

Investigation on the catalytic effects of AAEM during steam gasification and the resultant char reactivity in oxygen using Shengli lignite at different forms

Jianxin Mi¹ · Ningbo Wang¹ · Mingfeng Wang¹ · Pengju Huo¹ · Dan Liu¹

Received: 21 May 2014/Revised: 14 July 2015/Accepted: 22 July 2015/Published online: 25 September 2015
© The Author(s) 2015. This article is published with open access at Springerlink.com

Abstract The purpose of this study is to investigate the catalytic effects of alkali and alkaline earth metallic species (AAEM) on char conversion during the gasification in steam and the changes in ex-situ char reactivity in oxygen after the gasification in steam using different forms (i.e. H-form, Na-form) of Shengli brown coal. The surface area, AAEM concentration and carbon crystallite of chars were obtained to understand the change in char reactivity. It was found that not only Na concentration and carbon structure were the main factors governing the char reactivity in the atmosphere of steam and oxygen, but also they interacted each other. The presence of Na could facilitate the formation of disordering carbon structure in char, and the amorphous carbon structure would in turn affect the distribution of Na and thus its catalytic performance. The surface area and pore volume had very little relationship with the char's reactivity. Additionally, the morphology of chars from different forms of coals were observed using scanning electron microscope (SEM).

Keywords Steam gasification · H-form coal · Na-form coal · Char reactivity · Char structure

1 Introduction

Coal is the main energy source in China. The continuous improvement of living standards will continue to lead to drastic increases in the demand for energy. Coal gasification is the key and main technology of clean coal transformation and utilization technology (production of chemicals, hydrogen and liquid fuels etc.) (Bretz 1992; Gary and Russell 2001; Hayashi et al. 2002; McKendry 2002; Li 2004, 2007).

Gasification is particularly suitable for the utilization of low-rank coals, such as Shengli brown coal, due to its high gasification reactivity. In particular, the endothermic reaction between steam and carbon could efficiently transfer thermal energy to chemical energy stored in product gases (i.e. H₂, CO). The brown coal contain abundant

alkali and alkaline earth metallic (AAEM) species (mainly Na, K, Mg, Ca) which affects almost every aspect of gasification behavior (Takarada et al. 1995; Li et al. 2000a, b; Quyn et al. 2002a, b; Jamil Jamil and Li 2006). The presence of these AAEM species would thus be one of the most important considerations for deciding the proper route of Shengli brown coal utilization (Hayashi et al. 2002). For example, in the current combustion system, the AAEM species in the brown coal are largely responsible for those notorious problems such as fouling and slagging. In the advanced gasification/reforming power generation system (Li et al. 2000a; Wu et al. 2004), the AAEM species will be volatilized and mixed with the fuel gas, causing erosion/corrosion of the turbine components. However, these AAEM species remaining in char after the primary reaction are believed to act as effective catalysts for the subsequent char combustion and gasification reactions. Their retention in the char would substantially enhance the converting rate of the solid char. Therefore, the examination on the volatilization and catalytic performance of these inherent AAEM species during pyrolysis, gasification and combustion has been extensively conducted for possibly

✉ Jianxin Mi
mijianxin2007@126.com

¹ Hydrocarbon Research Center of Shaanxi Yanchang Petroleum (Group) Co. Ltd., Xi'an 710075, China

improving the utilization efficiency of coals (Zhu and Song 2008; Jin et al. 2010). However, most of the studies were focusing on the fast heating rate which resulted in quick and high devolatilization (Zhang et al. 2011a, b). At the same time, the fast heating rate inevitably caused high volatilizations of AAEM, which would be partially present in the product gases although cleaning process could remove most of them. To alleviate the negative effects of significant release of AAEM into the gas phase and reduce the cost of related cleaning equipment, it may be desirable to develop gasification technology at slow heating rates, especially for brown coal. The carbon matrix of brown coal is very vulnerable and could be thermally-cracked at relatively ease at slow heating rates. With slow heating gasification, the most reactive part of organic matter in the coal will be firstly gasified by steam or oxygen. The less reactive part (may be parent material for tar) and worst reactive part of organic matter stayed with most of inorganic matter as char. Therefore, the advantages of brown coal gasification at slow heating rates would be obtaining cleaner syngas with less tarry material and AAEM although the reaction rate and char conversion were expected to be slower than that of fast heating rate. As a matter of fact, the brown coal char with AAEM had a great potential to be used as activated carbon material (Chattopadhyaya et al. 2006). The multiple ending products from slow heating gasification of brown coal may have a bright future.

It has been known (Fu et al. 2012; Bernardo et al. 2012) that the physico-chemical structure of char (i.e. char surface area and pore volume, regularity of carbon structure) can also affect the gasification reactivity in addition to the AAEM species. The efficient use of Shengli lignite (one of the largest deposits in China) will be very critical in environmental and economic views. As a result, this study is to investigate the catalytic effects of AAEM during the slow heating gasification reactions using Shengli brown coal in a wide of experimental conditions. To further explore the difference in the property of chars prepared from the gasification in steam using different forms of coal at different temperatures, the reactivity of gasification char in oxygen was also examined in this work. As well the correlations between char structure and surface area to char reactivity were examined.

2 Experimental

2.1 Coal samples

A brown coal sample was obtained from the Shengli coal field, Inner Mongolia, China. The sample was partially dried at low temperature (<35 °C), crushed and then sieved

to obtain a sample of particle size between 96 and 150 μm . This coal sample was labeled as 'raw coal (RC)'. The raw coal's proximate and ultimate analysis are summarized in Table 1.

