Journal of Mechanical Engineering Research and Developments
ISSN: 1024-1752
Website: http://www.jmerd.org
Vol. 38, No. 1, 2015, pp. 112-120

The Characteristics and Kinetics of Municipal Solid Waste and Coal Co-Combustion

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ABSTRACT: The characteristics and kinetics of the co-combustion of municipal solid waste (MSW) and coal were experimentally studied using a thermal gravimetric analyzer. Combustion characteristics of the mixed samples of various combinations of MSW and coal were analyzed using Coats-Redfern combustion kinetics; the results showed that the MSW and coal in the mixes essentially maintained their respective combustion characteristics during the co-combustion process; the MSW in the mixes promoted the combustion characteristics of coal in the mixes. The co-combustion of the MSW-coal mixes exhibited two combustion stages, following second-order kinetics and first-order kinetics, respectively; the combustion of coal only exhibited one combustion stage that followed first-order kinetics. There existed a kinetic compensation effect between the activation energy Ea and pre-exponential factor A in the co-combustion of the MSW-coal mixes.

KEYWORDS: Municipal solid waste; Coal; Co-combustion; Coats-redfern combustion kinetics; Thermo gravimetric analysis (tga).

INTRODUCTION

With the continuous improvement in people's quality of life, the amount of municipal solid waste (MSW) has increased rapidly (Xu et al., 2013), reaching 170,809,000 t in 2012. Currently, in China the comprehensive utilization of MSW is very low, and approximately 90% is discarded or simply shifted to landfills (Ren, 2014), threatening the environment and human health. Therefore, the appropriate treatment of MSW has attracted more and more attention in recent years (Marshall et al., 2013; Zhou et al., 2014).

MSW is being increasingly used in power generation and cement production, which not only eases the energy shortage but also solves environmental pollution problems (Jin et al., 2013; Garg A et al., 2009 Silva R et al., 2010; Yan et al., 2014; Marisamy M et al., 2010). However, due to its high moisture content and low calorific value (Chen et al., 2014), MSW must be mixed with coal to meet the fuel requirements of power generation and cement production, and therefore, making studies of the combustion characteristics and kinetics of MSW-coal mixes important. In recent years, a large number of researchers have investigated the combustion characteristics of coal and MSW. Xing et al. (2013) and Liu et al. (2014) studied the combustion characteristics of kitchen waste at various heating rates and found that the index of combustion characteristics of kitchen waste increased with increasing heating rate. Yang et al. (2011) investigated the combustion characteristics of flammable individual components in MSW and determined the index of combustion characteristics for plastic, kitchen waste, paper and cloth. Wang et al. (2013) studied the combustion characteristics of a waste mix consisting of waste cotton, disposable chopsticks and grocery bags and established the regression equation for the activation energy of the waste mix. Liu et al. (2013) investigated the ignition characteristics of pulverized coal at different oxygen concentrations and found that the ignition temperature of pulverized coal decreased with increased oxygen levels. Gil et al. (2012) and Moon et al. (2013) studied the combustion characteristics of different varieties of coal and obtained the index of combustion characteristics of coal and the corresponding combustion kinetics formula. Moreover, some researchers studied the gas emission and pyrolytic characteristics of MSW and coal mixed, Zhu et al. (2013), Zhao (2002), Alfonso et al. (2013) studied the characteristics of the emission gas in a circulating fluidized bed and found that with the increase of dosage of living garbage, the emission of HCl was increased while others were reduced. Rita B S et al. (2015) studied the pyrolytic characteristics of MSWs using silica reactor under 650 ℃ and found that when the temperature up to 500 ℃, much of volatile coal had been pyrolyzed, the weight of the residual changed a little when the temperature up to 600°C; All of the previous studies primarily addressed the combustion characteristics and dynamics of single component MSW, waste mix or coal, while the co-combustion characteristics and combustion kinetics of MSW-coal mix were rarely investigated.

In the light of the limitation of the research about MSW and coal Co-Combustion, in this paper, combustion experiments were conducted using a thermal gravimetric analyzer. Though which we studied combustion parameters at various mixing ratios and then analyzed the Characteristics, Kinetics and kinetic compensation effect of Co-Combustion which aimed to provide a theoretical basis for industrial applications of MSW-coal mixes as fuel.

EXPERIMENT

Experimental Materials

The experimental materials were MSW and coal. The MSW samples were taken from the campus residential area and primarily composed of flammable domestic waste, including kitchen waste (vegetable leaves and meal leftovers, 55% (m/m), same as below), plastic (20%), fabric (10%) and waste paper (15%). The coal sample was quality bituminous coal produced by a coal mine in Chenzhou, Hunan Province with a heat value of 2,5856.9 kJ kg^{-1}. The technological process analysis of the MSW and coal was conducted according to "Sampling and physical analysis methods for domestic waste (GJ/T 313-2009)" and "Industry analysis methods of coal (GB/T 212-2008)". Briefly, the experimental materials were placed in a 110 ℃ oven and dried until reaching constant weight, and then the samples were pulverized and sieved. The powder that passed through a 100-mesh pore size sieve was collected as testing material. Elemental analysis was performed using an elemental analyzer. The technological process and elemental analysis results are shown in Table 1.

