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# The Influence of Sorption Pressure on Gas Diffusion in Coal Particles: An Experimental Study

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**Abstract:** Gas pressure changes during the process of coal mine gas drainage and CBM recovery. It is of great importance to understand the influence of sorption pressure on gas diffusion; however, the topic remains controversial in past studies. In this study, four samples with different coal ranks were collected and diffusion experiments were conducted under different pressures through the adsorption and desorption processes. Three widely used models, i.e., the unipore diffusion (UD) model, the bidisperse diffusion (BD) model and the dispersive diffusion (DD) model, were adopted to compare the applicability and to calculate the diffusion coefficients. Results show that for all coal ranks, the BD model and DD model can match the experimental results better than the UD model. Concerning the fast diffusion coefficient  $D_{ae}$  of the BD model, three samples display a decreasing trend with increasing gas pressure while the other sample shows a V-type trend. The slow diffusion coefficient  $D_{ie}$  of BD model increases with gas pressure for all samples, while the ratio  $\beta$  is an intrinsic character of coal and remains constant. For the DD model, the characteristic rate parameter  $k_{\phi}$  does not change sharply and the stretching parameter  $\alpha$  increases with gas pressure. Both  $D_{ae}$  and  $D_{ie}$  are in proportion to  $k_{\phi}$ , which reflect the diffusion rate of gas in the coal. The impacts of pore characteristic on gas diffusion were also analyzed. Although pore size distributions and specific surface areas are different in the four coal samples, correlations are not apparent between pore characteristic and diffusion coefficients.

**Keywords:** gas diffusion; gas pressure; unipore diffusion model; bidisperse diffusion model; dispersive diffusion model

## 1. Introduction

During the process of coal mine gas drainage and CBM recovery, the gas flow process can be divided into two stages. First, driven by the concentration gradient force, the gas adsorbed on the surface of coal matrix desorbs and then diffuses into the fracture/cleat system of coal. Second, the dissociative state gas permeates to the surface well or the underground borehole driven by the pressure gradient force. Therefore, two key factors that affect net gas movement result are the gas diffusion coefficient and the gas permeability in the fracture. The diffusion coefficient represents the essential parameter of diffusibility and related studies show that it could be affected by temperature [1,2], moisture [3], pressure [4,5], gas type [6–8], sample size [6,9,10], and coal sample features [11,12]. It should be noted that the coal seam gas pressure is in the dynamic condition during gas extraction. Hence, it is of great

significance to understand the impact of pressure on the gas diffusion coefficient. Several research papers on this topic have been conducted but arguments can be found on how gas pressure impacts the diffusion coefficients.

For example, some scholars believe that the diffusion coefficient is in direct proportion to gas pressure. Charrière et al. [2] used CH<sub>4</sub> and CO<sub>2</sub> to conduct the adsorption kinetics experiments when the pressure is equal to 0.1 MPa and 5 MPa respectively. They found that the diffusion coefficient increases with gas pressure. Pan et al. [3] performed CH<sub>4</sub> adsorption/desorption diffusion test within 0~4 MPa pressures range, and results show a direct ratio between diffusion coefficient and gas pressure. Jian et al. [13] carried out the desorption experiments within 0~4.68 MPa pressure range and the conclusion remains the same. However, some scholars reckon that the diffusion coefficient decreases with the increase in pressure. Cui et al. [8] found that the diffusion coefficient of CO<sub>2</sub> reduces when gas pressure is smaller than 3.6 MPa. Staib et al. [4] conducted the adsorption kinetics experiments and analyzed the results using the BD model. It was found that the diffusion coefficient  $D_a$  lowers when the pressure increases. Shi et al. [14] tested the influence of CO<sub>2</sub> injection on microporous diffusion coefficient after the adsorption of CH<sub>4</sub> was balanced. Findings show that the increasing injection pressure of CO<sub>2</sub> would cause the reduction of micropore diffusion coefficient. There are also a few scholars who concluded that gas pressure has small effects on the diffusion coefficient. Nandi et al. [15] conducted CH<sub>4</sub> adsorption/desorption experiments on bituminous and anthracite coals and they did not find an apparent relationship between pressure and gas sorption rate. To summarize, the research outcomes are listed in Table 1.

**Table 1.** Summary of diffusion coefficient changing trend with the increase in pressure.

Author	Coal Sample	Gas Category	Diffusion Model	Pressure Range	Diffusion Coefficient Changing Trend
Delphine Charrière	Bituminous coal	CO <sub>2</sub>	UD model	0.1 MPa, 5 MPa	Increase
Pan Zhejun	Bituminous coal	CH <sub>4</sub> , CO <sub>2</sub>	BD model	0~4 MPa	CH <sub>4</sub> increases and CO <sub>2</sub> remains unchanged
Jian Xin	Bituminous coal	CO <sub>2</sub>	UD model	0~4.68 MPa	Increase
Cui X.J	Bituminous coal	CH <sub>4</sub> , CO <sub>2</sub> , N <sub>2</sub>	UD model	<3.6 MPa	Decrease
Shi JQ		CH <sub>4</sub> -CO <sub>2</sub>	UD model	4.2 MPa	$D_i$ decreases
Gregory Staib	Bituminous coal	CO <sub>2</sub>	UD model, BD model, FDR model	0~4.5 MPa	$D_a$ decreases and small impact on $D_i$
Satyendra P. Nandi	Bituminous coal and anthracite coal	CH <sub>4</sub>	UD model	0~2.76 MPa	Small impact

By reviewing the previous studies, it can be concluded that the effect of pressure on gas diffusion coefficient remains controversial till now. It is difficult to compare the research outputs horizontally because of the diversified calculation models and experimental methods, such as experimental apparatus, gas pressure and gas type. Moreover, most of the coal samples used in the studies was bituminous coal, because gas diffusibility and diffusion coefficient in coal are closely correlated with the types of coals. It is unknown whether the results stand for coal with different metamorphic grades.

In the present study, we aim at investigating the influence of sorption pressure on gas diffusion and examining which previous finding is more convincing. To guarantee the comparability of the results, all the experiments are carried out under similar gas pressure range. Both adsorption and desorption kinetics test are conducted. Three widely used diffusion models are adopted to analyze the results and eliminate the possible differences induced by diffusion models. Four coal samples with different ranks are collected from typical mining areas in China, the test results are cross-compared to understand does the coal rank have impacts on the relationship between gas pressure and diffusion coefficients.

## 2. The Diffusion Models

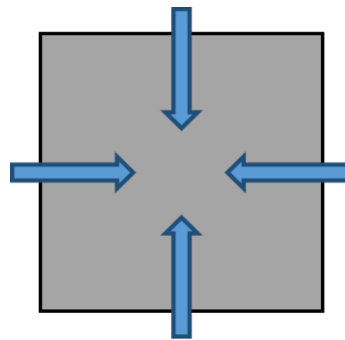
Three widely used diffusion models, i.e., the unipore diffusion (UD) model, the bidisperse diffusion (BD) model and the dispersive diffusion (DD) model, will be used in this study. The expressions and the assumptions are introduced as follows.

