The influence of pyrolysis temperature on lignite reaction kinetics and gas devolatilization process

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ABSTRACT: Pyrolysis is a clean method for lignite utilization, and it is greatly influenced by temperature and heating rate. The reaction mechanism and kinetic model were investigated by means of Differential Thermal-Gravimetric Analyzer and Fourier Transform Infrared spectrometer. It is found that lower heating rate leads to prolonged reaction process and less residue mass, whereas higher heating rate causes more intense reaction rate with different devolatilization gas compositions. In addition, the generations of CO2 and CO have different functional groups resources and corresponding temperature ranges. The temperature range discrepancies are mainly caused by the organic functional groups diversity, which is produced when chemical bridge bonds between the adjacent structural element molecules crack. Finally the reaction kinetic parameters are given by test datum regression, and the reliable index indicates that the calculation is credible.

INTRODUCTION

Coal utilization is the No.1 fossil fuel consumption in China at present. Among plenty of coal types, lignite is classified into the young coal with low coalification degree, and it accounts for about 13% of the coal total reserves. Lignite is characterized by high volatile content, low caloric value, low mechanical strength and intense chemical reactivity, so it is difficult to be directly used either as combustion fuel or in chemical processing. Recently China pays more attention to lignite utilization with the price rise on thermal coal market.

Lignite pyrolysis is a clean method for coal utilization with various technologies, including fixed bed reactor, fluidized bed reactor and moving bed reactor with heat carrier (Zhou, Q. & Zou, T. 2013). No matter which one is used, the pyrolysis process is significantly influenced by temperature and heating rate (Zou, L. et al. 2015, Canel, M. & Wanzl, M. 1994). Therefore, the reaction kinetic parameters and mechanism are close related to pyrolysis temperature. In this work, these relations are investigated by means of Thermal / Differential Thermal-Gravimetric Analyzer (TG/DTG).

TEST SYSTEM OF GAS DEVOLATILIZATION

Figure 1 shows the schematic diagram of the test system for gas devolatilization. High-purity nitrogen is used for sweeping (flow rate is 50 ml/min) and protection (15ml/min). Besides, the quality change rate of reactant is measured by means of TG/DTG, which could report the kinetic parameters for pyrolysis reaction. In order to investigate the mechanism and process characteristic accurately, the Fourier transform infrared spectrometer (FTIR) is used to test the volatile gas composition. During the test, pyrolysis temperature ranges from 25 to 1100 ˚C, and the heating rate are 5, 10, 20 and 30 ˚C/ min, respectively.
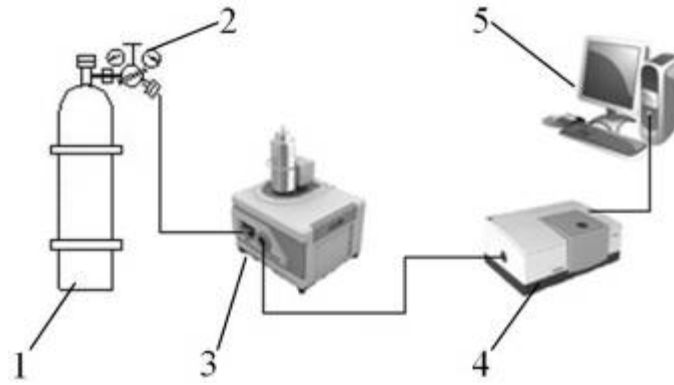
1-nitrogen gas cylinder, 2-flux control valve, 3-thermo gravimetric analyzer (TG/DTG), 4-infrared spectrometer, 5-data acquisition instrument.

Figure 1 Experimental system for gas devolatilization test

The lignite proximate and ultimate analysis is shown in Table 1, where M-moisture content, A-Ash content, V-volatile content, FC-fixed carbon content, LHV- low heat value, subscript ad-air dry basis. C, H, O, N, S are the element carbon, hydrogen, oxygen, nitrogen and sulfur respectively.

