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Kinetic fitting of methane adsorption rate and its influencing factors

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Abstract: In order to reveal the mechanism of the influence of coal matrix pores on methane adsorption rate, based on the high-pressure methane isothermal adsorption experiment of coal samples with different pore structures, the desorption law of methane in coal and its internal relationship with pore structure were studied by analyzing the change of methane adsorption amount at a single pressure point over time. Bangham kinetic model was used to fit the adsorption process, and constants representing the adsorption rate were obtained. The following understandings were obtained: (1) With the decrease of particle size, the adsorption equilibrium time is shorter, small particle size samples often have more complex pore structure, which makes the adsorption reaction between gas-solid interface more active, but the particle size itself cannot increase or reduce the size of the accumulated adsorption amount at the equilibrium, it only changes the length of time required to reach the adsorption equilibrium. (2) With the increase of the mesh number, the adsorption rate also increases, but the higher the coal rank, the greater the adsorption rate growth rate.

Keywords: Adsorption rate; Adsorption kinetics; Fick diffusion; Knudsen diffusion.

1. Introduction

Coal seam has a double pore structure, including many small micro-pore systems and large developed fracture systems [1-4]. Coalbed methane mainly occurs in coal pore cracks and matrix surfaces [5-7], and methane gas is the main component of coalbed methane. In the process of methane extraction, it can be simply divided into the following types according to gas state and flow form: In the three stages of desorption, diffusion and percolation, the adsorption state and the free state are transformed. Most of the methane in coal exists in the form of adsorption phase on the micropore surface of coal matrix [8-10]. Adsorption isotherms are usually used to describe the adsorption equilibrium, and adsorption kinetics is used to describe the adsorption rate, which can reflect the speed of adsorption reaction [11-12].

In the process of describing the adsorption rate by adsorption kinetics, different viewpoint models have been proposed by predecessors, including the quasi-first-order adsorption kinetics model, quasi-second-order adsorption kinetics model, Elovich kinetics model, Bangham adsorption kinetics equation, and intracelluar diffusion model [15-16]. Qin Yueping and Jiang Zhaolong et al. obtained a linear relationship between the reciprocal of the cumulative desorption of methane and the time function through isothermal adsorption experiments, and analyzed it through influencing factors such as particle size, so as to find out the influence of adsorption rate on the cumulative adsorption amount. However, the cumulative adsorption amount and time change in a curve, and only part of it is in line with the linear change. So this method has limitations. Elovich kinetic model believes that the adsorption rate decreases exponentially with the adsorption amount on the adsorbent surface, which is suitable for chemical reactions with large activation energy, so it is suitable for chemical adsorption. Ma Fengfeng et al. believed that the quasi-first-order adsorption kinetics model was suitable for describing the kinetic behavior at the initial stage of adsorption, but could not be used to describe the entire adsorption process. The quasi-second-order adsorption kinetics model was also based on the assumption that the adsorption rate was controlled by the chemisorption mechanism, so it was also not applicable here. Bangham equation is usually used to describe the pore diffusion mechanism in the adsorption process. The pore and fissure structure of coal matrix is self-consistent with the applicability of this equation. When the linear fitting of this equation is good, and the fitting coefficient R2 is greater than 0.9, it indicates that the pore diffusion model can better represent the actual adsorption situation.

2. Theoretical formula

Adsorption kinetics includes the mass transfer mechanism of methane and coal and the diffusion mechanism in pores. The mass transfer mechanism is mainly controlled by the properties of adsorbent and adsorbent, while the diffusion mechanism is mainly affected by the structure of adsorbent, including porosity, pore diameter, etc. Different pore diameters correspond to different diffusion mechanisms, which together constitute and affect the size of adsorption rate. According to the order of pore diameter from large to small, the diffusion mass transfer process in the pore can be divided into the following types: External diffusion: the diffusion process of methane gas molecules to the outer surface of the solid phase, which is usually very fast and the resistance can be ignored. Macropore diffusion: pore diameter is much larger than the mean free path of methane molecules, which can be described by Fick diffusion mechanism. Microporous diffusion: The pore size is similar to or smaller than the molecular free path of methane, which can be described by Knudsen diffusion mechanism. The Bangham adsorption kinetics model was used to obtain the adsorption rates of different coal samples. The effects of pore size, particle size and coal rank on the adsorption rates were obtained by fitting the distribution of pore size and isothermal adsorption curve.

