Creation and Generation Mechanism of Macromolecular Representation for Dongsheng Coal Vitrinite

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ABSTRACT: Insights into macromolecules of coal were critical for improving the understanding of the coal upgrading and coalification process. Here, the creation and generation of macromolecular representation for Dongsheng coal vitrinite was clarified using industry analysis, elemental analysis, and the peak fitting technology of 13C nuclear magnetic resonance (13C NMR), Fourier transform infrared spectrum, and X-ray diffraction. The structural parameters and macromolecular representation (C167H148N2O27) were innovatively calculated and created based on these characterization results and chemical shift correction, finally obtaining the plane macromolecular models whose 13C NMR spectrum was close to the experimental spectrum. The property parameters of basic structural units were $L_a$ (average lateral sizes) = 19.917 Å, $L_c$ (stacking heights) = 24.776 Å, $d_{002}$ (interlayer spacing) = 3.488 Å, $N$ (number of stacking layers) = 5.6213, and $L_a/L_c < 1$. Suffering from the dynamic metamorphism effects, the length of intermolecular aromatic lamellae for Dongsheng coal vitrinite was 7–8 aromatic rings in size. The aromatic clusters were dominated by benzene, naphthalene, and anthracene, and their numbers were 2, 4, and 2 per vitrinite model, respectively. Hydrogenated aromatic rings, ether bonds, and oxygen-methylene serve as the main bridge bonds to connect the aromatic clusters, where the short aliphatic chains were distributed around the edge of aromatic rings. Oxygen atoms exist in the form of hydroxyl, ether bond, carbonyl, and carbonyl groups, and their numbers were 2, 7, 4, and 8 per vitrinite model, respectively. The nitrogen atoms exist in the form of pyridine and pyrrole. The entropy weighting method was used to estimate the rationality of the macromolecular representation of long frame coal vitrinite, providing a new mathematical evaluation method for molecular simulation. Comparison of various macromolecular models from different geological conditions indicates that tectonic stress can promote the degree of aromatization and ring condensation. The thermal history and tectonic stress have a compensation effect for promoting the aromatization process. Aliphatic carbons were the most unstable units under thermal history and tectonic stress, and they are more easily removed from the aliphatic structure, followed by methyl. This finding of this paper can provide significance for coal liquefaction engineering in Dongsheng coalfield.

1. INTRODUCTION

Coal and mudstone-rich in organic matters are important oil source rocks\textsuperscript{1,2} and are very sensitive to environmental conditions such as thermal history, pressure, and tectonic stress. Tectonically-thermal events of multi-periods in the evolution of geological histories will inevitably lead to a series of physical, chemical, and structural alterations of coal organic macromolecules, which will undergo complex deformation and metamorphism.\textsuperscript{3,4} Accordingly, the metamorphic types of coal can be divided into three types, that is, low-temperature and high-pressure type, high temperature and high pressure type, and high temperature and low pressure type. Tectonically deformed coals (TDCs) were widely distributed in north and south China where the coal matrix not only exhibits brittle or ductile deformation but also undergoes certain extent of dynamic metamorphism.\textsuperscript{5,6} There exist distinct differences in the macromolecules of coal among different metamorphic deformation environments.\textsuperscript{7,8} Dongsheng coalfield is an important resource for coal liquefaction demonstration project whose macerals and liquefaction performances have been studied for a long time.\textsuperscript{9,20} There exists a synergistic effect for the liquefaction properties among different coal macerals.\textsuperscript{11–13} However, clarifying the molecular structure of coal macerals is the basis of understanding synergistic effect correctly. Researchers have studied the coal maceral composition, coal molecular structure, and coal aggregation structure chemistry of Shendong coal; however, the results are qualitative for primary structure coals.\textsuperscript{14–16} The molecular structure charac-

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teristics and the formation mechanism for mylonitic coal, which was formed with the coupling of thermal metamorphism and dynamic metamorphism have been minimally reported compared with the primary structure coals. Spectral analysis using spectrum of $^{13}$C nuclear magnetic resonance ($^{13}$C NMR), Fourier transform infrared (FTIR), and X-ray diffraction (XRD) has been successfully applied to create the macromolecular representations of coal, kerogen, and other solid organic materials. Within this series of technologies, the evaluation method frequently uses the comparison between the calculated and experimental spectrum to verify the macromolecular representations. There are few quantitative methods for evaluating the molecular structure of vitrinite based on numerical simulation.

