Effect of the Iron Component on Microcrystalline Structure Evolution of Hydrochloric Acid-Demineralized Lignite during the Pyrolysis Process

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ABSTRACT: Hydrochloric acid-demineralized Shengli lignite (SL+) and iron-added lignite (SL+-Fe) were thermally degraded using a fixed-bed device to better understand the effect of the iron component on the microcrystalline structure transformation properties of lignite during the pyrolysis process. The primary gaseous products (CO₂, CO, H₂, and CH₄) were detected by pyrolysis−gas chromatography. X-ray diffraction and Raman spectra were adopted to analyze the microcrystalline structure of lignite and chars. The results indicated that the iron component had a catalysis effect on the pyrolysis of SL+ below 602.6 °C. The pyrolysis gases released in the order of CO₂, CO, H₂, and CH₄, and the addition of the iron component did not change the sequences. The iron component promoted the generation of CO₂, CO, and H₂ in the low-temperature stage. During the high-temperature stage, the iron component inhibited the formation of CO and H₂. The formation of CH₄ was inhibited by the iron component throughout the pyrolysis process. The evolution characteristics of −OH, C=O, C≡C, and C−H functional groups were not significantly affected, and the fracture of aliphatic functional groups and C−O functional groups was inhibited by the iron component during the pyrolysis process. The iron component restricted the spatial regular arrangement tendency of aromatic rings and facilitated the decrease in the small-sized aromatic ring but inhibited the formation of large aromatic rings (≥6 rings) and the content decrease in side chains during the pyrolysis process. Notably, the effects of the iron component on the formation of gaseous products were associated with the microstructure evolution of lignite.

1. INTRODUCTION

In recent years, more low-rank coals have been developed and utilized due to the rapid consumption of high-quality resources in recent years. As a typical low-rank coal, the efficient utilization of lignite has attracted much attention. In addition to a complex structure, well developed voids, and a high water content, lignite also contains much higher amounts of volatile matter and oxygen-containing functional groups, restricting its large-scale utilization.¹ Coal classification conversion is one of the directions of efficient and clean utilization of lignite. As the initial and accompanying reaction of gasification, liquefaction, and combustion of coal, the pyrolysis process has an important effect on the subsequent conversion of coal.² The improvement of the pyrolysis conversion rate and product selectivity is also an important topic in the efficient and clean utilization process of lignite.

Previous studies showed that the iron component can promote the generation and transformation of coal pyrolysis products to a certain extent.³−⁶ These studies also indicated that the iron component can affect the thermal conversion temperature and evolution characteristics of Shengli lignite (SL+). The interactions of iron and organic matter during the pyrolysis process changed the conversion process of lignite.⁷,⁸ Because of complex nature and different structural components of lignite, the cognition about the effect of the iron component on the conversion properties of lignite during the pyrolysis process is still quite limited. Yang et al.⁷ and Zhang et al.¹⁰ considered that the presence of iron species caused a poor structural order of the microcrystalline arrangement of chars and changed the conversion process of coal. A study of Qi et al.¹ suggested that the iron component significantly changed the microcrystalline structure of carbon and increased the
disorder degree of carbon during pyrolysis. However, another study of Qi et al. showed that the iron component increased the number of active functional groups in chars and changed the structure of the aromatic ring. Therefore, it was considered that the iron component improved the reactivity of char by increasing the number of surface active sites. Gong et al. also concluded that the iron component could reduce the degree of graphitization and ordering of the carbon structure of char and improve the decomposition of the functional groups attached to aromatic groups, resulting in the formation of new free radicals during the pyrolysis process. However, the catalytic effect of the iron component on the dissociation of aromatic rings has been rarely reported. Geng et al. also concluded that the iron component promoted the activity of chars through the increased inactive sites. Lin et al. and Chen et al. both believed that the iron component and oxygen-containing functional groups in coal might form new higher-activity chemical structures, such as C–O–Fe and C–O–O–Fe, during the pyrolysis process. Liang et al. showed that the iron catalyst facilitated the bond breaking of the oxygen-containing groups in coal and reduced the oxygen content in char. The iron component definitely affected the product distribution and microcrystalline structural evolution of lignite to a certain degree during the pyrolysis process; however, the mechanism is still unclear.

