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Influence of pyrolysis condition and coal type on char gasification reactivity

Xianhua Wang, Hanping Chen, Haiping Yang,* Fudong Ju and Shihong Zhang

State Key Laboratory of Coal Combustion Huazhong University of Science and Technology, Wuhan 430074, Hubei Province, China

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ABSTRACT: The CO₂ gasification property of char particles was investigated with pressurized and ambient thermal analyzer with four typical Chinese industrial coals as samples. The influence of pyrolysis pressure and final temperature was analyzed and a new index (specific maximum gasification rate) of char CO₂ gasification reactivity was approached. The process of char gasification can be divided into two steps: the thermal cracking and CO₂ shifting of volatile hydrocarbon residues and the CO₂ shifting of carbon matrix. Higher pressure did not show positive effect on char gasification enhancing as pyrolysis pressure lower than 1.5 MPa, whereas it was accelerated with pressure increasing further as more volatile hydrocarbon left in char particles. Temperature showed variant influence on char gasification with different pyrolysis pressures. There exist some interaction between pyrolysis temperature and pressure. Furthermore, coal type played vital role on char gasification behavior and the specific maximum gasification rate showed great consistency with char gasification behavior. © 2011 Curtin University of Technology and John Wiley & Sons, Ltd.

KEYWORDS: pressurized pyrolysis; temperature; char gasification; specific reactivity

INTRODUCTION

The gasification reactivity of coal greatly depends on the reactivity of coal char obtained from coal pyrolysis.^[1] The gasification reaction mainly takes place on the surface of solid char, and the physico-chemical property of solid charcoal plays a vital role on the reactivity of char gasification.^[2–5] However, char derived from coal pyrolysis, and therefore the property of original coal particles and pyrolysis condition is critical to char structure.^[6–10] Liu, *et al.*^[11] observed that high pyrolysis pressure is favored for the formation of char with high porosity and non-uniform porous structure. Cloke, *et al.*^[1,12] investigated the pyrolysis/gasification of different coals, and they found that the characteristic of original coal displayed significant influence on the property of coal pyrolysis and char gasification. However, rarely related data on Chinese coals pressurized gasification was showed so far. In this regard, the gasification behaviors of coal char from typical Chinese coal samples were investigated, and the influence of pyrolysis pressure and temperature was involved as well.

Normally, CO₂ reduction percent of char that resulted from coal pyrolysis was used to show the gasification reactivity of coal.^[13] However, current reactivity indexes of coal char were mostly based on coal/char combustion in air/O₂, which was limited to a given condition, but cannot be used for general index.^[14–16] Furthermore, coal/char gasification was rarely involved, especially for char gasification with CO₂. Hence, a new index of char gasification reactivity based on char-CO₂ gasification was put forward, and it was used to mark the gasification behavior of char observed from coal pyrolysis under variant pressures and temperatures.

SAMPLE AND EXPERIMENTAL METHOD

Coal samples

Four typical Chinese industrial coal samples were involved, They are Xiaolongtan brown coal (XLT), ShenFu bituminous coal (SF), Pingzhai anthracite coal (PZ), and C (HS) as well. The original sample was ground and sieved with a 100-mesh screen. The physical property of original coal samples was referred to Table 1.

Char particles were obtained from coal pyrolysis in a temperature-programmed pressurized TGA (TG Thermal

*Correspondence to: Haiping Yang, State Key Laboratory of Coal Combustion Huazhong University of Science and Technology, Wuhan 430074, Hubei Province, China. E-mail: yhpj2002@163.com

Table 1. Proximate and ultimate analyses of coal samples.

	Proximate analysis (wt%, ad)				Ultimate analysis (wt%, ad)				
	M	V	A	FC	C	H	N	S	O
XLT	16.16	48.90	24.76	26.34	41.35	3.46	3.04	1.18	10.05
SF	10.19	31.62	5.84	52.35	68.84	5.06	0.91	0.28	8.88
PZ	2.83	9.42	6.82	80.93	78.38	3.29	0.99	2.34	5.35
HS	3.10	11.94	51.89	35.88	33.06	1.73	0.50	6.00	3.72

XLT, Xiaolongtan brown coal; SF, ShenFu bituminous coal; PZ, Pingzhai anthracite coal; HS, carbon coal.

