Research Article

Contribution of Ash Content Related to Methane Adsorption Behaviors of Bituminous Coals

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Methane adsorption isotherms on coals with varying ash contents were investigated. The textural properties were characterized by N\textsubscript{2} adsorption/desorption isotherm at 77 K, and methane adsorption characteristics were measured at pressures up to 4.0 MPa at 298 K, 313 K, and 328 K, respectively. The Dubinin-Astakhov model and the Polanyi potential theory were employed to fit the experimental data. As a result, ash content correlated strongly to methane adsorption capacity. Over the ash range studied, 9.35% to 21.24%, the average increase in methane adsorption capacity was 0.021 mmol/g for each 1.0% rise in ash content. With the increasing ash content range of 21.24% ∼ 43.47%, a reduction in the maximum adsorption capacities of coals was observed. In addition, there was a positive correlation between the saturated adsorption capacity and the specific surface area and micropore volume of samples. Further, this study presented the heat of adsorption, the isosteric heat of adsorption, and the adsorbed phase specific heat capacity for methane adsorption on various coals. Employing the proposed thermodynamic approaches, the thermodynamic maps of the adsorption processes of coalbed methane were conducive to the understanding of the coal and gas simultaneous extraction.

1. Introduction

Coalbed methane (CBM) as an unconventional energy resource has led to economic assessment in many countries [1–3]. However, the CBM industry still lacks an adequate understanding of the parameters determining methane production. Understanding of methane adsorption on coal is extremely significant in estimating CBM resource exploitation, and the methane-holding capacity of coal seams has become an important area of research [4–6].

The nature of coal is an important variable to be considered in the coal seam. Coal is a complex polymeric material with complicated porous structures. Most coal pores are less than 100 nm in diameter, making them favorable for gas adsorption but unfavorable for gas permeability. Gases in coal, mostly in adsorbed state within the micropores (<10 nm) [7], are primarily composed of CH\textsubscript{4} (98%), CO\textsubscript{2}, trace amount of hydrocarbons, and other gases [7,8].

To date, various researchers have identified the most important factors influencing methane storage, including coal type [9, 10], rank [9, 11], moisture content [12–14], temperature [4, 15], burial depth [6, 16], pore characteristics [3, 7, 17–19] and so on [3, 20–22]. Ash content is often considered to be the main parameter affecting methane adsorption capacity. Ash, expressed as mineral matter [22], takes two forms in coal: inherent and extraneous mineral matter. Ash infilling predominantly clays and carbonates have been found to block the coal pore system, including cleats and fractures, and significantly reduce gas production. Additionally, much of the ash is primarily detrital constituents deposited with the organisms in coals which would not cause blockages of transport pores. It is generally considered that there is a low ash content in coals, with the coal formed combined with a large number of the organisms. With the initial increase of ash content of coal, its micropores and micropore volume would increase, while the mesopore and macropore volumes would dramatically decline. A relationship of decreasing capacity to increasing ash content has been established. However, other studies suggest that the relationship with ash content is a second-order polynomial trend with a maximum occurring.

Therefore, to address this concern, methane adsorption isotherms of coals with varying ash contents were investigated in this study, and effect of ash content on methane adsorption capacity was also studied. The texture of coals was
determined by \( N_2 \) adsorption/desorption at 77 K. Methane adsorption was measured by a volumetric method and the Dubinin-Astakhov (D-A) model and the Polanyi potential theory were fitted to the equilibrium data. This study also presented the heat of adsorption, the isosteric heat of adsorption, and the adsorbed phase specific heat capacity for methane adsorption on the coals.

### 2. Experimental

#### 2.1. Sample Preparation.
The bituminous coals, collected from Pangpangta Colliery in Shanxi province (China), were selected as the samples. The coal samples were crushed to particles with size fraction of 40–60 mesh, subsequently dried in an oven overnight at 110°C, and stored in a sealed plastic container. Proximate analyses for the coals were given in Table 1. The coals contained significant amounts of fixed carbon and variable amounts of ash, and the samples with varying ash contents were considered in the evaluation of ash content effects on methane adsorption.

