

A Model-based Phenomenological Investigation of Char Combustion Kinetics through Thermogravimetry

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Abstract: Five coal char samples were burnt in thermobalance with ramp heating rate of 30 K/min. The pore structure of these char samples was studied through mercury intrusion method. Combined with the kinetic theory of gases, the data of surface area was used in fitting the results. As a result, the kinetic triplet was given. The analysis showed that five char samples share almost the same intrinsic activation energy of the overall reaction. The phenomenological implication of the derived combustion rate equation was given.

Keywords: Thermogravimetry, activation energy, pre-exponential factor, kinetic model function, char combustion.

Thermogravimetry (TG) can be used in the study of the reaction kinetics of coal chars¹. It works through measuring the continuous mass loss of the char sample held in the thermobalance in a temperature-program-controlled furnace. By fitting the data of the mass and the temperature, the kinetic parameters of combustion, *i.e.* char reactivity, can be obtained. In this paper, the combustion kinetics of five char samples were studied by using thermogravimetry and the kinetic triplet was also given.

Experimental

The samples were prepared from parent coals devolatilized in a drop tube furnace system (DTFS) in a stream of nitrogen at temperature of 1273 K. The proximate and ultimate analytic data of these five coal samples were listed in **Table 1**. The average diameter of the particles was about 75 μm .

The char samples were burnt in Dupont Thermal Analyst 2100 (TA Instruments). The ramping heat rate β remained at 30 K/min in each test. The test mass of each sample was about 2.0~3.0 mg, dispersed flatly in the pan (sample carrier) of about 8 mm in diameter and 1 mm in depth. The samples were all burnt in atmospheric air, whose flow rate was about 135 mL/min. All the char samples were burnt below 1000 K. The combustion reaction of the char samples was therefore all in kinetic-controlled zone².

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Table 1 The proximate and ultimate analytic data of parent coal samples

Samples	heating values kJ/g	proximate analysis(air dry basis)				ultimate analysis(dry basis)				
		inherent moisture	ash	volatile matter	fixed carbon	C	H	N	O	S
		%	%	%	%	%	%	%	%	%
Adaro	24.87	14.2	1.0	43.8	41	72.3	5.2	0.8	20.4	0.1
Chaohua	30.89	1.72	14.3	13.0	71.0	77.1	3.9	1.2	3.2	0.4
Hebi	29.17	1.40	16.8	14.2	67.6	74.7	3.6	1.3	3.2	0.3
Luoyang	28.80	1.70	16.2	11.5	70.6	75.1	3.3	1.3	3.5	0.4
Shanxi	29.34	2.70	14.5	10.2	72.6	77.9	3.4	0.8	2.8	0.4

To obtain the information of pore structures, these char samples were also tested with mercury intrusion with Atuoscan3 porosimetry (QUANTACHROME), whose work pressure was about 0~220 MPa. The pores above 3.5 nm in radius were measured according to Young-Laplace equation³. The porosity and pore surface area of char samples were obtained.

The expression of char combustion rate was derived as follows:

$$d\alpha/dt = AT^B \exp(-E/RT) \alpha^{m_1} (1-\alpha)^{m_2} \quad (1)$$

According to the kinetic theory of gases, this equation can finally be expressed as follows:

$$d\alpha/dt = AS_0C_0T^{-1/2} \exp(-E/RT) \alpha^{m_1} (1-\alpha)^{m_2} \quad (2)$$

where $K=AS_0C_0$, is referred to as pre-exponential factor. S_0 is the initial specific surface area of the char sample, C_0 , the concentration of oxygen in the air under standard ambient condition. E is the apparent activation energy, m_1 and m_2 are two exponents of the kinetic model function and A is a constant. α is the conversion of carbon in char sample. To explore the char reactivity of combustion, K , m_1 , m_2 and activation energy E in eqn (2) can be solved out with fitting curves to the TG data of each char sample.

Results and Discussion

The results of mercury intrusion experiments are listed in **Table 2**, which shows the porosity and specific surface area of each char samples. **Table 3** shows the results of the kinetic parameters of the char samples from the curve fitting with the square-least method.

