Journal of Thermal Analysis and Calorimetry, Vol. 95 (2009) 2, 633–638

THERMAL ANALYSIS STUDY OF THE EFFECT OF COAL-BURNING ADDITIVES ON THE COMBUSTION OF COALS

L. Fangxian[*]*, L. Shizong and C. Youzhi*

College of Materials Science and Engineering,Wuhan University of Technology, Wuhan 430070, The People 's Republic of China

Thermal analysis is widely used in combustion research for both fundamental and practical investigations. Efficient combustion of coals in cement industry is very important and necessary. In this research, the effects of three coal-burning additives on burning behaviour of bituminous coal and anthracite were studied with the help of thermogravimetry (TG) and differential scanning calorimetric (DSC) analysis. The kinetic study was carried out and the results were presented. The results showed that the coal-burning additives especially LSZ can reduce the ignition temperature, increase the ignition index D_i, combustion ending index D_f and affect the activation energy of the coal samples studied. The coal-burning additives especially LSZ can improve coal combustion effectiveness.

Keywords: *coal-burning additives, DSC, TG, thermal analysis*

Introduction

Coal is our major source of energy, and its utilization will proceed with further developments of more sustainable and energy efficient technologies. It is a physically heterogeneous and chemically complex mixture of organic and inorganic species, which undergoes appreciable physico-chemical changes when heat-treated [1]. Coal conversion comprises of combustion, gasification, pyrolysis and liquefaction, which essentially require thermal treatment under controlled process conditions, such as pressure, ambient atmosphere, coal type and heating rate [2, 3]. Pyrolysis is a fundamental process in the combustion, carbonization and gasification of coal. Volatile matter and the corresponding release profile, including the initial temperature, maximum rate of devolatilization and other factors which affect the release of volatiles, are very important properties which relate to the efficiency of these processes [4]. Thermoanalytical techniques such as TG, DTG, DTA, DSC, EGA and TMA cover a wide range of applications in research, development and economic assessment of coal combustion and have been used in a wide variety of areas related to proximate analysis, coal reactivity, and heat effect associated with coal pyrolysis, combustion and heat of hydrogenation [5, 6]. Thermal analysis data can be applied not only to the characterization of different coals, but also to the evaluation of combustion performance at high temperatures and heating rates [7].

Production and consumption of coal are very great and most of the raw coal mined every year is directly used as fuels in China [8], it is very important and necessary to improve the burning efficiency of the coals so as to save energy and to limit environmental pollution. Generally, high efficiency and low pollution are required for the coal burning. In order to achieve the above purposes, using coal-burning additives in the process of coal burning is an effective method. In recent years, the application of coal-burning additives has been quickly developed; the coals doped with the coal-burning additive have been used as fuels in power stations, cement industry and some other civil utilization in China. So the fundamental research work on the burning characteristics of coals doped with the coal-burning additives should be carried out so as to give theoretical guides to the application of the coal-burning additives. Yanhua *et al.* studied the effect of compounds in coal combustion characteristics. The experimental results show that iron compounds can intensify coal combustion reactions in the relatively low temperature zone. The prevailing mechanism is that ferric and ferrous chlorides behave like catalysts to change the chemical reaction kinetics for promoting the combustion process [9]. Li *et al.* investigated the kinetic study of the accelerating effect of coal-burning additives on the combustion of graphite. In their work, the catalytic and accelerating effects of three coal-burning additives on the burning of graphite were studied with the help of thermogravimetry (TG) analysis. The results show that the additives can change the carbon oxidation combustion course by catalytic action and change the activation energy, thus improving the combustion efficiency [10]. Catalyzed combustion of coals used in cement industry was studied by Junlin *et al.*, Fe_2O_3, MnO,

* Author for correspondence: lifangxian@sohu.com

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

CuO, $BaCO_3$ as the catalyst were selected, and a study on combustion of different kinds of coals was made by analyzing burn-out degree of coal, ignition index, burn-out index, the coal's volatility of volatimatter and so on. Through these experimental, both influences of different kinds of catalysts and their content on characteristics of combustion were discussed [11]. Shudong *et al.* studied the effects of coal combustion additives on coal combustibility. Four commercial additives and one prepared in their laboratory had been studied. The results show that all of the additives can enhance the combustion and increase the combustion rate of graphite and coal, while coal gangue is different from those of graphite and coal [12].

