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Kinetic Study of Pyrolysis Characteristics of Coal from Inner Mongolia Region

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Pyrolysis characteristics of different coals from Inner Mongolia region in China were analyzed by TGA technology under non-isothermal condition with a heating rate of 10 °C/min from room temperature to 980 °C in a nitrogen atmosphere. The maximum pyrolysis rate and characteristic peak temperatures were determined by TG-DTG technology. Thermogravimetric data at low and high temperature were analyzed respectively by the reaction rate model assuming the first-order kinetics and the third-order model F_3. Apparent activation energy and frequency factor of pyrolysis reaction of coal from Inner Mongolia region were estimated by Coast-Redfern integral method. The results showed that pyrolysis of coal from Inner Mongolia region at the low temperature have the characteristics of the lower value of mass loss, the larger apparent activation energy and frequency factor compared with that at the high temperature.

Keywords: Coal from Inner Mongolia region, Pyrolysis, Kinetic analysis.

INTRODUCTION

Coal is the main energy resource in China and Inner Mongolia in China is abundant in coal resources. The direct combustion of coal was the traditional way of utilization, along with poisonous and harmful gases and fine particulate matters, could cause great damage to the ecological environment[1]. Coal gasification, including two steps coal pyrolysis and coal gasification, is one of the dominant ways of coal conversion[2]. The process can convert coal into clean gas fuel, which can be more reasonable, clean and efficient utilization of coal resources. Thus, coal pyrolysis has a good influence on comprehensive utilization of coal[3]. Coal pyrolysis is a multifarious process in which there are a series of physical and chemical changes. Its products are mainly consisted of char, coal tar and gas[4]. Because of complexity, diversity and heterogeneity of coal, the process of coal pyrolysis can be influenced by many factors, such as chemical characteristics of coal, pore structure of coal and reaction conditions[5]. In the recent decade, coal pyrolysis process has much to do with coal rank[6], particle size[7], pyrolysis temperature[8], pressure[9,10], heating rate[10], coal blended with biomass[11] and some other factors.

To explore the pyrolysis properties of coal from Inner Mongolia region in China, pyrolysis characteristics and kinetics of three kinds of lignite and one kind of bituminous coal from Inner Mongolia region in China were investigated in this work by thermal gravimetric analysis (TGA) that is exercised to define the kinetic parameters. Up to now, TGA is the most used method for the research of coal pyrolysis. The experimental results of TGA are affected by some factors in TG methods, such as heating rates, samples and final temperature[12]. The effect of coal pyrolysis was discussed through making comparisons with several kinds of coal from different sites.

EXPERIMENTAL

Sample preparation: Three kinds of lignite and one kind of bituminous coal from Jalainur, Huolinhe, Pingzhuang and Ordos at Inner Mongolia region in China were chosen as the samples in pyrolysis experiment. They were respectively marked for L1, L2, L3 and B1. The samples were first crushed and then milled and sieved and the size fraction of the sample was 80 μm. Proximate and ultimate analyses results of the samples are given in Table-1.

Pyrolysis experiments: Proximate and ultimate analyses of the samples were carried out by element analyzers and sulfur analyzer. Proximate analyses of the samples were conducted in accordance with ASTM standards.

The TG-DTG measurements were carried out by a Netzsch-STA 409PC/PG thermal analyzer in a flowing nitrogen atmosphere (40 mL/min), about 10 mg of samples underwent thermal analysis with a heating rate of 10 °C/min from room temperature to 980 °C. The experiments were repeated under identical conditions to check the reproducibility of the results.

Kinetic analysis: The method of solving kinetic parameters in thermal analysis is mainly divided into integral method and differential method, the difference between them are that

TABLE-1
ULTIMATE AND PROXIMATE ANALYSES OF THE SAMPLES

	Ultimate (wt. %)					Proximate (wt. %)			
	C_d	H_d	N_d	S_d	0_d	Mad	Aad	Vad	Fcad
L1	63.07	3.88	0.60	0.14	23.54	11.11	10.61	35.94	43.46
L2	51.72	3.7	0.68	0.41	15.27	8.32	26.08	31.74	34.58
L3	61.03	3.96	0.57	0.34	27.49	4.39	6.52	40.85	48.26
B1	67.15	3.97	0.83	1.22	13.43	5.30	12.68	26.84	55.18

integral method can provide the kinetic parameters within the integral scope to reflect the datum as a whole. However differential method provides the kinetic parameters in given point, which can reflect the partial datum[13].

The calculation of the kinetic parameters is based on the following equation[14-16]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (1)$$

where α is percent conversion and k is the specific rate constant. The temperature dependence of k is expressed by the Arrhenius equations:

$$k(T) = Ae^{-\frac{E}{RT}} \quad (2)$$

where A is the Arrhenius constant regarded as frequency factor, s^{-1}; E is apparent activation energy, KJ/mol; T is absolute temperature, K; and R is the gas law constant, 8.314 J/mol K.

