

Article



Analysis of the Influence of Coal Petrography on the Proper Application of the Unipore and Bidisperse Models of Methane Diffusion

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Abstract: The analysis of phenomena related to gas transport in hard coal is important with regard to the energetic use of coal bed methane (CBM), the reduction of greenhouse gas emissions to the atmosphere (CO₂) and the prevention of natural hazards such as methane hazards and gas and rock outbursts. This article presents issues concerning the feasibility and scope of applying the unipore and bidisperse diffusion models to obtain knowledge concerning the kinetics of methane sorption and its diffusion in the carbon structure, depending on its petrography. Laboratory tests were carried out on coal samples which varied in terms of petrography. Quantitative point analyses were carried out, based on which content of groups of macerals was determined. The degree of coalification of coal samples was also determined based on measurements of vitrinite reflectivity R_0 and the volatile matter content V^{daf} . Sorption kinetics were also investigated, and attempts were made to adjust the unipore and bidisperse models to the real sorption kinetic courses. This allowed the identification of appropriate coefficients controlling the course of sorption in mathematical models. An attempt was also made to assess the possibility of applying a given model to properly describe the phenomenon of methane sorption on hard coal.

Keywords: hard coal; sorption; petrography; gas transport; diffusion models; coal bed methane; natural hazards

1. Introduction

Global economic development and the growth of civilization itself lead to greater consumption of electricity, resulting in a constant increase in the demand for it [1]. Its primary source is fossil fuels (mainly coal), the use of which causes the emission into the atmosphere of many harmful chemical compounds, including greenhouse gases (mainly CO₂), which cause global warming [2–4]. As a result of international agreements concluded under the United Nations Framework Convention on Climate Change (UNFCCC), countries are required to reduce greenhouse gas (GHG) emissions, especially CO₂, which has resulted in increased demand for "clean energy" sources. Currently, there is a growing awareness of the fact that methane molecules have a much greater impact on the greenhouse effect than carbon dioxide. This justifies research into the processes determining its emission into the atmosphere [5,6].

Coalbed methane (CBM) is a gas of natural origin, which was formed as a result of processes of conversion of organic matter into coal [7]. It occurs in coal seams mainly as adsorbed gas and in smaller amounts, also as free gas. This gas is of great importance worldwide as an alternative energy source [8–10]. Poland has some of the largest hard coal deposits in Europe, accompanied by the presence of methane. The unit methane content in



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Copyright: © 2021 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/). coal seams reaches several cubic meters per ton of coal ($m^3 CH_4/t$), which in the scale of the entire Upper Silesian Coal Basin (GZW), results in trillions of cubic meters of gas [11,12]. The capture of coalbed methane is desirable both from the point of view of energy, safety and environmental protection, because it is released during mining operations and is a source of danger and contributes to the increase in the greenhouse effect [13]. The study of gas transport phenomena in the coal structure is crucial for both the evaluation of coalbed methane production and CO₂ sequestration, due to the fact that the coal matrix is the main site for gas storage, sorption, and diffusion [14–16].

Gas sorption and desorption in coal is a complex process. For a long time, attempts were made to describe it using relatively simple mathematical models. They assumed that it was sufficient to take into account selected processes which were most important for the course of the phenomenon. For some coals, a good fit of the simulation results to the experimental data could be obtained. This may indicate that the processes included in the assumptions of the models are in fact the most significant for the course of the phenomenon, and the parameters of the model may be used to evaluate the properties of the material studied. The kinetics of the processes of methane accumulation and release within the coal structure depend on many factors. These coefficients are the effective diffusion coefficient (D_e) , the sorption capacity (a) and the half sorption time $(t_{1/2})$, which describe the kinetics of methane sorption on hard coal. Under certain assumptions, the key element affecting the rate of methane accumulation/release in hard coal will be the internal structure of the tested coal material [17]. One of the crucial parameters characterizing the kinetics of methane sorption in coal is the effective diffusion coefficient D_{e} . It is obtained from the solution of Fick's second law [18] using a number of simplifying assumptions. One of them is the assumption that the coal matrix contains only one type of pore—micropores. In reality, there are at most two different (interrelated) mechanisms related to the diffusion of methane from the microporous matrix and the flows occurring in the interstices and macropores [19]. In Poland, at present, the unipore model is used only to describe the kinetics of methane sorption on coal [20].

The literature survey conducted shows that there is a significant correlation between coal petrography and gas diffusion kinetics [21–26]. The change in porous structure is closely related to the change in the degree of coalification, and pores vary in shape and size [27]. The diffusivity of coal was found to decrease degree of coalification increased due to an increase in the proportion of micropores in its structure [28]. Based on research, the achievement of sorption equilibrium was found to be faster for low rank coals than for high rank coals [29].

The processes of gas desorption, sorption and migration were also modelled using numerical methods [21,30–33]. Determining the parameters of the bidisperse model allows it to be used for numerical analyses. By comparing the results for both descriptions of sorption kinetics, it was possible to assess the extent to which using a more accurate description can affect the quality of numerical modelling.

In this paper, an attempt is made to determine the possible scope of using the unipore and bidisperse model to obtain knowledge concerning the kinetics of methane sorption and its diffusion in the coal structure. Due to the range of different types and kinds of hard coal and its extended structure, it is not possible to precisely describe the kinetics of methane sorption in a universal way, based on simplified formulas that do not take into account the variability of its structure and the type of pores (micropores and macropores).