In this paper, the accelerating effects of three coal-burning additives on the burning of bituminous coal and anthracite are investigated with thermogravimetry (TG) and differential scanning calorimetry (DSC). The coal-burning additive of LSZ was prepared in our laboratory. At the same time a kinetic study is performed on the combustion mechanism of bituminous coal and anthracite by the three coal-burning additives. This would be of interest and use for the Chinese coal industry and for the related environmental considerations.

Experimental

The coal samples studied in this research was prepared according to ASTM Standards (ASTM D 2013-72) and was air dried and ground into fine powder and then passed through a 200-mesh screen. It is believed that for such a small particle size the effect of temperature distribution within the sample particle is eliminated. The bituminous coal and anthracite selected for this study is from the Hua Xin Cement Co., Ltd. Table 1 presents the proximate analysis of the two coal samples, and Table 2 presents their ash composition.

Simultaneous thermogravimetry (TG) and differential scanning calorimetry (DSC) of the coal samples was performed using a Netzsch STA 449C Thermal Analysis System.

The effects of experimental conditions on the TG and DTG curves were initially investigated using samples, in order to establish optimum sample size, air flow rate and heating rate for the present investigation. Due to the high reactivity of coal with oxygen, sample size must be small. With a large sample size, the heat released during the combustion process causes the temperature of the sample to increase in excess of the programmed temperature increase. However, the accuracy of TG decreases with decreasing sample size. Based on the results obtained, a sample mass of 6 mg was chosen for the present investigation. The air flow rate was found to have little effect on the burning profile, except that in static air, due to the lack of oxygen, the burning profile was broad and the intensity was very low. The optimum flow rate was determined to be 30 $cm^3\ min^{-1}$. From these preliminary results, 10°C min^{-1} was determined as the optimum heating rate in terms of peak sharpness and reproducibility.

Overall, the experimental conditions used were: sample size, 6 mg; reference, $A1_2O_3$; heating rate, 10°C min^{-1}; atmosphere, air; flow rate, 30 $cm^3\ min^{-1}$; crucibles, platinum.

The design of experiment is listed in Table 3.

Table 3 The design of experiment

Sample	Coal-burning additive	Content/%	Coals
1#	Undoped	0.0	bituminous coal
2#	LSZ	0.3	bituminous coal
3#	LSZ	0.4	bituminous coal
4#	LSZ	0.5	bituminous coal
5#	$NaNO_3$	0.3	bituminous coal
6#	$KClO_3$	0.3	bituminous coal
7#	Undoped	0.0	anthracite
8#	LSZ	0.3	anthracite
9#	LSZ	0.4	anthracite
10#	LSZ	0.5	anthracite
11#	$NaNO_3$	0.3	anthracite
12#	$KClO_3$	0.3	anthracite

Table 1 Proximate analysis of the bituminous coal and anthracite

Samples	Moisture/ %	Volatile matter/ %	Ash/ %	Fixed carb./ %	Calorific value/ kJ kg^{-1}
Bituminous coal	1.10	25.03	26.20	47.67	24616
Anthracite	0.67	10.12	23.16	66.05	25585

Table 2 Ash compositions analysis of bituminous coal and anthracite (mass%)

Samples	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO
Bituminous coal	49.80	29.11	11.43	3.26	1.25
Anthracite	42.67	28.53	17.05	4.44	1.23

Results and discussion

TG-DTG analysis procedures

The TG and DTG curves show the relative mass loss during heating in air and the rate of mass loss respectively. There are many methods to determine the ignition temperature in the coal combustion tests. In our research, the TG-DTG method was used. A vertical line is drawn from the peak of the DTG curve and intersects with the TG curves, and then from the cross-point a tangent of the TG curve is drawn. The cross-point between the tangent and the parallel lines of the beginning mass loss is defined ignition temperature.

