

# Thermogravimetric analysis on gasification reactivity of Hailar lignite

## Influence of inherent mineral matters and external ash

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**Abstract** Comparative studies on the Hailar lignite pyrolysis/gasification characteristics at N<sub>2</sub>/CO<sub>2</sub> atmosphere and the influence of inherent mineral matters, external ash and pyrolysis temperature on its reactivity during gasification at CO<sub>2</sub> atmosphere were conducted by non-isothermal thermogravimetric analysis, FTIR, and X-ray diffraction (XRD) analysis. Thermogravimetric test results show that the atmosphere of N<sub>2</sub> or CO<sub>2</sub> almost has no effects on the pyrolysis behavior, and the gasification reaction under CO<sub>2</sub> atmosphere occurs over 943 K at the heating rate of 40 K min<sup>-1</sup>. The external ash prepared at 1173 and 1223 K shows a certain catalytic effect on promoting the gasification reaction, although the inherent mineral matters of Hailar lignite are found in stronger catalytic effects on gasification than the external ash. The lignite gasification reactivity decreases with increasing pyrolytic temperature between 1073 and 1273 K.

**Keywords** Lignite · Gasification reactivity · Conversion fraction · Thermogravimetric analysis

### Introduction

Coal occupies about 70% of the total primary energy consumption in China and it is estimated that it will be kept

around 50% in 2050 [1, 2]. The amount of lignite resource is over 1,290 million tons and counts for 12.7% of the total coal reserves, and gasification can be regarded as a feasible thermochemical conversion technology to utilize lignite due to its high chemical activity and volatile matter. The gasification of lignite can be influenced by many factors, such as inherent mineral matters, particle size, heating rate, temperature, pressure, gasifying agents [3, 4]. Among the many gasification processes, the dual-bed gasification technology has been widely regarded as an advanced technology and was received considerable attentions. In the dual-bed gasification process, the circulating ash works as the solid heat carrier to supply part of the energy required for gasification reactions, and it is important that whether the ash influences the gasification behavior of the lignite.

Presently, the research on the effects of external ash on coal gasification is very few, and the discussions are mainly on the effects of inherent mineral materials. Skodras and Sakellaropoulos [5] and Samaras et al. [6] investigated the influence of mineral matters on the Greek lignite gasification by thermogravimetric analysis (TG) and fixed-bed reactor. They found that Ca, Na, K, and Mg elements have distinct catalytic effects on promoting gasification rate in CO<sub>2</sub> atmospheres. Köpsel and Zabawski [7, 8] found that the inherent mineral matters had some catalytic effects on the demineralized coal gasification. Otto et al. [9] found that ash from reactive coals can significantly enhance the gasification rates of chars derived from less reactive coals, while the effects of ashes on raw coal gasification and especially the effects of ash-producing temperature on that were not discussed.

Thermogravimetric analysis is one of the most commonly used thermal analysis techniques to study the thermal chemical behavior of carbonaceous materials. There are two modes of TG for estimating the reactivity of coal: isothermal

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[10–15] and non-isothermal [16–21]. In this work, the Hailar lignite from Inner Mongolia of China is taken as the initial raw material, and its gasification characteristics is investigated by non-isothermal TG, FTIR, and X-ray diffraction (XRD) methods. The main objective of the study is to investigate the catalytic effects of inherent mineral matters and external ash of different ash-producing temperatures on the gasification of lignite in CO<sub>2</sub> atmosphere, and the influences of pyrolysis temperature are also discussed.

## Experimental

### Preparation of coal samples

All the Hailar lignite samples were ground to less than 75 μm. The proximate and ultimate analysis and the ash constituent of the raw coal were listed in Table 1 and Table 2. The demineralized coal sample preparation procedures are like this: First, the raw coal samples were treated by mixed solution (the distilled water: 37% HCl : 40% HF = 50: 30: 20) at 333 K for 4 h to remove the inherent mineral matters; then the demineralized samples were washed with distilled water until no precipitation was detected by AgNO<sub>3</sub> solution, and the PH value of the washed water approaches 7. Finally, the demineralized samples are dried at 378 K and then preserve in sampling bag.

### Preparation of ash samples

Ash samples were prepared according to the GB/T 212-2008. Briefly, when the temperature of muffle furnace raised to 1123 K, the coal samples were put inside, then calcined at 1088 K for 40 min and the residues were denoted as Ash-1088. Then the Ash-1088 was recalcined in muffle furnace at 1173, 1223, and 1273 K for 50 min denoted as Ash-1173, Ash-1223 and Ash-1273, respectively.