This article presents the results of laboratory analyses of sorption and petrography for coal samples collected from mines located in the Upper Silesian Coal Basin. The coals selected for the analyses are characterised by a variable degree of coalification and diversified physical and chemical parameters. Within the scope of the paper, model runs were fitted to the measured kinetics of the sorption process on hard coal using unipore and bidisperse models, which allowed the determination of the corresponding coefficients found in the mathematical models. Thus far, only the first model has been used to describe the kinetics of methane sorption on hard coal, describing the sorption/diffusion kinetics using the effective diffusion coefficient from Crank's solution [20]. The research carried out within the scope of this paper will allow us to assess the quality of model descriptions and to determine the coal properties (maceral composition, degree of coalification) for which it is possible to apply the unipore model and, when it becomes necessary, to apply the bidisperse model. These considerations relate to coals from the Upper Silesian Coal Basin, whereas the results obtained, due to the diversity of samples analysed, may be applied to hard coals globally.

2. Diffusion Models

2.1. Unipore Diffusion Model

The most common and widely used physical model to describe sorption kinetics and methane diffusion phenomenon in hard coal is the unipore model [17,25,34–37]. It assumes that the carbon matrix is homogeneous and is composed of a single type of pores in which the diffusion and sorption processes occur at equal rates [32,38–40]. A number of assumptions and simplifications are required to make the unipore model practical [17,41].

The physical dependence that quantitatively describes the diffusion process is Fick's second law and is the basis for the derivation of the unipore model [18]:

$$\frac{\partial c}{\partial t} = D \cdot \nabla^2 c,\tag{1}$$

where *c*—substance concentration (mol/m³), *t*—time (s), *D*—diffusion coefficient (m²/s).

An analytical solution of the model, which relates to Fick's second law, can be found in Crank [20] and Timofiejew [42]:

$$\frac{\partial c(r,t)}{\partial t} = \frac{D}{1+K_H} \nabla^2 c(r,t) = D_e \nabla^2 c(r,t); \quad D_e = \frac{D}{1+K_H}$$
(2)

where D_e —effective diffusion coefficient (cm²/s), K_H —Henry's linear isotherm coefficient (mol/g × bar), *r*—distance from the centre of the grain (m).

With the required assumptions, the solution of Equation (2) under certain boundary and initial conditions, as described in the literature [20,37,42], takes the form:

$$\frac{M_t}{M_{\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} exp\left(-\frac{D_e n^2 \pi^2 t}{R_z^2}\right); \quad R_z = \frac{1}{2} \sqrt[3]{\frac{2d_1^2 d_2^2}{d_1 + d_2}}$$
(3)

where M_t —mass of gas deposited in time t (g), M_{∞} —total mass of gas deposited in grains (g), R_z —substitute grain radius (cm), d_1 and d_2 —grain boundary values for the examined grain class [cm].

2.2. Bidisperse Diffusion Model

The second model to be analysed is the bidisperse model. Its primary assumption is that the coal matrix is a spherical particle that is formed from an agglomeration of multiple microporous spheres with macropores around the microparticles [32], as shown schematically in Figure 1. This model was first developed and described by Ruckenstein [43].



Figure 1. Schematic representation of the coal matrix with micro- and macropores present as assumed by the bidisperse model [43].

The bidisperse model [28,30,34,44–48] assumes that the coal matrix consists of a microand macropore system, described by the diffusion coefficients D_i and D_a , respectively. Gas diffusion in the bidisperse system is driven by the concentration gradient between the outer and inner parts of the system.

The equations describing gas diffusion into macro- and microsphere particles are presented as follows [32]:

$$\frac{D_a\epsilon_a}{r_a^2}\frac{\partial}{\partial r_a}\left(r_a^2\frac{\partial C_a}{\partial r_a}\right) = \epsilon_a\frac{\partial C_a}{\partial t} + S_a\frac{\partial C_{sa}}{\partial t} + 4\pi nR_i^2\epsilon_i D_i\left(\frac{\partial C_i}{\partial r_i}\right)_{r_i=R_i} \tag{4}$$

where D_a —diffusion coefficient for macropores (cm²/s), D_i —diffusion coefficient for micropores (cm²/s), r_a —distance from the centre of macropores (cm), C_a —macropore fluid phase sorbate concentration (mol/cm³), C_{sa} —macropore adsorber phase concentration (mol/cm²), n—number of microspheres per unit volume of the macrosphere, R_i microsphere radius (cm), S_a —macropore surface (cm²/cm³), ϵ_a —macropore void fraction, ϵ_i —micropore void fraction, t—time (s).

$$\frac{D_i\epsilon_i}{r_i^2}\frac{\partial}{\partial r_i}\left(r_i^2\frac{\partial C_i}{\partial r_i}\right) = \epsilon_i\frac{\partial C_i}{\partial t} + S_i\frac{\partial C_{si}}{\partial t}$$
(5)

where C_i —micropore fluid phase sorbate concentration (mol/cm³), C_s —micropore adsorber phase concentration (mol/cm²), S_i —micropore surface (cm²/cm³), r_i —distance from the centre of micropores (cm).

The mathematical solutions of the above partial differential equations are complicated. To enable them to be easily fitted to experimental data, Ruckenstein [43] provided a simplified solution. Its basic assumption is that the sorption and diffusion processes occur much faster in macropores than in micropores; thus, the process was divided into two stages: a slower stage, occurring in micropores, and a faster stage, occurring in macropores. Accepting the above assumptions, the equations take the following form:

$$\frac{M_a}{M_{a\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} exp\left(-\frac{D'_a n^2 \pi^2 t}{R_a^2}\right)$$
(6)

where: M_a —mass of gas deposited in macropores in time t (g), $M_{a\infty}$ —total mass of gas deposited in macropores (g), R_a —macrosphere radius (cm), D'_a —effective diffusion coefficient for macropores (cm²/s).

$$\frac{M_i}{M_{i\infty}} = 1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} exp\left(-\frac{D'_i n^2 \pi^2 t}{R_i^2}\right)$$
(7)

where M_i —mass of gas deposited in micropores in time t (g), $M_{i\infty}$ —total mass of gas deposited in micropores (g), D'_i —effective diffusion coefficient for micropores (cm²/s).