A set of H-formed coal samples was prepared by acid-washing the raw coal, part of AAEM species can be ion-exchanged from the brown coal. Two different acid-washed coals were prepared. The ion-exchanged levels were expressed by the concentrations of HCl used during the washing process. 0.02 and 5 mol/L of HCl were used separately for preparing two different acid-washed coals, namely 0.02H-coal and 5H-coal respectively and their properties were also given in Table 1. In order to investigate the Na on the influence of gasification behavior of Shengli brown coal, a "Na-form" coal sample was prepared by physically impregnating NaCl into the 0.02H coal sample, the amount of loaded Na + was equal to that removed during acid washing process. Therefore, the Na concentration in Na-form coal was the same as that in raw coal.

The concentration measurement of AAEM for the different coals and chars basically followed the previous procedure (Li et al. 2000a, 2006). Briefly, the sample was ashed in air using a muffle furnace; the ash was then dissolved in a mixed acid of HNO_3 and HF (1:1 by volume). After the evaporation of HNO_3 and HF, the AAEM species will be remaining in the Teflon crucible. This was followed by using distilled water to dissolve the AAEM species. Finally, the AAEM species were quantified with an ICP (inductively coupled plasma). The AAEM species concentration of coal samples were thus obtained and shown in Fig. 1.

2.2 Gasification experiment

A fluidized-bed/fixe-bed quartz reactor shown in Fig. 2 was used in this study. The top frit could prevent the char particles from escaping out of the reactor while the bottom one acting as the gas distributor and fluidizing medium (300–355 μm silica sand) supporter. With the top frit, the volatilized AAEM species could be carried out by the fluidising gas while the char particles would be stopped in the reactor by the frit.

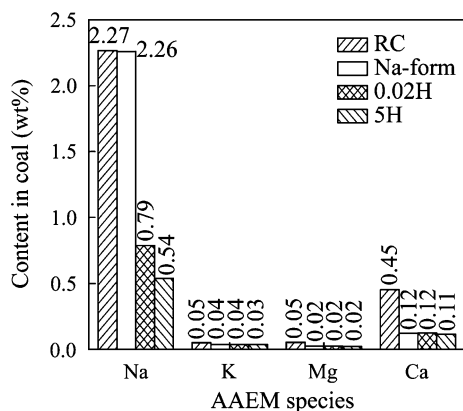
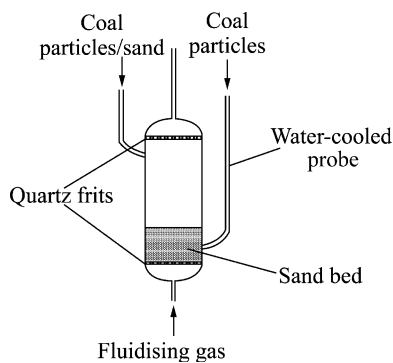
In order to achieve an identical reaction temperature distribution in the reaction zone (between top and bottom frit), we fixed the reactor in the middle of the electrical furnace with three independent heating zones. By adjusting the three temperature controller for the three heating zones, the temperature difference within the reaction zone could be as small as ± 5 °C.

In the slow heating rate gasification, the coal particles were fed into the quartz reactor at ambient temperature and the reactor was then heated up at a pre-set heating rate

Table 1 Properties of coal samples studied (wt%)

| Sample | Proximate analysis | | | | Ultimate analysis | | | | |
|---------|--------------------|----------|-----------|-----------|-------------------|-----------|-------------|-----------|-----------|
| | M_{ad} | A_{ad} | VM_{ad} | FC_{ad} | C_{daf} | H_{daf} | O^*_{daf} | N_{daf} | S_{daf} |
| RC | 6.48 | 8.16 | 40.20 | 45.16 | 72.45 | 4.99 | 20.99 | 0.95 | 0.62 |
| Na-form | 6.53 | 6.58 | 37.12 | 49.77 | 73.02 | 4.41 | 20.72 | 1.42 | 0.43 |
| 0.02H | 6.78 | 5.27 | 37.33 | 50.62 | 73.06 | 4.43 | 20.65 | 1.42 | 0.44 |
| 5H | 6.82 | 4.83 | 36.93 | 51.42 | 73.30 | 4.19 | 20.59 | 1.54 | 0.38 |

* by difference

**Fig. 1** AAEM species concentration of different coal samples**Fig. 2** A schematic diagram of the fluidized-bed/fixed-bed reactor used in this study (Quyn et al. 2002a, b)

(approximately 15 K/min) to the target temperature (700–900 °C). Mixture gases (1.8 L/min) of ultra-high purity argon and steam went into the reactor through the fluidizing gas tube, and the steam for the gasification was generated inside the reactor by continuously feeding water into the reactor with an HPLC pump. The concentration of steam in the fluidizing gas was always 15 % (by volume). After finishing the experiments as prescribed, the hot

reactor was then lifted out of the furnace from the top and cooled in the air naturally with continuous flow of inert gas.

2.3 Char analysis

2.3.1 Char yield

Char yields were calculated by the following equation:

$$y_c = \frac{M_{t,p} - M_{0,p}}{M} \times 100\% \quad (1)$$

where $M_{0,p}$ represents the weight of reactor with sand before experiments and $M_{t,p}$ refers to the weight of reactor including sand and char after experiments; M means the weight of coal sample used for the experiment.

