Pore Structure and Fractal Characteristic Analysis of Gasification-Coke Prepared at Different High-Temperature Residence Times

Yang Guo, Lu Zhou, Fanhui Guo, Xiaokai Chen, Jianjun Wu,* and Yixin Zhang*

ABSTRACT: An accurate and quantitative description of the pore structure of gasification-coke using fractal geometry could be of great significance to its industrial utilization. In this study, gasification-coke was prepared with low-quality coal blending at different high-temperature residence times to investigate the variation in the pore structure, fractal dimensions, reactivities, and their relationship. The pore structure parameters (e.g., specific surface area, pore volume, and average pore diameter) of gasification-coke were investigated by low-temperature N$_2$ adsorption/desorption and mercury intrusion porosimetry. Fractal dimensions $D_1$ and $D_2$ (at relative pressures of 0–0.5 and 0.5–1, respectively) were calculated using the fractal Frenkel–Halsey–Hill model, and the fractal dimension $D_1$ was obtained using the Menger sponge model. The results show that the pore structure systems of gasification-coke prepared at different high-temperature residence times are continuous and complete, which contributes to the gasification reaction. The variation trend of the macropore structure parameters is more complex than that of micropore and mesopore with the extension of the high-temperature residence time. It is found that $D_1$ is linearly correlated with the micropore specific surface area, indicating that $D_1$ is more suitable for reflecting the roughness of the micropore surface; $D_2$ is linearly correlated with the mesopore volume and can describe the volumetric roughness of the mesopore; and $D_3$ reflects the irregularities and surface roughness of the macropores. Gasification reactivity is closely related to the $D_2$ value, and the reactivity of the gasification-coke may be improved if the number of mesopores is increased by controlling the high-temperature residence time or other pyrolysis conditions. The research results will provide theoretical reference for controlling the gasification reaction of gasification-coke and gasifier design.

1. INTRODUCTION

China has abundant reserves of low-rank coals with high volatile content and low-quality coking coals with high sulfur content, being used mainly for power and heat production.$^{1,2}$ The conversion of coal into clean gas through the gasification process is a key technology for clean coal utilization and also forms the basis for the sustainable development of the coal chemical industry.$^{3,4}$ Fixed-bed gasification technology, one of the mature clean utilization technologies of coal, is facing the great challenge of lump coal shortage.$^{5,6}$ However, lump coke with low volatility can solve the problem of lump coal shortage in fixed-bed gasifiers. Lump gasification-c coke does not require strict strength and ash content like metallurgical coke.$^7$ Blending low-rank coal with caking coal to prepare lump gasification-c coke is effective in providing a solution to lump coal shortage. In addition, this method can realize the utilization of low-rank coal.$^8$ Gasification-c coke is produced by blending a larger proportion of low-rank coal, which makes its coking mechanism different from traditional metallurgical coke.$^9,10$ Yang et al.$^{11,12}$ put forward a new coking mechanism of gasification-c coke in terms of the physical texture to explain why gasification-c coke has high strength. The gasification reactivity of coke mainly depends on the physical structure of coke, the chemical structure of coke, the concentration and dispersion of alkali metals and alkaline earth metals with catalysis in coke.$^{13,14}$ The physical structure mainly refers to the pore structure which is one of the key factors influencing gasification. The pore structure of coke acting as the channel of mass transfer has a great influence on the diffusion of gasification agents and gasification products during the gasification process. Besides this, the pore structure provides an active site for the contact and reaction of gasification agents and coke.$^{15}$ The different coking mechanism may cause the pore evolution of gasification-c coke during the pyrolysis process to be different from that of traditional metallurgical coke. The effects of pyrolysis conditions on the pore structure of char/
cavities.26,27 It is of great significance to plastically deform, resulting in a smooth surface and large coke particles, wherein a high heating rate causes the particles in dimension of seepage and adsorption pores and explored the results of MIP and gas adsorption to calculate the fractal intrusion porosimetry (MIP).29

temperatures has a highly ordered structure.24,25 The pyrolysis increases. This indicates that the coke produced at high the carbon crystal size increase as the pyrolysis temperature

