Structure Characterization and CO₂ Gasification Kinetics of Tri-High Coal-Chars Derived from High-Temperature Pyrolysis

Lang Liu,∗‡† Bowen Kong,‡ Qingrui Jiao,‡ Jian Yang,‡ Qingcai Liu,‡ and Xiaoyu Liu‡

†Chemical Engineering Institute, Guizhou Institute of Technology, Guiyang, Guizhou 550003, China
‡College of Material Science & Engineering, Chongqing University, Shapingba, Chongqing, 400044, China

ABSTRACT: The pore structures and chemical composition features of two kinds of tri-high coal and their char samples prepared at a 750 °C temperature were analyzed. The results showed that the pyrolysis process has a great influence on the pore structure and the chemical composition of the char, and the influence is highly related to the coal ranks. The gasification kinetics of the two chars in pure CO₂ atmosphere was also studied. The results indicated that the classical random pore model (RPM) cannot be used to explain the gasification kinetics throughout the char gasification. A modified RPM, considering the inhibitory effect of ash on the gasification kinetics, was adopted to estimate the kinetics, and the kinetic constants and the corresponding activation energies were calculated. It was observed that it was necessary to include the effect of ash on the variations of char structures during the char gasification to get an accurate description of reaction rate versus carbon conversion throughout the gasification of the tri-high coal chars.

1. INTRODUCTION

Because of the increased demand for power and other applications,†‡ increasing coal consumption is needed and that has resulted in higher CO₂ emission. Therefore, the application of clean coal technology is necessary, for example, gasification. CO₂ and H₂O are the most common gasification agents for coal gasification, but the usage of H₂O is limited recently. Coal transforms to syngas (H₂ + CO) via gasification using CO₂ as a gasification agent,‡−⁵ which is one of the most critical processes in the highly efficient technologies⁶−⁸ to enable the cleaner and more efficient use of the tri-high coals.⁹,¹⁰ CO₂ gasification is usually divided into two steps: coal pyrolysis and char gasification, and char gasification is the rate-determining step in the overall coal gasification process.¹⁰ The char gasification will not only be impacted by the properties of the parent coal, such as coal rank, particle size, ash minerals, but also be highly improved by the char preparation conditions and operational conditions.¹¹−¹⁵ Meanwhile, pyrolysis, as the initial stage of coal gasification, is closely related to the coal composition and structure, which largely affect the char gasification characteristics. It is a complicated process involving the cracking of organic matter in the coal, the volatilization of low-molecular-weight pyrolysis products, the polycondensation of cracking residues, the decomposition and combination of volatile products during emission, and the further decomposition and reopolycondensation of the polycondensation products,¹⁶,¹⁷ which would affect the composition and structure of the char. The char composition and structure are directly related to the char reactivity.¹⁸,¹⁹ Understanding the kinetics of the CO₂ char gasification can help to better organize many industry processes, such as the conventional coal gasification and the integrated gasification combustion cycle. Thus, experimentally the CO₂ gasification mechanisms have been paid recent attention,²⁰−²² and their regular empirical reaction models were addressed, such as, for example, the volumetric model,²³ the hybrid model,²⁴ and the random pore model (RPM).²⁵,²⁶ The RPM seemed to be the most practical one, addressing the growth and coalescence of the char structure during the char gasification. However, because of the effect of the inherent ash in coals on the reactions occurring during CO₂ gasification, such as the formation of volatiles and tars and their subsequent pyrolysis reactions,²¹ and the variations of char porous structures and graph crystallites during the char gasification, it is difficult to explain the gasification reaction rate throughout the char gasification by the classical RPM.²⁷,²⁸

Tri-high coal, characterized by high-ash content, high-sulfur content, and high-ash fusion, is the most representative coal type in southwest China. Thus, the CO₂ gasification of two kinds of tri-high coal chars from Guizhou, China, in isothermal conditions was investigated kinetically by analyzing thermogravimetric data in this paper. A modified RPM, considering the inhibitory effect of ash on the gasification, was adopted to determine the kinetic constants and the corresponding activation energies, and the effect of composite and structure of coal char on the gasification was also considered.

