

文章编号: 0253-2409(2015)07-0769-10

## Effects of oxygen on the structure and reactivity of char during steam gasification of Shengli brown coal

SUN Jia-liang, CHEN Xu-jun, WANG Fang, LIN Xiong-chao, WANG Yong-gang

(School of Chemical and Environmental Engineering,  
China University of Mining & Technology (Beijing), Beijing 100083, China)

**Abstract:** The effects of oxygen on changes in char structure and reactivity during steam gasification of Shengli brown coal were examined. A stainless steel simulated entrained-flow reactor was employed to carry out gasification at 800 and 900 °C in 8 atmospheres: pure N<sub>2</sub>, 15% H<sub>2</sub>O, 25% H<sub>2</sub>O and 35% H<sub>2</sub>O balanced with N<sub>2</sub>; and 1% O<sub>2</sub>, 15% H<sub>2</sub>O+1% O<sub>2</sub>, 25% H<sub>2</sub>O+1% O<sub>2</sub> and 35% H<sub>2</sub>O+1% O<sub>2</sub> balanced with N<sub>2</sub>. The structure of chars was measured by Raman spectrum, and the intrinsic reactivity of chars with air was measured using a thermogravimetric analyzer (TGA) at low temperature (300 °C). The results show that the effects of oxygen on char structure are different at high temperature (900 °C) and low temperature (800 °C) in brown coal steam gasification. The volatilization of alkali and alkaline earth metallic (AAEM) is strongly influenced by char structure. The presence of O<sub>2</sub> during steam gasification has a similar effect on the volatilization of Na to the evolution of structure at different temperatures. Experimental data provided evidence that a mixed H<sub>2</sub>O/O<sub>2</sub> atmosphere could promote a decrease in subsequent char reactivity in air at 300 °C, and that char reactivity could correlate well with the band area ratio,  $I_{(G_R+V_L+V_R)}/I_D$ .

**Keywords:** brown coal; gasification; char structure; char reactivity; simulated entrained-flow reactor

**CLC number:** TQ546.2 **Document code:** A

Based on its economic and environmental properties, low-rank coal has the potential to be highly competitive in today's energy markets<sup>[1~5]</sup>. Compared with high-rank coal, low-rank coal in particular brown coal has high volatility and reactivity, and is a very good gasification feedstock. Low-rank coal has three distinguishing features, including abundant oxygen-containing functional groups, a proportionally larger transition pore and macropore structure, and more inorganic catalytic constituents<sup>[2~6]</sup> that allow it to be gasified at lower temperature (around 900 °C). Typically, a fluidized bed reactor is used to gasify low-rank coal; however, the process is always affected by the interaction between volatiles (such as CO, H<sub>2</sub>) and char, which can result in changes in char structure<sup>[7~9]</sup>, the volatilization of AAEM (especially Na)<sup>[4,8~13]</sup> and dispersion of the catalysts<sup>[12]</sup>. Further, the interaction is able to influence the gasification reaction characteristics<sup>[7~13]</sup>.

Many current gasification techniques are compromised to different degrees by the effects of volatile-char interaction that adversely impact the gasification rate of char, making it imperative to develop methods for minimizing the undesirable effects of this interaction. In this work, a novel brown coal gasification reactor was developed,

through which the reaction of char and the reforming of volatiles were decoupled (the novel process flow diagram for brown coal gasification was shown in Figure 1). The raw coal and gasifying agents (i. e. H<sub>2</sub>O and O<sub>2</sub>) flowed concurrently into the top of the reactor simultaneously with the gasification reaction. The char and volatiles were separated from the bottom of the reactor and then completely gasified and reformed with the secondary gasifying agents (O<sub>2</sub> and H<sub>2</sub>O, respectively). The novel gasification reactor enabled the gasification of char in the absence of volatiles at very low temperatures. During gasification, the gasifying agents, H<sub>2</sub>O and H<sub>2</sub>O+O<sub>2</sub>, demonstrated distinct effects on the structure and reactivity of char. In order to achieve high gasification efficiency and carbon conversion rate, the effects of oxygen on the structure and reactivity of char during steam gasification must be clearly understood.

The reactivity of char is determined by many factors, including distribution and volatilization of AAEM, changes in char structure, formation and decomposition of soot on the surface of char, and "thermal annealing". Significant research concerning changes in the structure and reactivity of char using a fluidized-bed/fixed-bed reactor in different gas atmospheres have been performed<sup>[3,13~15]</sup>. However,

**Received date:** 2015-02-03; **Received in revised form:** 2015-05-30.

**Foundation item:** The 12 th Five-Year Plan of National Science and Technology Support (2012BAA04B02).

**Corresponding author:** WANG Yong-gang (1960- ), Tel: +86 1062339882, Fax: +86 1062331897, E-mail: wyg1960@126.com.

本文的英文电子版由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18725813>).

the impact of oxygen on the steam gasification characteristics of Shengli brown coal in an entrained-flow reactor has not been systematically investigated. The changes in char structure, the relationship between AAEM and char structure, and the correlation between reactivity and char structure all need further investigation to provide theoretical guidance for the development of new technology. Accordingly, multiple gasification experiments on Shengli brown coal were carried out using a simulated entrained-flow reactor at 800 and 900 °C in different gasifying atmospheres. The evolution of char structure was investigated using the Raman technique, revealing the occurrence state of AAEM. Finally, the correlation between reactivity and char structure was explored.

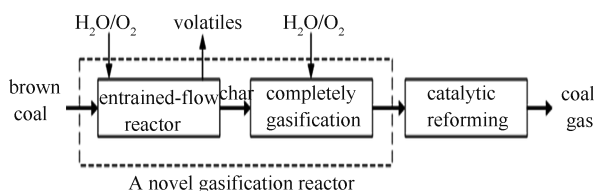


Figure 1 Novel process flow diagram for brown coal gasification

## 1 Experimental

### 1.1 Samples

The Shengli (SL) brown coal used as raw material was collected from Shengli deposits located in Inner Mongolia, China. The as-received brown coal samples were crushed, ground, and then dried at 60 °C for 24 h in a vacuum oven. The coal sample was then sieved to a particle size between 0.15 and 0.18 mm. The properties of the sample were C, 62.26%; H, 6.12%; N, 1.11%; S, 0.66%; O, 29.85%; V, 34.10% (ad); M, 5.89% (ad); and FC, 50.72% (ad), together with an ash yield of 9.29% (ad).

### 1.2 Gasification

Figure 2 shows the schematic diagram of the pilot entrained-flow reactor (EFR). The reactor included a heat-resisting stainless steel tube (3 000 mm long with 80 mm internal diameter), which was heated externally with electric furnace. The electric furnace contained three zones and was controlled by three thermocouples with temperature controllers, respectively. The deviation of temperature inside the reactor was controlled to less than  $\pm 5$  °C. An isothermal zone ( $\sim 2$  400 mm long) was measured by three thermocouples laid in the reactor. The coal samples were continuously fed into the EFR from a screw feeder, with a feed rate of 0.6 g/min under nitrogen flow as the primary carrier gas. The

nitrogen-oxygen mixed gas and the steam used a peristaltic pump supplied to the EFR. The steam flow was determined by measuring the water flow rate. Total gas flow was 36.2 L/min.

