International Conference on Applied Energy 2019
Aug 12-15, 2019, Västerås, Sweden
Paper ID: 0008

THE RELATIONSHIP BETWEEN COAL CHAR REACTIVITY AND CHAR STRUCTURE AT RAPID HEATING CONDITION BY TG AND HEATING STAGE-MICROSCOPY

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ABSTRACT

The coal char reactivity is usually evaluated in TG at a low heating rate under ex-situ conditions, which is far from the real condition in boiler and gasifier. In this work, the isothermal CO_2 gasification reactivity of in-situ chars which were pyrolyzed under different heating rates and terminal temperatures was measured by a rapid TG apparatus. Furthermore, the char structural parameters were correlated with the reactivity index. Results showed that heating rate had little effect on the gasification reactivity of the in-situ char when it exceeded 50°C /min. The carbon crystalline structure related closely to the reactivity index. Simultaneously, the HTSM experiments demonstrated that the reaction rates were slightly higher compared with TG.

Keywords: heating rate, in-situ char, rapid TG apparatus, structural parameters, heating stage microscope

NONMENCLATURE

Abbreviations	
TG	Thermogravimetry
HTSM	Heating stage microscope
Symbols	
m_0	initial mass of char (mg)
m_t	mass of char at the time t (mg)
m_{ash}	mass of ash (mg)
A_0	initial projected area
A_t	the area of the reaction time t
A_f	final projected area

1. INTRODUCTION

Thermogravimetry is one of the most common and precise methods for investigating gas–solid reactions[1]. As some researchers have reported, the pyrolysis heating rate and gasification temperature are dominant factors that have significantly influenced on gasification reactivity. However, the heating rate adopted in the previous work is lower than 50°C/min in TG which is far different from real condition[2]. Besides, different rates of chars are first prepared in different instruments and then gasified in TG.

There is no unified conclusion that whether there is an acceptable factor for evaluating the gasification reactivity of different carbonaceous materials, which guarantees a considerably high linear correlation coefficient between gasification reactivity and key factor. In addition, the gasification temperature has significantly on char gasification[3]. Generally, gasification experiments were mostly carried out in black-box equipment, resulting in huge challenges for the analysis of real reaction situation in gasifiers[4]. Therefore, there is need to apply a heating HTSM coupled with a TG to analysis the in-situ coal char gasification process.

The objective of this work is to study the effect of heating rate on pyrolysis and in-situ char gasification. Meanwhile, it will provide a more precision conclusion about char structure which influenced by rapid heating rate. Furthermore, many focal structure characterization indicators are correlated with gasification reactivity to identify the factor that plays key role in gasification reactivity. Besides, the evolution of coal char particles at various reaction temperatures is investigated by rapid TG and in-situ heating stage. The similarities and differences on the gasification characteristics of single in-situ char

Selection and peer-review under responsibility of the scientific committee of the 11th Int. Conf. on Applied Energy (ICAE2019).

particle in HTSM were compared with TG at the similar conditions.

2. EXPERIMENTAL SECTION

2.1 Material and methods

2.1.1 Preparation of coal and char samples

A Chinese typical coal, Piliqing bituminous coal (PLQ coal), was selected as raw materials. The coal samples were dried, ground and sieved to the size fraction of 120~150μm and less than 75μm. The proximate and ultimate analysis results of raw coal are given in Table 1. The preparation conditions of char samples with different heating rates were consistent with coal samples pyrolysis process in rapid TG.

Proximate analysis (wt. %)				Ultimate analysis (daf, wt. %)			
M_{ad}	A_d	V_{daf}	FC_d	C	H	O^a	N
12.2	7.68	36.24	58.86	77.13	3.98	17.63	0.67

Table 1 The proximate and ultimate analysis of the coal

2.1.2 Coal pyrolysis and in-situ char gasification experiment

The coal sample was sieved to particles less than 75μm in size. In each trial, a sample of about 6 mg was placed into an alumina crucible and heated up to the target temperature with an N_2 flow of 120 mL/min. The gas was then switched over to CO_2 flow of 120 mL/min for char gasification immediately. All experiments were tested at five different heating rates:10,20,50,100 and 200°C/min. The target temperatures were 850, 900,950,1000 and 1050°C respectively.