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2. RESULTS AND DISCUSSION

2.1. Structure Characteristics. 2.1.1. Morphology of Samples. The scanning electron microscopy (SEM) images of the selected samples are shown in Figure 1; it clearly revealed sizes, surface roughness and smoothness, irregularities in shape, and structures of visible surface pores of the selected samples. The surface of the raw coals particles was roughness with some lamellar structure features, and the pore structure was rarely. After pyrolysis, the surface of coals’ char particles became smooth, and the lamellar structure shrank and decreased. Figure 1 also shows that the char I surface showed a porosity development obviously, and the char I particles became coarse with some small embossed features, which were identified to be the parts of a small surface bulge on the char surface. However, it had not yet found more pore structure produced of the char II particles, probably because the agglomeration of the ash on the surface of the coal particles led to the smooth surface, which was not conducive to the growth of pore structures.

2.1.2. N₂ Adsorption–Desorption Isotherm Characteristics. Measurements of Brunauer–Emmett–Teller (BET) specific surface area and total pore volume of the selected samples are presented in Table 1. It can be found that the surface area of char I increased after pyrolysis, the raw coal I was 20.37 m²/g, the char I was 31.21 m²/g. This may be because of some of the pore growth and new pore formation, resulting in increase in char surface area during the pyrolysis process, and a similar trend was also observed in pore volumes of raw coal and char. The surface area and pore volume of char II decreased after pyrolysis, it could be because there was no pore growth and new pore formation, but aggregation of ash on the surface of raw coal during the pyrolysis process. These results were consistent with results from SEM images.

N₂ adsorption–desorption isotherms of the selected samples are shown in Figure 2. According to the IUPAC classification, there are six different types of isotherms adsorption–desorption curves.²⁹ The adsorption–desorption curves of raw coal I almost coincided, indicating that only a small number of pores exist. After pyrolysis, the adsorption–desorption curve of char I did not form a closed hysteresis loop, which may be because of the existence of only micropores. The isothermal adsorption–desorption curves of raw coal II and char II were similar to type III, but no closed hysteresis loop was formed. Moreover, when \( P/P_0 \) exceeded 0.4, both of the adsorption–desorption curves showed a large unclosed hysteresis loop, which indicated that micropores and mesopores coexisted in raw coal II and its char.²⁹ Figure 2a also shows that when the \( P/P_0 \) exceeded 0.4, the isothermal adsorption–desorption curves of raw coal II showed a weak hysteresis loop; after pyrolysis, the hysteresis loop of char II became larger, indicating that the porosity of particles increased after pyrolysis. These results are consistent with results from SEM analysis (Figure 1).

For the pore size distribution characteristics of selected samples (Figure 3), the pore structure of raw coal I sample mainly consisted of mesopores within the range of 2–5 nm, and the pore structure of char I mainly consisted of micropores and some mesopores within the range of 2–7 nm. These results indicated that pyrolysis is favorable to the formation of the micropores and the development of mesopores of coal I. However, the pyrolysis process has little effect on pore size distribution of coal II, and the pore structure of raw coal I and its char particles mainly consisted of micropores with pore size of less than 2 nm and small mesopores within the range of 3–5 nm.

2.1.3. X-ray Diffraction Pattern Analysis. Figure 4 shows the X-ray diffraction (XRD) patterns of the raw coal and the prepared char samples. Both the coal samples contain above 20% ash according to the proximate analysis of coal; thus, it can be seen that some minerals exist from the XRD patterns. The presence of a clear (002) band at ~26° and (100) band in

![Figure 1. SEM images of raw coals and their chars prepared at 950 °C under N₂ atmosphere.](Image)

| Table 1. BET Surface Areas and Total Pore Volume of the Selected Samples |
|-----------------------------|-------------|-------------|-------------|-------------|
| sample                     | raw coal I  | char I      | raw coal II | char II     |
| BET surface area (m²/g)     | 20.37       | 31.21       | 6.68        | 5.89        |
| total pore volume (mL/g)    | 0.044       | 0.083       | 0.030       | 0.020       |
the neighborhood of the graphite at $\sim 43^\circ$ indicated that the samples contained some graphite-like structures (crystalline carbon), shown in Figure 5, which suggested that the crystallites in the samples had intermediate structures between graphite and the amorphous state. The presence of the clear asymmetric (002) band around 26° suggested the existence of another band ($\gamma$) on its left-hand side, which was attached to the periphery of carbon crystallites.31,32 The 002 and 100 peaks of both of char I and char II were wider than those of their coal samples, which indicated that the pyrolysis process was favorable to the vertical stacking of the microcrystalline structure and the increasing of size of the carbon network plane. However, after pyrolysis, the $\gamma$ peaks in char I experienced limited change, which indicated that the aliphatic side chains of coal I did not crack at such pyrolysis temperature. Compared with coal II and its char, it can be seen that aliphatic side chains and other unstable macro-molecule groups crack to form low-molecular-weight groups, and volatilize, narrowing down the $\gamma$ peaks in char II. In addition, the aromatic layers were too thin to be detected, which resulted in no 100 peak being found in both coal II and its char.