Table 1. Proximate and ultimate analysis of living garbage and coal.

Material	Proximate analysis /%				Ultimate analysis /%				
	M_{ad}	A_{ad}	V_{ad}	FC_{ad}	w(C)	w(H)	w(O)	w(N)	w(S)
Kitchen waste	72.01	0.30	20.89	6.80	40.28	5.83	43.31	2.51	0.22
Plastic	0.41	0.34	91.82	7.43	60.89	8.18	3.43	0.05	0.13
Cloth	2.25	0.94	86.71	10.10	41.23	6.86	45.36	0.72	0.78
Waste paper	7.83	9.49	72.49	10.18	39.62	5.88	44.21	0.23	0.31
Coal	8.52	7.59	30.08	53.81	54.86	3.4	7.13	0.85	0.94

Note: M_{ad}, A_{ad}, V_{ad}, FC_{ad} are all dry base levels.

Experimental Apparatus and Methods

The STA-449C simultaneous thermal analyzer was from NETZSCH (German) and was able to conduct thermo-gravimetry (TG)-differential scanning calorimetry (DSC) and TG-differential thermo-gravimetry (DTG) simultaneously, with a maximum measuring temperature of 1650 ℃.

The experiment in this study focused primarily on the combustion characteristics and kinetics of MSW-coal mixes with different ratios of coal and MSW components. The mixes were made by adding 0%, 25%, 50%, 75% and 100% proportions of coal to the MSW powder, and 7.0 ± 0.1mg of each mix was weighed using an analytical balance (AUY220) and placed in an aluminum crucible. Air was passed into the thermal analyzer (flow rate of 25ml min^{-1}), and the temperature was increased to 900 ℃ at a heating rate of 10 ℃ min^{-1}(Ding et al., 2013). The thermos-gravimetric curve (TG curve) and differential thermo-gravimetric curves (DTG curves) of the combustion process of the mix samples were determined, which were subjected to kinetic analysis using the Coats-Red fern integral method to generate kinetic equations and parameters.

EXPERIMENTAL RESULTS AND ANALYSIS

TG Curve

TG-DTG curves of each mixture sample are shown in Figures 1 and 2.

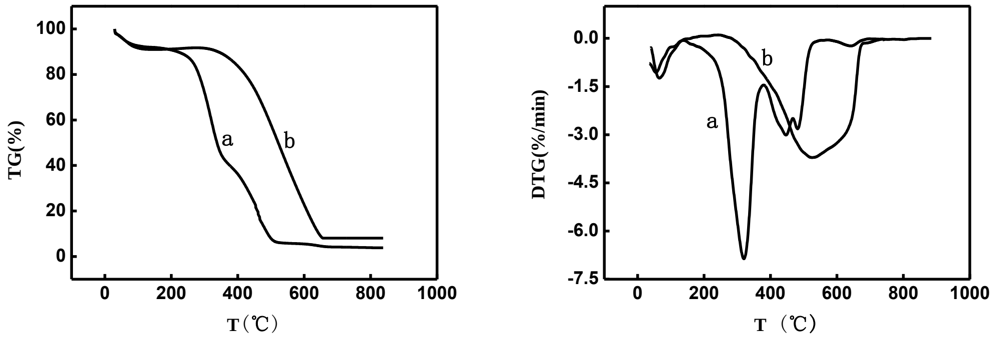

Figure 1. TG - DTG curve of living garbage and coal burning separately (a: Garbage; b: Coal).

The combustion processes of MSW and coal were quite different. The combustion process of MSW exhibited three distinct stages of weight loss, i.e., the water evaporation stage, the volatiles exudation and combustion stage and the fixed carbon combustion stage (Figure 1). Coal combustion stage did not exhibit a second peak, and the last two stages observed in MSW combustion overlapped, which is consistent with the report on coal combustion by Bo et al. (2012).

The combustion of all MSW-coal mix samples showed three distinctive weight loss stages (Figure 2). With increasing MSW content in the mix, the TG curvet shift to a high temperature zone, and the volatiles exudation and combustion stage was elongated while the fixed carbon combustion stage diminished, presumably because the volatiles in the MSW precipitated significantly at relatively low temperature. Ding et al. (2013) found that 40-60% of the volatiles in the MSW could be precipitated at 200-370 ℃. With increasing MSW content in the mix, the stage of volatiles exudation and the combustion zone were elongated, while the fixed carbon combustion stage gradually diminished.