2.1.3 In-situ CO_2 gasification experiments in the HTSM

Several (8~12) coal particles were spread on the center of sapphire slip which was placed in the heating furnace. Then the temperature of the char samples head up to target temperature at 100°C/min with a gas flow of N_2 (120mL/min), Once the prescribed temperature was reached, the atmosphere was switched to CO_2 quickly. Meanwhile, the microscope camera system recorded the whole rapid pyrolysis and isothermal gasification process continuously. Finally, the projecting plane evolution of coal char particles during gasification process was further measured and analyzed by ImageJ software.

2.1.4 Char samples characterization

The specific surface area and pore structure of chars were detected out by a Micrometrics ASAP2020 adsorption apparatus using N_2 was at 77 K. Carbon crystallite structure of char samples at different heating rate was characterized by PANalytical X'pert3 powder diffractometer with Cu Kα radiation. A step size of 0.02° at the speed of 4°/min over a 2θ angle range of 10-80°. The carbon structure characteristics of chars were performed by a Raman spectrometer with argon ion laser. The excitation line was 532 nm and Raman spectra in the wavenumber range 800–2000 cm^{-1} were acquired at a resolution of 2 cm^{-1}. The number of active sites, which could be quantitatively detected by CO_2 chemisorption in a setaram TG apparatus.

2.2 Calculation

Carbon conversion (*Xc*) in the isothermal gasification was calculated by the following equation:

$$X_c = \frac{m_0 - m_t}{m_0 - m_{ash}} \times 100\%$$

Simultaneously, in order to contact the TG gasification experiment, the carbon conversion of char particles in HTSM was defined as follows:

$$\mathrm{X} = \frac{\frac{\pi d_0^3}{6} - \frac{\pi d_t^3}{6}}{\frac{\pi d_0^3}{6} - \frac{\pi d_f^3}{6}} \times 100\% = \frac{A_0^{\frac{3}{2}} - A_t^{\frac{3}{2}}}{A_0^{\frac{3}{2}} - A_f^{\frac{3}{2}}} \times 100\%$$

3. RESULTS AND DISCUSSION

3.1 The effect of heating rate on pyrolysis process

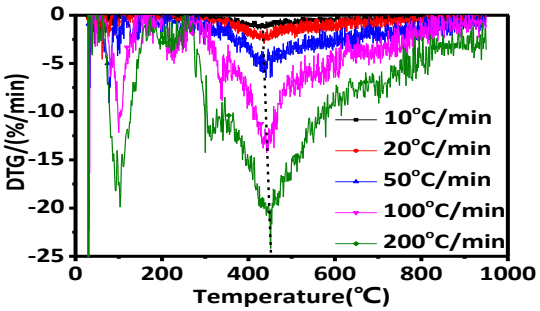

Fig 1 The DTG curves of parent coal at different heating rate during pyrolysis at the final temperature of 950°C

The Fig 1 showed that the maximum weight loss rate DTG_{max} evidently increased with an elevated heating rate during pyrolysis and its corresponding peak temperature slightly raised. The increase in heating rate causes the rapid formation of volatiles and further elevates the internal pressure of particles, thereby promoting the rapid release of volatiles. Moreover, the temperature gradient in coal particle was elevated at high heating rates because of its low thermal conductivity.

3.2 The effect of heating rate on in-situ char gasification

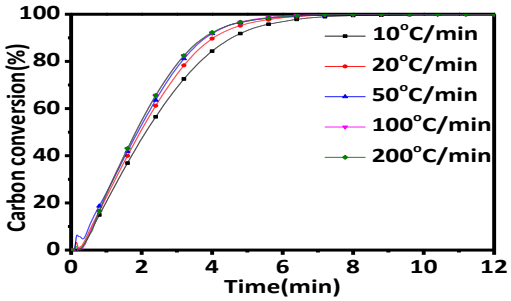

Fig 2 Carbon conversion and reaction time at different heating rates at 950 °C

As shown in Fig 2, gasification reactivity increased with the elevating of heating rate at 950°C. However, once the heating rate exceeded 50°C/min, it had little effect on the gasification reactivity of the in-situ char. Hence, the structure of in-situ char should be explored for the difference in the gasification reactivity. Furthermore, the key structural factors affecting the reactivity of gasification need to be further determined.