### 2.1. The Unipore Diffusion Model

The UD [13,16,17] model assumes that the coal particle has only one type of pore and the gas diffuses under the concentration gradient between exterior and interior of the coal particle. The UD model is illustrated in Figure 1. Both UD model and BD model follow the following assumptions: (a) the diffusion system is isothermal; (b) the geometric shape of the particle coal is the standard sphere; (c) coal and pore system are isotropic and homogeneous; (d) the pores are incompressible; (e) gas follows the linear adsorption rule; (f) gas diffusion in pores is in line with Fick's Second Law. It can be expressed as [18],

$$\frac{m_t}{m_\infty} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{Dn^2\pi^2t}{r^2}\right) \quad (1)$$

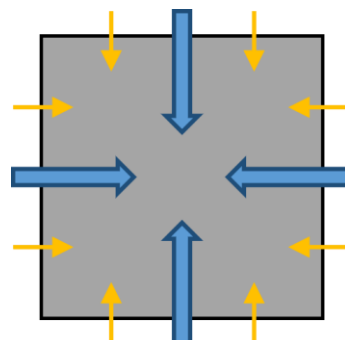
$m_t$  in the equation refers to the total gas adsorption/desorption quantity at time  $t$ ,  $m_\infty$  is the total quantity after the gas adsorption/desorption is balanced,  $r$  represents the radius of spherical coal particle,  $D$  refers to the diffusion coefficient ( $\text{m}^2/\text{s}$ ) and the value of  $\frac{D}{r^2}$  is defined as the effective diffusion coefficient  $D_e$  (1/s).



**Figure 1.** Concepts of gas diffusion under unipore diffusion (UD) Model [19].

### 2.2. The Bidisperse Diffusion Model

The BD model [5,8,9,14,20,21] assumes that the coal particle includes independent macropore and micropore systems, which are represented by  $D_a$  and  $D_i$  respectively. The gas diffusion under the two systems are driven by the concentration gradients between exterior and interior of the coal particle. The BD model is illustrated in Figure 2. The simplified BD model includes the fast macropore diffusion stage and the slow micropore diffusion stage [5,22].



**Figure 2.** Concepts of gas diffusion under bidisperse diffusion (BD) Model [19].

Concerning the fast macropore diffusion stage, the diffusion model is denoted as,

$$\frac{m_a}{m_{a\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D_a n^2 \pi^2 t}{r_a^2}\right) \quad (2)$$

$m_a$  in the equation refers to the total gas adsorption/desorption quantity at time  $t$  in the macropore,  $r_a$  and  $D_a$  represent the radius of macropore spherical coal particle and macropore diffusion coefficient ( $\text{m}^2/\text{s}$ ), respectively. The value of  $\frac{D_a}{r_a^2}$  is defined as the effective diffusion coefficient  $D_{ae}$  (1/s).

Concerning the lower micropore diffusion stage, the diffusion model is denoted as,

$$\frac{m_i}{m_{i\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} \exp\left(-\frac{D_i n^2 \pi^2 t}{r_i^2}\right) \quad (3)$$

$m_i$  in the equation refers to the total gas adsorption/desorption quantity in the micropore at time  $t$ ,  $r_i$  and  $D_i$  represent the radius of micropore spherical coal particle and micropore diffusion coefficient ( $\text{m}^2/\text{s}$ ), respectively. The value of  $\frac{D_i}{r_i^2}$  is defined as the effective diffusion coefficient  $D_{ie}$  (1/s).

The BD model is expressed as,

$$\frac{m_t}{m_{\infty}} = \frac{m_a + m_i}{m_{a\infty} + m_{i\infty}} = \beta \frac{m_a}{m_{a\infty}} + (1 - \beta) \frac{m_i}{m_{i\infty}} \quad (4)$$

$\beta = \frac{m_{a\infty}}{m_{i\infty} + m_{a\infty}}$  is the ratio of macropore adsorption/desorption to the total adsorption/desorption.

### 2.3. The Dispersive Diffusion Model

In recent years, the dispersive diffusion model was developed and it assumes that a distribution of characteristic times for diffusion. The diffusion is dispersed and represents the wide distribution of diffusion feature time. Therefore, theoretically, the DD model can avoid the simplification of pore structure and reflect the real physical experimental process. The DD model is expressed as,

$$\frac{m_t}{m_{\infty}} = 1 - \exp\left[-(k_{\phi} t)^{\alpha}\right] \quad (5)$$

$m_t$  in the equation refers to the total gas adsorption/desorption quantity,  $m_{\infty}$  is the total quantity after the gas adsorption/desorption is balanced,  $k_{\phi}$  is the characteristic rate parameter,  $\alpha$  is the stretching parameter ( $0 < \alpha < 1$ ). The research of Staib et al. [23] shows that  $\alpha$  is an intrinsic property of coal and is greatly influenced by the coal pore characteristic.

## 3. Diffusion Experiments

To carry out the diffusion experiments and analyze the impact of pressure on the methane diffusion, the iSorb HP (Quantachrome) instrument was used. The set maximum adsorption pressure is 6 MPa, the coal sample quality is 40 g and the experimental temperature is 315 K. Coal samples were collected from the HuiChun long frame coal at Jilin Province, Hedong coking coal at Shanxi Province, Xinmi lean coal at Henan Province, and Qinshui meager coal at Shanxi Province (Figure 3), with the four coal samples are denoted as HC, HD, XM and QS, respectively. The coal samples were ground into 0.2~0.25 mm particle samples and the prepared coal particles were dried under the 100 °C vacuum state for 24 h to remove moisture. The proximate analysis results are shown in Table 2.

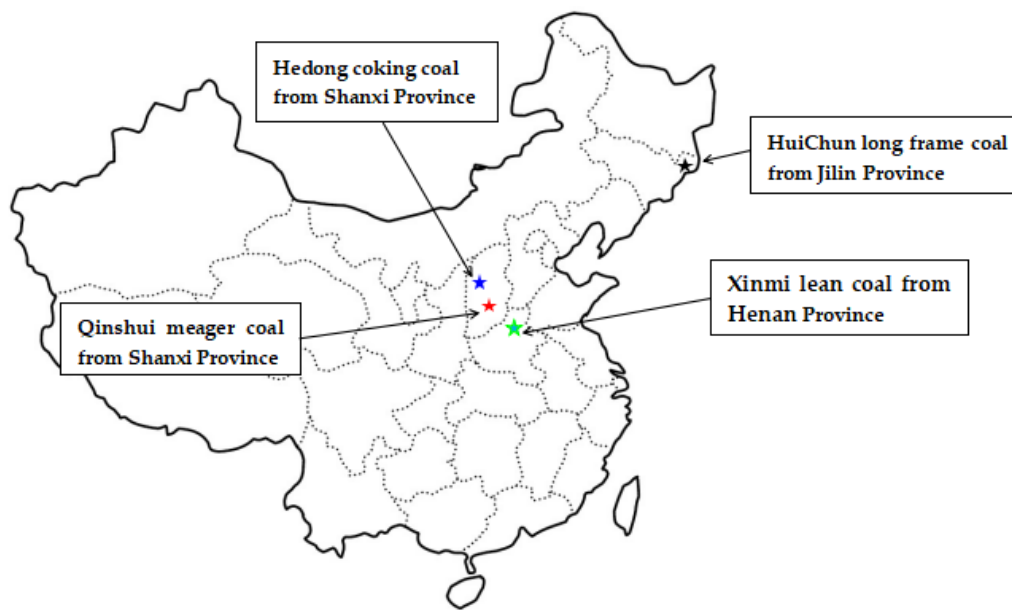


Figure 3. The diagram of coal samples collection places.

Table 2. Proximate analysis results.

Coal Sample	$M_{ad}$ (%)	$A_d$ (%)	$V_{daf}$ (%)	$F_c$ (%)
HC	8.40	32.47	47.40	11.73
HD	0.25	5.32	23.52	70.91
XM	2.65	7.83	17.25	72.27
QS	0.73	18.53	15.80	64.94

Manometric method is used in the experiments and the methane isothermal adsorption and diffusion kinetics are tested [24]. The gas state equation that implies the void volume of reference tank and coal samples tank is,

$$V = \frac{ZRTN_{He}}{P_{He}} \quad (6)$$

Four series data were recorded by pressure sensor in the experiments; (a) gas pressure in the reference tank before the gas is injected into the coal samples tank,  $P_{m1}$ ; (b) gas pressure in the reference tank after the gas is injected into the coal samples tank,  $P_{m2}$ ; (c) gas pressure in the coal samples tank before the reference tank gas is injected,  $P_{c1}$ ; (d) gas pressure in the coal samples tank after the reference tank gas is injected,  $P_{c2}$ .  $P_{m1}$ ,  $P_{m2}$  and  $P_{c1}$  are constant while  $P_{c2}$  is flexible.