#### 2.2. Characterization.
The textural characterization of the samples was obtained by \( N_2 \) adsorption/desorption isotherms, determined at 77 K with a NOVA1000e surface area and pore size analyzer (Quantachrome Company). Samples were degassed at 383 K for 24 h prior to analysis. Specific surface area (SSA) of the samples was measured from the Brunauer-Emmett-Teller (BET) method, and the mean pore size and the micropore volume were determined by nonlocal density functional theory (NLDFT) method. The total pore volume was evaluated at \( p/p_0 \approx 0.98–0.99 \), and the pore size distributions were obtained by density functional theory (DFT) equation [3, 23].

Proximate analysis was performed on a GF-A6 automatic proximate analyzer (Hebi Celestica Instruments Co., Ltd). All the samples were evaluated on a dry basis [3, 23].

#### 2.3. Methane Adsorption.
Methane adsorption measurements were performed using a volumetric method similar to that previously described [2, 3, 6, 23]. The purities of He and methane were 99.999% and 99.999%, respectively. Approximately 5 g of 40–60 mesh coal was dried at 110°C and evacuated for 3 h, prior to determination of void volume in the adsorption setup by helium calibration. Subsequent to helium calibration, samples were again evacuated for 3 h for methane adsorption. Methane was introduced into the adsorption setup to produce an adsorption isotherm under pressures up to 4.0 MPa in the temperature range 25–55°C. The test was repeated three times and the mean value of the equilibrium data was used to calculate the adsorption isotherm to ensure the validity of the experiment.

#### 2.4. Modeling Methane Sorption Data.
As the methane adsorption proceeds, the difference between excess adsorption amount (\( W_{\text{excess}} \), in mmol/g) and the absolute adsorption amount (\( W_{\text{absolute}} \) in mmol/g) becomes more obvious with the adsorption pressure becoming higher [3, 23, 24]. Since \( W_{\text{absolute}} \) cannot be directly measured, \( W_{\text{excess}} \) measured from the experiments is used for the calculation of \( W_{\text{absolute}} \):

\[
W_{\text{absolute}} = \frac{W_{\text{excess}}}{1 - \rho_{\text{gas}}/\rho_a}, \tag{1}
\]

where \( \rho_{\text{gas}} \) and \( \rho_a \) (in g/cm\(^3\)) are the density of the free gas phase and the adsorbed phase, respectively.

Since \( \rho_a \) cannot be determined directly, we use the following method to calculate the density of the adsorbed phase (\( \rho_a \)):

\[
\rho_a = \rho_b \exp\left[-\alpha(T - T_b)\right],
\]

where \( \rho_b \) is the density of methane at the boiling point (0.424 g/cm\(^3\)); \( T_b \) is the boiling point of methane (111.5 K); \( v_b \) is the specific mass at the boiling point (in mmol/g); \( v_a \) is the specific mass of the adsorbed phase (in mmol/g); and \( \alpha \) is the thermal expansion coefficient of the adsorbed phase (in K\(^{-1}\)). In our work, \( \alpha \) was determined by the empirical value of 0.0025.

The D-A equation was applied to fit the adsorption data. The adsorption parameters \( W_0, E, \text{and } n \) are optimized from the least-squares criteria. The relevant equation is expressed as

\[
W = W_0 \exp\left\{-\left(\frac{RT}{E} \ln\left(\frac{P_0}{P}\right)\right)^n\right\}, \tag{3}
\]

where \( W \) (in mmol/g) is the adsorption amount of methane; \( W_0 \) (in mmol/g) is the saturated adsorption amount of methane; \( T \) is 298.15 K, 313.15 K, and 328.15 K, respectively; \( R \) is the gas constant (8.314 J/mol·K); \( E \) is the characteristic energy of the adsorption system (in J/mol); \( P_0 \) (in MPa) refers to the quasi-saturated vapor pressure at the evaluated temperature, for the adsorption measurements are above

