Construction of Buertai coal macromolecular model and GCMC simulation of methane adsorption in micropores

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1. Details of the ash removal of coal samples

The coal samples were deashed as follows: First, 15.0000 g of coal powder (< 200 mesh) was weighed out using an electronic analytical balance and placed into a clean 250 mL beaker with 80 mL of dilute hydrochloric acid (5 mol/L). The beaker was placed in a water bath with a temperature of 60 °C and stirred with a glass rod for 1 hour. The mixture was then filtered using vacuum filtration. Second, the filtered mixture was transferred to a 250 mL plastic beaker where 80 mL of hydrofluoric acid was added slowly while stirring with a plastic rod for 1 hour. The solid coal particles were vacuum filtered and placed into a 250 mL glass beaker. Third, 80 mL of concentrated hydrochloric acid was poured into the beaker and stirred and heated as described above. Finally, the treated coal sample was washed with distilled water until the pH of the filtrate was 7. The filtered sample, namely demineralized coal, was dried in a vacuum oven for 24 hours prior to use.

2. The fitting results of the four bands of infrared spectrum

2.1. Aromatic structure absorption band analysis

Peaks observed in the 700–900 cm⁻¹ infrared band of the coal samples were fitted using the Origin 9.0 software. The fitted peaks for the samples are shown in Figure S1, and the attributes of each peak are presented in Table S1. As indicated by the results, the peak in this band mainly represents the substitution position on the
aromatic hydrocarbon, such as the one, two, three, and four substitution positions on the benzene ring.

**Figure S1.** Infrared spectrum of aromatic hydrocarbons in Buertai coal sample

**Table S1** Peak fitting results of infrared spectrum of aromatic hydrocarbons in Buertai coal samples

| number | Wave number (cm\(^{-1}\)) | half-peak width (cm\(^{-1}\)) | peak pattern | area | Relative area (%) | Corresponding group |
|--------|--------------------------|-------------------------------|--------------|------|-------------------|---------------------|
| 1      | 705.640                  | 7.15                          | Gaussian     | 0.004| 2.33              | Benzene ring substitution (5H) |
| 2      | 721.062                  | 8.20                          | Gaussian     | 0.015| 8.38              | Benzene ring disubstituted (4H) |
| 3      | 737.098                  | 12.61                         | Gaussian     | 0.024| 13.84             | Benzene ring disubstituted (4H) |
| 4      | 751.467                  | 10.71                         | Gaussian     | 0.023| 13.06             | Benzene ring disubstituted (4H) |
| 5      | 764.928                  | 12.47                         | Gaussian     | 0.014| 7.91              | Benzene ring trisubstituted (3H) |
| 6      | 786.575                  | 43.18                         | Gaussian     | 0.054| 31.04             | Benzene ring trisubstituted (3H) |
| 7      | 805.579                  | 8.18                          | Gaussian     | 0.005| 2.91              | Benzene ring trisubstituted (3H) |
| 8      | 819.933                  | 12.74                         | Gaussian     | 0.013| 7.67              | Benzene ring tetrasubstituted (2H) |
| 9      | 836.398                  | 8.43                          | Gaussian     | 0.005| 2.86              | Benzene ring tetrasubstituted (2H) |
| 10     | 852.425                  | 5.09                          | Gaussian     | 0.001| 0.81              | Benzene ring tetrasubstituted (2H) |
| 11     | 868.855                  | 7.67                          | Gaussian     | 0.002| 1.40              | Benzene ring five substitution (1H) |
| 12     | 886.911                  | 31.72                         | Gaussian     | 0.013| 7.73              | Benzene ring five substitution (1H) |
2.2. Absorption band analysis of oxygen-containing functional groups

Peaks in the 1000–1800 cm\(^{-1}\) infrared band of the coal samples were fitted, and the fitted peaks are shown in Figure S2 and the attributes of each peak in Table S2. It can be seen from the results that many functional groups occur within this band, and the spectrum is complicated. The 900–1300 cm\(^{-1}\) band is attributed to the C-O stretching vibration peak of the phenol, hydroxyl, ether, and ketone functional groups. The 1300–1610 cm\(^{-1}\) band represents the C=C stretching vibration peak of the aromatic compound and the deformation vibration peak of -CH\(_2\) and -CH\(_3\). The vibration peak near the 1395 cm\(^{-1}\) band is attributed to the symmetrical bending vibration of -CH\(_3\), and the 1610–1700 cm\(^{-1}\) band is attributed to the C=O stretching vibration peak. It is also noted that the absorption peak observed around 1600 cm\(^{-1}\), which is associated with phenolic compounds, is the strongest, indicating a high content of phenol ether compounds in the sample.

