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Research article

Upgrading of low rank coal by hydrothermal treatment: Coal tar yield during pyrolysis

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ABSTRACT

Hydrothermal treatment of coal was carried out in a lab autoclave at 533 K for 30 min and coal pyrolysis was completed in a tube reactor at 873 K for 15 min with the heating rate of 5 K/min. The thermal analysis of the raw and treated coal was compared by thermogravimetric analyzer. The distribution of carbon in coal was detected by solid state ^{13}C nuclear magnetic resonance. The free radical concentrations in coal were determined by electron paramagnetic resonance spectrometer. The results show that hydrothermal treatment is an effective method for upgrading and deoxygenation of low rank coal. The pyrolysis water yields decrease from 9.21 wt.% of the raw brown coal to 7.40 wt.% of the treated brown coal. The pyrolysis tar raises about 18% for the treated brown coal and 5% for the treated sub-bituminous. After hydrothermal treatment, the treated coal has lower contents of oxygen functional group and higher percentage of alkyl carbons in comparison with the raw coal, the free radical concentrations in treated coal increase, especially for brown coal, which is the result in the increment of tar yield.

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1. Introduction

Low-rank coals are very abundant in several regions throughout the world and they constitute a significant resource for both energy and chemical feedstock. However, in spite of their quantity and relatively low market price, low-rank coals have not been utilized to nearly the same extent as higher rank coals. The lack of interest in low rank coal is mainly due to their high-water (25–60 wt.%) and high oxygen functional group content [1,2]. Low-temperature pyrolysis of low rank coal is an economically efficient method for producing char to improve the combustion calorific value [3]. Coal tar hydrogen-cracking to prepare gasoline or diesel oil is coming to the foreground in recent years. The coal tar yield from pyrolysis of low rank coal is low and the pyrolysis water is high. Upgrading of low rank coal has strong economic and practical incentives.

Pretreatment of coal is a method for regulation of the quantity and quality of coal tar. The approaches toward the pretreatment [4–7] of low rank coal have been very diverse, but the commonly used pretreatment method is thermal treatment. Zeng et al. [8] investigated the effects of thermal pretreatment in helium on the pyrolysis behavior of Loy Yang brown coal and found that preheating the brown coal at >523 K leads to reduced tar and increased char yields. Dong et al. [9] treated brown coal by using common heat resources such as hot flue gas and superheated steam and indicated that the pretreatments at 473 K and 523 K in the mixture of steam and simulated flue gas elevate the light oil and phenol oil fractions in tar by 60 and 42 weight percentage points, respectively. Steam is able to depolymerize the coal macromolecular network by cleaving weak covalent bonds such as ether linkages that are thermally stable but hydrothermally unstable at elevated temperatures (>523 K) [10]. So steam pretreatment was used to improve the pyrolysis yields [11]. The water can participate in one or more roles with the existing of oxygen functional groups [12] in brown coal: as a catalyst, reactant, and solvent in the aquathermolysis chemistry at the treatment temperature. Compared with these methods, hydrothermal treatment was considered as an effective pretreatment method [13–15]. Water removed as liquid may dissolve and leach out some water soluble inorganics and hydrophilic organics containing oxygen functional groups with the waste water, thereby reducing the amount of ash producing constituents [16] and oxygen functional groups [17] in the upgraded solid during hydrothermal treatment. The heating value of the upgraded coal [18] is higher than that of the raw coal. Our previous research [19] also indicated that hydrothermal treatment could make the moisture holding capacity of brown coal decrease and reduce the oxygen functional groups.

Recently, many researchers focus on the effect of hydrothermal treatment on gasification of brown coal, hydrothermal treatment has an improvement in the slurryability of brown coal [20–23] and can reduce the viscosity of the coal–water slurry. Moreover, hydrothermal treatment not only promotes the hydro-liquefaction activity in coal liquefaction [24,25] but also increases the coal concentration of coal–solvent slurry [26], then, the oil production cost of liquefaction process is reduced. Shui [27,28] has studied the effect of hydrothermal treatment on modifying caking and coking properties of the sub-bituminous coal.

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Hydrothermal treatment is also an effective method for increasing the coke strength and the particle coke strength. However, little work was focused on the effect of hydrothermal treatment on increasing the pyrolysis tar yields. The paper aims to study the interrelation between hydrothermal treatment and the pyrolysis tar yields. The carbon distributions of coal organic structure were investigated to illustrate the reason of improving pyrolysis tar yield.

2. Materials and methods

2.1. Materials

Inner Mongolia brown coal (IM) and Sinkiang coal (SK, Chinese subbituminous coal) were used as the raw coal in this study. They were ground to less than 0.2 mm and stored under cryogenic environment. The proximate and ultimate analyses of the coal are shown in Table 2. The raw coal was dried under vacuum at 323 K for 8 h before the pyrolysis test.

The hydrothermally treated coal was prepared using a 500 ml autoclave. 80 g of coal and 48 ml of deionized water (the original coal state was simulated) were placed in the reactor, heated at the rate of 4 K/min to set the temperature to 533 K, stirred by a stirrer, and maintained for 30 min under its autogenic pressure. The treated coal was cooled to room temperature and removed from the reactor then. The products were filtered to remove excess water, and dried under vacuum at 323 K for 8 h.