Table 1 Lignite composition analysis

Proximate analysis		Ultimate analysis (%)	
M_{ad} (%)	7.95	C_{ad}	52.69
A_{ad} (%)	18.46	H_{ad}	4.27
V_{ad} (%)	45.23	O_{ad}	14.53
FC_{ad} (%)	28.36	N_{ad}	1.92
LHV_{ad} (MJ/kg)	16.4	S_{ad}	0.14

TEST RESULTS AND DISCUSSIONS

The TG/DTG pyrolysis curves are shown in Figure 2, in which the lignite mass reduction rate changes with temperature and heating rate β. It can be seen that the residue mass rises when β decreases and this phenomenon is more distinct when temperature exceeds 700 ˚C. This is caused by prolonged reaction process for lower heating rate. Condensation react account for most pyrolysis reactions over 700 ˚C, which transforms semi-coke into coke, and it is not as intense as volatile separate out from lignite. Hence, this kind of reaction requires more reaction time. In addition, Figure2 indicates that higher heating rate leads to more intense reaction rate. There are two peaks on DTG curves; the first one appearing around 100 ˚C is caused by inherent water evaporation. On the contrary, volatile separates out from lignite give rise to the second peak that appears around 300~600 ˚C, so the second peak indicates the most intense reaction temperature range.
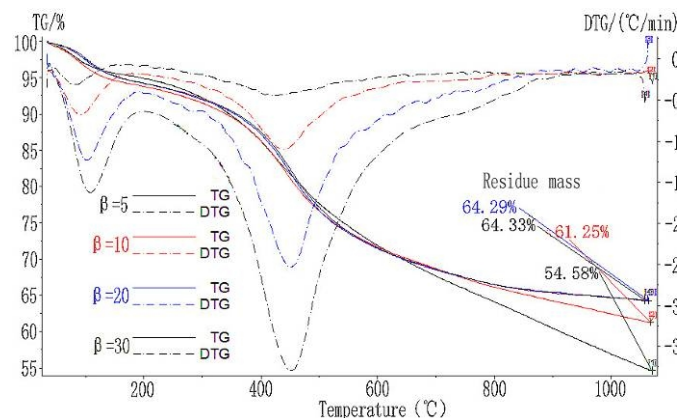