However, they did not investigate the effect of pyrolysis time on the pore structure or chemical structure of coal char to explain the change in coal char reactivity. He et al.21 investigated the influence of partial rapid pyrolysis on the properties of Chinese bituminous coal. They stated that the pretreatment of rapid pyrolysis had a fundamental effect on the coal char structure and reactivity. If coke is used for gasification, it is particularly important to study the relationship between the pyrolysis conditions and the pore structure of gasification-coke. The effects of pyrolysis temperature and time on the surface area and pore volume have a two-side effect. First, the precipitation of volatiles during pyrolysis increases the pore size, thereby increasing the pore volume. Alternatively, the reduction of the functional groups makes the coke structure segments more ordered, thereby reducing the pore volume and specific surface area.22,23 From another perspective, the interlayer spacing of the carbon is also reduced, while the carbon crystal size increase as the pyrolysis temperature increases. This indicates that the coke produced at high temperatures has a highly ordered structure.24,25 The pyrolysis pressure and heating rate also affect the morphology of the coke particles, wherein a high heating rate causes the particles to plasticly deform, resulting in a smooth surface and large cavities.26,27 It is of great significance to investigate the pore evolution of gasification-coke during pyrolysis which lays the foundation for the subsequent gasification process.

As mentioned above, the pore structure of gasification-coke has important effects on its gasification reactivity. An accurate and quantitative description of the pore structure of gasification-coke could be of great significance to its industrial utilization. However, traditional Euclidean geometry is difficult to describe the irregularity of the pore structure of gasification-coke accurately and quantitatively. Fractal geometry is a very appropriate tool that can be used to effectively describe the pore irregularities and surface roughness of gasification-coke during the pyrolysis process, which contributes to revealing the actual and detailed pore structure and fractal characteristics of gasification-coke prepared at different high-temperature residence times.28 Previous studies have shown that the fractal dimension is generally obtained by gas adsorption and mercury intrusion porosimetry (MIP).29–32 Wang et al.33 used the results of MIP and gas adsorption to calculate the fractal dimension of seepage and adsorption pores and explored the influence of coalification on the pore characteristics. The results show that coalification makes the pore structure more complex and the pore surface rougher. Xu et al.34 indicated that fractal theory is suitable for describing the pore structure and surface morphology of coal char. Sun et al.35 found that the surface fractal dimensions of coal are mainly determined by the carbon content and pore diameter. Deeper deposited coals have higher methane adsorption capacity, which could be due to their rougher surface and more condensed pore networks. The abovementioned research indicates that fractal theory is suitable for studying pore characteristics and pore evolution of coal and related products. Fractal geometry provides a new perspective in studying the effects of the pyrolysis process on the surface morphology and pore structure of gasification-coke.

The aim of this study is to provide further insights into the effects of high-temperature residence time on the pore structure of gasification-coke using fractal geometry. In this study, N2 adsorption/desorption and MIP were employed to characterize the pore structure of gasification-coke. Different fractal dimensions were obtained using the FHH model and the Menger sponge model, and the gasification reactivity of the gasification-coke was analyzed by thermogravimetric analysis. The variation in the gasification-coke pore structure, fractal dimensions, and reactivities and their relationship were investigated. The research results will provide a theoretical reference for controlling the gasification reaction of gasification-coke and gasifier design.

2. MATERIALS AND METHODS

2.1. Materials. Low-rank coal (long flame coal, LF) obtained from the Shannxi Province, high-sulfur coking coal (strong caking coal, CC), and inferior fat coal (weak caking coal, FC) from Inner Mongolia in China were used as parent coals in this study. The coals were crushed and sieved to obtain the same particle size fraction of 0.5–1 mm to prepare the gasification-coke. The ashes of raw coals were prepared according to the Chinese Standard GB/T1574–2001, and the main chemical compositions of the ashes were analyzed using an X-ray fluorescence spectrometer (XRF) according to ASTM D4326. According to the China National Standards GB/T 212–2008 and GB/T 19143–2003, proximate and ultimate analyses of raw coals are presented in Table 1.

2.2. Experimental Methods. 2.2.1. Gasification-Coke Preparation. The blending ratios of the three types of coal (CC, FC, and LF) were 40, 20, and 40 wt %, respectively. A total of 300 g of blended sample with 10 wt % moisture content was filled into a coke vessel (d × h = 90 × 80 mm). Subsequently, the dry bulk density of the blended sample reached 0.90 g/cm3 after pressing. The pyrolysis process was carried out in a muffle furnace under atmospheric pressure. Nitrogen gas (99.999% purity) at a certain flow rate was used as the inert gas flushing through the muffle. The temperature of the muffle was increased at a heating rate of 10 °C/min from room temperature to 1050 °C, and this temperature was then maintained for a desired time. In the pyrolysis process,
the effect of the high-temperature residence time on the gasification-coke pore characteristics was studied by varying the values from 1, 2, 3, 4, 5, and 6 h, while keeping all other parameters constant. The gasification-coke produced at different high-temperature residence times were recorded as Coke-1, to Coke-6. All the gasification-coke used for further analysis was prepared by sieving to obtain the same particle size fraction of 0.5–1 mm and dried at 105 °C for 24 h.