Hence, the total sorption at any time can be represented as the sum of the sorption of the macrosphere and microsphere in the form of the following equation:

$$\frac{M_t}{M_{\infty}} = \frac{M_a + M_i}{M_{a\infty} + M_{i\infty}} = \frac{\frac{M_a}{M_{a\infty}} + \frac{M_i}{M_{i\infty}} \left(\frac{M_{i\infty}}{M_{a\infty}}\right)}{1 + \frac{M_{\infty}}{M_{a\infty}}} = \frac{\frac{M_a}{M_{a\infty}} + \frac{\beta}{3\alpha} \frac{M_i}{M_{i\infty}}}{1 + \frac{\beta}{3\alpha}}$$
(8)

where α —dimensionless parameter specified:

$$\alpha = \frac{D_i' R_a^2}{D_a' R_i^2} \tag{9}$$

where β —dimensionless parameter specified:

$$\beta = \left[3\frac{(1-\epsilon_a)\epsilon_i}{\epsilon_a}\right] \left(\frac{D'_i R^2_a}{D'_a R^2_i}\right) \tag{10}$$

Accepting the presented assumptions, the equation for the bidisperse model, which takes into account the sorption and diffusion processes occurring independently in microand macropores, takes the form:

$$\frac{M_t}{M_{\infty}} = \frac{\left[1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} exp\left(-\frac{D'_a n^2 \pi^2 t}{R_a^2}\right)\right] + \frac{\beta}{3\alpha} \left[1 - \frac{6}{\pi^2} \sum_{n=1}^{\infty} \frac{1}{n^2} exp\left(-\frac{D'_i n^2 \pi^2 t\alpha}{R_i^2}\right)\right]}{1 + \frac{\beta}{3\alpha}} \tag{11}$$

3. Materials and Methods

3.1. Materials

Coal samples from the Upper Silesian Coal Basin (USCB), both from the Polish and Czech parts, were selected for the study. The samples were taken from the following mines: from the Polish part samples were taken from Sobieski (D-25, D-24), Piast (D-34), Mysłowice-Wesoła (D-37), Borynia (D-6), Zofiówka (D-22, D-23), and Pniówek (D-7); from the Czech part samples were taken from the ČR-Věřňovice mine (Cz. 4032, Cz. 4006). In the remainder of this article, samples will be named according to their symbols. The research material is characterized by varied petrography. Coals which differ in their degree of coalification and maceral composition were used for the tests. The samples were grouped according to their degree of coalification and summarized in Table 1.

Low-Rank Coal Samples	Medium-Rank Coal Samples	High-Rank Coal Samples		
Sobieski D-25	Borynia D-6			
Sobieski D-24	Zofiówka D-22	CR-Véřňovice Cz. 4006		
Piast D-34 Mysłowice-Wesoła D-37	Pniówek D-7 Zofiówka D-23	ČR-Věřňovice Cz. 4032		

Table 1. Coal samples selected for testing, taken from the Upper Silesian Coal Basin.

3.2. Petrographic Analysis—Research of Vitrinite Reflectivity and Maceral Composition

As part of the petrographic research, a quantitative point analysis and measurements of the coalification degree of selected coal samples from the USCB area were performed. The above analyses were conducted in accordance with recommendations of the International Committee for Coal and Organic Petrology (ICCP) regarding the petrographic analysis of hard coal and anthracite, contained in standards ISO 7404-2:2005—for preparing coal samples [49], ISO 7404-3:2001—for determining maceral group composition [50] and ISO 7404-5:2002—for reflectance of vitrinite [51]. Petrographic analyses were performed on granular polished sections according to the recommendation of ISO standards (ISO 7404-2; ISO 7404-3).

An AXIOPLAN polarizing microscope by ZEISS and a computer-controlled XYZ mechanical table were used to perform petrographic analyses. The image from under the optical microscope is transmitted to a monitor by a CCD camera. The relevant measurements were performed at $500 \times$ magnification using oil immersion.

To assess the content of individual maceral groups, quantitative point analyses were conducted. They included the determination of the content of the vitrinite, liptinite and inertinite groups as well as the mineral substance. Quantitative analyses were carried out on 1500 measurement points located in a square grid covering approx. 80% of the granular polished sections. The analyses of the maceral composition of individual samples are complemented by photographs of interesting fragments of the analysed coals.

For each of the analysed samples, the R_0 reflectivity was measured on the macerals from the vitrinite group colotelinite—free of impurities and inclusions. An Olympus BX50 polarization microscope at a magnification of $400 \times$ was used for the measurements. The granular polished sections were analysed in monochromatic light with a set wavelength of $\lambda = 546$ nm, reflected from the vitrinite surface, using oil immersion with a refractive index of n = 1.518. The results were obtained using the "LUCIA Vitrinite" image analysis system.

The volatile matter content was determined by the weight method based on the requirements of the Polish standard PN-G-04516 [52]. It consists of measuring the loss of volatile decomposition products of solid fuel, which is formed as a result of heating at 850 °C for 7 min without air access. An analytical sample with grain size below 0.2 mm, which is in accordance with the requirements of the standard, was used for the tests. The final result was obtained by converting the measured value to the dry, ash-free state (daf).

3.3. Sorption Analysis—Determination of Sorption Kinetics

A Hiden Isochema IGA-001 gravimetric sorption system was used for the precise analysis of sorption kinetics. The research on methane sorption was carried out on the basis of the gravimetric (weight) method, which, compared to the widely used volumetric method, is characterized by much greater accuracy and the possibility of registering the kinetics of the process.

