Study on the Differences of Chemical Structures and Pyrolysis Characteristics between the Jurassic and Carboniferous Coking Coals

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ABSTRACT: Using Jurassic coking coals and Carboniferous coking coals as raw materials, carbonization experiments were carried out on the cokes produced by them in a self-made furnace in a laboratory-scale coking furnace, finding that the coke quality of the Jurassic fat coals and coking coals was obviously inferior to that of the Carboniferous coking coals of the same brand. In this study, the reasons for this phenomenon were studied by elemental analysis, Fourier transform infrared spectroscopy analysis, and thermogravimetric analysis of experimental coal samples and by combining the differences in chemical structures of experimental coal samples with pyrolysis characteristic parameters. It was found that the key factor affecting the quality of cokes made from the Jurassic fat coals, coking coals, and highly volatile coking coals was that the coals contained too many oxygen-containing functional groups, which were decomposed into reactive oxygen species in the main pyrolysis stage of coal. These reactive oxygen species would consume too much free-moving hydrogen and then trigger a large number of condensation and cross-linking reactions, resulting in poor plastic mass and coke quality.

1. INTRODUCTION

Compared with other iron-making methods, blast furnace iron making is still the mainstream iron-making method in the world because of its mature process and higher thermal efficiency. The coke in the blast furnace plays four important roles: heat source, reaction reducing agent, column skeleton, and carburizing. Moreover, the column skeleton role makes it become an essential raw material for blast furnace iron-making.1 With the development of large-scale blast furnaces, enhanced smelting, and high injection technology, higher requirements for coke quality are put forward. The quality of coke depends on the quality of coking coal used.2,3 Therefore, studying and comparing the chemical structures and pyrolysis characteristics of different coking coals will help us to analyze the reasons for the differences in the properties of finished coke, such as reactivity strength (CRI) and post-reaction strength (CSR).

According to the distributions of coal accumulation periods in China, the coking coals in South China and North China are mainly Carboniferous and Permian.4 Xinjiang, which is located in northwest China, also has complete varieties of coking coals due to the special geological conditions of coal formation, which belong to Jurassic. Due to the time of coaling for coking coals being about 100 million years later than that of the Carboniferous coking coals, there are many differences in coal quality characteristics between the Jurassic and Carboniferous coking coals, which are mainly manifested in generally high reactivity and extremely easy oxidation, resulting in the cokes refined by Jurassic coking coals possessing defects like high reactivity, low strength after reaction, and serious pulverization. For example, Zhou5 found that in the coking experiment of the Jurassic coking coals in Xinjiang, the CRI and CSR of the cokes made from the Jurassic coking coals were >70 and <25%, respectively, so it was extremely difficult to apply them to medium and large blast furnaces of 1000 m³ or more.6 Consequently, it was impossible to produce cokes needed by large and medium blast furnaces only with local coking coals in Xinjiang.

A great deal of research has been done on Jurassic coals in Xinjiang. For example, Wang7 believed that the high vitrinite content in Xinjiang coking coals was the reason for the poor thermal strength of coke. Zhou5 also pointed out that the high vitrinite content of coals in Xinjiang led to the flow structure of the optical structure of the coke. The high porosity, thin pore wall, and high alkali metal content of the coke were the reasons for the high reactivity and poor strength after reaction. Hao8 et al. believed that the reason for the large and numerous pores, thin stomatal wall, and very high porosity of cokes processed in the Xinjiang coals was that the content of inert components in

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coals and cokes mainly focuses on a submicroscopic level, subduing mass (the particle size of studied coals was less than 3 mm) evenly, and then place it in a coking retort with an internal diameter of 100 mm and a length of 500 mm. The density and moisture of coal blends were limited to 0.95 g/cm³ and 10 wt %, respectively. A programmable controller was used to control the temperature in the coking furnace automatically, and the temperature was heated by the resistance wire. After the experimental temperature reached 700 °C, the coking retort was put into the furnace, combining with a heating rate of 10 °C/min. Subsequently, we maintained the target temperature for 5 h with a constant heating rate of 5 °C/min until it was heated to 1000 °C. Finally, the retort should be cooled to room temperature in the atmosphere.

After the experimental process ended, the GB1997-89 standard was applied to produce coke samples whose CRI and CSR indexes were both measured using the GB/T4000-1996 standard.9

2.3. Preparation of Demineralized Samples. In the FTIR analysis, to remove the potential effects of minerals on it, the coal samples needed to be acid-washed using HCl and HF solutions in an atmospheric environment as described in a previous study.10 Generally, the acid treatment under such conditions would not cause significant structural changes.11 The procedure was called demineralization. These demineralized samples were dried for 12 h in a vacuum room at 60 °C and stored under a nitrogen atmosphere.9

The equipment used for elemental analysis was the Elementar vario MACRO cube (Elementar Analyssysteme GmbH, Germany). The measured elements were carbon, hydrogen, nitrogen, and sulfur in the demineralized samples, and the oxygen element in the samples was obtained by the subtraction method. According to the GB/T 476-208 criterion, the ultimate analysis results of these demineralized samples were determined.