Gasification was performed in the EFR at 800 and 900 °C. The secondary gas (pure N<sub>2</sub>, 15% H<sub>2</sub>O, 25% H<sub>2</sub>O, 35% H<sub>2</sub>O balanced with nitrogen, and 1% O<sub>2</sub>, 1% O<sub>2</sub>+15% H<sub>2</sub>O, 1% O<sub>2</sub>+25% H<sub>2</sub>O, 1% O<sub>2</sub>+35% H<sub>2</sub>O balanced with nitrogen) was fed into the top of EFR. Deionized water was continuously injected into the reactor with a peristaltic pump in order to generate the steam. The gasification products were gathered in a collection train consisting of a filter, a cold trap kept at -78 °C, and a flue gas analyzer. Char was separated from gaseous products in the filter. Portions of tar and H<sub>2</sub>S gas were deposited in the CuSO<sub>4</sub> solution. The residual tar was condensed and dissolved in tri-chloromethane in a cold trap. After drying, the coal gas was measured by a flue gas analyzer.

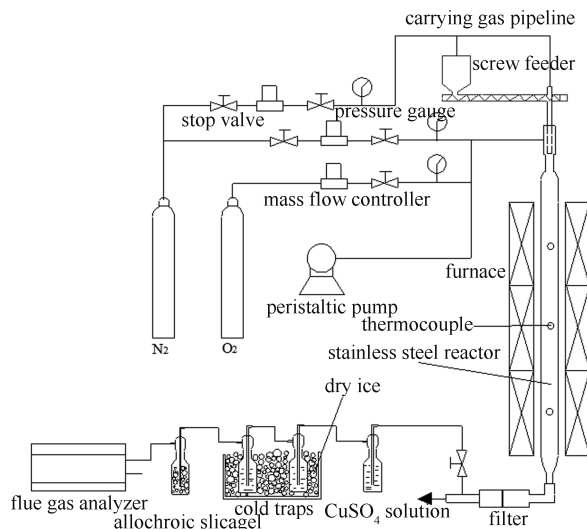


Figure 2 A Schematic diagram of the entrained-flow reactor used in this study

### 1.3 Raman spectrum

The char structure was analyzed by high-resolution Micro Raman spectrometer (MRS), with a given objective magnified 50 times focused at excited laser beams (532 nm visible laser lines). Spectral resolution was 0 ~ 0.65 cm<sup>-1</sup>. Changes in structure of 3 ~ 5 char particles were measured randomly each time. The recorded spectral range was 800 ~ 1 800 cm<sup>-1</sup>; each write time was 60 s. First, the Raman spectrum was handled using GRAMS/32 AI 6.0 software for baseline correction. Each Raman spectrum (800 ~ 1 800 cm<sup>-1</sup>) was deconvoluted into 10 Gaussian bands<sup>[16-20]</sup>, viz. G<sub>L</sub>, G, G<sub>R</sub>, V<sub>L</sub>, V<sub>R</sub>, D, S<sub>L</sub>, S, S<sub>R</sub>, R, the central positions of which were

1 700, 1 590, 1 540  $\text{cm}^{-1}$ , 1 465, 1 380, 1 300  $\text{cm}^{-1}$ , 1 230, 1 185, 1 060 and 960  $\sim$  800  $\text{cm}^{-1}$ , respectively. Briefly, the *G* band located at 1 590  $\text{cm}^{-1}$  was formed mainly by aromatic ring systems (brown coal or char). The *D* band (1 300  $\text{cm}^{-1}$ ) represented defect structure in the highly ordered carbonaceous materials, particularly aromatic compounds with not less than six fused rings. The  $G_R$  (1 540  $\text{cm}^{-1}$ ),  $V_L$  (1 465  $\text{cm}^{-1}$ ) and  $V_R$  (1 380  $\text{cm}^{-1}$ ) bands represented typical structures in amorphous carbon (especially smaller aromatic nucleus) and the semi-circular breathing of aromatic rings. The *S* band represented mainly cross-linked structures in coal char. The areas ratios of band were used for quantitatively characterizing the changes of char structure.

#### 1.4 Determination of inorganic constituents in the char

The content of alkali and alkaline earth metallic species in coal and char were measured using a Thermo Scientific iCAP 6 000 series (ICP). The coal/char sample was first ashed in a muffle furnace at 1  $^{\circ}\text{C}/\text{min}$  to the final temperature of 600  $^{\circ}\text{C}$  and maintained for 4 h. The ash was then digested in HF and  $\text{HNO}_3$  acids (1:1 ratio) at 110  $^{\circ}\text{C}$  for 24 h. The acidic mixture was subsequently evaporated at 80  $^{\circ}\text{C}$ . Finally, deionized water was used to dissolve the digested ash when there was no acid. The deionized water with AAEM species was injected into the ICP.

#### 1.5 Reactivity investigation

A Perkin-Elmer Pyris 1 thermogravimetric analyzer (TGA) was used to measure the reactivity of the char following the procedures established earlier<sup>[3,21]</sup>. Generally, about 7  $\sim$  10 mg of char was placed in a platinum crucible in the TGA. First, the temperature in nitrogen was set at 110  $^{\circ}\text{C}$  and held

20 min to fully dry the coal/char sample. The temperature was then increased to 300  $^{\circ}\text{C}$  in nitrogen. The reactivity measurement began as the gas atmosphere was switched from nitrogen to air. The specific reactivity (*R*) of char at any given time was calculated by:

$$R = -\frac{1}{W} \frac{dW}{dt} \quad (1)$$

where *W* is the char weight (daf) at any given time (*t*).

The char was heated to 600  $^{\circ}\text{C}$  and held for 30 min to burn out any remaining carbon composition after the weight loss was leveled off, and the resulting mass was taken as the weight of the ash<sup>[22]</sup>.

The char reactivity was also characterized by the following equation (2):

$$R_{0.5} = 0.5/\tau_{0.5} \quad (2)$$

where  $\tau_{0.5}$  is the time at which the conversion of char reached 50%. The reactivity of char increased with the increase of  $R_{0.5}$ . Similarly, specific reactivity measurements  $R_{0.02}$ ,  $R_{0.2}$ , and  $R_{0.8}$  were also used.

## 2 Results and discussion

### 2.1 Char yields

Figure 3 compares the char yields from gasification of SL brown coal in  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O}+\text{O}_2$  at 800 and 900  $^{\circ}\text{C}$ . It is obvious that the char yields from gasification in 15%  $\text{H}_2\text{O}$ , 25%  $\text{H}_2\text{O}$ , and 35%  $\text{H}_2\text{O}$  were higher than that in  $\text{H}_2\text{O}+1\% \text{O}_2$  mixture, and the difference was even greater at 900  $^{\circ}\text{C}$ . The char yields at 900  $^{\circ}\text{C}$  were lower than those at 800  $^{\circ}\text{C}$  in  $\text{H}_2\text{O}$  and  $\text{H}_2\text{O} + \text{O}_2$  atmospheres, respectively. This indicates that higher temperature promoted the gasification of brown coal in all gasifying atmospheres, and that oxygen enhanced the conversion of brown coal during steam gasification, due perhaps to the greater gasification rate of the char-O reaction.