The IGA-001 is an advanced gravimetric apparatus that records changes in sample mass over time associated with sorption processes occurring in porous materials, including coal. The sorption test stand described above is presented in Figure 2.



Figure 2. IGA-001 (intelligent gravimetric analyser) sorption test rig.

Coal samples with a grain size of 0.2-0.25 mm and a mass of approximately 150 mg were used for sorption testing. In the first stage, the sample was degassed and heated at 98 °C to remove adsorbed impurities and moisture.

After setting a certain pressure for the isotherm point, the sample mass is analysed continuously (real-time kinetic analysis). Data are collected until the previously set criterion approaches equilibrium. At this point, the software records the asymptotic adsorption and other equilibrium readings, and the pressure is automatically changed to a higher set point. The sorption kinetics are recorded continuously for each sorption isotherm point. The sorption isotherms for each coal samples were determined at 2 pressure points: 0.1 and 0.8 MPa, under continuously controlled temperature conditions of 25 °C. In the following part of the article, the sorption kinetics determined at 0.1 MPa will be analysed.

3.4. Identification Procedure

In order to determine the parameters describing the course of the sorption process on the basis of experimental data, an identification procedure was developed. The data obtained from experimental sorption tests were transformed to a system with the ratio $\frac{M_t}{M_{\infty}}(t)$ of gas adsorbed at the time *t* to the total mass of gas adsorbed in grains. Therefore, the experimental sorption curves were obtained, which were compared with the model described by Equation (3) in the case of the unipore model and Equation (11) in the case of the bidisperse model. The choice of the most appropriate of the two models depends on the structure of the analysed samples. The identification procedure is carried out as a task of minimisation of the error measure between the experimental and the model course of sorption curves. The error measure adopted in the task was the mean square error (MSE). In the identification problem defined in this way, the objective function *J* is minimised:

$$I = \sum_{j=1}^{M} (\hat{q}_j - q_j)^2$$
(12)

where \hat{q}_j is the measured value of the ratio $\frac{M_t}{M_{\infty}}$, q_j is the value of $\frac{M_t}{M_{\infty}}$ determined from the corresponding equation modelling the course of sorption at the same time, and Mis the number of measurements. The actual measurements were made at varying times, with a higher frequency at the initial stage of the process. The number of measurements depended on the time required to reach the equilibrium state which corresponds with the value of $\frac{M_t}{M_{\infty}} = 1$. The number of measurements ranges from about 250 to 500, depending on the experiment. The infinite sequences in the equations were approximated using the first 30 terms; it has been noted in previous studies that even approximation to 10 terms provides satisfactory results [53]. The parameter to be identified in the case of the unipore model is $\frac{D_e}{R_z^2}$, and after assuming a known value of R_z it is possible to determine the effective diffusion coefficient D_e . For the bidisperse model, which is described by a larger number of parameters, the following quantities were identified: $\frac{D'_a}{R_a^2}$, $\frac{D'_i}{R_i^2}$, α , $\frac{\beta}{\alpha}$ The function *fmincon* in MATLAB software was used to solve the identification task. This function searches for the minimum of a function with constraints using the interior-point method algorithm.

4. Results and Discussion

4.1. Petrographic Analysis

Hard coal, depending on the degree of coalification (determined on the basis of R_0 and V^{daf}), differs in colour in the microscopic view. The main difference can be seen in the grey shades of the individual macerals. In low rank coals, vitrinite is dark grey, liptinite is almost black, and inertinite is grey. In samples with higher coalification the macerals turn a slightly lighter shade of grey. In high rank coals vitrinite is almost white, while liptinite is completely invisible. During the microscopic research, photographic documentation of interesting fragments of the investigated coals was made. The above microscopic images are presented in the form of photographs in Figure 3a–j.



(**g**)

(**h**)

Figure 3. Cont.



Figure 3. (a) D-25—sporinite (macro and microscopic) surrounded by vitrinite and inertinite; (b) D-24—lamina of cracked vitrinite surrounded by trimacerite; (c) D-34—macro- and microsporinite among macerals of vitrinite and inertinite group; (d) D-37—telinite impregnated with micrinite; (e) D-6—fragment of coal composed of vitrinite and scattered macerals of inertinite and liptinite group; (f) D-22—fragment of lightly cracked coal composed of vitrinite and large macrospore and inertinite fragments; (g) D-7—vitrinite with bands of mineral matter, mainly clay; (h) D-23—fragment of coal composed of colotelinite, sporinite and small fragments of inertodetrinite; (i) Cz. 4032—vitrinite with macerals of inertinite group; (j) Cz. 4006—vitrinite with macerals of the inertinite group. Magnification 500×, reflected light, immersion.

Table 2 presents the results of petrographic microscopic analyses, along with quantitative point analysis and vitrinite reflectance. Furthermore, the results of some technical analyses such as moisture content W_a , ash content A and volatile matter content V^{daf} are included. The content of each group of macerals was converted to mineral matter free (mmf), and the content of mineral substance for each sample was also given.