3.3 The effect of heating rate on char structure

3.3.1 The effect of heating rate on carbon crystalline structure

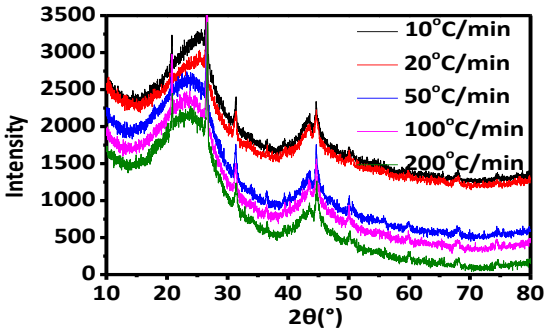

Fig 3 XRD spectra of pyrolysis chars prepared at different heating rate (pyrolysis temperature:950 °C)

As shown in Fig 3, with the increase of heating rate, the (002) peak intensity of the XRD spectra became weaker, and the shape became more asymmetrical and broader, meanwhile, the 002 band at a 2θ value became smaller, indicating a more highly disordered structure. However, once the heating rate exceeded 50°C /min, the (002) peak was basically no longer changing.

To further quantitatively determine the degree of graphitization of chars, the diffraction peak (002) was separated into two deconvoluted Gauss curves in previous studies[5]. The calculated results of all crystalline structure parameters for char samples at various pyrolysis heating rates are shown in Table 2. The law can be attributed to the number of free radicals and the amount of evolved gas in coal pyrolysis process.

3.3.2 The effect of heating rate on Raman spectroscopy for carbon structure

To evaluate the char structure, the ratios of each band were calculated and shown in Table 3. It was obviously that the I_{D1}/I_G ratios of five char samples increased with the increase of heating rate, while the I_G/I_{All} ratios were decrease. Moreover, once the heating rate exceeded 50°C/min, the ratios had slightly change. It seems that the evolution of chars detected by Raman spectroscopy is consistent with XRD analysis.

Rate °C /min	I_{D1}/I_G	I_{D2}/I_G	I_{D3}/I_G	I_{D4}/I_G	I_G/I_{All}
10	5.75	0.68	1.23	0.46	10.97
20	6.45	0.60	1.14	0.22	10.63
50	7.75	0.73	1.40	0.23	8.99
100	8.14	0.72	1.49	0.19	8.66
200	8.18	0.88	1.44	0.29	8.48

Table 3 Microstructure parameters ratios of five char samples at different heating rates

3.4 Correlations between char structural parameters of the in-situ char and reactivity index R_s

In order to further understand the in-situ gasification reaction, attempts are made to find the correlations

Rate(°C /min)	$d_{002,\ P}$ (Å)	$L_{c,\ P}$(Å)	$d_{002,\ G}$(Å)	$L_{c,\ G}$(Å)	X_P(%)	X_G(%)	$d_{002,\ a}$(Å)	$L_{c,\ a}$(Å)	$L_{c,a}/d_{002}$
10	3.71	9.69	3.43	40.57	87	13	3.67	13.56	3.69
20	3.74	9.04	3.49	27.46	83	17	3.70	12.17	3.29
50	3.87	8.93	3.50	19.31	79	21	3.80	11.06	2.91
100	3.89	9.03	3.50	16.37	78	22	3.80	10.68	2.81
200	3.87	9.04	3.50	15.10	75	25	3.78	10.55	2.79