In this study, M_{25} was used to evaluate the mechanical strength of gasification-coke. The mass ratio of gasification-coke (>25 mm particles) after the drum test (1/4 microdrum for 100 rotations at 25 rpm) can be defined as M_{25}. The gasification-coke strength after the reaction was evaluated by CSR and tested according to the China National Standards GB/T4000–2008. Proximate analysis, CSR, and M_{25} of gasification-coke are presented in Table 2.

Table 2. Proximate Analysis, CSR, and M_{25} of Gasification-Coke

| sample | M (wt%) | A | V | FC | CSR (%) | M_{25} |
|--------|---------|---|---|----|---------|-------|
| Coke-1 | 1.08    | 16.25 | 2.22 | 80.45 | 35.62 | 80.25 |
| Coke-2 | 0.86    | 17.81 | 1.82 | 79.51 | 38.13 | 82.41 |
| Coke-3 | 0.63    | 17.79 | 1.67 | 79.91 | 40.56 | 83.10 |
| Coke-4 | 0.52    | 18.55 | 1.53 | 79.40 | 38.89 | 85.96 |
| Coke-5 | 0.41    | 18.96 | 1.39 | 79.24 | 39.37 | 83.10 |
| Coke-6 | 0.33    | 19.13 | 1.25 | 79.29 | 40.02 | 83.94 |

“ad: air-dried base.

2.2.4. Fractal Dimensions from Low-Temperature N\textsubscript{2} Adsorption Isotherms. The FHH method is widely acknowledged as the most effective method for the characterization of irregular and complex pore structures.\textsuperscript{28,32,34} According to this method, the fractal dimensions can be calculated by the following equation using N\textsubscript{2} adsorption data.\textsuperscript{30,40}

\[
\ln \left( \frac{V}{V_0} \right) = C + A \ln \left( \ln \left( \frac{P}{P_0} \right) \right)
\]

(1)

\[ A = D - 3 \]

(2)

where V represents the volume of N\textsubscript{2} adsorbed by the gasification-coke under the equilibrium pressure; V_0 is the volume of N\textsubscript{2} adsorbed by the gasification-coke monolayer under the saturation pressure; P_0 is the gas saturated vapor pressure; A is a power-law exponent that is dependent on the fractal dimensions and mechanism of adsorption; C is the gas adsorption constant; and D denotes the fractal dimensions.

2.2.5. Fractal Dimensions from MIP. At present, the Menger sponge model is the main approach to calculate the fractal dimension D of the pore data of porous materials obtained from MIP.\textsuperscript{41,42} Based on the Washburn equation and the Menger sponge model, eqs 3 and 4 for calculating D are derived as follows:\textsuperscript{35,44}

\[
\ln(-dV_\rho/dR) \propto (2 - D) \ln R
\]

(3)

\[ D = 2 - K \]

(4)

where R represents the pore diameter of the gasification-coke; V_\rho is the mercury injection volume; D is the fractal dimension; and K is the slope of the fitting curve of ln(-dV_\rho/dR) vs ln(R).

2.2.6. Gasification Reactivity. The gasification reactivity of the gasification-coke was measured using an STA-409C thermogravimetric analyzer manufactured by the NETZSCH Company in Germany. Approximately 10 mg of the sample (60–80 mesh) was placed in a corundum crucible and heated at 20 °C/min to 1150 °C under a pure nitrogen flow of 60 mL/min. The N\textsubscript{2} atmosphere was switched to a CO\textsubscript{2} flow of 60 mL/min for gasification reaction after 5 min. The temperature was kept constant for 30 min. The measurements were repeated thrice, and the final results were the averages of the three independent results.