### Table 1: Proximate composition analysis of selected coal samples (mass fraction, %).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ash (dry basis)</th>
<th>Fixed carbon (dry basis)</th>
<th>Volatile matter (dry basis)</th>
<th>Moisture</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>9.35</td>
<td>67.18</td>
<td>23.47</td>
<td>1.08</td>
</tr>
<tr>
<td>A2</td>
<td>11.89</td>
<td>66.24</td>
<td>21.87</td>
<td>1.19</td>
</tr>
<tr>
<td>A3</td>
<td>15.27</td>
<td>63.97</td>
<td>20.76</td>
<td>1.03</td>
</tr>
<tr>
<td>A4</td>
<td>21.24</td>
<td>57.85</td>
<td>20.91</td>
<td>1.03</td>
</tr>
<tr>
<td>A5</td>
<td>26.82</td>
<td>52.82</td>
<td>20.36</td>
<td>1.18</td>
</tr>
<tr>
<td>A6</td>
<td>30.04</td>
<td>51.10</td>
<td>18.86</td>
<td>1.16</td>
</tr>
<tr>
<td>A7</td>
<td>35.62</td>
<td>46.01</td>
<td>18.37</td>
<td>1.20</td>
</tr>
<tr>
<td>A8</td>
<td>43.57</td>
<td>39.38</td>
<td>17.05</td>
<td>1.36</td>
</tr>
</tbody>
</table>

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the critical point of methane; and \( n \) is the structural heterogeneity factor. The \( P_0 \) can be estimated as

\[
P_0 = P_c \left( \frac{T}{T_c} \right)^2, \tag{4}
\]

where the subscript \( c \) refers to the critical point (for methane, \( P_c \) is 4.59 MPa and \( T_c \) is 190.56 K).

The prediction uncertainty is calculated from the following equation [23–25]:

\[
\delta = \sqrt{\frac{1}{N-1} \sum_{i=1}^{N} \left( \frac{W_i - W_{\text{cal}}}{W_i} \right)^2}, \tag{5}
\]

where \( N \) is the number of data and \( W_i \) is the data from the measured results.

Moreover, the Polanyi potential theory was employed to fit the experimental data. The relevant equations are

\[
\varepsilon = -\int_{P_s}^{P} V dP = -\int_{P_s}^{P} \frac{RT}{P} dP = -RT \ln \frac{P}{P_s},
\]

\[
\omega = \frac{WM}{22400 \rho_s},
\]

\[
P_s = P_c \left( \frac{T}{T_c} \right)^k,
\]

where \( \varepsilon \) is the adsorption potential (in J/mol); \( P_s \) (in MPa) refers to the quasi-saturated vapor pressure at the evaluated temperature, which is calculated by the Schwarz method; \( \omega \) is the volume of adsorbed phase at equilibrium (in cm\(^3\)/g); \( M \) is the molar mass of methane (in g/mol); \( k \) is a parameter specific to the adsorbate-adsorbent system; and, in this study, the value of \( k \) is 2.7.

The adsorption characteristic curve can be expressed as

\[
\varepsilon = A + B \omega + C \omega^2 + D \omega^3, \tag{7}
\]

where \( A, B, C, \) and \( D \) are constants.