No.	Sample	Wa (%)	A (%)	V ^{daf} (%)	R ₀ (%)	Wt mmf (%)	I mmf (%)	L mmf (%)	Minerals (%)
	Low rank coals								
1.	D-25	11.59	8.63	35.12	0.435	58.69	32.27	9.04	1.64
2.	D-24	8.04	8.03	36.73	0.47	47.56	39.68	12.75	5.68
3.	D-34	3.49	5.92	38.58	0.716	58.32	24.27	17.41	1.95
4.	D-37	3.17	12.08	38.96	0.735	64.99	28.89	6.12	6.60
	Medium rank coals								
5.	D-6	1.53	4.01	25.05	1.076	87.65	9.53	2.82	0.53
6.	D-22	1.12	5.80	25.37	1.113	81.55	15.87	2.57	3.28
7.	D-7	1.47	29.35	27.07	1.116	80.20	18.60	1.20	21.7
8.	D-23	0.99	6.21	19.80	1.361	73.82	24.09	2.09	6.83
High rank coals									
9.	Cz. 4006	0.62	7.54	13.62	1.94	91.29	8.71	0	3.11
10.	Cz. 4032	0.60	9.02	13.51	2.01	88.18	11.82	0	2.62

Table 2. Results	of	petrogra	phic	anal	lyses.
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Based on the research results, it was assumed that:

- Samples with $R_0 < 1\%$ should be treated as low rank coals (acc. to ASTM—Subbituminous and High Volatile Bituminous) [54].
- Samples with *R*₀ 1–1.4% should be treated as medium rank coals (acc. to ASTM—Medium Volatile Bituminous) [54].
- Samples with $R_0 > 1.4\%$ should be treated as high rank coals (acc. to ASTM—Low Volatile Bituminous) [54].

Vitrinite reflectivity R_0 for the analysed coal samples ranged from 0.435% to 2.01%. The lowest value of 0.435% was recorded for coal sample D-25, while the highest, i.e., 2.01%, was recorded for sample Cz. 4032. On the basis of the reflectivity test results and the assumptions made above, samples D-25, D-24, D-34 and D-37 were classified as low rank coals, samples D-6, D-22, D-7 and D-23 as medium rank coals, and samples Cz. 4006 and Cz. 4032 as high rank coals.

After analysing the obtained results of maceral composition, it was observed that the vitrinite content for all the tested samples ranged from 47.56% to 91.29%. For low rank coal samples, the values ranged from 47.56% to 64.99%, with the lowest value of 47.56% recorded for coal sample D-24. For medium rank coal samples, the values ranged from 73.82% to 87.65%, and for high rank coal samples from 88.18% to 91.29%. The highest vitrinite content of 91.29% was recorded for sample Cz. 4006.

The content of inertinite in the analysed samples ranged from 8.71% to 39.68%. The highest value was recorded for sample D-24, which is one of the low rank coals, while the lowest value, i.e., 8.71% was recorded for sample Cz. 4006, which is one of the high rank coals. The inertinite content for medium rank coals ranged from 9.53% to 24.09%.

In the samples with a high degree of coalification (Cz. 4032 and Cz. 4006), no macerals from the liptinite group were observed. This effect is known as the vitrinization of liptinite. Such a process causes the optical similarity of liptinite to vitrinite. Therefore, in microscopic observations in samples with R_0 above 1.3–1.4, macerals of the liptinite group are invisible. In the case of medium rank coals, liptinite was present in the range of 1.20% to 2.82%. Its highest values were observed for coal samples with a low degree of coalification. Their results ranged from 6.12% to 17.41%, and the highest value, i.e., 17.41% was obtained for the D-34 coal sample.

Based on the analysis of the results obtained for the volatile matter content V^{daf} and vitrinite reflectivity R_0 , it was found that coal with a low degree of coalification is characterized by a high volatile matter content, and the higher the reflectivity, the lower the V^{daf} . This relationship is not perfectly rectilinear, as V^{daf} is also affected by the content of individual maceral groups, especially the ratio of vitrinite to inertinite [55].

4.2. Sorption Analysis

Sorption studies were conducted on coal samples, which are characterized by varying degrees of coalification and maceral composition. As a result, the kinetics of methane sorption for selected samples at a pressure of 0.1 MPa were determined. For each of the determined sorption runs an attempt was made to fit the mathematical development of the unipore and bidisperse models. For both models, sorption runs were determined in the relationship $\frac{M_t}{M_{\infty}}(t)$, which were described based on Equations (3) and (11).

For both the unipore and bidisperse models, an unknown set of parameters $\frac{D_e}{R_z^2}$ and $\frac{D'_a}{R_a^2}$, $\frac{D'_i}{R_i^2}$, α , $\frac{\beta}{\alpha}$, controlling the course of the sorption and diffusion processes, respectively, was sought. Parameters were identified by fitting model runs with data obtained from laboratory tests. Fitting the model runs with the experimental results was performed by minimizing the mean square error (MSE).

The results of fitting the unipore model to the experimental data are shown in Figure 4a–j, and for the bidisperse model in Figure 5a–j. Experimental data are indicated by red dots, which correspond to measurements made as shown in Section 3.3, while model runs are indicated by blue solid lines. The value of the mean squared error (MSE) enables the assessment of the validity of the chosen model. A value closer to 0 corresponds to a better fit in relation to the experimental data, which indicates the relevance of using the selected model.



Piast (D-34) [unipore model], MSE = 0.0024261



(c)

Borynia (D-6) [unipore model], MSE = 0.00033297



(e)











Zofiówka (D-22) [unipore model], MSE = 0.0021516



Zofiówka (D-23) [unipore model], MSE = 0.00043067



Figure 4. Cont.



Figure 4. Fitting of the unipore model runs with experimental sorption data: (a) Sobieski (D-25); (b) Sobieski (D-24); (c) Piast (D-34); (d) Mysłowice-Wesoła (D-37); (e) Borynia (D-6); (f) Zofiówka (D-22); (g) Pniówek (D-7); (h) Zofiówka (D-23); (i) ČR-Věřňovice (Cz. 4006); (j) ČR-Věřňovice (Cz. 4032).