2.4. FTIR Measurements. The FTIR spectrometer was often used to characterize the chemical structures of coals and the functional groups in coals. In this study, a ThermoNicolet iS5 FTIR spectrometer (Thermo Fisher Scientific, MMAS, Waltham, MA, USA) was used for FTIR analysis of demineralized samples. The preparation method of the test sample was to mix 1 mg of the demineralized sample with 200 mg of KBr evenly, then to press it under a 10 MPa pressure for 2 min to make it turn into a small ball. The scanning wave number was in the range of 400–4000 cm⁻¹, the resolution was 4 cm⁻¹, and 32 scans per spectrum were performed.

2.5. TG Measurements. In order to reveal the differences of pyrolysis processes of different coking coals, the thermogravimetric analysis instrument of experimental coal samples was the NETZSCH STA449 C analyzer (Nestal, Selbu, Germany). A test sample size <74 μm was required, and the temperature range

### Table 1. Characteristic Analyses of Experimental Coal Samples**

| coal types | industrial analysis (a/o/%) | process analysis |
|------------|-----------------------------|-----------------|
| ST-QM      | 1.64 6.74 39.19 55.71 0.52 | 83.2 11.2 35.2 |
| ZL-QM      | 1.70 6.76 38.51 56.36 0.56 | 84.1 12.2 36.5 |
| ST-FM      | 1.38 9.74 31.65 64.35 1.67 | 92.8 27.2 27.0 |
| ZL-FM      | 1.46 7.56 32.48 63.58 0.62 | 96.1 25.8 31.1 |
| ST-JM      | 1.38 9.69 26.42 65.89 1.36 | 92.5 15.8 22.5 |
| ZL-JM      | 1.45 8.95 27.85 65.14 0.61 | 90.2 13.8 31.6 |
| ST-SM      | 1.26 9.58 17.12 72.83 0.86 | 32.3 4.2 25.5 |
| ZL-SM      | 1.25 9.29 17.68 72.68 0.52 | 36.8 5.1 26.4 |

**Note: In the table, subscripts d, ad, anddaf represent dry base, air dry base, and dry ash-free base, respectively.
was 25 °C (ambient temperature) to 1000 °C at a fixed heating rate of 10 °C/min under a continuous argon atmosphere with a flow rate of 50 mL/min in an alumina cell.

3. RESULTS AND DISCUSSION

3.1. Coal and Coke Quality Analyses. The specific industrial and technological analyses and total sulfur analysis data of the experimental coals are shown in Table 1.

According to Table 1, by comparing the Jurassic coking coals and Carboniferous coking coals of the same grade, it could be found that the main difference between them was reflected in the stage of fat coal and coking coal, as well as in the sulfur content, ash content, and shrinkage index of the gelatinous layer. However, there were no significant differences in volatile matter, cohesiveness index, and maximum thickness index of the gelatinous layer. According to the test data of carbonization experiments of coke in Section 2.2, Table 2 could be obtained.

Table 2. Quality Indexes of Coke Produced From Single Coal (ω/%)

| coke types  | A₀ | V₀ | FC₀ | S₀ | CRI | CSR |
|-------------|----|----|-----|----|-----|-----|
| ST-QM       | 9.25 | 1.03 | 88.61 | 0.40 | 61.3 | 25.8 |
| ZL-QM       | 9.38 | 1.01 | 88.95 | 0.41 | 60.1 | 26.6 |
| ST-FM       | 12.94 | 1.15 | 87.24 | 1.26 | 22.4 | 68.3 |
| ZL-FM       | 10.28 | 1.11 | 88.18 | 0.47 | 40.8 | 48.9 |
| ST-JM       | 12.85 | 1.12 | 85.42 | 1.02 | 17.6 | 73.4 |
| ZL-JM       | 12.13 | 1.15 | 86.10 | 0.46 | 36.8 | 54.5 |
| ST-SM       | 12.87 | 1.06 | 84.38 | 0.65 | 51.6 | 37.2 |
| ZL-SM       | 12.45 | 1.13 | 84.59 | 0.41 | 52.1 | 36.4 |

It could be seen from Tables 1 and 2 that the ash and sulfur content in coke was closely related to that in coal: the higher the ash and sulfur content in coal, the higher the ash and sulfur content in the corresponding coke. By comparing the coke refined by the Carboniferous and Jurassic coking coals of the same grade, it was found that the ash and sulfur content of the coke refined by the Jurassic fat coal and coking coal was obviously lower than that of the Carboniferous coal of the same grade, but the thermal strength index (CSR) of the coke refined by the Jurassic coking coal was also obviously lower. In order to study the cause of this difference, we further carried out the elemental analysis, FTIR analysis, and thermogravimetric analysis on experimental coal samples to study the differences in their chemical structures.

3.2. Elemental Analysis. According to the experiment in Section 2.3, the elemental analysis result of the coal samples is shown in Table 3.

According to the results in Table 3, with the increase in coal metamorphism, the evolution laws of elements were as follows:

1. The content of the C element kept increasing, while the content of H and O elements kept decreasing. This was mainly attributed to the increase in metamorphism time, which made the aliphatic chains and small molecular branch chains in coals constantly fall off and form more aromatic thick rings of large molecules.
2. The value of H/C in the two kinds of pulverized coals decreased with the increase in metamorphism degree.