Figure 2 TG/DTG pyrolysis curves for different heating rate

Figure 3 gives the three-dimensional characteristic chart of gas devolatilization at various heating rate. Where X axis is wave number which indicates the spectral band frequency (cm^{-1}), Y axis is absorbance that indicates the concentration for different gas composition, and Z axis is pyrolysis temperature (K). It can be seen that β has great effect on the gas devolatilization process and gas compositions. The absorbance units achieve climax when wave number is around 2200 and 2800 cm^{-1}.
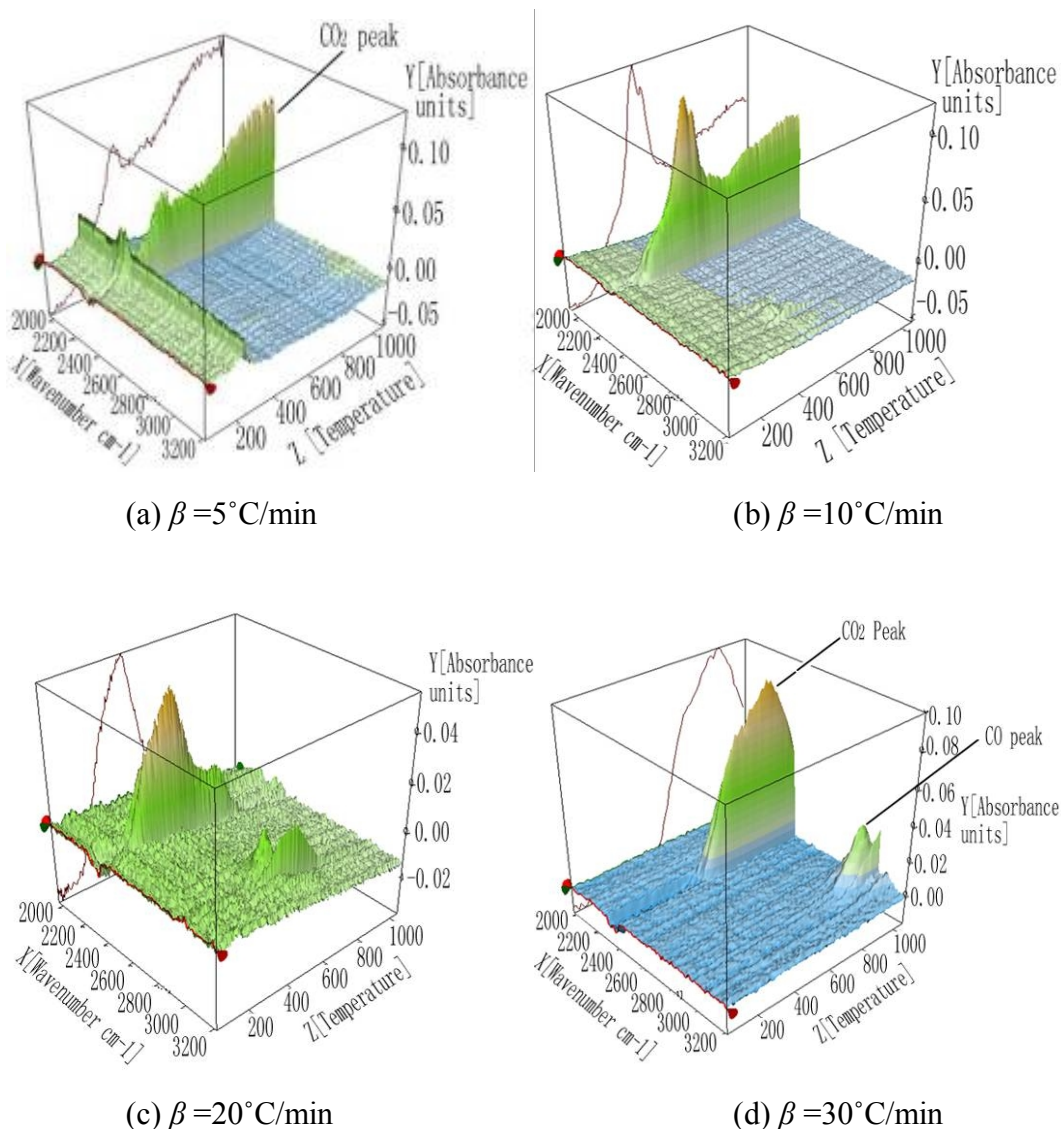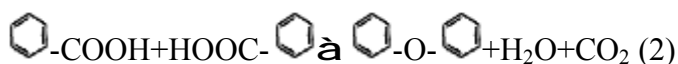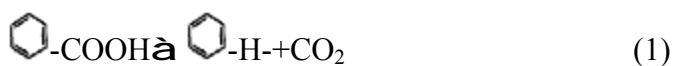

(a) β =5˚C/min   (b) β =10˚C/min

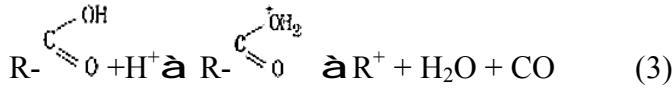(c) β =20˚C/min   (d) β =30˚C/min

Figure 3 3D characteristic chart of gas devolatilization

Besides, separation rate of CO_2 out of lignite reaches climax when pyrolysis temperature is around 300~600 ˚C. In comparison, the maximum separation rate of CO from lignite appears when temperature ranges from 600~800 ˚C. The temperature range discrepancies for CO_2 and CO acute devolatilization are caused by the organic functional groups diversity, which is produced when chemical bridge bonds between the adjacent structural element molecules crack (Chu, M. et al. 2012, Gonzalez, J.A. 2012). As to CO_2, it is generated by carboxyl functional groups (-COOH) break-up given in Equation (1) and Equation (2). Whereas CO is produced by carbonyl functional groups (C=O) break-up given in Equation (3). R denotes aromatic nucleus compositions in lignite.