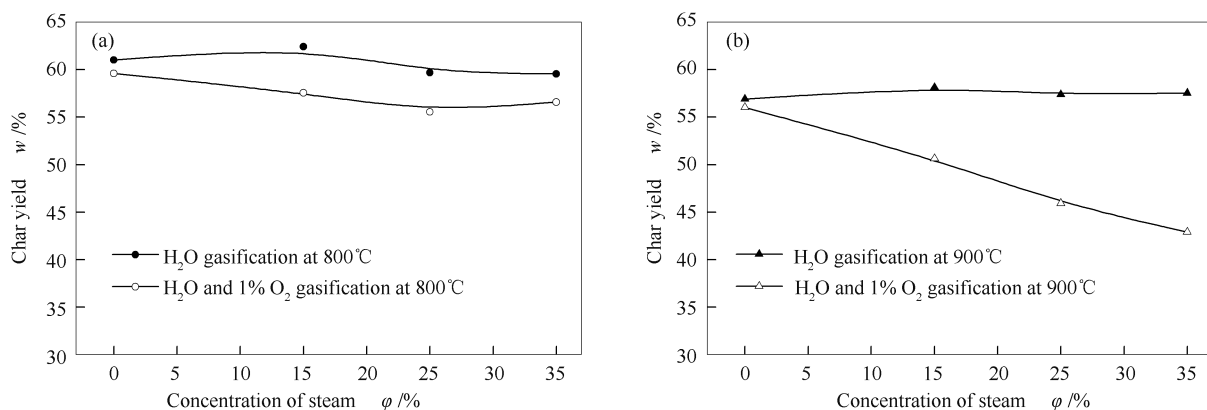


Figure 3 Char yields as a function of gasifying agent at 800 and 900  $^{\circ}\text{C}$   
(a) : 800  $^{\circ}\text{C}$ ; (b) : 900  $^{\circ}\text{C}$

## 2.2 Features of char structure

Figure 4 represents the changes in char structure reflected by Raman spectrum. From the description of Raman spectrum in section 1.3, the area ratios of these bands,  $I_{(G_R+V_L+V_R)}/I_D$ , could represent the relative ratio between the small and large fused rings in char<sup>[7]</sup>, shown in Figure 5 (a). Differences of  $I_{(G_R+V_L+V_R)}/I_D$  between the chars from gasification in  $H_2O$  and in  $H_2O+1\% O_2$  were very small at 800 °C, and gradually decreased with an increase of steam concentration, indicating that a few small fused rings were consumed or converted into larger fused rings in char. Steam was the primary factor responsible for changes in char structure, with oxygen playing a lesser role because H radicals cause the condensation of aromatic systems generated in the reaction of char with steam<sup>[7,12,23]</sup>, while oxygen was consumed on

the surface of chars. So steam reduced the ratio of  $I_{(G_R+V_L+V_R)}/I_D$ , and the addition of 1%  $O_2$  played less role in char structure. At 900 °C, there was a significant difference in  $I_{(G_R+V_L+V_R)}/I_D$  of char prepared from gasification in  $H_2O$  and  $H_2O+1\% O_2$ . The area ratios of these  $I_{(G_R+V_L+V_R)}/I_D$  bands of chars in  $H_2O+1\% O_2$  were lower than those in  $H_2O$ , indicating that more small fused-ring structures reacted with oxygen. The ratios of  $I_{(G_R+V_L+V_R)}/I_D$  of chars from gasification at 900 °C were lower than those of  $H_2O$  and  $H_2O+1\% O_2$  gasifying atmospheres at 800 °C, indicating that relative ratios between small and big fused rings were lower at high temperature. The reasons were that high temperature could promote the gasification. The reaction rate of small fused rings increased with an increase of temperature, leading to highly ordered char structure.

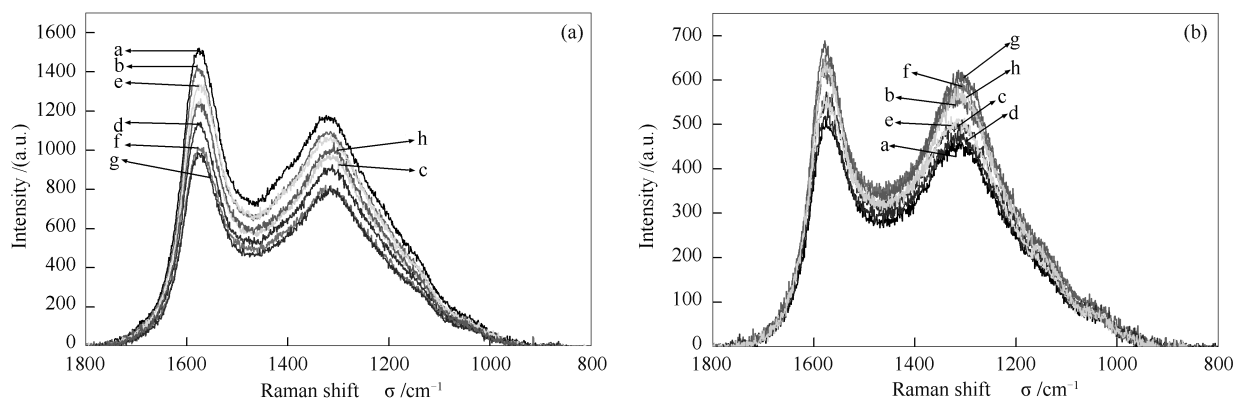


Figure 4 Raman spectra as a function of various gasification conditions for the chars prepared from the gasification of SL brown coal in  $H_2O$  and  $H_2O+1\% O_2$  at 800 and 900 °C  
(a): 800 °C; (b): 900 °C

a: 100%  $N_2$ ; b: 15%  $H_2O$ ; c: 25%  $H_2O$ ; d: 35%  $H_2O$ ; e: 1%  $O_2$ ; f: 15%  $H_2O+1\% O_2$ ; g: 25%  $H_2O+1\% O_2$ ; h: 35%  $H_2O+1\% O_2$

