CO₂ Gasification Kinetics and Structural Characteristics of Tri-High Coal Char Prepared at Elevated Temperature

Lang Liu, Bowen Kong, Jian Yang, Qingcai Liu, and Xiaoyu Liu

ABSTRACT: The combined effects of surface area, pore structure, degree of graphitization, and number of carbon functional groups on the gasification kinetics of tri-high coal char prepared at an elevated temperature were studied by a thermogravimetric analyzer and various characterization methods (scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) theory, X-ray diffraction (XRD), Raman spectroscopy, and Fourier transfer infrared spectroscopy). In the kinetic analysis, the CO₂ gasification of high-ash coal was not adequately described by the random pore model because ash influenced the char structure during pyrolysis and gasification. Meanwhile, the SEM and BET results indicated the promotion of micropore formation and mesopore expansion of the coal char during pyrolysis. The XRD, Raman, and FTIR results evidenced a significant increase of large aromatic groups during the pyrolysis process, attributable to the cracking of aliphatic groups and the polycondensation of the cracking residues. Overall, the porous structure and aromatic groups of coal char developed during the pyrolysis process improved the CO₂ gasification kinetics of the tri-high coal char.

INTRODUCTION

Tri-high coal is the most representative coal in Southwest China, which has the characteristics of high ash content, high sulfur content, and high ash fusion. Under the growing demand for power and other applications, tri-high coal has attracted an increasing share of attention. However, the utilization of such coals aggravates various environmental problems, such as SO₂ emission and high greenhouse gas emissions.1 Coal gasification, which efficiently converts coal into either clean energy (i.e., heat and electricity) or high value-added products, polycondensation of cracking products, and further decomposition and repolycondensation of the polycondensation products.18,19 All of these processes affect the porous structure, the single-crystal ordering (crystallite formation) of graphite, and the degree of graphitization in the coal char, which are directly related to the char reactivity and to the economics of coal gasification. Nevertheless, owing to the complexity of these chemical and physical decomposition processes, how the structure and composition of coal alter during the pyrolysis and thereby influence the gasification kinetics remains poorly understood, especially in tri-high coal gasification.

Therefore, whether the RPM adequately describes the char gasification kinetics under pyrolysis conditions that promote high-ash content is worthy of discussion.

As the initial stage of coal gasification, coal pyrolysis has a great influence on the composition and structure of the initial char, which has a great influence on the subsequent char gasification characteristics. Pyrolysis is a very complex process, which involves the following aspects: decomposition of organic matter, volatilization of low-molecular-weight cracking products, polycondensation of cracking residues, decomposition and combination of volatile products, and further decomposition and repolycondensation of the polycondensation products.18,19 All of these processes affect the porous structure, the single-crystal ordering (crystallite formation) of graphite, and the degree of graphitization in the coal char, which are directly related to the char reactivity and to the economics of coal gasification.

A tri-high coal from southwest China was selected to investigate whether the RPM adequately describes the gasification kinetics of the tri-high coal char. This paper also presented the evolution of the surface area, pore structure, and
crystalline features of tri-high coal during high-temperature pyrolysis by joint analytical measures, such as scanning electron microscopy (SEM), Brunauer–Emmett–Teller (BET) theory, X-ray diffraction (XRD), Raman spectroscopy,
and Fourier transfer infrared spectroscopy (FTIR), and the influence of these features on the char gasification kinetics.

**RESULTS**

**Experimental Results.** Figure 1 shows the time evolutions of the carbon conversions of the variously sized chars prepared at 950, 1000, and 1050 °C. Pyrolysis temperature exerted a noncomplicated effect on the char gasification process; specifically, raising the pyrolysis temperature generally improved the carbon conversion efficiency for a given particle size. The carbon conversion efficiency was also sensitive to the coal particle size. At a constant pyrolysis temperature, reducing the particle size is helpful to improve the carbon conversion rate in the char gasification process of coal char.

**Kinetic Analysis.** Figure 2 shows the reaction rates as functions of carbon conversion ratio at different temperatures, both obtained in the experiment (symbols) and calculated by the RPM (dotted lines). The reaction rate gradually rose to its maximum in the 0.1—0.2 range of carbon conversion ratios and then steadily declined during the char gasification. The squared correlation coefficients ($R^2$) between the experimental and theoretical results were generally very high (>0.92), indicating that the modeled data well fitted the experimental data.