2.3.2 Surface area and pore volume analysis

Gas adsorption techniques are commonly used to assess internal surface area of chars for correlation of coal reactivities, this method is N_2 adsorption at 77 K in mesopores as envisaged by the Brunauer–Emmet–Teller (BET) theory (Serrano-Talavera et al. 1997).

2.3.3 Carbon structure and morphology analysis

In order to investigate the effects of alkali metal and experimental conditions on the variation of crystallite structure of chars prepared from above coals, the XRD scans were conducted on a X'Pert-Pro MPO using Cu K α radiation, voltage: 40 kV, current: 40 mA. The X-ray intensities were measured in the range of $10^\circ \leq 2\theta \leq 80^\circ$. These scan were recorded automatically by the X'Pert HighScorePlus™ software.

In this study, we also used scanning electron microscope (SEM) to observe the morphology of the chars, at resolution of $\times 15,000$.

2.3.4 Ex-situ char reactivity measurement

The reactivity of chars prepared from the gasification experiments was then measured with a PerkinElmer Pyris1 TGA equipped with a high temperature furnace. The experimental procedure (Senel et al. 2001) can be outlined as follows: approximately 10 mg of char sample was placed in a platinum crucible and heated in oxygen (21 % oxygen in nitrogen) from ambient temperature to 110 °C to remove the moisture of the char and held for 30 min; The temperature was then increased to 380 °C at the rate of 15 °C/min, holding for 360 min at 380 °C. The sample was heated further to 650 °C at 15 °C/min with holding time of 30 min to complete the combustion of the carbonerous material (Quyn et al. 2003; Cakal and Anal 2007). 10 mg of char samples was used as such amounts only occupied about 1/4th height of platinum crucible and the absolute height of char particle layer was less than 1 mm. Thus the reactivity of char with oxygen was less affected by diffusing resistance. Before choosing 380 °C as the main reaction temperature, higher temperatures than 380 °C were tried for shortening the reaction time, but the phenomenon of combustion was always observed.

The specific reactivity of char was evaluated as the rate of weight loss per unit weight of the char at any time. The specific reactivity (R_x) of char was calculated according to the following formula:

$$R_x = -\frac{1}{W_0} \left(\frac{dW}{dt} \right) \quad (2)$$

where W_0 is the initial weight of char and W is the weight of char at any time.

3 Results and discussion

3.1 Changes in char yields of different forms of coals during the gasification in steam

Figure 3 compared the char yields of different coals as a function of gasification temperature in the fluidized-bed/-fixed-bed reactor at the slow heating rate. The char yields generally decreased with increasing reaction temperature from 700 to 900 °C in 15vol % steam. It has been noticed that the char yield of 0.02H sample was significantly lower than that of 5H sample before 800 °C. The char yields from Na-form coal was broadly between the acid-washed coal and raw coal.

The coal after being acid-washed by high concentration of HCl (i.e. 5 M in this paper) could lose not only AAEM (performing catalytic roles for gasification reactions), but also some reactive organic compounds (humic acid material), which was the main reason for the lower observed

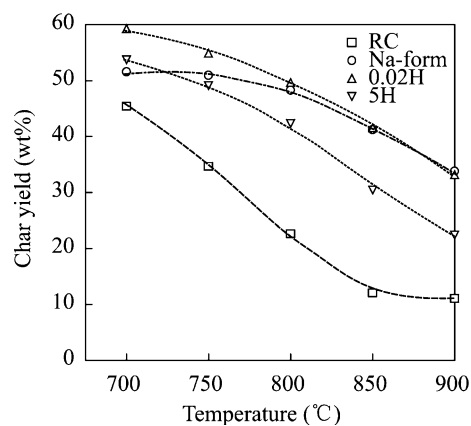


Fig. 3 Yields of char from the gasification as a function of temperature (holding time, 15 min)

char yields from 0.02H-form coal than 5H-form coal before 800 °C (Kashimura et al. 2004). It appears that the effects of additional loss of AAEM and humic acid material on the char yields were ignorable when the gasification temperatures were higher than 800 °C. With the impregnation of 1.48 % Na into 0.02H-form coal, the coal reactivity were significantly improved and led to the apparent reduction in char yields. However, the char yields of Na-form coal were still much higher than those of raw coal although they had the similar contents of Na (see Fig. 1), implying that some other AAEM species (such as Ca and Mg) existing in raw coal have also taken part in the catalytic reactions. As a matter of fact, another possibility was that the externally-loaded Na might exist differently from the original one in raw coal regarding to its distribution and occurring forms (Kershaw et al. 2000). The following discussion will further disclose that the AAEM concentrations in the resultant chars were also in the same order as that in original coals.