The adsorption gas quantity at the  $i$  pressure step and time  $t$  in the adsorption diffusion process is,

$$N_{ti} = (N_{m1} - N_{m2}) - (N_{c2} - N_{c1}) = \left( \frac{P_{m1}V_m}{Z_{m1}RT} - \frac{P_{m2}V_m}{Z_{m2}RT} \right) - \left( \frac{P_{c2}V_c}{Z_{c2}RT} - \frac{P_{c1}V_c}{Z_{c1}RT} \right) \quad (7)$$

Therefore, the adsorption diffusion ratio of each pressure step is,

$$\frac{m_t}{m_\infty} = \frac{N_{ti}M_{CH_4}}{N_{\infty i}M_{CH_4}} = \frac{N_{ti}}{N_{\infty i}} \quad (8)$$

$\infty$  in the equation represents the required time when the  $i$  pressure step is balanced.

While the total adsorption quantity at the pressure balance point is,

$$Q_{ad} = \frac{22.4 \times 1000 \times \sum_{i=1}^n N_{\infty i}}{m_{CH_4}} \quad (9)$$

Therefore,  $\frac{m_t}{m_\infty}$  is equal to the gas adsorption quantity at the  $i$  pressure step and time  $t$  divided by the gas adsorption quantity when the  $i$  pressure step is balanced. Formula (9) is used to calculate the adsorption gas quantity at each balanced gas point and the adsorption/desorption isothermal lines [19] of coal samples are shown in Figure 4.

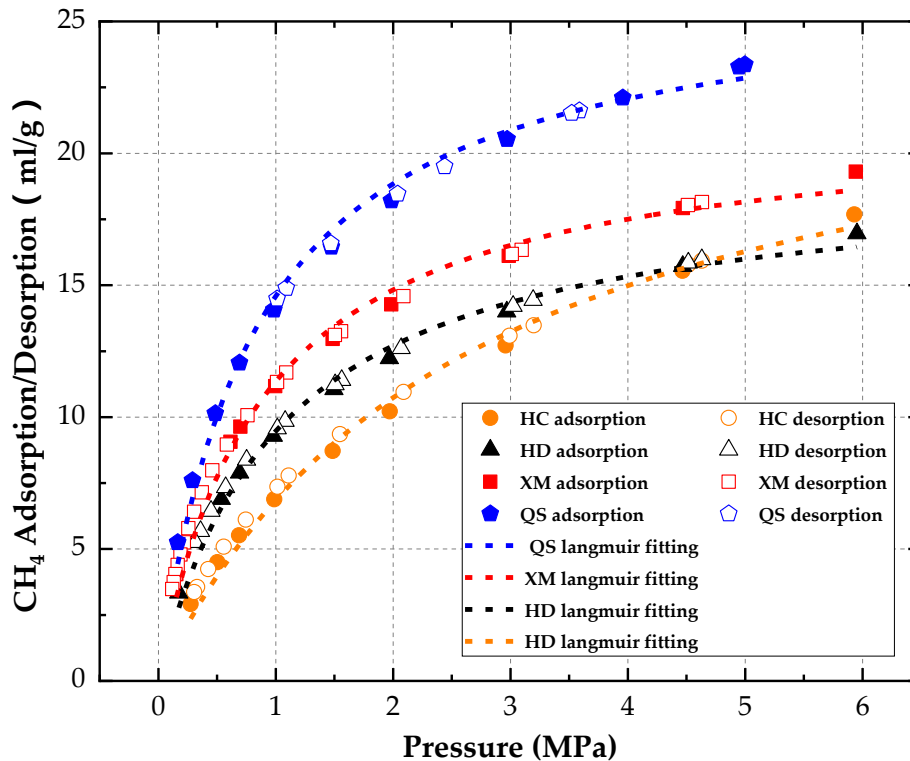


Figure 4. Adsorption-desorption isotherm of coal samples.

Langmuir model (Equation (10)) is used to fit the adsorption and desorption data of  $\text{CH}_4$  and the correlation  $R^2$  is listed in Table 3. It can be seen that the adsorption and desorption characteristics of  $\text{CH}_4$  are represented well by the Langmuir model. The adsorption characteristic parameters are calculated in Table 3.

$$X = \frac{aP}{b + P} \quad (10)$$

$a$ ,  $b$  in the equation are the adsorption characteristic parameters.  $a$  represents the Langmuir adsorption quantity and  $b$  refers to the Langmuir adsorption pressure.  $X$  is the adsorbed gas quantity and  $P$  refers to the gas pressure.

Table 3. Adsorption characteristic parameters of coal samples.

Coal Sample	$R^2$	$a/(\text{mL/g})$	$b/\text{MPa}$
HC	0.9935	24.81	2.62
HD	0.9891	19.33	1.04
XM	0.9930	21.37	0.88
GH	0.9933	25.46	0.67

Overall, similar to the previous findings [25,26], no apparent hysteresis phenomenon is found in the absorption/desorption process, in other words, the absorption/desorption process of  $\text{CH}_4$  can be reversed.

## 4. Analysis and Discussion

### 4.1. Model Applicability Analysis

Based on the Equation (8), the diffusion ratio can be calculated at any moment. The approximate method was used to fit the experimental results when applying the UD and BD models. In the process of fitting the UD and BD models, findings show that the calculation results are adequately convergent when the infinite series  $n$  is expanded to the fifth term. This can ensure the accuracy of model fitting results and further reduces the calculation difficulties. Therefore, all data was processed by setting  $n$  expand to five as the standard for calculation.

Taking the gas balance pressure increases from 0.7 MPa to 1 MPa as an example, the experimental results and the fitting diffusion lines of coal samples are shown in Figure 5.

It is shown in Figure 5 that the fitting line by the UD model is below the experimental line before some critical moment regardless of the coal samples, indicating that the fitting value is smaller than the actual value. After a certain time, the fitting line keeps above the experimental line and implies that fitting value is larger than the actual value. Therefore, the experimental results cannot be restored by the fitting line regardless of moderating the UD coefficient. The fitting effect of the BD model is superior to the UD model and the fitting line of the DD model is closer to the actual line. It suggests that the whole gas adsorption/desorption process cannot be accurately described by the UD model due to the complicated pore structures. The fitting line through the BD model includes the double structure of macropore and micropore and thus shows a higher coincidence degree with the experimental results. The DD model shows the best coincidence degree with the real experimental results. Therefore, the BD model and DD model are selected to calculate the gas diffusion characteristic parameter.