By comparing the Jurassic coking coals and Carboniferous coking coals of the same grade in Table 3, it could be found that the H and O content and the H/C value of the Jurassic fat coals and coking coals were significantly higher than those of the Carboniferous coking coals of the same grade. Generally, the higher the H/C value is, the lower the metamorphism degree is. Therefore, it indicated that there were more aliphatic chains and small molecular branch chains in the Jurassic fat coals and coking coals, which made the metamorphism degree lower than that of the Carboniferous coals of the same grade. The difference of Jurassic coking coals lies between the middle volatile fat coals and coking coals.

3.3. FTIR Analysis. This paper referred to the baseline processing method of the FTIR spectra of coals proposed by Ibara and et al. Origin 9.0 software was used for baseline processing of FTIR spectra of experimental coal samples. The spectra of experimental coal samples after baseline removal are shown in Figure 1.

![Image](https://doi.org/10.1021/acsomega.1c06332)

Figure 1. FTIR spectra of experimental coal samples.

3.3.1. Distribution and Variation of Functional Groups. Different absorption peaks in the FTIR spectra of coals corresponded to different functional groups, and the larger the area of the absorption peak, the higher the content of functional groups corresponding to the peak. Based on previous research results, functional groups corresponding to common absorption peaks in FTIR spectra of coals are summarized in Table 4.

In combination with Figure 1 and Table 4, it could be seen that the coal ranks of the Carboniferous and Jurassic coking coals showed some similar properties during the transition from gas coal to lean coal, such as: (1) the peak with a wave number of about 3050 cm⁻¹ represented the stretching vibration of aromatic CH, and there was no obvious peak in the gas coal stage of the two kinds of pulverized coal (ST and ZL). With the increase in metamorphism degree, the peak began to appear in the stage of fat coal, and then the peak strength gradually increased. (2) The value of H/C in the two kinds of pulverized coals decreased with the increase in metamorphism degree, which made the metamorphism degree lower than that of the Carboniferous coals of the same grade.
increased in the stages of coking coal and lean coal, indicating that from the stage of gas coal to lean coal, the aliphatic structure in coal gradually changed to an aromatic structure. (2) The wave number of about 1620 cm\(^{-1}\) represented the expansion of the aromatic ring C=O\(_2\). Generally, the intensity of this peak increases with the increase in the metamorphism degree. However, it could be seen from Figure 1 that the intensity of this peak was the strongest in the gas coals of the two types of coking coals and the lowest in the fat coals, which then gradually increased in the coking coals and lean coals. This is because the gas coal contained a high oxygen content (as shown in Table 4), so coal contained a large number of oxygen-containing functional groups. The phenolic, hydroxyl, and carboxyl groups in these oxygen-containing functional groups would increase the peak strength at 1620 cm\(^{-1}\). However, in the fat coal stage, the oxygen content in the coals decreased sharply due to the further removal process of aliphatics and acids. Therefore, the reduction of the absorption peak strength at 1620 cm\(^{-1}\) in the fat coals was caused by the removal of a large number of oxygen-containing functional groups. The continuous increase in the absorption peak strength at 1620 cm\(^{-1}\) of coking coals and lean coals was due to the continuous improvement of the aromatizing process and the increase in aromatic ring C=C bonds in coals.

### 3.3.2. Peak-Differentiation-Imitating of FTIR Spectra.

The FTIR spectra of coals were relatively complex. According to relevant studies, absorption peaks in the FTIR spectra of coals were usually the result of multiple peak overlapping. According to the study of Feng et al., relevant semi-quantitative information could be obtained by peak-differentiation-imitating of the FTIR spectra of coals. Therefore, we needed to conduct peak-differentiation-imitating processing for absorption peaks in Figure 1. In this paper, the peak fit module in Origin 9.0 software was used to perform Gaussian and Lorentz peak-differentiation-imitating on the FTIR spectra of experimental coal samples.

Generally, the FTIR spectra of coals could be divided into four absorption bands, namely, the hydroxyl absorption band with a displacement of 3600–3100 cm\(^{-1}\), the aliphatic structure absorption band with a displacement of 3000–2800 cm\(^{-1}\), the absorption band of oxygen-containing functional groups with a displacement of 1800–1000 cm\(^{-1}\), and the absorption band of aromatic structures with a displacement of 900–700 cm\(^{-1}\). In this paper, only the peak-differentiation-imitating spectra of four absorption bands of the Jurassic coking coals (ZL-FM) were used as a legend to show the peak-differentiation-imitating results, which were summarized in Figure 2.