3.2 Char surface area and pore volume

Figure 4 shows the specific surface area and pore volume for the chars from different forms of coals at different temperatures. The surface area of chars with increasing gasification temperature was slowly decreasing, whereas the pore volumes of chars from different coals all reduced to a similar value of 0.05 mL/g at 900 °C, indicating that the sizes of char pores were in opposite trend to their surface areas at 900 °C. That is, the pore size of the char from Na-form coal was the largest whilst that of the char from 5H-form coal was the smallest at 900 °C. Different from the trend in char reactivity, the highest surface area and pore volume came from the char of 5H-form coal and the char from Na-form coal produced the lowest surface area and pore volume. In other words, the high char reactivity did not mean high char surface area or pore volume

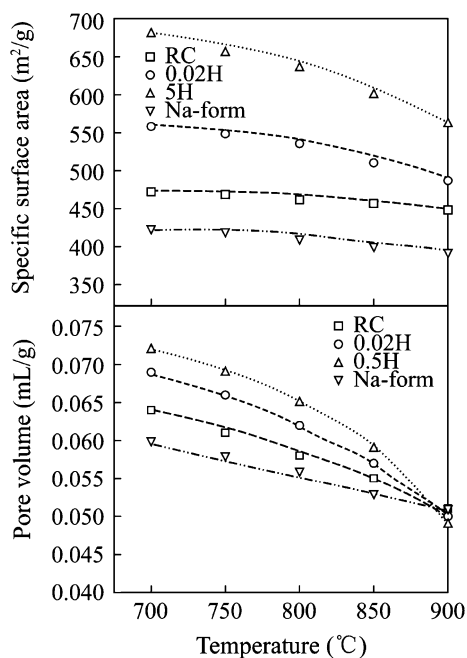


Fig. 4 Change in the surface area and pore volume during the gasification as a function of temperature

(Zhuo et al. 2000; Çakal et al. 2007). This strongly suggests that some other factors were governing the change in the char reactivity. The Na-form char and raw coal char featuring the low surface area and pore volume as well as big pore size further suggests that the presence of Na (or other metallic species) have intensified the gasification reaction locally around the metal species and caused the pore collapse and coalescence (Tomita and Ohtsuka 2004). On the contrary, the 5H-form and 0.02H-form coals matrix has been partially freed from those inorganic matters to different extents, thus forming fairly abundant and small pores.

3.3 Carbon structure

As the temperatures for the gasification were not mild and the carbon functional groups (i.e. containing oxygen) have been mostly decomposed (Cetin et al. 2004), the carbon ordering degree of chars was measured by using XRD technique.

Figure 5 shows the XRD spectrogram of gasification char samples prepared at 800 °C. The order of peak 002 intensity is: 5H-form coal > 0.02H-form coal > Raw coal > Na-form coal. The crystallite structure parameters of the chars (average stacking height L_c , carbon crystallite width L_a and interplanar spacing d_{002}) prepared at the gasification temperature of 800 °C were given in Table 2. At the same temperature, the higher Na

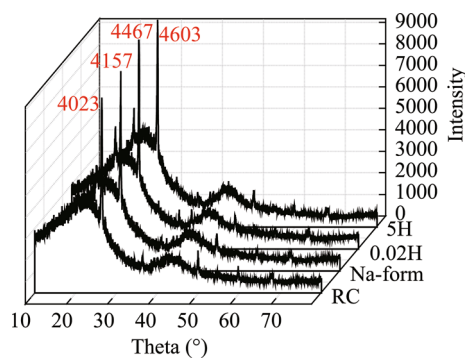


Fig. 5 The XRD analysis for gasification char samples prepared at 800 °C

Table 2 Crystallite structure parameters of char samples prepared at 800 °C

| Char sample | Crystallite structure parameters | | |
|-------------|----------------------------------|--------|-----------|
| | L_c | L_a | d_{002} |
| RC | 0.6325 | 0.4083 | 0.9433 |
| Na-loaded | 0.6130 | 0.4025 | 0.9384 |
| 0.02H | 0.9141 | 0.6758 | 0.7325 |
| 5H | 1.1267 | 0.7806 | 0.6240 |

concentration (Raw coal and Na-loaded coal) resulted in lower L_c and L_a but a higher d_{002} values. The lower Na concentration caused a larger increase in L_c than L_a , which means that the longitudinal growth in adjacent BSUs (Basic Structural Units) dominated the development of microcrystalline carbon structure. The phenomenon suggests that the presence of AAEM has inhibited the process of graphitization during coal gasification, resulting in the less ordered carbon crystalline structure (Fan et al. 2006). These metal species may be bonded to coal/char matrix and fixed upon BSU, which destroys the parallelism of the layer and the constancy of the interlayer spacing, thus decreasing the intensity and sharpness of the 002 scatter beam. The ordering carbon structure seems to be one of the main reasons explaining that the H-form coal had low conversion (in Fig. 3) and low ex-situ char reactivity (in Fig. 4). Besides the high reactivity of amorphous carbons structure itself, the homogenous carbon arrangement of chars from Na-form coal could have also facilitated the catalytic activity of AAEM species by well distributing them. On the other hand, it should also be stressed that the evolution of char was not taking place independently from AAEM species which has intimately interacted with carbon and led to the eventual “char”.

3.4 The morphology of chars

For further gaining information on the change of char particle surface property due to the difference in Na contents, the direct observation of char surface morphology was conducted using SEM. Figure 6 shows SEM pictures of three samples at resolution of 15,000 times. As shown in Fig. 6a and b, the surfaces of chars from raw coal and Na-form coal were very coarse, and smooth, plate-type structures were observed on the surface of 5H-form char particles in Fig. 6c. On the other hand, some white spots were seen on the surface of the Na-loaded char samples. These spots were the central activation points that play an important role in the gasification reaction. The alkali metals were inclined to form intercalation compounds with carbon, which could increase the interlayer distance and cause volume expansion. The C–C bonds are thus weakened and the gasification reaction was enhanced. This could explain why the char containing Na had the good reactivity compared to other samples (Zhuang et al. 1996; Zhou 2002; Manquai et al. 2009). Furthermore, the size of white spots in Fig. 6b was fairly bigger than that in Fig. 6a, contributing to the difference in char yields for raw coal and Na-form containing the similar amount of Na as raw coal.

