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Low temperature pyrolysates distribution and kinetics of Zhaotong lignite

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ABSTRACT

This paper aims to determine the distribution of all species produced from Zhaotong lignite under low temperature pyrolysis and to derive an appropriate kinetic model. A fixed bed reactor system with no carrier gas is used. For the products (tar, gas and semi-char) distribution determination, experiments are carried out over different operating factors. The characteristics of pyrolysates are analyzed with Gas Chromatograph (GC), Gas Chromatograph/Mass Selective Detector system (GC/MSD), Fourier transform infrared spectroscopy (FTIR), nitrogen adsorption–desorption isotherm analysis and Scanning Electron Microscope (SEM). The kinetic model of Coats–Redfern is used, as a basis, to predict the experimental evolution curves. It is seen here that temperature, heating rate and particle size play a pivotal role in low temperature pyrolysates distribution. Meanwhile, it is suggested that atomic ratios of H/C and O/C have some correlativity with the yield of products. The prediction of Costs–Redfern integral model is discussed with the experimental fractions, which indicates that the model is suitable to explain the reaction mechanism of lignite during low temperature pyrolysis.

1. Introduction

Lignite reserve in the world reaches 4000 billion tons, accounting for 40–50% of global coal reserves. In China, there are 130 billion tons of proven lignite reserves. About 12.6% of these proved lignite reserves are contributed by Zhaotong (ZT), Yunnan Province [1]. ZT lignite was formed in late Neogene period. Dominated by young lignite, ZT lignite is characteristic of low degree of coalification, high chemical activity, developed pores, and high oxygen ($O_{daf} \approx 20\%$) and water (30–50%) contents. However, Because of its low calories and poor thermo-stability, it is not appropriate for long distance transport. Currently, it is only used as power fuel in local regions rather than in/as gasification materials widely. Moreover, export sales directly are a large proportion for ZT lignite. Only few (<30%) are processed locally into products with high char and value added, coal gasification products and liquidation products [2]. Therefore, adopting reasonable measures to make full use of the rich lignite resources in Yunnan Province has become one of the urgent problems for local researchers of China [3].

Recently, high-efficient utilization of lignite is attracting more and more attention from both China and foreign energy industries [4–8]. Low-temperature pyrolysis is a good choice. Compared to coal gasification and liquidation, it is superior for simple processing, mild processing conditions, low production cost and comprehensive utilization of products. However, low-temperature pyrolysis of lignite is susceptible to both coal properties and external pyrolysis conditions (e.g. heating rate, final pyrolysis temperature, particle size, and carrier gas) [9]. Studying the effect of pyrolysis conditions on yield, composition and properties of pyrolysates, analysis on pyrolysis process and mechanism of lignite could be helpful to deepen understanding on mechanism of low-temperature lignite pyrolysis. These researches have some theoretical and technical significance in guiding green high-efficient comprehensive utilization of lignite [10]. Existing researches on upgrading lignite utilization mainly focus on reactor, technological process, heating method, dry upgrading and dynamics. There are still few researches on low-temperature lignite pyrolysis and pyrolysis mechanism [11–15] and thus, generation features of products as well as morphology and characteristic changes of coal and semi-char during pyrolysis are still unclear, especially when the low-temperature pyrolysis process is processing without any additional carrier gas and pressure. Therefore, the key factor controlling product quality during lignite upgrading process is to systematically understand the generation features of low-temperature pyrolysis products of lignite (e.g. tar, pyrolysis gas and semi-char), which is proceeded in a reactor system with no carrier gas.

In this paper, effect of heating rate, final pyrolysis temperature and coal particle size on low-temperature pyrolysis characteristics of lignite were studied systematically in an independently

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developed pyrolysis oven without any carrier gas. Meanwhile, generation features of low-temperature pyrolysis products (tar, pyrolysis gas and semi-char) were analyzed through TG, GC, GC/MS, BET, SEM, FTIR and chemical means. Morphology and functional structure changes of semi-char were investigated. Mechanism function and kinetic parameters of lignite during low temperature pyrolysis were established. All of these were attempted to reveal the nature of low-temperature pyrolysis of ZT lignite.

2. Experiment

2.1. Materials

2.1.1. Geological setting

The Tertiary Zhaotong Coalfield, 20 km long and 15 km wide, with a total area of 230 km^2 and coal province area of 140 km^2 (Fig. 1), is located in a basin along NE–SW trend in northeastern Yunnan province, China [16].

The Neogene Miocene Series, Pleistocene Series and Holocene Series, widely developed in the basin, overlapped angular unconformity on the Devonian, Carboniferous, Permian, Triassic, Jurassic and Cretaceous. The coal-bearing stratum in Yunnan Luliang Basin is neogene Pliocene Ciying Formation of Neocene. The Basin has three workable seams with the total mining thickness of 80–130 m, 80 billion tons of coal reserve, which make its unique position of Neogene Coal-rich Basins in Yunnan Province [17].