### 2.5. Thermodynamics

#### 2.5.1. Heat of Adsorption

The heat release during the adsorption process is known as the heat of adsorption (\( H_{\text{ads}} \)) [26]. With coal possessing a heterogeneous surface, \( H_{\text{ads}} \) is essential for methane adsorption and changed greatly with the variation of surface loading (\( W/W_0 \)). \( H_{\text{ads}} \) is presented in a Clausius-Clapeyron equation, which has been used for the evaluation of \( H_{\text{ads}} \) [26]. \( H_{\text{ads}} \) is extracted by Clausius-Clapeyron equation from the experimental adsorption data:

\[
H_{\text{ads}} = RT^2 \left[ \frac{\partial (\ln P)}{\partial T} \right]_W. \tag{8}
\]

Invoking the D-A model (3) in (8), an explicit expression for \( H_{\text{ads}} \) can be written as (9) for \( T > T_c \) (the subscript \( c \) refers to the critical point, as shown in (4)) [26]. Consider

\[
H_{\text{ads}} = 2RT + E \left[ \ln \frac{W_0}{Cv_g} \right]^{1/n} + \alpha \frac{T}{n} \left( \ln \frac{W_0}{Cv_g} \right)^{1-n/n}, \tag{9}
\]

where \( W_0 \) (in mmol/g) is the saturated adsorption amount of methane; \( E \) is the characteristic energy of the adsorption system (in J/mol); \( \alpha \) is the specific mass of the adsorbed phase (in mmol/g); \( C \) is the methane surface loading (in g/g); \( H_{\text{ads}} \) is the heat of adsorption (in J/mol).

#### 2.5.2. Isosteric Heat of Adsorption

Since \( \beta E_0 \) can be related to the isosteric heat of adsorption (\( Q_{st} \)) at the fractional filling \( \phi \) of \( e^{-1} \) using the enthalpy of vaporization \( \Delta H_s \) at the boiling point, \( Q_{st} \) can be expressed as [12, 13, 27]

\[
Q_{st,\phi=\epsilon^{-1}} = \Delta H_s + \beta E_0, \tag{10}
\]

where \( Q_{st} \) is the isosteric heat of adsorption at the fractional filling \( \phi \) of \( e^{-1} \) (in J/mol); \( \Delta H_s \) is the enthalpy of vaporization of methane at the boiling point (in J/mol); \( E_0 \) is the characteristic adsorption energy (in J/mol); \( \beta \) is the affinity coefficient.

#### 2.5.3. Adsorbed Phase Specific Heat Capacity

The adsorbed phase, different from the gaseous and the liquid phase, has been assumed to be equal to the liquid phase for a long time, as well as similar to the gaseous phase. Therefore, the specific heat capacity (\( c_{p,a} \), in J/mol · K) is necessary to be determined for the adsorbed phase. To date, the \( c_{p,a} \) is thermodynamically defined as the temperature derivative of the differential adsorbed phase enthalpy (\( h_a \), in J/mol) at constant surface loading (\( W \)) [26]; that is,

\[
c_{p,a} = \left( \frac{\partial h_a}{\partial T} \right)_W. \tag{11}
\]

Since the \( H_{\text{ads}} \) can also be presented as the difference between the gaseous phase enthalpy and the adsorbed phase enthalpy by definition, \( c_{p,a} \) can be written as

\[
H_{\text{ads}} = h_g - h_a, \tag{12}
\]

\[
c_{p,a} = \left( \frac{\partial h_g}{\partial T} \right)_p - \left( \frac{\partial h_{\text{ads}}}{\partial T} \right)_W = c_{p,g} - \left( \frac{\partial h_{\text{ads}}}{\partial T} \right)_W, \tag{13}
\]

where \( h_g \) is the enthalpy of gaseous phase (in J/mol); \( h_a \) is the enthalpy of adsorbed phase (in J/mol); \( c_{p,g} \) is the specific heat capacity of gaseous phase (in J/mol · K).