Knudsen coefficient (Kn) relates the flow state of rarefied

gas to the aperture, and is defined as the ratio of the average molecular free path λ of gas molecules to the characteristic length d (aperture) of objects in the flow field (Equation 1) :

$$\mathrm{Kn} = \frac{\lambda}{d} \quad (1)$$

The mean free path of gas λ (Equation 2) :

$$\lambda = \frac{\mathrm{K_B T}}{\sqrt{2}\pi\delta^2 \mathrm{p}} \quad (2)$$

Where, KB: Boltzmann constant, 1.3805×10-23J/K; T: Temperature (K); δ: collision diameter of gas molecules, methane molecular diameter is 0.38 nm; P: Pressure (MPa).

When Kn<0.01, the gas flow form belongs to Darcy seepage. When 0.01<Kn<0.1, the gas flow form belongs to Fick diffusion. When 0.1<Kn<10, the gas flow form is called transition flow; When 10<Kn, the gas flow form is called free molecular flow, namely Knudsen diffusion.

2.1. Adsorption kinetics

Bangham model (Equation 3)

$$\frac{dq_t}{dt} = \mathrm{k}\frac{q_m - q_t}{t^n} \quad (3)$$

after cleaning up

$$\ln\left(\ln\frac{q_m}{q_m - q}\right) = \ln k + n\ln t \quad (4)$$

Where, q_m: adsorption capacity at equilibrium, ml/g; q_t: instantaneous accumulated adsorption capacity, ml/g; t: Time, s.

By $\ln\left(\ln\frac{q_m}{q_m - q_t}\right)$ of $\ln t$ drawing to draw a straight line, and by linear slope and intercept and the type of the constants k and n. k is the constant representing the adsorption rate, and n is the constant related to the adsorption material.

2.2. Diffusion theory

The single-hole diffusion model of Fick's law can effectively describe gas diffusion, and the analytical formula is as follows (Equation 5) :

$$\frac{Q_t}{Q_\infty} = 1 - \frac{6}{\pi^2}\sum_{n=1}^{\infty}\frac{1}{n^2}e^{-\frac{n^2\pi^2 Dt}{r^2}} \quad (5)$$

$$D_e = \frac{D}{r^2}$$

Where: Qt: diffusion at time t, mg; Q_∞ is the gas diffusion at the equilibrium moment, mg; D is gas diffusion coefficient, m2/s; r is the diffusion path, m, the diffusion path is estimated to be the radius of the particle, r=0.75×10-3m; De is the effective diffusion coefficient, s-1.

Knudsen diffusion is based on the theory of molecular motion. In the pore of radius r, the molecular diffusion coefficient of methane caused by wall scattering is (Equation 6) :

$$D_K = \frac{2}{3}r\sqrt{\frac{8RT}{\pi M}} \quad (6)$$

$$D_K = 9700\mathrm{r}\sqrt{\frac{T}{16}}$$

Where, DK: Knudsen diffusion coefficient, m2/s: r: aperture, cm: T: absolute temperature, K; M: Molar mass of methane molecule, 16g/mol; R: Universal gas constant, 8.3145 J·mol-1·K-1.

The one between Fick diffusion and Knudesn diffusion is excessive diffusion, and the intermolecular collision of gas and the collision between gas and pore wall occur at the same time. The diffusion coefficient is expressed as (Equation 7) :

$$D_r = (D_K^{-1} + D_e^{-1})^{-1} \quad (7)$$

Then, the total diffusion path of methane gas molecules in coal samples can be expressed as (Equation 8):

$$\mathrm{D} = \alpha D_e + \beta D_K + \gamma D_r \quad (8)$$

Where, α: 0.01<Kn<0.1 corresponds to the percentage of aperture, dimensionless; β: Kn>10 percent of the corresponding aperture, dimensionless; γ: 0.1<Kn<10 corresponding to the percentage of aperture, dimensionless.