Paleozoic coal seams in Ordos Basin are preserved in multiple northeast and north-northeast (NE-NNE) trending fault basins. Since Mesozoic, it has experienced five tectonic evolution stages: initial fault depression, slow fault depression, strong fault depression, continuous fault depression, and pull-apart fault depression. Tectonic movement destroys the coal seam structures, and thus, mylonitic coal is widely developed here. Investigations of petrography of Carboniferous-Permain series in Ordos Basin indicated that the early coal seam was mainly subjected to burial metamorphism with the increasing temperature and pressure with the increase in the burial depth, which exceeded the temperature and pressure of the original deposition. Zhao et al. considered that the tectonic activity in the eastern margin of Ordos Basin is weak, and the overlying strata are continuously thickened after the sedimentary period of the Upper Paleozoic in the Ordos Basin. Therefore, the organic matter of the Upper Paleozoic in this stage mainly undergoes deep metamorphism. The deep metamorphism process belongs to the low temperature and high pressure type, and its temperature rise is mainly caused by the increase in buried depth of strata with the normal geothermal gradient. The characteristics of the macro-molecular structure of mylonitic coal under low-temperature and high-pressure environment and the differences with the primary coal were seldom reported, which is critical to understand the mechanism of coalification and the synergetic effect at the molecular level. Thus, the characteristics of molecular structure functional groups and coalification mechanism under low temperature and high stress in this area can be understood by comparing the molecular structure differences of coals under different temperatures and stress conditions on the same maturity level, which can provide great significance for Shendong coal liquefaction demonstration project.

Here, the mylonitic coal from no. 2 coal seam of Dongsheng coalfield in Ordos was selected as the research object. The single maceral vitrinite was enriched via the drifting centrifugation method. The analytical tools mentioned above were also carried out to reveal the molecular structure parameters of vitrinite in the Dongsheng coal molecular structure model. Then, the initial macromolecular representations were created based on these structure parameters. The entropy weighting method was introduced to estimate the macromolecular representations, attempting to evaluate the representations using the comprehensive evaluation method based on the current spectrum correction method. Finally, the macromolecular structure model of vitrinite in primary coal under the same metamorphic conditions and the vitrinite in Wumuchang coal under high-temperature and low-pressure conditions were compared to discuss the generation mechanism of macromolecules for vitrinite of mylonitic coal under the low-temperature and high-pressure conditions.

2. SAMPLES AND EXPERIMENTS

2.1. Coal Samples and Basic Chemical Properties. The coal sample was the long-flame coal with the $R_{\text{max}} = 0.58\%$ (following ASTM Standards D2797/D2797M-11a and ASTM Standard D388-12). The primary structure of the sample is invisible, and the joints are densely developed. The densely developed joints and fragments can be seen in the cross section where the blocks are easily formed. The sample was crushed and ground to $\sim 200$ mesh and dried in a vacuum box. Then, the single maceral vitrinite was enriched via sink-float separation using the zinc chloride as specific gravity solution (high density: $1.35 \text{ g/cm}^3$; low density: $1.28 \text{ g/cm}^3$). The content of vitrinite was up to $93\%$ under microscopic analysis (Figure 1). Then, proximate and ultimate analyses were conducted for the enriched vitrinite sample following GB/T212-2008 and GB/T476-2008. The relative contents of C, H, O, N, and S were 78.21, 4.15, 16.41, 1.09, and 0.14%, respectively, which can be used to quantitatively estimate their atomic ratio.

2.2. Experimental Procedure. An improved microscale sealed vessel (SV) pyrolyzer was used to obtain the pyrolysis samples. The powder samples were sealed after vacuuming in the glass tube whose mass was measured by the difference method. A total of 15 device sample glass tubes were pyrolyzed by temperature programmed according to the heating rate of $10 \degree \text{C/h}$. The time and heating rate were linear whose sampling temperature range was $350$–$510 \degree \text{C}$. The $^{13}$C NMR, FTIR, and XRD were conducted for the vitrinite and semi-char samples.

2.2.1. $^{13}$CP/MAS-NMR. The $^{13}$C NMR here was conducted using the wide-cavity solid-state NMR spectrometer (AVANCE III 400 MHz). The experimental parameters were as follows: solid double resonance probe, $6 \text{ mm ZrO}_2$ rotor, and $6 \text{ kHz}$ revolution speed. The detecting resonance frequency of nuclear of $^{13}$C was $75.425 \text{ MHz}$ with the spectral width of $3000 \text{ Hz}$. The sampling time was $0.05 \text{ s}$ with the scan times, pulse length, and cycle delay time of 7000, 4 $\mu$s, and 4 $\mu$s, respectively. The cross-polarization contact time of hydrocarbon was $0.005 \text{ s}$. Then, the $^{13}$C NMR spectrum was obtained for the vitrinite and pyrolyzed samples (Figure 2). The spectral graph deconvolution subprogram within the