Table 1 reports the experimentally observed rate constants $k$ and the structural parameters $\psi$ obtained by the RPM in all cases. As expected, the rate constant $k$ increased with increasing temperature and with decreasing particle sizes. As shown in Table 1 and Figure 2, the modeled and experimental data well agreed for smaller coal char particles (48—106 μm) but diverged for the larger particles (154—355 μm). This is attributable to the structural parameter $\psi$ in the RPM, which cannot be accurately estimated for large-sized particles. During the parameter estimation, the value sometimes approached zero (lower boundary), given as the second term in the RPM equation (eq 3). In such cases, the model reduces to the volumetric model, as reported in previous studies. When the ash contents of the selected coal reached 20.8%, the coal particle size exceeded 154 μm, and the ash greatly influenced the char preparation and gasification processes. Consequently, the RPM model failed to capture the variations in the char structures during the char gasification process, especially in the postraction stage.

| sample     | $k$    | $\psi$ | $k$    | $\psi$ | $k$    | $\psi$ | $k$    | $\psi$ |
|------------|--------|--------|--------|--------|--------|--------|--------|--------|
| 950 °C char | 0.008  | −      | 0.009  | −      | 0.010  | −      | 0.012  | −      |
| 1000 °C char| 0.010  | −      | 0.017  | −      | 0.032  | −      | 0.033  | −      |
| 1050 °C char| 0.019  | −      | 0.025  | −      | 0.043  | −      | 0.044  | −      |

$\text{−−}$, Negative (lower boundary).

Figure 3. SEM images of the raw coal and char samples prepared from pyrolysis at 950, 1000, and 1050 °C.
Moreover, the char particles of different sizes prepared at different temperatures exhibited different structural parameters [porous structure, single-crystal ordering of graphite (crystallites), and degree of graphitization]. These parameters are directly related to the char kinetics. The structures of the initial char samples prepared under different pyrolysis temperatures and their influence on the gasification reactivity were then characterized by SEM, BET, XRD, Raman, and FTIR. The samples were raw coal of particle size 48–65 μm, and its chars were prepared at 950, 1000, and 1050 °C under an N2 atmosphere.

**Morphology of Samples.** SEM images of the selected samples are shown in Figure 3. The sizes, smooth and rough surfaces, and irregularities in the shapes and structures of the visible surface pores are clearly revealed. The surface of the raw coal resembled a regular rock with no visible surface pores. After pyrolysis, the char surface was obviously porous. The chars prepared at 1000 and 1050 °C were coarse with some small embossed features, which were identified as parts of a small surface bulge. Increasing the char pyrolysis temperature promoted the emergence of pores and embossed features by intensifying the thermal condensation. The char samples prepared at 1000 and 1050 °C contained more pores of larger size than the sample prepared at 950 °C, possibly because the pores integrated and merged at higher temperatures. These actions increased the surface areas of the chars prepared at higher temperatures, thereby increasing their gasification rates in the gasification process (see Figures 1 and 2).

**Table 2. BET Surface Areas and Total Pore Volume of the Selected Samples**

| Sample        | BET surface area (m²/g) | Total pore volume (mL/g) |
|---------------|-------------------------|-------------------------|
| Raw coal      | 13.5                    | 0.035                   |
| 950 °C char    | 253.5                   | 0.16                    |
| 1000 °C char   | 312.3                   | 0.25                    |
| 1050 °C char   | 320.4                   | 0.27                    |

N2 Adsorption–Desorption Isotherm Characteristics. Table 2 lists the BET specific surface areas and total pore volumes of the selected samples. Obviously, the surface area of the raw char was very small, and the surface areas of the processed chars increased with the char generation temperature. The specific surface areas of the raw coal, char prepared at 950 °C, and char prepared at 1050 °C were 13.5, 253.5 and 320.4 m²/g, respectively. The increased char surface area at high pyrolysis temperatures may be attributable to pore growth and new pore formation. The pore volume of raw coal and coal char showed a similar trend, which were consistent with the SEM images.

