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Study of the microtextural transformation of coal char during supercritical water activation

Xianxian Zhou [a,b], Xuan Qu [a], Rong Zhang [a], Jicheng Bi [a,*]

[a] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Shanxi 030001, PR China
[b] University of Chinese Academy of Sciences, Beijing 100049, PR China

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ABSTRACT

Low-rank coal chars with different structures were prepared in a fixed-bed pyrolyzer. These coal chars were activated in a semi-continuous tubular supercritical water (SCW) reactor to produce activated carbon. Raman spectra data showed that the amount of aromatic carbon increased with pyrolysis temperature. After SCW activation, smaller aromatic ring units gradually disappeared in SCW, while large aromatic rings in the carbon matrix evolved into the pore structure. Corresponding to the results of nitrogen adsorption, different structures had different reaction rates as a result of SCW exposure, which led to the production of different pore textures. One of the possible pathways in the SCW activation process is proposed. Although there is a strong association between the ratio of cross-linked structures and BET surface area at higher pyrolysis temperatures, the texture of activated carbon is mainly related to the degree of coal conversion achieved.

1. Introduction

At temperatures and pressures above the critical point, the physical properties of water are completely different from those in the liquid or vapor phase [1,2]. In the vicinity of the critical point, the density, viscosity and dielectric constant of water decrease remarkably, leading to an increase in the diffusivity of its molecule and the mobility of gases and organic compounds dissolved in it. Consequently, supercritical water penetrating the porous structure of the char can extract and convey the molecules of the activation products from particles inside. As a result, supercritical water could be used as an activator for the production of activated carbon.

As one of the most important industrial carbon materials, activated carbon is widely used in many fields [3]. It is known for its large surface area, tailored pore structure, thermostability, and stable acid/base properties. The development of micro- and meso-pores is of great importance during the production of activated carbon, for it allows itself to absorb large amounts and various types of chemicals from gases or liquids. Besides its significant contribution to adsorption, activated carbon with a well-developed mesoporous structure has many new applications [4–6]. Compared with normal techniques such as the template method, which is used to produce mesoporous materials [7], supercritical water (SCW) activation shows significant advantages in producing activated carbon with mesopores [8] and sufficient strength [9] at higher burn-offs.

Many works have been carried out with various types of char (including coal [8,10], lignocellulosic biomass [11–13] and polymers [14,15]) to explain the pore development mechanism during the SCW activation process. Material such as anthracite coal char, which contains large amounts of aromatic layer structures, is activated at a temperature of 700 °C for approximately 6 h to achieve a better burn-off; however, in anthracite char, the development of the pore structure is hindered owing to the diffusion limitation caused by its fine micro-porosity, which means the concentration of SCW inside the particle will decrease and the reaction mainly occurs outside the particle. Lignite coal char with a less aromatic structure and more substitute groups shows higher reactivity and needs a lower temperature and less time (around 650 °C and 1 h, respectively) to be activated during SCW. The Brunauer–Emmett–Teller (BET) surface area increases from 488 to 825 m^2/g with the addition of 10 wt.% KOH. Compared with coal, a biomass whose structure is looser, it needs lower activated temperature (around 550–600 °C). In most studies, the SCW activation process produces a larger development of micro-porosity at lower burn-off temperatures; however, the small micro-porosity in biomass char increases more quickly than it does in coal char owing to its open pore structure, which provides carbons with large micro-pores and some mesopores. Polymers such as phenolic fiber and phenolic-resin carbon spheres show a highly and uniformly developed micro-pore structure. High water flow rates slightly enhanced the development of micro-porosity but had little effect on the development of mesopores. Chars from different sources are activated under the same conditions but they

* Corresponding author at: No. 27 Taoyuan South Road, Taiyuan, Shanxi 030001, PR China. Tel.: +86 3514072379.
E-mail address: bijc@sxicc.ac.cn (J. Bi).

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obtained different pore structures. These results show that the reaction rate of chars with different carbon structures in SCW is more or less different.

In the literature, all works focus on comparing SCW with steam in producing activated carbon; little attention has been paid to the detailed analysis of the effect of the carbon-containing precursor itself on the activating process [16]. Kang [13] et al. used thermogravimetric (TG)/differential scanning calorimetry (DSC) analysis to analyze the texture difference between three kinds of biomass. They concluded that biomass material with compact structures that are cross-linked at low temperatures (<374 °C) are more suitable for producing activated carbon with mesopores, because organic high polymer can be easily extracted by SCW, which is one of the most important parts in constructing cross-linked units, which results in low yield and porosity.

Coal has become more important both as an energy source and as the source of organic chemical feedstock in recent years. Low-ranking coal in particular, with its widespread distribution and high water content, is more suitable to be converted in SCW [8]. Supercritical water gasification shows higher conversion efficiencies under lower temperatures and obtains a product gas with high percent of hydrogen and methane. However, there was still approximately 30 wt.% coal char which could not be converted at 700 °C within 10 min. As a result, the char structure (include carbon content, organic matrix, and pore structure) should be deeply investigated for the effective use of these low-grade fuels.