Figure 1. Solid vitrinite obtained from the sink-float separation using the zinc chloride as specific gravity solution (reprinted with permission).
OriginPro7.5 FTP was based on the calibration method of the baseline compensation. The chemical shift of carbon groups and second derivatives of these spectrums were used to determine the position and number of initial deconvolution fitting peaks.\(^{17-19}\) According to the unique structure of vitrinite molecules, the peak shape was optimized, and the peak position was assigned. The peak position fitting map was obtained, and the fitting degree was 0.9942, as shown in Figure 3. The chemical shift calculation in this paper is carried out on ACD/C NMR Predictor 3.5 software, which is widely used in the characterization and prediction of\(^{13}\)C chemical shifts in organic compounds.\(^{29,30}\)

### 2.2.2. FTIR

In this paper, the FTIR spectra were conducted using a Fourier transform infrared spectrometer (VERTEX-70) produced in Bruck, German. 80 mg of KBr is taken in an agate bowl, 0.9 mg of the coal sample is added to fully grind, and it is mixed with the coal samples. The transparent chips are pressed into the transparent sheets of 0.1−1.0 mm in thickness. The experimental parameters were as follows: wavenumber range of 400−4000 cm\(^{-1}\), resolution rate of 2 cm\(^{-1}\), and cumulative scan number of 32. The high-quality spectrum was obtained by comparing the scan background of blank KBr slice for 32 times. Then, the sub-peak spectrums of 2800−3000 and 1000−1800 cm\(^{-1}\) can be obtained via OriginPro7.5 FTP software, as shown in Figures 4 and 5, respectively.\(^{29,30}\)

### 2.2.3. XRD

The vitrinite was grinded to \(-300\) mushes using the X-ray diffractometer produced by Bruker (Karlsruhe, Germany). The Cu K\(\alpha\) target was used with the voltage, current, and width of divergence slit of 40 kv, 30 mA, and 1 mm, respectively. The width of receiving slit and stepwise scanning width were 0.16 mm and 0.04°, respectively, with the scanning speed of 2°/min. Low-angle diffraction was utilized with the diffraction angle of 4−64°. Jade software was used to analyze the XRD spectrum. The XRD spectrum is depicted in Figure 6a−c, where the basic structural units (BSU) structural parameters of elongation (\(L_a\)), stacking degree (\(L_c\)), aromatic layer network spacing (\(d_{002}\)), and aromatic nuclear carbon atomic network stacking layers (\(N\)) can be calculated based on the following eqs 1−4:\(^{28}\)

\[
L_a = \frac{K_1 \lambda}{\beta_{(002)} \cos \theta_{(100)}} \quad (1)
\]

\[
L_c = \frac{K_2 \lambda}{\beta_{(002)} \cos \theta_{(002)}} \quad (2)
\]

\[
d_{\text{kl}} = \frac{\lambda}{2 \sin \theta_{(\text{kl})}} \quad (3)
\]

\[
N = \frac{L_c + d_{002}}{d_{002} + \phi} \quad (4)
\]

where the \(\lambda\) was the wavelength of X-ray, in \(\mu\)m. The \(hk\) and \(\theta_{hk}\) were the crystal face index and the corresponding \(\theta\) value, respectively (Figure 6a,b). The \(\phi\) is the carbon atomic network thickness, which is approximated by carbon atomic diameter.

\[
\beta = \frac{\text{area of peak}}{\text{high of peak}} \quad (5)
\]

where the \(K_1\) and \(K_2\) were nucleus shape factors, \(K_1 = 1.84\) and \(K_2 = 0.94\) (Figure 6c).

### 2.3. Entropy Weighting Method

Entropy weighting method is an objective weighting method based on “difference

![Figure 2. \(^{13}\)C NMR spectrum of vitrain and pyrolyzed coals.](image)

![Figure 3. \(^{13}\)C NMR curve-fitted spectrum of vitrain.](image)

![Figure 4. FTIR analysis of SV during 2800−3000 cm\(^{-1}\) (reprinted with permission).\(^{30}\)](image)

![Figure 5. Curve-fitted FTIR during 1000−1800 cm\(^{-1}\) (reprinted with permission).\(^{30}\)](image)
3. RESULTS AND DISCUSSION

3.1. Characterization and Analysis for the Carbon Structure. The $^{13}$C NMR spectrum of vitrinite suggested that the carbon skeleton of vitrinite macromolecule can be divided into three regions, that is, aliphatic carbon region (0–90), aromatic carbon region (90–165), and carbonyl region (165–220). The spectra showed that the peak intensity of the aromatic region was greater than that of the aliphatic region, indicating that vitrinite macromolecular aromatic carbon was the main structural component. Then, 12 structural parameters can be calculated based on the integral peak area (Tables 1 and 2), where aromatic carbon is an important parameter for calculating the total number of carbon atoms in the macromolecular structure. The ratio of aromatic bridge carbon to aromatic pericarbon $X_{BP}$ was an essential parameter to calculate the size of the aromatic clusters. From Table 2, $f_{al}^*$ was 0.321, higher than $f_{al}$ (0.110), indicating that the aliphatic carbons in vitrinite macromolecule were dominated by chain alkanes and cycloalkanes. The content of methyl was rather low.