Based on the eqns. 1 and 2, the pyrolysis characteristics of the samples in this work have been analyzed by Coast-Redfern integral method[14]. The kinetic equation for coal pyrolysis is:

$$\ln\frac{G(\alpha)}{T^2} = \ln\frac{AR}{\beta E} - \frac{E}{RT} \quad (3)$$

where G(α) is kinetic mechanism function under integral form and β is heating rate, K/s.

As the change of temperatures have affection on the experimental mechanism, the pyrolysis experimental process has been divided into low temperature and high temperature[15]. At low temperature, the pyrolysis process is regarded as the first order reaction, so the kinetic equation for coal pyrolysis at low temperature is:

$$\ln\left(-\frac{\ln(1-\alpha)}{T^2}\right) = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \quad (4)$$

The pyrolysis process at high temperature is under the control of the third-order model F_3, so the kinetic equation for coal pyrolysis in high temperature is[14]:

$$\ln\left[\frac{(1-\alpha)^{-2}}{T^2}\right] = \ln\left(\frac{AR}{\beta E}\right) - \frac{E}{RT} \quad (5)$$

RESULTS AND DISCUSSION

Pyrolysis characteristics of the samples: TG and DTG curves obtained from pyrolysis experiments of the samples are, respectively given in Figs. 1 and 2. Fig. 1 displays differences to some extent due to variation in pyrolysis properties of different coal kinds and compositions. When the mass losses on the TG profiles are examined for the samples, two major regions are distinguishable in certain temperature ranges. The region 1 is observed below 270 °C and the region 2 is in the ranges from 270 to 980 °C. Mass loss are about (4-6 %) and (31-39) % in the regions 1 and 2, respectively. As can be observed, the main mass loss (31-39 %) occurs in the region 2.

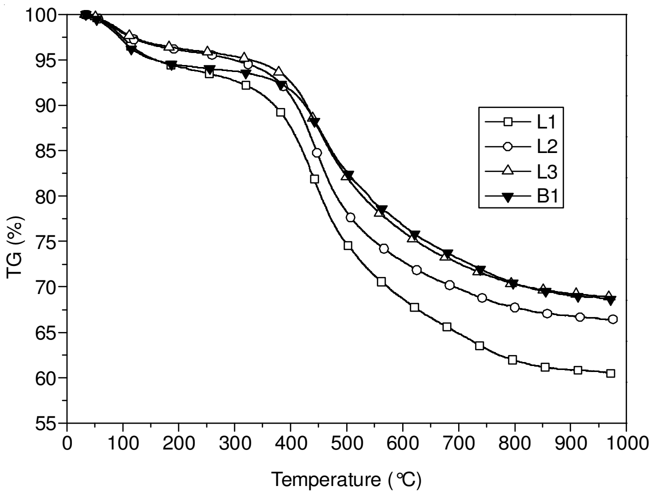

Fig. 1. TG curves of pyrolysis experiments

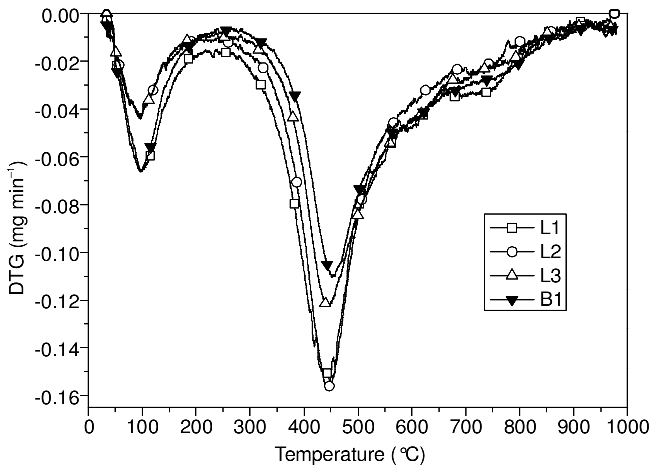

Fig. 2. DTG curves of pyrolysis experiments

According to the curves in Fig. 2, the DTG curves have two peaks which differ in position and value. The region 1 mentioned in the above refers to the release of moisture from the samples and shows that the peak temperature corresponding to the maximum rate of mass loss are from 95 to 99 °C. It is until 230 °C that mass loss of the coal especially lignite with increasing of temperature was due to release of not only moisture, but also low volatile species which includes mainly free radicals and low molecular mass compounds[5,17]. It is proved that the release temperature of volatile of lignite in this work is about 230 °C. But it is similar for bituminous coal until the pyrolysis temperature is more than 270 °C. At the end of pyrolysis experiments, mass loss of bituminous coal is smaller than that of three kinds of lignite, for higher carbonized ratio of bituminous coal relative to others.