The complex nature of coal structure makes it difficult to use a single technique to determine its composition [17]. However, advances in the characterization of amorphous carbons by Raman spectroscopy over the last four decades have been of great interest in many fields [18]. Most research work has focused on the assignment of peaks gained by Raman investigation. Some studies have tried to correlate the crystal parameters such as d_{002} with the peak ratio [19,20]. It is worth noting that the Raman spectra of highly disordered carbonaceous materials such as amorphous carbon or low-temperature pyrolysis coal char differ from those of highly polycrystalline graphite [19]. So Raman spectral parameters, originally derived from highly ordered carbon materials, such the widths, full width at half-maximum, peak position and ratios of intensities of the G (graphite) and D (defect) bands as well as other bands, which have been used to investigate the correlation with other characteristics such as graphite crystallite size [21,22] and pore size [23] are not suitable for analyzing coal char. Li and coworkers [24–26] worked on curve-fitting Raman spectra of Victorian brown coal char and acquired quantitative correlations between Raman spectra and structural parameters, which offer us a useful way to understand the carbon microstructures. To the best of our knowledge, no work has been done on the char microtexture transformation during SCW activation by Raman spectroscopy and studied the relationship between reaction characteristics and pore structure.

The objective of this study is to investigate microtexture transformation of chars derived from lignite pyrolysis during supercritical water activation in order to determine the influence of char structure on pore development and BET surface area.

2. Experimental

2.1. Material

Pulverized coal sample were supplied from Ulanqab, located in the middle of Inner Mongolia of China. All the samples were stored in standard room conditions. Table 1 is the proximate and ultimate analyses of the raw coal and coal char. It can be seen from the ultimate analysis that the raw coal contained a high oxygen content, which means that the coal has high reactivity and that its structure will be more severely affected by temperature. Three different particle sizes were used to investigate the effect of ash content on the textural characteristics. Sample 1 was 0.25–0.35 mm, sample 2 was 0.15–0.25 mm, and sample 3 was 0.01–0.15 mm. An increase in the ash content can be found with the decrease of the particle size. The most obvious difference lies in the sulfur content, which is due to the high content of pyritic sulfur in the ash.

Table 1
Proximate and ultimate analyses of the raw coal and coal char.

Sample	Proximate analysis (wt.% ad)				Ultimate analysis (wt.% daf)				
	M	V	A	FC	C	H	S	N	O[a]
1	8.95	30.80	26.57	33.69	62.63	4.79	2.34	1.24	28.99
2	9.14	32.36	26.85	31.66	65.05	4.68	3.08	1.26	25.92
3	10.04	32.71	34.40	22.85	64.51	4.55	6.37	1.25	23.32
Char 3	3.51	23.79	43.8	28.90	72.34	3.70	8.97	1.48	13.51
Char 4	3.61	21.61	43.0	31.78	74.76	3.65	8.62	1.51	11.46
Char 8	1.62	18.69	48.8	30.89	84.32	3.09	10.80	1.51	0.29

[a] By difference.

2.2. Preparation of coal char and activated carbon

In this study, 20 g of raw coal was pyrolyzed (carbonization) in a simple iron retort reactor under nitrogen atmosphere. It is well known that the temperature, heating rate, and residence time would influence the pyrolysis process. In order to obtain different structures of coal chars, a simple orthogonal optimal experiment (Table S1) was designed, with four factors (A, B, C, D) and three levels (i = 1, 2, 3). Factor A was the pyrolysis temperature (400, 500, 600 °C); B was the pyrolysis time (0, 30, 60 min); C was the heating rate (2, 10, 20 °C/min), and D was the particle size of the raw coal (0.25–0.35 mm, 0.15–0.25 mm, and 0.01–0.15 mm). The experimental pyrolysis scheme is shown in Table 2. Nine kinds of coal chars were prepared under these conditions.

The experimental setup for activating char by SCW is shown in Fig. 1. About 1.5 g of coal char was loaded in the reactor, and a sintered silica plate (mean pore size 10 μm) was used to fix both sides. A flow rate of 8.6 mL/min was delivered to the reactor with an HPLC metering pump. The flow of water was preheated in the preheater and then passed through the coal char layer. Then, the stream at the outlet of the reactor was cooled inside a coiled stainless steel tube immersed in a water bath at 20 °C. The pressure in the reactor was maintained and adjusted with a back-pressure regulator. When the experiment was finished at the desired reaction time, the system was depressurized and the reactor was cooled under nitrogen flow. Once the reactor was cooled to room temperature, the solid product was removed and stored in a desiccator for further analysis.

2.3. Analytical methods

2.3.1. Thermogravimetric/differential thermogravimetric analysis

The pyrolysis behavior of the lignite was determined by a thermogravimetric analyzer (SetaramSestys, France). The sample was heated at the rate of 2 °C/min to 900 °C under a flow of N_2 (60 mL/min).

Table 2
Raman shift of bands D and G and BET surface area of orthogonal experiment.

Experiment number		N_2 pyrolysis coal char			After SCW activation			
	AiBiCiDi	D (cm^{-1})	G (cm^{-1})	Gap (cm^{-1})	D (cm^{-1})	G (cm^{-1})	Gap (cm^{-1})	BET (m^2/g)
1	$A_1B_1C_1D_1$	1370	1589	219	1332	1591	259	493
2	$A_1B_2C_2D_2$	1367	1587	220	1350	1600	250	470
3	$A_1B_3C_3D_3$	1360	1601	241	1351	1598	247	344
4	$A_2B_1C_2D_3$	1365	1599	234	1339	1604	265	609
5	$A_2B_2C_3D_1$	1363	1593	230	1351	1602	251	348
6	$A_2B_3C_1D_2$	1363	1598	235	1341	1599	258	350
7	$A_3B_1C_3D_2$	1356	1599	243	1348	1602	254	458
8	$A_3B_2C_1D_3$	1354	1597	243	1348	1602	254	583
9	$A_3B_3C_2D_1$	1356	1600	244	1343	1602	259	345
Raw coal 1		1372	1580	208				<20
Raw coal 2		1372	1590	218				
Raw coal 3		1372	1590	218				