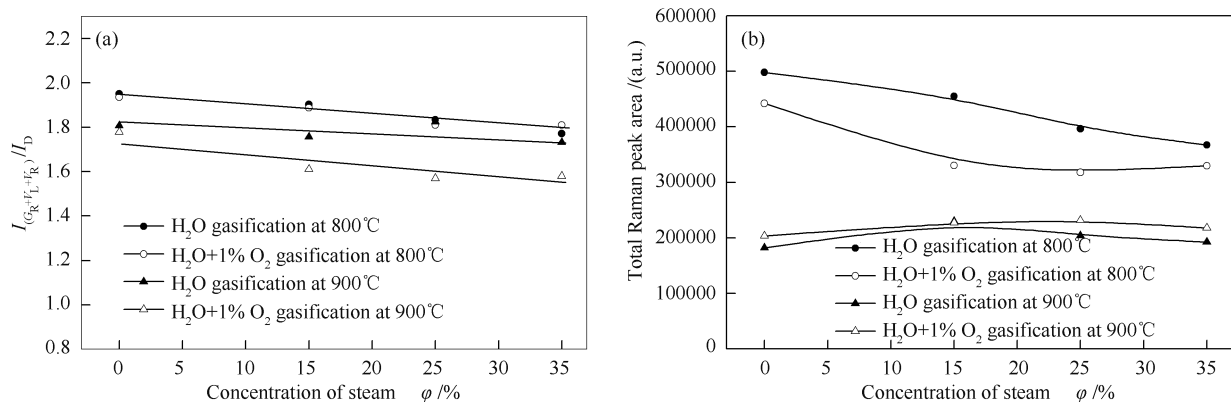


Figure 5  $I_{(G_R+V_L+V_R)}/I_D$ (a),  $I_T$ (b) as a function of various gasification conditions for the chars prepared from the gasification of SL brown coal in  $H_2O$  and  $H_2O+1\% O_2$  at 800 and 900 °C

The  $I_T$  denotes the total area of Raman spectrum between 800 and 1800  $cm^{-1}$  of chars during gasification. The aromatic ring system and oxygen-

containing groups are the determining factors for Raman intensity<sup>[16]</sup>. The oxygen-containing groups with resonance effects are the main factors influencing

Raman intensity in brown coal gasification at relatively low temperatures. Figure 5 (b) shows the total  $I_T$  Raman peak areas of chars prepared from gasification in  $H_2O$  and  $H_2O + 1\% O_2$  at 800 and 900 °C. The Raman intensity of chars during gasification in  $H_2O$  decreased with increasing concentrations of steam at 800 °C. Furthermore, the Raman intensity decreased much more sharply in the  $H_2O + 1\% O_2$  atmosphere. These decreases are due mainly to the deoxidation reaction between char and  $H_2$  produced from steam gasification, which in turn decreases oxygen-containing groups in chars<sup>[17,24,25]</sup>. The decrease in Raman intensity of chars during gasification in a mixture of steam and oxygen indicates that oxygen reduced the oxygen-containing groups in chars. The  $I_T$  of chars prepared from gasification in  $H_2O$  (15%, 25%, 35%  $H_2O$  balanced with  $N_2$ ) were higher than those prepared from pyrolysis (gasification in  $N_2$ ), then decreased with increasing steam at 900 °C due to the oxidation reactions resulting in an increase of oxygen-containing groups when steam was present. The deoxidation reaction with char and  $H_2$  could decrease the oxygen-containing groups with an increasing concentration of steam, resulting in the reduction of  $I_T$ . In other words, the oxidation and deoxidation of char simultaneously occurred in steam gasification at high temperature (900 °C). The  $I_T$  of chars during gasification in  $H_2O$  and 1%  $O_2$  was greater than that in  $H_2O$  at 900 °C, being different from those at 800 °C. This is due to an increase of oxygen-containing structures created by oxidation reaction. These results indicate that the effects of oxygen on char structure were different at high temperature (900 °C) and at low temperature (800 °C) in brown coal steam gasification. The  $I_T$  of chars from gasification in both atmospheres at 900 °C were less than those at 800 °C, verifying that high temperature promoted the breakage of O-containing structures, and that temperature was the primary factor influencing the changes in char structure.

### 2.3 Retention of AAEM species

Figure 6 shows the volatilization of AAEM species (i. e. Na, Mg and Ca) during gasification of SL brown coal in various gasifying atmospheres at 800 and 900 °C in a simulated entrained-flow reactor. During steam gasification, the volatiles were first produced, and then free radicals and light molecules were generated by thermal cracking of nascent volatiles. The reaction of steam with char or volatiles could produce free radicals. The free radicals replacing AAEM species held in the char might

explain the volatilization of AAEM species<sup>[11]</sup>. When the brown coal was gasified in  $H_2O$  atmosphere alone, the concentration of Na in char at 900 °C was lower than that at 800 °C, indicating that the volatilization of Na was a strong function of temperature. Increasing temperature would increase the generation of H radicals either on the surface of chars or in the gas phase<sup>[12]</sup>. The H radicals would in turn displace Na from the bond of Na-char in the char structure.

At lower temperature (i. e. 800 °C), the retention of Na for chars prepared from gasification in  $H_2O$  and 1%  $O_2$  mixture atmosphere was less than that in  $H_2O$  alone. By contrast, at higher temperature (i. e. 900 °C), the retention of Na for chars prepared in a  $H_2O$  and 1%  $O_2$  mixture atmosphere was greater than that in  $H_2O$  alone. This interesting phenomenon might be attributed to a different reaction pattern of char- $O_2$  during steam gasification at 800 and 900 °C. In  $H_2O$  atmosphere, the addition of  $O_2$  would promote the generation of H radicals that volatilize Na<sup>[14,26]</sup>, as well as consumption of some oxygen-containing groups on the char surface. These factors are believed to contribute to reduction in Na-holding capacity of the chars. On the other hand,  $O_2$  could directly influence the bonding between Na and the char matrix. The Na-O intermediate formed by  $O_2$  would constitute stronger bonding of Na with the char matrix and enhance the Na holding capacity of the chars. These changes for volatilization of Na were similar to the evolution of O-containing structures in chars (Figure 5(b)). The Raman spectroscopic data in Figure 5(b) shows that the concentrations of O-containing structures in chars from gasification in  $H_2O + 1\% O_2$  atmosphere were higher than that in  $H_2O$  atmosphere at 900 °C. On the contrary, the concentrations of O-containing structures in chars from gasification in  $H_2O + 1\% O_2$  atmosphere were lower than that in  $H_2O$  atmosphere at 800 °C. These O-containing structures could act as sites for binding Na to prevent its volatilization. Figure 6 (a, a') indicates that the role of  $O_2$  in retaining Na during steam gasification at 800 °C was different from that at 900 °C. During gasification in a mixture of  $H_2O$  and 1%  $O_2$ , the factors enhancing the volatilization of Na were dominant at 800 °C; by contrast, more Na was retained at 900 °C. The evolution of Na is strongly dependent on changes in char structure.

Figures 6 (b, b') and 6 (c, c') show the respective changes in concentration and retention of Mg and Ca under various reaction conditions. The changes in concentration and retention of Mg in chars were minimal during gasification, which were

attributed to its divalency<sup>[27]</sup>. The energy needed to destroy two bonds in order to release Mg is greater than that required to release monovalent Na. In agreement with various studies<sup>[3,14,15]</sup>, Na is volatilized primarily due to the interaction of free radicals with char, whereas Ca is slightly different.

The  $\text{CaCO}_3$  in chars are higher mobile than CaO. So the agglomerates of  $\text{CaCO}_3$  are formed due to the high mobility. Finally, the Ca would be directly released from the char in form of crystallites formed by the  $\text{CaCO}_3$  aggregations at relative low temperature.