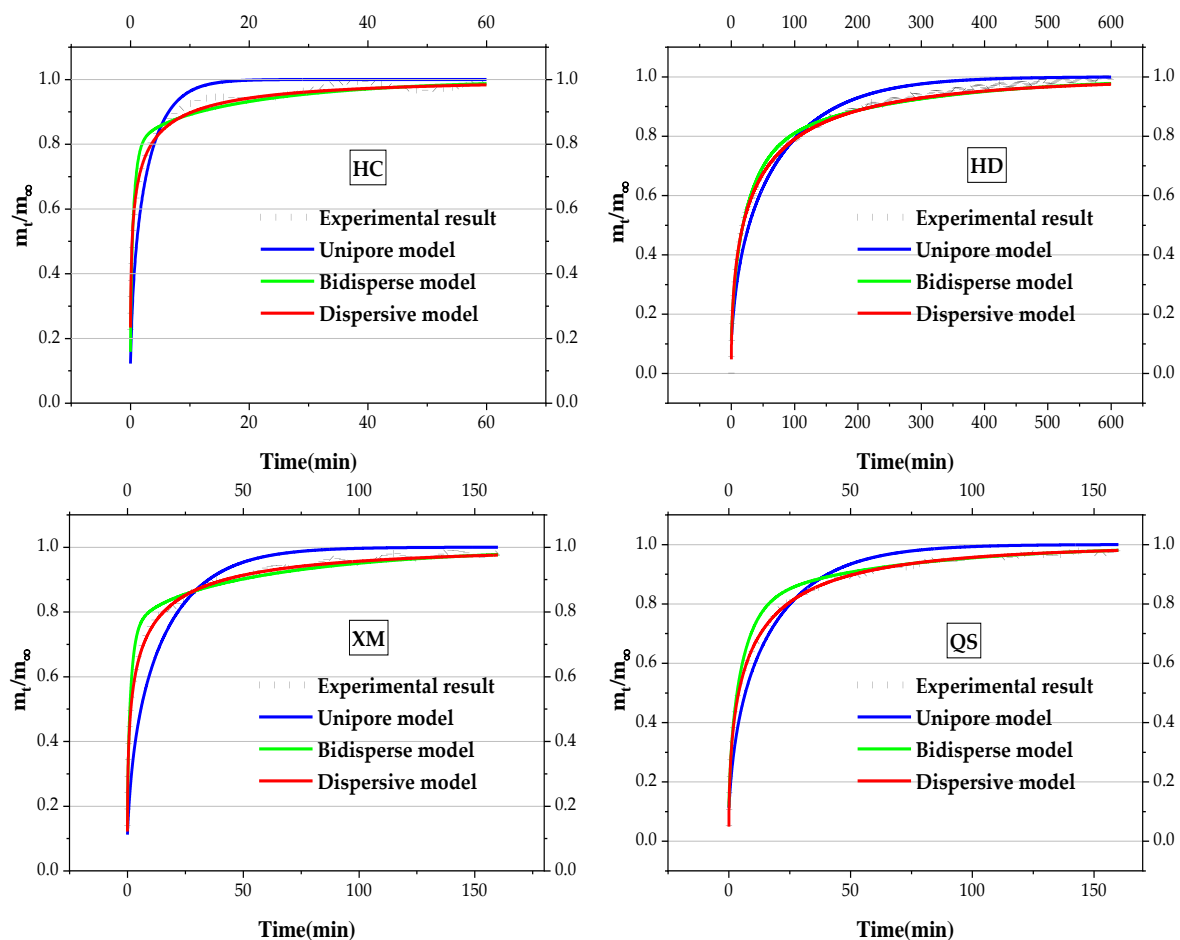


Figure 5. Experimental results and fitting diffusion lines of coal samples.

### 4.2. Analysis of Pressure's Effect on the Gas Diffusion

#### (1) The BD Model

Equation (4) implies that the BD model includes three unknown parameters, including fast effective diffusion coefficient  $D_{ae}$ , slow effective diffusion coefficient  $D_{ie}$  and the ratio of macropore adsorption/desorption to the total adsorption/desorption  $\beta$ . Using Equation (4) to calculate the BD characteristic parameters and analyze the impact of pressure on  $D_{ae}$  (Figure 6) and quadratic polynomial is to fit the results, the fitting goodness and calculated coefficient are shown in Table 4. As can be seen from Figure 6, the macropore diffusion coefficient  $D_{ae}$  decreases with the increase in pressure in three out of four sample coals (i.e, HC, XM and QS). Concerning the HD,  $D_{ae}$  shows a V-shape trend, which first decreases and then increases as the increases in pressure. Figure 6 also shows that the impact law of pressure on  $D_{ae}$  is better illustrated by the quadratic polynomial. When comparing the values of  $\bar{D}_{ae}$ , in both the adsorption and desorption processes,  $\bar{D}_{ae}(HC) > \bar{D}_{ae}(XM) > \bar{D}_{ae}(QS) > \bar{D}_{ae}(HD)$ . The difference of  $\bar{D}_{ae}$  in the absorption versus the desorption process becomes larger from HC to QS. No significant increasing trend of HC, XM and QS is found when the pressure increases, It is suspected that the set maximum pressure is not in the threshold level.

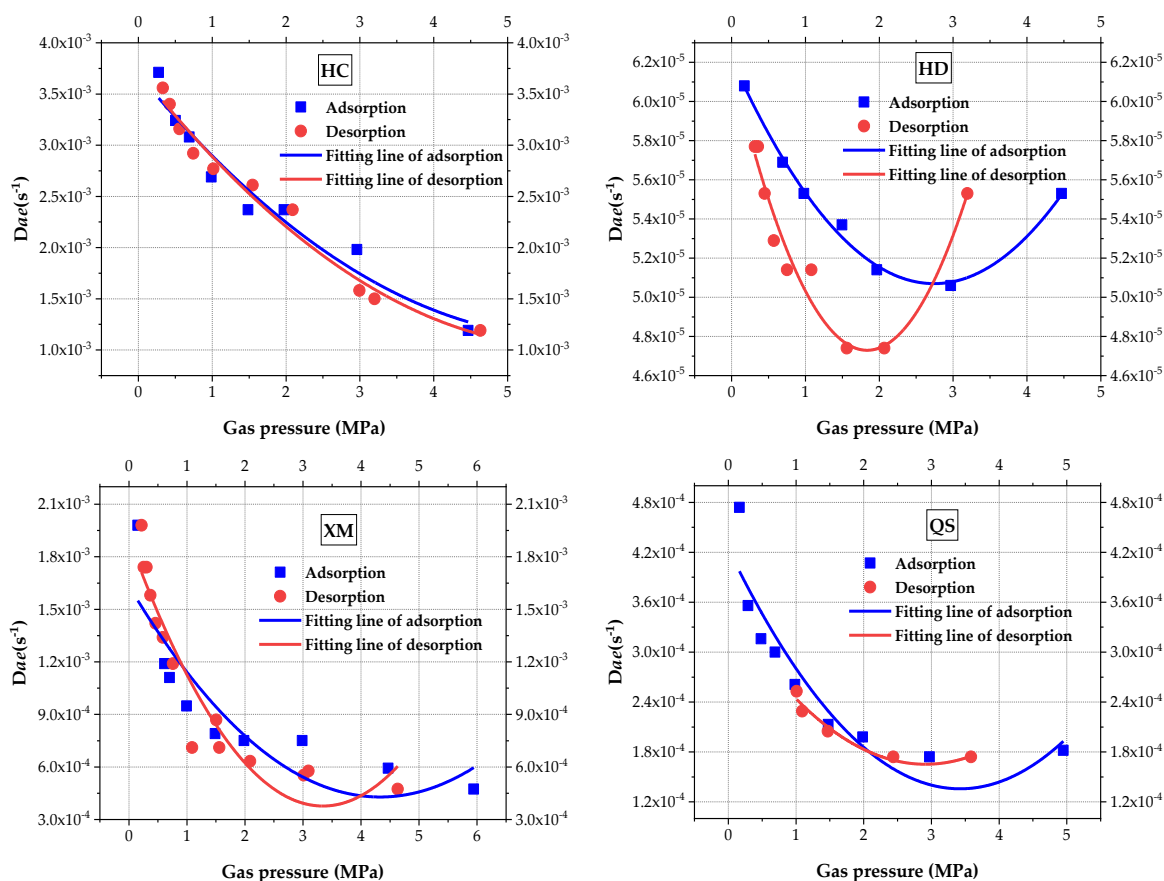


Figure 6. The diagram of the variation of macro-diffusion coefficients with pressure.