3.2. Analysis for BSU Structural Parameters. As a perfect crystal, there exist clear diffraction peaks for (002), (100), (101), (004), (103), (110), and (112). As coal is anisotropic, only (002) peak is obvious for low-rank coal in the X-ray diffraction spectrum (Figure 6a,b). The (100) peak is rather broad (Figure 6a,b) and corresponds to the condensation of the aromatic ring. The steeper the peak is, the narrower the peak is, corresponding to the condensation of the aromatic ring. The steeper the peak is, the narrower the peak is, corresponding to the condensation of the aromatic ring.
the \(L_a\) (Figure 6c). The (100) peak corresponds to \(2 \theta_{(002)} = 15-30^\circ\), attributing to the orientation of crystal nucleus spatial arrangement. The larger the \(\theta_{(002)}\) is, the smaller the \(d_{(002)}\) is. The higher this peak is, the narrower the peak is, corresponding to the more regular arrangement of the aromatic layers. \(L_a\), \(L_c\), and \(d_{(002)}\) can reflect the size and arrangement regularity of coal macromolecules. From results of PFM in OriginPro7.5, the \(\rho_{(100)}\), \(\rho_{(002)}\), \(2 \theta\) \((100)\), and \(2 \theta\) \((002)\) were 0.2011, 0.0646, 44.95408–44.99298, and 25.32883–25.34828\(^\circ\), respectively. Thus, the \(L_a\), \(L_c\), \(d_{(002)}\) and \(N\) were 19.917, 24.776, 3.488 \(\AA\), and 5.6213 and 0.8038, respectively, based on eqs 1–6. The \(L_a/L_c\) was <1, indicating that the Dongsheng coal vitrinite here have suffered from dynamic metamorphism.\(^\text{39–41}\) Assuming the aromatic lamina as a parallelogram structure, Mathews et al.\(^\text{42}\) calculated the attribution range of aromatic lamina size \((1 \times 1–8 \times 8)\) (some parameters are shown in Table 3) and arrangement in the macromolecular structure.

| aromatic sheet | min size (\(\AA\)) | max size (\(\AA\)) | average size (\(\AA\)) | size range (\(\AA\)) |
|----------------|---------------------|---------------------|------------------------|----------------------|
| 1 \(\times\) 1 | 2.8                 | 4.9                 | 3.9                    | 3.0–5.4              |
| 2 \(\times\) 2 | 4.9                 | 7.1                 | 6.0                    | 5.5–7.4              |
| 3 \(\times\) 3 | 7.4                 | 11.3                | 9.3                    | 7.5–11.4             |
| 4 \(\times\) 4 | 9.8                 | 15.6                | 12.7                   | 11.5–14.4            |
| 5 \(\times\) 5 | 12.3                | 19.8                | 16.0                   | 14.5–17.4            |
| 6 \(\times\) 6 | 14.7                | 24.1                | 19.4                   | 17.5–20.4            |

3.3.3. Determination of Oxygen and Heteroatoms. During the evolution process of oxygen-containing functional groups in coal, methoxy shedding was the earliest, followed by carboxyl. There was an obvious shedding evolution of hydroxyl groups in the early stage of immature stage. Then, the shedding is relatively slow in a relatively long evolution stage. It falls off sharply after the coking coal stage and disappears basically in the overmature stage. The carboxyl group gradually falls off with the increase in the coalification degree where preservation can continue to the anthracite stage.\(^\text{35}\) The Dongsheng coal vitrinite belonged to the long flame coal stage. The occurrence state of oxygen functional groups involved ether bond, hydroxyl, carboxyl, and carbonyl groups based on the FTIR peak separation parameters of 1000–1800 cm\(^{-1}\) (Table 5). Their quantities were 7, 2, 8, and 4, respectively,

![Table 4. Types and Quantities of Aromatic Unit Structure](https://pubs.acs.org/store/acsomega/1bc6975)

| Type | Quantity |
|------|----------|
| ![Structure 1] | 1        |
| ![Structure 2] | 3        |
| ![Structure 3] | 1        |
| ![Structure 4] | 4        |
| ![Structure 5] | 2        |
Based on the integral peak area (Table 3), the atomic ratio of C, O, and N was 83.5:13.1:0.99 based on the results of elementary analysis. As the total number of carbon atoms was 167, the number of O and N atom was 27 and 2, respectively. Therefore, seven ether bonds, two hydroxyl groups, eight carboxyl groups, and four carbonyl groups were considered in the modeling of the macromolecular representations. Pyrrole nitrogen and pyridine nitrogen are the main forms of nitrogen.36−38 In the structural modeling, one nitrogen atom exists in the form of pyridine and the other in the form of pyrrole (Table 4). As Dongsheng vitrinite had low sulfur content, thus the sulfur element was not considered in the modeling process.

