Influence of cooling rate on structure and combustion reactivity of char during char preparation process

Huanying Chi¹, Sheng Su¹,²*, Jun Xiang ¹,², Pengfeng Yu³, Haizhou Huang³, Tingting Guo⁴ and Hanjian Li¹

¹ State key laboratory of coal combustion, School of Energy and Power Engineering, Huazhong University of Science and Technology, Wuhan, Hubei, 430074, China
² China-EU Institute for Clean and Renewable Energy at Huazhong University of Science and Technology, Wuhan, Hubei, 430074, China
³ Huadian Electric Power Research Institute Co., Ltd., Hangzhou, Zhejiang, 310030, China
⁴ China Datang Corporation Science and Technological Research Institute, Beijing, 100040, China

*susheng@mail.hust.edu.cn
*Corresponding author’s e-mail: susheng_sklcc@hotmail.com

Abstract. Different chars with various cooling rates were obtained in the novel concentrating photothermal reactor to investigate the influence of cooling rate on the structure and combustion reactivity of char. The chars were prepared at 900°C with holding time of 10s, 30s and 120s, respectively. Subsequently, the cold (ex-situ) chars were prepared from the hot (in-situ) chars by controlling different cooling rates of 180°C/s (fast cooling rate), 30°C/s (sub-fast cooling rate), 6.8°C/s (moderate cooling rate) and 1.3°C/s (slow cooling rate). The ex-situ chars were then employed for the combustion in 30%O₂/70%CO₂ atmosphere at 900°C for 180s. For comparison, the in-situ char was conducted by instantaneously switching the reaction atmosphere. For the chars with holding time of 10s, the mass fraction of in-situ char was higher than the char yield of ex-situ char, and the char yield was decreased with the decrease of cooling rate. The char yield with slow cooling rate was decreased by 11.16% than that with fast cooling rate. The maximum and average mass loss rate of char in O₂/CO₂ was decreased as the cooling rate decreased. Reduced influence of cooling rate on the aromatic ring systems of char with holding time of 30s and its reactivity was displayed, while almost no difference of those with holding time of 120s was illustrated. The reactivity was closely related to the chemical structure of the char, but no positive correlation was found between the combustion reactivity and the specific surface area of char. The residues proportion of volatile components was the decisive factor of char reactivity.

1. Introduction
The char combustion duration accounts for about 70-80% of the entire coal combustion process[1]. The structure and reactivity of chars have been widely investigated, which are of significant guidance for the design and optimization of coal combustion boilers. The chars were prepared after pyrolysis process and followed by cooling process. Generally, there are different cooling methods for char preparation. After pyrolysis for certain holding time, the reactor was usually taken out of the high-temperature furnace and moved to dry ice or liquid nitrogen with ultra-fast cooling rate[2], or to room environment to be cooled...
down naturally[3-5]. Otherwise, the chars would stay in the original position, just waiting for the temperature of electric furnace naturally cooling down[6]. Different cooling methods have different advantages and disadvantages, and there are no fixed requirements of char preparation.

The preparation methods of chars had great influence on their structure and reactivities. Some researchers[7, 8] found that the hot chars (in-situ chars, without cooling) had more microporous structure and larger specific surface area than the cold chars (ex-situ chars). Xu et al.[2] believed that the "cold quenching" effect might occur during cooling process and further changed their reactivities. The reactivities of chars decreased significantly as the cooling rates increased. Moreover, the cooling rate slightly affected the chemical structure of chars, while the specific surface area was remarkably significantly decreased with the increase of the cooling rate owning to the destruction of pore structure. By contrast, Fang et al.[1] concluded that the reactivity of char decreased with the decrease of cooling rate and indicated that char deactivation during the cooling process was independent of specific surface area. The conclusions for influence of cooling rates on the structure of chars are different and need further clarify to guide industrial application.

In this study, the real-time mass loss of coal during devolatilization process was investigated on the novel concentrating photothermal experimental reactor. The ex-situ chars with different holding times were cooled with various cooling rates, and further characterized by N2 adsorption technique and Raman spectra. The combustion reactivities of the ex-situ chars were compared with those of the in-situ chars with same holding time. The effects of cooling rate on the structure and reactivity were analyzed and quantified.