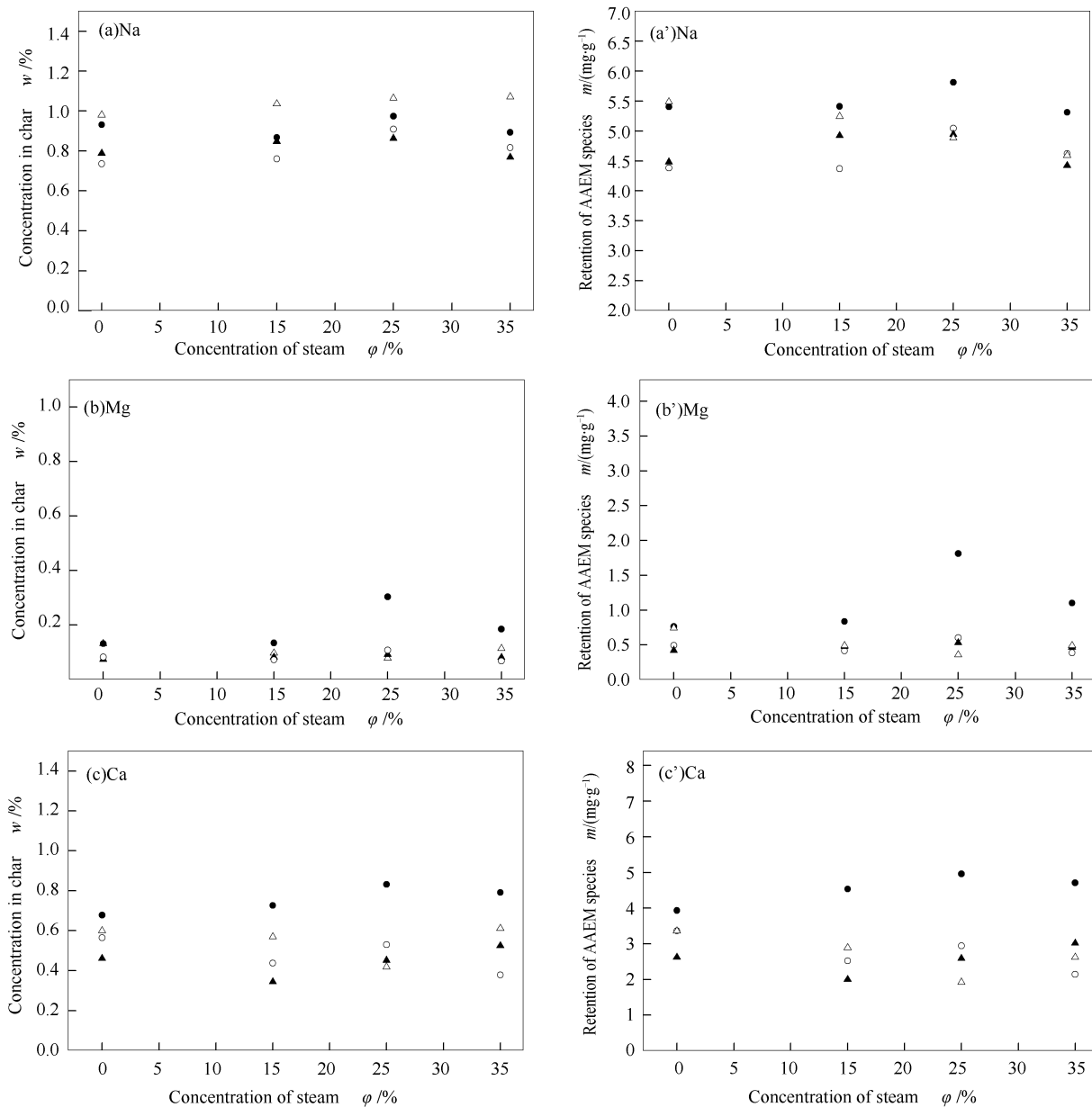


Figure 6 Concentration (a, b, c) and retention (a', b', c') of the alkali and alkaline earth metallic species (a, a') Na, (b, b') Mg and (c, c') Ca in the chars as a function of gasifying atmosphere during gasification at 800 and 900 °C  
 ●:  $\text{H}_2\text{O}$  gasification at 800 °C; ○:  $\text{H}_2\text{O}$  and  $\text{O}_2$  gasification at 800 °C;  
 ▲:  $\text{H}_2\text{O}$  gasification at 900 °C; △:  $\text{H}_2\text{O}$  and  $\text{O}_2$  gasification at 900 °C

It should be noted that temperature also seriously influences the volatilization of Ca during gasification in  $\text{H}_2\text{O}$  atmosphere alone (Figure 6 (c, c')). The concentrations and retentions of Ca in char prepared from gasification in  $\text{H}_2\text{O}$  atmosphere were higher than

those in  $\text{H}_2\text{O}+1\% \text{O}_2$  at the same temperature (i. e. 800 °C). When 1%  $\text{O}_2$  was added to  $\text{H}_2\text{O}$  gasifying atmosphere, it is believed that more breakages of char structure was occurred, more H radicals were generated, thereby reducing the concentrations of Ca

in chars. However, retentions of Ca in chars prepared from gasification in  $\text{H}_2\text{O}$  were lower than those prepared in  $\text{H}_2\text{O}+1\% \text{O}_2$  at  $900\text{ }^\circ\text{C}$  as the concentration of  $\text{H}_2\text{O}$  was less than 15% ; when the concentration of  $\text{H}_2\text{O}$  was higher than 15% , this result was opposite. The likely reason for the high retention of Ca during gasification of coal in  $\text{H}_2\text{O} + 1\% \text{O}_2$  at higher temperature in the less than 15%  $\text{H}_2\text{O}$  could be that some O-containing structures were formed, which in turn enhanced the Ca-holding capacity. More  $\text{CO}_2$  and H radicals could be produced with the concentration of  $\text{H}_2\text{O}$  being more than 15% .  $\text{CO}_2$  would inhibit the decomposition of  $\text{CaCO}_3$ , and  $\text{CaCO}_3$  aggregations were possibly formed. Therefore more Ca species were released from chars. As such,  $\text{O}_2$  played different roles in the volatilization of Ca in chars gasified in a  $\text{H}_2\text{O}+1\% \text{O}_2$  atmosphere at different temperatures. The results presented in Figure 6 clearly show that the gasifying atmosphere and temperature influence the volatilization of AAEM species during gasification by changing the structure of char.

## 2.4 Reactivity of chars

Figure 7 shows reactivity measured by TGA at  $300\text{ }^\circ\text{C}$  for the chars from gasification at 800 and  $900\text{ }^\circ\text{C}$  in 15%  $\text{H}_2\text{O}$ , 25%  $\text{H}_2\text{O}$ , and 35%  $\text{H}_2\text{O}$ , balanced with nitrogen; and 15%  $\text{H}_2\text{O}+1\% \text{O}_2$ , 25%  $\text{H}_2\text{O}+1\% \text{O}_2$ , and 35%  $\text{H}_2\text{O}+1\% \text{O}_2$ , respectively. Figure 7 shows as well that reactivity in air at  $300\text{ }^\circ\text{C}$  tended to decrease with increasing concentrations of  $\text{H}_2\text{O}$  for the chars from gasification in a  $\text{H}_2\text{O}$  atmosphere at  $800\text{ }^\circ\text{C}$ . These findings proved that steam decreased char reactivity measured at  $300\text{ }^\circ\text{C}$  during gasification at  $800\text{ }^\circ\text{C}$  due to the formation of condensed char structure by H radicals. The chars collected in  $\text{H}_2\text{O}+1\% \text{O}_2$  had lower reactivity with air at  $300\text{ }^\circ\text{C}$  than those produced in  $\text{H}_2\text{O}$  (Figure 7), corresponding with the retention of Na (Figure 6(a, a')). This was because the addition of  $\text{O}_2$  enhanced the generation of H radicals in  $\text{H}_2\text{O}$  atmosphere, thus changing the char structure. H radicals would cause condensation of the aromatic ring systems and result in a more ordered structure of char with lower reactivity.