Thus, invoking the expression for \( H_{\text{ads}} \) from (9) in (13), the \( c_{p,a} \) can be rewritten as (14) for super-critical condition

\[
c_{p,a} = c_{p,g} - 2R + \frac{\alpha^2 (1-n)}{n^2} E T \ln \left( \frac{W_0}{Cv_g} \right)^{(1-2n)/n}. \tag{14}
\]

### 3. Results and Discussion

#### 3.1. Textural Characterization

Coal pore morphology is mainly represented by micro- and mesopores with a well-connected and ink-bottle shaped morphology. Most coal pores are less than 100 nm in diameter, making them favorable for gas adsorption but unfavorable for gas permeability. Based on the knowledge of coal nature, its pore structure is characterized by \( N_2 \) adsorption/desorption isotherms. Figure 1 displayed \( N_2 \) adsorption/desorption isotherms at
77 K as a function of ash content. According to the BET classification, adsorption isotherms of this kind belonged to type III describing the physical adsorption process of N\textsubscript{2}. The isotherms exhibited remarkable hysteresis loops at higher relative pressures ($P/P_0 > 0.2$). It was obvious that the isotherms of samples A4 and A5 dramatically increased on reaching a relative pressure of unity. Moreover, the adsorption volume of sample A4 was the highest among the eight samples, while the adsorption volume of A1 was the lowest.

Figure 2 presented the textural parameters for the coal samples, and the pore size distributions obtained by applying the DFT equation were shown in Figure 3. The variation of ash contents led to differences in the SSA, micropore volume, and total pore volume. Among the samples, the A1 displayed the lowest SSA and micropore volume, indicating that the development of porosity of A1 was incomplete. Compared with the others, the A4 sample had highest SSA and micropore volume, being 7.95 and 2.29 times higher than the sample A1, respectively.

Many of the physical properties of the coal show a "U-shaped" curve with a minimum or a maximum in the mid-bituminous coal rank, and the effect of ash content
on the pore structure was no exception. With increases in ash content range of 9.35%–21.24%, the SSA increased, going through a maximum in the ash content up to 21.24% and decreasing with further increases in ash content, as well as the micropore volume and the total pore volume. The initial decrease in porosity was related to a decrease in macro- and mesoporosity, while the subsequent increase was related to an increase in microporosity. The decreased micropore volume and total pore volume suggested that either the opened pores were closed or some micropores initially opening have been blocked by the ash.

The pore size distributions demonstrated in Figure 3 showed that the pore structures of the specimens were predominantly microporous structures (<10 nm) [7]. The pore volumes of the samples in Figure 3(a) were increased as a function of ash content compared with that of A1 sample. It was observed that the pore volume could be strongly influenced by ash content. As illustrated in Figure 3(b), in the case of ash content further increasing, the volume in microporous range was decreased as compared with the samples in Figure 3(a), for ash-rich coals were often more macroporous than ash-low coals in Figure 3(b). As mentioned above, the micropores were blocked by the continued increase of ash content, after being the highest total pore volume.

3.2. Methane Adsorption Isotherms. Figure 4 displayed the measured data of methane adsorption on the samples at 25°C, 40°C, and 55°C under pressures up to 4.0 MPa. The methane adsorption isotherms were Type I of IUPAC. Differences in SSA and ash content can result in variation of methane adsorption capacities. The adsorption capacities of coals increased with increasing ash content up to 21.24%, passing through a maximum, and then decreased sharply with further increases in ash content. Among the samples, the sample A4 possessed the highest methane adsorption capacity and the A1 sample possessed the lowest methane adsorption capacity.

The methane adsorption isotherms at lower relative pressures represent behavior dominated by Van der Waals forces, whereas the isotherms at higher relative pressures characterize actions dominated by capillary condensations. Thus, the D-A model, based on the Polanyi potential theory and applied when the adsorption process follows a pore filling mechanism, was appropriate to fit the adsorption data and provided good agreement with the experimental data. The adsorption parameters of the D-A model were described in Table 2. The parameter \( n \) in D-A model describes the surface heterogeneity. It has been reported that the surface of the adsorbent is less heterogeneous when the \( n \) value is approaching 3 more (\( n < 3 \)). The value of \( n \) generally changed along with the variation of ash content of the samples. The parameter \( E \) in D-A model is the characteristic energy that described the strength of interaction between adsorbate and adsorbent.