![Figure S2. Curve-fitting FTIR spectrum of oxygen-containing functional groups in Buertai coal](image)
Table S2 Peak fitting results of infrared spectrum of the oxygen-containing functional groups in Buertai coal samples.

| number | Wave number (cm⁻¹) | half-peak width (cm⁻¹) | peak pattern | area | Relative area (%) | Corresponding group |
|--------|---------------------|------------------------|--------------|------|-------------------|---------------------|
| 1      | 1050.72             | 56.90                  | Gaussian     | 0.14 | 2.24              | -CH₂                  |
| 2      | 1102.69             | 61.18                  | Gaussian     | 0.25 | 3.97              | -CH₃                  |
| 3      | 1159.57             | 83.19                  | Gaussian     | 0.29 | 4.59              | C-O vibration of ether alcohol and ether |
| 4      | 1192.60             | 97.02                  | Gaussian     | 0.19 | 3.05              | C-O vibration of phenol and ether |
| 5      | 1240.76             | 99.95                  | Gaussian     | 0.35 | 5.61              | C-O vibration in phenol and ether |
| 6      | 1281.01             | 75.90                  | Gaussian     | 0.24 | 3.85              | CH₃-symmetric bending vibration |
| 7      | 1346.13             | 68.14                  | Gaussian     | 0.26 | 4.11              | CH₃-symmetric bending vibration |
| 8      | 1395.63             | 44.61                  | Gaussian     | 0.33 | 5.28              | CH₃-symmetric bending vibration |
| 9      | 1446.46             | 62.08                  | Gaussian     | 0.39 | 6.26              | CH₃-symmetric bending vibration |
| 10     | 1507.19             | 50.32                  | Gaussian     | 0.15 | 2.37              | C=C vibration of aromatic hydrocarbons |
| 11     | 1573.67             | 72.44                  | Gaussian     | 0.81 | 12.81             | C=C vibration of aromatic hydrocarbons |
| 12     | 1636.58             | 67.08                  | Gaussian     | 2.38 | 37.66             | C=O stretching vibration |
| 13     | 1696.02             | 64.65                  | Gaussian     | 0.51 | 8.14              | C=O stretching vibration |

2.3. Aliphatic structure absorption band analysis

The peaks in the 2800–3000 cm⁻¹ infrared band of the coal samples were fitted, and the fitted peaks are shown in Figure S3 and the attributes of each peak in Table S3. It can be seen from the results that the vibration peak of -CH₂ in the coal samples is greater than the vibration peak of -CH₃, which indicates that samples contain more methylene than methyl groups.
Table S3 Peak fitting results of infrared spectrum of aliphatic hydrocarbons in Buertai coal samples

| number | Wave number (cm⁻¹) | half-peak width (cm⁻¹) | peak pattern | area     | Relative area (%) | Corresponding group     |
|--------|--------------------|------------------------|--------------|----------|------------------|-------------------------|
| 1      | 2956.86            | 25.78                  | Gaussian     | 0.030    | 13.44            | Anti-symmetric RCH₃     |
| 2      | 2923.39            | 25.46                  | Gaussian     | 0.098    | 42.84            | Anti-symmetric R₂CH₂    |
| 3      | 2852.57            | 17.14                  | Gaussian     | 0.036    | 15.77            | Symmetric RCH₂          |
| 4      | 2895.99            | 64.80                  | Gaussian     | 0.064    | 27.93            | R₃CH                    |

2.4. Hydroxyl structure absorption band analysis

Peaks in the 3000–3600 cm⁻¹ infrared band of the coal samples were fitted, and the fitted peaks are shown in Figure S4 and the attributes of each peak in Table S4. As indicated by the results, the hydroxyl groups in the sample mainly include an associative hydroxyl group and a hydroxyl-ether hydrogen bond.
Figure S4. Infrared spectrum of the hydroxyl functional groups of Buertai coal

Table S4 Peak fitting results of infrared spectrum of the hydroxyl absorption band of Buertai coal samples

| number | Wave number (cm⁻¹) | half-peak width (cm⁻¹) | peak pattern | area | Relative area (%) | Corresponding group                      |
|--------|--------------------|------------------------|--------------|------|-------------------|------------------------------------------|
| 1      | 3440.93            | 81.24                  | Gaussian     | 3.60 | 20.82             | Self-associated hydroxyl                 |
| 2      | 3502.06            | 89.70                  | Gaussian     | 4.11 | 23.77             | Self-associated hydroxyl                 |
| 3      | 3557.66            | 52.14                  | Gaussian     | 0.55 | 3.18              | OH-Π hydrogen bond                       |
| 4      | 3385.64            | 88.65                  | Gaussian     | 3.76 | 21.72             | Associated phenolic hydroxyl group       |
| 5      | 3321.62            | 99.75                  | Gaussian     | 2.54 | 14.69             | Hydroxyl-ether hydrogen bond             |
| 6      | 3238.77            | 109.22                 | Gaussian     | 2.28 | 13.17             | Hydroxyl-ether hydrogen bond             |
| 7      | 3150.60            | 91.51                  | Gaussian     | 0.45 | 2.61              | Hydroxyl cyclic polymer                  |
### 3. NMR data