2. Experimental Processes

2.1 Coal Sample
A typical Chinese coal (Zhundong coal) was ground and sieved to obtain the size ranging from 74 µm to 105 µm. The proximate and ultimate analyses of coal are shown in Table 1.

| Proximate analysis (wt.%, ad) | Ultimate analysis (wt.%, ad) |
|-----------------------------|-----------------------------|
| M  \ V  A  FC  C \ H \ O*  N \ S | 14.34 24.91 6.85 53.91 61.45 4.29 12.20 0.46 0.41 |

*By difference.

2.2. The novel concentrating photothermal experimental reactor
Experiments were carried out on the novel concentrating photothermal experiment reactor, schematically shown in Figure 1.

Figure 1. Schematic diagram of the concentrating photothermal experimental reactor
800 ml/min of Ar was introduced into the reactor as reaction gas, and 400 ml/min of Ar was fed into the balance as shielding gas. 100±2mg coal powders were pressed (10MPa) to form cylindrical pellets, which were placed in the focus spot of the concentrating photothermal lamps and suspended by the balance (Sartorius, BSA-224s) with accuracy of ±0.1mg through a connecting rod. The surface temperature of coal was detected by φ0.5 mm thermocouple with accuracy of ±0.1℃. Detailed setup about the experimental reactor has been provided elsewhere[9, 10]. The coal could be heated quickly as soon as the lamps powered on. The power would be stopped immediately after certain holding time and the temperature of the whole reaction chamber dropped quickly without any heat source.

2.3. Experimental Processes
Ex-situ chars with different holding times were prepared at 900℃ in Ar atmosphere, and then cooled with various cooling rates by controlling the decrease rate of voltage for the concentrating photothermal lamps at 180°C/s (fast cooling rate), 30°C/s (sub-fast cooling rate), 6.8°C/s (moderate cooling rate) and 1.3°C/s (slow cooling rate), respectively. The combustion reactivities of these ex-situ chars were conducted with the applied voltage of lamps once the reaction gas switched to 30% O2/70% CO2 simultaneously. For in-situ chars, the reactivities were evaluated in 900℃ after preparation with same certain holding times, and the reaction gas (Ar) was immediately switched to 30% O2/70% Ar.

2.4. Char characterization
The pore structural properties of ex-situ chars were obtained by using the N2 adsorption-desorption analyzer (JW-BK100A), and the specific surface areas were calculated with Brunauer-Emmett-Teller (BET) method. Raman spectra of chars were recorded by the Laser Raman spectrometer (Thermofisher DXR2) equipped with Nd-YAG laser (λo = 532 nm). The power of the laser was 5 mW and a 10× objective lens was used to focus the laser beam on the samples. The scans from 50 to 3500 cm−1 were performed on the samples.

3. Results and discussion
3.1. Effect of cooling rate on the char yield with different holding times
Figure 2 shows the mass loss and mass loss rate of coal particles in devolatilization process on the concentrating photothermal experimental reactor. The maximum mass loss rate was at about 10s. With the holding time of 30s, the release content of volatile matter exceeded 90% of the total volatile matter of coal, and the devolatilization process was almost complete at 120s. The holding time of 10s, 30s and 120s were selected for char preparation.

![Figure 2. Mass loss and mass loss rate of coal on the concentrating photothermal experimental reactor](image)

The mass fraction of in-situ char with holding time of 10s was 84.38%, while the char yields with fast, sub-fast, moderate, slow cooling rates were 73.16%, 68.67%, 64.08%, and 62.00%, respectively.
The char yield of ex-situ char with fast cooling rate was 86.71% of the in-situ char, while the char yield with slow cooling rate was 73.49% of the in-situ char. The char yield with slow cooling rate was decreased by 11.16% than that with fast cooling rate. Notably, coal could be pyrolyzed above 670K, accompanied by the broken of chemical bonds[11]. Obviously, the mass loss rate of char with holding time of 10s was high, the devolatilization of char with slow cooling rate could be continued in high temperature for relatively longer duration, which could further lead to decrease of char yield.

With holding time of 30s, the mass fraction of in-situ char was 64.15%, and the char yields with various cooling rates were 63.90%, 62.98%, 62.72%, and 61.54%, respectively. The char yields of ex-situ chars with fast cooling rate and slow cooling rate were 99.62% and 95.93% of the in-situ char. The char yield with slow cooling rate was decreased by 2.37% than that with fast cooling rate, which was only about one-fifth of char with holding time of 10s. This was mainly because the devolatilization process was almost complete with holding time of 30s, and most of the volatile matter had been released. The additional mass loss of char during cooling process was limited with slow cooling rate, which was explained that the influence of cooling rate was reduced with the holding time of 30s.