The chars produced in 1%  $\text{O}_2$  show higher reactivity with air at  $300\text{ }^\circ\text{C}$  than those prepared in 100%  $\text{N}_2$  at  $900\text{ }^\circ\text{C}$ , due mainly to the changes of structure forming more O-containing structures in chars. The data in Figure 8(a) once again proved that steam also tended to reduce the reactivity of chars collected at  $900\text{ }^\circ\text{C}$ . However, the addition of 1%  $\text{O}_2$  in  $\text{H}_2\text{O}$  at  $900\text{ }^\circ\text{C}$  also lowered the reactivity of char with air at  $300\text{ }^\circ\text{C}$  (Figure 8(b)). As the retention of

Na (Figure 6) was comparable for these chars at  $900\text{ }^\circ\text{C}$ , the dominant factor explaining differences in char reactivity had to be char structure, shown in Figure 5(a). In a word, the data from Figure 7 and Figure 8 indicate that the mixed  $\text{H}_2\text{O}/\text{O}_2$  atmosphere can promote a decrease in subsequent char reactivity in air at  $300\text{ }^\circ\text{C}$ .

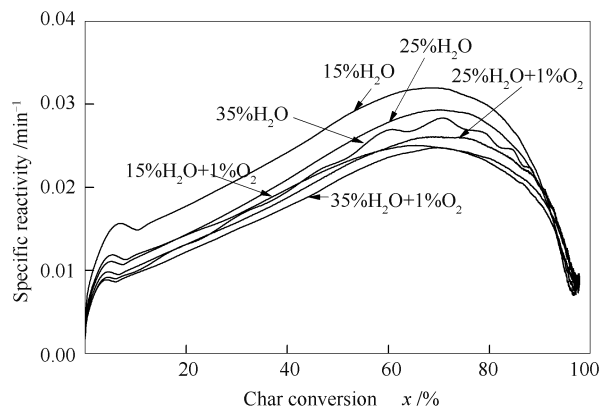


Figure 7 Char reactivity measured in air using TGA at  $300\text{ }^\circ\text{C}$  chars were collected from gasification at  $800\text{ }^\circ\text{C}$  in 15%  $\text{H}_2\text{O}$ , 25%  $\text{H}_2\text{O}$ , 35%  $\text{H}_2\text{O}$  balanced with nitrogen, and 1%  $\text{O}_2 + 15\% \text{H}_2\text{O}$ , 1%  $\text{O}_2 + 25\% \text{H}_2\text{O}$ , 1%  $\text{O}_2 + 35\% \text{H}_2\text{O}$  balanced with nitrogen

The catalytic effects of Mg and Ca for the oxidation of SL brown coal char with air are relatively minor. With low concentration, Na has far more significant effects on char reactivity than either Mg or Ca for the chars from brown coal<sup>[28,29]</sup>. Ultimately, changes in char reactivity with air at  $300\text{ }^\circ\text{C}$  are owing to the evolution of char structure.

## 2.5 Correlation of reactivity and structure of char

Figure 9 shows the reactivity of chars was correlated with structure. The Raman band area ratios represent the comparative ratios between small fused rings and large aromatic rings in chars. The reactivity of chars prepared from gasification in various gasifying atmospheres at 800 and  $900\text{ }^\circ\text{C}$  were measured using TGA with air at  $300\text{ }^\circ\text{C}$ . The index of gasification was usually calculated by the time the conversion of char reached fifty percent, which can reflect the reactivity of chars. The indexes of gasification denoted, respectively, by  $R_{0.02}$ ,  $R_{0.2}$ , and  $R_{0.8}$  were calculated employing the time at which conversion reached two percent, twenty percent, and eighty percent, according to Formula (2). These reaction indexes could evaluate reactivity at the beginning and ending reactions of chars. The correlation of reactivity and structure of char can be obtained from the diagram, plotted by the indexes with band area ratios  $I_{(G_R+V_L+V_R)}/I_D$  (all temperatures

and gasifying atmospheres). The results indicate that the gasification index increased with an increase of the band area ratio,  $I_{(G_R+V_L+V_R)}/I_D$ , shown in Figure 9 (a), (b), (c), and (d). Further, the results show

strong correlations between char reactivity and Raman spectrum data, with the key reactivity role played by char structure. The reactivity of chars can be evaluated by means of Raman spectrum.

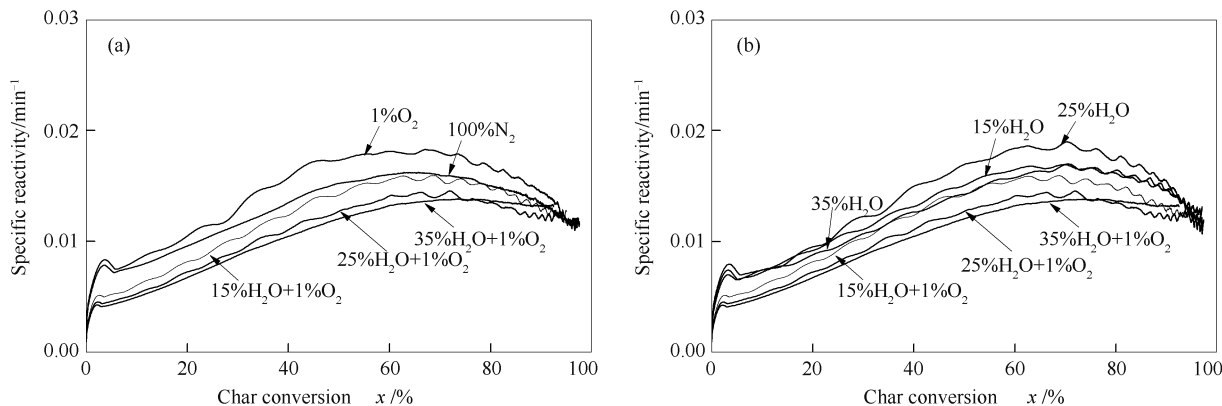


Figure 8 Reactivity of chars measured with air using TGA at 300 °C  
chars were produced from gasification at 900 °C in 15% H<sub>2</sub>O, 25% H<sub>2</sub>O, and 35% H<sub>2</sub>O balanced with nitrogen, and 1% O<sub>2</sub>, 1% O<sub>2</sub>+15% H<sub>2</sub>O, 1% O<sub>2</sub>+25% H<sub>2</sub>O, and 1% O<sub>2</sub>+35% H<sub>2</sub>O balanced with nitrogen