3.5 AAEM retention and concentration

Figure 7 illustrates AAEM retention as a function of gasification temperatures for different coal forms. Kalium was not included as its content was too low to accurately detect. The volatilization of Mg and Ca of each coal sample were little affected by the reaction temperature from 700 to 900 °C. Comparatively, about 30 % of Na was volatilized from both the raw coal and the Na-loaded coal samples, and 20 and 10 % of Na was released for

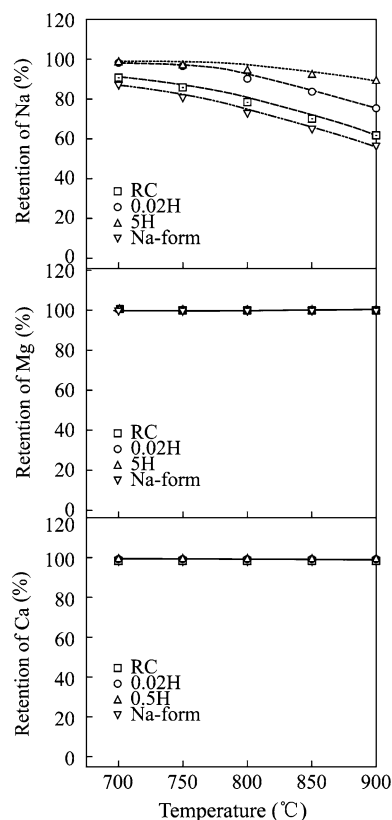


Fig. 7 Changes in Na/Mg/Ca retention in char as a function of gasification temperature in steam

0.02H-form and 5H-form coal samples respectively at 900 °C.

The aim of coal gasification was to produce light gases (H_2 , CO , CO_2 and CH_4) while inevitably producing tarry materials and light hydrocarbons from the primary reactions in the reacting zone. These relatively large molecules of hydrocarbons would be easily cracked at higher temperatures, forming free radicals (especially H radicals)

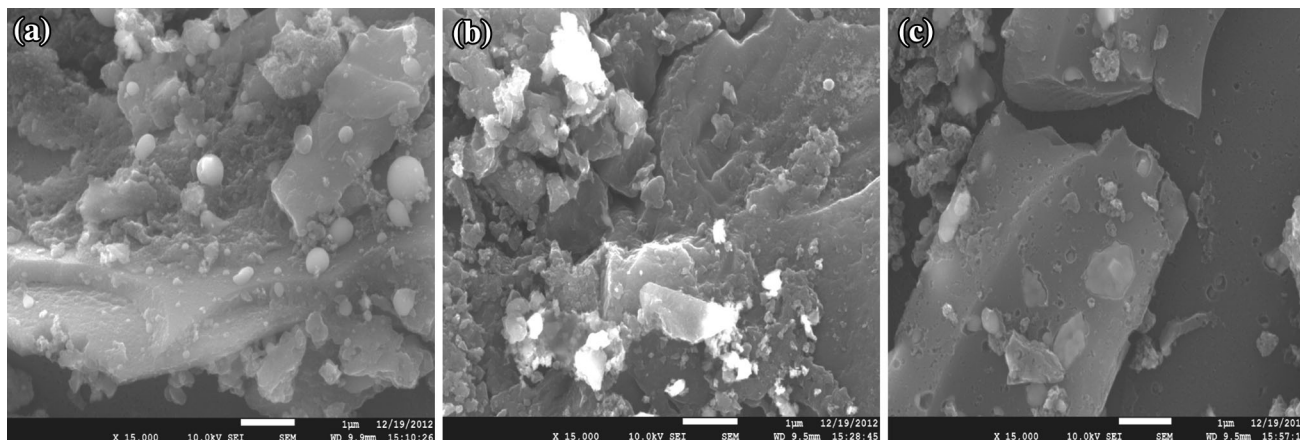


Fig. 6 Scanning electron microscopy images of raw-char. **a** Raw char: 900 °C; **b** Na-form char: 900 °C; **c** 5H-form char: 900 °C

(Woon and Sang 1995). The radicals may replace the AAEM species which were initially chemically bonded to the char. The substituted AAEM would then escape from the char matrix and flow out of the reactor with gaseous products, which was the main reason for the decreasing Na retention in char and for the presence of inorganic impurities in the product gas (Jensen et al. 2000).

Valence of AAEM species was the key factor dominating the ease of volatilizations. The alkaline earth metal (Ca and Mg) has two single electrons, thus they bonded with coal or char divalently (i.e. C–Ca/Mg–C). Clearly the double bonding would be much more stable than the single bonding of alkali with carbon (C–Na). In other words, the volatilization of Ca and Mg required the simultaneous cracking of two bonds, the probability of which was obviously much lower than the breaking of a single bond of C–Na. The different volatilizing extents of Na for different coal samples (5H-form coal, 0.02H-form coal, raw coal and Na-form coal) demonstrates that the remaining Na in coal after acid wash was in fairly stable forms.