**Table S5** Chemical shifts and resonance assignments in the $^{13}$C-NMR spectrum of Buertai coal

| Chemical shift/ppm | Type       | Chemical shift/ppm | Type       |
|--------------------|------------|--------------------|------------|
| 16                 | R−CH$_3$  | 75～90             | R−O−R     |
| 20                 | Ar−CH$_3$ | 100～129           | Ar−H      |
| 23                 | CH$_2$−CH$_3$ | 129～137       | bridgehead |
| 33                 | CH$_2$    | 137～148           | Ar−C      |
| 36～50              | C, CH     | 148～165           | Ar−O      |
| 50～60              | O−CH$_3$, O−CH$_2$ | 165～190    | COOH      |
| 60～70              | O−CH     | 190～220           | C=O       |

**Table S6** $^{13}$C-NMR peak-sharing simulation of absorption peak parameters of Buertai coal

| Number | Chemical shift/ppm/peak pattern | Relative area | Carbon atom attribution                          |
|--------|---------------------------------|---------------|-----------------------------------------------|
| 1      | 15.08 Gaussian                  | 1.72          | Lipid methyl                                   |
| 2      | 23.55 Gaussian                  | 1.23          | Aryl methyl                                    |
| 3      | 25.88 Gaussian                  | 6.85          | Methylene group attached to a lipid methyl group |
| 4      | 30.47 Gaussian                  | 1.81          | Methylene                                      |
| 5      | 83.30 Gaussian                  | 2.75          | Oxygen-bonded carbon in the ring               |
| 6      | 105.77 Gaussian                 | 3.32          | Protonated aromatic carbon                     |
| 7      | 117.98 Gaussian                 | 5.21          | Protonated aromatic carbon                     |
| 8      | 124.75 Gaussian                 | 40.33         | Protonated aromatic carbon                     |
| 9      | 131.12 Gaussian                 | 15.65         | Bridged aromatic carbon                        |
| 10     | 139.23 Gaussian                 | 11.51         | Lateral aromatic carbon                        |
| 11     | 153.66 Gaussian                 | 5.60          | Oxygen substituted aromatic carbon             |
| 12     | 172.63 Gaussian                 | 1.09          | Carboxyl carbon                                |
| 13     | 189.42 Gaussian                 | 2.93          | Carboxyl carbon                                |
4. **HRTEM data**

**Table S7** Classification of parallelogram-shaped aromatic fringes using HRTEM fringe data

| Aromatic sheet | Min L/Å | Max L/Å | Mean/Å | Grouping/Å |
|----------------|---------|---------|--------|------------|
| Naphthalene    | 2.8     | 4.9     | 3.9    | 3.0-5.4    |
| 2×2            | 4.9     | 7.1     | 6.0    | 5.5-7.4    |
| 3×3            | 7.4     | 11.3    | 9.3    | 7.5-11.4   |
| 4×4            | 9.8     | 15.6    | 12.7   | 11.5-14.4  |
| 5×5            | 12.3    | 19.8    | 16.0   | 14.5-17.4  |
| 6×6            | 14.7    | 24.1    | 19.4   | 17.5-20.4  |
| 7×7            | 17.2    | 28.4    | 22.8   | 20.5-24.4  |
| 8×8            | 19.6    | 32.6    | 26.1   | 24.5-28.4  |

**Figure S5.** Example of the longest and shortest measurement method for a 4 × 4 aromatic layer
5. Verification of the coal macromolecular structure model

![Model building flowchart](image)

**Figure S6.** Model building flowchart

6. Spatial configuration optimization of the macromolecular structure model of Buertai coal

6.1. Optimization of the spatial configuration of the coal macromolecules based on molecular mechanics

Molecular mechanics optimization was performed using the Materials Studio 8.0 software. The Buertai coal macromolecular structure model shown in Figure 5 was opened in the Visualizer module. After hydrogenation saturation, the Clean tool was selected to optimize the coal structure to obtain the initial three-dimensional structure.
Molecular mechanics calculations were then performed using the Focite module to obtain a stable three-dimensional configuration. For the simulation, the Smart Minimizer method under the Geometry Optimization option was used, and the charge was selected by Forcefield assigned. The number of iteration steps was set to $1 \times 10^4$, the force field was selected as COMPASS, the precision was set to Fine, and the standard of Force was $5 \times 10^{-3}$ kcal·mol$^{-1}$·Å$^{-1}$. Energy was set at $1 \times 10^{-4}$ kcal·mol$^{-1}$; the non-bond interaction energy uses the Atom-based summation method. The specific parameter settings are shown in Figure S7. The molecular structure model of the optimized coal macromolecules using molecular mechanics is shown in Figure S8.