### 3.3.4. Model Construction and Correction.

The initial molecular structure model (C_{167}H_{148}N_{2}O_{27}) of Dongsheng coal vitrinite was created based on the above 13C NMR and FTIR experiments. In order to make it closer to the real structure of Dongsheng coal and eliminate the influence of isomers, the chemical shift of the initial molecular structure model was calculated on ACD Predictor software via importing it into gNMR software. Under the condition of keeping the ratio of aromatic structure and aliphatic structures constant, the bonding relationship was constantly adjusted, finally obtaining the macromolecular representation of Dongsheng coal vitrinite, which was in good agreement with the experimental spectrum (Figure 7).17−19 The comparison between calculated spectrum of this macromolecular representation and experimental spectrum of Dongsheng coal vitrinite is depicted in Figure 8, as well as their structural parameters in Tables 6 and 7. The element content and aromaticity of the structural model were consistent with the experimental results, and the calculated spectra were generally in good agreement with the experimental spectra. The agreement was poor in the carbonyl region with chemical shifts of 170−220, which was due to the "sideband effect" of carbonyl in the experimental process.44−47

#### Table 5. Peak Parameters of Oxygen Functional Groups for Dongsheng Coal Vitrinite

| peak no. | peak width (cm⁻¹) | center (cm⁻¹) | area ratio (%) | attribution                        |
|----------|-------------------|---------------|----------------|-----------------------------------|
| 1        | 54.14             | 1049.79       | 1.37           | C−O−C                           |
| 2        | 80.57             | 1113.87       | 5.63           | C−O of ether                     |
| 3        | 72.35             | 1178.69       | 8.83           | hydroxy benzene                  |
| 4        | 58.13             | 1226.87       | 4.96           | C−O of ether                     |
| 5        | 74.03             | 1274.42       | 10.72          | C−O of aryl ether                |
| 6        | 67.45             | 1336.66       | 8.38           | C−O of ether                     |
| 7        | 47.69             | 1372.62       | 3.54           | CH_{3}−Ar, R                     |
| 8        | 56.92             | 1401.40       | 6.71           | CH_{3}                           |
| 9        | 66.57             | 1452.62       | 9.31           | CH_{2}, CH_{2}−                  |
| 10       | 46.08             | 1505.00       | 4.02           | C=CC of aromatic hydrocarbon     |
| 11       | 57.10             | 1549.06       | 11.28          | C=CC of aromatic hydrocarbon     |
| 12       | 63.43             | 1595.27       | 12.77          | unsaturated carboxylic acid      |
| 13       | 76.07             | 1641.73       | 9.32           | unsaturated carboxylic acid      |
| 14       | 47.50             | 1702.77       | 3.07           | unsaturated carboxylic acid      |

Figure 7. Molecular structural model of Dongsheng coal vitrinite.
The H/C ratio, as listed in Table 5, was the ratio of atom number instead of the ratio of atom mass. Actually, the ratio of atom number was 0.9192 for the macromolecular representation of Dongsheng coal vitrinite. It was 0.6367 for the Dongsheng coal vitrinite sample. The higher hydrogen content of the macromolecular representation was induced from the aromatic adding hydrogen saturation process for the initial carbon skeleton. The carbon skeleton model was created based on the $^{13}$C NMR, FTIR, XRD, and element analysis. For the real vitrinite sample, there exist unsaturated structures such as C=C bonds and unsaturated aliphatic acids; thus, the macromolecular representation here overestimates the hydrogen content of the vitrinite sample. We use the entropy method to quantitatively evaluate the congruence degree between the representation and experimental results.

### 4. COMPREHENSIVE EVALUATION OF THE MACROMOLECULAR REPRESENTATION

When considering the contribution of each structural parameter to the vitrinite structure of Dongsheng coal, each index of each structural parameter corresponds to the contribution of this index to the whole structural model when acting alone. The focus is on the contribution of each structural parameter combination to the vitrinite structure of Dongsheng coal. Thus, it is necessary to analyze the weight of each parameter and obtain its weight. Then, the structural parameter can be multiplied and added by the weight. Finally, the combination entropy of the structural model can be obtained. The proportions of 12 structural parameters of vitrinite of Dongsheng coal and its pyrolysis coal can be calculated by spectral peak separation, as shown in Table 7.