### Table 4. Band Assignments Derived From FTIR Spectra in Coals

| wave numbers (cm\(^{-1}\)) | corresponding groups                                      |
|---------------------------|------------------------------------------------------------|
| 3415–3350                 | –OH (or –NH) of hydrogen bonding, phenols                  |
| 3025–3050                 | aromatic CH stretching vibration                            |
| 2975–2955                 | asymmetric stretching vibration of aliphatic CH\(_3\)       |
| 2925–2919                 | asymmetric stretching vibration of aliphatic CH\(_2\)       |
| 2855–2850                 | aliphatic CH\(_2\) stretching vibration                   |
| 1705–1695                 | carboxyl/xarboxyl (C=O)                                     |
| 1640–1605                 | Aromatic rings C=O or C=C stretching                       |
| 1470–1450                 | Aliphatic chain CH\(_3\), CH\(_2\)                        |
| 1274–1260                 | C–O stretching vibration of phenols, alcohols, esters, and ethers |
| 1165–1155                 | phenol, ether C–O stretching vibration                     |
| 1098–1095                 | alcohol C–O stretching vibration or aromatic ring C–H     |
| 1035–1030                 | alky ether                                                 |
| 876–872                   | aromatic substituted hydrocarbon CH (an adjacent H)        |
| 815–801                   | aromatic substituted hydrocarbon CH (two adjacent Hs)      |
| 750                       | aromatic substituted hydrocarbon CH (four adjacent Hs)     |

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**Figure 2.** Curve-fitted FTIR spectra of different absorption zones for the Jurassic fat coals (ZL-FM): (a) the 3600–3100 cm\(^{-1}\) zone; (b) the 3000–2800 cm\(^{-1}\) zone; (c) the 1800–1000 cm\(^{-1}\) zone; and (d) the 900–700 cm\(^{-1}\) zone.
3.3.2.1. Unfolding and Semi-quantitative Analysis of Oxygen-Containing Functional Groups. Generally, the content of oxygen-containing functional groups in coals could be evaluated by the peak area of this region (1800−1000 and 3600−3100 cm$^{-1}$).22 Referring to previous studies,23 we assigned the attribution of each sub-peak in Figure 2a,c and then summarized it in Table 5. Table 5 showed that the hydroxyl groups in coals were mainly divided into OH−π, OH−OH, OH−OR, and OH bonds. The carbon−oxygen functional groups in coal were mainly divided into carboxylic acid (−COOH), conjugate carbon−oxygen double bonds (C=O) including ketones, aldehydes, and lipids, and carbon−oxygen single bonds (C−O) including phenols, ethers, and alcohols.

The evolution of different carbon−oxygen bonds with the O/C atomic ratio of coal is shown in Figure 3.

Figure 3a shows that in the Jurassic and Carboniferous coking coals, with the loss of the O/C ratio, the areas of the carboxylic acid absorption peaks gradually reduced in the two types of pulverized coals. When they got to the stage of lean coal, the carboxylic acid had been completely removed, which indicated that the carboxylic acid in coking coals was poor and the content was low. Thus, this kind of carbon−oxygen bond in the coalification process of coking coals was the first to be removed.

Figure 3b shows that in the Jurassic coking coals and Carboniferous coking coals, the areas of C=O absorption peaks corresponding to the conjugated carbon−oxygen double bond increased with the decrease in O/C atomic ratio in coal from the gas coal to coking coal; that is, the content of conjugated C=O functional groups in coal increased gradually. This was because the conjugated C=O functional groups in coal had high stabilities, and the amount of removal was small in the coalification process of coking coal. Meanwhile, other oxygen-containing functional groups in coal would be gradually transformed into conjugated C=O functional groups.12 Therefore, when the decomposition amount was lower than the generation amount, the content of conjugated C=O functional groups in coal would gradually increase. For the Carboniferous coking coals, the content of conjugated C=O functional groups in coking coals reached the maximum value, indicating that the unstable oxygen-containing functional groups in coal had been basically removed. With the further metamorphism of coal, the decomposition rate of conjugated C=O functional groups in coal would be greater than the generation rate. Therefore, during the transition from Carboniferous coking coal to lean coal, some stable oxygen-containing functional groups were mainly removed. However, for the Jurassic coking coals, the removal

Table 5. Assignments of the FTIR Absorption Wave Number for the 1800−1000 cm$^{-1}$ Zone and the 3600−3100 cm$^{-1}$ Zone of Coal

| wave number (cm$^{-1}$) | the corresponding groups | wave number (cm$^{-1}$) | the corresponding groups |
|-------------------------|--------------------------|-------------------------|--------------------------|
| 3545                    | OH−π bond                | 1445−1455               | aliphatic ethers CH$_2$, CH$_3$ |
| 3445                    | OH−OH bond               | 1405−1410               | −OH                     |
| 3315                    | OH−OR bond               | 1375−1380               | aromatic CH$_3$          |
| 3215                    | OH bond                  | 1335−1345               | CH$_2$−C=O               |
| 1705−1710               | carboxylic acid          | 1245−1255               | C=O                     |
| 1650                    | conjugated C=O           | 1210−1215               | C=O−/−OH/ether           |
| 1620                    | (C≡C)$_2$/C=O            | 1170−1180               | phenol/ether (C=O)       |
| 1575−1585               | Aromatic ring stretching | 1085−1090               | alkyl ether              |
| 1495−1505               | (C≡C)$_2$                | 1032−1035               | alkyl ether              |

Figure 3. Relationship between different carbon and oxygen functional groups and the O/C atomic ratio in experimental coal samples: (a) −COOH functional group; (b) C=O functional group; and (c) C−O functional group.
of stable oxygen-containing functional groups would be
dominant in the lean coal stage, indicating that the Jurassic
coking coals still contained many unstable oxygen-containing
functional groups such as hydroxyl groups.

