

Effects of fractal surface on rheological behavior and combustion kinetics of modified brown coal water slurries

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Abstract The paper reports the effects of surface fractal structures on the rheological behavior and combustion kinetics of raw brown coal and three modified coal water slurries (CWSs). The results show that the fractal structures and physicochemical properties of samples are dependent on various modification processes. The apparent viscosities of the coal water slurries increase with increasing surface fractal dimensions (D), especially with decreasing shear rates. Furthermore, it has been proved that the ignition temperatures and apparent activation energies of modified CWSs are lower than that of raw coal water slurry. Compared with the traditional qualitative analysis of the effect of pore structures on CWSs properties, D can more efficiently indicate the quantificational effect of pore structures on the rheological behavior and combustion kinetics of CWSs.

Keywords Coal water slurry · Modification processes · Fractal surface · Rheological behavior · Combustion kinetics

1 Introduction

With more than 60 wt% solid in small particle size (<50 μm) and low apparent viscosities (1200 MPa s), coal water slurry (CWS) has been extensively developed as a coal-based clean fuel in many countries (Phuoc et al. 2014). CWS fuel has been widely used due to its great efficiency in substituting crude fuel used in several industries of China (Cui et al. 2007; Chen et al. 2014). The physicochemical properties of coals, stabilizers and chemical dispersants have important effects on the preparation and combustion properties of CWS. Especially, the degree of coalification, such as moisture, oxygen, volatile, ash, carbon, function group, particle size distribution and

surface chemistry, are all the key factors for CWS preparation (Logos and Nguyen 1996; Dincer et al. 2003; Boylu et al. 2004; Atesok et al. 2005; Meikap et al. 2005; Zhou et al. 2012; Zhu et al. 2014). In recent years, researchers mainly focused their interests on the reliable preparation of high concentration CWS (Tiwari et al. 2003; Das et al. 2009), and improving rheological behavior, promoting stability of additives (stabilizers and dispersants) and decreasing viscosity of CWS (Xu et al. 2006; Qiu et al. 2007; Zhou et al. 2007; Das et al. 2009; Chen et al. 2011; Li et al. 2012; Panda and Swain 2014). Low-rank coals such as brown coal, which is difficult to prepare high concentration CWS, has been modified to optimize its character and enhance its value-added for applications (Christian 2003; Li et al. 2014; Yu et al. 2014).

Although the complex pore structures of solid particles have important effects on CWS preparation and combustion properties of modified coals, the present researchers mostly focused on qualitative analysis of pore structures (Yavuz et al. 1998; Burdukov et al. 2002; Tahmasebi et al. 2012). The special attention has been paid to the relationship of the fractal dimensions and the coal pore structures such as volume distribution and porosity (Lee and Pyun

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2005; Mahamud and Novo 2008a, b), but most studies are concentrated on the change of fractal dimensions with pore structures in brown coals (Mahamud et al. 2004; Yao et al. 2009; Ge et al. 2013). However, the effects of pore fractal structures on the rheological behavior and combustion kinetics of modified brown coal water slurries (CWSs) were seldom reported. Based on the fractal theory, it is valuable to quantitatively evaluate the complicated and nonlinear porosity of coal particles, and clarify the impacts of surface fractal dimensions (D) on modified CWSs properties.

The present work introduces the effects of surface fractal dimensions (D) on their rheological behavior and combustion kinetics of raw brown coal and three modified CWSs. In particular, a new strong relationship among D and rheological behavior and combustion characteristics of CWSs has been obtained via the analysis of the physicochemical properties of CWSs. It is concluded that the pore fractal structures have obviously effect on the combustion characteristic of CWSs, and the physicochemical changes of brown coal in modification processing are beneficial for modified CWSs. The results are helpful for expanding application range of the modified brown coals.

2 Experimental

The raw brown coal (marked as BRYM) provided by the Shenhua coal International Trade Co., Ltd. in China and the other three modified coals (marked as BR1, BR2 and BR3 respectively) were thoroughly used in our experiments. Prior to use as modified brown coal, three modification methods including drying to dewater by using low-temperature fluidized bed, coal pyrolysis at low temperature, and coal briquetting have been done, respectively. In the experiments, BR1 was treated as dewatered coal by using fluidized bed dryers with flue gas blending under N_2 gas at the mixture ratio of 1:1 (flue/gas). In the modification processing, raw brown coal was milled to no more than 3 mm in size and dried at the temperature of 260 °C with 2 % relative values of moisture content. BR2 (particle size of 0–6 mm) was prepared by pyrolysis processing at 450 °C with a heating rate of 15 °C/min for 1 h in a tubular-furnace with 0.35 Pa vacuum system under N_2 atmosphere, and the required pressure was less than 0.5 Pa in experimental processing. BR3 was conducted on hydraulic molding machine with 3000 mL per batch capacity, and the pulverized raw coal was mixed with water (1:1 in weight) and pressed under about 300 kN for 1 h as the optimum condition of modification process.

The particle size analysis of coal was performed by using a laser particle size analyzer (LS-C(1), China). The

specific surface areas and pore diameters of the coal samples were determined by N_2 volumetric adsorption analyzer (SSA4300, China). Nitrogen adsorption isotherms were determined at 77 K up to a P/P_0 value of 0.98 (where P is the equilibrium pressure and P_0 is the saturation pressure of the adsorbate under the measurement temperature). The sample was dried at 373 K for 120 min at a pressure $<10^{-4}$ torr to clean the surface. The adsorption and desorption curves of the nitrogen and the pore diameter distribution of coal samples are shown in Figs. 1 and 2, respectively.

The surface morphology of samples was observed by using scanning electron microscopy (SEM, Hitachi S-3400N II, Japan). A functional group analysis was conducted by a Fourier transform infrared (Nicolet 6700, USA) with the resolution of 1 cm^{-1} . The sample was conducted by the KBr pellet method in a spectra selected range of 3800–600 cm^{-1} which were assigned to the aliphatic hydrogen, hydrogen bonding alcohols, phenols and oxygen containing structures, respectively.