The N2 adsorption–desorption isotherms and pore size distributions of the selected samples are shown in Figure 4. The International Union of Pure and Applied Chemistry (IUPAC) classification describes six types of isotherms in adsorption–desorption curves.24 The isothermal adsorption–desorption curve of raw coal (Figure 4a) resembled a type III isotherm, indicating a small number of mesopores. Real adsorption–desorption isotherms are usually combinations of the six types of curves defined by IUPAC. The isothermal adsorption curves of all char samples exhibited the features of type I and type II isotherms. At near-zero relative pressures, the adsorption capacity increased rapidly owing to the micropore structure. Increasing the relative pressure increased the adsorption capacity via multilayer adsorptions in the pore. At high relative pressures, the adsorption amount increased rapidly. The adsorption had apparently not saturated even when the relative pressure approached 1 because capillary condensation occurred. Moreover, the desorption volume was obviously higher than the adsorption volume, and hysteresis loops appeared at P/P0 ratios above 0.4, indicating a continuous and complete pore structure (comprising both micropores and mesopores) in all chars.24 The hysteresis loop was weak in the isothermal adsorption–desorption curve of the char prepared at 950 °C and larger in the curve of the sample prepared at 1000 °C (Figure 4a), indicating increased porosity of the char samples. The isothermal adsorption–desorption curve of the 1050 °C char was slightly higher than, but otherwise similar to, that of the 1000 °C char. As shown in Figure 4b, pyrolysis significantly increased the adsorption of the samples, and the effect increased with increasing pyrolysis temperature. Examining the pore size distribution characteristics of the selected samples, the raw coal sample mainly consisted of small (2–4 nm-diameter) mesopores, whereas the char samples mainly consisted of micropores with pore sizes below 2 nm and small mesopores of diameters 3–5 nm. This observation indicates that pyrolysis promoted the formation of micropores and the development of mesopores, consistent with the BET specific surface areas and total pore volumes.

**Figure 4.** (a) N2 adsorption–desorption isotherms and (b) pore size distributions of the raw coal and char samples prepared by pyrolysis at 950, 1000, and 1050 °C (A: Adsorption isotherms; D: Desorption isotherms).  

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Therefore, the chars acquired their porosity via micropore formations and expanding mesopores during the pyrolysis process, which were facilitated by a high pyrolysis temperature.

**XRD Pattern Analysis.** The XRD patterns of the selected samples are shown in Figure 5. The proximate analysis revealed 22.08% ash content in the raw coal, and mineral signals appeared in the XRD patterns. The samples also contained some graphitelike structures (crystalline carbon), as indicated by the clear asymmetric (002) band in the raw coal sample. The (100) band in the neighborhood of graphite at ~43° suggests the existence of another band (γ) on the left-hand side. The γ band around 20° or 26° has been reported by numerous authors and has been attributed to saturated structures such as aliphatic side chains attached to the periphery of the carbon crystallites.26,27

Figure 6 shows the XRD patterns after smoothing and processing by Peakfit4.2. Overall, the 002 peaks were wider in the char samples than in the raw coal and gradually widened with increasing pyrolysis temperature. This indicates that higher pyrolysis temperatures favored the vertical stacking of the microcrystalline structures. Owing to the very thin aromatic layer, no 100 peak was found in the raw coal sample. The presence of these peaks in the char samples indicates that pyrolysis increased the size of the carbon network plane. At 950 °C, the γ peak hardly changed from that of raw coal, indicating that the aliphatic side chains were not cracked at this temperature. When the temperature rose to 1000 °C, the aliphatic side chains and other unstable macromolecule groups dissociated to form low-molecular-weight groups. Such dissociation and volatilization narrowed the γ peaks at 1000 and 1050 °C.

The crystallite structural parameters $L_m$, $L_d$, and $d_{002}$ were calculated by Bragg’s law and the Scherrer equation26,29 as shown in Table 3. The $d_{002}$ and $L_d$ values depended on the pyrolysis temperature, but $L_m$ did not. This result consolidates that the aliphatic side chains and other macromolecule groups dissociated into low-molecular-weight groups at elevated temperature, some of which volatilized. The cracking residues then acted as lubricants between the aromatic layers, promoting the relative sliding and alignment of the microchip layers. The consequent parallel stacking of the microchip layers decreased the horizontal dimension $L_m$ of the aromatic microcrystal. Meanwhile, the vertical dimension $L_d$ was significantly reduced by polycondensation of the aromatic layers in the longitudinal direction. Polycondensation and aromatization of the cracking residues, dehydrogenation of hydrogenated aromatics, and pyrolysis of heterocycles occurred during the pyrolysis process, increasing the number of aromatic ring structures, disordering the stacking and lamellae, and hence increasing the interlayer spacing between the crystallite layers ($d_{002}$).