The impact of gas pressure on  $D_{ie}$  is analyzed and is shown in Figure 7. Linear regression is used to fit the results and, results of the fitting goodness and calculated coefficient are given in Table 5. It can be clearly seen that the slow efficient diffusion coefficient  $D_{ie}$  increases with the increase in pressure for all four samples. The impact law of pressure on  $D_{ie}$  is better explained by the linear regression. When comparing the values of  $\bar{D}_{ie}$ , the order is  $\bar{D}_{ie}(HC) > \bar{D}_{ie}(XM) > \bar{D}_{ie}(QS) > \bar{D}_{ie}(HD)$  in the adsorption process and  $\bar{D}_{ie}(HC) > \bar{D}_{ie}(QS) > \bar{D}_{ie}(XM) > \bar{D}_{ie}(HD)$  in the desorption process.



Table 4. Goodness of fit and diffusion coefficient.

Coal Sample	$R^2$		$\bar{D}_{ae}$	
	Adsorption	Desorption	Adsorption	Desorption
HC	0.950	0.977	$2.58 \times 10^{-3}$	$2.50 \times 10^{-3}$
HD	0.991	0.948	$5.49 \times 10^{-5}$	$5.29 \times 10^{-5}$
XM	0.764	0.906	$9.53 \times 10^{-4}$	$1.11 \times 10^{-3}$
QS	0.873	0.961	$2.75 \times 10^{-4}$	$2.07 \times 10^{-4}$

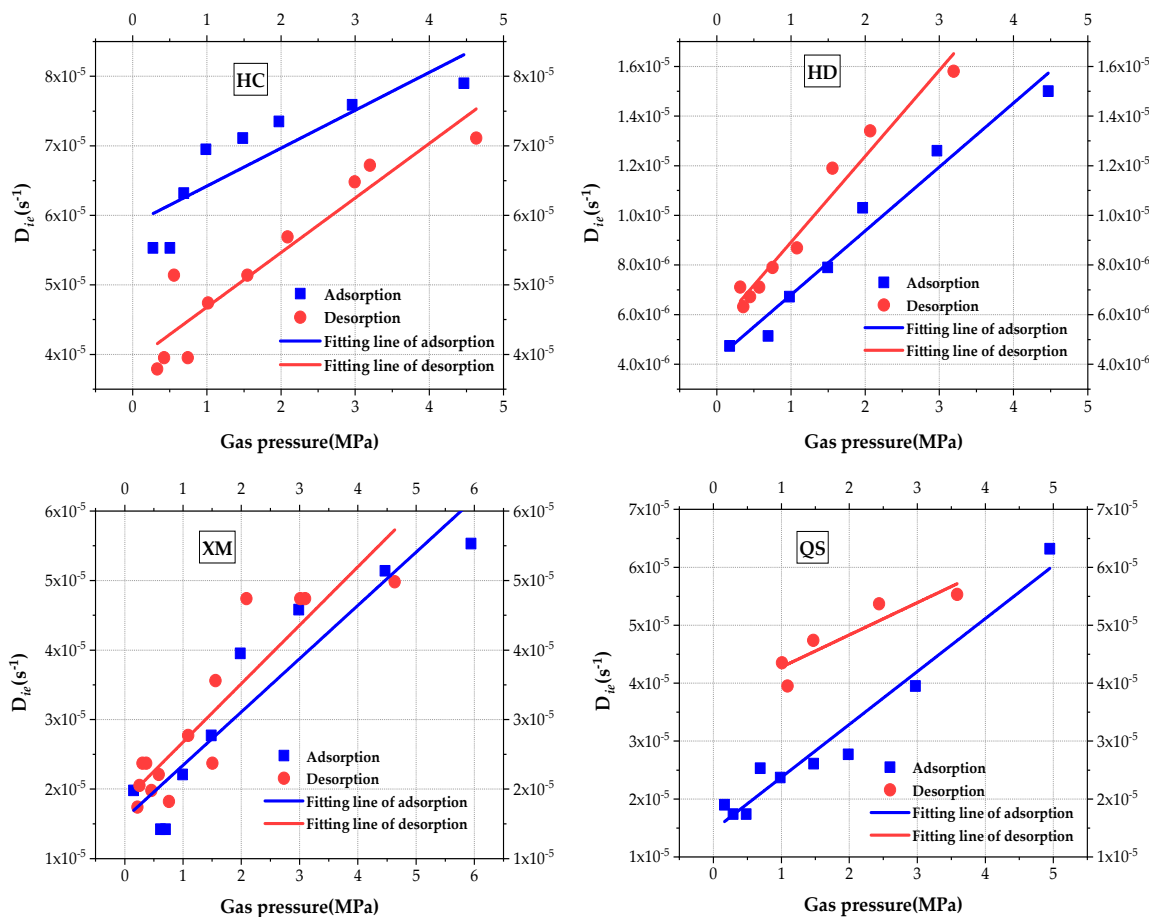


Figure 7. The diagram of variation of micro-diffusion coefficient with pressure.

Table 5. Goodness of fit and diffusion coefficient.

Coal Sample	$R^2$		$\bar{D}_{ie}$	
	Adsorption	Desorption	Adsorption	Desorption
HC	0.747	0.886	$6.79 \times 10^{-5}$	$5.27 \times 10^{-5}$
HD	0.968	0.967	$8.92 \times 10^{-6}$	$9.44 \times 10^{-6}$
XM	0.875	0.824	$3.22 \times 10^{-5}$	$3.03 \times 10^{-5}$
QS	0.955	0.828	$2.88 \times 10^{-5}$	$4.79 \times 10^{-5}$

The calculation results show that  $\beta$  is 0.74~0.76 for HC, 0.58~0.6 for HD, 0.67~0.69 for XM and 0.69~0.7 for QS, respectively, implying that the diffusion characteristic parameter  $\beta$  keeps constant in the adsorption/desorption process. This further indicates that  $\beta$  which represents the intrinsic property would not show a significant fluctuation with the change in pressure.

(2) The DD Model

The DD model includes two unknown characteristic parameters, the characteristic rate parameter  $k_\phi$  and the stretching parameter  $\alpha$ . The influencing law of pressure on the  $k_\phi$  and  $\alpha$  are re-analyzed, and calculated based on the gas diffusion experimental results and Equation (5). The results are shown in Figures 8 and 9, respectively.

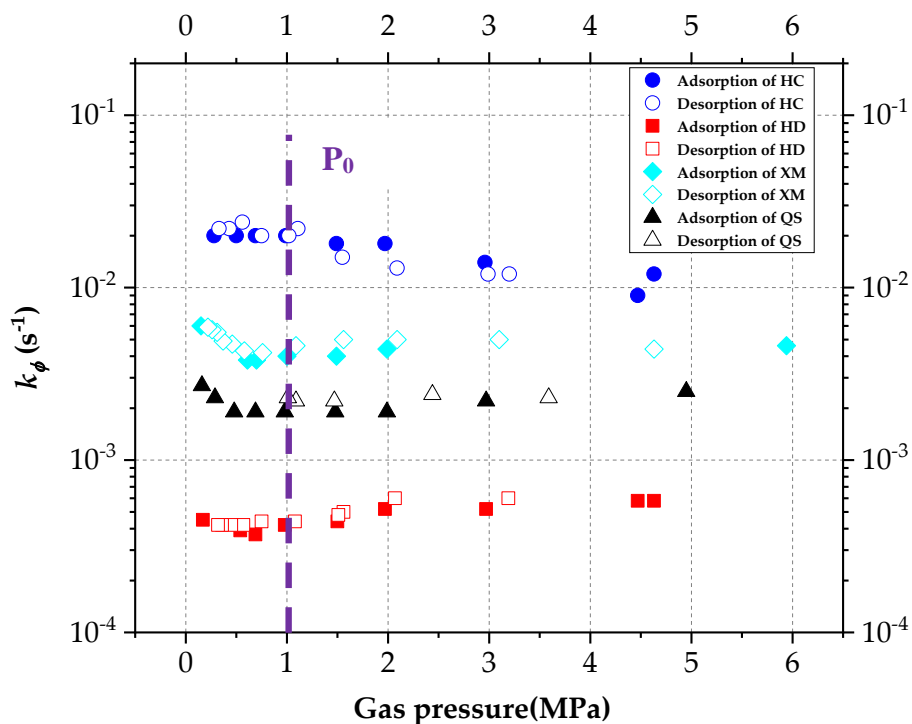


Figure 8. The diagram of variation of characteristic rate parameter  $k_\phi$  with pressure.