⬡-COOH**à** ⬡-H-+CO_2 (1)

⬡-COOH+HOOC-⬡**à** ⬡-O-⬡+H_2O+CO_2 (2)

R- (structure) $+H^+$ à R- (structure) à $R^+ + H_2O + CO$ (3)

KINETIC MODEL AND ITS PARAMETERS

The pyrolysis process is assumed to be composed of n stage reaction, where n is positive integer (Tia, S. et al. 1991). Its reaction kinetic model is described in Equation (4). The pyrolysis kinetic equation (5) could be deduced by performing logarithm on both sides of Equation (4) (Vamvuka, D. et al. 2003).

$$dx/dt = A \cdot e^{-E/(RT)} \cdot (1-x)^n \qquad (4)$$

$$\ln\left[\frac{1-(1-x)^{1-n}}{T^2(1-n)}\right] = \ln\left[\frac{AR}{bE}\left(1-\frac{2RT}{E}\right)\right] - \frac{E}{RT} \qquad (5)$$

Where x-mass ratio of residue to original lignite; t-time, second; A-frequency factor; E-activation energy, kJ/kmol; R-universal gas constant, 8.314 kJ/(kmol·K); T-temperature, K; β-heating rate, °C/min; n-reaction stage number. Parameters E and A could be calculated by means of linear regression from Equation (5). Figure 4 shows the regression curves of kinetic parameters when heating rate is 5 and 30 °C/min, respectively, where the reaction stage number n is assigned with value 2 and 3. Besides, the exact reaction kinetic parameters regressed from Equation (5) is given in Table 2 and Table 3, where k and a are the slope and intercept of regression curve in Figure 4, respectively, R^2 is reliable index.