By comparing the two types of coking coals of the same grade
in Figure 3b, it could be found that the content of conjugated
C＝O functional groups in the two types of coals at the gas coal
stage was similar. However, in the stages of fat coal and coking
coal, the content of stable conjugation C＝O functional groups
in the Jurassic fat coals and coking coals was lower than that in
the Carboniferous coking coals of the same brand. This result
indicated that the unstable oxygen-containing functional groups
in the Jurassic fat coals and coking coals could be transformed
into relatively stable oxygen-containing functional groups with
the same content as that of the Carboniferous fat coals and
coking coals by further coalification.

According to Figure 3c, the absorption peak areas of C＝O
functional groups in the Jurassic and Carboniferous coking coals
showed a certain linear correlation with the O/C atomic ratio,
indicating that the O/C ratio could reflect the content of C＝O
functional groups in coal to a certain extent. By comparing
the same grade of the Jurassic and Carboniferous coking coals, it
could be found that the absorption peak areas of C＝O
functional groups in the Jurassic fat coals and coking coals
were all larger than those in the same grade of the Carboniferous
fat coals and coking coals, indicating that the specificity of the
Jurassic coking coals was also reflected in that there were more
C＝O functional groups in the Jurassic coking coals than those in
the Carboniferous coking coals.

3.3.2.2. Unfolding and Semi-quantitative Analysis of
Aliphatic Hydrocarbons. According to relevant literature,24
the five sub-peaks in Figure 2b belonged to the asymmetric
stretching vibration peak of aliphatic CH$_3$ located near 2955 cm$^{-1}$, the asymmetric stretching vibration peak of aliphatic CH$_2$ located near 2955 cm$^{-1}$, the stretching vibration peak of aliphatic CH located near 2895 cm$^{-1}$, and the symmetric stretching vibration peaks of aliphatic CH$_2$ and CH$_3$ located near 2868 and 2855 cm$^{-1}$, respectively.

Generally, the content of aliphatic CH$_x$ in coal could be
measured by the peak areas of the above sub-peaks. The larger
the peak areas were, the more aliphatic functional groups
related to the peaks were. The index commonly used to
evaluate the degree of the aliphatic chain length and branched
chain in coal was the content ratio of asymmetric CH$_3$ and CH$_2$
functional groups in coal, which could be obtained from the peak
area ratio ($A_{2922}/A_{2955}$) corresponding to the two peaks.25

Combined with the peak-differentiation-imitating results of the
experimental coal samples, the variation trend of the CH$_2$/CH$_3$
value in the experimental coal samples with the atomic ratio
of H/C in the coals was drawn as a graph, as shown in Figure 4.

Relevant studies showed that the larger the CH$_2$/CH$_3$ value in
calcs was, the longer the aliphatic chain in coals was, and the
fewer the corresponding branch chains.26

As could be seen from Figure 4, the asymmetric CH$_2$/CH$_3$
ratio in both types of coking coals increased with the decrease
in the H/C atomic ratio, indicating that the aliphatic chains in both
Jurassic and Carboniferous coking coals evolved in the same
way; that is, with the deepening of coal metamorphism, the
lengths of aliphatic chains in coals increased while the number of
branch chains in aliphatic chains decreased. By comparing
the same grade of the Jurassic and Carboniferous coking coals
in Figure 4, it could be found that the CH$_2$/CH$_3$ value of Jurassic
fat coals and coking coals was lower than that of the

Carboniferous coking coals of the same grade, indicating that
the difference of the Jurassic coking coals was also reflected in
the fact that there were more aliphatic side chains in the coals of
both stages.

3.3.2.3. Unfolding and Semi-quantitative Analysis of
Aromatic Hydrocarbons. The aromatic structures in coal include
the aromatic CH stretching vibration of the high wave-number segment, the aromatic core C＝C vibration, the aromatic ring stretching vibration of the middle wave-number segment, and the aromatic hydrocarbon displacement deformation vibration of the low wave-number segment.27,28 The 900—
700 cm$^{-1}$ absorption band could not only reflect the content of aromatic hydrocarbons but also evaluate the degree of aromatic
substitution and condensation of aromatic nuclei according to the
number of adjacent hydrogen on benzene rings.12

In Figure 2d, (1H－(C－H)$_w$) referred to the external plane
substitution of the aromatic hydrocarbon with only one H atom in
the benzene ring, (2H－(C－H)$_w$) referred to the external plane
substitution of the aromatic hydrocarbon with two H atoms in the benzene ring, and (4H－(C－H)$_w$) referred to the
external plane substitution of the aromatic hydrocarbon with four H atoms in the benzene ring. The area proportions of the
three fitting absorption peaks in the experimental coal samples
are shown in Table 6.