The implementation process of entropy method includes standardization of indexes (homogenization of heterogeneous indexes), calculation of information entropy, and calculation of difference coefficient and weight, where the specific solving process can be referred to in the previous work. From the data in Table 6, the weight values of the 12 structural parameters characterizing the coal structure are obtained by programming with Matlab data analysis software (Table 8).

From the weight value of these parameters, it could be inferred that the aliphatic structures have the highest weights due to their high activities. The aliphatic structures were easy to break down into small molecules. The weight of the aromatic ring ($f_a$) was the lowest due to the relatively stable aromatic ring. Its variation was relatively small, which conforms to the characteristics of differential driving. Therefore, the weight effectively characterizes the differences in various functional groups in the process of model structure construction, reflecting the degree of control over the overall structure. Combination entropy can be calculated via the following equation

$$v_i = \sum_{j=1}^{n} a_j p_{ij}$$

where the $p_{ij}$ was the $j$th evaluation index value for the $i$th scheme to be evaluated. The $q_j$ was the weight of the index $j$, and the $v_i$ was the evaluation value for scheme $i$. Via calculation, the comprehensive evaluation coefficient $v_i$ was 7.3536 for Dongsheng coal vitrinite, which was close to the comprehensive evaluation coefficient calculated based on $^{13}$C NMR experimental structural parameters (7.6505). The structural model obtained by the standardized entropy method well reflected the experimental results. The entropy method has considered 12 structural parameters here, covering the main functional groups of coal molecules. Thus, the macro-molecular representation was comprehensively and objectively evaluated, which was basically consistent with the results obtained by the observation spectrum.

For the evaluation of the molecular structure model, the similarity between the structural spectrum and the experimental spectrum (Figure 7) is often used to evaluate the structural rationality of the model lacking the quantitative and systematic evaluation methods. Furthermore, the comparison method faces challenges when dealing with the singular value of structural parameters. The results of intuitive observation were more qualitative and difficult to consider the information of all functional groups. The entropy method used here was to normalize the structural parameters of Dongsheng coal vitrinite and a series of pyrolysis coals. All functional group parameters are selected to quantitatively investigate the agreement between the macromolecular representation and the experimental results. Thus, the entropy method was more comprehensive and practical. From Figure 7, it could be inferred that the calculated spectrum and experimental spectrum were in good agreement for the regions of aromatic clusters and aliphatic structures. However, they do not match well for the regions of hydroxyl groups with chemical shifts of 50−75 and carbonyl groups with chemical shifts of 170−220. The intuitive observation can only consider the main part of coal molecular structure. The chemical shifts of coal molecular structure functional groups are continuously distributed between 0 and 220 due to their varying chemical environments. The specific functional groups have unique chemical shifts. According to the interval set theorem, the common points of a series of intervals whose lengths gradually tend to zero can be selected to characterize the location

![Figure 8. Experimental and calculated $^{13}$C NMR spectrum.](image)

**Table 6. Structural Parameters of Dongsheng Coal Vitrinite**

| sample                | $f_a$ | H/C   | O/C   | N/C   | molecular formula | molecular weight |
|-----------------------|-------|-------|-------|-------|-------------------|------------------|
| Dongsheng coal vitrinite | 0.5680 | 0.9192 | 0.1617 | 0.0120 | C_{167}H_{148}N_{2}O_{27} | 2614.9591 |
characteristics of these intervals. Therefore, the chemical displacement of 0–220 was actually divided into 12 sub-interval sequences by selecting 12 structural parameters data of the coal structure, and the interval length in each sub-interval sequence converges to zero, which determined that the entropy method can be used to characterize the continuous interval of chemical displacement 0–220. It was more quantitative than the observation spectrum method.

5. CHARACTERISTIC OF REPRESENTATION AND GENERATION MECHANISM

The metamorphism of coal can be classified into three types according to the relationship between the pressure and thermal history, that is, low temperature and high pressure type, high temperature and high pressure type, and high temperature and low pressure type. The plutonic metamorphism belonged to low temperature and high pressure type as the heat mainly comes from the increase in the burial depth of the stratum, where the ground-temperature gradient is normal. For the Dongsheng coal field, tectonic movement destroys the coal seam structures, and thus, mylonitic coal is widely developed here. Investigations of petrography of Carboniferous-Permian series in Ordos Basin indicated that the early coal seam was mainly subjected to burial metamorphism with the increasing temperature and pressure with the increase in burial depth which exceeded the temperature and pressure of the original