Table 2. Structure parameters of resulting chars at different pyrolysis heating rates

between the relevant char structural parameters and

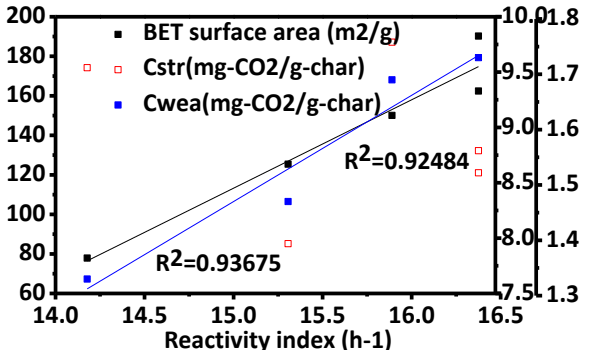

Fig 4 Correlations between the BET surface area, CO_2 chemisorption parameters and reactivity index

gasification reactivity. As shown in Fig 4, the correlation coefficient between the C_{str} values and reactivity index was the lowest, while the correlation coefficient of C_{wea} was 0.94. Therefore, the C_{wea} can be considered as a reasonable factor to estimate the reactivity compared with C_{str} and BET surface area.

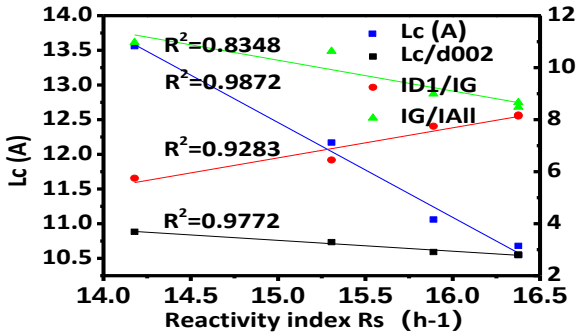

Fig 5 Correlations between the carbon crystalline structure, Raman parameters and reactivity index

Correlations between carbon structure and reactivity index of different heating rate were shown in Fig 5. XRD and Raman spectra jointly showed that the increasing of heating rate could lead to the carbon crystallite structure of coal char to develop toward a reduced degree of graphitization within a certain range. However, the heating rate exceeded 50°C/min, it had negligible reduction. Moreover, the linear correlation coefficients were higher than 0.97. Thus, we can conclude that heating rate has influences on the BET surface area, number of active sites and carbon crystalline structure. The carbon crystalline structure is the best factor to estimate the gasification reactivity of in-situ chars at different heating rate.

3.5 The difference of gasification reaction between TG and HTSM

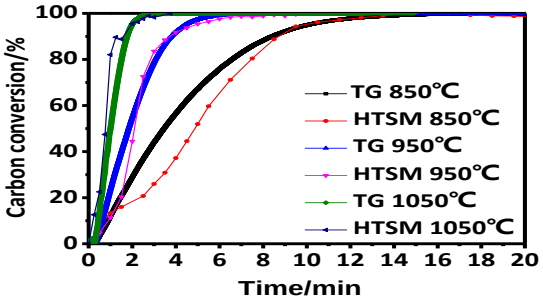

Fig 6 The average carbon conversion versus time in TG and HTSM at different gasification temperature

As shown in Fig 6, the gasification temperatures drastically affected the reaction rate. The result was also verified by TG data. However, the in-situ heating stage experiments demonstrated that the gasification reaction rates were slightly higher compared with TG gasification at different temperatures. As mentioned above, the inter-particle diffusion resistance was significant and the mass transfer couldn't be ignored in TG experiments. The CO inhibition effect was also conspicuous because of its accumulation inside the sample bed at high temperatures. Moreover, a large initial mass might be associated with diffusional limitation.

3.6 Conclusions

The main following conclusions that can be drawn from this work include:

(1) The DTG_{max} evidently increased with an elevated heating rate and its corresponding peak temperature rises. In addition, the gasification reactivity increases with the increase of heating rate at 950°C. However, it has little effect on the gasification reactivity of the in-situ char when the heating rate exceeds 50°C/min.

(2) Carbon Crystalline Structure is a dominant factor which can estimate the gasification reactivity of in-situ char of different heating rates.

(3) The in-situ heating stage microscope experiments demonstrated that the gasification reaction rates were slightly higher compared with TG gasification experiment at different temperatures, which could be attributed to CO inhibition effect and inter-particle interaction.

ACKNOWLEDGEMENT

This work was supported by the Joint Foundation of Natural Science Foundation of China and Shanxi Province (U1510201). National Natural Science Foundation of China (Nos. 21476247 and 21761132032).

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