2.2. Methods

2.2.1. Pyrolysis

All pyrolysis tests were carried out in a quartz tubular reactor. The reactor was made of quartz tube with an internal diameter of 20 mm and an overall length of 340 mm. The gas–liquid separator was connected with the reactor through ground glass. 15 g of coal was placed in the reactor, heated at 873 K for 15 min with the heating rate of 5 K/min. The product adhering to the inner wall of the gas–liquid separator and the connection tubes was collected by rinsing with methylbenzene. The water in liquid was determined by ASTM D95-2010. The yields of tar, water and char of coal pyrolysis can be calculated by the following formulas (1)–(3). The yields of gas were calculated by difference.

$$w_{tar} = \frac{m_l - V_w \rho_w}{m_{coal}} \times 100\% \quad (1)$$

$$w_w = \frac{V_w \rho_w - m_{coal} M}{m_{coal}} \times 100\% \quad (2)$$

$$w_{char} = \frac{m_{char}}{m_{coal}} \times 100\% \quad (3)$$

where w_{tar} is the yield of coal pyrolysis tar, %; w_w is the yield of pyrolysis water, %; w_{char} is the yield of pyrolysis char, %; m_l is the mass of liquid from coal pyrolysis by dry and ash-free basis, g; m_{coal} is the mass of coal for pyrolysis by dry and ash-free basis, g; m_{char} is the mass of pyrolysis char by dry and ash-free basis, g; V_w is the volume of water in the liquid, ml; ρ_w is the density of water at 298 K and 0.1 MPa, g/cm^3; and M is the moisture of coal for pyrolysis, %.

The gas analysis was monitored by gas chromatograph (GC) of GC 126 (INESA instrument, China), equipped with two detectors, namely thermal conductivity detector (TCD) and flame ionization detector (FID), was used to quantify the main gaseous species. The gas sampling bags were vacuumed and purged several times before the sampling.

2.2.2. Analysis of the raw and treated coal

The proximate analyses of the coals were determined by standard methods (ISO1171:2010 and ISO562:2010). The elements Carbon, Hydrogen, Nitrogen and Sulfur were analyzed by an elemental analyzer (Elementar Vario Micro Cube, Germany) and the percentage of oxygen was calculated by difference.

The thermal analysis of the coals was determined by a TGA/DSC thermo-gravimetric (TG) analyzer (METTLER TOLEDO, Switzerland). 15 mg of coal was placed in the thermo-balance and heated to 1073 K at a heating rate of 5 K·min^{-1} under a nitrogen flow of 100 ml·min^{-1}. The temperature is corresponding to the maximum weight loss rates of the coals were determined from the first derivatives of the weight loss curves with respect to temperature (DTG). The characteristic temperatures were designated as follows:

Ti	temperature of initial pyrolysis
Tm	temperature of maximum rate of pyrolysis
Tt	temperature of terminal pyrolysis

The solid-state C-13 nuclear magnetic resonance (NMR) was carried out by a Bruker Avance II 500 NMR spectrometer (Germany) at a frequency of 125.77 MHz for carbon and a frequency of 500.12 MHz for proton. Dry and powdered coals were packed into a 4 mm rotor. The C-13 NMR spectra were recorded at a spinning speed of 10 kHz using a triple resonance probe and the total suppression of sidebands sequence (TOSS). The measurement conditions were as follows: the contact time was 2.5 ms, with a recycle delay of 5 s and a scan number greater than 2000. The total signal intensity and the proportion contributed by each carbon grouping were determined by integration using the five spectral areas [29] delineated in Table 1.

Electron paramagnetic resonance (EPR) was determined at room temperature and atmospheric pressure using a Brucker EMX-8/2.7 spectrometer (Germany). EPR scan parameters were kept the same during all the experiments: modulation frequency, 100 kHz, X-band; modulation amplitude, 1 Gauss (G); microwave frequency, about 9.8 GHz; microwave power, 6.375 mW; time constant, 5.12 ms; scan time, 20.97 s; receiver gain, 2500; scan range, 100 G. The free radical characteristics of superfine pulverized coal particles were analyzed with Bruker computer software, WinEPR Acquisition. The main EPR spectra parameters such as g-values (which can reflect the locations of the unpaired electrons in the paramagnetic molecules), linewidth (ΔH, the peak to peak distance of derivative curve, which reflects the relaxation time of spinning electrons), and the free radical concentrations (Ng, which reflects the contents of paramagnetic centers) were analyzed. Moreover, the radical concentrations were quantified using a standard curve of 2,2-diphenyl-1-picryhydrazyl (DPPH, g = 2.0036) as the reference [30].

3. Results and discussion

3.1. Preliminary evaluation of the raw coal and hydrothermally treated coal

Table 2 shows the proximate and ultimate analyses of the raw and treated coals.

The carbon contents of the treated coal are more than that of the raw coal and the hydrogen contents increase after hydrothermal treatment.

Table 1
Chemical shift limits and assignments of the four spectral regions into which the CP/MAS ^{13}C NMR spectra were divided.

Label	Chemical shift range (ppm)	Dominant forms of carbon
A0	200–164	Carboxylic carbon, esters and amides
A1	164–130	Protonated aromatic carbon
A2	130–107	Carbon substituted aromatics and unsaturated carbon and oxygenated aromatics and unsaturated carbon
S1	107–53	Oxygenated alkyl, alkyl-amino, methoxyl, acetal and ketal carbon
S2	53–0	Methyl, methylene, methine and quaternary carbon

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