| structural parameters | chemical shift | vitrinite (%) | 350 °C (%) | 440 °C (%) | 510 °C (%) |
|------------------------|---------------|--------------|-----------|-----------|-----------|
| f_L                    | 165–240       | 0.000000     | 0.010626  | 0.020431  | 0.008907  |
| f_M                    | 150–165       | 0.010225     | 0.036475  | 0.016348  | 0.014789  |
| f_S                    | 137–150       | 0.009430     | 0.048143  | 0.067584  | 0.038850  |
| f_T                    | 129–137       | 0.041272     | 0.000000  | 0.000000  | 0.027255  |
| f_U                    | 100–129       | 0.146483     | 0.180884  | 0.178463  | 0.190269  |
| f_V                    | 50–90         | 0.032205     | 0.005279  | 0.00662  | 0.009937  |
| f_W                    | 22–90&50–60   | 0.103186     | 0.034569  | 0.012664  | 0.026068  |
| f_X                    | 0–22&50–60    | 0.039126     | 0.011262  | 0.021894  | 0.012298  |
| f_Y                    | P + S + B     | 0.060928     | 0.084618  | 0.083932  | 0.080895  |
| f_Z                    | N + H, 90–165 | 0.207412     | 0.265840  | 0.267514  | 0.271726  |
| f_A                    | 90–240        | 0.207412     | 0.276466  | 0.287946  | 0.280634  |
| f_B                    | 0–90          | 0.142313     | 0.045832  | 0.034558  | 0.038366  |

Table 8. Structural Parameters Weights of SV

| parameter | f_a | f_a c | f_a P | f_a S | f_a B | f_a H | f_a N | f_B | f_P | f_S | f_B | f_H | f_N |
|-----------|-----|-------|-------|-------|-------|-------|------|-----|-----|-----|-----|-----|-----|
| weight    | 0.048 | 0.0586 | 0.0474 | 0.0477 | 0.0488 | 0.0965 | 0.0538 | 0.1174 | 0.1552 | 0.1136 | 0.0997 |

Figure 9. Structural parameters of (a) aromatic carbons, (b) aromatic ring carbons, (c) protonated aromatic carbons, and (d) aliphatic carbons for low rank coal formed in different metamorphic deformation environments.
deposition. The Wumuchang coal vitrinite was generated in the environment of high temperature and low pressure due to its shallow buried depth and existence of abnormal heat source. The buried depth was 309–542 m with the existence of Yanshanian magmatic intrusion. High temperature and high pressure type is caused by an abnormal heat source, such as high-temperature intrusive rock mass invading near coal measure strata under the condition of deep burial of strata. The generation background of Shendong coal vitrinite was similar to that of the Dongsheng coal vitrinite, and their difference lies in the tectonic deformation. Shendong coal vitrinite was generated from the unaltered coal seams.

Here, three macromolecular representations, that is, Dongsheng coal vitrinite in this paper, Wumuchang coal vitrinite macromolecule ($R_o = 0.46\%$) formed in the high-temperature and low-pressure environment, and Shendong coal vitrinite macromolecule ($R_o = 0.51\%$) formed in the stable tectonic environment will be compared to highlight the variations of the main structural parameters (Figure 9). The similar H/C ratio, aromatic rate, and FTIR hydrogen index indicated that the thermal maturity of these three coal vitrinite macromolecules was similar (Table 9), and thus, their structural difference was induced from the different degree of tectonic deformation. The generation mechanism of the molecular structure of mylonitic coal formed in low-temperature and high-pressure environment can be revealed by comparing the molecular structure of the primary coal formed in high-temperature and low-pressure environment in the similar rank stage. As the Dongsheng coal vitrinite was enriched from the no. 3 coal of Shanxi Formation, the sedimentary environment was the delta deposits developed on the sedimentary background of epicontinental sea. Generally, the transition from Delta estuary sand bar and tributary bay to delta plain facies was mainly composed of sandstone, sandy mudstone, and coal seam. The Wumuchang coal vitrinite was collected from the no. 11 coal seam of Damoquai formation. The lithology was mainly composed of sandstone and close to that of Dongsheng coal vitrinite. They were similar in the sedimentary environment. However, their difference mainly lies in the buried depth and heat source. The Shendong coal vitrinite was identified to Dongsheng coal vitrinite in the coal formation process, and their difference was originated from the alteration of the mine structure. Thus, the effects from the sedimentary environment were not slight, and the temperature—pressure conditions play a critical role in the differences of macromolecule structures.