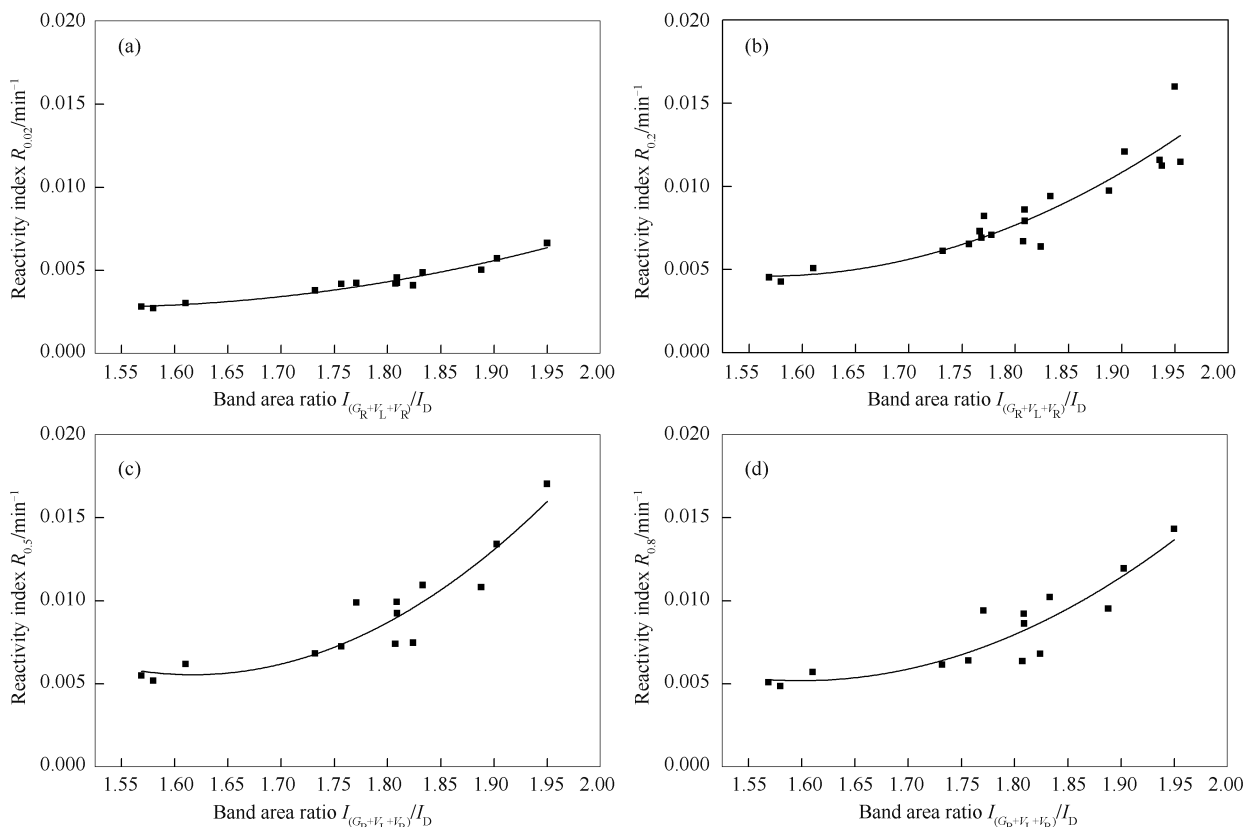


Figure 9 Correlation between reactivity and char structure characterized by  $I_{(G_R+V_L+V_R)}/I_D$  from Raman spectrum  
(a):  $R_{0.02}$ ; (b):  $R_{0.2}$ ; (c):  $R_{0.5}$ ; (d):  $R_{0.8}$

### 3 Conclusions

Shengli brown coal was gasified in a stainless steel entrained-flow reactor at 800 and 900 °C in atmospheres containing inert (N<sub>2</sub>), reducing (H<sub>2</sub>O) and oxidizing (O<sub>2</sub>) gasifying agents. Based on the

experimental results, the following conclusions can be drawn:

Steam was the primary factor explaining the lesser changes in char structure and effects of oxygen when gasification temperature was 800 °C; however,



the effects of oxygen played a larger role at 900 °C. The O-containing groups in chars were determined by oxidation and deoxidation during brown coal gasification. The effects of oxygen on char structure differed at high temperature (i. e. 900 °C) and low temperature (800 °C) in brown coal steam gasification.

The volatilization of alkali and alkaline earth metallic species were strongly influenced by the char structures. The role of O<sub>2</sub> in retaining Na during steam gasification at low temperature (i. e. 800 °C) was different from that at high temperature (i. e. 900 °C). O<sub>2</sub> promoted the volatilization of Na at 800 °C, but contrastively increased the retention of Na

during gasification at 900 °C in a mixture of H<sub>2</sub>O and 1% O<sub>2</sub>.

Char-air reactivity at 300 °C revealed that the mixed H<sub>2</sub>O/O<sub>2</sub> atmosphere could promote the decreasing char reactivity. Changes in the reactivity of chars were due mainly to the variation in char structure during gasification.

Char reactivity correlated well with the band area ratio,  $I_{(G_R+V_L+V_R)}/I_D$ , indicating that char structure played the key role in changes in char reactivity.

Ultimately, the factors influencing volatilization of AAEM and char reactivity with air at 300 °C largely changes in char structure.

