

Experimental Study of Micropore Size Distribution in Coals

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Abstract. In this paper, the experimental study of the micro-pore structure and distribution of the long flame coal mined in Hami, is carried out. The distribution of the pore size, the pore volume and specific surface area of all kinds of pore in the sample coal is measured, by BET static nitrogen adsorption technique, and the results are analysed. The results show: There are continuous sizes of pores, and no upper limit of pore size, in the sample coal. In smaller size pore range of the sample coal, micro-pore structures are mostly pores with one end closed, and are scarcely pores with two ends opened. The pores in 2~100nm size range have a higher percentage, and the pores in 2~100nm size range have strong distribution intensity and concentration, in the sample coal. Low temperature pyrolysis has little influence on the microscope structure of the pores, for the pores less than 500nm pore size.

Keywords: long flame coal, micropore structure, specific surface area, pore size

1. Introduction

Coal is a complex polymeric material with a complicated porous structure. The pore size, pore volume, surface area and gas-specific sorption characteristics of the coal, these parameters of the pore can control adsorption capacity for gases such as methane and carbon dioxide. Because of that, the micropore size and distributions characteristics of the coal is highly important to the prediction of coal gas outbursts in coal mines, the economic recovery of natural gas from coal seams, characterization of coals as a pre-cursor for activated carbon, and CO₂ sequestration using CO₂ injection[1][2].

Various methods have been used to study the micro-pore structure of coals, in particular, the pore size distribution and specific surface area. Nitrogen adsorption are commonly used to quantify these parameters. Gan et al. demonstrated that pore volume distribution is dependent upon the rank of coal. In the Gan et al. [3][4], study, total pore volumes were divided into: micropores (0.4–1.2 nm), transitional pores (1.2–30nm), and macropores (30–2960nm). The current study utilizes the IUPAC classification[5][6]. Lower-rank coals (carbon content < 75%, brown coal and long flame coal) contain mainly macropores, coals in the 76–84% fixed carbon content range contain mainly micro-pores and transitional pores, and high rank coals (carbon content > 84%) contain mainly micropores. For the lower-rank coals, the pore diameters smaller than 100 nm, have an important role in adsorbed-gas storage and migration.

In this paper, the characteristics of the micro-pore structure and distribution of the long flame coal mined from Hami, are studied. The pore size measured ranges from 0nm to 500nm, for the coal samples. The results will be used as the theoretical foundation to develop and utilize the long flame coal.

2. Method of experiment

The coal samples are the long flame coal mined in Hami. The coal samples are prepared by sieving to a top size of 3mm. No.1 coal samples are raw coal particles. No.2 coal samples are drying at the air temperature of 293°C for 30s in the constant temperature drying oven. Before the experiment, Both No.1 and No.2 coal samples have been put into the constant temperature drying oven, and heated for 3 hours, at the air temperature of 110°C.

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The micro-pore structure, the distribution of the pore size, pore volume and specific surface area of all kinds of pore in the coal samples, are measured by BET static nitrogen adsorption technique, using surface area and pore size analyzer. The relative pressure of the nitrogen gas ranges from 0.05 to 0.35. The pore size measured ranges from 0 nm to 500 nm, for the coal samples.

3 Analysis of experiment results

3.1 Specific surface area and pore volume

Table1. Structure parameters of pores of NO.1 coal samples

Structure parameters of pore	BET mono-layer	BET multi-layers	BJH adsorption	BJH desorption
Specific surface area (m ² /g)	2.268	2.327	2.495	2.234
Total pore volume (cm ³ /g)	0.008		0.00863	0.00847
Average pore diameter (nm)			13.838	15.163
Utmost pore diameter (nm)			1.992	2.528
Average pore diameter of adsorption (nm)	14.601			

Table2. Structure parameters of pores of NO.2 coal samples

Structure parameters of pore	BET mono-layer	BET multi-layers	BJH adsorption	BJH desorption
Specific surface area (m ² /g)	2.115	2.168	2.529	2.054
Total pore volume (cm ³ /g)	0.008		0.00820	0.00772
Average pore diameter (nm)			12.961	15.029
Utmost pore diameter (nm)			2.121	2.278
Average pore diameter of adsorption (nm)	14.724			