The $R_o$ of the Dongsheng coal, Wumuchang coal, and Shendong coal was similar ($R_o = 0.46$–0.58\%), and thus, variations in their macromolecular representations were induced from the different metamorphic deformation environments. For primary coal, the aromatic carbon ratio was the highest and lowest of high temperature and low pressure and of low temperature and high pressure, respectively. The $R_o$ was lowest for Wumuchang coal vitrinite, indicating that thermal history was the dominant factor controlling aromatization. Although the maturity of Dongsheng coal vitrinite and Shendong coal vitrinite was close, the basic parameter unit ductility of BSU manifests as $L_a(Dongsheng) \gg L_a(Shendong)$ indicating that the dynamic metamorphism was in favor for the basic parameter unit ductility. Normally, $L_a$ increases slowly from low rank to high rank. The anomaly here was due to the fact that the stress polycrystallization promoted the rearrangement of BSUs of coal, where the increase in order led to the increase in the aromatic dense ring system. Tectonic stress can also promote aromatization and ring condensation to some extent (Figure 9a). The evolution process of aromatic rings was consistent with that of aromatic carbon, and also, the total amount of aromatic rings tended to be consistent for low-temperature high-pressure dynamic type and high-temperature low-pressure type. The tectonic stress can promote the increase in protonated aromatic carbon, while the high-temperature effect can increase the ratio of non-protonated aromatic carbon (Figure 9b). The non-protonated aromatic carbon of the low-temperature and high-pressure dynamic type was higher than the low temperature and high pressure type, where the increase in bridged aromatic carbon indicated the increase in the aromatic ring system. The smaller aromatic rings were connected by aromatic bridge carbon to form aromatic ring units with larger ductility.

In terms of aromaticity, thermal history and tectonic stress have mutual compensation effect on aromatization. The evolution of hydroxyl-ether oxygen carbon is abnormal here for these three coals, and the content of low temperature and high pressure dynamic type and high temperature and low pressure type is higher than that of low temperature and high pressure type, which was found more common in medium and high rank coal in China. This was due to the fact that high thermal history and tectonic stress can promote the oxygen functional groups in coal macromolecular representation. Both the steric effect induced from the short-chain aliphatic hydrocarbons and the low-temperature and high-pressure environment were not conducive to the escape of small molecules, resulting in the combination of oxygen-containing components and unstable components in the benzene ring structure to form new oxygen-containing functional groups (Figure 9c). The thermal history and tectonic stress have a compensation effect for promoting the aromatization process (Figure 9d). Aliphatic carbons were the most unstable units under thermal history and tectonic stress and more easily removed from the aliphatic structure, followed by the methyl content. Both the thermal history and tectonic stress have slight effects for the variations in methylene and quaternary carbons. From variation in the aliphatic structures, there exist lipid materials such as ethyl for Dongsheng coal vitrinite. However, the content of lipid materials was rather low for Shendong coal vitrinite. The content of epoxy resin carbon of Shendong coal vitrinite was higher than that of Dongsheng coal vitrinite, indicating that the epoxy substances such as ethyl and methyl were easy to be removed from the epoxy resin during the conversion of lignite to bituminous coal.

### 6. Conclusions

Insights into macromolecules of coal were critical for improving the understanding of the coal upgrading and coalification process. Here, the creation and generation of macromolecular representation for Dongsheng coal vitrinite were clarified using industry analysis, elemental analysis, and

| sample     | molecular formula | H/C | aromaticity | A-factor |
|------------|-------------------|-----|-------------|----------|
| Dongsheng  | C_{167}H_{148}N_{2}O_{27} | 0.0739 | 0.57 | 0.91 |
| Wumuchang  | C_{122}H_{106}N_{3}O_{18} | 0.0716 | 0.56 | 0.84 |
| Shendong   | C_{194}H_{146}N_{31}O_{2} | 0.0623 | 0.65 | 0.89 |
the peak fitting technology of $^{13}$C NMR, FTIR, and XRD. The entropy weighting method was used to verify the macromolecular representation of Dongsheng coal vitrinite based on the traditional spectrum comparison method. The results indicated that Dongsheng coal vitrinite possessed benzene, naphthalene, and anthracene as aromatic structural units, whose numbers were 2, 4, and 2, respectively. Ether bond, hydrogenated aromatic ring, and ortho methylene were the main bridge bond connecting aromatic structures. Oxygen atoms exist in the form of hydroxyl, ether bond, carbonyl, and carboxyl, and their numbers are 2, 7, 4, and 8, respectively.

Then, the macromolecular representation was created based on these results. Compared with the method of spectral comparison, the entropy weighting method takes into account the main functional group information of molecular structure analysis, which is more quantitative, objective, and comprehensive to evaluate the model structure. From the comparison analysis, which is more quantitative, objective, and comprehensive to evaluate the model structure. From the comparison, the entropy weighting method was used to verify the macro-

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**Notes**

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