The CWSs with 60 wt% solid concentration were composed of pulverized coal (60 wt%), water, chemical dispersant and stabilizer (<1 wt%) at room temperature. The chemical dispersant (naphthalene sulfonic acid-formaldehyde condensate, NSF) and stabilizer ($FeSO_4$) were added to a proportion of 0.7 wt% and 0.03 wt% in the air-dried coal, respectively. The water was added with a 40 wt% proportion of CWSs. The apparent viscosity was measured by using a rotary viscometer (NXS-11A, China). The slurry sample was first put into a cylinder, keeping shearing at 100 S^{-1} for 5 min, the shear rates increased from 10 to 100 S^{-1} , and the viscosity data were recorded every 30 s during 5 min period. The apparent viscosity at 100 S^{-1} was calculated by an average of the ten viscosity values recorded and the temperature was controlled at $25 \pm 0.1\text{ }^\circ\text{C}$ in whole process.

The CWSs combustion kinetics was carried out on a thermo gravimetric analyzer (STA449F3, Germany) at the heating rates of 15, 25, 50 °C/min respectively, and the weight of the CWS sample was about 15 mg at an air flow rate of 40 mL/min. The air-dried basis moisture content of brown coal and three modified coals were 23.53 %, 7.83 %, 4.6 % and 8.8 % respectively. All samples employed in the experiments had an average particle size range from 10 μm to 50 μm . The industrial analysis of coal samples was given in Table 1. As a low-rank raw coal, air-drying water-based (Mt) value of BRYM was much higher (26.13 wt%). In the modified processing, dewatering was very important and the total moisture in coal was consisted of inherent and surface moisture. The inherent water is the indication of the quality of a coal, and the surface moisture will disappear when the coal is dried under standard conditions. The coal with high water content can make the surface hydrophobicity weaken, so that it may lead to polar

Fig. 1 SEM images of four coal samples grinding for 4 h. **a** Raw brown coal; **b** modified-coal sample by using fluidized bed; **c** modified coal sample by low-temperature pyrolysis and carbonization and **d** pulverized coal by dried compression

hydrophilic surface adsorbed on coal. The non-polar hydrophobic group can conflict with adding water, which is not conducive for coal dispersion in CWSs. The purpose of dewatering is to decrease inherent water for improving the physicochemical properties and pulping of raw brown coal. The M_{ad} of modified-coal samples and total moisture (M_t) of coal significantly decreases, while air-dried basis volatile (V_{ad}) decreases slightly, and the dry ash-based fixed carbon (FC_d) content increases in all various processes.

Coal particles characterized of very complicated surface morphologies and porosity can be accurately described by a novel fractal theory (Mahamud and Novo 2008a, b). In this paper, the novel fractal model is used to calculate D value of coal particles. The equation is $D = 3 - r$. D is the surface fractal dimension which is limited as follows:

$$0 \leq D \leq 3,$$

where D is denoted as a measure of surface roughness. The slope of “ $-r$ ” is used to calculate the fractal dimension. “ $-r$ ” can be calculated according to the Avnir equation (Avnir and Jaroniec 1989):

$$\theta = K[\ln(P_0/P)]^{-r},$$

where θ is the relative adsorption amount of N_2 gas, $\theta = V/V_m$, in which V is the N_2 adsorption volume (cm^3/g , in Table 3) at the relative adsorption pressure of P/P_0 , and V_m is the monolayer N_2 adsorption volume (cm^3/g) based on the specific surface area calculation. V_m is calculated by the following equation:

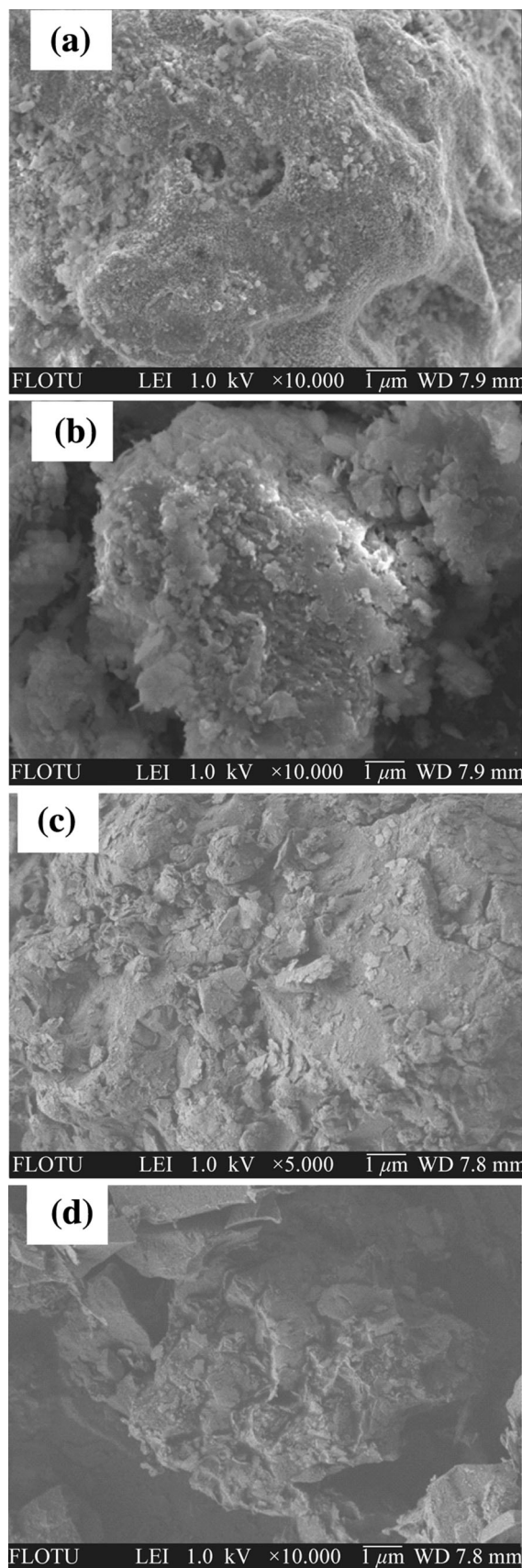
$$V_m = \frac{1}{A + B},$$

where A and B are the slope and intercept of liner by Plots of $P/P_0/(V(1 - P/P_0))$ versus P/P_0 reconstructed from the N_2 gas adsorption isotherms and all the curves (Fig. 4) come from the experiment of specific surface areas and pore diameters of coals determined by N_2 volumetric adsorption analyzer.