2.2. Kinetic Analysis. Figure 5 shows the carbon conversions versus gasification time char at different temperatures (950–1200 °C). The results showed that the effects of temperature on the char gasification are pretty straightforward; the elevation of gasification temperature generally resulted in increasing carbon conversion efficiency. The increase of temperature led to the increase of the carbon conversion throughout the char gasification process.

Figure 6 shows the reaction rate versus carbon conversion at different temperatures, obtained via experiments (symbols), modeling by the RPM (dot lines). It showed that the reaction rate portrayed a gradual rise till a maximum located in the carbon conversion at around 0.2 and then went down steadily during the char gasification. In our previous work,10 we studied the derivations and variations of char structures throughout the char gasification process. The results indicated that both the porous structure and carbon crystallites would affect the char CO$_2$ gasification kinetics; the slower gasification rates might be explained by collapsing the pore structure and/or the slow transfer of CO$_2$ to new carbon sites, which required a certain degree of mobility.10,23 Figure 6 also shows that the RPM was not able to capture the salient features of the experimental reaction rate versus
carbon conversion curves throughout the gasification process in the whole range of temperature values. The rate constant $k$ and the structural parameter $\psi$ in the RPM for all experiments are reported in Table 2. As expected, rate constant $k$ increased with increasing temperature. However, the structural parameter $\psi$ for the RPM cannot be accurately estimated; its value sometimes approached zero during the parameter estimation, and the second term in the RPM equation (eq 3) was always 1, collapsing this model to the volumetric model, which was consistent with published studies.\textsuperscript{23,33} It was because the ash content of the selected coal was as high as above 20%, which had a great influence on the char preparation process and gasification process, and led to the variations of char structures.

Figure 5. Profiles of carbon conversion vs gasification time, in response to variation of the temperatures.

Figure 6. Profiles of reaction rate vs carbon conversion obtained at different temperatures. Symbols, experimental data; solid lines, fitting results by the RPM.

Table 2. Gasification Kinetic Parameters Modeling by the RPM

| sample | parameter | temperature, °C | 950 °C | 1000 °C | 1050 °C | 1100 °C | 1150 °C | 1200 °C |
|--------|-----------|----------------|--------|---------|---------|---------|---------|---------|
| char I | $R^2$     |                | 0.41   | 0.68    | 0.91    | 0.94    | 0.95    | 0.94    |
|        | $k$       |                | 0.0069 | 0.016   | 0.047   | 0.098   | 0.15    | 0.21    |
|        | $\psi$    |                | 6.07   | 3.79    | 0.38    | 0.46    | 0.41    | 0.68    |
| char II| $R^2$     |                | 0.66   | 0.48    | 0.82    | 0.59    | 0.81    | 0.62    |
|        | $k$       |                | 0.0036 | 0.0083  | 0.019   | 0.035   | 0.068   | 0.087   |
|        | $\psi$    |                | 0.54   | 0.73    | 0.25    | 1.82    | 1.30    | 1.59    |

Figure 7. Fitting results by the mRPM. Symbols, experimental data; dot lines, fitting results by the mRPM.
Table 3. Gasification Kinetic Parameters Modeling by the mRPM

| sample  | parameter | 950 °C  | 1000 °C  | 1050 °C  | 1100 °C  | 1150 °C  | 1200 °C  |
|---------|-----------|---------|----------|----------|----------|----------|----------|
| char I  | R²        | 0.94    | 0.99     | 0.99     | 0.99     | 0.99     | 0.99     |
|         | k         | 0.0037  | 0.0093   | 0.037    | 0.082    | 0.13     | 0.18     |
|         | ψ         | 62.85   | 37.07    | 7.44     | 4.96     | 4.69     | 4.84     |
|         | n         | 2.61    | 2.36     | 2.42     | 2.24     | 2.23     | 2.15     |
| char II | R²        | 0.91    | 0.81     | 0.94     | 0.92     | 0.95     | 0.95     |
|         | k         | 0.0033  | 0.0058   | 0.014    | 0.033    | 0.040    | 0.071    |
|         | ψ         | 10.40   | 24.90    | 11.68    | 21.34    | 28.90    | 29.58    |
|         | n         | 3.79    | 3.40     | 2.75     | 3.07     | 2.64     | 3.17     |

Table 4. Activation Energy (Eₐ) and Pre-Exponential Factor (k₀) in Gasification Reaction Based on the mRPM

| parameter | char I | char II |
|-----------|--------|--------|
| ln k₀     | 16.27  | 13.76  |
| Eₐ kJ/mol | 258.69 | 235.90 |

Figure 8. Relationship between ln k and 1/T in gasification of the char samples.

shows the curves of the linear regression of gasification values of kinetics parameters, summarized in Table 4. Specifically, Eₐ = 258.69 kJ/mol for gasification kinetics of char I modeling by the mRPM, and Eₐ = 235.90 kJ/mol for char II.