**Raman Spectral Analysis.** Typical first-order region Raman spectral profiles, collected between 800 and 2000 cm$^{-1}$ for each char sample, are shown in Figure 7. Two characteristic peaks at ~1330 cm$^{-1}$ (D band) and ~1590 cm$^{-1}$ (G band) in the Raman spectra were experimentally determined.30 The peaks in each Raman spectrum were fitted by the curve-fitting software Peakfit4.2. The peaks resolved into four Lorentzian bands (designated as the G, D1, D2, and D4 bands) and one Gaussian band (the D3 band), as shown in Figure 7. The mathematical fitting procedures were based on the procedures outlined in the studies by Larouche et al.,31 Dippel et al.,32 Jawhari et al.,33 Cuesta et al.,34 and Nistor et al.35 The D1 band at ~1350 cm$^{-1}$ refers to the broadening of the G peak resulting from the disordering of carbon, and the D2 band at 1615–1625 cm$^{-1}$ is the acromion of G peak at 1615–1625 cm$^{-1}$, which refers to the E2g vibration mode of the surface graphite layer.31,36 The D3 band at ~1500 cm$^{-1}$ is the amorphous sp$^3$-bonded form of carbon, D4 at ~1250 cm$^{-1}$ is attributed to the amorphous mixed sp$^2$–sp$^3$ bonded forms of carbon, and the G band refers to the graphitic band.25,36,37

Figure 8 shows the pyrolysis temperature dependences of the area ratios of the D1, D2, and D4 bands on the G band (denoted as $I_{G}/I_{all}$). The $I_{G}/I_{all}$ ratio remained almost unchanged from that of raw coal at 950 °C but decreased significantly at 1000 °C. This sudden decline reflects the cracking of numerous cross-linking bonds in the pyrolyzed sample, such as aliphatic side chains (as shown in the XRD results). The reduced cross-linking density lowered the $I_{G}/I_{all}$ ratio. Moreover, as the cross-linking bonds were almost completely cracked at 1000 °C, the $I_{D}/I_{G}$ values were similar in the chars prepared at 1000 and 1050 °C. The formation of large aromatic structures from the cracking residues by polycondensation increased the $I_{D}/I_{G}$ ratio. Higher temperatures favor the polycondensation reaction, so the $I_{D}/I_{G}$ value increased with temperature. During pyrolysis, the volatilization and polycondensation of low-molecular-weight groups into large aromatic structures decreased the relative contents of the sp$^2$ and sp$^3$ bonding carbon atoms, thereby reducing $I_{D}/I_{G}$. As expected, the $I_{G}/I_{all}$ ratios also reduced with increasing pyrolysis temperature (from raw coal to the char prepared at 1050 °C). This trend is attributable to the increased spacing between the crystallite layers and the formation of more amorphous char structures at higher temperatures. These results confirm the relationship between the G band and the crystalline component in the carbons. The mild decline of $I_{G}/I_{all}$ with increasing pyrolysis
temperature is consistent with the previous literature. The Raman spectral results were also consistent with the XRD pattern results.

**FTIR Spectral Analysis.** To better understand the structures of the raw coal and char samples, the changes in the carbon functional groups between the raw coal and chars prepared at different pyrolysis temperatures were investigated by FTIR spectroscopy. The FTIR spectra of the selected samples are presented in Figure 9. The spectra were characterized by six principal bands at 3700–3200, 2960–2850, 1620, 1380, 1250–1000, and 900–700 cm⁻¹. The bands between 3750 and 3200 cm⁻¹ were assigned to −OH stretching in organic compounds with oxygen functional groups typically found in coal, including phenols, alcohols, and carboxylic acid. Meanwhile, the bands at 2960–2850,
1620, and 1380 cm\(^{-1}\) were attributed to aliphatic C–H stretching, aromatic C\(=\)C stretching, and aliphatic –CH\(_3\) bending, respectively. The bands between 1250 and 1000 cm\(^{-1}\) were assigned to Si–O–Al bending vibrations, and the bands between 900 and 700 cm\(^{-1}\) were caused by aromatic out-of-plane C–H bending.\(^{26,36,38,39}\)