The Shengli coal field in Inner Mongolia, the largest lignite field in China, has more than 22.4 billion tons of lignite reserves. The efficient utilization of SL is of great significance to the economic development of Inner Mongolia. In this study, hydrochloric acid-demineralized SL and its iron-added lignite (SL-Fe) were pyrolyzed in a fixed-bed pyrolysis device at 900 °C. The distribution of gaseous products and microcrystalline structure evolution were analyzed to establish an iron-component catalytic mechanism model during the pyrolysis process of lignite.

2. EXPERIMENTAL SECTION

2.1. Preparation of the Coal Sample. Lignite from the no. 2 mine in the Shengli Coal field of Inner Mongolia was selected as the experimental sample. Raw lignite with a particle size in the range 0.18–0.42 mm was dried at 105 °C for 4 h and labeled SL. Some minerals and organic components in SL were removed by the solution method. SL was mixed with hydrochloric acid (18%) at room temperature at a ratio of 1 g: 10 mL. After 24 h stirring, the mixture was filtered, and the filter cake was washed with water until the filter fluid contained no Cl⁻ (AgNO₃ test) and dried at 105 °C for 4 h to obtain hydrochloric acid-demineralized lignite and named SL.

The catalyst and coal sample in full contact could be prepared by the blending method and impregnation method (transition-metal soluble salts). It is generally believed that the impregnation method can infiltrate transition-metal ions into the void of pulverized coal to achieve the best catalytic effect. Therefore, iron component-added hydrochloric acid-demineralized lignite was prepared by the impregnation method following the literature procedure in this report. FeCl₃·6H₂O was dissolved in water and mixed with SL, based on a 5.0% iron content accounting for the mass of the coal sample. The mixture was stirred for 12 h and dried at 105 °C for 24 h and named SL-Fe. The iron component (3.5%) was added to hydrochloric acid-demineralized lignite according to the X-ray fluorescence (ZSX Primus II, Rigaku) results. Compared with the blending method results, the iron content by the impregnation method was lower than calculated; however, it did not show any significant effect on the study of the pyrolysis process.

According to GB/T 212 2008, proximate analysis and ultimate analysis of samples were performed using an industrial coal analyzer (China 5E-MF6200) and elemental analyzer (Germany Elementar: Vario EL Cube). The results are shown in Table 1, indicating that 35.23% of ash in SL was removed by hydrochloric acid. The ash content increased by 9.56% after adding the iron component, confirming complete loading of the iron component by the impregnation method.

2.2. Pyrolysis Experiment. The pyrolysis experiments of SL and SL-Fe were carried out in a fixed-bed pyrolysis device (Tianjin Xianquan Company). The final pyrolysis temperature was 900 °C at a heating rate of 4 °C/min and a holding time of 90 min in a 0.2 MPa and 600 mL/min flow rate argon pyrolysis atmosphere. The chars obtained from SL and SL-Fe were labeled SL-900 and SL-Fe-900, respectively. The proximate analysis and ultimate analysis of chars were carried out according to GB212-91, and the results are listed in Table 2. The pyrolyzed gaseous products were detected in real time using pyrolysis–gas chromatograph (Py-GC, GC-8A, Shimadzu Corporation of Japan). The working conditions of GC are as follows: TCD detector, cylinder temperature of 160 °C, sampler temperature of 180 °C, hot wire temperature of 200 °C; and gas collection interval of 7 min.

### Table 1. Proximate Analysis and Ultimate Analysis of Samples

| samples       | yield of char (wt %) | M_d | A_d | V_d | FC_d | ultimate analysis (wt %) | C   | H   | N   | S   | O*   |
|---------------|----------------------|-----|-----|-----|------|--------------------------|------|-----|-----|-----|------|
| SL            | 60.0                 | 1.36| 18.7| 5.69| 75.6 | 70.5                     | 1.49 | 0.45| 1.06| 7.84|      |
| SL-Fe-900     | 62.9                 | 1.37| 24.2| 7.23| 68.6 | 71.3                     | 1.48 | 0.76| 1.92| 0.35|      |

Note: A-ash content; V-volatile content; FC-fixed carbon; d-dried basis; and *-by difference.