The major mass loss, along with complicated chemical reactions and release of tar, bond water and gaseous products, devolatilization and semicoke formation, occurs in the region 2 mentioned in the above. In other words, carbonization of coal mainly occurs at this region. Initially, tar formation begins between 400 and 600 °C with release of gaseous hydrocarbon and carbohydrate[18]. The maximum rate of mass loss of the samples emerge between 439 and 453 °C. When the pyrolysis temperature is above 700 °C, hydrogen and other gases particularly methane, arene and carbon monoxide forms with the dissociation and breakdown of aromatic compounds[5,19]. Moreover, the mass loss of part of the samples observed at temperatures from 600-650 °C up to 900 °C is put down to the decomposition of mineral matter, such as quartz, kaolinite, montmorillonite and calcite[20].

The pyrolysis characteristic parameters of the samples are given in Table-2. $\Delta T_{1/2}$ is the temperature range corresponding to $(dw/dt)/(dw/dt)_{max} = 1/2$. If T_s and $\Delta T_{1/2}$ are less, the release peak of volatile would focus on smaller range earlier, which is beneficial to ignition of coal. According to the data in Table-2, it is proved that the reason why ignitability of lignite is usually better than bituminous coal. R is the release characteristic parameters of volatile. Furthermore, comparing with R in Table-2, it is proved to be so[21].

TABLE-2
PYROLYSIS CHARACTERISTIC
PARAMETERS OF THE SAMPLES

Sample	T_s/°C	$(dw/dt)_{max}$ /(mg min^{-1})	T_{max}/°C	$\Delta T_{1/2}$/°C	R/10^{-8}
L1	234.17	0.15198	439.96	134.02	1.10
L2	230.34	0.15636	443.96	114.95	1.33
L3	239.80	0.12247	444.45	144.52	0.80
B1	270.26	0.10974	453.43	152.64	0.59

Kinetic analysis results: The temperature range for kinetic parameters of coal pyrolysis is determined by tangent method that can be obvious to exhibit the main mass loss process. Based on the results of coal pyrolysis experiments, kinetic parameters of coal pyrolysis obtained by eqns. 4 and 5 are summarized in Table-3.

TABLE-3
KINETIC PARAMETERS OF COAL PYROLYSIS

Sample	Temp. range (°C)	Mass loss (%)	E/KJ mol^{-1}	A (s^{-1})	R
L1	374.48-439.96	7.49	60.31	26	0.9992
	439.96-555.52	11.38	48.67	17	0.9978
L2	377.58-443.96	7.38	69.42	134	0.9984
	443.96-565.47	11.02	59.25	121	0.9972
L3	395.37-444.45	4.83	75.05	294	0.9992
	444.45-564.53	10.17	50.53	18	0.9997
B1	398.06-453.43	4.627	81.69	728	0.9996
	453.43-595.38	10.04	43.95	4	0.9988

In Table-3, it is shown that the value of mass loss at the low temperature is lower than that at high temperature for all the samples and the apparent activation energy is larger, but the pyrolysis of unstable groups such as methoxy and carboxyl contribute to the larger frequency factor in the low temperature, which makes mass loss faster and more easily. However the apparent activation energy in the high temperature is lower, it is difficult for the pyrolysis of polymethylene groups participating at the high temperature. The result is that the frequency factor in the high temperature is low and the mass loss spends more time. Comparing with three kinds of lignite, the frequency factor change of bituminous coal between low and high temperature is larger, so it exhibits that it is stronger for bituminous coal in low temperature. Moreover, It can be admitted that the activation energies calculated for the samples are the sum of effective activation energies form various types of chemical reactions as well as physical changes occurring simultaneously during pyrolysis. Low value of the frequency factor reveals that the reaction is non-spontaneous in nature but the driving factor is that the reaction is controlled by the diffusion of the components in the system[22].

Conclusion

Pyrolysis of coal from Inner Mongolia region in China under nitrogen atmosphere were investigated by thermogravimetric analysis. Based on the results of coal pyrolysis experiments, study on kinetic analysis was examined by Coast-Redfern integral method. The following conclusions were drawn.

In the samples, the release temperature of volatile of all the lignite are lower than that of bituminous coal and the maximum rate of lignite mass loss are larger. Moreover, the release characteristic parameters of lignite volatile are superior to that of bituminous coal. Thus, pyrolysis process of lignite tend to occur at lower temperature, which shows that ignitability of lignite is more superior and pyrolysis process of lignite spends less time, in other words, pyrolysis technology has a better influence on comprehensive utilization of lignite.

From the viewpoint of pyrolysis kinetics, pyrolysis of the samples at the low temperature has the characteristics of the lower value of mass loss and the larger frequency factor, which makes mass loss faster and more easily. But the frequency factor change of bituminous coal between low and high temperature is larger, so it exhibits that it is stronger for bituminous coal in low temperature.

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