3. Sample collection and experiment

3.1. Sample basic information

Coal samples were taken from Changyan coal (SM) of Shenmu, Yulin, Shaanxi Province, lean coal (WY) of Wuyang, Changzhi, Shanxi Province, and anthracite (CZ) of Chengzhuang, Jincheng, Shanxi Province. The original coal sample size is about 30cm×30cm×20cm. After sealed storage, samples are prepared according to different experimental requirements. The industrial analysis results of each coal sample are shown in Table 1:

3.2. Pore development characteristics

The pore volume, pore size and specific surface area distribution of coal samples were measured by CO2 and N2 gas adsorption experiments and high-pressure mercury injection experiments. The QuadraSorb adsorption Station and PoreMaster mercury injection instrument produced by Canta Instrument Company of the United States were adopted. The pore development results are shown in Table 2. As shown in 3:

Table 1. Vitrinite reflectance and industrial analysis results of coal samples

Sample	Site	Proximate analysis			R^o_{max} (%)	Rank
		Mad (%)	Vad(%)	Aad(%)		
SM	Yujialiang Mine	6.18	29.51	3.78	0.65	Canneloid
WY	WuYang Mine	1.00	13.20	8.92	2.06	Lean coal
CZ	ChengZhuang Mine	2.56	9.87	7.44	3.01	Anthracite

Table 2. Pore volume and its proportion of coal samples

Sample No	Stage PV/(mL/g)				Stage SSA/(m^2/g)			
	<2 nm	2-50 nm	> 50 nm	Total PV	<2 nm	2-50 nm	> 50 nm	Total SSA
SM	0.0633	0.0218	0.0370	0.1121	210.89	7.65	0.34	218.88
WY	0.0515	0.0010	0.0243	0.0768	172.15	0.24	0.02	172.41
CZ	0.0894	0.0009	0.0079	0.0982	305.01	0.23	0.01	305.25

According to the International Union of Theoretical and Applied Chemistry (IUPAC), the pore size of porous

materials was divided into three types, which were smaller than 2nm. Mesoporous pores of 2~50nm and macroporous pores of more than 50nm. Under the constant temperature of 30℃ and the pressure of 145psi, 290psi, 580psi, 870psi, 1160psi, 1450psi and 1740psi, the pore diameter -Kn number -pressure relationship is obtained as shown in Fig.1 (data Table 3). The light cyan represents Fick diffusion. Yellow represents excessive diffusion, while white represents Knudsen diffusion. White only accounts for a small part, almost negligible, in the lower left corner of the coordinate axis. Therefore, Fick diffusion is the main diffusion of coal samples under the above conditions.

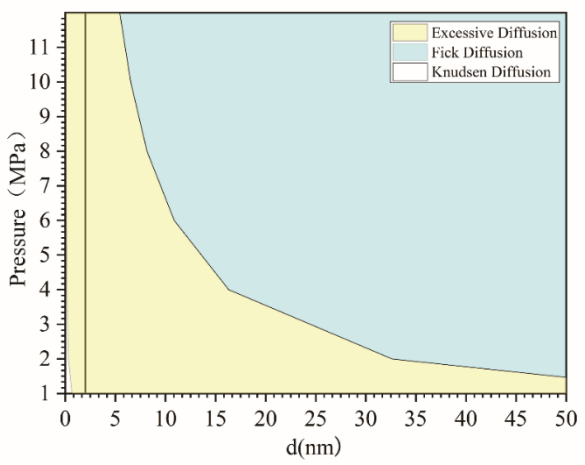

Fig. 1 Pore distribution -Kn number - pressure relationship

Table 3. Pore sizes (nm) corresponding to different Kn values under different pressures

Pressure(psi)	Kn=10	Kn=1	Kn=0.1	Kn=0.01
145	0.65	6.52	65.25	652.49
290	0.32	3.26	32.62	326.25
580	0.16	1.63	16.31	163.12
870	0.11	1.09	10.87	108.75
1160	0.08	0.82	8.16	81.56
1450	0.07	0.65	6.52	65.25
1740	0.05	0.54	5.44	54.37

