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Full Length Article

Porosity changes in progressively pulverized anthracite subsamples: Implications for the study of closed pore distribution in coals

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ABSTRACT

Coal samples for low-pressure nitrogen (N_2) adsorption measurement in previous work cover a large particle size range (from 0.075 to 4.75 mm). However, minimal attention has been paid to the effect of coal particle size on pore structure using gas adsorption methods. Anthracite coal collected from the Zhina Coalfield, China, was crushed, subsampled, and sieved to eight particle size ranges: 1–2 mesh (8000–25400 μm), 40–50 mesh (270–380 μm), 50–70 mesh (212–270 μm), 70–90 mesh (160–212 μm), 90–160 mesh (96–160 μm), 160–200 mesh (75–96 μm), 200–300 mesh (48–75 μm), and > 300 mesh (< 48 μm). The adsorption–desorption isotherms of each subsample were measured using N_2 at 77.35 K to compare differences in pore structure characteristics. The results of the N_2 adsorption tests show that particle size has a significant effect on pore volume, specific surface area, and pore size distribution of coal. Specifically, decreasing coal particle size results in continuous increase in macro- and mesopore volumes and specific surface areas. This can be attributed to the fact that smaller-sized coal particles open more of the previously closed pores, which are then accessible to adsorping gas. The contribution of closed pores to the total pore volume is 94.94% in the pore aperture range of 3.1–370 nm. The volume of closed macropores varies from 48.96 to 84.69% of the total closed pore volume. According to optical microscope and SEM observations of the Zhina Coalfield subsamples, massive gas pores exist in an isolated form with poor connectivity; some plant tissue pores are filled by pyrites and clay minerals, and may be totally occluded. Thus, gas pores contribute the dominant amount of the closed pore volume. In addition, different Zhina Coalfield subsamples show varied hysteresis loop shapes, indicating that closed pores in coal possess a variety of pore morphologies and sizes. To improve the accuracy and comparability of the pore structure of coal, we propose > 300 mesh as the preferred particle size of coal for all low-pressure N_2 adsorption measurement in future work. Furthermore, caution must be used in evaluating coal bed methane resource recovery potential as coal possesses high closed porosity; failure to account for this will result in an overestimation of the amount of gas that can be recovered from coal seams during production.

1. Introduction

Pore characteristics include volume, specific surface area, genetic type, and size distribution. The International Union of Pure and Applied Chemistry (IUPAC) divides pores into three subtypes: micropore ($d < 2$ nm), mesopore ($2\text{ nm} \le d \le 50$ nm), and macropore ($d > 50$ nm), where d is the pore aperture or diameter [1]. Coal is a chemically and structurally heterogeneous material with a complex pore structure characterized by a broad pore size distribution (PSD) [2]. Porosity plays a key role in all aspects of coal development and utilization, such as coalbed methane (CBM) extraction, gasification, beneficiation, combustion, liquefaction, and production of activated carbon, metallurgical coke, and carbon molecular sieves as well as geological sequestration of carbon dioxide [3,4].

The nature and structure of coal pores has been discussed in the literature for at least sixty years now [3,5,6]. Bond [5] proposed a

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physical structure model for coal, in which pores were interconnected by a maze of narrow capillary constrictions (tortuous tubes) and connected to the coal external surface. This model was challenged by Mahajan [3] and Larsen and Wernett [6], who suggested that a significant proportion of pores in coal may not be connected to the external coal surface and are inaccessible to gas and fluids. Further research on closed pores in coal is ongoing. Alexeev et al. [7] verified the existence of closed pores in coal and concluded that the contribution of closed pores to total pore volume exceeds 60% in most cases (> 80% for anthracite). He et al. [8] concluded that the volume of closed pores varied from 13 to 36% of the total pore volume and that the volume fraction of closed pores shows no correlation to the maceral composition. Cai et al. [9] found that the closed porosity is generally no less than 40% of the total porosity for the high rank coal, and no less than 30% for middle and low rank coal. Pan et al. [10] demonstrated that closed pore volume increases and its contribution to the proportion of the total porosity decreases with increasing mechanical deformation. Niu et al. [11] concluded that the closed pore volume shows a tendency of first increasing, then decreasing during coalification. This is caused by the appearance of massive gas pores generated by pyrolysis of organic matter (pyrolysis effect). Currently, the consensus is that coals contain both open pores, connected to an external surface, and closed pores, not connected to an external surface.

Low-pressure nitrogen (N_2) adsorption is a widely used method to determine pore volume, specific surface area, and PSD of coal and other carbonaceous materials [2,12–15]. However, the N_2 adsorption method has its own limitations. It can only provide information regarding open porosity as N_2 can only enter the open pores and not the closed pores [4,8–10].

Experimental evidence demonstrates that coal porosity and PSD are controlled by a variety of factors, including coal maceral composition and coal rank. As coal rank increases, the volume of macropores decreases, whereas the volume of micropores increases significantly [2,14,16,17]. Vitrinite predominantly contains micropores, whereas inertinite predominantly contains meso- and macropores [17–21]. Coal porosity is also related to the mineral matter content, and the presence of mineral matter reduces coal porosity [17,20,21].

