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Research article

Fractal characteristics of pore structures in 13 coal specimens: Relationship among fractal dimension, pore structure parameter, and slurry ability of coal

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ABSTRACT

The fractal characteristics of pore structures in 13 different coal specimens were investigated. Insights into the relationship among fractal dimension, pore structure parameter, and slurry ability of coal were provided. N_2 adsorption/desorption at 77 K was applied to analyze the pore structure of coal. Two fractal dimensions, D_1 and D_2, at relative pressures of 0 to 0.45 and 0.45 to 1, respectively, were calculated with the fractal Frenkel–Halsey–Hill model. Results reveal that the value of D_1 is mainly affected by the influence of meso- and macro-pores with an average pore size range of 10 nm to 220 nm on the specific surface area; therefore, D_1 can be utilized to quantitatively describe the surface roughness of these meso- and macro-pores in coal. Meanwhile, the value of D_2 is mainly related to the effects of fine mesopores with an average pore size range of 2 nm to 10 nm on the total pore volume; therefore, D_2 can be utilized to quantitatively describe the volumetric roughness of these mesopores in coal. D_1 has no apparent linear correlation with the pore structure parameters and maximum solid loading of coal, and D_2 has a positive linear correlation with the specific surface area and total pore volume of coal. The increase in specific surface area, total pore volume, and D_2 has negative effects on the slurry ability of coal. High-rank coals with high ash content and low volatile matter relatively have higher D_1 and lower D_2. Meanwhile, with increasing coal rank, D_2 has a decreased trend. The fine mesopores with an average pore size range of 2 nm to 10 nm in coal have direct effects on the pore structure parameters and D_2 of coal; thus, the slurry ability of coal may be improved if the number of these mesopores in coal is reduced by modification processes, such as microwave irradiation, hydrothermal treatment and so on.

1. Introduction

The development of large-scale, high-temperature, and high-pressure coal water slurry (CWS) gasification technology is beneficial to the staged conversion and classification utilization of coal resources. As a type of clean coal-based liquid fuel, CWS has a great prospective application in industrial coal gasification. CWS is prepared with pulverized coal, water, and additives and is a highly concentrated and heterogeneous liquid–solid suspension [1–3]. Currently, CWS is widely utilized in China as liquid fuel and a gasification material, and the representative devices are the CWS boiler developed by Zhejiang University and the gasifier developed by Texaco, respectively [4,5]. The slurry ability of coal is mainly affected by its physicochemical properties, including coal rank, chemical compositions (e.g., inherent moisture, oxygen-containing functional group, and ash), pore structure [e.g., average pore diameter (APD), specific surface area (SSA) and total pore volume (TPV)], surface characteristics (e.g., wetting properties, Zeta potential, and contact angle), and particle size distribution [6–11]. Moreover, the additives employed as dispersants or stabilizers in CWS can also improve the slurry ability of coal [12–14].

Coal is a carbon-based organic solid material and contains many different inorganic mineral impurities. Coal is structurally heterogeneous, porous, and amorphous. The surface morphology and pore structure of coal are complex and irregular because coal contains different pore structures, such as cracks, capillaries, and open and closed pores. The physical characteristics of coal (i.e., mechanical, adsorption, wetting, and permeation properties) as well as the migration of the reactant and product during coal processing and utilization (e.g., modification and dehydration of lignite, combustion, pyrolysis, and gasification of coal) are affected by its complicated surface morphology and pore structures. Moreover, the surface morphology and pore structure of coal have important effects on its slurry ability. Therefore, accurately and quantitatively describing the surface morphology and pore structure of coal is important in industrial application. However, traditional Euclidean geometry fails to analyze the irregularity and disorder of surface morphology and pore structure because of its limitations in theory. Numerous studies [15–20] have demonstrated that because the surface morphology and pore structure of coal have the property

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of self-similarity for a certain range of scales, fractal geometry is a powerful and reasonable tool that can be used to describe their irregularity and disorder. Different methods can be applied to calculate the fractal dimension of coal; these methods include gas adsorption, small-angle X-ray scattering, mercury porosimetry, image analysis, and small-angle neutron scattering [21–27]. Gas adsorption is widely utilized to analyze the fractal characteristics of coal because it is simple and convenient [28–31].

Over the past several decades, fractal geometry has been applied to study the irregularity and disorder of coal. Bale et al. [32] applied fractal geometry to the study of the pore structure of Beulah lignite and to the calculation of surface fractal dimension. Zhang et al. [30] applied the Frenkel–Halsey–Hill model to analyze the fractal characteristics of 58 types of coal from 14 mining areas. Based on the results, they concluded that the fractal dimension should be calculated with adsorption data when capillary condensation controls the adsorption process. Coal rank and maceral content have obvious effects on the surface fractal dimension of coal; they decrease with increasing carbon and hydrogen contents and decreasing ash yield ratio. Mercury porosimetry and gas adsorption were employed by Wang et al. [31] to investigate the pore structure and fractal characteristics of differently ranked coal specimens. They found that the fractal dimensions of seepage and adsorption pores increase with increasing coal rank, thereby indicating that coalification makes the pore structure more complex and the pore surface rougher. Liu et al. [33] obtained the surface and pore fractal dimensions of super-fine pulverized coal particles through N_2 adsorption and small-angle X-ray scattering. The results showed that the surface fractal dimension increases with the increase in pulverized coal particle size, and the pore fractal dimension increases with the decrease in average pore diameter (APD). By analyzing the fractal dimensions of coal particles, they concluded that super-fine pulverized coal particles are good for coal combustion. Overall, fractal geometry provides a new method and perspective in studying the effects of the surface morphology and pore structure of coal on its processing and utilization.