The obtained Eₐ of char I is lower than that of char II, indicating that the gasification reaction of char II requires lesser energy than char I and the activity of the carbon matrix of char II is higher than that of char I, which is consistent with the result of XRD. However, char I displays a higher pre-exponential factor (k₀) than that of char II, revealing that a higher gasification rate is attained in the gasification process. Moreover, the BET and SEM results show that char I has more pore structure than char II. These results indicate that the reaction rate of char gasification is a result of the combination of composite and structure of char, and pore structure plays a major role.

3. CONCLUSIONS

In this paper, the surface areas, pore structures, and carbon crystalline features of two kinds of coal and their char samples prepared at a 750 °C temperature were analyzed. A classical RPM and a modified RPM (mRPM) were also applied. The BET and SEM results showed the pyrolysis process is favorable to the development of the pore structures of char I, but not for char II. The XRD results showed that the aliphatic side chains of coal I did not crack at 950 °C during pyrolysis, but the aliphatic side chains of coal I did.

The mRPM is able to capture all the salient features of the reaction rate versus carbon conversion for both kinds of tri-high coal char samples throughout the char gasification in the whole range of temperatures.

The value of the estimated activation energies by the mRPM of char I was 258.69 kJ/mol, which is higher than that of char II, 235.90 kJ/mol. In combination of the results of BET, SEM, and XRD, gasification reactivity is the result of the interaction of pore structure and the chemical composition of the chars.

4. EXPERIMENTAL SECTION

4.1. Materials. The proximate and ultimate analysis of the two coals used in this paper is summarized in Table 5, and named coal I and coal II, respectively. The volatile contents of the two coals are low, accounting for around 10%; the ash contents of the two coals are high, exceeding 20%, and the carbon contents are also very high, exceeding 85%. In this paper, the coal samples were ground and sieved to 100 μm. Char preparation was carried out at 950 °C under a nitrogen atmosphere in a fixed bed reactor, and the char CO₂ gasification was carried out in a thermogravimetric analyzer at 950–1200 °C. In the char gasification process, 10 ± 0.5 mg of coal char was placed in a crucible boat, and then heated at 20 K/min to the design temperatures under a nitrogen atmosphere. Thereafter, the gas was switched to CO₂ and the gasification process was allowed to proceed. Finally, the
samples were held isothermal for 90 min. The combined gas flow rates of N\(_2\) and CO\(_2\) were 50 mL/min.

4.2. Char Characterizations. 4.2.1. Scanning Electron Microscopy. The SEM experiments were conducted on a FEI Company Nova Nano SEM 450 and the microscope was operated between 5 and 25 kV. To prepare the samples for examination, silver paste was applied to an SEM stub, and the samples were sprinkled onto the paste.

4.2.2. Brunauer—Emmett—Teller. The BET specific surface areas and pore volumes of char samples were obtained using the N\(_2\) adsorption—desorption isotherms at 77 K by an ASAP 2020 apparatus. Prior to the analysis, the char samples were degassed at 200 °C for 3 h. The specific surface area was calculated using the BET method. The total pore volume, \(V_t\), was determined as the volume of nitrogen adsorbed at a relative pressure of 0.99. The micropore volume was obtained by applying the \(t\)-Plot method. The mesopore volume was obtained by subtraction of the volume of nitrogen adsorbed at a relative pressure of 0.10 from the volume of nitrogen adsorbed at a relative pressure of 0.95. The density functional theory method was used to interpret the data related to the pore size distribution.