**Table 1** Proximate analysis and ultimate analyses of Hailar lignite

Proximate analysis/wt <sub>ad</sub> %				Ultimate analysis/wt <sub>ad</sub> %				
M	VM	A	FC	C	H	O	N	S
8.35	37.71	9.24	44.70	61.17	4.62	16.38	0.06	0.18

*ad* air dry basis

**Table 2** Ash compositions of Hailar lignite (wt%)

SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	Fe <sub>2</sub> O <sub>3</sub>	CaO	MgO	TiO <sub>2</sub>	K <sub>2</sub> O	Others
36.22	14.47	13.18	13.01	2.82	0.48	4.83	14.99

Pure SiO<sub>2</sub> particles were used here as a reference to determinate whether the Ash-1173, Ash-1223, and Ash-1273 samples showed the catalytic effects on Hailar lignite gasification reaction because it had been proved to be inert during gasification. The Hailar lignite was mixed with SiO<sub>2</sub>, Ash-1173, Ash-1223 and Ash-1273 samples at a mass ratio of 1:2 and the mixed samples were denoted as HS, HA-1173, HA-1223, and HA-1273.

### Preparation of char samples

Char samples were prepared by the steps below: the coal samples of 6.0 g in the crucible with a cap were sent to muffle furnace for 50 min at 1073, 1173, and 1273 K, respectively. Then the char samples were taken out from the muffle furnace and cooled down to room temperature. The char samples were denoted as Char-1073, Char-1173, and Char-1273.

### Thermogravimetric analysis

The non-isothermal thermogravimetric analyses were carried out with a Netzsch STA-449C thermogravimetric analyzer: a sample of about 5 mg was weighted and put into an open alumina crucible for each run. The samples were heated from ambient temperature to an end temperature of 1473 K at a fixed heating rate of 40 K min<sup>-1</sup> at CO<sub>2</sub> atmosphere for gasification and N<sub>2</sub> atmosphere for pyrolysis. The flow rates of N<sub>2</sub> and CO<sub>2</sub> were set at 50 mL min<sup>-1</sup>.

### FTIR characterization

Infrared spectra of both Hailar lignite and the demineralized Hailar lignite were obtained by FTIR spectrometer (Bruker EQUINOX 55). The coal samples and the dried KBr were ground at a ratio about 1:100. The spectra were obtained with 32 scans at a resolution of 4 cm<sup>-1</sup>.

### XRD characterization

Ash-1173, Ash-1223 and Ash-1273 samples were characterized by XRD (X' Pert MPD Pro, made by PANalytical B.V. Almelo, the Netherlands) using monochromatic Cu Kα radiation at 40 kV and 30 mA ( $\lambda = 1.5406 \text{ \AA}$ ) to identify and quantify the phases insides the ashes. Scans were conducted at a scanning range from 5° to 60° 2θ with a scanning rate of 2°/min and a step size of 0.033°.

### Thermogravimetry data processing

The thermogravimetry (TG, %) and differential thermogravimetry (DTG, %/min) data were obtained by the following Eqs. 1 and 2, respectively.

$$TG = \frac{m_t}{m_0} \times 100\% \quad (1)$$

$$DTG = \frac{d\left(\frac{m_t}{m_0}\right)}{dt} \times 100\% \quad (2)$$

The conversion fraction ( $X$ ) and reactivity ( $\frac{dX}{dt}$ ) were defined by Eqs. 3 and 4:

$$X = \frac{m_t - m_f}{m_0 - m_f} \times 100\% \quad (3)$$

$$\frac{dX}{dt} = \frac{d\left(\frac{m_t - m_f}{m_0 - m_f}\right)}{dt} \times 100\% \quad (4)$$

where  $m_t$  is the instantaneous sample weight at the time  $t$ ,  $m_0$  is the initial sample weight,  $m_f$  is the weight of remaining ash after complete reaction.