Table 6. Area Proportions of Aromatic C－H Out-of-Plane
Deformation Bands in Experimental Coal Samples (%)

| coal types | 870 cm$^{-1}$ | 815 cm$^{-1}$ | 750 cm$^{-1}$ |
|------------|--------------|--------------|--------------|
| ST-QM      | 26.47        | 43.86        | 29.67        |
| ZL-QM      | 25.57        | 44.06        | 30.37        |
| ST-FM      | 30.40        | 38.38        | 31.22        |
| ZL-FM      | 27.64        | 42.19        | 30.18        |
| ST-JM      | 32.03        | 36.07        | 31.90        |
| ZL-JM      | 28.54        | 40.41        | 31.05        |
| ST-SM      | 34.81        | 32.97        | 32.22        |
| ZL-SM      | 34.82        | 32.85        | 32.33        |

Previous studies showed that the absorption peak near 870 cm$^{-1}$
represented the condensation degree of aromatic nuclei in
calcs, and the larger the area proportion of this peak was, the
more the polycyclic aromatic hydrocarbons in coal with high
ring numbers was. The absorption peaks near the wave numbers
of 815 and 750 cm$^{-1}$ were mainly related to the number of
substituted aromatic rings in coal. The larger the proportion of
the absorption peak area was at 815 cm$^{-1}$, the smaller the
proportion was at 750 cm$^{-1}$, indicating that there were more
substituted aromatic rings in coal. Consequently, it could be seen from Table 6 that the evolutions of the Jurassic and Carboniferous coking coals showed the evolution law that the numbers of substituted aromatic rings decreased while the sizes of condensed aromatic rings increased.

It was worth noting that by comparing the same grade of the Jurassic and Carboniferous coking coals, the absorption peak areas at 870 and 750 cm\(^{-1}\) in the Jurassic fat coals and coking coals were lower than those in the Carboniferous coking coals of the same grade, and the absorption peak areas at 815 cm\(^{-1}\) were higher than those in the Carboniferous coking coals of the same grade. It showed that the condensation degree of aromatic nuclei in the Jurassic fat coals and coking coals was lower than that in the Carboniferous coking coals of the same grade, but the number of substituted aromatic hydrocarbons was higher than that in the Carboniferous coking coals of the same grade.

3.3.3. Calculation of the Aromatic Carbon Ratio. Coal is usually complex and uneven in structure, so it is difficult to exactly describe its molecular structure. However, the rate of aromatic carbon in coal can be used to describe the basic structural units of coal in terms of the average structure characteristics of carbon atoms (usually, the higher the aromatic carbon rate is, the greater the aromatic carbon content in coal is and the higher the corresponding degree of aromatization is).\(^{30}\)

Therefore, the aromatic carbon ratio of the coal used in the experiment was calculated in this paper.

According to the literature,\(^{12}\) for bituminous coals in the coking coal stage, it could be assumed that there were only two types of carbon atoms in coals, namely the aromatic carbon (\(C_{ar}\)) and the fatty carbon (\(C_{al}\)). The H atom content corresponding to these two types of carbon atoms could be calculated by dividing the absorption peak areas of the 900–700 cm\(^{-1}\) region and the 3000–2800 cm\(^{-1}\) region by the corresponding extinction coefficient, as shown in formulas 3.1 and 3.2. The extinction coefficient is the coefficient that converts the area of FTIR absorption peaks of coal into the concentration of chemical structures corresponding to each absorption peak. According to Solomon and Carangelo,\(^{31}\) for bituminous coals, the extinction coefficient of the former was 744 ABS cm\(^{-1}\) mg cm\(^{-2}\) and that of the latter was 684 ABS cm\(^{-1}\) mg cm\(^{-2}\). Therefore, based on the peak-differentiation-imitating result of each interval in Figure 2 and the above analyses, formula 3.3 could be used to calculate the aromatic carbon ratio (\(f_a\)) of coal:

\[
H_{ar} = \frac{A(3000 - 2800 \text{ cm}^{-1})}{744} \tag{3.1}
\]

\[
H_{al} = \frac{A(3000 - 2800 \text{ cm}^{-1})}{684} \tag{3.2}
\]

\[
f_a = 1 - \frac{C_{al}}{C} \tag{3.3}
\]

\[
\frac{C_{al}}{C} = \left(\frac{H_{al}}{H} \times \frac{H}{C}\right) \frac{H_{al}}{C_{al}} \tag{3.4}
\]

\[
\frac{H_{al}}{H} = \frac{H_{al}}{H_{ar} + H_{al}} \tag{3.5}
\]

In the formulas, \(C_{al}/C\) is the ratio of the fat carbon content to total carbon content and \(H/C\) is the ratio of \(H/\)C atoms in coal, which could be obtained from Table 3. \(H_{al}/H\) is the ratio of aliphatic hydrogen to total hydrogen and \(H_{al}/C_{al}\) is the ratio of hydrogen to carbon atoms in the aliphatic groups of coal.

According to relevant literature reports,\(^{32}\) an empirical value of 1.8 is usually appropriate. The aromatic carbon ratio \(f_a\) could be obtained according to formulas 3.1–3.5. The relationship between the \(f_a\) and \(H/C\) ratio in the experimental coal samples is shown in Figure 5.

![Figure 5. Relationship between the aromatic carbon fraction and H/C ratio of experimental coal samples.](https://doi.org/10.1021/acsomega.1c06332)

It could be seen from Figure 5 that \(f_a\) in the Jurassic and Carboniferous coking coals presented a good linear relationship with the \(H/C\) atomic ratio, which indicated that \(f_a\) was an indicator that could be used to measure the maturities of the Jurassic and Carboniferous coking coals. It was worth noting that by comparing the \(f_a\) of the two types of pulverized coals of the same brand, it could be found that the \(f_a\) of the Jurassic fat coals and coking coals was less than that of the Carboniferous coking coals of the same brand. The result showed that the aromatic carbon atomic content of basic structural units of the Jurassic fat coals and coking coals was lower than that of the Carboniferous coking coals of the same grade. That is, compared with conventional coking coals of the same grade, the aromatic degree and metamorphism degree of the Jurassic fat coals and coking coals were lower.