The adsorption and desorption characteristics of the nitrogen, the micro-pore structure, the distribution of the pore size, the pore volume and the specific surface area of all kinds of pore in the sample coals, are measured by the BET static nitrogen adsorption technique, for the pores in the ranges of 1.70 nm~300.00 nm of pore diameter in the coal sample. The structure parameters of the pores of the coal samples obtained by measuring and calculating, and be listed in the table1 and table2. The values of utmost pore diameter show that 1.9 nm~2.6 nm diameter of pore is most in all kinds of the pores. The parameters calculated by the different calculation method, are nearly equivalent each other. The pore volume of No.1 and No.2 coal samples is about 0.008 cm³ / g, and the specific surface area of No.1 and No.2 coal samples is about 2.4 (m²/g). It indicates that the coal samples have a copious quantity of micropore structure. The average pore diameter of the No.2 coal samples is less, and the pore volume is a little bigger, than the No.1 coal samples. The main cause is that the micropore structure has a slight change and a few new micropore structure formed, because of the dehydration, the thermal decomposition and the spillage of the volatile in the No.1 coal samples, being heated in short time.

3.2 Adsorption/desorption isotherms

The solids with micro-pore structure immersed in nitrogen gas, the capillary condensation of the gas should occur, as the pressure of the nitrogen gas reaches a certain level. As the pressure of the gas increasing, the diameter of the micro-pores where condensation occurring increase, adsorption and condensation process until the maximum diameter of micro-pores. Under these conditions, if the gas pressure is reduced, the nitrogen of the adsorption in the solid should be desorbed, When the pressure is reduced to the value corresponding to the size of the Kelvin diameter, the capillary evaporation will occur. For different pore structure, the occurrence of the condensation and evaporation phenomena may be at the same relative pressure, or not. If the occurrence of the condensation and evaporation phenomena are at the same relative

pressure, two branches of the adsorption/desorption isotherms overlap. If the occurrence of the condensation and evaporation phenomena are at the different relative pressure, two branches of the adsorption/desorption isotherms detach, the detachment circle of the two branches is named as hysteresis loop. The shape of the hysteresis loop represents the structure characteristics of the pores in the solid. The structure characteristics of the pores in the solid can be estimated, observing the hysteresis loop of the adsorption/desorption isotherms.

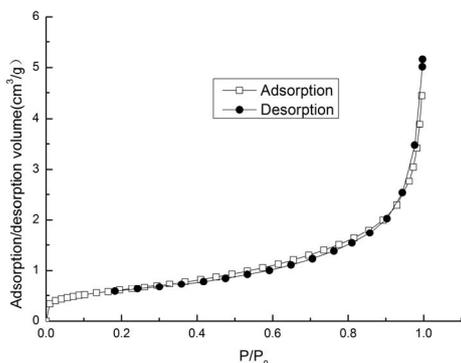


Fig.3 the adsorption/desorption isotherms for the No.1 coal samples

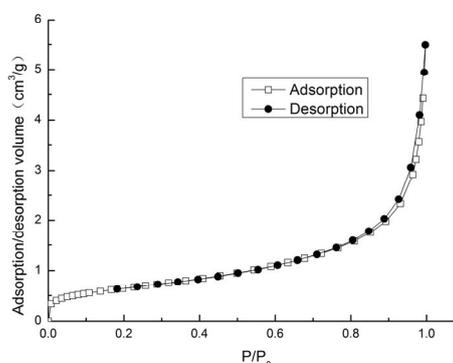


Fig.4 the adsorption/desorption isotherms for the No.2 coal samples

Fig.3 and Fig.4 represent the adsorption/desorption isotherms of the No.1 and No.2 coal samples. The characteristics of the adsorption/desorption isotherms can be seen in the figures. The adsorption/desorption isotherms of the coal samples are anti-S-shaped curves. At the relative pressure lower than 0.1, the quantity of the adsorption increases with the relative pressure gradually increasing, the adsorption/desorption isotherms form the convex shape curves.