3 Results and discussion

The results from the proximate analysis and ultimate analysis of samples are shown in Tables 1 and 2.

The particle sizes and porosity parameters of the four coals are shown in Table 3. When the grinding time is prolonged from 0.5 to 4 h, the average particle size of BRYM, BR1, BR2 and BR3 coal decreases from 45.34 to



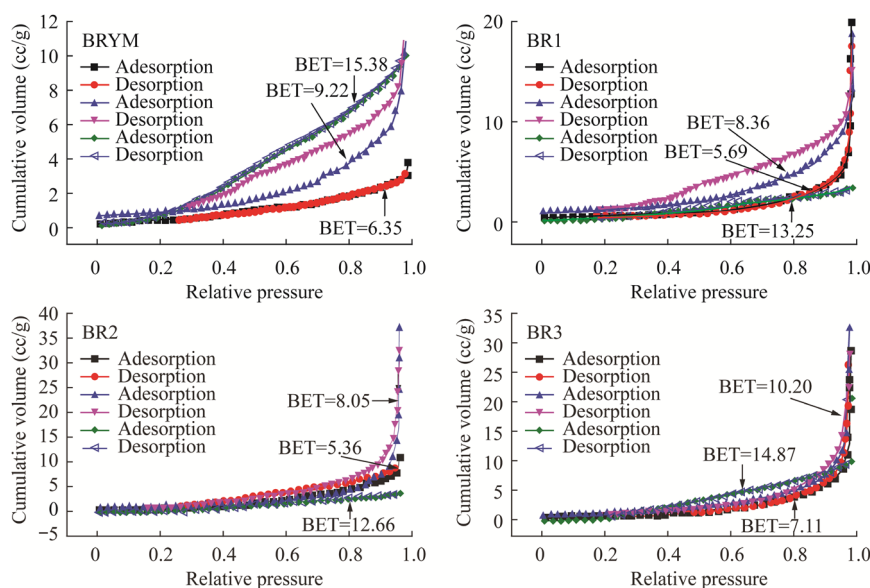


Fig. 2 Adsorption and desorption curves of the nitrogen of coal samples

Table 1 Proximate analysis of coals (wt%)

Index of samples	M_{ad}	V_{ad}	A_{ad}	FC_d	M_t	$Q_{net,ad}$ (kcar/kg)
BRYM	23.53	48.99	9.79	51.01	26.13	16.67
BR1	7.83	43.61	9.34	56.27	16.38	23.04
BR2	4.6	42.62	10.89	57.39	15.77	24.58
BR3	8.8	46.62	9.04	53.38	17.07	21.23

Table 2 Ultimate analysis of coals (wt%)

Index	C_d	H_d	O_d	N_d	S_{td}	C/H	C/O
BRYM	64.58	4.85	29.08	1.12	0.38	13.32	2.22
BR1	66.5	4.23	28.02	0.83	0.42	15.72	2.37
BR2	67.47	4.5	26.74	0.81	0.48	14.99	2.52
BR3	65.07	4.46	29.11	0.93	0.44	14.59	2.24

16.48, 52.12 to 22.54, 59.84 to 20.14 and 40.24 to 12.35 μm respectively. In the meantime, the total specific surface area of BRYM, BR1, BR2 and BR3 coal increases from 6.35 to 15.38, 5.69 to 13.25, 5.36 to 12.66 and 7.11 to 14.87 m^2/g respectively. The total specific surface areas and pore volumes of the four coals all increase with the decrease of the particle size, while the mean pore diameters decrease.

3.1 Pore fractal structure of the modified brown coals

3.1.1 SEM images analysis

The SEM images of coal samples are given in Fig. 1. There are different surface morphologies in the four coals. The

raw coal appears brittle-sponge and most irregular particles are loosely stacked with smooth particle surface full of large and irregular pores (Fig. 1a). BR1 shows the more rough surface covered with small holes and the texture is regular-terrace and granular (Fig. 1b). Due to the low-temperature carbonization, BR2 surface is rougher (Fig. 1c). But BR3 presents the large surface cracks with large gaps and is very loose after dried and compressed (Fig. 1d).

The residual liquids and gases in the coal pore structure would be removed as the coal matrix was distorted or damaged by substituting the liquids and gases in coal by resin. The resin was also designed to improve the image contrast between the voids and coal microstructure (Charrière and Behra, 2010). Overall, the cracks collapsed from the original cracks changes with the change of modification degree. When the roughness of particle surfaces increases, the flat shapes become more solid. The change of physicochemical properties of brown coal is also a key reason for this phenomenon during the modification process. In addition, the porosity increases with the coal rank. Another reason lies in that large pores are broken into small pores through dry and compression. Additionally, this modification processing may lead to the increase of the specific

Table 3 Particle sizes and porosity parameters of coal samples

Coal samples	Grinding time (h)	Volume-average particle size (μm)	Specific surface area (m^2/g)	Specific pore volume (cm^3/g)	Mean pore diameter (nm)	Pore fractal dimension
BRYM	0.5	45.34	6.35	0.018	9.68	2.31
	2	25.14	9.22	0.021	8.21	2.35
	4	16.48	15.38	0.028	7.55	2.47
BR1	0.5	52.12	5.69	0.012	8.64	2.24
	2	32.58	8.36	0.017	7.68	2.31
	4	22.54	13.25	0.026	7.26	2.38
BR2	0.5	59.84	5.36	0.013	8.99	2.26
	2	38.41	8.05	0.019	7.34	2.30
	4	20.14	12.66	0.023	7.21	2.37
BR3	0.5	40.24	7.11	0.019	8.69	2.30
	2	20.14	10.20	0.022	7.32	2.35
	4	12.35	14.87	0.027	7.47	2.41