In this study, the reactivity index \( (R_\alpha, \text{min}^{-1}) \) was used to investigate the gasification reactivity of gasification-coke at different high-temperature residence times.\textsuperscript{35,46}

\[
\alpha = \frac{m_0 - m_t}{m_0 - m_f}
\]

(5)

where \( \alpha \) represents the carbon conversion (%); \( m_0 \) refers to the initial mass of gasification-coke (mg); \( m_f \) is the gasification-coke quality at time \( t \) (mg); and \( m_t \) is the residual mass of gasification-coke after the gasification reaction (mg).

\[
R_\alpha = \frac{0.5}{t_{0.5}}
\]

(6)

where \( t_{0.5} \) denotes the time (min) required to reach 50% of the carbon conversion.

3. RESULTS AND DISCUSSION

3.1. Characteristics of the Pore Structure of Gasification-Coke. 3.1.1. Low-Temperature N\textsubscript{2} Adsorption/Desorption Analysis. The adsorption/desorption isotherms

https://dx.doi.org/10.1021/acsomega.0c02399

ACS Omega 2020, 5, 22226–22237
of the gasification-coke prepared at different high-temperature residence times are shown in Figure 1. The adsorption isotherms of gasification-coke have similar trends. According to the IUPAC classification, the adsorption isotherms of gasification-coke are observed to be type II. This means that there are three sections in the nitrogen adsorption process of the gasification-coke: monolayer adsorption, multilayer adsorption, and capillary condensation. This also means that the pore size in the gasification-coke is distributed from nanometer to micrometer. In addition, the isotherms increase slowly in the low-pressure region \((P/P_0 \leq 0.5)\) due to the monolayer adsorption controlled by the van der Waals force occurring in this region. Multilayer adsorption occurs in the high-pressure region \((P/P_0 > 0.5)\), which is controlled by surface tension. Considering the differences in gas adsorption mechanisms between the low-pressure and high-pressure regions, the fractal dimensions of the gasification-coke could be determined as \(D_1\) and \(D_2\), respectively.

The pore shape of the cokes can also be obtained by analyzing the hysteresis loops in the adsorption/desorption isotherms. All isotherms of the gasification-coke have hysteresis loops, and all the hysteresis loops belong to type B, implying that micropores and mesopores are mainly cylindrical pores. It is worth noting that the adsorption/desorption isotherms of Coke-1 and Coke-2 are nonoverlapping at relatively low pressure conditions, suggesting that the pores in Coke-1 and Coke-2 are well connected. However, the adsorption/desorption isotherms of other cokes overlap at the relatively low pressures, which indicates the presence of cylindrical pores with closed ends and wedge-shaped pores in the gasification-coke. The prolongation of the high-temperature residence time causes the volatile substances to slowly escape from the blended coal particles, which facilitates the formation of cylindrical pores.

The micropore and mesopore information (from the HK and BJH models, respectively) of the gasification-coke are shown in Figures 2 and 3. The data obtained show that the SSA and pore volume of the gasification-coke change greatly with the increase in high-temperature residence time. The mesopore SSA changes from 2.85 to 10.65 m\(^2\)/g and the micropore SSA ranges from 16.85 to 56.65 m\(^2\)/g. The micropore SSA is significantly larger than that of the mesopore, indicating the greater contribution of micropores to the SSA than the mesopores. The mesopore volume varies from 0.0086 to 0.045 cm\(^3\)/g and micropore volume changes from 0.0056 to 0.036 cm\(^3\)/g. The total APD initially decreases and then increases with the extension of the high-temperature residence time, which is consistent with the changing trend of micropore and mesopore APDs. The dominant micropore size is between 0.5 and 1 nm, with a major peak at approximately 0.75 nm for
Coke-1, 0.57 nm for Coke-2, 0.55 nm for Coke-3, 0.48 nm for Coke-4, 0.64 nm for Coke-5, and 0.69 nm for Coke-6. The cokes display a multimodal micropore size distribution, while the mesopore size distribution tends to be unimodal with a main size between 2 and 18 nm. The abovementioned results indicate that the increase in high-temperature residence time increases the number of micropores and mesopores in the gasification-coke and the pore size becomes smaller, but the opposite trend is observed when the residence time is longer than 4 h. Almost all the curves (except the plot of residence time vs mesopore SSA) in Figure 2 show a maximum or minimum at a high-temperature residence time of 4 h. The volatile components in blended coal cannot escape completely when the high-temperature residence time is short (≤2 h).
Therefore, the residual volatiles block some of the mesopores in the gasification-coke, which reduces the SSA of the mesopores.\textsuperscript{34} As the high-temperature residence time increases (>2 h), the gas generated by the release of volatile matter in the blended coal expands the gasification-coke particles, making the pore structure more complicated and increasing the amount of both micropores and mesopores.\textsuperscript{49,50} Moreover, with the increase in high-temperature residence time, the volatile matter lodged at the pore mouth is removed and more pores are opened, thereby causing the increase in the SSA and volume of micropores and mesopores.\textsuperscript{10} However, the micropore SSA, micropore volume, and mesopore volume of the gasification-coke slightly decrease when the high-temperature residence time is more than 4 h. The reason for such results could be that the prolongation of the high-temperature residence time could lead to an increase in the degree of gasification-coke graphitization. The progress of graphitization causes the crystalline structure of the gasification-coke to reach unity, causing the mesopores and macropores in the gasification-coke to collapse, along with the disappearance of some micropores.\textsuperscript{24}