In the kinetic model, the pre-exponential factor K is derived from the kinetic theory of gases and therefore is a known constant, while the pre-exponential factor and activation energy have to be determined simultaneously in many other models. The macropore surface area S_m (listed in **Table 2**) is deliberately taken as the initial specific surface area S_0 in eqn (2). The result of mercury intrusion indicates that the pore surface S and the pore radius r have the relationship $dS/dr \propto r^{1-D}$, where D is referred to the fractal dimension. Different values of D are found between the micropore and the

macropore from the experiment results. r_{tr} in **Table 2** is the transition radius between micropore and macropore. It is known that the total surface of char particles consists of macropore surface and micropore surface. Although most surface area is contributed by micropore surface, it has been found that much micropore surface area is inaccessible to oxygen during the char combustion, even when the reaction is controlled in kinetic regime⁴. Besides, C_0 in eqn (2) represents the oxygen concentration of both the bulk flow and gases in macropores. Therefore, the surface area affecting the char combustion is equivalent to the sum of macropore surface area. The products of A and S_m of the all samples are listed in **Table 4**.

Table 3 shows that, except for sample Adaro, the activation energies of other four char samples are almost in the same values, which fall within the range of that obtained by Gopalakrishnan and Bartholemew⁵ (109~134 kJ/mol). These values are also close to the values given by Suuberg⁶, Charpeney⁷ *et al.*. The Adaro char may still have some volatile matter on account of the higher volatile matter content of its coal sample (see **Table 1**). As a result, the activation energy value of Adaro char sample is a bit lower than others.

Now we may phenomenologically interpret the physiochemical implication of the item $AS_0C_0T^{-1/2}exp(-E/RT)$ in eqn. (2). Since the mean thermal velocity of oxygen molecule is proportional to $T^{-1/2}$, we can predicate that $AS_0C_0T^{-1/2}$ represents the molar flux of oxygen molecules through the macropore surfaces of char particles. The item $exp(-E/RT)$ gives the fraction of oxygen molecules, whose kinetic energy exceeds the activation energy of the overall reaction.

Table 2 The pore structure of five char samples

Samples	Porosity ϵ	Specific surface area $S_0(\text{m}^2/\text{g})$	Transition radius $r_{tr}(\text{nm})$	Macroscopic pore surface $S_m(\text{m}^2/\text{g})$
Adaro	0.369	20.09	20	5.10
Chaohua	0.162	7.34	38	2.27
Hebi	0.148	3.09	53	1.68
Luoyang	0.279	8.66	47	3.05
Shanxi	0.202	2.54	76	1.02

Table 3 The kinetic parameters of char combustion obtained from curve fitting

Samples	$\ln(K)(\text{K}^{-0.5})$	m_1	m_2	Activation energy $E(\text{kJ/mol})$	Correlation index, R^2
Adaro	15.85	0.79±0.05	1.62±0.03	102.01±1.43	0.962
Chaohua	15.04	0.04±0.01	1.05±0.04	119.63±2.88	0.975
Hebi	14.74	0.32±0.01	1.01±0.02	117.06±1.76	0.993
Luoyang	15.34	0.28±0.01	1.00±0.01	119.82±2.72	0.989
Shanxi	14.25	0.68±0.02	1.02±0.03	110.39±3.68	0.994

Table 4 The value of AS_0 used in resolving eqn (2)

Samples	Adaro	Chaohua	Hebi	Luoyang	Shanxi
AS_0	4.30×10^5	1.91×10^5	1.42×10^5	2.57×10^5	8.06×10^4

The values of exponents m_1 and m_2 , which differ greatly from char to char, determine the tendencies of the weight-loss curves of the char samples. Thus the whole product of $S_0 a^{m_1} (1-a)^{m_2}$ can be regarded as the change process of reactive surface area during the char combustion. The evolution of the surface area during the char combustion process is directly related to the pore structure of the char sample. On the other hand, as the chars are burnt in the kinetic-controlled zone, the combustion of these char samples is free from the diffusive effects. These two exponents are therefore recognized to be determined by the pore structure properties of the chars, such as fractal dimension, tortuosity factor and so on.

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