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Low temperature pyrolysis properties and kinetics of non-coking coal in Chinese western coals

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A B S T R A C T

Chinese western low-rank coals known as for its favorable characteristics play a key role in the production of coal oil. In this work, based on the changes in element occurrence during low-temperature pyrolysis of coal, the kinetic and thermodynamic characteristics of coal at 400–500 °C temperatures with 10 °C/min heat rate were studied, which resulted in the drastically cracking of aliphatic groups. However, a significant amount of oxygen-containing functional groups were also found during coal pyrolysis at low temperature followed pseudo-first-order kinetics. According to the low-temperature thermal kinetics analysis of different coals, the activation energy of coking coal is higher than that of non-coking coals, and the activation of non-coking coals is relatively low under the same pyrolysis conditions. The objective of this work is to provide theoretical data about the pyrolysis characteristics of non-coking coal at low temperature and increase the non-coking coal proportion in coking proceeding.

1. Introduction

Coal as the primary energy resource of China will dominate energy structure pattern in a period of time, furthermore, coal is the most important pillar industry in the China's region, and study of the cleaning utilization of coal in China's western region is significant and realistic to rapidly develop western provinces. Currently, the coking coal is obviously dwindling, and the situation is serious, so it is important to explore new resources for coking. Moreover, non-coking coal reserves are abundant in our country in some areas, for example Shanxi, Inner Mongolia, Xinjiang, Ningxia, Gansu and other provinces [1,2]. The non-coking coal resources in Inner Mongolia are abundant, and how to make full utilization of non-coking coal resources is significant and realistic. Some researches have shown that using a 3% non-coking coal instead of 1/3 coking coal for blending coking, the coke quality had no significant decrease, but more than 5% mixing ratios of non-coking coal, the wear resistance strength of coke decreased, and the thermal cracking phenomenon was obviously with the caking property decreasing [3,4]. Therefore, based on non-coking coal used in coking, in order to improve a greater proportion of non-coking coal in coking processing, the studies of pyrolysis properties are necessary since it can provide new insights into the evolution of non-coking coal composition and physicochemical structure. In last few decades, many papers have been published on structural characterization of coals and studies have been conducted on the macromolecular structures of coals, as the knowledge of these structures will directly affect the understanding of their reactivity in liquefaction reactions [5,6].

As pyrolysis is the initial phase in the most coal conversion processes, many works have focused on the development of a general description of coal thermal decomposition [7,8]. There are many factors important for pyrolysis process such as pyrolysis temperature, pressure, atmosphere, heating rate, petrographical composition, mineral content, catalyst and so on [9–17]. However, it is still necessary to investigate pyrolysis process because of coal structure heterogeneity and complexity.

Based on the requirement of coal pretreatment cost, a low temperature heat treatment technology in a Thermo-Gravimetric (TG) system and a fixed-bed reactor was used to research the low temperature pyrolysis characteristics and kinetics mechanism of no-coking coal in

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China's region. The objective of this work is to provide theoretical data which can better understand the pyrolysis characteristics of non-coking coal at low temperature to increase the non-coking coal proportion in coking proceeding.

2. Experiment

2.1. Materials

A low rank coal (non-coking coal) and a coking coal (ShanDong coal) were used in this study. The non-coking coal collected from ShenMu, DongSheng, and FuGu in Chinese west areas. The ShanDong coal is a kind of coking coal used to compare with non-coking coal in the present study. The coal samples with layers of wrapping plastic bags were saved in water, in order to avoid the impact of natural oxidation in the experiments. Experimental samples also included vitrinite and inertinite enrichment after the phase separation of the coals. The topic properties of the basic properties of coals were shown in Table 1.

G value is an index for evaluating coal plasticity, and according to G values, the main uses of the coal can be preliminary determined. According to Table 1, the V_{daf} and G values of ShenMu coal are 36% and 0 respectively which show that it is non-coking coal, while the V_{daf} and G values of DongSheng coal are 44% and 0 which shows that it is lignite.