4.2.3. X-Ray Diffraction. XRD curves of the samples were obtained in the Ultima IV XRD using the Cu KR radiation (\(\lambda = 0.1542 \text{ nm}\)). The spectra were recorded in the 2\(\theta\) range of 10°–90° with a scanning speed of 2° min\(^{-1}\). The XRD data were smoothed and processed by PeakFit4.2 according to Zhang et al.,\(^{33}\) and the crystallite structures of the samples such as the horizontal dimension of the aromatic microcrystal (\(L_h\)), the vertical dimension (\(L_v\)), and the average distance between the polyaromatic layers (\(d_{\text{out}}\)) were calculated by Bragg’s law and Scherrer equation.\(^{35}\)

4.3. Kinetic Modeling. The carbon conversion degree (\(x\)) of char defined as the mass ratio of the gasified char at any time to the initial char mass can be expressed as follows.

\[
x = \frac{w_0 - w_f}{w_0 - w_{\text{ash}}}
\]

(1)

Reaction rate (\(r\)) was calculated from mass ratio versus time profiles using eq 2.

\[
r = \frac{-1}{w_0 - w_{\text{ash}}} \frac{dw}{dt} = \frac{dx}{dt}
\]

(2)

where \(w_0\) is the initial mass of char, \(w_f\) is the instantaneous char mass at reaction time \(t\), and \(w_{\text{ash}}\) is the mass of ash.

The RPM\(^{37,38}\) was used to estimate the CO\(_2\) gasification kinetics, which was valid to summarize together with derivations and development of the pore structure of the char for the evaluation of char gasification kinetics.

The overall reaction rate was

\[
r = \frac{dx}{dt} = k(1 - x)\sqrt{1 - \psi \ln(1 - x)}
\]

(3)

where \(k\) is the reaction rate constant.

Here, \(E_a\) — activation energy, \(k_0\) — pre-exponential factor. \(\psi\) is a parameter related to the pore structure of the initial char structure.

\[
\psi = \frac{4\pi L_0 (1 - \epsilon_0)}{S_0^2}
\]

(5)

where \(S_0\) — initial surface area; \(L_0\) — the total pore length per unit volume; \(\epsilon_0\) — the initial porosity.

However, the inherent high ash in coal in the tri-high coal would have a great influence on the char gasification process, which would lead the variations of char structures, failing to follow the RPM during the char gasification process, especially in the postreaction stage.\(^{37,38}\) It could result in the following: (1) the fitting degree between the experiment and modeling data is poor; and (2) the structural parameter \(\psi\) for the RPM cannot be accurately estimated; its value approached zero (lower boundary) during the parameter estimation, and the second term in the RPM equation was always 1, collapsing this model to the volumetric model.\(^{23,33}\)

During the gasification, the inner and outer surfaces of coal char pores will accumulate ash, which have a non-negligible inhibitory effect on the gasification process, and the effect of the ash on the process is related to the carbon conversion. Thus, in this paper, the RPM was modified by introducing an empirical formula \(G(x)\), which is used to characterize the inhibitory effect of ash, to better fit the experimental data obtained by gasification of the tri-high coal char with high ash by CO\(_2\).

\[
G(x) = e^{\psi(1 - x)^m}
\]

(6)

where \(m\) is a constant to characterize inhibition.

The modified RPM (mRPM) is shown as follows

\[
\frac{dx}{dt} = G(x)k(1 - x)\sqrt{1 - \psi \ln(1 - x)}
\]

(7)

If we defined \(n = m + 1\), we can get.

\[
\frac{dx}{dt} = ke^{\psi(1 - x)^n} \sqrt{1 - \psi \ln(1 - x)}
\]

(8)

### Author Information

**Corresponding Author**

*E-mail: l.liu@git.edu.cn.*

**ORCID**

Lang Liu: 0000-0002-0720-0828

**Notes**

The authors declare no competing financial interest.

\[\text{Table 5. Proximate and Ultimate Analysis of Raw Coals}\]

| sample | fixed carbon (wt %, db) | volatile | ash (wt %, db) | ultimate analysis (wt %, daf) |
|--------|-------------------------|----------|----------------|--------------------------------|
| coal I | 69.13                   | 9.42     | 21.45          | C 89.2                        |
|        |                         |          |                | H 2.25                        |
|        |                         |          |                | N 0.52                        |
|        |                         |          |                | O\(^b\) 5.56                  |
|        |                         |          |                | S 2.47                        |
| coal II| 60.95                   | 13.79    | 25.26          | C 86.95                       |
|        |                         |          |                | H 3.73                        |
|        |                         |          |                | N 1.89                        |
|        |                         |          |                | O\(^b\) 5.12                  |
|        |                         |          |                | S 2.31                        |

\(^{a}\)db, dry basis; and daf, dry and ash-free. \(^{b}\)Oxygen content by difference.
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