Figure 1 showed the process of fixing ignition temperature. The combustion characteristic parameters of TG and DTG curves include: the initial temperature T_i and the corresponding time t_0, maximum combustion rate $(\mathrm{d}m/\mathrm{d}t)_{max}$ and the corresponding time t_m, the final temperature of the burning T_f and the corresponding time t_f and $\Delta t_{1/2}$ which is the temperature difference between two temperatures at $(\mathrm{d}m/\mathrm{d}t)/(\mathrm{d}m/\mathrm{d}t)_{max}=1/2$. $\Delta t_{1/2}$ is named as half peak width, which represents concentrated degree of combustion product releasing. According these parameters the ignition index D_i and combustion ending index D_f which are presented by Junlin [13] of Wuhan University of Technology can be calculated. The definition of D_i and D_f is as follow:

$$D_i = \frac{(\mathrm{d}m/\mathrm{d}t)_{max}}{t_0 t_m} \quad (1)$$

$$D_f = \frac{(\mathrm{d}m/\mathrm{d}t)_{max}}{\Delta t_{1/2} t_m t_f} \quad (2)$$

The larger value of index D_i and D_f which combined with the characteristic of ignition and burning-out of coals, the better combustibility.

The combustion characteristic parameters of TG and DTG curves were showed in Tables 4 and 5.

It can be observed that for samples doped with coal-burning additives the ignition temperature of the bituminous coal and the anthracite were all reduced. For example the ignition temperature reduced from 413–386, 384–397 and 451–388°C, 427 and 445°C for LSZ, $NaNO_3$ and $KClO_3$, respectively, with respect to the bituminous coal and the anthracite when

Table 4 The combustion characteristic parameters of bituminous coal

Sample	1#	2#	3#	4#	5#	6#
T_i/°C	413	386	405	409	384	397
T_m/°C	479	484	509	508	484	501
T_f/°C	545	556	583	588	561	572
$(\mathrm{d}m/\mathrm{d}t)_{max}$/mg s^{-1}	–4.85	–5.038	–5.40	–4.58	–5.12	–4.34
t_0/s	2419	2217	2407	2465	2310	2401
t_m/s	2823	2803	3020	3050	2921	3000
t_f/s	3230	3228	3464	3545	3400	3435
$\Delta t_{1/2}$/s	923	966	882	1014	945	1079
$D_i(10^{-7})$/mg s^{-3}	7.09	8.11	7.42	6.09	7.59	6.02
$D_f(10^{-10})$/mg s^{-4}	5.76	5.76	5.85	4.80	5.46	3.90

Table 5 The combustion characteristic parameters of anthracite

Sample	7#	8#	9#	10#	11#	12#
T_i/°C	451	388	450	445	427	445
T_m/°C	543	485	526	535	516	535
T_f/°C	617	559	585	603	586	607
$(\mathrm{d}m/\mathrm{d}t)_{max}$/mg s^{-1}	–4.74	–4.95	–4.90	–4.90	–5.09	–5.38
t_0/s	2717	2315	2685	2710	2515	2650
t_m/s	3260	2880	3130	3250	3066	3190
t_f/s	3695	3340	3490	3633	3495	3620
$\Delta t_{1/2}$/s	972	899	903	901	946	856
$D_i(10^{-7})$/mg s^{-3}	5.35	7.43	5.83	5.56	6.60	6.36
$D_f(10^{-10})$/mg s^{-4}	4.05	5.73	4.97	4.61	5.02	5.44