3.4. Thermogravimetric Characteristics and Pyrolysis Characteristic Parameters. The thermal weight loss (TG) and differential thermal weight loss (DTG) curves formed by the pyrolysis of experimental coal samples are shown in Figure 6.

![Figure 6. TG and DTG curves of studied coals during pyrolysis.](https://doi.org/10.1021/acsomega.1c06332)
The TG curves in the figure represented the change in the masses of the coal samples with temperature, while the DTG curves represented the instantaneous weight loss rate of the coal samples, which could be used to measure the severity of the reaction of the coal samples at a certain time.

It could be seen from Figure 6 that the DTG curves of all experimental coal samples roughly showed the same trend of change, and there were two small mass rate loss peaks at about 100 and 720 °C, which were caused by the separation of physical adsorption water from coal and the dominant H2 gas from secondary degassing reaction in coal samples. However, it was worth noting that there was an obvious mass rate loss peak on the DTG curves of all experimental coal samples at about 450 °C, and the corresponding TG curves of coal samples also significantly decreased. This peak was mainly due to the massive fracture of bridge bonds and covalent bonds in the molecular structures of coals, resulting in a large number of depolymerization and decomposition reactions. Gaseous products such as H2O, CO2, CH4, and short-chain aliphatic hydrocarbons were formed, and the escape of these gases led to a reduction in the quality of the experimental coal samples.

The thermal stabilities of coal samples were usually related to their pyrolysis characteristic parameters. According to the above phenomenon, the TG and DTG curves of experimental coal samples were processed according to the analysis method of pyrolysis characteristics of coal samples by Liu et al. to obtain pyrolysis characteristic parameters of coal samples for semi-quantitative analysis. This paper only took the determination method of pyrolysis characteristic parameters of the Jurassic fat coals as an example, as shown in Figure 7.

![Figure 7. TG and DTG curves of Jurassic fat coals.](https://doi.org/10.1021/acsomega.1c06332)

In Figure 7, \( V_w \) is the peak of water loss rate, the temperature corresponding to this peak \( T_w \) is the maximum water loss temperature, and \( M_a \) is the mass of adsorbed water in coals. \( T_s \) is the initial temperature of pyrolysis and \( T_h \) is the initial temperature of high-rate pyrolysis. \( M_i \) is the weight loss rate of low-rate pyrolysis, \( V_{\text{max}} \) is the maximum weight loss rate peak, \( T_{\text{max}} \) is the maximum weight loss rate temperature, \( T_j \) is the end temperature of high-rate pyrolysis, and \( M_d \) is the weight loss rate of high-rate pyrolysis. \( V_p \) is the weight loss rate peak of secondary polycondensation reaction, \( T_p \) is the maximum weight loss rate temperature of secondary polycondensation reaction, \( T_e \) is the end temperature of secondary polycondensation reaction, \( M_p \) is the weight loss rate of secondary polycondensation reaction, and \( \Delta M \) is the total weight loss rate during pyrolysis.

As shown in Figure 7, the pyrolysis process of coals was divided into three major stages, namely, the drying stage (room temperature—\( T_i \)), the pyrolysis stage (\( T_i \sim T_f \)), and the polycondensation stage (\( T_f \sim 1000 \) °C). By analyzing the pyrolysis process of coal samples, it could be concluded that there were three weight loss rate peaks and five mass weight loss rates in the pyrolysis process of experimental coal samples, which are shown in Table 7, and seven characteristic temperatures are shown in Table 8.

As could be seen from Tables 7 and 8, (1) The maximum weight loss rate of coal samples in the pyrolysis process occurred in the high-rate pyrolysis stage. In the Jurassic and Carboniferous coking coals, with the increase in the coalification degree, the peak value of the three weight loss rate peaks all decreased and the weight loss rate of each pyrolysis stage also decreased correspondingly, which was closely related to the decrease in the aliphatic hydrocarbon content, the decrease in heteratomic functional groups, and the increase in the macromolecular structure aromatic hydrocarbon content in coal. Compared to the same brand of Jurassic and Carboniferous coking coals, it could be found that in the Jurassic fat coals and coking coals, the peak value of the maximum weight loss rate, the high rate of pyrolysis stage of the weightlessness rate, and the total weight loss rate of the pyrolysis process were higher than those of the Carboniferous coking coals of the same brand. The result showed that the reaction rate and reaction intensity of the Jurassic fat coals and coking coals were obviously higher than those of the Carboniferous coking coals of the same grade in the stage of high pyrolysis rate. This was because the reactions involved in the high-rate pyrolysis stage of coal mainly included the decomposition reaction of aliphatic chains and the oxygen-containing functional groups dominated by epoxy hydroxyl groups and the reaction of unstable covalent bonds breaking to form small molecular aromatic compounds. According to the above FTIR analysis result, the content of aliphatic side chains and oxygen-containing functional groups in the Jurassic fat coals and coking coals was higher than that in the Carboniferous coking coals of the same brand. At the same time, the condensation degree of aromatic nuclei in coal was lower than that of the Carboniferous coking coals of the same grade, so the Jurassic fat coals and coking coals showed more intense thermal decomposition phenomena in the high-rate pyrolysis stage.

