



Fractal and pore structure analysis of Shengli lignite during drying process

Jiewu Tang, Li Feng^{*}, Yajun Li, Jie Liu, Xiangchun Liu

Key Laboratory of Coal Processing and Efficient Utilization of Ministry of Education, School of Chemical Engineering and Technology, China University of Mining & Technology, Xuzhou, Jiangsu, 221116, China

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ABSTRACT

Pore structure is one of the key factors that influence the dewatering, burning and conversion of lignite. In this study, the pore structure variation and fractal dimension of Shengli lignite in the drying process (150 ~ 500 °C) were investigated. The pore structure of lignite samples, including specific surface area, average pore diameter and pore shape etc., were obtained by N₂ adsorption/desorption at 77 K. And two fractal dimensions D₁ and D₂ were calculated using the Frenkel-Halsey-Hill (FHH) method at relative pressures of 0 to 0.5 and 0.5 to 0.95, respectively. The results show that the general pore structure of lignite samples varies slightly in the drying process. Mesopores are mainly the open cylindrical pores and cracks pores, and micropores are mainly one dead end pores. The pore size distribution of mesopores is unimodal, and that of micropores appears to be multimodal. The variation trend of specific surface area is opposite to that of average pore diameter in the drying process. And before the drying temperature reaches 300 °C, the specific surface area, average pore diameter and mesopore volume show a “V” shape variation trend. The evolution mechanisms of pore structures during process mainly included moisture evaporated, pore shrinkage and decomposition of functional groups. The changes in D₁ were similar to those in specific surface area of mesopores development, reflecting the roughness of mesopore surface. The variation trend of D₂ and micropore volume tends to be the same, indicating the volumetric roughness of micropore. And the analysis of scanning electron microscope images of processed lignite, indicating that FHH modal is suitable to describe the pore structure change of lignite in the drying process.

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1. Introduction

Lignite, a multi-phase porous low-rank coal, plays an important role in the energy field [1–3]. As is known, high water content is the bottleneck of lignite utilization. It is the main barrier to the thermal efficiency of lignite in the process of power generation [4,5], 20–25% energy is wasted to remove the water in lignite. Under such a circumstance, it is imperative that some rational drying process should be employed to improve the utilization efficiency of lignite. However, the pore structure of lignite after drying is very complicated [6], which not only influences its physical properties such as mechanical and adsorptive properties, but also the energy transfer and reactivity in the process of burning [7]. Therefore, it is of great significance to study the pore structure of lignite after drying which lays the very foundation for the subsequent transformation and utilization. The conventional Euclidean geometry [8], however, cannot describe the surface morphology of irregular objects accurately and quantitatively, not to mention the evolution and surface features of the pore structure of lignite after drying.

Consequently, a proper theory or method is needed to describe the pore structure of lignite after drying accurately and quantitatively.

Gas adsorption is the classic method to study the pore structure. Gas adsorption generally includes two specific methods, which are low-temperature (77 K) N₂ adsorption and CO₂ adsorption method at room temperature (298 K). Comparatively speaking, low-temperature N₂ adsorption is more widely used since chemical adsorption is more unlikely to happen for N₂ due to its chemical inertness [9]. In recent years, great efforts have been made on the research of pore structure by means of N₂ adsorption, but the focus of these efforts is mainly placed upon some parameters of pore structure. For example, Nie [10] explored the pore structure characteristics of different low-rank coals by means of scanning electron microscopy (SEM) and low-pressure N₂ adsorption. They analyzed the pore size distribution of coal samples and concluded that the pore size distribution of mesopore is multimodal, and that of micropore appears to be unimodal. Zhang [11] analyzed the variations of pore structure parameters such as the porosity, pore size distribution and specific surface area in the heating process of calcium-enriched bio-oil. The result indicated that when the temperature is between 450 and 600 °C, the specific surface area, total pore volume and average pore size all tend to decrease; when the temperature exceeds 700 °C, the specific surface area and pore volume begin to increase.

^{*} Corresponding author.

E-mail address: cumthgf163.com (L. Feng).

Han [12] analyzed the change of shale pore structure in the process of heating. The results show that the pore volume and specific surface area increase as the temperature rises. From these researches it can be concluded that N_2 adsorption method can represent the change of pore structure in the process of treatment. However, it fails to represent the roughness of pore surface and pore structure on its own which determines the adsorption capacity of porous materials to some degree [13]. Therefore, other theories and methods are needed to make a comprehensive study.

The fractal geometry theory is used to describe the roughness of irregular complex pore structure. The definition and application of fractal is put forward by Mandelbrot in 1982 [14]. Since then, it is widely employed. Hausdorff fractal dimension (D) is generally used to describe the pore fractal characteristics. For porous materials, the value of D is between 2 and 3: if the value of D is 2, it means the surface is smooth; if the value of D is 3, it means that the surface is rough. Therefore, the bigger the value of D is, the rougher the surface is; and conversely the smaller the value of D is, the smoother the surface is. D can be determined by means of SEM method, X-ray method, and gas adsorption method [15–17]. Gas adsorption method is more widely used compared with the first two [18]. Recently, fractal theory has been widely employed. Song [19] explored the change of the surface roughness of lignite when treated with alkali liquor under the guidance of fractal theory. The results show that D increases as the density of alkali liquor rises and the surface of lignite sample tends to be rougher. Liu [20] studied the relationship between D and the adsorption capacity of eleven coal samples to methane. The results show that coalification makes coal surfaces and pore networks comparatively smoother and more regular for lower rank coals ($V_{daf} > 15\%$), but rougher and more complex for higher rank coals. This justifies the difference in D and adsorption capacity to methane. Xu [21] analyzed the change of pore structure of coal samples in the heating process of 950–940 °C. The results indicate that two different adsorptions exist in the coal samples, reflecting two different fractal characteristics. All the above studies indicate that fractal theory is beneficial to the researchers in terms of the relationship between pore structure and function or the change of pore structure in the process of treatment. However, the change of pore structure differs when the coal samples are treated with different upgrading methods. Besides, rare efforts have been made on the research of the relationship between D and micropore or mesopore structure.