3.3. Isothermal adsorption curve

In this paper, the temperature of the isothermal adsorption experiment was set at 30℃, and seven pressure points were set, respectively 145psi, 290psi, 580psi, 870psi, 1160psi, 1450psi and 1740psi. The isothermal adsorption and desorption experiments were carried out on coal samples of different coal ranks and particle sizes in CZ, SM and WY using TerraTek Company's isothermal isothermal adsorption and desorption desorption instrument, and the isothermal adsorption and Langmuir fitting curves were obtained, as shown in Figure 2,3. Theoretically, the adsorption of methane by coal is not applicable to the Langmuir theory of monolayer, but the isotherms obtained belong to type I adsorption isotherms, so the Langmuir equation can be used to fit, and the fitting results are in line with its development trend.

4. Results and discussion

Fig. 2 shows the isothermal adsorption lines of three coal samples with different particle sizes and their Langmuir fitting lines. It can be seen that with the increase of pressure, the accumulated adsorption capacity of methane also increases, and the slope of the curve increases gradually. The Langmuir equation was fitted to the scatter plot of the accumulated adsorption capacity, and the R2 of CZ coal was greater than 0.99 after fitting. The fitting degree R2 of SM coal sample was >0.86, and R2 of 200 mesh and 60-80 mesh was >0.99. The column R2 in WY coal sample is greater than 0.97, and the rest are greater than 0.99. It is concluded that the Langmuir equation can be well matched with the methane adsorption data in coal. Among the three coal samples, the adsorption capacity of columnar sample is the lowest under the same time pressure. The adsorption capacity of CZ anthracite is 60-80 mesh >200 objective, while that of the remaining two coal samples is 200-mesh >60-80 objective.

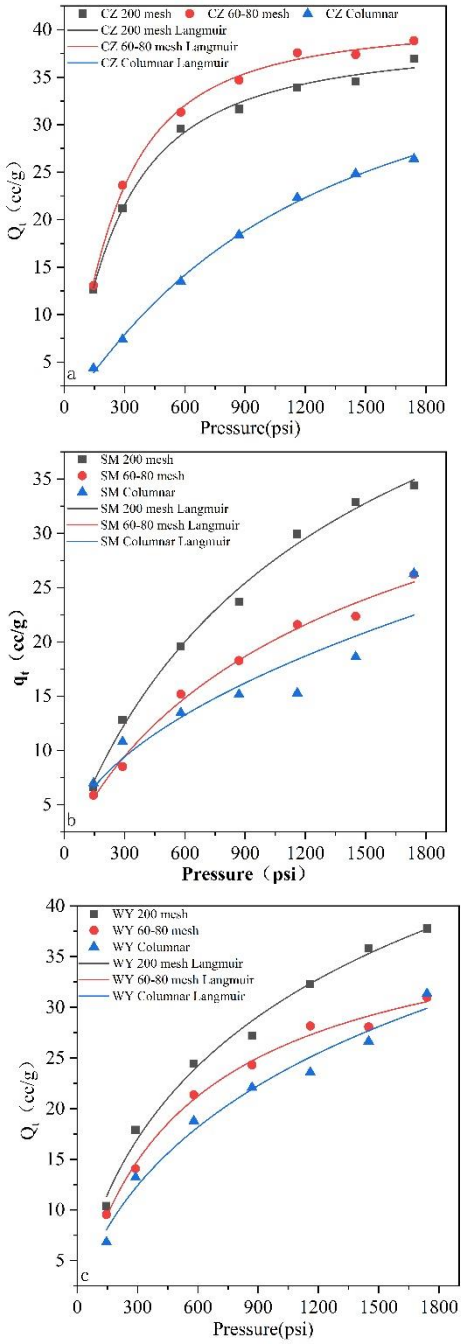

Fig. 2 Isothermal adsorption fitting curves of three coal samples with different particle sizes

Most researchers show that with the decrease of particle size, the adsorption rate increases and the adsorption capacity per gram also increases, corresponding to Figure 2 (b) and (c). When Liu Shengdong explored the influence of particle size on the adsorption characteristics of coal, he found that within the range of experimental pressure, the adsorption capacity of