![Figure S7. Molecular mechanics simulation parameter settings](image-url)
6.2. Optimization of the spatial configuration of the coal macromolecules based on molecular dynamics

To find the lowest energy configuration of the Buertai coal macromolecular structure model, following the molecular mechanics calculations, it was necessary to simulate the annealing dynamics in order to find the energy minimum over the entire potential energy surface and the corresponding structural model. In the Materials Software, first the Forcite module was selected, then the Anneal option was selected for the task item, perform was selected under the regular ensemble (NVT), the precision was set to Fine, the COMPASS force field was used as the force field, and Nose was chosen for the temperature controller. The number of cycles was set at 10, the charge was selected from Use Current, the initial temperature was 298 K, and the maximum temperature was 500 K; the total number of simulated steps was set to $1 \times 10^5$ steps, the time step was 1 fs, and the total simulation time was $1 \times 10^3$ ps. The model of each output was optimized so that the energy of the final structure model was the lowest. The specific parameter settings are shown in Figure S9. By comparing
the output energy data, the energy minimum configuration was selected, and according to the energy minimization principle, the selected configuration was the optimal configuration. Figure S10 shows the molecular structure model of Buertai coal macromolecules obtained through molecular dynamics optimization.

Figure S9. Molecular dynamics simulation parameter settings

Figure S10. Model of coal macromolecular structure following molecular dynamics optimization (a) left view; (b) plane view; (c) right view.

The energy of the Buertai coal macromolecular structure before and after optimization is shown in Table S8. Following the molecular dynamics optimization, the model curvature increased, the structure was tight, the arrangement of the
aromatic layers was approximately parallel, and the total energy was greatly reduced. The bond expansion energy $E_{\text{bond}}$ decreased from 1541 to 56.09 kJ·mol$^{-1}$, the bond angle energy $E_{\text{angle}}$ increased from 70.42 to 89.69 kJ·mol$^{-1}$, and the torsion energy $E_{\text{torsion}}$ increased from 1733.24 to 1760.08 kJ·mol$^{-1}$. Following molecular dynamics optimization, van der Waals forces can be greatly reduced in terms of the non-valence bond energy, and the Coulomb energy can be reduced accordingly, indicating that van der Waals energy plays an important role in the coal macromolecular structure. After optimization, the valence bond energy could be seen, the maximum energy was the bond torsion energy, the minimum energy was the bond inversion energy, and the bond angle tended to the middle. Thus, the three-dimensional structure of the coal macromolecule is mainly affected by the bond torsion energy and the bond angle energy.

**Table S8 Energy comparison before and after molecular dynamics optimization**

|                  | $E_{\text{valence energy/KJ/mol}}$ | $E_{\text{non bond energy/KJ/mol}}$ |
|------------------|-----------------------------------|-------------------------------------|
|                  | $E_{\text{Total}}$ | $E_{\text{Bond}}$ | $E_{\text{Angle}}$ | $E_{\text{Torsion}}$ | $E_{\text{Inversion}}$ | $E_{\text{Hydrogenbond}}$ | $E_{\text{Van der Waals}}$ | $E_{\text{Electrostatic}}$ |
| Initial          | 4894.18              | 1541.30              | 70.42             | 1733.24          | 1.224                | 0                     | 428.26                    | -62.03                    |
| Final            | 1694.04              | 56.09               | 89.69             | 1765.08          | 7.88                 | 0                     | 86.69                    | -226.62                   |

6.3. Coal macromolecule optimal structure model

In order to obtain the optimal structure model for coal macromolecules, the Amorphous cell module in the simulation software was selected to set the period boundary parameters, and the parameters were set according to Figure S11.
7. The results of the liquid nitrogen adsorption experiment.

Table S9 Textural properties of Buertai coal sample.

| Samples  | \(^aS_{\text{BET}}\) (m\(^2\cdot\text{g}^{-1}\)) | \(^bV_t\) (cm\(^3\cdot\text{g}^{-1}\)) | \(^cV_{\text{mic}}\) (cm\(^3\cdot\text{g}^{-1}\)) | \(V_{\text{mic}}/V_t\) (%) |
|----------|--------------------------------|----------------|----------------|-----------------|
| Buertai  | 9.121                        | 0.012          | 0.00068        | 5.67            |

\(^a\)The specific surface area calculated using the BET method at p/p\(_0\)=0.05~0.30. \(^b\)Total pore volume acquired at p/p\(_0\)=0.99. \(^c\)Micropore volume determined by t-plot method.

Figure S11. Density simulation parameters

Figure S12. (a) \(\text{N}_2\) adsorption-desorption isotherms for Buertai coal, (b) Pore size distribution of Buertai coal.