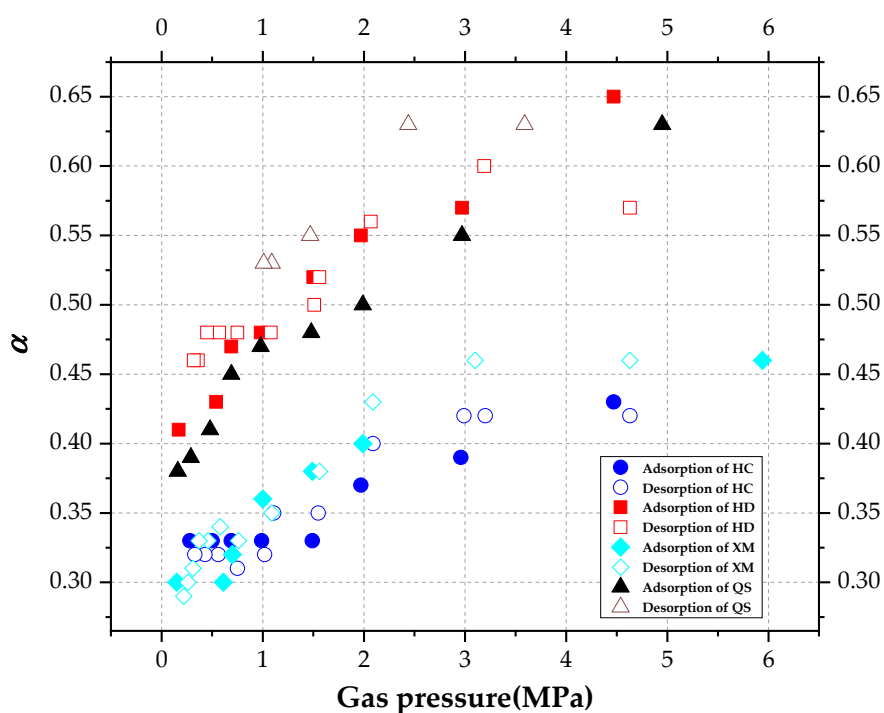


Figure 9. The diagram of variation of stretching parameter  $\alpha$  with pressure.

Gregory Staib et al. [23,27] found that  $k_{\phi}$  decreases with the increase in pressure which ranges from 0~3 MPa in their studies. In terms of the vitrinite-rich coal samples,  $\alpha$  increases with gas pressure while for the inertinite-rich coal samples, no significant changing trend is found for  $\alpha$ . Figure 8 shows that in our study,  $k_{\phi}$  keeps unchanged in the pressure fluctuation process. Concerning XM and QS,  $k_{\phi}$  slightly decreases with the increase in pressure when the pressure is less than  $P_0$ , but it keeps constant while the pressure is larger than  $P_0$ .

As shown in Figure 9,  $\alpha$  increases with pressure. The mean values of  $\alpha$  were calculated in Table 6. The mean value of  $\alpha$  is ordered as  $\bar{\alpha}(\text{HD}) > \bar{\alpha}(\text{QS}) > \bar{\alpha}(\text{XM}) > \bar{\alpha}(\text{HC})$  in the absorption process, while the order is  $\bar{\alpha}(\text{QS}) > \bar{\alpha}(\text{HD}) > \bar{\alpha}(\text{HC}) > \bar{\alpha}(\text{HM})$  in the desorption process.

Table 6. Stretching parameter  $\bar{\alpha}$ .

Coal Sample	Adsorption	Desorption	R <sup>2</sup>
HC	0.355	0.356	0.876
HD	0.510	0.506	0.825
XM	0.376	0.353	0.908
QS	0.473	0.560	0.898

### (3) Analysis of the correlation of diffusion characteristics parameters

The five diffusion characteristics parameters of the BD and DD models are treated by the homogenization procedure and the results are shown in Table 7. It can be seen that  $\bar{D}_{ae}$ ,  $\bar{D}_{ie}$  and  $\bar{k}_{\phi}$  are the largest for HC, in the middle for XM and QS, and the smallest for HD. The linear regression results of  $\bar{k}_{\phi}$  on  $\bar{D}_{ae}$  and  $\bar{k}_{\phi}$  on  $\bar{D}_{ie}$  are shown in Figures 10 and 11, respectively.

Table 7. Average gas diffusion parameters of experimental coal samples.

Coal Sample	$\bar{D}_{ae}$ (s <sup>-1</sup> )	$\bar{D}_{ie}$ (s <sup>-1</sup> )	$\bar{k}_{\phi}$ (s <sup>-1</sup> )	$\bar{\alpha}$	$\bar{\beta}$
HC	$2.54 \times 10^{-3}$	$5.94 \times 10^{-5}$	$1.78 \times 10^{-2}$	0.36	0.75
HD	$5.38 \times 10^{-5}$	$9.21 \times 10^{-6}$	$4.73 \times 10^{-4}$	0.51	0.59
XM	$1.05 \times 10^{-3}$	$3.11 \times 10^{-5}$	$4.69 \times 10^{-3}$	0.35	0.68
QS	$2.51 \times 10^{-4}$	$3.56 \times 10^{-5}$	$2.16 \times 10^{-3}$	0.51	0.70

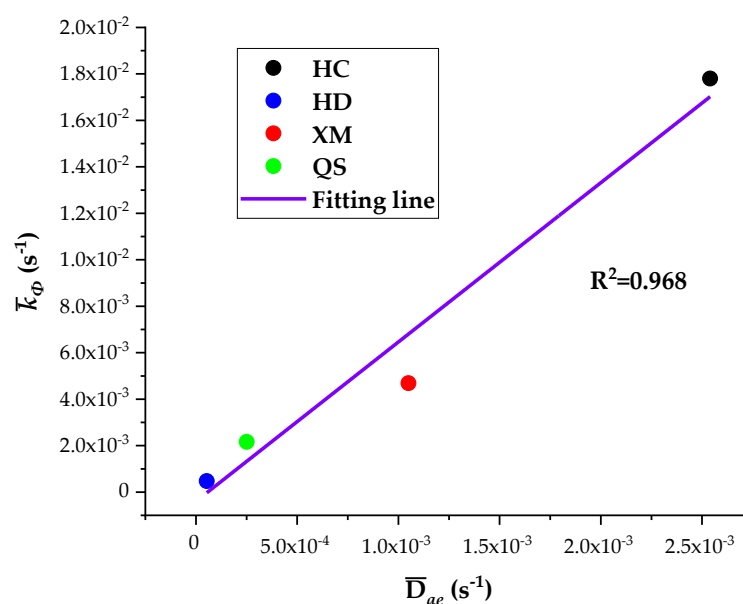
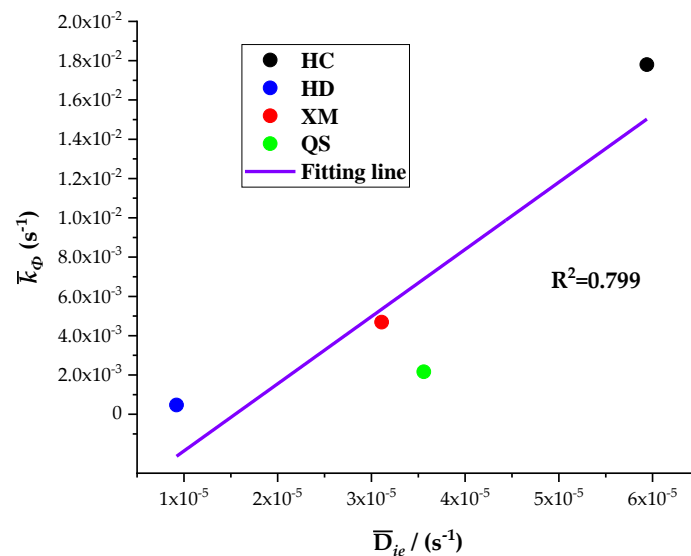


Figure 10. The linear regression of  $\bar{k}_{\phi}$  on  $\bar{D}_{ae}$ .