## Results and discussions

### TG and DTG results of pyrolysis and gasification of Hailar lignite

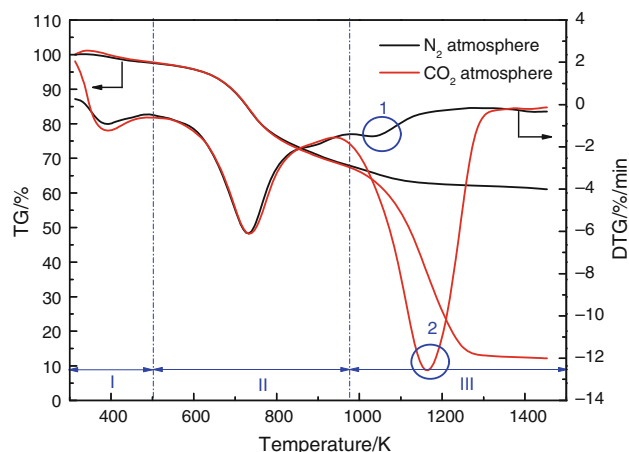
TG and DTG results of pyrolysis and gasification of Hailar lignite are shown in Fig. 1. It can be seen that the gasification process in  $\text{CO}_2$  atmosphere can be separated into three stages. The first stage is the drying stage ( $<513$  K) and the TG curve shows a slightly downward trend, and there is a small peak in the DTG curve. The basic decomposition products are water and the adsorbed gases, such as  $\text{CO}$ ,  $\text{CO}_2$ , and  $\text{CH}_4$ . The second stage is the pyrolysis stage ( $513 \sim 943$  K). The DTG curve has a peak value at 733 K, and the corresponding weight loss is about 31.58%. The decomposition products in this stage are complex, mainly consists of the gaseous hydrocarbon and tar, besides the  $\text{CO}$ ,  $\text{CO}_2$  and  $\text{CH}_4$ . The third stage ( $943 \sim 1473$  K) is mainly the char gasification step, and the main products are  $\text{CO}$  and  $\text{CO}_2$ . The total weight loss of coal samples in  $\text{CO}_2$  atmosphere is 87.35% at the end temperature of 1473 K, higher than 38.85% in  $\text{N}_2$  atmosphere, due to the gasification of char in  $\text{CO}_2$ . The TG as well as the DTG curve almost has the same tendency in the weight loss both in  $\text{N}_2$  atmosphere and in  $\text{CO}_2$  atmosphere from the initial temperature to 943 K, and the weight losses are quite similar (31.73% and 31.85, respectively). Thus, the experimental results indicate that atmosphere has little effects on the pyrolytic behaviors of Hailar lignite. The major differences between the two DTG curves are marked as 1 and 2 in Fig. 1. There is a weak peak of DTG curve in  $\text{N}_2$  atmosphere at about 1033 K, while the major peak in  $\text{CO}_2$  atmosphere appears at about 1163 K. The peak 1 may be attributed to the decomposition of the mineral matters of

calcite as mentioned in reference [22, 23] that calcite will decompose and release  $\text{CO}_2$  at about 1033 K. The peak at 1163 K in DTG curve for  $\text{CO}_2$  atmosphere can be attributed to the gasification of the nascent char. The decomposition of calcite may also be partly attributed to this peak, since the decomposition temperature of calcium carbonate in pure  $\text{CO}_2$  is about 1173 K.

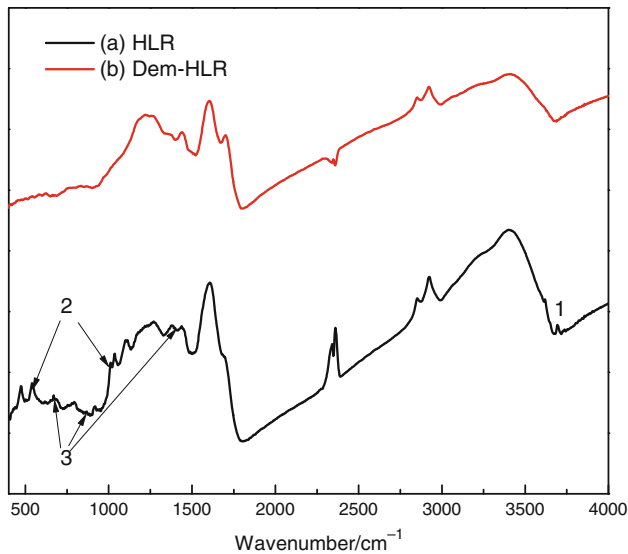
### The effects of inherent mineral matters on lignite gasification

