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Study on the structural evolution of semi-chars and their solvent extracted materials during pyrolysis process of a Chinese low-rank coal



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G R A P H I C A L A B S T R A C T

Proposed conversion process of the chemical structure of Shenfu low-rank coal during low-temperature pyrolysis, especially considering the solvent extracted metaplast materials (SEMMs) in semi-chars.



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ABSTRACT

The structural evolution of coal during pyrolysis process has been studied for a long time but remains unclear, mainly due to the extraordinary complexity of coal structure. The present study aimed to further identify the chemical structural evolution of different parts in the semi-chars obtained by low-temperature pyrolysis of a Chinese low-rank coal (Shenfu coal). Semi-chars and their solvent extracted materials (oil, resin, asphaltene and preasphaltene) were analyzed by ¹³C nuclear magnetic resonance (NMR) mass spectrometry, diffuse reflectance Fourier transform-infrared spectroscopy (DRIFTs) and ultraviolet (UV) fluorescence spectroscopy, separately. The results showed that 23.8% weight loss occurred during the whole pyrolysis process at 435 °C and half of the weight loss was achieved in the initial five minutes. By contrast, amount of the extracts in semi-chars (solvent extracted metaplast materials) decreased more dramatically in the initial stage of the pyrolysis, and 51.8% of the extracts disappeared in the initial one minute. Oil and preasphaltene showed higher thermal sensitivity than asphaltene and resin. Considerable content of metaplast materials with 1-2 rings (especially in oil and/or asphaltene) were produced along with the pyrolysis process. Condensed aromatic structures in semi-chars were relatively stable and mainly decomposed in the initial stage of pyrolysis which could be attributed to the dramatically decomposition of some active aromatic structures with ≥ 4 rings (especially the components in extracts such as preasphaltene). The results provided a new insight into the structural evolution of coal during lowtemperature pyrolysis process, which specially considered the detailed information of the solvent extractable metaplast materials in semi-chars.

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1. Introduction

Low-rank coals (LRCs) such as lignite and subbituminous coal have gained special attention due to their high moisture and low calorific value in recent years [1-3]. Thermal conversions such as upgrading [4], liquefaction [5] and gasification [6,7], etc. are recently the main methods for the clean and efficient utilization of LRCs. Extensive researches [8-10] have shown that pyrolysis plays an important role in these thermal conversions and the chemical structure of coal is one of the most important factors influencing the pyrolysis characteristics. Thus, study on the chemical structural evolution of LRCs during pyrolysis process (so-called semi-char) is particularly important, which can give excellently theoretical basis for efficient utilization of LRCs. In the past decades, models of the pyrolysis such as FG-DVC (functional groupdepolymerization, vaporization, cross-linking) model [11], CPD (chemical percolation devolatilization) model [12,13], etc. have been successfully established and used for the prediction of coal pyrolysis behavior [14,15]. Unfortunately, due to the extraordinary complexity of coal and its derived semi-chars, their detailed chemical structural evolution remains unclear [16] and is still the important purpose in recent years [17,18]. Hence, further in-depth and systematic study on structural characteristics of the semi-chars needs to be conducted.

Based on the host-gust model of coal, mobile phase and fixed phase (immobile phase) constitute the chemical structure of coal [19,20]. In particular, only the mobile phase and the peripheral structures of the fixed phase can be decomposed during the initial stage of pyrolysis [21,22]. The extracts and residues obtained through solvent extraction are considered as the representatives of mobile phase and fixed phase in coal, respectively [23]. Because the chemical structures of these two parts of coal are extremely different from each other, the characteristics of their pyrolysis are rather different [24–26]. Relevant works from Zou et al. [25] suggested that the pyrolysis process of those extraction residues exhibited lower water yield, higher gas yield and similar char yield by comparing with raw coal. Through re-pyrolysis of solvent extracted material, Stanger et al. [24] pointed out that volatile tars from extracts were higher in molecular weight than those produced from pyrolysing the raw coal. Meanwhile, the extract from semi-char has been considered as important part of the metaplast material which is responsible for the fluidity of coal during the whole pyrolysis process [11,27]. Furthermore, the recent researches from our group showed that even different parts in the extract itself from LRCs had notably diverse chemical structures [23,28]. However, few works were reported about the detailed structural evolution of the components in mobile phase of LRC during pyrolysis process. Thus, combined with solvent extraction, chemical separation and suitable analytical methods, the structural characteristics of the semi-chars would be finely revealed.