Max 500, Thermal Cahn, USA). Coal sample (~1 g) was heated to pre-set temperature at selective pressure with heating rate of 10 °C/min and Ar (100 ml/min) as purging gas. The pre-set pressure and temperature involved were (0.1, 0.8, 1.5, 3, and 5 MPa) and (500, 650, 800 and 1000 °C), respectively. SF coal—was selected as typical sample for the analysis the influence of pyrolysis pressure and final temperature on char gasification. The chemical component of char particles and the corresponding pyrolysis condition are listed in Table 2. It can be observed that the volatile content diminished greatly with pyrolysis temperature increasing; however, it increased with pyrolysis pressure enhancing, especially for final temperature higher than 650 °C. With respect to different coal samples, more hydrocarbon content showed for XLT char; it is similar with that of the original coal sample.

Experimental method and set-up

The gasification behavior of char particles was measured at atmospheric pressure. Isothermal char gasification experiments were performed using an ambient thermobalance (STA 409 C, NETZSCH, Germany) at 1000 °C with carbon dioxide as gasify agent. About 20 mg of char particles was charged into alundum container, which was then placed on the thermal balance (sensitivity is 0.1 µg). Then, the sample was heated to 1000 °C quickly at 50 °C/min in inert atmosphere with Ar protection (100 mL/min). Then, gasify agent CO₂ (100 mL/min) took the place of Ar and initialized char gasification. It was kept for 1 h to finish char CO₂ gasification.

Maximum specific gasification reactivity ($R_{s,max}$)

Maximum specific weight loss rate is the function of mass loss rate and the content of fixed carbon. The calculation equation can be written as follows:

$$R_{s,max} = -\frac{1}{W_0} \times \left(\frac{dW}{d\tau} \right)_{max} / FC \quad (1)$$

Where W_0 is the original mass of the sample at dried and free ash basis (mg), τ is the gasification time, as CO₂ input time was taken as initial point. W is the mass

of char at any given time (τ). FC is the fixed carbon content in char on dry and ash free basis, in case there is a need to eliminate the impact caused by inorganic matters and moisture in char sample. The higher the $R_{s,max}$ value, the better is the gasification reactivity of char.

RESULT AND DISCUSSION

Influence of pyrolysis pressure on char gasification

The gasification profile of SF char observed at variant pressures is plotted in Fig.1. It can be observed that the gasification rate was greatly enhanced while gasification was ongoing, and it stretched to its maximum value as carbon conversion reached ~10%. The gasification of hydrocarbon residue on char surface might play the main role; however, with char gasification continuing, it decreased gradually, and different changing trends were displayed with pyrolysis pressure variant. As pressure is lower than 3 MPa, gasification rate of char was kept constant at ~6 wt%/min till carbon conversion reached 80%, and then, it decreased quickly to zero. However, for char obtained at 5 MPa, it was gasified promptly, and the gasification rate increased greatly and achieved its maximum rate (14.4%/min) as carbon conversion reached ~14.5%. After that, it decreased largely to an equal value of char derived from lower pressure (<3 MPa) as carbon conversion was about 35%, and then similar property was showed with char gasification taking place. The high volatile content of char (5 MPa) might be the main reason for the high gasification velocity, whereas the CO₂ shifting of fixed carbon was quite slow.

The gasification of char particles can be described into two steps: cracking/CO₂ shifting of hydrocarbon residue and CO₂ gasification of fixed carbon. The former stage is homogeneous reaction, and it is quite rapid, whereas the fixed carbon gasification is mainly gas–solid reaction–heterogeneous reaction; it is mainly controlled by the rate of gas diffusing with limited reaction velocity. As more volatile content was left in char particles when SF coal pyrolysis was at higher pressure

Table 2. Proximate analysis of char observed from different coal types.

Char	XLT _{1000,0.1}	XLT _{1000,0.3}	PZ _{1000,0.1}	PZ _{1000,0.3}	HS _{1000,0.1}	HS _{1000,0.3}	SF _{1000,0.1}	SF _{1000,0.3}	SF _{1000,0.8}	SF _{1000,1.5}	SF _{1000,3}	SF _{1000,5}	SF _{500,0.1}	SF _{500,0.3}	SF _{500,0.8}	SF _{500,1.5}	SF _{500,3}	SF _{500,5}	SF _{800,0.1}	SF _{800,0.3}	SF _{800,0.8}	SF _{800,1.5}	SF _{800,3}	SF _{800,5}
V _{daf}	21.96	24.37	0	24.37	3.57	0	8.74	10.80	11.78	11.89	20.14	33.05	19.18	10.91	10.91	10.91	30.56	20.78	15.23	15.23	15.23	15.23	15.23	15.23
A _d	30.24	29.58	21.35	22.65	61.72	62.78	9.06	9.05	8.96	8.95	8.18	6.95	8.27	9.04	9.04	9.04	7.19	8.12	8.64	8.64	8.64	8.64	8.64	8.64
FC _{daf}	78.04	75.63	100	100	96.43	100	91.26	89.20	88.22	88.11	79.86	66.95	80.82	89.09	89.09	89.09	69.44	79.22	84.77	84.77	84.77	84.77	84.77	84.77
C _{daf} /H _{daf}	89.51	120.73	119.02	102.45	67.26	107.26	165.03	212.08	217.84	226.28	241.29	23.66	43.77	90.12	90.12	90.12	26.35	44.04	134.98	134.98	134.98	134.98	134.98	134.98