For the chars with holding time of 120s, the char yields were all about 61.00% with different cooling rates, and they were similar with the mass fraction of in-situ char. The volatile matter of coal had been completely released with holding time of 120s and cooling rate had basically no influence on the char yields.

3.2. Effect of cooling rate on the char structure with different holding times

3.2.1 Effect of cooling rate on the specific surface area of char.
Figure 3 shows the specific surface areas ($S_{BET}$) of coal/chars with different cooling rates. It could be seen that the $S_{BET}$ of raw coal was 5.65 m$^2$/g and it was smaller than the other chars. During the devolatilization process of coal with certain cooling rate, $S_{BET}$ was increased as the volatile released and then decreased owning to the collapses of pore structure in high temperature.

![Figure 3. The specific surface area of coal/chars with different cooling rates](image)

For the chars with holding time of 10s, the $S_{BET}$ with fast cooling rate was 12.48 m$^2$/g, which was only slightly larger than that of raw coal. The specific surface areas of chars increased as the cooling rate decreased from fast, sub-fast to medium cooling rate, mainly because more pores formed accompanied with the release of the volatile matter in the chars in high temperature for relatively longer duration than those with fast cooling rate. For the chars with holding time of 30s, the $S_{BET}$ with fast cooling rate was 238.95 m$^2$/g, which was the largest specific surface area among all the chars. The specific surface area of chars gradually decreased when the cooling rate slowed down. It indicated that after the devolatilization basically completed, with the decrease of cooling rate, remarkable collapse of
pores would be occurred for longer duration in high temperature and led the decrease of specific surface area. Similarly, for the chars with holding time of 10s, the $S_{BET}$ with slow cooling rate was lower than that with medium cooling rate, which revealed that the pore collapse had occurred and resulting the decrease of specific surface area. For the chars with holding time of 120s, the volatile matter had been completely released and the $S_{BET}$ with different cooling rates were similar for the formation of stable pore structure.

3.2.2 Effect of cooling rate on the aromatic ring systems of char.

The curve-fitting method proposed by Li [12] was carried out and 10 Gaussian bands were synthesized from first order Raman spectra of chars between 1800 cm$^{-1}$ to 800 cm$^{-1}$. The D band at 1300 cm$^{-1}$ can typically represent medium to large ($\geq$6) aromatic ring systems in char, whereas the Gr band at 1540 cm$^{-1}$, the Vl band at 1465 cm$^{-1}$, and the Vr band at 1380 cm$^{-1}$ together mainly represent the small (3–5) aromatic ring systems. Thus, the Raman band area ratio between the (Gr + Vl + Vr) bands and the D band can reflect the ratio of small aromatic ring systems to large ones. The total Raman peak area $I_{All}$ and Raman band ratio $I_{(Gr+Vl+Vr)}/I_D$ of coal/chars with different cooling rates are shown in Figure 4.

![Figure 4. Total Raman peak area $I_{All}$ (a) and Raman band ratio $I_{(Gr+Vl+Vr)}/I_D$ (b) of coal/chars with different cooling rates](image)

With the increase of holding time, the chemical bonds of macromolecular structure in coal would be broken during the devolatilization process, which could increase the total amount of chemical bonds and lead the $I_{All}$ to increase first. As the volatile matter released, the total amount of chemical bonds remained in the chars decreased, resulting of the $I_{All}$ decreased. During the whole devolatilization process, more and more small aromatic rings were consumed or converted into larger ones and led the $I_{(Gr+Vl+Vr)}/I_D$ gradually decreased. The $I_{All}$ and the $I_{(Gr+Vl+Vr)}/I_D$ were stable when the volatile released completely. As the cooling rate decreased, the $I_{All}$ and the $I_{(Gr+Vl+Vr)}/I_D$ of the chars with holding time of 10s were decreased. It indicated that with holding time of 10s, the char with slow cooling rate could release more volatile matter and would be more condensed in high temperature for longer duration. For the chars with holding time of 30s/120s, the $I_{All}$ and the $I_{(Gr+Vl+Vr)}/I_D$ of the chars with different cooling rates were slightly changed. In addition, for the chars undergoing rapidly release of volatile matter, different cooling rates would lead to different structural evolution laws. The $I_{All}$ of chars with fast and sub-fast cooling rates increased firstly and then decreased, while the $I_{All}$ with medium and slow cooling rates showed a tendency to decrease first and then stabilize. The conversion of chars with medium and slow cooling rates could cause the lack of detailed structural evolution of chars.