### Table 2. Proximate Analysis and Ultimate Analysis of Chars

| samples       | yield of char (wt %) | M_d | A_d | V_d | FC_d | ultimate analysis (wt %) | C   | H   | N   | S   | O*   |
|---------------|----------------------|-----|-----|-----|------|--------------------------|------|-----|-----|-----|------|
| SL-Fe-900     | 62.9                 | 1.37| 24.2| 7.23| 68.6 | 71.3                     | 1.48 | 0.76| 1.92| 0.35|      |

Note: A-ash content; V-volatile content; FC-fixed carbon; d-dried basis; and *-by difference.
2.3. Microcrystalline Structure Analysis. Fourier-transform infrared (FT-IR) spectra were recorded with the KBr pellet technique using a NEXUS 6700 infrared spectrometer (Nicolet, USA) in the detection range from 4000 to 400 cm$^{-1}$ at a resolution of 4 cm$^{-1}$.

The micro-structural parameters of the lignite sample and chars were investigated using a SmartLab 9 kW instrument (Rigaku, Japan) equipped with a highly sensitive D/teX Ultra 250 detection system and Cu Kα radiation (40 kV, 200 mA). Powder X-ray diffraction (XRD) patterns of the samples were recorded in the 2θ range from 10 to 90°, at a scanning speed of 5°/min.

Raman spectra were recorded using an inVia microscope (Renishaw, UK), at a laser wavelength of 532 nm and a laser power of 0.3 mW in the range 120–3200 cm$^{-1}$.

3. RESULTS AND DISCUSSION

3.1. Pyrolysis Characteristics. Figure 1 shows the pyrolysis conversion curves of SL$^+$ and SL$^+$-Fe based on the combustible mass. The conversion process can be mainly divided into three stages based on reaction temperature: 200.0–602.6 °C (I), 602.6–692.0 °C (II), and 692.0–900.0 °C (III). In stage I, the higher conversion rate of SL$^+$-Fe indicates that the iron component facilitated the pyrolysis in this stage. In stage II, the basically coinciding conversion curves of lignite indicate that the iron component had no catalytic effects on the pyrolysis of lignite. In stage III, a slightly lower conversion rate of SL$^+$-Fe indicates that the iron component inhibited the pyrolysis of lignite in this stage.

Figure 2 shows the generation rate curves of four pyrolysis gases (CO$_2$, CO, H$_2$, and CH$_4$) during the pyrolysis process of SL$^+$ and SL$^+$-Fe analyzed by GC. The pyrolysis gases released in the order of CO$_2$, CO, H$_2$, and CH$_4$, and the addition of the iron component did not change the order of released gases.

CO$_2$ is the major gaseous product in the early stages of pyrolysis at low temperatures and is mainly generated from the cracking and reforming of C═O and −COOH functional groups. As shown in Figure 2a, CO$_2$ starts to escape at approximately 118.1 °C, and the escape rate peaked in the range 350–380 °C. After the addition of the iron component to the hydrochloric acid-demineralized lignite, the precipitation temperature of CO$_2$ decreased, and the temperature region shortened, and the precipitation rate increased significantly. It is speculated that the iron component facilitated the cracking and reforming of C═O and −COOH functional groups at low temperatures during the pyrolysis process.

CO is formed during the cracking of carboxyl, carbonyl, phenol hydroxyls, and ether functional groups and is generated from the aldehyde group cracking in the low-temperature stage. In the higher-temperature stage, CO is generated from the decomposition of the methoxyl group, the secondary reaction of tar formation (fracture of the ether bond between the aromatic ring and ring), and fracture of ether, the hydroxyl group, and the oxygen-containing heterocyclic ring structure. As shown in Figure 2b, CO began to escape at approximately 188.7 °C, with the maximum escape rate in the range 350–380 °C. The CO formation rate enhanced during 188.7–358.7 °C and then decreased at the higher-temperature range after the addition of the iron component. The results showed that iron species promoted the decomposition of

![Figure 1](http://pubs.acs.org/journal/acsodf)

![Figure 2](http://pubs.acs.org/journal/acsodf)
aldehyde groups at low temperature and inhibited the decomposition of functional groups to generate CO at high temperature.