In the present work, microwave-assisted extraction was conducted for the separation of mobile phase and fixed phase in the semi-chars which were derived from pyrolysis of Shenfu coal under various residence time at 435 °C. The extracted portions were further divided into four parts, namely, oil, resin, asphaltene and preasphaltene. ¹³C nuclear magnetic resonance (¹³C NMR) mass spectrometry, diffuse reflectance Fourier transform infrared spectroscopy (DRIFTs) and ultraviolet (UV) fluorescence spectroscopy were applied for the characterization of the derived materials. Curve-fitting analyses of IR and ¹³C NMR spectrum were conducted to evaluate the structural composition of the samples. UV fluorescence spectroscopy was used to further investigate the evolution of aromatic ring systems in the samples during pyrolysis process.

2. Experimental

2.1. Materials

Coal used in this work was from Shenfu coal field in Shanxi province, China. The coal sample was firstly dried at 105 °C to constant weight and ground to less than 74 µm before use. The results of its

ultimate and proximate analyses can be seen in our previous work [28]. In brief, the volatile and moisture in Shenfu coal (SF) were 33.85% and 6.85% (wt.%, air-dry basis), respectively, and its carbon and oxygen element were 68.78% and 14.06% (wt.%, air-dry basis), respectively.

2.2. Pyrolysis process

The pyrolysis experiment was conducted in a horizontal quartz reactor (length = 600 mm, diameter = 50 mm). A quartz boat containing coal (0.25 \pm 0.01 g, sample thickness < 200 µm) was placed in the cooling zone of reactor and 1 L/min pure nitrogen (99.999%) was inlet into the reactor at least 20 min to guarantee the oxygen-free atmosphere. When the target temperature (435 °C) was reached, the quartz boat was quickly pushed into the reaction zone. After specific residence time (30 s–40 min), the semi-char (SC) was immediately pulled back to the cooling zone and stayed for a while. The semi-chars obtained were weighed and stored in nitrogen atmosphere for subsequent processing.

2.3. Microwave-assisted extraction of coal and semi-chars

Selected semi-chars (SC-1, SC-5, SC-16 and SC-30, see in Fig. 1) and raw coal (RC) were subsequently extracted with the help of microwave heating using tetrahydrofuran (THF) as solvent. The detailed extraction and separation procedures can be seen elsewhere in our previous work [23]. In brief, extracts from the samples were separated into four parts, namely, oil, resin, asphaltene (asp.) and preasphaltene (pre.).

2.4. Characterization of derived materials

Diffuse reflectance Fourier transform infrared spectroscopy (DRIFTs) of the four fractions (oil, resin, asp. and pre.) were measured on a VERTEX 70 FTS 60 spectrometer. Samples mixed with KBr (1:100) were finely ground and placed in a diffuse reflectance test apparatus. The region of the IR spectra was $4000-400 \text{ cm}^{-1}$ and the resolution of the spectroscopy was 4.0 cm^{-1} . Aromatic systems in the derived fractions were identified by UV fluorescence spectroscopy. In this work, UV fluorescence spectra of the samples were recorded using an Agilent Cary Eclipse spectrometer. The synchronous spectra were recorded with a constant energy difference of -2800 cm^{-1} , a slit width of 2.5 nm, a scan speed of 400 nm/min and a scan range of 200-600 nm. A ¹³C crosspolarization magic spinning (CP/MAS) solid-sate NMR spectrometer (Bruker, AVANCE III 600) was used to analyze the RC and SCs and were recorded at a resonance frequency of 150.9 MHz, and with a spinning rate of 14 kHz, a contact time of 3 ms, and a recycle delay time of 5 s. The deconvolution of IR and NMR spectroscopy were conducted using PeakFit v4.12 (developed by U.S. SeaSolve Software Inc.).



Fig. 1. Char conversion rates of the semi-chars with different residence time.

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