20-40 particle size was the largest, that of 40-60 mesh was the smallest, and that of 60-80 mesh and 12-20 mesh were basically equal, which was corresponding to Figure 2 (a). Zhang Li and Ruppel T C et al argued that the particle size of coal sample had little effect on the adsorption capacity of coal. Macroscopically speaking, small particle size makes it take shorter time for coal samples to reach adsorption equilibrium. Microscopically speaking, small particle size samples often have more complex pore structure, which makes the adsorption reaction between gas-solid interface more active. However, particle size itself cannot increase or reduce the accumulated adsorption amount at equilibrium, but it only changes the length of time required to reach adsorption equilibrium.

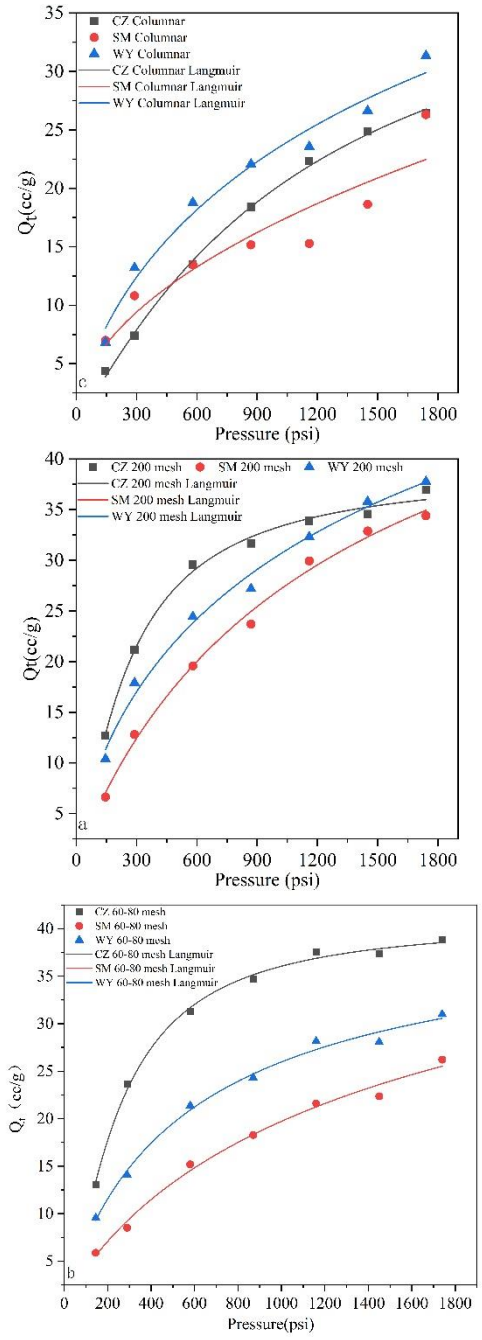

Fig. 3 Langmuir fitting diagram of isothermal adsorption of three coal samples with the same particle size

Fig. 3 (a), (b) and (c) respectively show the cumulative isothermal adsorption and Langmuir equation fitting lines of 200 mesh, 60-80 mesh and columnar coal samples with the same particle size. Among 200 mesh particle size, SM coal sample has the lowest adsorption capacity, CZ starts to be greater than WY, and WY surpasses CZ when the pressure increases to 1400psi. There is no reverse superposition in 60-80 mesh, and the larger the coal rank is, the larger the adsorption capacity will be. In the column sample, WY was always the largest, and SM was larger than CZ at the beginning. When the pressure reached about 500psi, CZ exceeded WY and the gap widened.