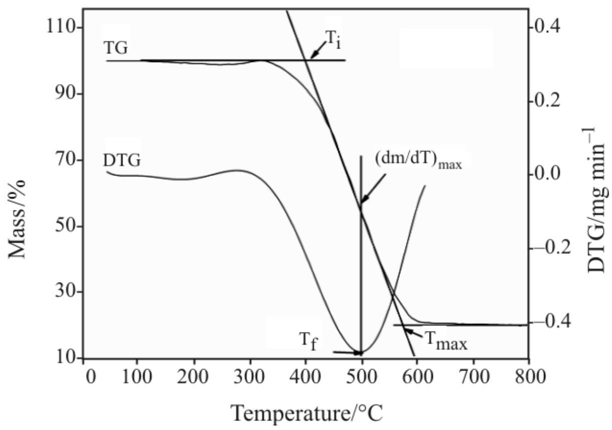

Fig 1 TG-DTG curve of sample 1#

the 0.3%-doped of coal-burning additives was added. The 0.3%-LSZ-doped was the best obviously reduce the ignition temperature for the two kind's coals. In general, those coals with low ignition temperature and high mass loss in the lower temperature range can be considered as easy to ignite and burn out.

Above all the combustion characteristic parameters the D_i and D_f is the most important in the cement industry. The Table 4 showed the effect of coal-burning additives on the bituminous coal. The D_i and D_f were 7.09 and 5.76 without the coal-burning additives. When adding the same content of coal-burning additives the D_i were 8.11, 7.59, 6.02 and the D_f were 5.76, 5.46, 3.90 for LSZ, $NaNO_3$ and $KClO_3$, respectively. So the LSZ can best improve the combustibility of the three coal-burning additives. At the same time it can be observed that adding different content of LSZ from 0.3 to 0.4%, 0.5%, the D_i reduced from 8.11 to 7.42, 6.09 and the D_f changed from 5.76 to 5.95, 4.80. So the 0.3%-LSZ-doped was the most proper. The same change can be seen from Table 5 for the anthracite.

DSC analysis procedures

DSC measurements were carried out simultaneously with TG and were used to estimate the heat of change during the thermal treatment.

Figure 2 showed the DSC curve of the bituminous coal with coal-burning additives. It can be observed that the shape of curve changed after adding coal-burning additives. The temperature which the maximum combustion rate corresponded to reduced 542.83–538.24, 538.79 and 533.64°C for LSZ, $NaNO_3$, and $KClO_3$. Figure 3 showed the DSC curve of the anthracite with coal-burning additives. The shoulder became narrow after adding coal-burning additives. The temperature which the maximum combustion rate corresponded to reduced 576.26–559.55, 562.06 and 573.76°C for LSZ, $NaNO_3$ and $KClO_3$.