*V, volatile content; A, ash; C, carbon content in char; H, Hydrogen content; d, dried basis; daf, dry and free ash basis.
Note: coal_r, P, it indicated that char sample was observed from coal sample pyrolysis at final pyrolysis temperature ($T^{\circ}\text{C}$) and pressure (P(MPa)), respectively.

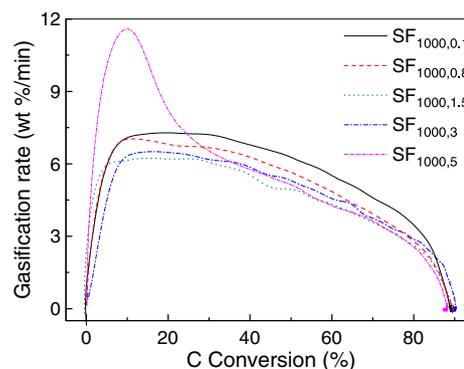


Figure 1. Gasification profiles of ShenFu bituminous coal char resultant at variant pressures. This figure is available in colour online at www.apjChemEng.com.

(refer to Table 2), the gasification rate was much higher (5 Mpa), whereas for char observed from lower pressure (<3 Mpa), minor difference was shown for the first range as similar volatile content showed in the char particles. However, the gasification rate of the second range for pressurized char is a little lower than that of ambient char, as the forming of macromolecule structure is enriched at higher pressure.^[17]

Influence of pyrolysis temperature on char gasification

The gasification profile of SF char observed at variant final temperatures was plotted in Figs. 2 and 3. For ambient char (Fig. 2), the gasification rate increased quickly and reached the maximum value (8–9 wt%/min) as carbon conversion was at ~10%, then, it kept constant with carbon advancing (10–30%). This was mainly the cracking and CO₂ shifting of hydrocarbon residues. It was a homogeneous reaction (gas–gas), and gasification velocity was quite fast. However, after that,

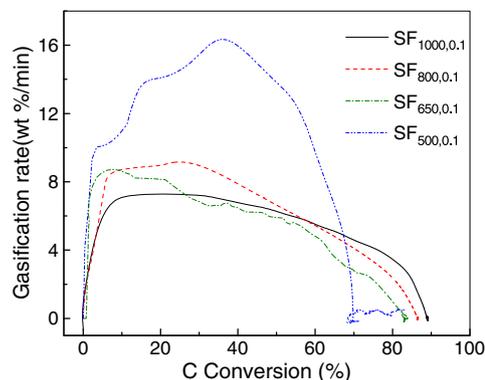


Figure 2. Gasification profiles of ShenFu bituminous coal char observed at different temperatures and 0.1 Mpa. This figure is available in colour online at www.apjChemEng.com.

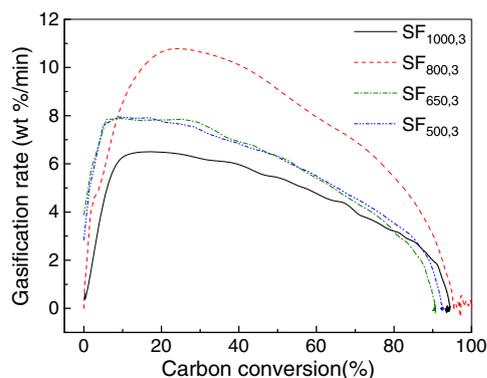


Figure 3. Gasification profiles of ShenFu bituminous coal char observed at different temperatures and 3 MPa. This figure is available in colour online at www.apjChemEng.com.

the gasification was slowed down. The gasification shifted to second range and was mainly controlled by CO_2 diffusing. Correspondingly, the reaction rate was a little lower. As carbon conversion was over $\sim 80\%$, the velocity reduced quickly to zero. It might be attributed to the inner carbon structure wherein the carbon structure was much compact. Furthermore, the inorganic matters left in char particles might wrap carbon particles making it difficult for the contacting of CO_2 and carbon matrix in the final stage.