Figure 2 shows the differences of the FTIR spectra between the Hailar raw coal and the demineralized coal samples. In Fig. 2a, the absorption bands near  $1450\text{--}1410$ ,  $880\text{--}860$ , and  $720\text{--}680$   $\text{cm}^{-1}$  in the spectra of the raw coal can be identified as carbonates [24–26]. Considering the metal elements of ash sample in Table 2, the alkaline, alkaline-earth compounds and transition-metal compounds, such as  $\text{Na}_2\text{CO}_3$ ,  $\text{CaCO}_3$ ,  $\text{FeCO}_3$  may exist in the Hailar lignite because of the high concentration of carbonates. The absorption bands of silicate minerals near  $1100\text{--}800$  and  $600\text{--}400$   $\text{cm}^{-1}$  and those of kaolinite near  $3700\text{--}3600$   $\text{cm}^{-1}$  [27–29] can also be identified in the spectra of raw coal. On the contrary, the absorption bands of silicates, kaolinite and carbonate have almost disappeared at all after the demineralization as shown in Fig. 2b. To be mentioned, the peak around  $2358$   $\text{cm}^{-1}$  is the adsorbed  $\text{CO}_2$  in raw coal, and the adsorbed  $\text{CO}_2$  is removed after the demineralization.

The conversion fraction ( $X$ ) as well as reactivity ( $\frac{dX}{dt}$ ) of the Hailar lignite and the demineralized samples are shown in Fig. 3. The results show that the reactivity ( $\frac{dX}{dt}$ ) of the demineralized sample is similar to that of the lignite less than 973 K. For the case higher than 973 K, the gasification of the raw coal sample terminated at about 1263 K,



**Fig. 1** TG and DTG curves of the Hailar lignite pyrolysis and gasification

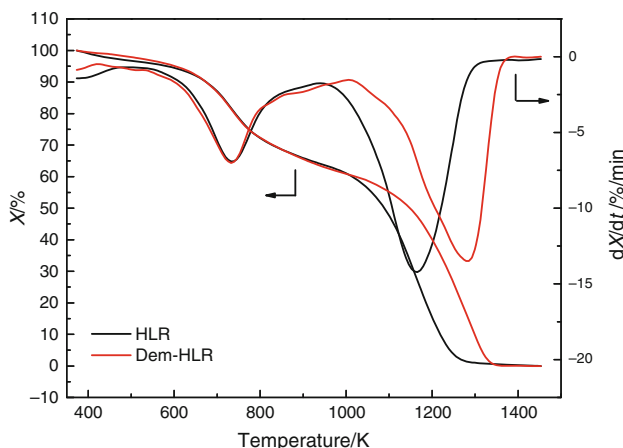


**Fig. 2** FTIR spectra of lignite investigated: **a** demineralized Hailar lignite (Dem-HLR); **b** Hailar lignite (HLR): 1 Kaolinite; 2 silicate minerals; 3 Carbonates

60 K prior to that of the demineralized sample, and the temperature corresponding to the maximum conversion fraction ( $X$ ) temperature of the raw coal sample is 1163 K, lower than that of the demineralized one (1281 K). This indicates that the raw sample perform a higher reactivity ( $\frac{dX}{dt}$ ) than that of the demineralized sample. It also indicates that the inherent mineral matters of Hailar lignite have strong catalytic effects on gasification process.

#### The effects of external ash on lignite gasification

Figure 4 shows the effects of Ash-1173, Ash-1223, and Ash-1273 samples on the gasification of Hailar lignite and the effects of  $\text{SiO}_2$  as inert matter is also illustrated for comparison. It can be seen that the maximum value of  $\frac{dX}{dt}$  is

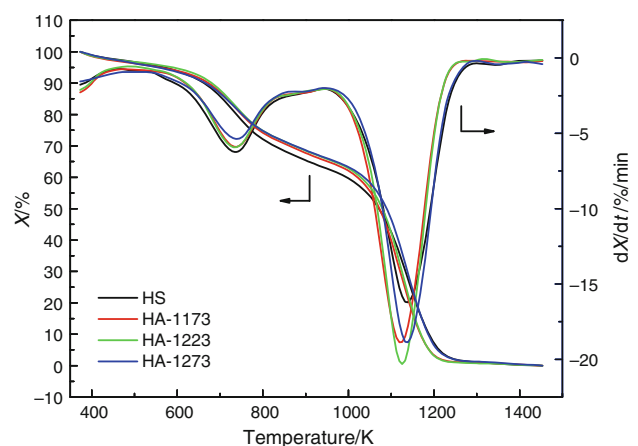


**Fig. 3** Curves of the conversion fraction ( $X$ ) and reactivity ( $\frac{dX}{dt}$ ) of the raw lignite and the demineralized lignite versus temperature