Based on the analysis of the graphs (Figure 4a–j) and the results of the mean squared error (MSE) (Table 3), it was found that there is a relatively good fit of the model run for the unipore model with the experimental data for samples Cz. 4032, Cz. 4006, D-23, D-7 and D-6 for which the MSE values were 0.00018; 0.00066; 0.00043; 0.00092; 0.00033, respectively. For the samples D-25, D-24, D-34, D-37 and D-22, the fit is not satisfactory and the MSE values were 0.005143; 0.00730; 0.00243; 0.00293; 0.00215, respectively. Based on the above observations, it can be concluded that there is a relatively good fit for the unipore model for high rank coals and partially for medium rank coals. A dependence of the level of fit of the model run with the experimental data depending on the maceral composition was also observed. A satisfactory fit is found for coals with high vitrinite content, i.e., for samples Cz. 4032, Cz. 4006, D-23, D-7 and D-6. The exception was sample D-22 which, despite its high vitrinite content of 81.55%, does not have a satisfactory fit. This may be due to the presence of cracks, which can be seen on the microscopic image (Figure 3f) and which disrupt the pore structure of this sample causing inhomogeneity.

Analysis of the dependence $\frac{D_e}{R_z^2}$ shows that for high rank coals its values are lower and range from 1.758×10^{-6} to 2.559×10^{-6} (s⁻¹). For medium rank coals these values increase and ranged from 2.344×10^{-6} to 9.287×10^{-6} (s⁻¹), while the highest values were recorded for low rank coals, from 5.990×10^{-6} to 2.714×10^{-4} (s⁻¹). Therefore, it can be concluded that the dependence $\frac{D_e}{R_z^2}$, which determines the rate of sorption processes in hard coal (its kinetics), depends on the degree of coalification and the maceral composition. The increase in the degree of coalification has the effect of reducing the $\frac{D_e}{R_z^2}$ dependence, which results in lower sorption kinetics of methane on hard coal. However, this is not a linear dependence, which is influenced by the varying maceral composition of the coals.

Based on the analysis of the literature, it can be stated that the petrography of coal has a significant influence on the course of sorption processes in its structure. The literature describes the dependence of the maceral composition and the degree of coalification on the course of diffusion and sorption processes [19,21,22,31,48,56–58]. The diffusivity of hard coal is related to both pore size distribution and porosity in terms of macroscopic equation. The organic matter has a strong methane-adsorption capacity. On the basis of research described in the literature [59,60], it was found that the methane permeability for organic pores first decreases and then increases with the increase of pore size.





Mysłowice-Wesoła (D-37) [bidisperse model], MSE = 0.00032896













(a)

Piast (D-34) [bidisperse model], MSE = 0.00017337



Borynia (D-6) [bidisperse model], MSE = 0.0001372



(e)

Pniówek (D-7) [bidisperse model], MSE = 0.00041555



Figure 5. Cont.



Figure 5. Fitting of the bidisperse model runs with experimental sorption data: (a) Sobieski (D-25); (b) Sobieski (D-24);
(c) Piast (D-34); (d) Mysłowice-Wesoła (D-37); (e) Borynia (D-6); (f) Zofiówka (D-22); (g) Pniówek (D-7); (h) Zofiówka (D-23);
(i) ČR-Věřňovice (Cz. 4006); (j) ČR-Věřňovice (Cz. 4032).

pressure 0.	1 MPa.					
No.	Sample	$rac{D_e}{R_z^2} [\mathbf{s}^{-1}]$	R_z (cm)	$D_e \ (\mathrm{cm}^2/\mathrm{s})$	MSE	
Low-rank coals						

Table 3. The unipore diffusion model fitting parameters for the methane adsorption rate data at

110.	Sumple	$R_z^2 \begin{bmatrix} 0 & 1 \end{bmatrix}$	$\mathbf{R}_{\mathbf{Z}}$ (cm)	D_{ℓ} (cm 73)	NICL		
Low-rank coals							
1.	D-25	$1.793 imes10^{-4}$	0.011157	$2.232 imes 10^{-8}$	0.00514		
2.	D-24	$2.714 imes10^{-4}$	0.011157	$3.379 imes10^{-8}$	0.00730		
3.	D-34	$5.990 imes10^{-6}$	0.011157	$7.457 imes 10^{-10}$	0.00243		
4.	D-37	$6.840 imes10^{-6}$	0.011157	$8.515 imes10^{-10}$	0.00293		
Medium-rank coals							
5.	D-6	$5.087 imes10^{-6}$	0.011157	$6.333 imes 10^{-10}$	0.00033		
6.	D-22	$2.344 imes10^{-6}$	0.011157	$2.918 imes10^{-10}$	0.00215		
7.	D-7	$9.287 imes10^{-6}$	0.011157	$1.156 imes10^{-9}$	0.00092		
8.	D-23	4.791×10^{-6}	0.011157	$5.964 imes 10^{-10}$	0.00043		
High-rank coals							
9.	Cz. 4006	1.758×10^{-6}	0.011157	$2.188 imes 10^{-10}$	0.00066		
10.	Cz. 4032	2.559×10^{-6}	0.011157	$3.185 imes10^{-10}$	0.00018		