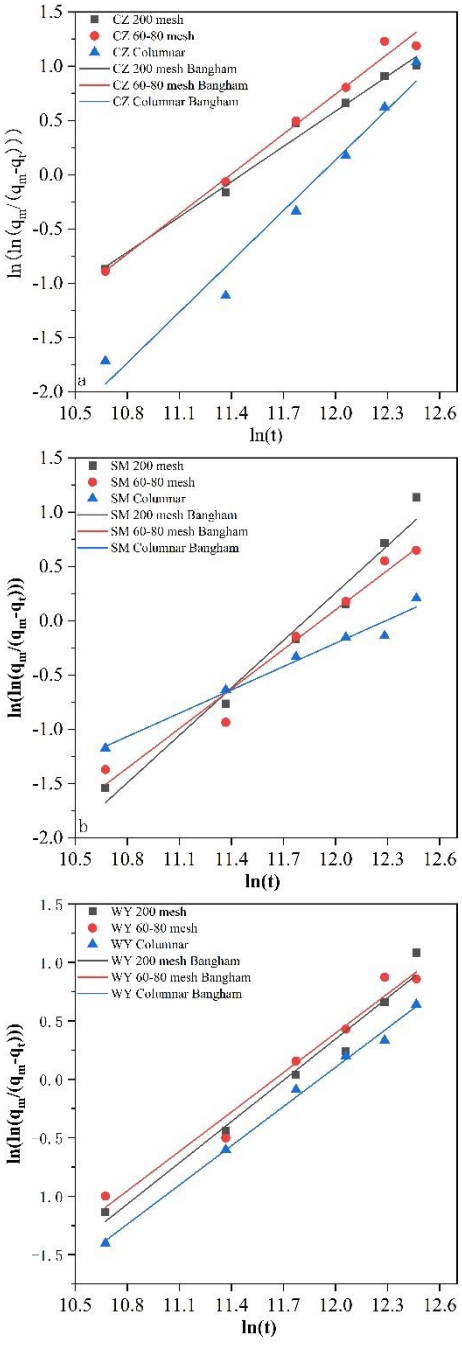

Fig. 4 Bangham fitting diagram of three coal samples with different particle sizes

Fig. 4 and Fig. 5 show the Bangham fitting diagram of the three coal samples under full pressure with different particle sizes and the Bangham fitting diagram of the three coal samples with different particle sizes respectively. The fitting data are shown in Table 4 and Table 5, and the Bangham fitting correlation R2 in Fig. 4 is greater than 0.96, and the fitting degree R2 in Fig. 5 is greater than 0.94, indicating that the two have good fitting degree. The results show that the Bangham diffusion model is suitable for methane adsorption

in coal. Wherein, the fitted slope k value represents the methane adsorption rate in coal.

Fig. 4 Among the three coal samples, WY's columnar coal sample has the highest fitting degree R2=0.99; CZ coal sample has a decreasing slope with the increase of mesh number; on the contrary, other coal samples have an increasing slope with the increase of mesh number; however, with the increase of coal rank, The slope size changes from the higher the number of coal rank, the larger the slope, to the higher the number of coal rank, the lower the slope, indicating that the slope k value is related to the coal rank and the number of coal rank, or to the porosity corresponding to the coal rank.