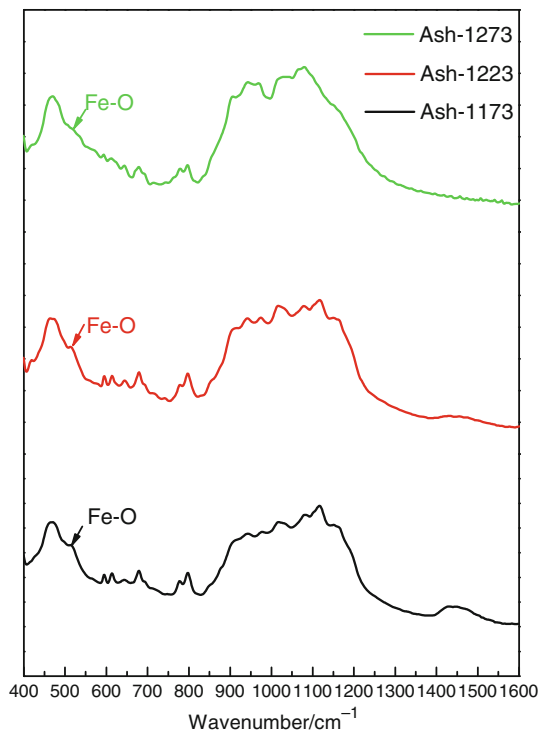
–16.19%/min for HS sample appeared at 1137 K, and the maximum value for HA-1173, HA-1223 and HA-1273 samples are –18.44, –19.68, and –18.37%/min at the temperatures of 1122, 1125, and 1137 K, respectively. The temperature corresponding to the maximum conversion rate of HA-1173 and HA-1223 samples is obviously lower than that of HS sample ranged from 1073 K to the end temperature, while the sample of HA-1273 almost has no difference to that of HS. The result indicates that Ash-1173 and Ash-1223 can promote the gasification conversion of raw coal, while Ash-1273 almost has no catalytic effect on lignite gasification.

To explain the different catalytic effects among the different external ash samples, FTIR analysis was conducted as shown in Fig. 5. It can be seen that the peak of  $520 \text{ cm}^{-1}$  [30], representation of Fe–O vibration in the sample is distinctly weaker for Ash-1273 than the peaks for the other two samples treated under lower temperatures of 1173 and 1223 K. The Fe–O vibration belongs to  $\text{Fe}_2\text{O}_3$ , which has been confirmed by XRD analysis. As proved by other researches that  $\text{Fe}_2\text{O}_3$  has certain catalytic effects by oxygen transfer mechanism on coal gasification reaction [31–35], and thus the decrease of the content of  $\text{Fe}_2\text{O}_3$  in the sample of Ash-1273 makes the catalytic effect on gasification decrease.

To further explain the catalytic effects of the ashes, XRD analysis was conducted as shown in Fig. 6. It shows that the element Ca in the ash sample of Ash-1273 has been partly transformed to calcium sulfate and silicates and thus lost much catalytic activity. Additionally, the figure shows that the minerals such as augite, aluminian and akermanite–gehlenite with lower catalytic activity on gasification exist by the peak around  $2\theta = 30^\circ$  in the XRD patterns of these ash samples. The peak intensity around  $2\theta = 30^\circ$  for Ash-1273 becomes stronger than those for Ash-1173 and

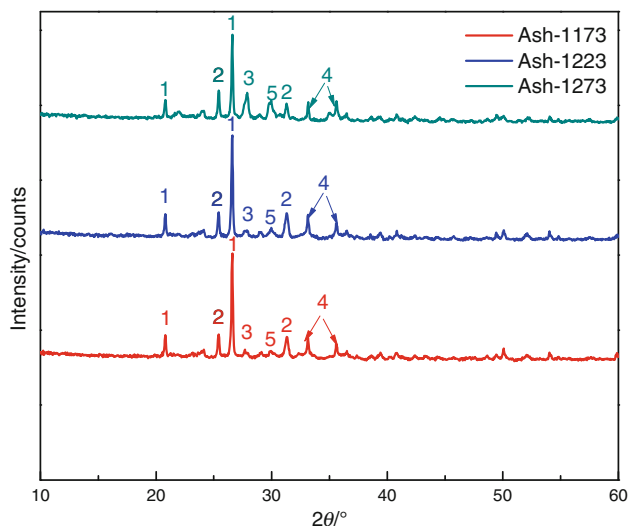


**Fig. 4** Curves of the conversion fraction ( $X$ ) and reactivity ( $\frac{dX}{dt}$ ) of HS, HA-1173, HA-1223, HA-1273 versus temperature