Dewatering technology has been the highlight of lignite upgrading research [22,23]. But most efforts have been focused on the change of oxygen-containing functional groups and water-holding capacity when lignite samples are dewatered [24,25]. Quite rare efforts have been made to study the relationship between pore fractal characteristics and pore structure of lignite sample in the drying process. In this paper, by means of low-temperature N_2 adsorption/desorption, SEM and fractal theory, the change of pore structure and the mechanism of the change are analyzed in the drying process. Meanwhile, the pore fractal characteristics are studied to establish the relationship between pore structure and D of the lignite samples, which provides theoretical reference for the subsequent transformation and utilization of dried lignite.

2. Experiments and methods

2.1. Material

The lignite sample in this experiment was taken from Shengli mine, Inner Mongolia, China. The lignite sample was crushed with a crusher at firstly, and screened with plansifter under 80 meshes, then it was sealed up for the use of subsequent experiments. The proximate analysis and ultimate analysis of the lignite was shown in Table 1.

Table 1

Proximate and ultimate analyses of the lignite.

Sample	Proximate analysis w/%				Ultimate analysis w daf/%				
	M_{ad}	A_d	V_{daf}	FC_{daf}	C	H	N	S	O ^a
SL	10.91	25.57	45.86	25.57	65.71	4.92	1.26	2.42	25.69

^a By difference.

2.2. Experimental methods

2.2.1. Drying (150 °C–500 °C) experiments

Drying experiments were conducted in the tube furnace (made in China, Electric Furnace Model: OTL-1200, Voltage Rating: 220 V, Power Rating: 3.5 kW, Temperature Rating: 950 °C, Program Controller Model: TCW-32B). Firstly, lignite sample (0.7 g, as received basis) was put it in the cupel; then the cupel was placed into tube furnace. Secondly, turn on the mass flow controller of the cylinder where N_2 is stored and let N_2 flow into the furnace slowly for 2–3 min before the drying experiments begin so as to vent the air out of the furnace. The technical parameters in the drying process were set by the program controller, at the heating rate of 5 °C/min, the lignite sample was dried for 2 h at the constant temperature of 150 °C, 200 °C, 250 °C, 300 °C, 350 °C, 400 °C, 450 °C, and 500 °C, respectively, which were recorded as SL150, SL200, SL250, SL300, SL350, SL400, SL450, and SL500. Let the lignite samples cool down to room temperature in the tube furnace; then took the samples out and keep them under seal for the subsequent analyses. The schematic illustration of the drying device employed in the experiment is shown in Fig. 1.

2.2.2. N_2 adsorption/desorption experiments

The BEL-Max Automatic Specific Surface Area/Pore Analyzer manufactured by BEL Company of Japan was employed to conduct the analysis. About 0.7 g lignite sample was put into the sample tube, which in turn was degassed under vacuum condition at the temperature of 150 °C for 4 h; after degassing treatment, the sample tube was put in liquid nitrogen (77 K) to be analyzed. The BEL-Max Analyzer can draw out the adsorption/desorption isotherm automatically, which then can be analyzed by means of Brunauer-Emmett-Teller (BET) and Barrett-Joiner-Halenda (BJH), and Horvath Kawazoe (HK) models. Through the analysis of specific surface area (SSA), average pore diameter (APD), pore size distribution (PSD), and pore volume, including micropore volume and mesopore volume, can be obtained.

2.2.3. Calculation of fractal dimension

The fractal Frenkel-Halsey-Hill (FHH) is widely acknowledged to be the simplest and most effective method to describe the irregular and complex pore structure [26,27]. Fractal dimension (D) can be calculated

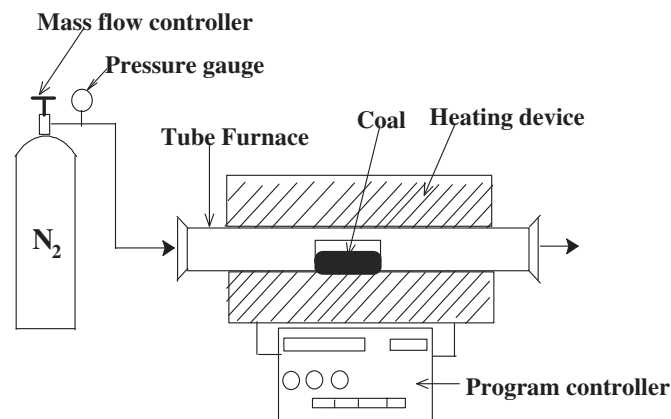


Fig. 1. Schematic illustration of the Tube Furnace drying experimental.

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