The char conversion and retention of AAEM together decided the AAEM concentration in the eventual char and the AAEM concentrations in char had a direct effect on char conversion and reactivity. Due to the very low content of K and low catalytic performance of Mg and Ca, Na

concentration was particularly calculated and plotted versus char ex-situ reactivity (as shown in Fig. 8) for observing the relationship between them. The first point of each curve in Fig. 8 indicated the Na concentration of resultant char produced from the gasification in steam. As mentioned above, the Na concentrations for the chars from Na-form coal and raw coal were also higher than 0.02H-form and 5H-form coals. This again strongly suggests the main role of AAEM for enhancing the carbon–steam and carbon–oxygen reactions.

However, for each sample (each curve) in Fig. 8, it seems that the ex-situ char reactivity was not closely related to Na concentration. In some cases (such as the chars from 5H-form coals at 800 and 900 °C), the ex-situ char reactivity in oxygen was almost constant when the Na concentrations increased for more than 10 wt%. The large difference in ex-situ char reactivity for the given Na concentration in Fig. 8 has indicated the high importance of carbon structure to physicochemical forms and distribution of Na and thus the char reactivity. Actually, the catalytic role of alkali and alkaline species during gasification reactions might be largely affected by their distributions and statuses in some cases (Hayashi et al. 2000). The extent of which would rely on the specific char structure, such as the carbon functional groups and ordering degree. During the gasification in steam, the relatively reactive part of carbon has been consumed preferentially and the fairly inert carbon structure was left as char. Indeed, the effect of carbon structure on the catalytic performance of Na could be further observed by carefully examining the waved shape of reactivity curves in Fig. 8.

The reactivity for most of chars especially being produced from RC and Na-form coals presented a broad peak with increasing Na concentration in the char. It is not difficult to understand the increasing char reactivity (the left part of peak) as the Na concentration increased. With the further increase in Na concentration to a certain point, the char reactivity started to drop. This phenomenon has also been observed by some previous studies (Meijer et al. 1991; Asadullah et al. 2010). It was believed that the char generally consisted of two different carbon structures (ordering and disordering). Those AAEM (such as Na) would initially bond with disordering carbons and thus catalyzed the oxidation reaction. Thus at the early stage of char conversion (the left part of curve), the disordering carbon was consumed quickly. With the reduction in the proportion of amorphous carbon remaining in the char, the Na had to immigrate, accumulate and anchor on the ordering carbons. The low reactivity of high ordering carbon itself and the low catalytic performance of Na (owing to the accumulation and weak interaction with carbon) would lead to the decreasing char reactivity shown on the right of curve. The almost constant reactivity for

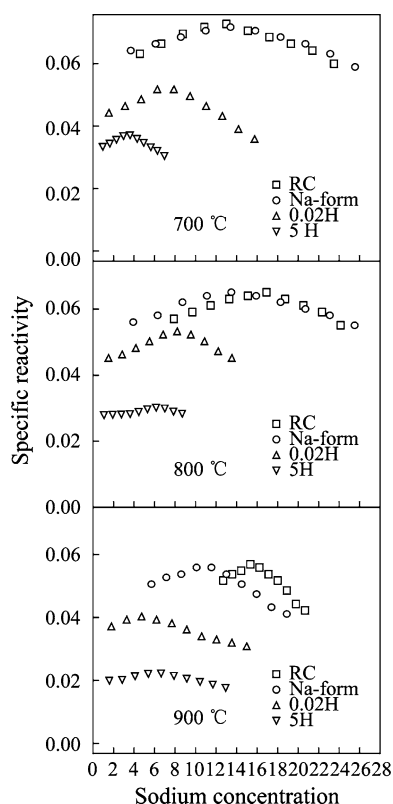


Fig. 8 Ex-situ char reactivity in oxygen as a function of Na concentration in char (Na, % Na in char)

chars from 5H-form coals at 800 and 900 °C indicated that the chars containing little AAEM were non-selectively gasified/consumed in the atmosphere of oxygen, being consistent with some previous reports (Fanjul et al. 2001). A very small peak was observed for the char from 5H-form coal at 700 °C, which might be related to the high Na retention for the char as shown in Fig. 7.

3.6 Changes in ex-situ reactivity of chars from the gasification in steam

To further explore the difference in the property of chars prepared from the gasification in steam using different forms of coal at different temperatures, the chars from 700, 800 and 900 °C were subjected to reactivity measurements using TGA. The reaction atmosphere was oxygen (21 vol.% O₂ in N₂) and the chars experienced the same temperature program as indicated in the experimental section. From Fig. 9, It can be seen that the chars from raw coal and Na-form coal showed the similarly highest reactivity while the reactivity of char from 5H-form coal gave the lowest reactivity. The effect of gasification temperature

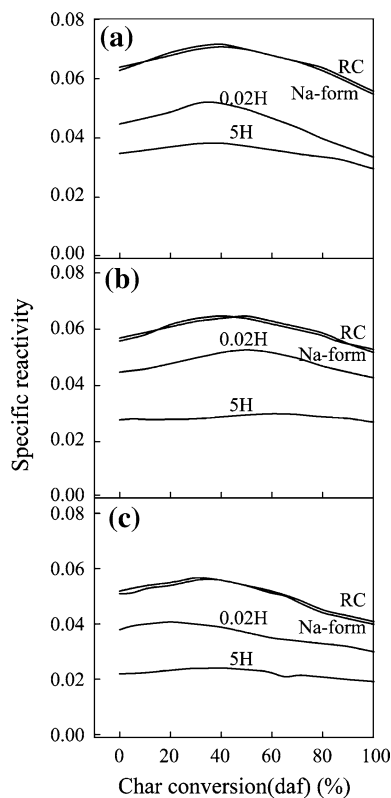


Fig. 9 Ex-situ reactivity (in oxygen) of chars as a function of char conversion. **a** The chars were prepared from the gasification in steam at 700 °C; **b** The chars were prepared from the gasification in steam at 800 °C; **c** The chars were prepared from the gasification in steam at 900 °C

on the ex-situ char reactivity was also easily observed; and the datum points of char reactivity were overall shifting down from Fig. 9a–c.