(a) β=5, n=2   (b) β=5, n=3

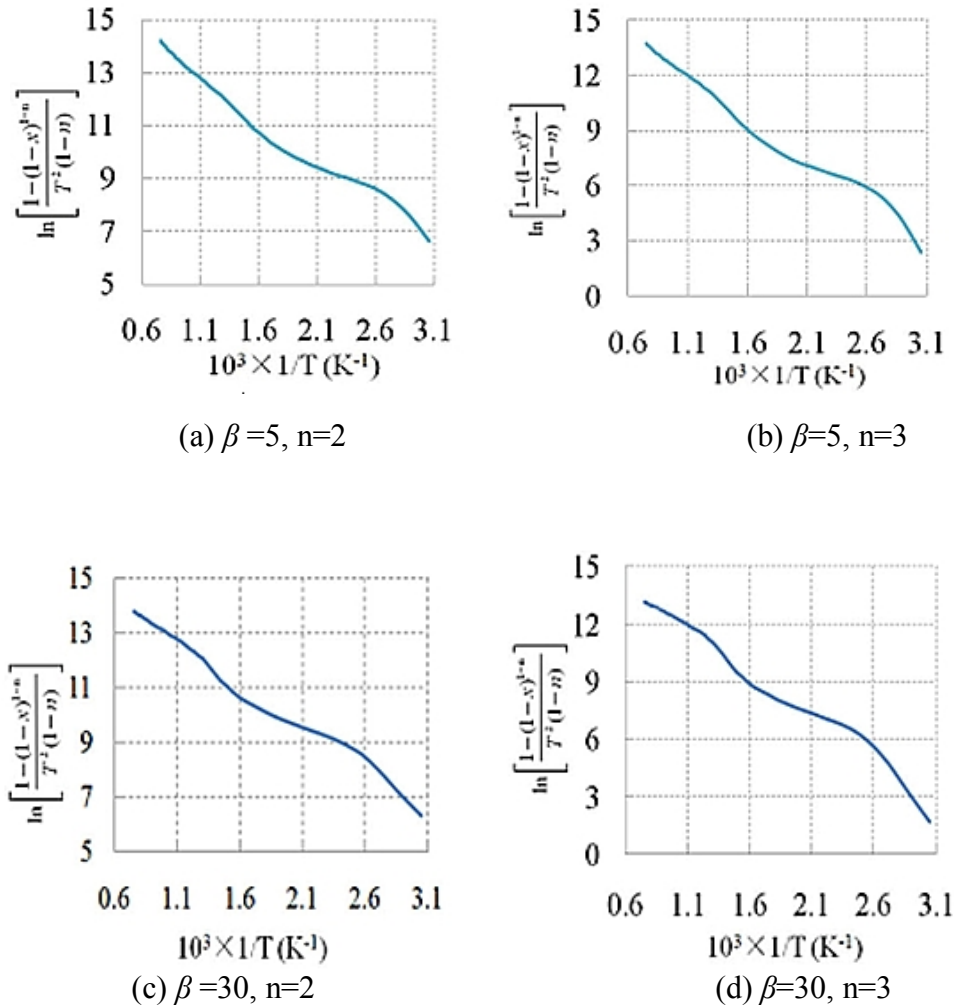(c) β=30, n=2   (d) β=30, n=3

Figure 4 Regression curves of reaction kinetic parameters

The calculation results given in Table 2 and Table 3 indicate that the activation energy for three stage reaction, namely n=3, is slightly higher than that of two stage reaction. Both of two kinetic models' results show that activation energy E gradually increases with heating rate β increment, and E is around its peak when reaction temperature T ranges from 300 to 600 ˚C. Hence, the reaction is also intense in this temperature range that is shown in Figure 2.

Table 2 Reaction kinetic parameters when β =5 ˚C/min

No.	Items	T=20~300˚C		T=300~600˚C		T=600~1100˚C	
		n=2	n=3	n=2	n=3	n=2	n=3
1	k	2346	3745	4183	6160	4023	4888
2	a	14.38	15.02	17.43	18.94	17.15	17.33
3	R^2	0.946	0.913	0.998	0.997	0.996	0.997
4	E (kJ/mol)	19.5	31.1	34.8	51.2	33.4	40.6
5	A ($\times 10^2$)	15.4	11.3	1.13	0.34	1.46	1.43

Table 3 Reaction kinetic parameters when β =30 ˚C/min

No.	Items	T=20~300˚C		T=300~600˚C		T=600~1100˚C	
		n=2	n=3	n=2	n=3	n=2	n=3
1	k	2777	4586	4407	6545	2962	3366
2	a	15.34	16.87	17.72	19.43	16.02	15.70
3	R^2	0.945	0.915	0.992	0.991	0.999	0.998
4	E (kJ/mol)	23.1	38.1	36.6	54.4	24.6	28.0
5	A ($\times 10^2$)	39.6	12.6	5.3	1.3	21.7	32.7

CONCLUSIONS

The lignite pyrolysis reaction mechanism was investigated and its reaction kinetic procession was tested. It is found that pyrolysis temperature and heating rate have great effect on reaction rate and devolatilization gas compositions. Higher heating rate leads to more intense reaction rate, and the most acute reaction temperature range is 300~600 ˚C, in which reaction rate arrives at its climax. In addition, CO_2 is generated by carboxyl functional groups break-up in 300~600 ˚C, whereas CO is produced by carbonyl functional groups crack within 600~800 ˚C in contrast. Finally the pyrolysis kinetic parameters were calculated from curve regressions. The results show that activation energy gradually increases with heating rate increment, and it is around the peak corresponding to the acute reaction temperature range.

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