**Figure 11.** The linear regression of  $\bar{k}_\phi$  on  $\bar{D}_{ie}$ .

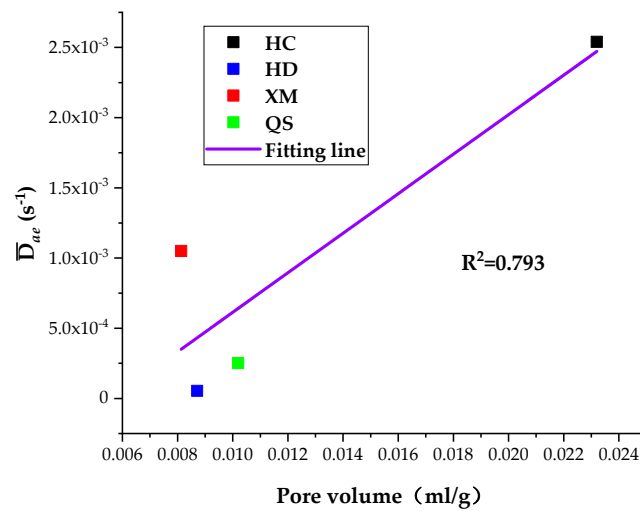
The results show a good linear correlation of  $\bar{D}_{ae}$ ,  $\bar{D}_{ie}$  and  $\bar{k}_\phi$  in our experimental results, and the goodness of fit is the best for  $\bar{D}_{ae}$  and  $\bar{k}_\phi$ . It suggests that both the diffusion coefficients  $D_{ae}$  and  $D_{ie}$  and characteristic rate parameter  $k_\phi$  are suitable for describing the coal gas diffusion rate. The analysis above suggests that the fast diffusion coefficient  $D_{ae}$  decreases with the increase in pressure while the slow diffusion coefficient  $D_{ie}$  increases with the increase in pressure.  $k_\phi$  keeps fixed and thus may be considered as a combined effect of  $D_{ae}$  and  $D_{ie}$ .

#### 4.3. Analysis of the Relationship between Pore Structure Characteristics and Gas Diffusion

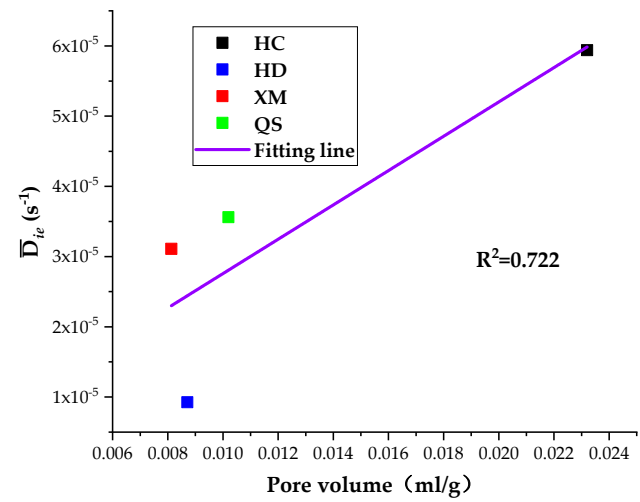
By analyzing and summarizing the impact, law of  $CH_4$  diffusion under different pressures, we found the diversity of gas diffusion coefficients in both absorption and desorption process for different coal samples. Because the coal pore structures might directly affect the diffusion process of gas [28], experiments on the low temperature nitrogen absorption and mercury penetration were conducted to test the characteristics of coal pore structure.

The Quadrasorb instrument is used for the low temperature nitrogen absorption experiment and the PoreMaster60 mercury porosimeter instrument is applied for the mercury penetration. coal samples particles with 1~3 mm in size are prepared and dried. The low temperature nitrogen absorption method is suitable for testing the distribution of coal micropore ranging from 0~25 nm, which determines the coal specific surface area [28]. Because the mercury penetration method is not accurate in testing the micropore, it is only suitable for analyzing the pores which are bigger than 25 nm. Therefore, in this study, the computation of pore volume is calculated by the low temperature nitrogen absorption method when the pore size ranges from 0~25 nm and by the mercury penetration method if the pore size is bigger than 25 nm. The specific surface area and pore volume are given in Tables 8 and 9, respectively.

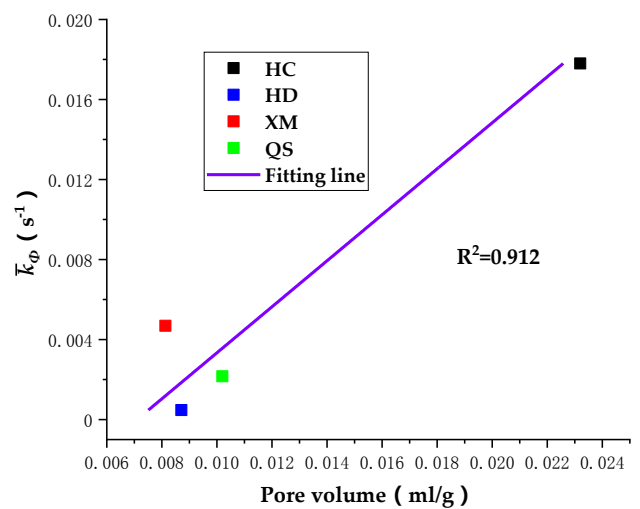
To further understand the impact of coal pore structure characteristics on the gas diffusion, we run the linear regressions of  $\bar{D}_{ae}$ ,  $\bar{D}_{ie}$  and  $\bar{k}_\phi$  on pore volume. As shown in Figure 12, the correlation between the pore volume and the diffusion coefficients is, largest for  $k_\phi$  ( $R^2 = 0.912$ ), middle for  $D_{ae}$  ( $R^2 = 0.793$ ) and smallest for  $D_{ie}$  ( $R^2 = 0.722$ ).



a) The impact of pore volume on  $\bar{D}_{ac}$



b) The impact of pore volume on  $\bar{D}_{ie}$



c) The impact of pore volume on  $\bar{k}_\phi$

**Figure 12.** The impact of pore volume on  $\bar{D}_{ac}$ ,  $\bar{D}_{ie}$  and  $\bar{k}_\phi$ .

Table 8. Specific surface area of coal samples.

Coal Sample	Pore Size/nm	(0~25)
HC	Specific surface area/(m <sup>2</sup> /g)	11
HD		0.234
XM		0.380
QS		0.177

Table 9. Pore volume of coal samples.