The first half part of the adsorption/desorption isotherms is relatively gentle. With the adsorption capacity increasing slowly, the adsorption occurs on the microporous pore wall, and gradually achieves the monolayer adsorption saturation. Subsequently, the liquid nitrogen condensed wets the micropore walls, and adsorption layer thickness on the wall of the micropore increases, with the relative pressure gradually increasing. When the thickness of the adsorption layer on the micropore wall increases until the thickness corresponding critical relative pressure, capillary condensation will occur in the micropores. With relative pressure increasing, the small diameter of pore was first filled with liquid nitrogen condensed. At the same time, the diameter of pore filled with liquid nitrogen condensed increases gradually, and the thickness of the adsorption layers on the wall of all kinds of sizes of pore constantly thickens.

Therefore, in the range 0.85~0.9 relative pressure, an inflexion appears in the tail half part of the adsorption/desorption isotherms. Subsequently, with the adsorption capacity increasing rapidly, the adsorption capacity increases. This result proves there are the successive holes system structure in the No.1 and No.2 samples, no limit in pore size.

The figures show the two branches of the adsorption/desorption isotherms at low relative pressure are coincident or near coincident. It represents there are a majority of pores with one end closed, and is scarcely pores with two ends opened the No.1 coal samples. The very small hysteresis loop in the desorption/desorption isotherms, indicates that there are mainly a series of closed micropores in the No.1 coal samples.

There is a clear hysteresis loop in the adsorption/desorption isotherms at higher relative pressure, it indicates that there are open micropores, or airtight micropores, because the airtight holes have not impact to the hysteresis loop structure of the adsorption/desorption isotherms. These indicate that the long-flame coal heated in short time changes slightly in the micropore structure.

3.3 Pore size distribution curves

Fig.5 and Fig.8 detail the differential and integral curves of the pore size distribution in the process of the BJH adsorption and desorption. The figures show that larger proportion of total volume is the specific volume of the pores in the range 2~100nm diameter, and the curves close to a straight line and the larger the slope in the curves, which also shows there are the distribution of all kinds of sizes micropore, and uneven distribution in the coal samples.

The test data show that the micropore volume in the 2~50nm diameter range has 0.244% in the total pore volume, the micropore volume in the 50~100nm diameter range has 0.244% in the total pore volume, in the No.1 coal samples.

According to the pore size distribution curves of the BJH adsorption and the integral curves of the pore size distribution, we can estimate the pore diameter sizes mainly is in the 2~50nm diameter range.

According to (the International Association of Fine Applied Chemistry,IUPAC), the large holes (> 50nm); the middle hole (2~50nm); small hole (<2nm), the pore sizes of the No.1 and No.2 coal samples is mainly concentrated in the middle hole range.