Efforts were made to understand the changes in the trends of char conversion during the gasification in steam (Fig. 3) and ex-situ char reactivity in oxygen (Fig. 9) by considering three factors (char surface area and pore volume, AAEM retention and concentration, regularity of carbon structure). The three factors were normally the most important contributors affecting the reactivity of chars. It is known that porous structure (large surface area and pore volume), high AAEM concentration, and amorphous carbon structure would be in favor of the char reactivity. But their relative importance would be varied depending on the situations (Miura et al. 1989).

4 Conclusions

Shengli brown coal in different forms (H-form and Na form) has been gasified in fluidised-bed quartz reactor to examine the effect of AAEM (particularly Na) on the char yields at different temperatures. The ex-situ reactivities of chars produced from the gasification in steam were further measured by TGA. The changes in char reactivity during the reactions with steam or oxygen were mainly attributed to the Na content and the char structure. The surface area and pore volume appears not to be the critical factor for affecting the char reactivity during the reactions with steam and oxygen. The presence of Na in coal/char could facilitate the formation of disordering carbon structure in char at high temperatures, and the amorphous carbon structure would in turn decide the distribution of Na and thus its catalytic performance.

The volatilization of Na was at different extents for different forms of coals at different gasification temperatures in steam. In contrast, the release of divalent Ca and Mg was negligent. The surface area and pore volume had very weak relationship with the char's reactivity. Additionally, some large Na clusters were clearly observed on the surface of chars from Na-form coal gasification using SEM.

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

- Asadullah M, Zhang S, Min ZH, Yimsiri P, Li CZ (2010) Effects of biomass char structure on its gasification reactivity. *Bioresour Technol* 101(20):7935–7943