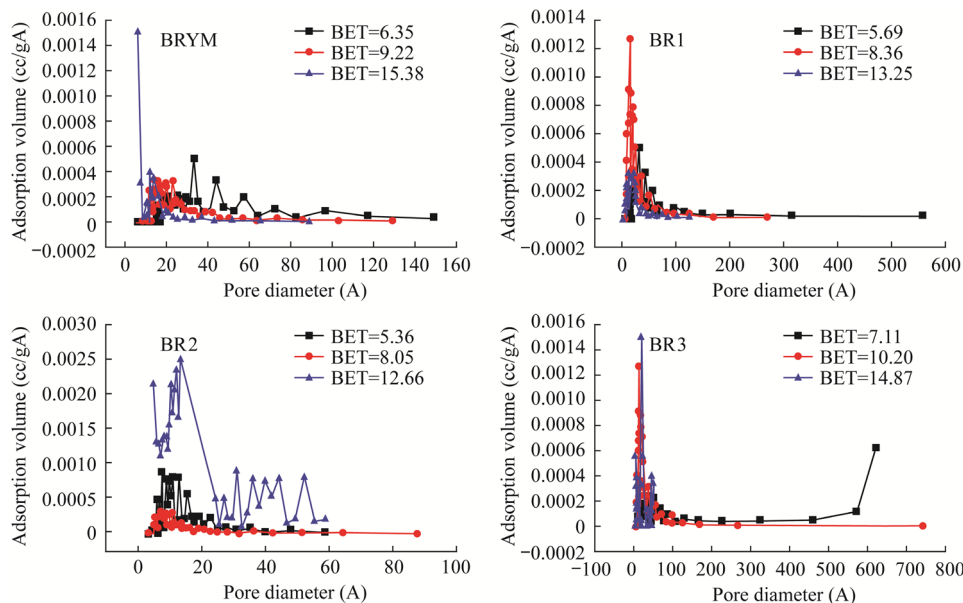


Fig. 3 Pore diameter distribution of coal samples

surface. During the modification process, the cleavage of bridge results into the partial collapse of mesopore structure whose change can be observed by optical microscopy in the modified coal samples.

3.1.2 Fractal dimensions calculation

Figure 2 gives the adsorption and desorption curves of the nitrogen of coal samples, and some adsorption and desorption curves are not coincident which indicated that the pore structure was more complex. Figure 3 indicates that the total pore volumes and specific surface areas of BRYM, BR1, BR2, and BR3 increase from 6.35 to 15.38, 5.69 to

13.25, 5.36 to 12.66, and 7.11 to 14.87 m^2/g , D of the four coals increases from 2.31 to 2.47, 2.24 to 2.38, 2.26 to 2.37 and 2.30 to 2.41 m respectively.

Figure 4 shows the plots of $P/P_0/(V_1 - P/P_0)$ versus P/P_0 reconstructed from the N_2 gas adsorption isotherms.

P is N_2 partial pressure, and P_0 is the saturated N_2 vapor pressure at liquid nitrogen temperature. Convert the Avnrin equation into a logarithm form:

$$\ln \theta = \ln K - r \ln[\ln(P_0/P)],$$

where $\theta = V/V_m$ that is $\theta = V(A + B)$. V is given in Table 3, while A and B is the slope and intercept of the lines in Fig. 4. Fit a linear regression to the data points on

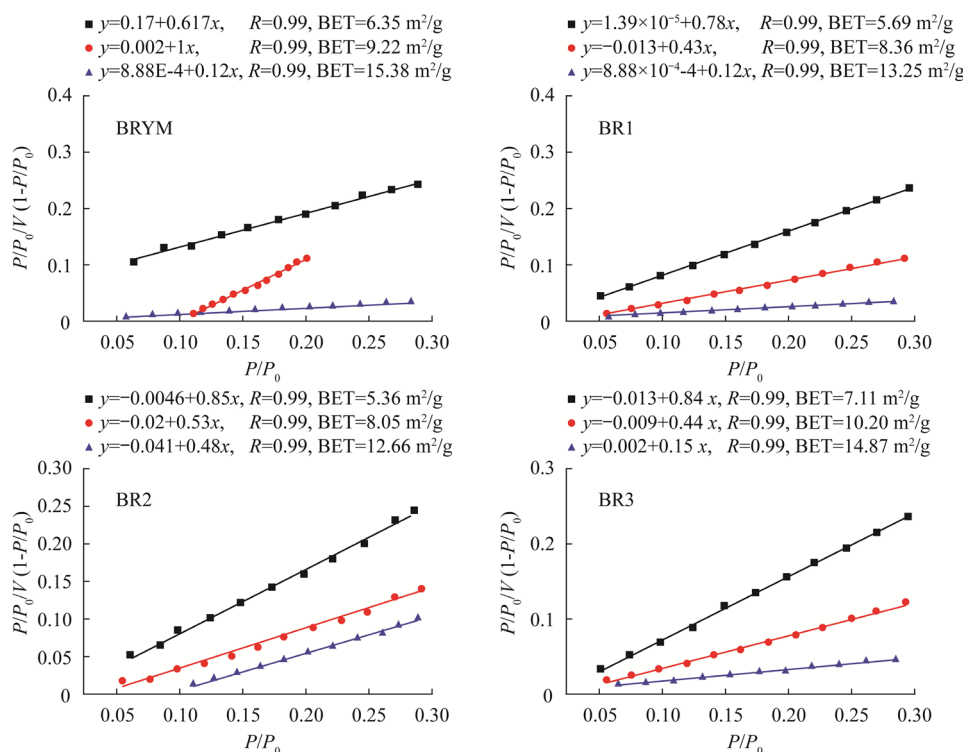


Fig. 4 Plots of $P/P_0/(V(1 - P/P_0))$ versus P/P_0 reconstructed from the N₂ gas adsorption isotherms