(2) Although the weight loss rates of the Jurassic fat coals and coking coals in the main pyrolysis stage were 17.37 and 16.12%, respectively, higher than those of the Carboniferous fat coals and coking coals in the main pyrolysis stage of 15.79 and 14.04%, the maximum weight loss rate temperature (\( T_{\text{max}} \)) and the end temperature (\( T_f \)) of high-rate pyrolysis reaction during pyrolysis were lower than those of the Carboniferous coking coals of the same grade, indicating that the thermal decomposition processes of the Jurassic fat coals and coking coals were fast and short. This was because the occurrence of intense pyrolysis reaction led to the formation of a large number of free...
Table 7. Weight Loss of Experimental Coal Samples at Different Pyrolysis Stages and the Weight Loss Rates of Characteristic Weightlessness Peaks

| coal types | weight loss rate (%/min) | weight loss ratio (%; daf) |
|------------|--------------------------|---------------------------|
|            | $V_w$ | $V_{max}$ | $V_f$ | $M_w$ | $M_f$ | $M_p$ | $M_p$ | $\Delta M$ |
| ST-QM      | 0.12  | 1.64     | 0.13  | 1.63  | 3.21  | 17.02 | 8.47  | 31.45 |
| ZL-QM      | 0.12  | 1.61     | 0.13  | 1.61  | 3.13  | 16.95 | 8.32  | 30.82 |
| ST-FM      | 0.11  | 1.23     | 0.12  | 1.47  | 2.95  | 12.84 | 6.61  | 24.46 |
| ZL-FM      | 0.11  | 1.34     | 0.10  | 1.54  | 3.01  | 14.36 | 6.31  | 25.72 |
| ST-JM      | 0.11  | 0.94     | 0.14  | 1.42  | 2.43  | 11.61 | 6.31  | 21.22 |
| ZL-JM      | 0.11  | 1.08     | 0.09  | 1.46  | 2.51  | 13.61 | 5.95  | 23.48 |
| ST-SM      | 0.10  | 0.49     | 0.05  | 1.31  | 2.13  | 7.51  | 4.06  | 15.23 |
| ZL-SM      | 0.10  | 0.50     | 0.05  | 1.29  | 2.11  | 7.65  | 4.16  | 15.56 |

Table 8. Characteristic Temperatures in TG/DTG Curves of Studied Coal Samples (°C)

| coal types | $T_w$ | $T_i$ | $T_{max}$ | $T_f$ | $T_p$ | $T_h$ |
|------------|------|------|-----------|------|------|------|
| ST-QM      | 102.1| 198.7| 404.1     | 453.2| 560.1| 705.7|
| ZL-QM      | 101.5| 199.6| 404.7     | 455.4| 561.4| 707.3|
| ST-FM      | 101.3| 202.4| 416.2     | 471.4| 571.1| 720.3|
| ZL-FM      | 100.8| 200.6| 414.5     | 466.1| 565.7| 714.5|
| ST-JM      | 100.6| 205.1| 423.2     | 481.6| 581.2| 731.6|
| ZL-JM      | 100.5| 203.5| 418.3     | 475.8| 575.3| 722.3|
| ST-SM      | 101.8| 206.5| 432.1     | 493.2| 595.8| 738.1|
| ZL-SM      | 102.3| 206.3| 431.4     | 492.3| 596.9| 737.7|

4. CONCLUSIONS

(1) The specificity of the Jurassic coking coal in Xinjiang was mainly reflected in fat coal and coking coal with medium-volatile content. The low degree of condensation of aromatic nuclei and high content of oxygen-containing functional groups and aliphatic side chains in coal were not conducive to the stability and development of the plastic mass during coal pyrolysis.

(2) The key factor restricting the quality of coke refined by low-quality coking coal was the excessive oxygen-containing functional groups in coal. When a large number of oxygen-containing functional groups decomposed in the main pyrolysis stage of coking coal, a large number of reactive oxygen species would be formed accordingly, which would consume a large amount of free movement H and then cause intense condensation and cross-linking reactions, which are not conducive to the development of the coke microcrystalline structure.

(3) The aromatic carbon ratio ($f_a$) of coal could be used as an important index to evaluate the coal metamorphism degree.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.1c06332.

Expansion characteristic indexes of studied coals; determination results of ash composition of experimental coal samples ($\omega$/%); kinetics parameters of studied coals during fierce pyrolysis stage; evolution of FTIR spectra in the 3600–3100 cm$^{-1}$, 3000–2800 cm$^{-1}$, 1800–1000 cm$^{-1}$, and 900–700 cm$^{-1}$ zones for the studied coals; relationship between the number of single carbon rings in the basic structural units and the H/C ratio of experimental coal samples; basic chemical structure unit of coal; and Arrhenius curve of Jurassic fat coal (ZL-FM)(PDF)

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Notes

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