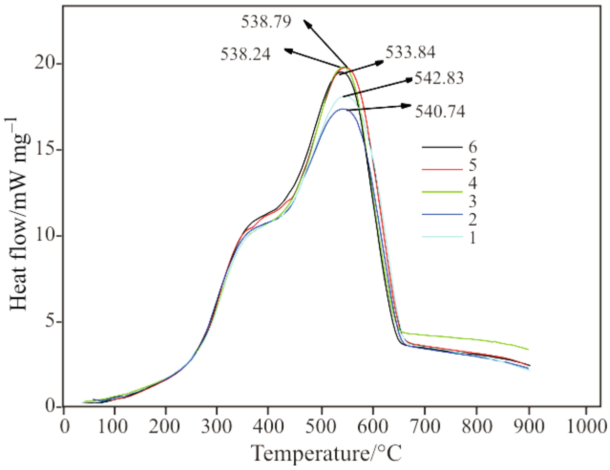

Fig. 2 DSC curve of the bituminous coal

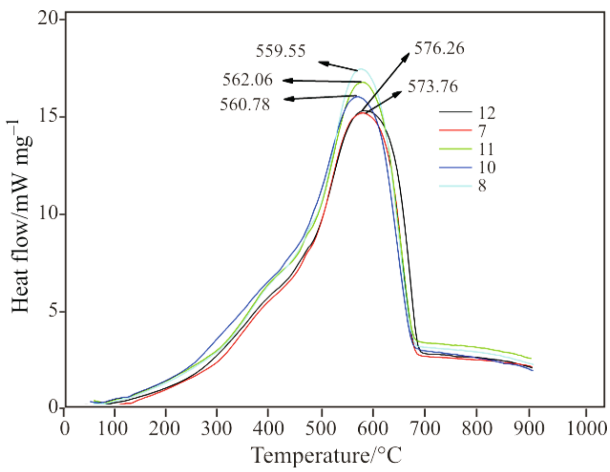

Fig. 3 DSC curve of the anthracite

The kinetics of combustion with coal-burning additives

Combustion parameters describe the combustion process simply and intuitively, but it does not reveal the mechanism. The kinetic study will help us understand the action mechanism of coal-burning additives on the burning of coals. In the process of the kinetic study, the combustion process is approximately regarded as a simple reaction, and no diffuse obstacle exists under the conditions of this experiment. The Arrhenius equation is used to describe the apparent reaction rate (Eq. (3)).

$$k=Ae^{-E/RT} \quad (3)$$

The differential method of Freeman and Carroll is used to obtain the kinetic parameters with the thermogravimetry data.

$$\frac{d\alpha}{dT}=\frac{A}{\varphi}e^{-E/RT}(1-\alpha)^n \quad (4)$$

where k is the apparent reaction rate, A the pre-exponential factor, E the activation energy, R the gas constant, T the temperature, α the remainder percentage, φ the linear heating rate and n the reaction order. Based on experience, n=1, and by itegral

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

According to Eq. (5)

$$y=\ln\left[-\frac{\ln(1-a)}{T^2}\right],\ a=\ln\left[\frac{AR}{\varphi E}\left(1-\frac{2RT}{E}\right)\right],\ b=\frac{E}{R},\ x=\frac{1}{T}$$

In this experimental condition a can be considered as a constant, so the Eq. (5) can be expressed $y=a+bx$. By using Eq. (5) to deal with the thermogravimetry data, a straightline chart of $\ln[-(\ln(1-a))/T^2]$ *vs.* $1/T$ can be obtained (shown in Fig. 4), in which $-E/R$ is the slope of the line and a is the intercept [14, 15]. The pre-exponential factor A can be calculated from E. The obtained kinetic parameters of combustion were listed in Table 6.

The activation energy values obtained by Freeman and Carroll and Arrhenius models in the main combustion reaction region are given in Table 6. It can be seen that the coal-burning additives LSZ and $NaNO_3$ reduce the apparent activation energy of combustion of bituminous coal and anthracite obviously, only $KClO_3$ makes it little change. Lower activation energies were the indication of easy combustibility of coal samples. It was concluded that adding the coal-burning additives affected the activation energy of the coal samples studied. The coal-burning additives can change the combustion process by the catalytic action, resulting in an increase of the overall combustion rate. The above results indicate that the coal-burning additives especially LSZ can improve coal combustion effectiveness.

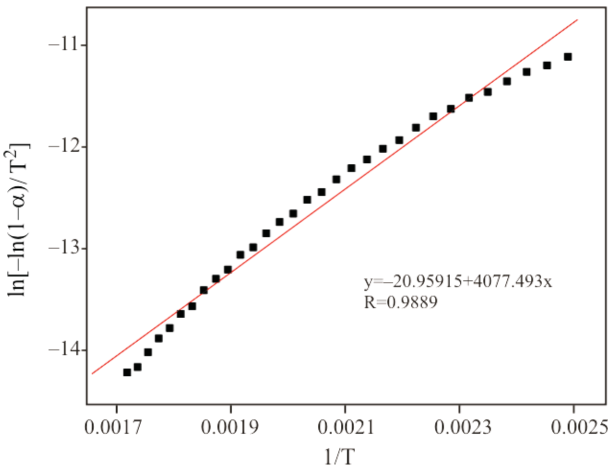

Fig. 4 Chart of $\ln\left[-\frac{\ln(1-a)}{T^2}\right]$ *vs.* $\frac{1}{T}$ of sample 1#