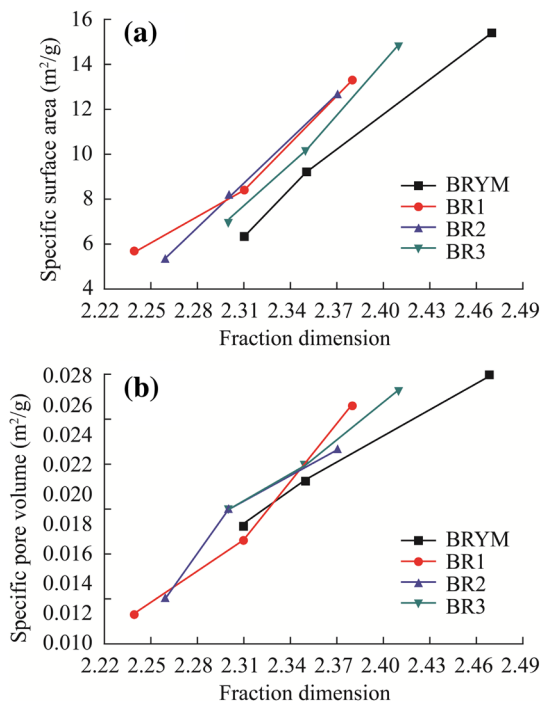


Fig. 5 Specific surface areas and pore volumes versus pore fractal dimensions

the graph of “ $\ln \theta$ ” versus “ $\ln [\ln(P_0/P)]$ ”, the slope is “ $-r$ ” which is the key data for equation “ $D = 3 - r$ ” (Table 3). The intercept of “ $\ln K$ ” is an adsorption constant

for the specific coal with the specific particle size distribution. Based on the limited experimental data, an attempt can be made to estimate the D by using the Avnir equation. The experimental data are probably of quantificational to explain the rheological and combustion properties of CWSs.

Table 3 shows that D of BRYM, BR1, BR2, and BR3 increases from 2.31 to 2.47, 2.24 to 2.38, 2.26 to 2.37 and 2.30 to 2.41 when the average particle size decreases from 45.34 to 16.48, 52.12 to 22.54, 59.84 to 20.14 and 40.24 to 12.35 μm respectively. Generally speaking, D of coal particles all increase with the decrease of the particle sizes because of the more complex inner surfaces and pore networks. Figure 5a indicates that the specific surface areas of BRYM, BR1, BR2, and BR3 increase from 6.35 to 15.38, 5.69 to 13.25, 5.36 to 12.66 and 7.11 to 14.87 m²/g, while, Fig. 5b demonstrates the total pore volumes of the four coals increase from 0.018 to 0.028, 0.012 to 0.026, 0.013 to 0.023 and 0.019 to 0.027 cm³/g, and D of the four coals increase from 2.31 to 2.47, 2.24 to 2.38, 2.26 to 2.37 and 2.30 to 2.41 m respectively.

3.1.3 Mechanism analysis

Fractal dimension can be elaborately shown in the reflection of the complexities of pore shapes. In general, higher fractal dimensions correspond to the more complex

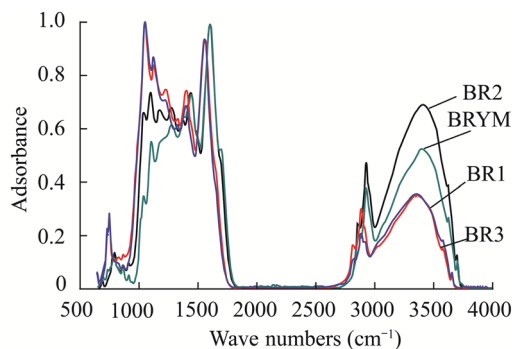


Fig. 6 FT-IR spectrums of the four coals

pore shapes (Xiao et al. 2012). In order to construct the relationship between the modification processes and the fractal dimensions of modified coals, the Fourier infrared spectroscopy was used to analyze the physical and chemical change of coals during the heating processing (Fig. 6a, b).

Many physical and chemical phenomena occur in the modification process including the plasticity and depolymerization. All those phenomena can affect pore structures, especially for the coals with high volatile content. The band recorded in the range of 3000–3500 cm^{-1} is mainly hydrogen bonding alcohols and phenols. 3401 cm^{-1} is hydrogen bond absorption formed by phenolic hydroxyl dipolymer. BR2 is characterized by a high concentration of hydroxyl functionalities from both phenolic and carboxylic structures, as seen from the band in the 3000–3500 cm^{-1} regions (Fig. 6). This phenomenon may be explained as the following.

In mild pyrolysis processing, the raw coal releases CO_2 , CH_4 , carboxyl oxygen and aliphatic hydrocarbon detached from raw coal resulting in low carbon and hydrogen content at less than 450 °C. The oxygen-containing functional groups decompose and macromolecular structure breaks with the increase of the pyrolysis temperature. Decreasing volatile matter caused the oxygen and hydrogen elements decreased sharply, but the carbon exists with a relatively stable aromatic carbon and the compounds originated from the cleavage of covalent C=C bonds interconnecting bicyclic aromatic rings (Wang et al. 2008). So the band ratio between 3000–3500 in BR2 becomes bigger than the original one as shown in Fig. 6.