Previous studies have shown that pore size distribution may have a significant impact on the gas sorption rate for coal samples. A sample that is homogeneous in terms of pore size distribution can be well fitted by simple diffusion models based on the unipore structure [30,61]. This was confirmed in the research presented in this paper, which was proved by the indication of a good fit of the unipore model to the experimental data for highly coalified samples Cz. 4006 and Cz. 4032. They were characterized by a maceral composition with a visible predominance of vitrinite, which is characterized by a micropore structure. A thesis describing the influence of coal petrography on sorption properties was also presented by Ceglarska-Stefańska [48], describing the effect of pore size distribution dependence in individual macerals. Furthermore, this thesis showed that vitrinite is a microporous material, while inertinite contains a significant proportion of meso- and macropores. Studies on the effect of maceral composition on sorption processes were also conducted by Crosdale [21], who found that inertinite-rich coals, especially fusinite and semifusinite, exhibit high gas emission rates, while vitrinite-rich coals exhibit slower emission rates. The studies described in this paper confirm the above thesis. The analysed coal samples for which high values of vitrinite content were obtained required more time to reach the sorption equilibrium state. For samples Cz. 4006 and Cz. 4032 with vitrinite contents of 91.29% and 88.18%, the values of effective diffusion coefficient D_e 2.188×10^{-10} and 3.185×10^{-10} cm²/s were obtained, which were determined based on the unipore model. Low values of the effective diffusion coefficient result from slower sorption processes occurring in these samples. The above observations also confirm the thesis concerning the predominance of the processes occurring in the micropores in the structures having a predominance of macerals from the vitrinite group. Modelling by Crosdale [21] indicates that bright and dull coals behave differently during gas desorption. The applicability of the unipore model to the desorption of bright coals suggests that the micropore system plays a dominant role here. The desorption described by the bidisperse model is suitable for dull coals rich in inertinite, especially semifusinite.

The low level of fit of the mathematical development of the unipore model with the experimental data for coals with a low degree of coalification is indicative of their extensive pore structure (Table 3). This is evident in the analysis of the maceral composition of these samples. For the low rank coals, the vitrinite content ranged from 47.56% to 64.99% and inertinite content ranged from 24.27% to 39.68% (Table 2). As stated in this paper and the literature presented above, an important parameter that differentiates coal in terms of its sorption properties is the content of each maceral group. Vitrinite is a microporous maceral with high sorption capacity, and sorption processes occur quite slowly in it. Inertinite, especially one with large and hollow cells, has high macroporosity and negligible microporosity. Therefore, for coals with different maceral composition and a low degree of coalification, it is necessary to treat their structure as bidisperse, for which sorption and diffusion processes occur simultaneously in micro- and macropores.

The fit of the bidisperse model runs to the experimental data for each of the analysed samples gave good results, as shown in the graphs (Figure 5a–j). This is further confirmed by the low values of the mean squared error MSE obtained, which ranged from 5.152×10^{-5} to 0.00721 (Table 4).

No.	Sample	$rac{D_a^{'}}{R_a^2} [\mathbf{s}^{-1}]$	$rac{D_i^{'}}{R_i^2} [\mathbf{s}^{-1}]$	α	$\frac{\beta}{\alpha}$	MSE		
	Low-rank coals							
1.	D-25	$1.923 imes 10^{-4}$	7.192×10^{-7}	0.788472	0.0682	0.00503		
2.	D-24	$2.836 imes10^{-4}$	$2.244 imes10^{-7}$	0.014057	0.0392	0.00721		
3.	D-34	$3.725 imes 10^{-5}$	$7.137 imes10^{-6}$	0.386631	6.1462	0.00017		
4.	D-37	$3.471 imes 10^{-5}$	5.273×10^{-6}	0.492207	4.6148	0.00033		
Medium-rank coals								
5.	D-6	$1.330 imes 10^{-5}$	3.289×10^{-3}	0.001063	7.2988	0.00014		
6.	D-22	$2.115 imes 10^{-5}$	$2.197 imes 10^{-3}$	0.006380	20.3650	0.00010		
7.	D-7	$1.841 imes 10^{-5}$	$8.396 imes10^{-4}$	0.004401	2.2815	0.00042		
8.	D-23	$1.486 imes 10^{-5}$	$8.205 imes 10^{-4}$	0.003880	7.7398	0.00011		
High-rank coals								
9.	Cz. 4006	3.295×10^{-5}	1.237×10^{-3}	0.001090	38.9386	5.152×10^{-6}		
10.	Cz. 4032	1.695×10^{-5}	$1.970 imes 10^{-3}$	0.001132	33.0460	$6.649 imes 10^{-6}$		

Table 4. The bidisperse diffusion model fitting parameters for the methane adsorption rate data at pressure 0.1 MPa.

Table 4 summarizes the fitting parameters of the bidisperse model along with the value of the mean squared error MSE. The values of effective diffusivity of macropores $\frac{D'_a}{R_a^2}$, effective diffusivity of micropores $\frac{D'_i}{R_i^2}$, and dimensionless parameters are presented: α represents the ratio of the time scales of the processes taking place in the micro- and macropores, and $\frac{\beta}{\alpha}$ specifying the information concerning the ratio of the micro- and macropores uptakes at equilibrium [43].

The hypothesis, presented above in connection with the unipore model, that the rate of methane sorption on hard coal decreases with an increase in the degree of coalification appears to be correct. It was confirmed by the obtained values of $\frac{D'_a}{R_a^2}$ and $\frac{D'_i}{R_i^2}$ for the samples with a high degree of coalification, where the dominance of effective micropore diffusivity

 $\frac{D'_i}{R_i^2}$ responsible for the sorption processes occurring in the micropores, where the process is slower, is visible. One example is the sample Cz. 4032 for which the effective diffusivity of micropores $\frac{D'_i}{R_i^2}$ was 1.970×10^{-3} (s⁻¹), while the effective diffusivity of macropores $\frac{D'_a}{R_a^2}$ was 1.695×10^{-5} (s⁻¹), which confirms the advantage of micropores in its structure. This is also confirmed by the maceral composition results obtained (Table 2). For the analysed high rank coals, there is a predominance of vitrinite (88.18–91.29%) over other macerals.

In the case of medium rank coals, for which vitrinite content ranged from 73.82 to 87.65% and inertinite content from 9.53 to 24.09%, the advantage of sorption processes occurring in micropores over macropores was also observed. For these samples, the effective micropore diffusivity $\frac{D'_i}{R_a^2}$ ranged from 3.289×10^{-3} to 2.197×10^{-4} (s⁻¹), while the effective macropore diffusivity $\frac{D'_a}{R_a^2}$ ranged from 1.330×10^{-5} to 2.115×10^{-5} (s⁻¹). The highest value of effective macroporous diffusivity of 2.115×10^{-5} (s⁻¹) was observed for sample D-22. As mentioned before, its structure shows areas of cracks (Figure 3f), which may explain the increased value of this parameter.