The maximum adsorption capacities (\( W_0 \)) of the coal samples in the study varied from 0.45 to 0.70 mmol/g. The study revealed that the ash content had different effects on the methane adsorption capacities of the coal samples. Over the ash range studied, 9.35% to 21.24%, the average increase in methane adsorption capacity was 0.021 mmol/g for each 1.0% rise in ash content. For the coals with ash content range of 21.24%–43.57%, the ash content acting as a diluent strongly influenced the methane adsorption capacity (decreased about 0.0985 mmol/g for each 10% rise in ash content).
Figure 4: Methane adsorption isotherms obtained by applying the D-A model at 298 K, 313.15 K, and 328.15 K, respectively. (a) A1, (b) A2, (c) A3, (d) A4, (e) A5, (f) A6, (g) A7, and (h) A8; solid line, fitted by the D-A model.
Table 2: Adsorption parameters of the D-A model of methane adsorption at 298 K.

<table>
<thead>
<tr>
<th>D-A model</th>
<th>A1</th>
<th>A2</th>
<th>A3</th>
<th>A4</th>
<th>A5</th>
<th>A6</th>
<th>A7</th>
<th>A8</th>
</tr>
</thead>
<tbody>
<tr>
<td>$W_0$ (mmol/g)</td>
<td>0.45</td>
<td>0.54</td>
<td>0.59</td>
<td>0.70</td>
<td>0.66</td>
<td>0.64</td>
<td>0.52</td>
<td>0.48</td>
</tr>
<tr>
<td>$E$ (kJ/mol)</td>
<td>5.34</td>
<td>4.44</td>
<td>5.92</td>
<td>5.14</td>
<td>6.06</td>
<td>5.22</td>
<td>4.64</td>
<td>5.76</td>
</tr>
<tr>
<td>$\eta$</td>
<td>1.38</td>
<td>1.31</td>
<td>1.94</td>
<td>1.37</td>
<td>1.63</td>
<td>1.60</td>
<td>1.38</td>
<td>1.68</td>
</tr>
<tr>
<td>Mean relative deviation $\delta$ (%)</td>
<td>1.62</td>
<td>1.95</td>
<td>1.53</td>
<td>1.09</td>
<td>0.69</td>
<td>0.52</td>
<td>1.33</td>
<td>0.69</td>
</tr>
</tbody>
</table>

3.3. Heat of Adsorption ($H_{ads}$). The heat of adsorption ($H_{ads}$) values for the samples was evaluated using (8) and (9) and these were plotted in Figure 7 against the surface loading ($W/W_0$). Since the heat of vaporization ($h_{fg}$) is an increasing function of temperature above the critical point, $H_{ads}$ increased with temperature for the supercritical states as shown in Figure 7. Since the derived expression (9) requires the adsorption isotherm parameters ($W_0$, $E$, $\eta$, and $\alpha$) in calculating the $H_{ads}$, Table 2 presented the adsorption parameters of the D-A model of methane adsorption at 298 K as an example. It was observed that the $H_{ads}$ varied with the surface loading for all the samples, and the $H_{ads}$ values of samples A3, A5, and A8 were found larger compared with the others. From Figure 7, it can be also seen that the $H_{ads}$ varied with coal surface loading and approached a limiting value when the adsorption process proceeded towards the saturation uptake limit. This variation of $H_{ads}$ with the surface loading was due to the surface heterogeneity of the coal. The $H_{ads}$ decreased as surfaces became less heterogeneous and the surface coverage increased.