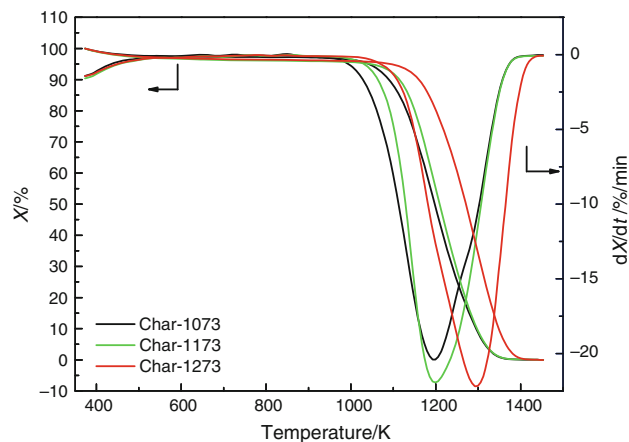


**Fig. 5** Comparison of FTIR spectra of different ash samples

Ash-1223, which indicates that more Fe<sub>2</sub>O<sub>3</sub> is transformed into the minerals above at higher temperature. So the Ash-1173 and Ash-1223 show more catalytic effects on the gasification than Ash-1273.



**Fig. 6** Comparison of XRD patterns of different ash samples: 1 quartz (SiO<sub>2</sub>); 2 calcium sulfate (CaSO<sub>4</sub>); 3 calcium aluminum silicate Ca(Al<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>); 4 hematite (Fe<sub>2</sub>O<sub>3</sub>); 5 Augite (Ca<sub>0.61</sub>Mg<sub>0.76</sub>Fe<sub>0.49</sub>(SiO<sub>3</sub>)<sub>2</sub>), aluminian (Al<sub>0.2</sub>Ca<sub>0.9</sub>Fe<sub>0.1</sub>MgO<sub>6</sub>Si<sub>1.8</sub>), akermanite–gehlenite (Ca<sub>2</sub>(Mg<sub>0.5</sub>Al<sub>0.5</sub>)(Si<sub>1.5</sub>Al<sub>0.5</sub>O<sub>7</sub>))



**Fig. 7** Curves of the conversion fraction ( $X$ ) and reactivity ( $\frac{dX}{dt}$ ) versus temperature for Char-1073, Char-1173 and Char-1273

**Table 3** Indicative temperatures of different char samples

	Char-1073	Char-1173	Char-1273
$T_{X=0.5}/K$	1198	1210	1266
$T_{(\frac{dX}{dt})_{max}}/K$	1195	1199	1295

### The effects of pyrolysis temperature on lignite gasification

A gasification process involves an initial pyrolysis stage and a subsequent char gasification stage. The conditions in the pyrolysis stage can influence the char yield and the char gasification reactivity. The curves of conversion fraction ( $X$ ) and reactivity ( $\frac{dX}{dt}$ ) versus temperature for Char-1073, Char-1173, and Char-1273 are shown in Fig. 7. Herein, the two values of  $T_{X=0.5}$  and  $T_{(\frac{dX}{dt})_{max}}$  representing the temperature when the mass loss is 50% and the temperature when the mass loss rate reaches the maximum value, are used as indicative temperatures to estimate the reactivity of char [36, 37]. As shown in Table 3, the both values of  $T_{X=0.5}$  and  $T_{(\frac{dX}{dt})_{max}}$  increase with the increasing pyrolysis temperature in the coal pyrolysis process for char-producing. Figure 7 shows that the char-producing temperature in the range from 1073 to 1173 K has slightly influence on the char gasification reactivity, while the char-1000 sample obtained under 1273 K shows a rather low gasification reactivity compared to the other two char samples.

### Conclusions

- (1) The Hailar lignite gasification process in CO<sub>2</sub> atmosphere by the TG analysis can be divided into three stages: drying, pyrolysis and char gasification. The

gasification reaction starts at the temperature higher than 943 K at the test conditions.

- (2) The external ash prepared at 1173 and 1223 K shows a certain catalytic effect on promoting the gasification reaction, although the inherent mineral matters of Hailar lignite are found in stronger catalytic effects on gasification than the external ash. The external ash obtained at 1273 K almost has no catalytic effects on lignite gasification.
- (3) The char obtained under different pyrolysis temperature has different indicative temperatures during gasification. The char prepared in lower temperature from 1073 to 1173 K has a higher gasification reactivity than that in higher temperature of 1273 K.

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