H$_2$ is generally believed to be the product of secondary pyrolysis of coal, which is the result of polymerization of aromatic substances and hydrogenated aromatic ring dehydrogenation at high temperature.$^{25,26}$ As shown in Figure 2c, the initial escape temperature of H$_2$ was approximately 277.9 °C, with the maximum escape rate in the range 690–710 °C. The generation rate of H$_2$ increased at less than 593.8 °C and then decreased at the higher-temperature range due to the addition of the iron component. The iron component promoted the decomposition of aromatic structures at less than 593.8 °C and inhibited further polymerization of free radicals and their agglomeration to inhibit the generation of H$_2$ in the higher-temperature range.

CH$_4$ is mainly generated from the dissociation of methoxy groups and aliphatic side chains in lignite at low temperature and from aromatic side chain breaking at high temperature.$^{27}$ As shown in Figure 2d, the initial escape temperature of CH$_4$ was approximately 286.0 °C, and the escape rate peaked in the range 470–530 °C. The CH$_4$ formation rate reduced after the addition of the iron component. The iron component inhibited the dissociation of aliphatic side chains and aromatic side chains during the pyrolysis process.

### 3.2. FTIR Characterization

Figure 3 shows the FTIR spectra of SL$^+$ and chars, indicating the presence of three main molecular structures in the organic matters of lignite and chars, namely, the aliphatic structure, aromatic structure, and oxygen-containing functional group structure.$^8$ The FTIR spectra of lignite can be mainly divided into four frequency regions on the basis of absorbance assignments: 3675–3000 cm$^{-1}$ (I), 3000–2800 cm$^{-1}$ (II), 1850–1000 cm$^{-1}$ (III), and 900–650 cm$^{-1}$ (IV).$^{29–31}$

As shown in Figure 3, some differences were observed in the FTIR spectra of SL$^+$ and chars. In frequency region I, the peak at approximately 3426 cm$^{-1}$ in all the three samples corresponds to the hydroxyl groups (–OH). The absorbance of –OH groups from SL$^+$, SL$^+$-900, and SL$^+$-Fe-900 is slightly different, indicating that the iron component had no significant effect on these functional groups during the pyrolysis process. In frequency region II, an obvious weakening of characteristic absorbance was observed for the aliphatic C–H at approximately 2935 and 2859 cm$^{-1}$ in chars, indicating that the pyrolysis process decreased the amount of aliphatic functional groups in lignite. The slightly stronger peaks of SL$^+$-Fe-900 in this section suggest that the iron component prevented the separation of some aliphatic functional groups and is consistent with the escape characteristics of CH$_4$. In frequency region III, the absorbance of C=O stretching at approximately 1707 cm$^{-1}$ and the aromatic C=C vibration around 1610 cm$^{-1}$ decreased after pyrolysis, indicating that the C=O and C=C functional groups dissociated during the pyrolysis process. The intensity of the absorbance peaks of C=O and C=C functional groups did not show any obvious change due to the addition of the iron component. The weakening absorbance of the C=O stretching in the range 1300–1000 cm$^{-1}$ indicates that alcohols, phenols, ethers, and/ or esters could be reduced during the pyrolysis process. The absorption intensity of C=O increased due to the addition of the iron component, indicating that these species inhibited the decomposition of C=O, and the results are consistent with the release characteristics of CO. In frequency region IV, the absorbance in the range 900–650 cm$^{-1}$ is mainly attributed to various aromatic C–H group out-of-plane bending vibrations of lignite and chars. The weakening absorbance of the aromatic C–H group suggests that these chemical bonds dissociated during the pyrolysis process; however, the addition of the iron component had little effect on the variations of the aromatic C–H group.