- Bernardo M, Lapa N, Goncalves M, Mendes B, Pinto F, Fonseca I, Lopes H (2012) Physico-chemical properties of chars obtained in the co-pyrolysis of waste mixtures. *J Hazard Mater* 219:196–202
- Bretz EA (1992) Clean coal technologies: a status report. *Electric World* 2:37–42
- Cakal GÖ, Anal J (2007) Physical and chemical properties of selected Turkish lignites and their pyrolysis and gasification rates determined by thermogravimetric analysis. *Appl Pyrolysis* 80:262–268
- Çakal GÖ, Yücel H, Gürüz AG (2007) Physical and chemical properties of selected Turkish lignites and their pyrolysis and gasification rates determined by thermo-gravimetric analysis. *J Anal Appl Pyrolysis* 80(1):262–268
- Cetin E, Moghtaderi B, Gupta R (2004) Influence of pyrolysis conditions on the structure and gasification reactivity of biomass chars. *Fuel* 83(16):2139–2150
- Chattopadhyaya G, Macdonald DG, Narendra N (2006) Preparation and characterization of chars and activated carbons from Saskatchewan lignite. *Fuel Process Technol* 87(11):997–1006
- Fan X, Yang F, Zhang W, Zhou ZJ, Wang FC, Yu ZH (2006) Variation of the crystalline structure of coal char during pyrolysis and its effect on gasification reactivity. *J Fuel Chem Technol* 34(4):395–399
- Fanjul F, Granda M, Santamaría R, Menéndez R (2001) Assessment of the oxidative stabilisation of carbonaceous mesophase by thermal analysis techniques. *J Anal Appl Pyrolysis* 58: 911–926
- Fu P, Hu S, Xiang J, Sun LS, Bai XY (2012) Evolution of char structure during steam gasification of the chars produced from rapid pyrolysis of rice husk. *Bioresour Technol* 114:691–697
- Gary JS, Russell CM (2001) Gasification technologies: the path to clean, affordable energy in the 21 century. *Fuel Process Technol* 71(1–3):80–81
- Hayashi JI, Takahashi H, Iwatsuki M, Essaki K, Tsutsumi A, Chiba T (2000) Rapid conversion of tar and char from pyrolysis of a brown coal by reactions with steam in a drop-tube reactor. *Fuel* 79(3):439–447
- Hayashi JI, Iwatsuki M, Morishita K, Tsutsumi A, Li CZ, Chiba T (2002) Roles of inherent metallic species in secondary reactions of tar and char during rapid pyrolysis of brown coals in a drop-tube reactor. *Fuel* 81:1977–1987
- Jamil K, Li CZ (2006) Volatilisation and catalytic effects of AAEM species on reactivity of char from pyrolysis and gasification of Victorian brown coal. *J Energy Environ* 5:31–44
- Jensen PA, Frandsen FJ, Dam-Johansen K, Sander B (2000) Experiment investigation of the transformation and release to gas phase of potassium and chlorine during straw pyrolysis. *Energy Fuels* 14(6):1280–1285
- Jin H, Lu YJ, Liao B, Guo LJ, Zhang XM (2010) Hydrogen production by coal gasification in supercritical water with a fluidized bed reactor. *Int J Hydrog Energy* 35(13):7151–7160
- Kashimura N, Hayashi JI, Li CZ, Sathe C, Chiba T (2004) Volatilisation and catalytic effects of alkali and alkaline earth metallic species during the pyrolysis and gasification of Victorian Brown coal. *Fuel* 83:97–107
- Kershaw JR, Sathe C, Hayashi JI, Li CZ, Chiba T (2000) Fluorescence spectroscopic analysis of tars from the pyrolysis of a Victorian brown coal in a wire-mesh reactor. *Energy Fuels* 14(2):476
- Li CZ (2004) *Advances in the science of Victorian brown coal*. Oxford, UK
- Li CZ (2007) Some recent advances in the understanding of the pyrolysis and gasification behavior of Victorian brown coal. *Fuel* 86(12–13):1673–1679
- Li CZ, Sathe C, Kershaw JR, Pang Y (2000a) Fates and roles of AAEM species during the pyrolysis of a Victorian brown coal. *Fuel* 79(3):427–438
- Li CZ, Sathe C, Kershaw JR, Pang Y (2000b) Fates and roles of alkali and alkaline earth metals during the pyrolysis of a Victorian brown coal. *Fuel* 79(3):427–438
- Li X, Hayashi JI, Li CZ (2006) FT-Raman spectroscopic study of the evolution of char structure during the pyrolysis of a Victorian brown coal. *Fuel* 85(12/13):1700–1707
- Manquai KL, Snape C, McRobbie I, Barker J, Pellegrin V (2009) Comparison of the combustion reactivity of TGA and drop tube furnace chars from bituminous coal. *Energy Fuels* 23(9):4269–4277
- McKendry P (2002) Energy production from biomass (part 3): gasification technologies. *Bioresour Technol* 83(1):55–58
- Meijer R, Weeda M, Kapteijn F, Moulijn JA (1991) Catalyst loss and retention during alkali-catalysed carbon gasification in CO₂. *Carbon* 29(7):929–941
- Miura K, Hashimoto K, Silveston PL (1989) Factors affecting the reactivity of coal chars during gasification, and indices representing reactivity. *Fuel* 68(11):1461–1475
- Quyn DM, Wu HW, Li CZ (2002a) Volatilisation and catalytic effects of AAEM species on reactivity of char from pyrolysis and gasification of Victorian brown coal. Part II. Effects of chemical form and valence. *Fuel* 81:151–158
- Quyn DM, Wu H, Li C-Z (2002b) Volatilisation and catalytic effects of AAEM species on reactivity of char from pyrolysis and gasification of Victorian brown coal. Part I. Volatilisation of Na and Cl from a set of NaCl-loaded samples. *Fuel* 81(2):143–149
- Quyn DM, Wu H, Hayashi JI (2003) Volatilisation and catalytic effects of AAEM Species during the pyrolysis and gasification of Victorian brown coal. *Fuel* 82:587–593
- Senel IG, Gürüz AG, Yucel H, Angelo WK, Sarofim AF (2001) Characterization of pore structure of Turkish coals. *Energy Fuels* 15(2):331–338
- Serrano-Talavera B, Munoz-Guillena J, Linarez-Solano A, Salinas-Martines de Lecea C (1997) Biodegradation aspects of Polycyclic Aromatic Hydrocarbons. *Energy Fuels* 11:785
- Takarada T, Ishikawa H, Abe H, Nakaike Y (1995). Alkali volatilisation during pyrolysis and gasification of coal. In *Proceedings 8th International conference on coal science*. Elsevier, Amsterdam 687–691
- Tomita A, Ohtsuka Y, 2004. *Gasification and combustion of Brown coal*. Oxford: 223
- Woon JL, Sang DK (1995) Catalytic activity of alkali and transition of metal salt mixtures for steam-char gasification. *Fuel* 74(9):1387–1391
- Wu H, Hayashi JI, Quyn DM, Li CZ (2004) Volatilisation and catalytic effects of AAEM species during the pyrolysis and gasification of Victorian brown coal. Part V, Combined effects of Na concentration and char structure on char reactivity. *Fuel* 83:23–30
- Zhang S, Hayashi JI, Li CZ (2011a) 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-H₂O and char-O₂ reactivities. *Fuel* 90:1655–1661
- Zhang S, Min ZH, Tay HL, Asadullah M, Li CZ (2011b) Effects of volatile-char interactions on the evolution of char structure during the gasification of Victorian brown coal in steam. *Fuel* 90:1529–1535
- Zhou S (2002) Inquiry on coke quality indexes. *Iron Making* 21:22–25
- Zhu WK, Song WL (2008) Catalytic gasification of char from co-pyrolysis of coal and biomass. *Fuel Process Technol* 89(9):890–896
- Zhuang Q, Kyotani T, Tomita A (1996) Desorption behavior of surface oxygen complexes on carbon in an inert gas and in O₂-gasification atmosphere. *Energy Fuels* 10(1):169–172
- Zhuo Y, Lemaigmen L, Reed GP, Dugwell DR, Kandiyoti R (2000) Attempt to correlate conversions in pyrolysis and gasification with FT-IR spectra of coals. *Energy Fuels* 14(5):315