Several researchers focused on the relationship between the fractal characteristics and slurry ability of coal and obtained useful conclusions. Cheng et al. [9] studied the effects of the fractal dimensions of three ultrafine CWSs on the rheological behaviors and combustion dynamics. They observed that with decreasing particle size, the SSAs and fractal dimensions of CWSs increase, resulting in an increase in apparent viscosities and a decrease in ignition temperatures and apparent activation energies. They calculated the fractal dimensions of 10 types of coal and discussed the effects of fractal dimension, moisture content, oxygen content, and grindability on CWS properties [34]. Results showed that with increasing fractal dimension, SSA and pore volume increase; therefore, the maximum solid concentration of CWS decreases, and apparent viscosity increases. The increase in fractal dimension, moisture content, and oxygen content and the decrease in grindability are harmful to CWS properties. However, according to our previous study and other references [25,28,30,35], because the pore structure of coal is highly complicated, applying piecewise linear fitting to the calculation of fractal dimensions is necessary to reveal the real fractal characteristics of coal. Moreover, the coal-forming conditions of coal from different areas are significantly different, resulting in the difference in the pore structure of coal. Therefore, investigating the fractal characteristics of different coal is necessary.

The pore structure and fractal characteristics of 13 coal specimens from the Permian geologic era were studied through low-temperature nitrogen adsorption, and the piecewise linear fitting method was employed to calculate their fractal dimensions. The relationship among fractal dimensions, coal properties and slurry ability of coal was discussed. The aim is to determine the relationship among fractal dimension, pore structure parameter, and slurry ability of coals from the Permian geologic era and thus provides a new method and approach in investigating the fractal characteristics of coal and improving its slurry ability.

2. Experimental

2.1. Material

The 13 coal specimens utilized in this study are as follows: Shenhua (SH), Xuzhou (XZ), Datong2# (DT2), Huangling (HL), Lianyungang (LYG), Yanzhou (YZ), Pingdingshan (PDS), Australia (AZ), Datong1# (DT1), Xiyang (XY), Tianchi (TC), Shigang (SG), and Xiaotun (XT). The coal samples were ground in a bowl mill and sieved to <74 μm.

2.2. Methods

2.2.1. Preparation and determination of CWS properties

CWSs were prepared by mixing coal powder, deionized water, and an additive (0.8 wt% based on air-dried coal powder weight). CWS apparent viscosity was measured with a rotational viscometer (NXC-4C, Chengdu Instrument Factory, China). Details of the CWS preparation and determination of CWS properties can be found in reference [36]. Maximum solid loading (MSL), which is defined as the solid content of CWS with a viscosity of 1000 mPa s at a shear rate of 100 s^{-1}, was applied to the appraisal of the slurry ability of CWS. High MSL of CWS means good slurry ability [37,38].

2.2.2. Low-temperature nitrogen adsorption experiment

An automatic surface area and pore analyzer (TriStar 3020, Micromeritics, USA) was employed to determine the pore structure of coal. N_2 gas adsorption/desorption isotherms at 77 K were measured for relative pressure (P/P_0) ranging from 0.01 to 0.99. The multipoint Brunauer–Emmett–Teller method was applied to calculate SSA. Pore size distribution was determined according to the Barrett-Joyner-Halenda method.

2.2.3. Calculation of fractal dimension

According to the fractal Frenkel–Halsey–Hill model, the fractal dimension can be calculated with the formula [16,39]

$$\ln\left(\frac{V}{V_0}\right) = C + A\left[\ln\left(\ln\frac{P_0}{P}\right)\right], \tag{1}$$

where V is the volume of the gas adsorbate at equilibrium pressure P, V_0 is the volume of gas in the monolayer, P is the gas equilibrium pressure, P_0 is the saturation pressure of the gas, A is a power-law exponent that is dependent on D and the mechanism of adsorption, and C is the constant of gas adsorption. The value of A can be calculated by plotting the gas adsorption isotherm data in terms of ln V versus $\ln(\ln(P_0/P))$. The slope of the straight line should be equal to A. Fractal dimension D can be calculated with two different formulas: $A = (D - 3)/3$ and $A = D - 3$. However, fractal dimensions calculated with $A = (D - 3)/3$ are usually <2, and this value is beyond the definition of fractal dimension, whereas fractal dimensions calculated with $A = D - 3$ are in the range of 2 and 3 [30]. Therefore, fractal dimension D is calculated with $D = 3 + A$.

3. Results and discussion

3.1. N_2 gas adsorption/desorption isotherms

Fig. 1 shows that the adsorption isotherms of the 13 coal specimens exhibit a type IV with H3 type hysteresis loop based on the classification method proposed by International Union of Pure and Applied Chemistry (IUPAC), thus indicating the existence of mesopores in coal [40,41]. Although the isotherms of the different coal specimens have different shapes, these coal specimens can be classified into three groups according to the similarity in hysteresis loop. Group A includes SH, XZ, and YZ, and their hysteresis loops are wide and conspicuous. Group B includes DT2, HL, LYG, PDS, and AZ, and their hysteresis loops are narrow.