### 3.3. XRD Characterization

Figure 4 shows the XRD spectra of the crystalline carbon (graphite-like structure) of SL$^+$ and chars. SiO$_2$, Al$_2$O$_3$, and FeO are the main types of inorganic substances found in the samples. The microcrystalline structural characteristics will be discussed in the latter part. The carbon structural characteristics of lignite and chars were acquired in the peak ranges 25–27° and 43–45° in the XRD spectra, representing the 002 and 100 peaks, respectively.$^{32,33}$ The 002 and 100 bands revealed a certain degree of graphitization for the carbon structure of chars.

Crystallite structure parameters, the aromacity ($f_a$), interlayer distance ($d_{002}$), stacking height ($L_z$), and aromatic layer size ($L_c$), were used to quantitatively describe the carbon structure. In the study of the lignite structure, the larger $f_a$ means the higher oriented trend spatial arrangement of aromatic rings and the higher proportion of aromatic carbon atoms forming 002 surface networks.$^{34}$ $d_{002}$ is inversely proportional to the degree of graphitization and the ordering degree of the microcrystalline structure.$^{29}$ The increase in $L_z$ and $L_c$ means the deepening of the aromatic ring lateral polycondensation degree of char in longitudinal and transverse orientation, respectively.

The crystallite structure parameters were determined by Bragg’s law and the Scherrer equation, and the calculated...
results are listed in Table 3. The crystal plane space ($d_{002}$) of lignite samples and chars is higher than that of pristine graphite (0.336–0.337 nm), indicating a relatively low degree of graphitization and a poor microcrystalline structure in SL$^+$ and chars. The calculated values of the aromatic microcrystalline structure of lignite and chars indicate that $f_a$, $d_{002}$, $I_D$, and $I_G$ of SL$^+$/900 were higher than those of SL$^+$, while $d_{002}$ was slightly lower, indicating that the graphitization degree of SL$^+$ deepened by the pyrolysis process. The lower $f_a$, $I_D$, and $I_G$ and higher $d_{002}$ of SL$^+$/Fe-900 suggest that the addition of iron effectively inhibited the graphitization tendency of the char structure during the pyrolysis process. This result is consistent with some previous literature reports. $^{3,11}$

| samples           | $f_a$   | $d_{002}$/nm | $I_D$/nm | $I_G$/nm |
|-------------------|---------|-------------|----------|----------|
| SL$^+$            | 0.598   | 0.3747      | 1.5285   | 1.2343   |
| SL$^+$/900        | 0.788   | 0.3626      | 1.6470   | 2.0967   |
| SL$^+$/Fe-900     | 0.470   | 0.3684      | 1.4971   | 1.7144   |

*Note: $f_a$—aromaticity; $d_{002}$—interlayer space; $I_D$—degree of stacking of aromatic layers; and $I_G$—aromatic layer size.*

### 3.4. Raman Spectroscopy

The chemical structure of SL$^+$ and chars was analyzed by Raman spectroscopy to further explore the role of the iron component in the pyrolysis process. Figure 5a shows the baseline-corrected Raman spectra in the range from 800 to 1800 cm$^{-1}$. The vibration regions attributed to the G-peak (1580–1600 cm$^{-1}$) and D-peak (1340–1380 cm$^{-1}$) existed in the Raman spectrum. During the structural investigating process of highly ordered carbonaceous materials with exciting laser in the visible range, the G-peak and D-peak usually referred to the Graphite and Defect bands, respectively. $^{12,25–37}$ However, in the Raman spectra of coal samples, the G-peak mainly represents the larger aromatic ring structure, and the D-peak is mainly attributed to the medium-to-large-sized aromatics having six or more fused benzene rings but not satisfying the graphite structure. $^{1,11,37–39}$ Studies have shown that the intensity of Raman peaks can be affected by electron-rich functional groups containing O, N, and S, and relation to the char structures, especially the aromatization. $^{37–39}$ As shown in Figure 5a, the intensity of the G-peak and D-peak decreased during the pyrolysis process. In addition, the Raman spectrum of SL$^+$/Fe-900 shows the lowest intensity. The contents of N and S of chars barely changed but that of O sharply decreased during the pyrolysis process after the addition of the iron component according to Table 1, indicating that the evolution of functional groups containing oxygen is one of the major factors corresponding to the difference in the Raman intensity.