The released volatile matters will lead to some changes of the pore shape with the decrease of the pore surface area and the mean pore sizes during modification processing. Additionally, physical and chemical changes are also the main reason for the variation of the surface fractal dimensions. The changes of macropores are observed in the two different ways during the modification processes. One is that some micropores become simple so that the fractal dimensions are reduced, and the other is that the

macropores become more complex leading to bigger D (McMahon et al. 1999). Figure 2 shows the evolutions in the micropores, mesopore and macropores of coal samples during modification processes, and the above changes have appreciable effect on the D values. The morphology of BRYM shows that the raw coal becomes more complex in the micropore structure than the modified coals. Based on the studies and analyses mentioned above, the aromatic compounds of modified coals, aromatic nucleus and basic structural unit of condensation increase in the total amount, and a number of oxygen-containing functional groups of coal reduce to the orderly arrangement of internal elements. The contents of hydroxyl and carboxyl of modified brown coals change in the trend line, and then the contents gradually increase with the modification degree comparing with the raw coal. The removal rate of carboxyl is significantly higher than that of hydroxyl in the same modification conditions, especially in the pyrolysis modification processing in which the carboxyl group contents of coals decrease. It indicates that the carboxyl group and phenol hydroxylation are mainly removed in the pyrolysis modification processing, and the structures of oxygen-containing functional groups are changed and the chemical structure of coals are partly changed which can change the appearance of coal particles. One main reason is that the first external characteristics of the modified brown coal makes some micro-pores less complex with the decrease of fractal dimensions, thus the increase of the pore surface area improves the D values. The second reason is that another external performance shows that the macropore shapes become more complex after pyrolysis, leading to the decrease of D . It is concluded that D is a significantly important parameter to characterize the roughness of coal surface, and D of coal samples varies under different modified conditions and those features can make great influence on the slurry ability of CWSs.

3.2 Rheological behavior of modified CWSs

The apparent viscosities and rheological behaviors of the four CWSs with 60 wt% concentration are shown in Fig. 7. It may be seen that the apparent viscosities of four CWSs change obviously with the varied shear rates after being ground for 4 h when D reaches the maximum. By contrast, the apparent viscosities of the four CWSs show less change after being ground for 0.5 h. The apparent viscosities of raw CWS dramatically increase when D increases to the maximum after being grinding for 4 h, and the extent of the decrease is gradually diminished with the increase of shear rates while the three modified CWSs are all appeared to pseudoplastic fluids characteristics.

Figure 7 shows the apparent viscosities of the four CWSs increasing with the increase of D . The apparent

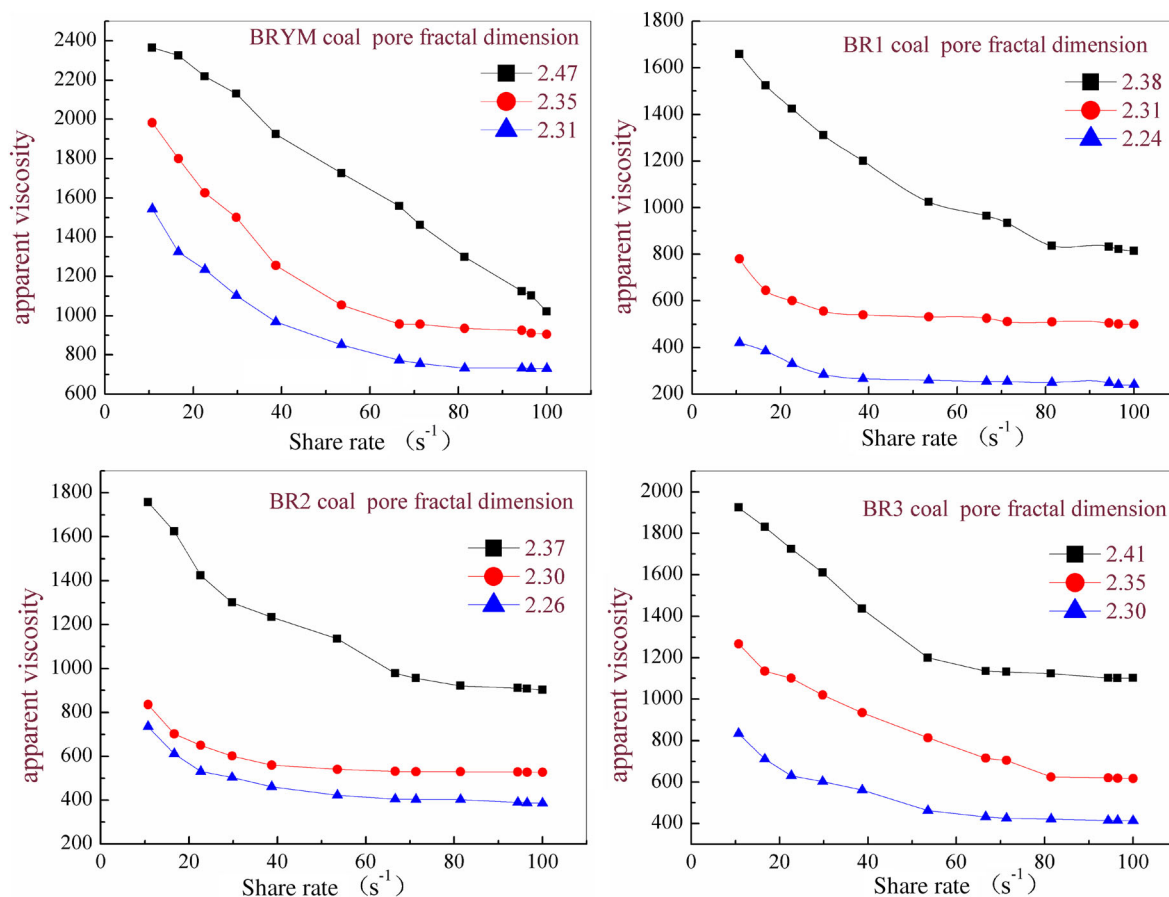


Fig. 7 Rheological behavior of the four CWSs

viscosities of BRYM, BR1, BR2, and BR3 increase from 1544 to 2361, 420 to 1658, 735 to 1758 and 835 to 1925 MPa s at a low shear rate of $10\ s^{-1}$ respectively, while these increase from 730 to 1021, 240 to 815, 386 to 902 and 414 to 1102 MPa s at a high shear rate of $100\ s^{-1}$ respectively. The experimental results indicate that D of modified CWSs is smaller than that of raw brown CWS at the same grinding time, so that the apparent viscosities of the modified CWSs decrease. The first reason is that the pore volume and specific surface area both increase with the increase of D , resulting in a reduced free water amount among coal particles and an enhanced water-adsorption capacity of coal particles. More attention should especially be paid to the result which the raw brown coal is at the low rank with the above obvious characteristics. The other reason is that the volume-average particle size decreases with increasing D , which can increase free water among coal particles and volumetric particle amount, and this is beneficial to decreasing the apparent viscosities of the modified CWSs.