Table 6 The kinetic parameters of combustion

Sample	Temperature range/°C	Activation energy/kJ mol^{-1}	Correlation coefficient/%
1#	T_i~T_f	33.90	98.89
2#	T_i~T_f	30.56	99.06
3#	T_i~T_f	31.05	99.64
4#	T_i~T_f	32.27	99.11
5#	T_i~T_f	30.91	99.33
6#	T_i~T_f	33.90	99.79
7#	T_i~T_f	39.31	99.67
8#	T_i~T_f	29.27	99.24
9#	T_i~T_f	38.53	99.79
10#	T_i~T_f	37.07	99.78
11#	T_i~T_f	34.00	99.71
12#	T_i~T_f	38.51	99.69

Conclusions

- Thermal analysis techniques can be successfully applied to the study of coal combustion. The thermal analysis parameter can be used to characterize and compare the reactivity with coal-burning additives of different coals.
- The coal samples with different coal-burning additives have different combustibility. The ignition temperature of the bituminous coal and the anthracite were all reduced and the D_i and D_f were increased after adding coal-burning additives. The 0.3%-LSZ-doped was the best in reducing ignition temperature and improving the D_i and D_f.
- The kinetic of the effect of coal-burning additives on the combustion of the bituminous coal and the anthracite was studied. Adding the coal-burning additives affected the activation energy of the coal samples studied. The coal-burning additives can change the combustion process by the catalytic action, resulting in an increase of the overall combustion rate.

Acknowledgements

The authors are grateful to Key Laboratory of Silicate Materials Science and Engeering of Wuhan University of Technology.

References

1 K. E. Ozbas, M. V. Kök and C. Hicyilmaz, J. Therm. Anal. Cal., 71 (2003) 849.
2 M. V. Kök and C. Keskin, J. Therm. Anal. Cal., 649 (2001) 1265.

3 L. Wachowski and M. Hofman, J. Therm. Anal. Cal., 2 (2006) 379.
4 X. Li, G. Matuschek, M. Herrera, H. Wang and A. Kettrup, J. Therm. Anal. Cal., 719 (2003) 601.
5 A. G. M. Vasandani and M. Raza Shah, J. Therm. Anal. Cal., 41 (1994) 1053.
6 S. Kizgut, K.Baris and S.Yilmaz, J. Therm. Anal. Cal., 2 (2006) 483.
7 N. Qihong and S. Shaozeng, J. Combust. Sci. Technol., 1 (2001) 72.
8 L. Liang, L. Lu-ping, Z. Jie-ming, Y. Hong-jie and B. Xiang-yan, J. Chang Sha University of Science and Technology (Natural Science), 4 (2005) 44.
9 L. Yanhua, C. Defu and L. Yintan, J. XI'AN Jiaotong University, 9 (2000) 21.
10 L. Li, Z.-C. Tan, S.-H. Meng, S.-D. Wang and D.-Y. Wu, J. Therm. Anal. Cal., 62 (2000) 681.
11 X. Junlin, W. Guiming and Y. Hong, Bull. Chin. Ceram. Soc., 2 (2002) 58.
12 W. Shudong and W. Diyong, J. Fuel Chem. Technol., 3 (1998) 248.
13 X. Jun-lin, H. Feng and Y. Run-zhang, J. Wuhan University Technol.-Mater. Sci., 1 (2002) 72.
14 H. Sis, J. Therm. Anal. Cal., 3 (2007) 864.
15 B. Arias, C. Pevida, F. Rubiera and J. J.Pis, J. Therm. Anal. Cal., 3 (2007) 860.

Received: March 25, 2008
Accepted: May 12, 2008
OnlineFirst: August 15, 2008

DOI: 10.1007/s10973-008-9124-x