Previous studies have suggested that the disorder degree of lignite and chars is relatively high, and the detailed information of the char structure is mainly hidden near the G-peak and D-peak. Therefore, investigating char properties directly by Raman spectra is very difficult. In this study, the Raman spectra were fitted into 10 Gaussian bands to obtain the detailed char structure information. $^{38,40}$ One example for the spectral fitted curves is given in Figure 5b. As the bands of G, G$\nu$, V$\nu$L, and R virtually represent the curve-fitting residuals and account for a small percentage of the Raman peak in any case, the Raman data is actually focused on four groups/bands (G, G$\nu$ + V$\nu$L + V$\nu$R, D, and S). $^{37}$ The features of the char chemical structure can be studied using the band area ratio $I_D/I_G$, $I_{(GR+VL+VR)}/I_D$, and $I_S/I_G$. The $I_D/I_G$ ratio has been extensively used as an important parameter to study the crystalline or graphite-like carbon structures. The $I_{(GR+VL+VR)}/I_D$ ratio is regarded as a brief measure of the ratio between the small aromatic ring systems having three–five fused benzene rings and the medium-to-large aromatic ring systems ($\geq$6 rings). The S band mainly represents sp$^3$-rich structures such as alkyl–aryl C–C structures and the methyl group attached to an aromatic ring. $^{38}$ The $I_S/I_G$ ratio is mainly used to describe the cross-linking density or the content of substituent groups in char.

Figure 6 shows the $I_D/I_G$, $I_{(GR+VL+VR)}/I_D$, and $I_S/I_G$ ratio of SL$^+$ and chars calculated from the curve fitting of Raman spectra. For the chars in this study, the growth of the $I_D/I_G$ ratio indicates the relative increases in the concentrations of aromatic rings having six or more fused benzene rings during pyrolysis. The relatively lower $I_D/I_G$ ratio of SL$^+$/Fe-900 to SL$^+$/900 suggests that the iron component inhibits the formation of medium-to-large aromatic ring systems ($\geq$6 rings). The decrease in the $I_{(GR+VL+VR)}/I_D$ ratio of chars...
indicates a transition from the relatively small to large aromatic ring systems or disappearance of small-sized aromatic rings during pyrolysis. The lowest \(I_{(GR+VL+VR)}/I_D\) ratio of SL\(^*\)-Fe-900 suggests that the iron component facilitates the reduction of the small-sized aromatic ring. The decrease in the \(I_D/I_G\) ratio of chars indicates that SL\(^*\) transforms from a side chain-rich structure to a fewer-substituent group structure during pyrolysis. The slightly higher \(I_G/I_O\) ratio of SL\(^*\)-Fe-900 indicates that the iron component inhibits the reduction of side chains during this pyrolysis process.

4. CONCLUSIONS

In conclusion, the effects of the iron component on the structure characteristics and pyrolysis behaviors of SL\(^*\) were comprehensively investigated. The Py-GC results suggest that the iron component promoted the conversion of lignite at temperature less than 602.6 °C and is unfavorable to pyrolysis at higher temperature. The pyrolysis gases released in the following order: CO\(_2\), CO, H\(_2\), and CH\(_4\), and the addition of the iron component did not change the sequences of released gases. The iron component promoted the generation of CO\(_2\), CO, and H\(_2\) in the low-temperature range and inhibited the formation of CO and H\(_2\) in the high-temperature range. The formation of CH\(_4\) was inhibited by the iron component throughout the pyrolysis process. The FTIR spectra showed that the evolution characteristics of −OH, C==O, C=C, and C−H functional groups were not significantly affected, and the dissociation of aliphatic functional groups and C−O functional groups was inhibited by the iron component during the pyrolysis process. The XRD and Raman spectra results indicate that the iron component restricted the regular spatial ring arrangement of aromatic rings, the formation of large aromatic rings (\(≥6\) rings), and the decrease in the content of side chains but facilitated the reduction of small-sized aromatic rings during the pyrolysis process. The addition of the iron component as a pretreatment method for pyrolysis can potentially establish the mechanistic pathway.

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Notes

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