It is clear that the result correlates with the change in the mechanical properties of brown coal upon drying and compression, and it is suggested that there exists some type of

pore collapse suffered by brown coal on drying and compression. The average particle size decreases with the increase of D , resulting in an increased particle amount and segmented free water among coal particles. Taking into consideration of industrial application for CWS, an increasing of CWS apparent viscosity has dual influences: the dramatic increase of CWS apparent viscosity at the low shear rate is beneficial to keep the longtime stability during the CWS transportation and storage, while it is unfavorable to the atomization during the CWS spraying into combustors.

Another main reason for decreasing the apparent viscosities of the modified CWS is that the oxygen-containing functional groups decompose and macromolecular structure breaks in modification processing. Decreasing volatile matter causes the oxygen and hydrogen elements decrease sharply, but the carbon exists with a relatively stable aromatic carbon and these compounds are originated from the cleavage of covalent C=C bonds interconnecting bicyclic aromatic rings. As shown in Fig. 6, the basic group becomes more than that of the raw brown coal which can weaken the adsorption capacity of coal to water, therefore the apparent viscosities of the modified CWSs decrease.

It is believed that the coals used in the experiments have different surface property at the same rank. Although the chemical additives are applied in tests to ensure the dispersity of coal particles, the modified processing makes the improvement to the physical characteristics of the CWSs, such as the calorific value and pore structure of the resultant product. As to the oxygen contents given in Table 1, BRYM is much more hydrophilic while the qualities of the three modified coals are relatively improved. BRYM tends to absorb much more water than the modified coals in the CWS system. The increased water-adsorption capability of BRYM can be found in the measured viscosity values. Therefore, the rheological behavior of CWS is affected by pore structures, particle sizes and surface properties of coal.

3.3 Combustion dynamics of modified CWSs

The combustion dynamics of the four CWSs can be determined on the differential thermo gravimetric (DTG) curves obtained at different heating rates. The CWS combustion processing can be divided into three steps: the moisture evaporation, the volatile release and ignition, and the coal char combustion and burnout. The most important characteristic temperatures of a burning profile are ignition temperature and peak temperature (Kücükbayrak et al. 2001; Umar et al. 2005). The peak temperature which is the point on the burning profile at the maximum rate of weight loss is usually denoted as a reactivity measurement of the sample (Haykırı-Acma et al. 2001).

As shown in Fig. 8, the ignition temperature of the four CWSs all decrease with the increase of D . For all modified CWSs, compared with raw CWS, the ignition temperature significantly increases because of the loss of volatile matters contents and the removal of moisture during the modified process. Generally, the DTG peak temperature is the maximum combustion rate (T_{max}) related to the coal reactivity and the reactive coal has a lower T_{max} .

The ignition temperature of CWS is determined by a vertical line which is firstly made upwards through the DTG peak point to meet the TG oblique line, and then a tangent line to TG oblique line made to meet the extended TG initial level line. Thereby, the ignition temperature is defined by the temperature at the intersection point (Umar et al. 2006). As shown in Fig. 8, the ignition temperature of the four CWSs all decrease with the increase of D , but increase with the increase of heating rates. When D of BRYM, BR1, BR2, and BR3 increases from 2.31 to 2.47, 2.24 to 2.38, 2.26 to 2.37 and 2.30 to 2.41 respectively, the ignition temperature of CWSs made of BRYM, BR1, BR2, and BR3 decreases from 475 to 442, 481 to 461, 482 to 451 and 480 to 446 °C at the heating rate of 50 °C/min, while at the heating rate of 15 °C/min decreases from 438 to 389, 462 to 441, 467 to 440 and 462 to 437 °C respectively. The results show that the CWS ignition temperature is reduced with the decrease of heating rate. It can be explained that the heat exchange, not only from furnace wall to coal particles but also from particle surfaces to inner nucleus, increases with the decrease of heating rate (Cheng et al. 2008). The pore fractal dimension is defined as quantitative