Minimal work has been performed on the effect of particle size on pore structure and porosity of coal by gas adsorption methods. The particle size range of coal samples used in low-pressure N_2 adsorption experiments in previous works is variable. For example, the following particle sizes have been recorded and studied: 0.150–0.180 mm [22], 0.212–0.380 mm [2], ~0.15 mm [23], 0.23–0.45 mm [12,24], ~0.25 mm [13,17,25,26], ~4.75 mm [25], 0.18–0.25 mm [15,27,28], and ~0.075 mm [14]. These studies determined the total pore volume in coals by gas adsorption methods, taking into account only the open pores and neglecting the contribution of closed pore volume for various particle sizes of the tested coals.

The purpose of the current study is to investigate the effect of particle size on the porous structure of coal. In this study, a coal sample, collected from Upper Permian Longtan Formation in the Zhina Coalfield, Southwestern China, was prepared by crushing and sieving to sizes of 1–2 mesh, 40–50 mesh, 50–70 mesh, 70–90 mesh, 90–160 mesh, 160–200 mesh, 200–300 mesh, and > 300 mesh. Low-pressure N_2 adsorption measurements with varying particle sizes of coal subsamples were carried out to obtain information about the effects of variations in pore characteristics. The pore variables tested include volumes and specific surface areas of mesopores and macropores, and PSD. Furthermore, the relationship between closed pore volume and coal particle size is investigated.

2. Samples and analysis

2.1. Sample collection

Guizhou Province, located in Southwest China (Fig. 1), has the highest potential for CBM extraction in Southern China. The main coal-bearing strata in this region are the Upper Permian Longtan and Changxing Formations (Fig. 2). A fresh coal sample was collected from the No. 27 coal seam in the Upper Permian Longtan Formation in the Zhicheng coal mine, Zhina Coalfield, western Guizhou Province (Fig. 1). The selected sample was a 4 kg block of tectonically undeformed coal, which was carefully packed and dispatched for analysis.

2.2. Analytical procedures

2.2.1. Coal sample preparation

Prior to the N_2 adsorption measurement, the raw coal was crushed and then sieved into eight different particle size subsamples: 1–2 mesh, 40–50 mesh, 50–70 mesh, 70–90 mesh, 90–160 mesh, 160–200 mesh, 200–300 mesh, and > 300 mesh. After crushing these subsamples were stored in sealed bags to avoid oxidation.

For microscopic analysis by reflected light, the sample was prepared following the American Society for Testing and Materials (ASTM) Standard D2797-04. Prior to the maceral analysis, the raw coal was crushed to a maximum particle size of 1.0 mm (18 mesh size), embedded in epoxy resin, and polished.

2.2.2. Testing methods

2.2.2.1. Coal rank and coal quality analyses. The mean maximum vitrinite reflectance (%$R_{o,max}$) of the polished coal sample was measured using a Leitz MPV-III photometer system following ASTM Standard D2798-05. Following reflectance measurements, maceral analyses were undertaken using the point counting method based on ISO 7404-3 (2009). A total of 500 points per sample were counted at a stage interval of 1.0 mm under white light using a magnification of ×500. Proximate and ultimate analyses were performed on the coal sample following the ASTM standards D3172-13 and D3176-15, respectively. The analytical results are given in Table 1.

Table 1 lists the coal sample analysis data, including the maceral, proximate, and ultimate analyses, and coal vitrinite reflectance. The mean maximum reflectance value of vitrinite ($R_{o,max}$) is 2.95% and the volatile matter yield (V_{daf}) is 8.44%, which indicates that the coal belongs to anthracite. The carbon, oxygen, hydrogen, and nitrogen contents are 90.62%, 3.92%, 3.14%, and 1.20%, respectively. The ash yield (A_{ad}) of the coal is 14.16%, and its moisture content (M_{ad}) is 1.84%.

2.2.2.2. Particle size measurement. The particle size distributions of the crushed and sieved coal subsamples were measured using a laser diffraction particle size analyzer (Model LS 100Q, Beckman Coulter, USA) for a size range of 0.375–948.3 μm. The distribution of particle size is expressed as the percentage of each size by volume yielding a distribution curve where the total area under the curve represents the total particle volume (sums to 100%) [29]. The characteristic diameters including the median diameter (d_{50}) and boundary diameters (d_{10}, d_{90}) were used to express the particle size distribution. The numbers (i.e., 10, 50, and 90, respectively) in d_{10}, d_{50}, and d_{90} stand for the cumulative volume percentage of particles below the specified diameters. Fig. 3 shows the particle size distributions of these coal subsamples for different particle sizes. As shown in Table 2, subsamples ZCK2, ZCK3, ZCK4, ZCK5, ZCK6, ZCK7, and ZCK8 correspond to the sizes of 40–50 mesh, 50–70 mesh, 70–90 mesh, 90–160 mesh, 160–200 mesh, 200–300 mesh, and > 300 mesh, respectively, with the median diameters of 668.1 μm, 438.1 μm, 292.2 μm, 182.0 μm, 103.9 μm, 76.97 μm, and 31.31 μm, respectively. Thus, the median diameters decrease with increasing sieve mesh number.

2.2.2.3. Low-pressure N_2 adsorption. Low-pressure N_2 adsorption measurements were conducted on an Autosorb-iQ surface area and porosity analyzer (Quantachrome Instruments, USA). Prior to adsorption analyses, all subsamples were dried at 105 °C for 12 h to remove moisture in a constant temperature drying oven. Subsamples