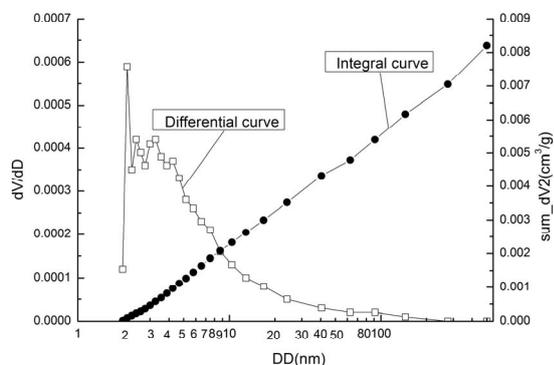


Fig.5 Pore size distribution curves of BJH adsorption for No.1 coal samples

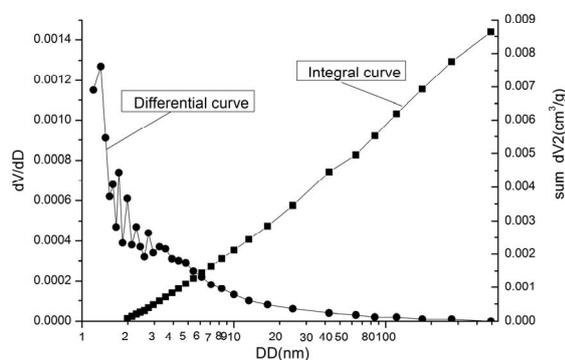


Fig.6 Pore size distribution curves of BJH adsorption for No.2 coal samples

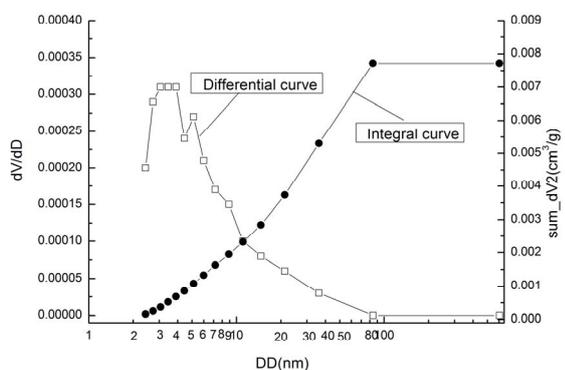


Fig.7 Pore size distribution curves of BJH desorption for No.1 coal samples

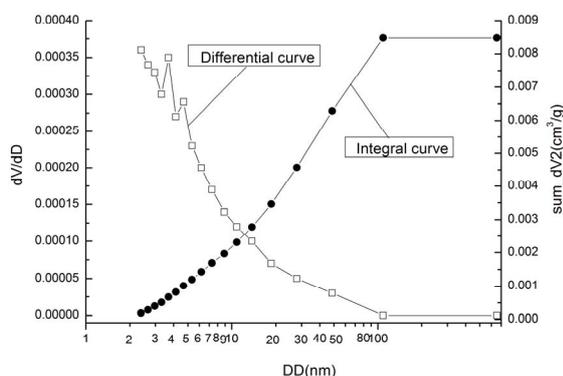


Fig.8 Pore size distribution curves of BJH desorption for No.2 coal samples

The differential distribution curves of the pore size have peak at the 2nm of pore, and the intensity and concentration of the pore size distribution is strong in the range of 2~5nm pore size, in the No.1 and No.2 coal samples. The peak width and the number is very different in the differential distribution curves, for the No.1 and No.2 coal samples. It indicates that the long-flame coal heated in short time change slightly in the pore structure.

The test data of the BJH pore size distribution of the adsorption show that the specific surface area in the 2~50nm diameter range has 0.0752% in the total specific surface area, the specific surface area in the 2~50nm diameter range has 88.5% in the total specific surface area, the specific surface area in the 50 ~ 100nm diameter range has 2.25% in the total specific surface area, in the No.1 coal samples.

The specific surface area in the 2~50nm diameter range has 0.0752% in the total specific surface area, the specific surface area in the 2~50nm diameter range has 88.6% in the total specific surface area, the specific surface area in the 50~100nm diameter range has 2.3% in the total specific surface area, in the No.1 coal samples.

There are little distinction between the No.1 and No.2 coal samples in the micro-pore. The pore volume and the specific surface area is nearly equal for the No.1 and No.2 coal samples. It indicates the low-temperature pyrolysis of the coal samples have no significant impact to the micro-pore structure of the pores less than 500nm.

4 Conclusion

- (1) The micropore structure has a slight change and a few new micropore structure formed, because of the dehydration, the thermal decomposition and the spillage of the volatile in coal samples, which were heated in short time.

- (2) There are a majority of pores with one end closed, and is scarcely pores with two ends opened the No.1 coal samples.
- (3) There are the distribution of all kinds of sizes micropore, and uneven distribution in the coal samples. The pore sizes of the No.1 and No.2 coal samples is mainly concentrated in the middle hole range. The low-temperature pyrolysis of the coal samples have no significant impact to the micro-pore structure of the pores less than 500nm.

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6 References

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