3.1.2. Mercury Intrusion Porosimetry Analysis. The SSA, pore volume, APD, and porosity of macropores are shown in Figure 4. The macropore SSA varies from 0.129 to 5.169 m\textsuperscript{2}/g, the pore volume ranges from 1.046 to 1.168 cm\textsuperscript{3}/g, the porosity changes from 60.26 to 64.80%, and the APD varies from 0.9037 to 32.46 μm. The variation tendency of the macropore SSA is consistent with that of the micropores and mesopores. The macropore size distribution curves are shown in Figure 5. When the high-temperature residence time is extended from 2 to 4 h, the gasification-coke displays a multimodal macropore size distribution, whereas unimodal macropore size distribution is observed when the residence time is 1, 5, and 6 h. This indicates that Coke-2, Coke-3, and Coke-6.

![Figure 5. Macropore size distribution curves.](image-url)

![Figure 6. SEM results of the gasification-coke prepared at different high-temperature residence times.](image-url)
Coke-4 have a wider macropore size range than the other gasification coke.

### 3.1.3. SEM Results

The pore morphology of the gasification coke was analyzed using some representative SEM images. As can be seen from Figure 6, although there are some small particles covering and accumulating near the pores, the surface of Coke-1 is smoother than that of other cokes (except for Coke-6), which is one of the reasons for the smaller fractal dimension of Coke-1. In addition, it can be seen that there are few pores (micropores, mesopores, and macropores) in Coke-1. As the high-temperature residence time increases, the pore network becomes more developed and the pore surface is covered by more small mineral particles. According to the results of Table 3, the three raw coals are rich in silicon, aluminum, and ferrum. The minerals containing these

| raw coals | SiO$_2$ | Al$_2$O$_3$ | Fe$_2$O$_3$ | CaO | MgO | K$_2$O | Na$_2$O | TiO$_2$ | SO$_3$ | P$_2$O$_5$ | others |
|-----------|---------|-------------|-------------|-----|-----|--------|--------|--------|-------|--------|--------|
| CC        | 49.50   | 34.77       | 5.66        | 3.03 | 0.69 | 0.55   | 0.47   | 1.29   | 2.71  | 0.66   | 0.67   |
| FC        | 43.19   | 40.68       | 5.01        | 3.52 | 1.31 | 0.61   | 0.18   | 1.39   | 3.44  | 0.31   | 0.36   |
| LF        | 40.25   | 14.89       | 11.22       | 16.37| 2.08 | 0.32   | 0.99   | 0.56   | 12.12 | 0.44   | 0.76   |

Figure 7. Representative plots of ln(V) versus ln(ln(P$_0$/P)) on the basis of the N$_2$ adsorption isotherms.

Figure 8. $D_1$ and $D_2$ of the gasification-coke prepared at different high-temperature residence times.
elements are converted and precipitated at the high-temperature condition, and the high content of silicate and aluminosilicate minerals in raw coals has a more important influence on the pore structure of gasification-coke. The mineral particles formed by melting minerals may close some pores in gasification-coke. However, the extension of the high-temperature residence time reduces mineral particles accumulated in the pores and parts of pores were opened. Compared to Coke-4, small particles on the surface of Coke-5 are eliminated and some macropores of Coke-5 collapse to form cracks or evolve into macropores. Compared to Coke-5, the pore surface of Coke-6 becomes smoother and the pore structure becomes simpler. The above results concur with the conclusions drawn from N₂ adsorption/desorption and MIP results.