With pyrolysis temperature decreasing, the maximum gasification rate increased straightly. For char obtained at 500°C and ambient pressure, the maximum gasification rate reached 16 wt\%/min at carbon conversion of 38% , attributable to the high volatile content in char particles ($\sim 33\%$). It confirmed the result that the cracking and CO_2 shifting of volatile residue account for the first step of char gasification. However, for char observed at 3 MPa, different trend was shown (Fig. 3). The value of maximum gasification rate increased and achieved the maximum value at 800°C , and then it decreased with its final temperature increasing. It might be attributed to the higher surface area and enriched porosity of char obtained at 800°C and 3 MPa.^[10] In comparison with ambient char, pyrolysis pressure enhancing showed a different influence on char gasification property with temperature increasing. Firstly, it enhanced the gasification of char sample when pyrolysis temperature was higher than 650°C , as higher pressure blocked the releasing of volatile compounds and more hydrocarbon left in char particles resulted in higher gasification rate. But contrary result was shown when pyrolysis temperature is lower than 650°C as the temperature was too low for volatile evolving out, hence, the influence of pressure on the chemical compound was neglected (Table 2). However, pressure showed great influence on physical structure as the volatile hydrocarbon tend to liquefy before releasing out under higher pressure. It easily blocked the pore

on char surface and was unfavorable for mass and heat transfer. Therefore, the gasification rate of $\text{SF}_{500, 0.1}$ is much higher than that of $\text{SF}_{500, 3}$. Furthermore, it can be derived that there existed some interaction between the influence of pyrolysis pressure and final temperature on the behavior of char gasification.

Influence of coal type on char gasification

The gasification profile of char observed from different coal types at ambient char is plotted in Fig. 4. For XLT char, the conversion rate increased greatly and achieved the maximum value ($\sim 40\text{ wt\%/min}$) as carbon conversion rate was lower than 30% . It might be attributed to the fact that higher volatile residue was shown in XLT char sample. It was similar with that of $\text{SF}_{500, 0.1}$. However, after that, the gasification rate decreased quickly as it was mainly CO_2 gasification of carbon elements in char, and the reaction was quite slow.

For PZ char particles, the gasification rate increased greatly and achieved the maximum gasification rate (15 wt\%/min), whereas carbon conversion was at $\sim 10\%$. Then, it decreased to 0.0175 wt\%/min at carbon conversion of 25% and was kept constant till char gasification finished. It was different from the gasification of SF char as lower volatile content showed in the original PZ coal, and almost no hydrocarbon compounds was left in the resulted char particles (Table 2). Hence, the gasification of PZ char was mainly the CO_2 shifting of carbon matrix. It was controlled by the physical structure and gasify agent diffusing. HS char showed similar gasification rate shape with XLT char gasification, whereas the maximum value is less lower (30 wt\%/min), but compared with PZ and SF char, it was much higher. It might be attributed to catalytic influence caused by the high inorganic matters in HS char (Table 1).^[18,19] However, as carbon conversion rate was higher than 70% , the gasification

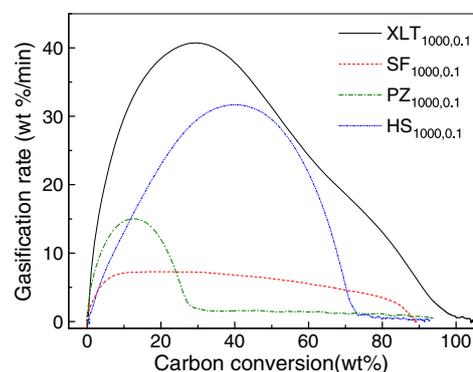


Figure 4. Gasification profiles of char resulted from different coal samples pyrolyzed at 0.1 Mpa. This figure is available in colour online at www.apjChemEng.com.