3.4. Isosteric Heat of Adsorption. The isosteric heat of adsorption of methane was calculated from the characteristic heat of adsorption employing (10). As shown in Figure 8, the range of the values of isosteric heat of adsorption for the coals was small, between 12.6 and 14.2 kJ/mol, regardless of the ash content, and the maximum of the differences was 1.6 kJ/mol. Moreover, for a single sample at various adsorption temperatures, the differences of values of isosteric heats of adsorption of methane were located between 0.25 and 0.95 kJ/mol, much smaller than 1.6 kJ/mol. The range and magnitude of these isosteric heats of adsorption values suggested a physical adsorption mechanism rather than a chemisorption mechanism. Since the isosteric heat of adsorption should decrease as the surfaces became less heterogeneous and the surface coverage increased [26], herein, it was suggested that the changes in the isosteric heat of adsorption were due to the heterogeneity of the pore surfaces of the coals.

3.5. Adsorbed Phase Specific Heat Capacity. The adsorbed phase specific heat capacity ($c_{p,ads}$) is function of pressure, temperature, and amount of adsorbate adsorption, whereas the bulk specific heat capacity ($c_p$) depends only on pressure and temperature [26]. Therefore, it is necessary to evaluate the $c_{p,ads}$ values for thermodynamic analysis of any adsorbate-adsorbent system, such as methane-coal system. Equation (14) was developed for this purpose.

The $c_{p,ads}$ values were evaluated for methane adsorption onto the coal samples and plotted against ash content in Figure 9 for constant pressure, $P = 0.1$ MPa. Due to the availability of adsorption uptake data of methane-coal system, it was reasonable to determine the $c_{p,ads}$ values for supercritical temperatures. The $c_{p,ads}$ values were pressure and temperature dependent, and they were closer to the gaseous phase values. It was observed that the isobaric $c_{p,ads}$ values were increasing with temperatures and also in the similar trend in case of all the samples. It was also observed that the $c_{p,ads}$ values were dependent on the adsorption parameters and these plots.

**Figure 5**: Saturated adsorption capacity $W_0$ related to specific surface area ($\square$) and micropore volume ($\blacksquare$).
Figure 6: Characteristic curves for methane on (a) A1, (b) A2, (c) A3, (d) A4, (e) A5, (f) A6, (g) A7, and (h) A8 at 298 K, 313.15 K, and 328.15 K, respectively.
FIGURE 7: Heat of adsorption ($H_{ads}$) for methane/coal systems against surface loading ($W/W_0$) at various temperatures. ◼, 298.15 K; ⧫, 313.15 K; and ▲, 328.15 K. (a) A1, (b) A2, (c) A3, (d) A4, (e) A5, (f) A6, (g) A7, and (h) A8.
demonstrated the dependence on the characteristics energy \((E)\) and the heterogeneity parameter \((n)\).

### 4. Conclusion

Methane adsorption behaviors on coals with varying ash contents were studied in this work. The adsorption characteristics of methane were performed at 298 K, 313 K, and 328 K, respectively, and pressures up to 4.0 MPa by a volumetric method. The D-A model and the Polanyi potential theory were fitted to the experimental data, respectively, and the fitting results showed that the D-A model fitted the data well, and the characteristic curve was independent of temperature. The methane adsorption on coals involved in coordination with their physical structures and ash contents. As a result, there was a positive correlation between the saturated adsorption capacity and the SSA and micropore volume of samples. Further, ash content correlated strongly to methane adsorption capacity. Over the ash range studied, 9.35% to 21.24%, the average increase in methane adsorption capacity was 0.021 mmol/g for each 1.0% rise in ash content. For the coals with ash content range of 21.24%~43.57%, the ash content acting as a diluent strongly influenced the methane adsorption capacity (decreased about 0.0985 mmol/g for each 10% rise in ash content).

Further, this study presented the heat of adsorption, the isosteric heat of adsorption, and the adsorbed phase specific heat capacity for the adsorption of methane onto various coals. Employing the proposed thermodynamic approaches, this paper showed the thermodynamic maps of the adsorption processes of CBM for understanding the coal and gas simultaneous extraction.

### Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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