3.2. Characteristics of Fractal Dimensions of Gasification-Coke. 3.2.1. Fractal Dimensions from the Analysis of N₂ Adsorption Isotherms. The FHHI model was applied to obtain plots of \(\ln(\ln(P/P_0))\) vs \(\ln(V)\) from the N₂ adsorption isotherms. It can be seen from Figure 7 that the corresponding \(R^2\) values of all curves exceed 0.94, and the fitting effect is good. All the fitting curves can be divided into two segments with the demarcation point of \(P/P_0 = 0.5\), which further explains that there are two different fractal features in the pores of the gasification-coke.

\(D_1\) and \(D_2\) are obtained from the slope of the fitting curve, and the variation in \(D_1\) and \(D_2\) with the high-temperature residence time is shown in Figure 8. The results show that the values of \(D_1\) and \(D_2\) are between 2 and 3, which is consistent with the definition of the fractal dimension. Monolayer adsorption occurs in the region contained within \(P/P_0 \leq 0.5\), and the N₂ molecules are slowly adsorbed on the gasification-

coke pore surface. Therefore, \(D_1\) can be used to describe the surface fractal features of the pores in the gasification-coke. Figure 9(A) and (B) shows that the micropore SSA and \(D_1\) present a better correlation than mesopore SSA. This indicates that \(D_1\) represents the roughness of the micropore surface. As the high-temperature residence time increases, the values of \(D_1\) initially increase and then decrease slightly, indicating that the micropore surface of the gasification-coke gradually becomes rougher and then becomes smoother. The volatile matter in blended coal has sufficient time to polycondense to form disordered carbon deposits on the pore surface, resulting in a rougher micropore surface. The results comply with the conclusions drawn from Figure 6. However, as the amount of micropores increases, the carbon layer becomes more ordered, which explains why \(D_1\) slightly decreased subsequently.

Multilayer adsorption occurs in the region contained within \(1>P/P_0>0.5\), and N₂ molecules are gradually adsorbed and filled in the pores of the gasification-coke. Therefore, \(D_2\) can be used to describe the fractal characteristics of the mesopore volume, which reflects the complexity of the mesopore structure. Furthermore, the results in Figure 9(C) and (D) also confirm the significant correlation between \(D_2\) and mesopore volume. The values of \(D_2\) initially increase and then decrease as the high-temperature residence time increases. When the high-temperature residence time is 4 h, the value of \(D_2\) reached 2.83, indicating that the interior of the mesopore structure became quite complex at this time, which is related to the increasing number of mesopores.

3.2.2. Fractal Dimension From the Analysis of MIP. The Menger sponge model was occupied to obtain the plots of \(\ln(R) vs \ln((-dV_p/dR))\) from the MIP date. As shown in Figure 10, the fitting level of all the curves is good and the corresponding \(R^2\) values are over 0.98. In Figure 11, the values of \(D_3\) are between 2 and 3, which is consistent with the definition of the fractal dimension. Thus, \(D_3\) can sufficiently reflect the irregularities and surface roughness of the macropores. With the increase in the high-temperature residence time, the variation of \(D_3\) is complicated, indicating that the structure and number of macropores change intricately.

3.2.3. Relationship Between Fractal Dimensions and Gasification Reactivity. Figure 12 shows the influence of the high-temperature residence time on the gasification reactivity of gasification-coke. It is shown that the \(R_t\) initially increases and then decreases, implying that the gasification reactivity of gasification-coke initially rises and then declines. The pyrolysis process of blended coal causes certain changes in the chemical structure, mineral matters, surface morphology, and so on. These changes in turn affect the pore structure of the gasification-coke. The changes in the pore structure are important factors affecting the gasification reactivity of gasification-coke. Figure 12 shows that Coke-3 and Coke-4 have higher gasification reactivity and a larger \(D_2\) compared to other gasification-coke. In addition, gasification-coke with lower gasification reactivity has a smaller \(D_2\). This indicates that the fractal dimension \(D_2\) of the mesopores may affect the gasification reactivity of gasification-coke to some extent. Therefore, we attempted to explore the relationship between the reactivity and the three fractal dimensions.