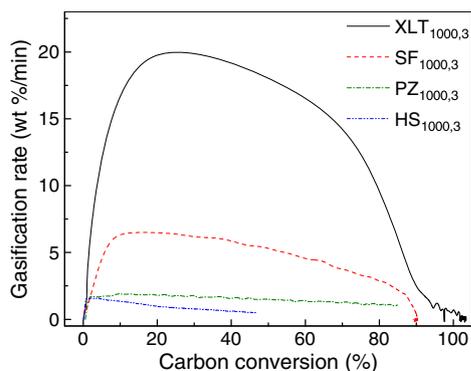


Figure 5. Gasification profiles of char obtained from different coal samples pyrolyzed at 3 Mpa. This figure is available in colour online at www.apjChemEng.com.

rate decreased to zero, and no CO₂ gasification took place anymore. This might be the cause that the ash content in HS coal was very high, and the fixed carbon residue in solid char particle was wrapped by inorganic compounds, and it was quite difficult for the contacting of Carbon–CO₂. With respect to the pressurized char (3 Mpa, Fig.5), the gasification rate of the resultant char was reduced largely. This might be related to the difference of physico-chemical structure of char samples caused by pyrolysis pressure as higher external pressure inhibited the forming of more surface pores, whereas higher pressure enhanced the graphitization of char particle, hence, the reactivity of CO₂ shifting was lowered obviously.

Maximum specific gasification reactivity

The maximum specific CO₂ gasification reactivity ($R_{s, \max}$) of char particles observed under variant condition is listed in Table 3. It can be observed that $R_{s, \max}$ decreased with pyrolysis pressure increasing and reached the minimum value at 3 Mpa, after that it increased greatly with pyrolysis pressure increasing further to 5 MPa, and obtained the maximum value at 5 MPa. It showed the similar result with gasification rate of char gasification. With respect to char obtained

at different temperatures, $R_{s, \max}$ decreased with final temperature increasing, and achieved the maximum value at pyrolysis temperature of 500 °C for ambient char. As pyrolysis pressure was 3 MPa, no obvious change was shown for $R_{s, \max}$ as temperature increased from 500 °C to 650 °C, but it increased greatly with temperature increasing further to 800 °C. However, when temperature was increased further, $R_{s, \max}$ decreased greatly. This was consistent with the trend of maximum gasification rate with temperature difference.

The XLT brown coal char showed highest gasification reactivity. The order of ambient char gasification reactivity was XLT > HS > PZ > SF, whereas it was XLT > HS > SF > PZ for pressurized char. Similar order was shown with the maximum gasification rate of char obtained from variant coal types. It indicated that $R_{s, \max}$ is efficient to indicate the gasification reactivity of char observed from variant pyrolysis condition and coal type.

CONCLUSION

The CO₂ gasification of char can be divided into two separate steps: thermal cracking and CO₂ shifting of volatile hydrocarbon residues with higher gasification rate and CO₂ shifting of fixed carbon in char particles with lower gasification velocity.

Pressure increasing is not favorable for the enhancing of char gasification as pressure is lower than 1.5 MPa, whereas contrary result showed with pressure increasing further. At ambient pressure, lower temperature pyrolysis pressure is favorable to achieve higher gasification rate, but for char resulting from higher pyrolysis pressure (3 MPa), it increased first and achieved the maximum value at 800 °C.

Gasification is easily achieved by XLT coal char CO₂-shifting, whereas for PZ and HS coal char, it is more difficult to attain gasification because of their lower hydrocarbon residue and compact physical structure. Specific maximum gasification rate ($R_{s, \max}$) was approached, and consistent result showed the gasification property as pyrolysis condition and coal type variant. Hence, it is effective to show coal gasification reactivity.

Table 3. $R_{s, \max}$ of solid chars CO₂ gasification.

Char	XLT _{1000, .1}	XLT _{1000,3}	PZ _{1000,0.1}	PZ _{1000,3}	SF _{1000,0.1}	SF _{1000,3}	HS _{1000,0.1}	HS _{1000,0.8}
$R_{s, \max}$ (h ⁻¹)	10.92	4.98	8.22	1.56	3.78	3.6	8.22	0.42
Char	SF _{500,0.1}	SF _{650,0.1}	SF _{800,0.1}	SF _{1000,0.1}	SF _{500,3}	SF _{650,3}	SF _{800,3}	SF _{1000,3}
$R_{s, \max}$ (h ⁻¹)	10.68	5.52	6.00	3.78	4.44	4.38	5.76	3.60
Char	SF _{1000,0.1}	SF _{1000,0.8}	SF _{1000,1.5}	SF _{1000,3}	SF _{1000,5}			
$R_{s, \max}$ (h ⁻¹)	3.78	3.66	3.54	3.60	5.16			

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