu, China) were used as samples in the study. The proximate and ultimate analysis data of the samples are shown in Table 1. It shows that the natural coke has lower ash content, lower sulfur content, lower volatile matter content and higher calorific value.

Basic experimental conditions are as follows:

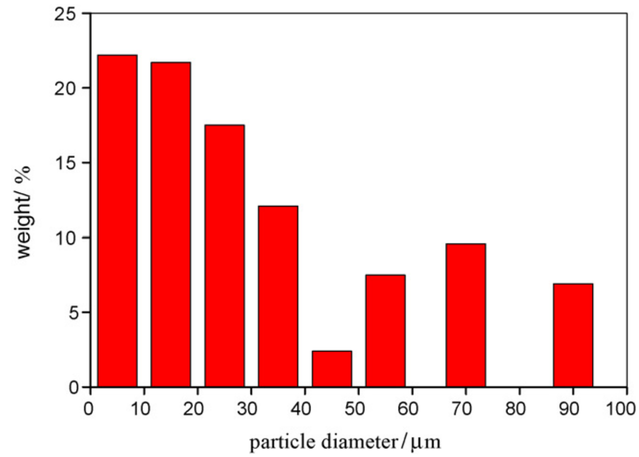

Fig. 1. Sample particle size distribution of natural coke.

- 0.1 MPa,
- nitrogen flow rate of 200 ml min^{-1},
- heating rate of 20 °C min^{-1},
- final temperature of 1000 °C.

In the tests for investigating the influence of the heating rate and the pressure on pyrolysis characteristic of natural coke, the heating rate was 5, 10, 20, 25 °C min^{-1}, and the pressure was 0.1, 0.2, 0.5, 1, 2 MPa, respectively.

The samples were comminuted using KER-1/100A pulverizer. As to the influence of particle diameter on the pyrolysis process of Peicheng natural coke, the samples were divided into three groups according to its diameter distribution: <44, 44–75, 75–125 μm. In the other experiments, the particle diameter of samples is less than 100 μm with the average particle diameter of 31 μm. Fig. 1 gives the particle size distribution of the coke samples. It can be seen that more than 70% of the particles are below 40 μm. Coal is changed into natural coke under high temperature and pressure. Although natural coke is usually dull, compact and hard, it is porous and hydrated. Each experiment sample is weighted about 100 mg.

2.2. Experimental apparatus

Cahn's Thermax500 pressurized thermogravimetric analyzer was used to perform the pressurized-pyrolysis experiments. The pyrolysis conditions are as follows:

- system atmosphere: N_2 (>99.999%);
- flow rate of carrier gas: 200 ml min^{-1};
- sample weight: 100 mg.

Table 1
The proximate and ultimate analyses of Peicheng natural coke and Hanqiao coal

Sample	Proximate analysis (%) (mass, air dry)				Ultimate analysis (%) (mass, daf)					$Q_{net,ad}$ (MJ kg^{-1})
	M	A	V	FC	C	H	O	N	S	
Natural coke	0.81	16.15	9.05	73.99	93.12	1.99	3.21	1.10	0.58	26.59
Coal	1.77	23.52	28.73	45.98	80.47	5.10	12.19	1.46	0.78	23.08