As seen in Figure 13, there is a significant positive correlation between \(D_2\) and the gasification reactivity of gasification-coke. However, \(D_1\) and \(D_3\) have a weak positive correlation between the reactivity and the three fractal dimensions.
correlation with the gasification reactivity. The gasification-coke and CO$_2$ gasification reactions are typical heterogeneous reactions. The pores provide a transport channel for gaseous reactants and products and play a significant role in the gas-phase mass transfer process.\textsuperscript{17,57} As conveyed before, $D_2$ reflects the fractal dimensions of the mesopore volume. The higher $D_2$ values represent more mesopores and higher heterogeneity of the mesopore distribution. This could provide more transmission channels for the transfer of CO$_2$ gas from the external surface to the internal surface, and also improves the transmission efficiency.\textsuperscript{58,59} Gasification reactivity is closely related to the $D_2$ value, and a larger $D_2$ value could indicate an increased reactivity of gasification-coke. Thus, the reactivity of gasification-coke may be improved if the number of mesopores

**Figure 10.** Representative plots of $\lg(R)$ versus $\lg(-dV/dR)$ on the basis of MIP.

**Figure 11.** $D_2$ of the gasification-coke prepared at different high-temperature residence times.

**Figure 12.** Gasification reactivity of coke at different high-temperature residence times.
is increased by controlling the high-temperature residence time or other pyrolysis conditions.

4. CONCLUSIONS

In this study, the fractal characteristics and pore structure of gasification coke prepared at different high-temperature residence times were analyzed using gas adsorption, MIP, and fractal theory. Furthermore, based on the physical significance of the fractal dimensions, the relationship between the reactivity and the three different fractal dimensions was also discussed. The conclusions drawn are as follows:

1. The pore structure systems of gasification-coke prepared at different high-temperature residence times are continuous and complete. The variation trend of the macropore structure parameters is more complex than that of micropores and mesopores with the extension of the high-temperature residence time.

2. The fractal theory based on the FHH and Menger sponge models is suitable for describing the pore structure of gasification-coke. It is found that \( D_1 \) indicates the roughness of the micropore surface; \( D_2 \) can describe the volumetric roughness of the mesopores; \( D_3 \) reflects the irregularities and surface roughness of the macropores.

3. The degree of change of \( D_1 \) (19.58% varies) is evidently larger than that of \( D_2 \) (12.96% varies) and \( D_3 \) (9.439% varies). This indicates that the high-temperature residence time has a greater effect on the roughness of the mesopore volume than on the macropore and micropore surfaces.

4. Gasification reactivity is closely related to the \( D_2 \) value, and a larger \( D_2 \) value could indicate an increased reactivity of gasification-coke. The reactivity of gasification-coke may be improved if the number of mesopores is increased by controlling the high-temperature residence time or other pyrolysis conditions.

**AUTHOR INFORMATION**

**Corresponding Authors**

**Jianjun Wu** — School of Chemical Engineering and Technology and National Engineering Research Center of Coal Preparation and Purification, China University of Mining and Technology, Xuzhou 221116, P.R. China; Email: jjuw@163.com

**Yixin Zhang** — National Engineering Research Center of Coal Preparation and Purification, China University of Mining and Technology, Xuzhou 221116, P.R. China; Email: yixinzhang@cumt.edu.cn

**Authors**

**Yang Guo** — School of Chemical Engineering and Technology and National Engineering Research Center of Coal Preparation and Purification, China University of Mining and Technology, Xuzhou 221116, P.R. China

**Lu Zhou** — School of Chemical Engineering and Technology and National Engineering Research Center of Coal Preparation and Purification, China University of Mining and Technology, Xuzhou 221116, P.R. China

**Fanhui Guo** — School of Chemical Engineering and Technology and National Engineering Research Center of Coal Preparation and Purification, China University of Mining and Technology, Xuzhou 221116, P.R. China

**Xiaokai Chen** — School of Chemical Engineering and Technology and National Engineering Research Center of Coal Preparation and Purification, China University of Mining and Technology, Xuzhou 221116, P.R. China

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.0c02399

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was financially supported by the National Natural Science Foundation of China (No. 51704292 and 51974311) and the National Key Research and Development Program of China (No. 2019YFC1904302).

**REFERENCES**

1. Kern, S.; Pfeifer, C.; Hofbauer, H. Gasification of lignite in a dual fluidized bed gasifier — Influence of bed material particle size and the amount of steam. *Fuel Process. Technol.* 2013, 111, 1–13.

2. Zhang, Y.; Yang, G.; Jiang, Y.; Guo, F.; Zhao, X.; Wu, J. The mechanism of the ash fusion characteristics of gasification coke affected by SiO2/Al2O3 ratio and CaO content in blending coals. *Int. J. Coal Prep. Util.* 2019, 1675647.