## References

- [1] TREMEL A, SPLIETHOFF H. Gasification kinetics during entrained flow gasification-Part I: Devolatilisation and char deactivation[J]. Fuel, 2013, **103**: 663-671.
- [2] QUYN D M, WU H W, LI C Z. Volatilisation and catalytic effects of alkali and alkaline earth metallic species during the pyrolysis and gasification of Victorian brown coal. Part I. Volatilisation of Na and Cl from a set of NaCl-loaded samples[J]. Fuel, 2002, **81**(2): 143-149.
- [3] TAY H L, KAJITANI S, ZHANG S, LI C Z. Effects of gasifying agent on the evolution of char structure during the gasification of Victorian brown coal[J]. Fuel, 2013, **103**: 22-28.
- [4] BAYARSAIKHAN B, SONOYAMA N, HOSOKAI S, SHIMADA T, HAYASHI J I, LI C Z, CHIBA T. Inhibition of steam gasification of char by volatiles in a fluidized bed under continuous feeding of a brown coal[J]. Fuel, 2006, **85**(3): 340-349.
- [5] ZHANG L X, MATSUHARA T, KUDO S, HAYASHI J I, NORINAGA K. Rapid pyrolysis of brown coal in a drop-tube reactor with co-feeding of char as a promoter of in situ tar reforming[J]. Fuel, 2013, **112**: 681-686.
- [6] YE D P, AGNEW J B, ZHANG D K. Gasification of a south Australian low-rank coal with carbon dioxide and steam: Kinetics and reactivity studies[J]. Fuel, 1998, **77**(11): 1209-1219.
- [7] ZHANG S, MIN Z H, TAY H L, ASADULLAH M, LI C Z. Effects of volatile-char interactions on the evolution of char structure during the gasification of Victorian brown coal in steam[J]. Fuel, 2011, **90**(4): 1529-1535.
- [8] LI C Z. Importance of volatile-char interactions during the pyrolysis and gasification of low-rank fuels-A review[J]. Fuel, 2013, **112**: 609-623.
- [9] WU H W, LI X J, HAYASHI J I, CHIBA T, LI C Z. Effects of volatile-char interactions on the reactivity of chars from NaCl-loaded Loy Yang brown coal[J]. Fuel, 2005, **84**(10): 1221-1228.
- [10] KAJITANI S, TAY H L, ZHANG S, LI C Z. Mechanisms and kinetic modelling of steam gasification of brown coal in the presence of volatile-char interactions[J]. Fuel, 2013, **103**: 7-13.
- [11] WU H W, QUYN D M, LI C Z. Volatilisation and catalytic effects of alkali and alkaline earth metallic species during the pyrolysis and gasification of Victorian brown coal. Part III. The importance of the interactions between volatiles and char at high temperature[J]. Fuel, 2002, **81**(8): 1033-1039.
- [12] LI X J, WU H W, HAYASHI J I, LI C Z. Volatilisation and catalytic effects of alkali and alkaline earth metallic species during the pyrolysis and gasification of Victorian brown coal. Part VI. Further investigation into the effects of volatile-char interactions[J]. Fuel, 2004, **83**(10): 1273-1279.
- [13] ZHANG S, HAYASHI J I, LI C Z. Volatilisation and catalytic effects of alkali and alkaline earth metallic species during the pyrolysis and gasification of Victorian brown coal. Part IX. Effects of volatile-char interactions on char-H<sub>2</sub>O and char-O<sub>2</sub> reactivities[J]. Fuel, 2011, **90**(4): 1655-1661.
- [14] TAY H L, LI C Z. Changes in char reactivity and structure during the gasification of a Victorian brown coal: comparison between gasification in O<sub>2</sub> and CO<sub>2</sub>[J]. Fuel Process Technol, 2010, **91**(8): 800-804.
- [15] QUYN D M, HAYASHI J I, LI C Z. Volatilisation of alkali and alkaline earth metallic species during the gasification of a Victorian brown coal in CO<sub>2</sub>[J]. Fuel Process Technol, 2005, **86**(12/13): 1241-1251.
- [16] LI X J, HAYASHI J I, LI C Z. FT-Raman spectroscopic study of the evolution of char structure during the pyrolysis of a Victorian brown coal [J]. Fuel, 2006, **85**(12/13): 1700-1707.
- [17] TAY H L, KAJITANI S, ZHANG S, LI C Z. Inhibiting and other effects of hydrogen during gasification: Further insights from FT-Raman spectroscopy[J]. Fuel, 2014, **116**: 1-6.
- [18] TAY H L, KAJITANI S, WANG S, LI C Z. A preliminary Raman spectroscopic perspective for the roles of catalysts during char gasification [J]. Fuel, 2014, **121**: 165-172.
- [19] LI X J, HAYASHI J I, LI C Z. Volatilisation and catalytic effects of alkali and alkaline earth metallic species during the pyrolysis and gasification of Victorian brown coal. Part VII. Raman spectroscopic study on the changes in char structure during the catalytic gasification in air [J]. Fuel, 2006, **85**(10/11): 1509-1517.
- [20] LI X J, LI C Z. Volatilisation and catalytic effects of alkali and alkaline earth metallic species during the pyrolysis and gasification of Victorian brown coal. Part VIII. Catalysis and changes in char structure during gasification in steam[J]. Fuel, 2006, **85**(10/11): 1518-1525.
- [21] QUYN D M, WU H W, HAYASHI J I, LI C Z. Volatilisation and catalytic effects of alkali and alkaline earth metallic species during the pyrolysis and gasification of Victorian brown coal. Part IV. Catalytic effects of NaCl and ion-exchangeable Na in coal on char reactivity[J]. Fuel, 2003, **82**(5): 587-593.

- [22] LI C Z, SATHE C, KERSHAW J R, PANG Y. Fates and roles of alkali and alkaline earth metals during the pyrolysis of a Victorian brown coal[J]. *Fuel*, 2000, **79**(3/4): 427-438.
- [23] KEOWN D M, HAYASHI J I, LI C Z. Drastic changes in biomass char structure and reactivity upon contact with steam[J]. *Fuel*, 2008, **87**(7): 1127-1132.
- [24] FUSHIMI C, WADA T, TSUTSUMI A. Inhibition of steam gasification of biomass char by hydrogen and tar[J]. *Biomass Bioenergy*, 2011, **35**(1): 179-185.
- [25] LUSSIER M G, ZHANG Z, MILLER D J. Characterizing rate inhibition in steam/hydrogen gasification via analysis of adsorbed hydrogen[J]. *Carbon*, 1998, **36**(9): 1361-1369.
- [26] JOCHEN S, TORE M. Reduction of a detailed reaction mechanism for hydrogen combustion under gas turbine conditions[J]. *Combust Flame*, 2006, **144**(3): 545-557.
- [27] QUYN D M, WU H W, P. BHATTACHARYA S, LI C Z. Volatilisation and catalytic effects of alkali and alkaline earth metallic species during the pyrolysis and gasification of Victorian brown coal. Part II. Effects of chemical form and valence[J]. *Fuel*, 2002, **81**(2): 151-158.
- [28] LI C Z. Some recent advances in the understanding of the pyrolysis and gasification behaviour of Victorian brown coal[J]. *Fuel*, 2007, **86**(12/13): 1664-1683.
- [29] WU H W, HAYASHI J I, CHIBA T, TAKARADA T, LI C Z. Volatilisation and catalytic effects of alkali and alkaline earth metallic species during the pyrolysis and gasification of Victorian brown coal. Part V. Combined effects of Na concentration and char structure on char reactivity[J]. *Fuel*, 2004, **83**(1): 23-30.

## 氧气对胜利褐煤水蒸气气化半焦结构及反应性的影响

孙加亮, 陈绪军, 王芳, 林雄超, 王永刚

(中国矿业大学(北京)化学与环境工程学院, 北京 100083)

**摘要:** 为了研究氧气对半焦的结构变化和反应性的影响,采用不锈钢模拟气流床反应器,在8种不同气氛,800和900℃条件下,进行了胜利褐煤水蒸气气化实验。利用拉曼光谱和热重分析仪分别表征了半焦的结构和本征反应性。结果表明,在800和900℃条件下,添加的氧气对半焦结构变化的影响方式不同;半焦结构的变化是影响碱金属和碱土金属(AAEM)挥发的主要因素。在不同温度下,添加的氧气对Na挥发的影响和对结构的作用类似, $H_2O/O_2$ 混合气氛促使气化所得半焦的反应性进一步降低。半焦的反应活性指数与拉曼光谱谱带比值  $I(G_r+V_L+V_R)/I_D$  具有很好的相关性。

**关键词:** 褐煤; 气化; 半焦结构; 半焦反应性; 模拟气流床反应器

**中图分类号:** TQ546.2      **文献标识码:** A