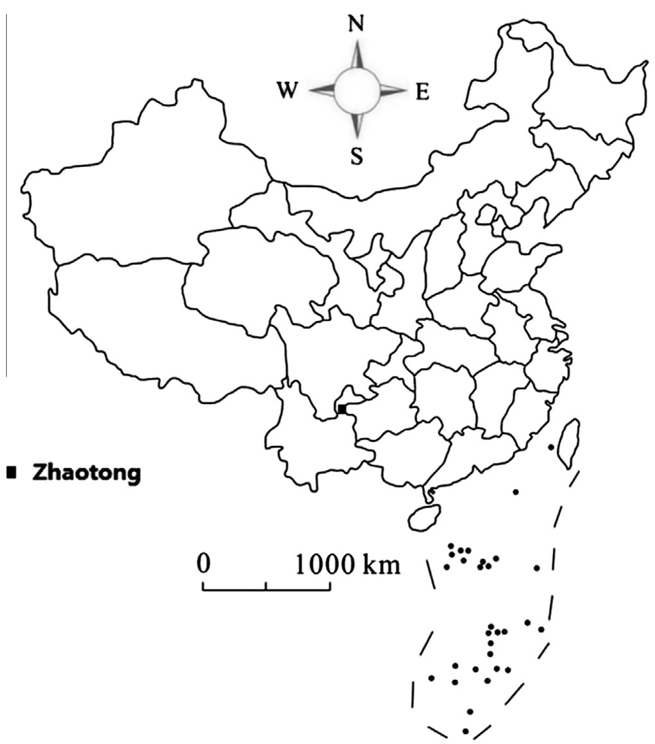

Fig. 1. Location of Zhaotong Coalfield in Yunnan Province, South-northern China.

2.1.2. Coal characteristics

The investigations were performed on lignite sample taken from Zhaotong deposit in Yunnan province, China. Table 1 shows the proximate and ultimate analyses of Zhaotong lignite (ZT). All the information reported in the table was provided by the State Key Laboratory of Coal Conversion, Shanxi Institute of Coal Chemistry, The Chinese Academy of Sciences.

2.2. Experimental procedure

The experimental device for low-temperature pyrolysis of ZT lignite is a self-researched fixed bed reactor as shown in Fig. 2. It is composed of pyrolysis system, control system and detection system. The pyrolysis system mainly consists of the low-temperature pyrolysis reactor of lignite. The control system mainly includes temperature controller and relief damper. The detection system mainly includes Gas Chromatography (GC).

About 20 g ZT lignite particles of certain size was putted into the quartz pyrolysis reactor (inner diameter = 21 mm). Before the pyrolysis beginning, air in reactor was blow out with helium (He) until its content reaches 99.9% at the outlet of the system and then He was shut off. Temperature-programmed pyrolysis experiments were typically performed at a heating rate of 10 °C/min from room temperature to 600 °C and kept for 30 min.

2.3. Analytical instruments

Composition of pyrolysis gas was analyzed using GC-950 and GC 9890A. The GC-950 had two TCDs and two channels. Its parameters are: sample injector temperature: 50 °C; carrier gas: H_2; flow rate of carrier gas: 40 ml/min; column temperature: 40 °C. O_2, N_2, CH_4 and CO in pyrolysis gas was tested by 5A molecular sieve column, while CO_2, C_2H_4 and C_2H_6 in pyrolysis gas were tested by GDDX-502 column. Parameters of GC 9890A include: sample injector temperature: 80 °C; carrier gas: N_2; flow rate of carrier gas: 40 ml/min; column temperature: 80 °C. H_2 in pyrolysis gas was tested by 5A molecular sieve column.

Composition of generated tar was analyzed by Agilient 6890/5973 GC/MS (America). Chromatographic conditions are: HP-5MS capillary column: 30 m × 0.25 mm × 0.25 μm; carrier gas: high-purity He; flow rate of carrier gas: 0.6 mL/min; sample injector temperature: 320 °C; injection volume: 0.1 μL; split ratio: 120:1; temperature programming: 50 °C (6 min); starting temperature: 50 °C; final temperature: 260 °C; heating rate: 5 °C min^{-1}; heating time: 40 min. MS conditions include: electron impact source (EI source); electron energy: 70 eV; filament current: 25 μA; scanning range: 50–1000 μm; ion source: 250 °C; mass scanning range: 30–500 amu.

Surface functional groups of samples were detected by Nicolet 6700 Fourier transform infrared spectrometer (American). The scanning range varies from 400 to 4000 cm^{-1} and the scanning rate is 10 kHz. The resolution is 4 cm^{-1}.

Surface morphology of samples was observed by JSM-6700F field emission scanning electron microscope. The acceleration voltage is 0.5–30 kV and resolution is 1.0 nm (15 kV)/2.2 nm (1 kV).

Table 1
Proximate and ultimate analyses of lignite.

Proximate analyses/wt.%				Ultimate analyses/wt.% (daf)				
Moisture (ar[a])	Ash (ar)	Volatile matter (daf[b])	Fixed carbon(daf)	C	H	O[c]	N	S
32.70	19.94	55.57	44.43	59.78	4.86	33.44	1.35	0.55

[a] ar, as received basis.
[b] daf, dry ash-free basis.
[c] By difference.