Figure 10 shows the fitted FTIR spectra of the raw coal and char samples in selected wavenumber regions (4000–2600 and 1800–650 cm\(^{-1}\)). The area ratios of \(C_\text{al}\) and \(C_\text{ar}\) in each range are given in Table 4. As the pyrolysis temperature increased, the area ratios of \(C_\text{al}\) and \(C_\text{ar}\) decreased and increased, respectively. This trend can be explained by the cracking of aliphatic groups into low-molecular-weight groups followed by their partial volatization, which reduced the area ratio of \(C_\text{al}\) as the temperature increased.

3450 and 3250 cm\(^{-1}\) were attributed to –OH stretching. In the spectrum of raw coal, aliphatic C–H was responsible for the broad band at 2960 cm\(^{-1}\) and the two narrow bands at 2920 and 2850 cm\(^{-1}\); as expected, these peaks narrowed with temperature. Several absorption bands attributed to aromatic and aliphatic groups were located between 1800 and 650 cm\(^{-1}\). An aromatic C\(=\)C stretching band at 1620 cm\(^{-1}\), two aromatic C–H vibration bands at ~890 and ~780 cm\(^{-1}\), and an aliphatic –CH\(_3\) bending band at 1380 cm\(^{-1}\) were also found. The area ratios of \(C_\text{al}\) and \(C_\text{ar}\) in each range are given in Table 4. As the pyrolysis temperature increased, the area ratios of \(C_\text{al}\) and \(C_\text{ar}\) decreased and increased, respectively. Again, this trend can be explained by the cracking of aliphatic groups into low-molecular-weight groups followed by their partial volatization, which reduced the area ratio of \(C_\text{al}\) as the temperature increased.
pyrolysis temperature increased. Meanwhile, polycondensation of the cracking residues into large aromatic structures increased the aromatic group contents ($C_{ar}$). As a high pyrolysis temperature is beneficial to polycondensation, $C_{ar}$ was an increasing function of temperature. These results were consistent with the XRD and Raman analysis results.

**DISCUSSION**

As evidenced in the kinetics and the structural characterization of raw coal and its char products, the char kinetics were influenced by the developed surface areas, pore structures, and crystalline carbon features. Owing to the development and generation of micropores and mesopores during the pyrolysis process, the particle structures were more porous in the char samples than in raw coal. Meanwhile, the cracking of aliphatic groups into low-molecular-weight groups and the polycondensation of cracking residues into large aromatic structures largely affected the crystallite structures and functional groups of coal char during the pyrolysis process. The reactivity of coal

**Figure 10.** Infrared spectra of the raw coal and char samples with their corresponding curve-fitted bands in the ranges 4000–2600 (a) and 1800–650 cm$^{-1}$ (b). Ar and Al denote aromatic and aliphatic components, respectively.
char was affected by the combined action of these structural transformations.

The gasification of tri-high coal char under CO2 at elevated temperatures was monitored by a thermogravimetric analyzer (TGA). The TGA results showed a gradual rise in the gasification rate, followed by a steady decrease as the gasification proceeded. The kinetics of the char-CO2 gasification reactions were then studied by the RPM. The RPM could not fully describe the CO2 gasification of high-ash coal because the high-ash content greatly influenced the char structure during pyrolysis and gasification.

The surface areas, pore structures, and carbon crystalline features of the raw coal and char samples prepared at different temperatures were also analyzed. The surface areas and pore structures of the chars were well developed during the pyrolysis process. Meanwhile, the residual low-molecular-weight groups produced by the cracking of aliphatic side chains acted as lubricants, promoting the parallel stacking of microchip layers. The polycondensation of aromatic layers in the longitudinal direction significantly increased the stacking height and the interlayer spacing. The changing aromaticity and crystalline structure during pyrolysis and gasification were well developed during the pyrolysis process.

In summary, the pyrolysis process enhanced the surface areas and pore structures of the chars and promoted the formation of large aromatic groups, thereby improving the reactivity of the tri-high coal chars.