2.2. Experimental methods

The experimental methods in this chapter mainly include the analysis of the basic characteristics of macerals, vitrinite reflectance, and oxygen functional groups of raw coal samples for chemical analysis and all the main experiment apparatus and equipments were shown in Table 2. The proximate and ultimate analyses of the coal sample were according to the national standard GB212-2008. Determination of caking index G value was conducted in accordance with the national standard of GB/T5447-1997. The characterization is that the quantity test sample and anthracite are mixed and fastly heated to form coke, and the strength of coke is used to measure bonding ability of coal sample. G is calculated using the following equation:

$$G = 10 + [(30m_1 + 10m_2)/m]$$

where G is caking index, m is all coke slag amount after coking treatment, m_1 is the screen residue quality after first drum test, m_2 is the screen residue quality after second drum test.

Oxygen functional groups can be defined as total acid, carboxyl and hydroxyl content which was determinated by chemical analysis. Fourier transform infrared (Nicolet 6700, USA) with the resolution of 4 cm^{-1} was used for the functional group analysis and the sample is conducted by the KBr pellet method in a spectra selected range of 4500–200 cm^{-1}. Vitrinite reflectance and its reflectance distribution is measured by using Germany Leica binocular partial reflective microscope and the HD type full automatic micro photometer developed by Hainan University for experiments. Acordance to the requirements of GB/T6948-2008 in the determination of coal vitrinite random reflectance under non-polarized light, the HD software will automatically measure in terms of the average maximum random reflectance of vitrinite reflectance. Determination of coal macera is in accordance with GB/T8899-1998. Barium hydroxide method is used to determine the contents of total acid base in coal, the total acidic group reacts with an excess of $BA(OH)_2$, and then the standard concentrations HCl is carried out to react with excess $Ba(OH)_2$, finally, the standard concentration NaOH is used to drop in. Reaction equation as follows:

$$Ba(OH)_2 + 2HA \rightarrow BaA_2 + 2H_2O$$

The combustion runs dynamics were carried out in a thermo gravimetric analyzer (STA449F3, German NETZSCH Company) at three different heating rates (10 °C min^{-1}, 20 °C min^{-1} and 30 °C min^{-1}), and the samples weigh about 15 mg at a high purity nitrogen flow rate of 100 mL/min. The chamber was again first purged with high-purity nitrogen at 100 mL min^{-1} for 30 min. Then, the sample was heated from 25 °C to 400 °C, 420 °C, 450 °C, 500 °C respectively, holding for 10 min at a heating rate of 10 K min^{-1}.

3. Results and discussion

3.1. The property of micro-components

Table 3 shows the industrial analysis and petrographic analysis of coal samples.

The air dry basis moisture content of vitrinite and inertinite of the samples is lower than raw coal, but the ash content of inertinite is generally quite higher than raw coal. The reasons maybe that the ash of the raw coal transfer to inertinite increasing the ash content and the net ash content of inertinite was higher than the ash content of vitrinite. The dry ash-free basis volatile of vitrinite from three coals was

Table 1
The basic properties of coal samples.

Coals	Proximate analysis/%			Elemental analysis/%				Reflectivity/%	G
	M_{ad}	A_d	V_{daf}	FC_{daf}	H_{daf}	N_{daf}	$S_{t,d}$	R/%	
ShenMu	10.23	6.04	35.99	74.33	4.833	1.112	0.489	0.487	0.03
FuGu	11.44	5.09	37.96	75.59	5.113	1.343	0.408	0.492	0
DongSheng	22.03	7.45	43.85	64.77	4.694	1.240	0.455	0.287	0
ShanDong	2.81	8.87	40.59	75.96	5.228	1.409	0.946	0.749	79.86

Notes: M, moisture; A, ash; V, volatile matter; FC, fixed carbon; ad, air dry basis; d, dry basis; daf, dry ash free basis.