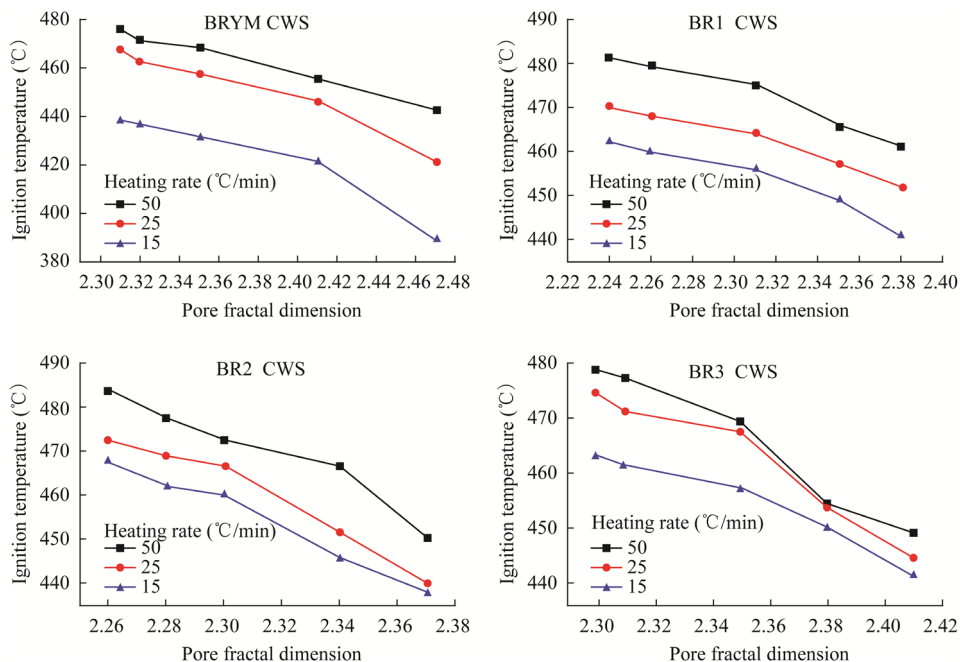


Fig. 8 Ignition temperatures of the four CWSs

characterization for pore structures, and the pore fractal dimension is larger, meaning the more micropores which lead to increase specific surface areas. The large specific surface areas can provide more interface for oxygen which is conducive to volatilization and heterogeneous ignition. So as to reduce the coal particle size, particle resistance is reduced, and the lower ignition temperature shows that the coal is more inflammable and the apparent activation energy becomes smaller.

Under different heating rates, the apparent activation energy of sample changes slightly (Vamvuka et al. 2004). Based on Freeman–Carroll method, the DTG curves obtained at different heating rates are used to calculate the apparent activation energy of four CWSs. The combustion dynamics equation of CWSs is transformed according to the following equation:

$$\ln[\beta(da/dT)] = \ln[Af(a)] - E/RT,$$

where E is the apparent activation energy, β is the heating rate, a is the conversion ratio of weight loss, and A is the pre-exponential factor. According to the DTG curves at the different heating rates; the linear regression is fit to the data points on the graph of “ $\ln[\beta(da/dT)]$ ” versus “ $-1/T$ ”. The apparent activation energy of E is calculated by the line slope. Figure 9 shows E of the four CWSs when the conversion ratio reached 40 %. The E of four CWSs of BRYM, BR1, BR2, and BR3 decreases from 103 to 41, 101 to 38, 95 to 35 and 104 to 39 kJ/mol when D from 2.24 to 2.38, 2.31 to 2.47, 2.26 to 2.37 and 2.30 to 2.41 respectively.

As shown in Figs. 8 and 9, the ignition temperature of modified CWSs increases compared with the origin one and the modified CWS (BR1 and BR3) apparent activation energy are larger than BRYM, so the modified CWSs (BR1 and BR3) are not easier to be ignited than the raw CWS. The reason may be explained as the follows.

The release of CO_2 , CH_4 , carboxyl oxygen from raw coal and aliphatic hydrocarbon detached from raw coal results in low carbon and hydrogen content in pyrolysis

processing. The oxygen-containing functional groups decompose and macromolecular structure breaks with the pyrolysis temperature increasing. Decreasing volatile matter will cause the oxygen and hydrogen elements decrease sharply, but the carbon exists with a relatively stable aromatic carbon and these compounds are originated from the cleavage of covalent $\text{C}=\text{C}$ bonds interconnecting bicyclic aromatic rings. As shown in Fig. 3a, b, the band ratio between 3000 and 3500 in modified coals becomes bigger than the original one. The change of oxygen-containing functional groups in modified coals make their surface structure complex, and the spatial distribution of the network pore structure become more complex which will form a three-dimensional surface. The three-dimensional trends are favorable to the particle surface in contact with oxygen, then the modified CWS are easier to be ignited than the raw CWS.

By simple thermal drying at the temperature of 100–110 °C, moisture gets slowly accumulated on the dried surface of brown coal, while the pores and micropores are not destroyed, and their physical structures are not been altered during the stage. The total content of carboxylic acid functionality is more than that of the matured coals and most of the functionalities are in reactive form, which can be decomposed below 400 °C (Mukherjee et al. 2004). During the stage of decarboxylation, an elimination reaction occurs very smoothly if a moderately good electron acceptor adjacent to the carboxyl exists. Conclusively, almost all the chemical changes can cause the change of the apparent activation energies of coals.

4 Conclusions

The complicated nonlinear porosity structure of coal particles is greatly related with the properties of CWS. It is estimated by the Avnir equation that the effects of surface fractal structures in different CWS samples have good correlations with the properties of CWS.

- (1) The pore fractal dimensions, specific surface areas and pore volumes of raw brown coal and modified coals all go up with the increase of grinding time and the decrease of average particle sizes. All the apparent viscosities increase with the increase of D while the increasing acceleration is gradually enlarged with the decrease of shear rates. On the whole, the rheological behavior of the CWS prepared from coal with low D is better than that of CWS prepared from coal with high D .
- (2) The porosity structure and reactivity of the modified coals change due to the physical and chemical changes occurring in the different modification

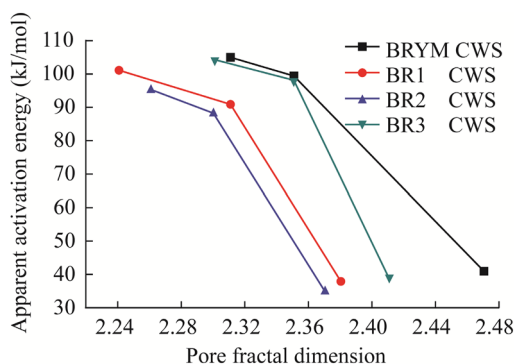


Fig. 9 Apparent activation energies of three ultrafine CWSs

processing. The ignition temperature and the peak temperature of modified coals obviously decrease with the increase of D . The above results indicate the modified CWSs easier to be burnt compared with the raw CWS. On the other hand, the apparent activation energies of the three modified CWSs all decrease with increasing value of D . The main reason lies in the larger interface area between coal particles and faster diffusion rate of O_2 . It can be clearly predicated that the pore fractal structures greatly affect the combustion dynamics of the modified CWSs and D is more efficiently quantificational for the indication of the relationship between pore structure and CWSs properties.

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