### EXPERIMENTAL SECTION

#### Materials

Table 5 summarizes the proximate analysis of the Chinese tri-high coal investigated in the present study. The raw coal samples were ground and sieved into particles of different sizes: 48–65, 75–106, 154–200, and 280–355 μm. The char was prepared at 950, 1000, or 1050 °C under a nitrogen atmosphere in a fixed bed reactor. During the char preparation process, a 20 g sample of coal char was placed in a corundum crucible and then heated at 20 °C/min to the designed temperature under a nitrogen atmosphere. Finally, the sample was held at that temperature for 30 min.

Meanwhile, the char samples prepared at different temperatures were named 950 °C char, 1000 °C char, and 1050 °C char.

The char CO2 gasification was carried out in an STA449F3 TGA; 10 mg of the sample of coal char was placed in a crucible boat and then heated at 20 °C/min to the designed temperature (1000 °C) under a nitrogen atmosphere (50 mL/min). The gasification was started by switching the gas flow to CO2 (50 mL/min). Finally, the sample was held at the designated temperature for 120 min. The temperatures of the char preparation and gasification processes are given in Table 6.

#### Table 4. Area Ratios of Aliphatic Carbon (C_al) and Aromatic Carbon (C_ar) in Each Region (a, 4000–2600 cm⁻¹; b, 1800–650 cm⁻¹)

| groups                        | raw coal | 950 °C char | 1000 °C char | 1050 °C char |
|-------------------------------|----------|-------------|--------------|-------------|
| aliphatic C–H (2960–2850 cm⁻¹) | 11.34    | 6.96        | 6.90         | 3.03        |
| aliphatic —CH₃ (1390 cm⁻¹)    | 12.54    | 10.54       | 9.78         | 5.64        |
| aromatic carbon C–H, C–O      | 11.31    | 18.62       | 18.73        | 22.01       |

#### Table 5. Proximate and Ultimate Analyses of Tri-High Coal

| coal        | fixed carbon (%) | volatiles (%) | ash (%) | ultimate analysis (wt %, daf) |
|-------------|------------------|---------------|---------|-------------------------------|
|             |                  |               |         | C                  | H   | N    | O    | S   |
| raw coal    | 70.02            | 7.08          | 22.90   | 90.48              | 4.05| 0.33 | 1.02 | 4.12|

a db, dry basis; daf, dry and ash-free. b oxygen content by difference.
\[
r = \frac{dx}{df} = k(1 - x)\sqrt{1 - \psi \ln(1 - x)}
\]

where \(\psi\) is the structural parameter of the initial char structure and \(k\) is the rate constant of the gasification reaction.

**Char Characterization by SEM and BET.** A Nova Nano SEM 450 microscope (FEI Company, United States) and an ASAP 2020 BET apparatus was employed to analyze the surface areas and pore structures of the samples.

**Char Characterization by XRD.** An Ultima IV diffractometer irradiated with Cu KR radiation (\(\lambda = 0.1542\) nm) was used to detect the crystallite structures of the samples.

The specific methods of the SEM, BET, and XRD analyses can be obtained in our previous work.\(^{30}\)

**Char Characterization by Raman Spectroscopy.** All selected samples (10–20 randomly chosen particles) were analyzed in a D8R Raman spectrometer (Thermo Scientific) equipped with a Nd-YAG laser (532 nm) and a confocal microscope with three objective lenses. The laser power on the sample surface was controlled to approximately 6 mW. The spot diameter of the laser beam reaching the sample was 1.2 \(\mu m\). The spectra were recorded in the 800–2000 cm\(^{-1}\) wavenumber range, covering the first-order bands of the samples. All spectra were processed by a linear baseline correction, and the bands were fitted in the 800–2000 cm\(^{-1}\) region by PeakFit4.2 software. Finally, the positions, intensities, widths, and areas of the bands were determined.

**Char Characterization by FTIR.** The FTIR spectra were recorded from 4000 to 650 cm\(^{-1}\) (40 averaged scans with a resolution of 2 cm\(^{-1}\)) on a vertex 80 FTIR spectrometer (Bruker, province, country) with a UATR attachment using KBr pellets. The pellets were made from a mixture of demineralized char sample and KBr in the ratio of 1:150. All KBr pellets. The pellets were made from a mixture of KBr with a UATR attachment using a Random Pore Model for the Kinetics of Char Gasification. BioResources 2014, 34, 3975–3977.

**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.

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