For the analysed coals with a low degree of coalification, the maceral composition was different compared to the previously discussed samples, where a higher content of inertinite was observed. Vitrinite content ranged from 47.56% to 64.99% and inertinite content ranged from 24.27% to 39.68%. The predominance of sorption contribution in macropores over micropores is evident for these samples. The values of effective micropore diffusivity $\frac{D'_i}{R_a^2}$ ranged from 2.244 × 10⁻⁷ to 7.137 × 10⁻⁶ (s⁻¹), while the effective macropore diffusivity $\frac{D'_a}{R_a^2}$ ranged from 3.471 × 10⁻⁵ to 2.836 × 10⁻⁴ (s⁻¹). Attention should be paid to sorption runs for samples D-24 and D-25 (Figure 5a,b). They show higher dynamics than the others, which are connected with a larger share of sorption in macropores for which the values of effective macropore diffusivity were 2.836 × 10⁻⁴ and 1.923 × 10⁻⁴ (s⁻¹), respectively.

Ruckenstein and Dang [32,43] stated that the parameter α (Table 4) represents the ratio of the time scales of the processes taking place in the micro- and macropores. For α values falling within the range of 0.001 to 100, it is apparent that the simultaneous diffusion of micro- and macropores controls the adsorption process. Studies by Roberts and York [62] have shown that sorption and diffusion processes occur in both micro- and macropores when the value of α occurs between 0.1 and 1.0. The results of the α coefficient presented in the article show that the diffusion processes for the analysed coal samples should be considered in terms of the bidisperse structure. Its values ranged from 0.001090 to 0.788472. Lower values for α occurring at the limit of 0.001 occurred for coals with a high degree of coalification and a certain predominance of sorption processes in micropores. Conversely, higher values of 0.5–0.8 were observed for low rank coals, in which the predominance of sorption processes in macropores was determined. Therefore, it can be stated that lower values of α coefficient were found for coal samples in which sorption processes took place predominantly in micropores, whereas higher values, closer to 1, were found for coals in which macropores were dominant in sorption processes.

Ruckenstein and Dang [32,43] defined the $\frac{\beta}{3\alpha}$ dependence shown in Equation (11), specifying the information concerning the ratio of the micro- and macropores (M_i/M_a) uptakes at equilibrium $\frac{M_t}{M_{\infty}} = 1$. They also defined that for low values of $\frac{\beta}{3\alpha}$ there is negligible adsorption of micropores, while for high values there is neglible adsorption of macropores. Thus, the adsorption ratio of micropores and macropores (M_i/M_a) at sorption equilibrium can be described by the equation [32]:

$$\frac{M_i}{M_a} = \frac{\beta}{3\alpha} \tag{13}$$

where M_i —the adsorption rate of methane in micropores at equilibrium, M_a —the adsorption rate of methane in macropores at equilibrium.

The determined value of $\frac{\beta}{\alpha}$ (Table 4) is obtained by fitting the bidisperse model to the experimental data obtained as a result of the research. The analysis of the research results presented in the article (Table 4), to some extent confirms the above thesis. For coals in which sorption processes were found to be dominant in macropores, the $\frac{\beta}{\alpha}$ results ranged from 0.0682 to 6.1462, which may indicate a lower proportion of micropores in their structure. On the contrary, for coals with predominance of sorption processes in the micropores, the values of the $\frac{\beta}{\alpha}$ coefficient ranged between 33.0460 and 38.9386, which may confirm a smaller share of macropores in their structure.

5. Conclusions

On the basis of the studies carried out, it has been stated that the mechanism of the occurrence of processes of sorption and diffusion of methane on hard coal is related to the petrography of coal, in particular to the maceral composition and the degree of coalification. The applicability of one of the models (unipore or bidisperse) describing the phenomenon of gas sorption and diffusion in a carbon structure is related to its structure and the relationship between micro- and macropores. The above fact supports the need for research on the applicability of the compared models. Based on the research conducted, the following conclusions were formed:

- 1. The pore size distribution has a significant impact on the rate of gas sorption processes in the coal structure. Coals homogeneous in terms of pore size distribution can be well fitted with simple diffusion models based on the unipore pore structure. Such coals are characterized by a high degree of coalification and a homogeneous maceral composition with a visible predominance of one of the maceral groups. The possibility of using the unipore model to describe the sorption of bright coals suggests that the micropore system plays a dominant role in their structure.
- 2. Bidisperse sorption is indicated for dull coals rich in inertinite, especially semifusinite. Coals with a complex structure, in which sorption and diffusion occur simultaneously in micro- and macropores, must be described by a bidisperse model, which has a better fit to the real course of sorption kinetics.
- 3. The application of the unipore model is possible for high rank coals, characterized by structures with vitrinite predominating. Conditionally, it can be applied to medium rank coals on the condition of high vitrinite content, indicating the predominance of micropores in the structure.
- 4. For low rank coals, it is necessary to use a bidisperse model to properly describe the course of sorption processes. The bidisperse model provides a good fit for all analysed coal types, regardless of the ratio of individual maceral groups.
- 5. Hard coal with a low degree of coalification is characterized by a high volatile matter content V^{daf} , and as the vitrinite reflectivity R_0 increases, V^{daf} decreases. This correlation is not perfectly rectilinear, as V^{daf} is also affected by the content of individual maceral groups, especially the ratio of vitrinite to inertinite.

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