3. Gini, C. Suitability of coal gasification technologies for the chemical industry. *Przem. Chem.* 2014, 93, 1393–1400.

4. Zhang, Z.; Pang, S.; Levi, T. Influence of AAEM species in coal and biomass on steam co-gasification of chars of blended coal and biomass. *Renew. Energ.* 2017, 101, 356–363.

5. Fanhui, G.; Miao, Z.; Guo, Z.; Li, J.; Zhang, Y.; Wu, J. Properties of flotation residual carbon from gasification fine slag. *Fuel* 2020, 267, 117043.

6. Guo, F.; Wu, J.; Zhang, Y.; Hou, K.; Jiang, L. Characterization of gasification-coke prepared with coal by-product and a high ratio of low-rank coal addition. *Energ. Source. Part A.* 2020, 1.

7. Liu, X.; Yuan, Z. Life cycle environmental performance of by-product coke production in China. *J. Cleaner Prod.* 2016, 112, 1292–1301.
elevated temperatures. Fuel Surface morphology and pore structure. Gasification properties and kinetics of biomass chars and anthracite atmospheres at elevated pressures. ACS Omega http://pubs.acs.org/journal/acsodf Pyrolysis conditions on the structure and gasification reactivity of Collie bituminous coal. Energ. Fuel. Characteristics of coal partial gasification on a circulating fluidized bed reactor. Energy. Fuel. 2017, 31, 2557−2564.

Fuels exhibit a range of complex behaviors, including reactive transport, due to their heterogeneous nature. Understanding these processes is crucial for optimizing the performance and efficiency of energy conversion systems. This manuscript investigates the impact of pyrolysis conditions on the structural and gasification reactivity of Collie bituminous coal, providing valuable insights into the mechanisms governing these processes.

The study demonstrates the importance of considering the interplay between pyrolysis conditions and coal structure. The results highlight the significance of optimizing operational parameters to achieve desired outcomes, such as efficient energy extraction or enhanced product quality. This work contributes to the broader understanding of coal pyrolysis and gasification, offering practical implications for the design of advanced energy technologies.
during gasification in supercritical water. *J. Supercrit. Fluid.* 2018, 136, 102–109.

(50) Jiao, H.; Wang, M.; Kong, J.; Yan, D.; Guo, J.; Chang, L. Contribution of single coal property to the changes of structure and reactivity of chars from blending coking. *J. Anal. Appl. Pyrol.* 2018, 134, 114–121.

(51) Lee, C.; Jenkins, R.; Schobert, H. Structure and reactivity of char from elevated pressure pyrolysis of Illinois No. 6 bituminous coal. *Energ. Fuel.* 1992, 6, 40–47.

(52) Li, C.; Zhao, J.; Fang, Y.; Wang, Y. Pressurized fast-pyrolysis characteristics of typical Chinese coals with different ranks. *Energ. Fuel.* 2009, 23, 5099–5105.

(53) Koranyi, A. The relationship between specific reactivity and the pore structure of coal chars during gasification. *Carbon* 1989, 27, 55–61.

(54) Wang, M.; Roberts, D.; Kocjanek, M.; Harray, D.; Chang, L.; Li, C. Raman spectroscopic investigations into links between intrinsic reactivity and char chemical structure. *Energ. Fuel.* 2014, 28, 285–290.

(55) Hurt, R.; Sarofim, A.; Longwell, J. Role of microporous surface area in uncatalyzed carbon gasification. *Energ. Fuel.* 1991, 5, 290–299.

(56) Liu, S.; Rezaei, R.; Lucas, A.; Harris, J.; Wall, F. Modelling of a pressurised entrained flow coal gasifier: the effect of reaction kinetics and char structure. *Fuel* 2000, 79, 1767–1779.

(57) Wang, Y.; Bhatia, K. A generalised dynamic model for char particle gasification with structure evolution and peripheral fragmentation. *Chem. Eng. Sci.* 2001, 56, 3683–3697.

(58) Zou, J.; Zhou, Z.; Wang, F.; Zhang, W.; Dai, Z.; Liu, H.; Yu, Z. Modeling reaction kinetics of petroleum coke gasification with CO. *Chem. Eng. Process.* 2007, 46, 630–636.

(59) Liu, X.; Nie, B. Fractal characteristics of coal samples utilizing image analysis and gas adsorption. *Fuel* 2016, 182, 314–322.