3.3. Effect of cooling rate on the reactivity of chars with different holding times.

Figure 5 shows the mass loss rates of in-situ and ex-situ chars with different cooling rates in 30%O$_2$/70%CO$_2$ atmosphere. For the chars with holding time of 10s, the average mass loss rates of in-
situ and ex-situ chars with various cooling rates were 0.43%/s, 0.37%/s, 0.34%/s, 0.32%/s, 0.31%/s, respectively. The average mass loss rate of in-situ char in O2/CO2 was higher than that of ex-situ chars, and it decreased with the decrease of cooling rate. For the in-situ char during the devolatilization process in Figure 2, the mass loss rate at 10s was the largest during the whole devolatilization process. When the reaction gas switched to O2/CO2, the maximum mass loss rate of the in-situ char with the holding time of 10s was the largest among all the chars. For the ex-situ chars with holding time of 10s in Figure 5(a), more volatile matter remained in char with fast cooling rate than that with slow cooling rate, which increased first and then decreased. As the cooling rate slowed down, the maximum mass loss rate gradually decreased. For the chars with holding time of 30s in Figure 5(b), the average mass loss rates of in-situ and ex-situ chars with different cooling rates were 0.32%/s, 0.32%/s, 0.31%/s, 0.31%/s, 0.30%/s, respectively. The cooling rates had little influence on the combustion reactivities of chars. As shown in Figure 2, the mass loss rate at 30s was decreased than that at 10s. The mass loss rate of in-situ char increased first and then gradually decreased when the reaction gas switch to O2/CO2. The char yields of chars with different cooling rates only differed by 2.37%. In other words, the difference of volatile matter contents of chars was limited, which led little difference of mass loss rates of chars with different cooling rates. With holding time of 120s in Figure 5(c), the average mass loss rate of ex-situ chars with different cooling rates were all about 0.30%/s, and they were nearly same with that of in-situ char. Almost no influence of the in-situ and ex-situ chars with different cooling rates on their combustion reactivities.

Overall, for the chars that undergoing fast pyrolysis, the cooling rate had great influence on the char structure and combustion reactivity. The slower the cooling rates, the longer time of the char stay at high temperature, resulting of more volatile matter released and decrease of reactivity. For the chars with holding time of 10s, the specific surface area of chars with fast cooling rate was small, but exhibited larger average and maximum mass loss rate in O2/CO2. For the chars with holding time of 30s, the specific surface area with fast cooling rate was the largest but the reactivity was not much larger than others. It indicated that the specific surface area did not play a major role on the combustion reactivities. After the volatiles were almost released, with the holding time of 30s/120s, the cooling rate had little effect on the total Raman peak area $I_{All}$ and the Raman band ratio $I_{Gr+Vr+Vf}/I_D$, and the reactivities of the chars were similar. The residues proportion of volatile matter was the decisive factor of char reactivity. The chemical structure played a leading role in the reactivities of chars.

4. Conclusions
In this work, coal conversion and char preparation were carried out on the novel concentrating photothermal experimental reactor. Effects of cooling rate on structure and combustion reactivity of char during char preparation process were studied. The main results in this study were as follows.

(1) The mass fraction of in-situ char with holding time of 10s was higher than the char yield of ex-situ chars with various cooling rates. The char yield decreased as the cooling rate decreased.

(2) For the chars with holding time of 10s, the specific surface area of chars with fast cooling rate
was small, but exhibited larger average and maximum mass loss rate in O₂/CO₂. For the chars with holding time of 30s, the specific surface area with fast cooling rate was the largest but the reactivity was not much larger than others. It indicated that the specific surface area did not play a major role on the combustion reactivities.

(3) The influence of cooling rate on aromatic ring systems of the ex-situ char with holding time of 30s/120s and their reactivity was smaller than those with holding time of 10s. The residues proportion of volatile components was the decisive factor of char reactivity.

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