Coal Sample	Pore Size Ranges/nm	(0~10)	(10~100)	(100~1000)	(>1000)	Total
HC	Pore volume/(mL/g)	$1.21 \times 10^{-2}$	$8.10 \times 10^{-3}$	$2.50 \times 10^{-3}$	$5.00 \times 10^{-4}$	$2.32 \times 10^{-2}$
HD		$3.89 \times 10^{-4}$	$4.52 \times 10^{-3}$	$2.50 \times 10^{-3}$	$1.30 \times 10^{-3}$	$8.71 \times 10^{-3}$
XM		$7.55 \times 10^{-4}$	$3.27 \times 10^{-3}$	$2.60 \times 10^{-3}$	$1.50 \times 10^{-3}$	$8.13 \times 10^{-3}$
QS		$3.14 \times 10^{-4}$	$6.25 \times 10^{-3}$	$2.60 \times 10^{-3}$	$1.00 \times 10^{-3}$	$1.02 \times 10^{-2}$

Table 8 shows that the specific surface area is larger in HC relatively to other coal samples, indicating that the porosity in HC is well developed than other coal samples. It is shown in Table 7 that  $\bar{D}_{ae}$ ,  $\bar{D}_{ie}$  and  $\bar{k}_\phi$  of CH<sub>4</sub> is the largest in HC, suggesting the porosity development level is correlated with the diffusion rate. However, Figure 13a shows that  $\bar{D}_{ae}$  of HD, QS and XM significantly increases when  $\bar{D}_{ae}$  is smaller than  $1.6 \times 10^{-11}$  while the specific surface area keeps unchanged. Figure 13b,c show that the impact of specific surface area on  $\bar{D}_{ie}$  and  $\bar{k}_\phi$  is small in all coal samples excluding HC. It is worth to mention that our experimental results can only be considered as reference due to the small number of coal samples. The impact of coal structure on the diffusion parameters requires further study. In conclusion, the fluctuation of diffusion coefficients with respect to the gas pressure is correlated to the variation of pore characteristics, but the reason is still mysterious due to lack of evidence.

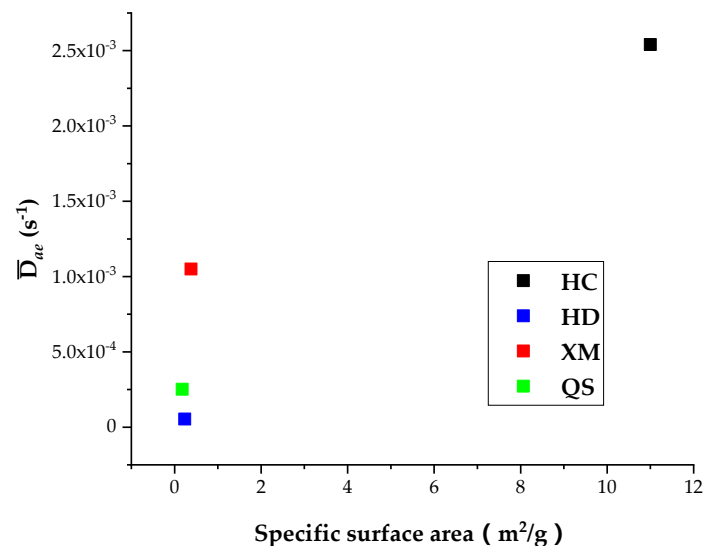
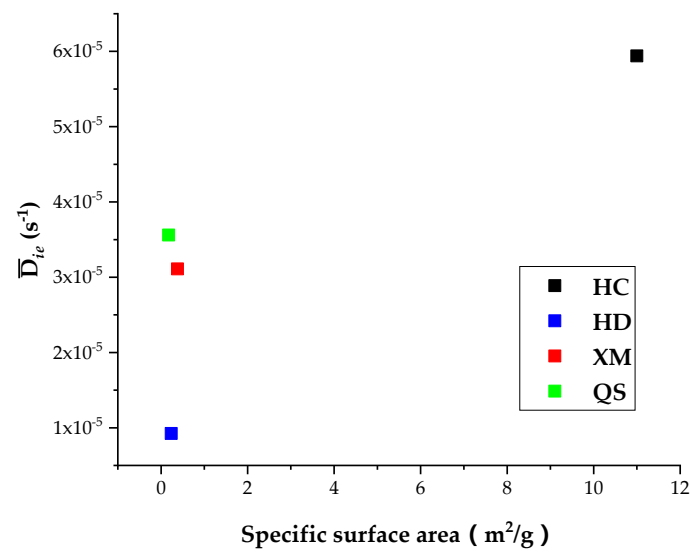
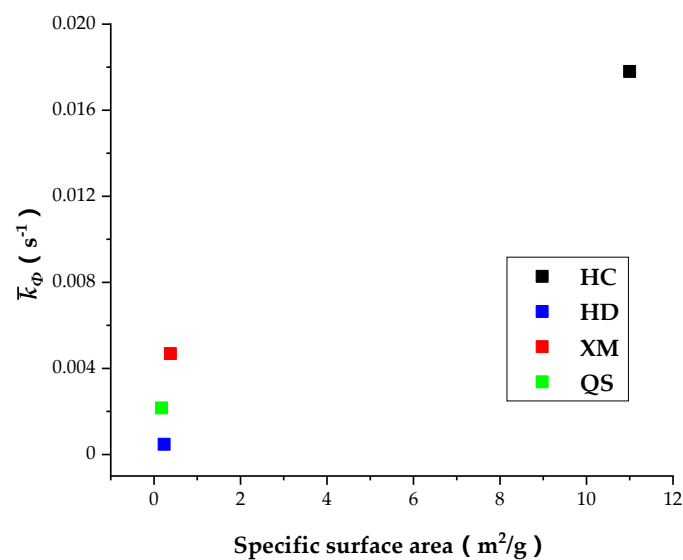
a) The impact of specific surface area on  $\bar{D}_{ae}$ 

Figure 13. Cont.

b) The impact of specific surface area on  $\bar{D}_{ie}$ c) The impact of specific surface area on  $\bar{k}_\phi$ **Figure 13.** The impact of specific surface area on  $\bar{D}_{ae}$ ,  $\bar{D}_{ie}$ , and  $\bar{k}_\phi$ .

#### 4.4. Discussion on the Influence of Inconstant Diffusion Coefficients on CBM Recovery

Previous studies have demonstrated that the BD diffusion cannot be overlooked and replaced by UD diffusion if diffusion is a constraint of gas production, especially for the coal seam with relatively large cleat spacing [24]. In this study, we found the BD and DD models are more accurate in describing the diffusion process, while pressure has apparent influence on the diffusion coefficients. From this point of view, the inconstant diffusion coefficients will have impacts on the CBM recovery rate. In terms of BD coefficients, most samples show an increase of fast diffusion coefficient  $D_{ae}$  but a decrease of slow diffusion coefficient  $D_{ie}$  during the drop of coal seam pressure. The increase or decrease of diffusion coefficient will certainly accelerate or hinder gas flow, but these two effects might be compromised for the BD model and the ultimate effect depends on the net value of these two effects. For the DD model,  $k_\phi$  keeps at a stable level, this phenomenon proves the above speculation as  $k_\phi$  can be seen as a

combination of  $D_{ae}$  and  $D_{ie}$ . However, the stretching parameter  $\alpha$  decreases during pressure dropping, which indicates the CBM recovery rate will be reduced due to the change of diffusion coefficient.

## 5. Conclusions

- (1) Compared with the UD model, the BD and DD models are more accurate in describing the whole gas adsorption/desorption process.
- (2) The fast efficient diffusion coefficient  $D_{ae}$  decreases with the increase in pressure for three out of four coal samples (i.e. HC, XM and QS) while it shows a V-shape with the increasing pressure for HD. The slow efficient diffusion coefficient  $D_{ie}$  is positively correlated with the pressure for all coal samples. The diffusion characteristic parameter  $\beta$  keeps constant in the adsorption and desorption process for all coal samples.
- (3)  $k_{\phi}$  keeps fixed when the pressure changes and the stretching parameter  $\alpha$  increases with the increase in pressure.
- (4) Both the effective diffusion coefficient  $D_{ae}$  and  $D_{ie}$  and the characteristic rate parameter  $k_{\phi}$  can be used to describe the gas diffusion rate. The impact of pore volume on  $D_{ae}$ ,  $D_{ie}$  and  $k_{\phi}$  differs in the four coal samples while  $D_{ae}$ ,  $D_{ie}$  and  $k_{\phi}$  are slightly affected by the specific surface area. The influence of pore structure characteristics on gas diffusion ability still requires further study.

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