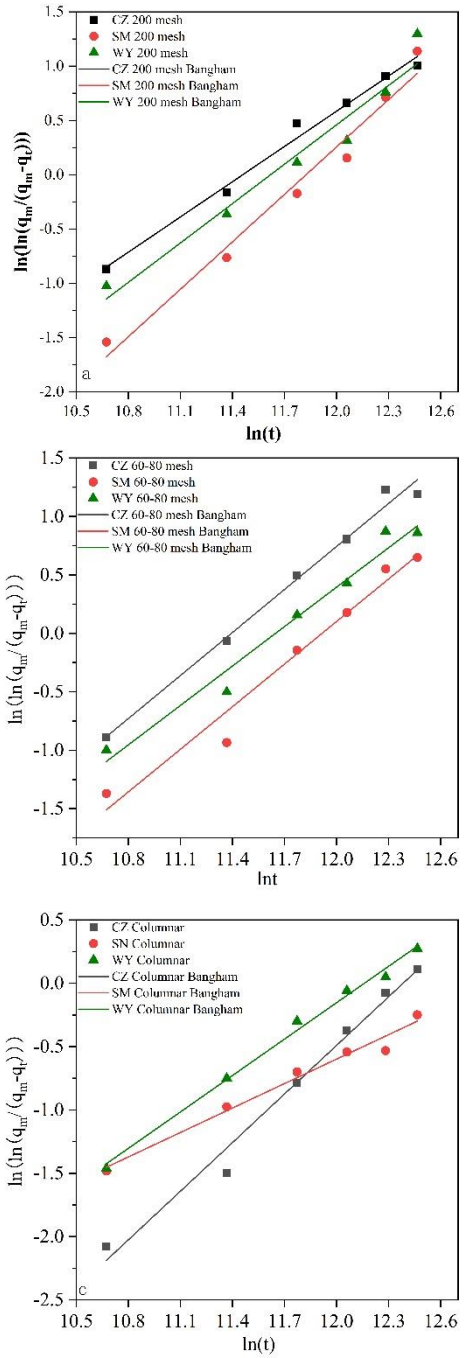

Fig. 5 Bangham fitting of three coal samples with particle size

Figure 5 shows the Bangham fitting condition of the three coal samples with the same particle size. In the case of 200 mesh and 60-80 mesh, the fitting lines did not cross, showing CZ, WY and SM from top to bottom. In the column, CZ was at the top, SM was greater than CZ at the initial stage, and CZ exceeded SM at the middle and late stage of intersection. The slope corresponding to the three shows that SM>WY>CZ when particle size is 200 mesh, SM>CZ>WY when particle size is 60-80 mesh, and CZ>WY>SM when particle size is 60-80 mesh, the higher the coal rank is, the higher the adsorption rate is. When particle size is 60-80 mesh, the adsorption rate is low coal rank > high coal rank > middle coal rank; when particle size is 200 mesh, the adsorption rate is low coal rank > middle coal rank > high coal rank. It shows that the adsorption rate increases with the increase of mesh number, but the higher the coal rank, the higher the adsorption rate increases. That is, the higher the coal rank, the higher the percentage of micropore surface area in the total pore surface area, and the slope k is positively correlated with the percentage of micropore surface area.

Table 4. Bangham fitting of three coal samples with different particle sizes and full pressure fitting lines and correlation

Sample	Mesh	Slope	Intercept	Equation	R^2
CZ	200	1.08	-12.40	y=1.08x-12.4	0.99
CZ	60-80	1.22	-13.97	y=1.22x-13.97	0.99
CZ	column	1.42	-18.56	y=1.42x-18.56	0.97
SM	200	1.45	-17.22	y=1.45x-17.22	0.98
SM	60-80	1.21	-14.47	y=1.21x-14.47	0.97
SM	column	0.66	-8.80	y=0.66x-8.8	0.98
WY	200	1.17	-13.77	y=1.17x-13.77	0.98
WY	60-80	1.12	-13.09	y=1.12x-13.09	0.97
WY	column	1.08	-13.32	y=1.08x-13.32	0.99

Table 5. Bangham fitting line and correlation between coal samples with grain size and full pressure

Sample	Mesh	Slope	Intercept	Equation	R^2
CZ	200	1.08	-12.40	y=1.08x-12.4	0.98
SM	200	1.45	-17.22	y=1.45x-17.22	0.97
WY	200	1.20	-14.05	y=1.20x-14.05	0.95
CZ	60-80	1.22	-13.97	y=1.08x-12.4	0.98
SM	60-80	1.21	-14.47	y=1.22x-13.97	0.97
WY	60-80	1.12	-13.09	y=0.55x-18.56	0.97
CZ	column	1.34	-15.84	y=1.34x-15.84	0.98
SM	column	0.68	-8.32	y=0.68x-8.32	0.97
WY	column	0.98	-11.65	y=0.98x-11.65	0.99

5. Conclusion

(1) Small particle size makes the coal sample take a shorter time to reach the adsorption equilibrium. From the microscopic point of view, small particle size samples often have more complex pore structure, making the adsorption reaction between gas-solid interface more active, but the particle size itself can not increase or reduce the size of the

accumulated adsorption amount at the equilibrium, it only changes the length of time required to reach the adsorption equilibrium.

(2) With the increase of the mesh number, the adsorption rate also increases, but the higher the coal rank, the greater the adsorption rate growth rate.

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