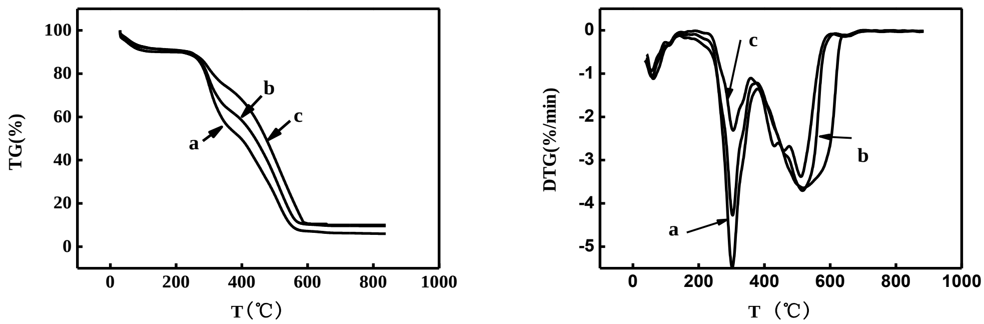

Figure 2. TG-DTG curve of different ratio of living garbage and coal mixed combustion (a: 75% garbage; b: 50% garbage; c: 25% garbage).

Table 2. Weightlessness analysis of living garbage and coal mixed combustion.

	Water evaporation		**Volatile precipitation and combustion**		**Fixed carbon combustion**	
Sample	Weightlessness rate (%)	Temperature range(℃)	Weightlessness rate (%)	Temperature range (℃)	Weightlessness rate (%)	Temperature range (℃)
Garbage	8.11	50~150	52.15	240~380	36.78	380~520
75%Garbage	8.66	50~150	40.93	240~400	46.22	400~595
50%Garbage	8.68	50~150	32.45	240~400	52.69	400~635
25%Garbage	8.88	50~150	17.19	240~400	66.36	400~670

	Water evaporation		Volatile and fixed carbon combustion	
	Weightlessness rate (%)	Temperature range (℃)	Weightlessness rate (%)	Temperature range (℃)
Coal	9.01	50~180	82.94	320-705

The thermo gravimetric analysis results based on TG experimental data and Figure 1 and Figure 2 are shown in Table 2. The temperature of volatiles exudation of coal was approximately 80 ℃ higher than that for MSW, indicating that the volatiles in coal were more difficult to precipitate than the volatiles in MSW. With increasing MSW content in the mix, the burnout temperature decreased gradually, the burnout rate increased from 91.95% to 97.04%, indicating that the MSW component in the mix promoted the combustion of coal and that the ash content of the MSW was lower than that for coal, which is consistent with the results of the technological process analysis.

Combustion Characteristics

Combustion characteristic parameters can be used to evaluate the properties of fuel combustion, which include (1) ignition temperature T_i (℃); (2) burnout temperature T_F (℃); (3) maximum burning rate $(dm/dt)_{max}$ (% ·min^{-1}); and (4) temperature of maximum combustion rate T_{max} (℃). The smaller the T_i, the more easily the fuel burns, and the better the ignition performance. The smaller the T_F, the more easily the fuel burns out. The higher the $(dm/dt)_{max}$, the more intensely the fuel burns. The smaller the T_{max}, the faster the fuel burns. The T_i was defined using the TG-DTG joint definition method [Xiong et al., 2013].The T_F is the temperature when the weight of fuel becomes constant. Through analyzing the TG-DTG curves of the mix, the major combustion parameters of the mix were obtained and are listed in Table 3 (note that t_i, t_{max}, t_F are the times for samples to reach the T_i, T_{max} and T_F (min), respectively).

Table 3. Main combustion characteristic parameters of living garbage and coal blends.

Sample	Ti/ ℃	ti/min	(dm/dt)max/(% ·min-1)	Tmax/ ℃	tmax/min	TF/ ℃	tF/min
Garbage	268.6	24.7	6.86	315	29.2	520	49.2
75%Garbage	269.7	24.8	5.48	308	28.5	595	56.7
50%Garbage	270.8	24.9	4.27	310	28.7	635	60.7
25%Garbage	271.5	25.1	3.65	516	48.6	670	64.2
Coal	419.4	39.3	3.71	526	49.6	705	69.7

Major Parameters of Combustion Characteristics

The T_i is the temperature at which the material starts to burn, reflecting the degree of difficulty for the material to ignite. The T_i of the MSW-coal mixes were all near 270 ℃ (Table 3), similar to the T_i of MSW. The time for the mixes to ignite (approximately 25 min) was also similar to the value for MSW, indicating that the ignition characteristics of the mixes were similar to that of MSW.

The $(dm/dt)_{max}$ and T_{max} reflect the intensity of the combustion of the material. When the MSW content in the mixes were higher than 50%, the T_{max} of the mixes were all approximately 310 ℃, similar to MSW alone, and appeared in the volatiles exudation and combustion stage zone. However, when the MSW content in the mix was reduced from 100% to 50%, the $(dm/dt)_{max}$ decreased from 6.86% min^{-1} to 4.27% min^{-1}, mainly because when the $(dm/dt)_{max}$ appeared in the volatiles exudation and combustion stage, decreasing the MSW content in the mix meant that the content of the volatiles decreased and the exudation of the volatiles was mild; therefore, the $(dm/dt)_{max}$ decreased. When the MSW content in the mix was 25%, the T_{max} was 516 ℃, which was similar to that of coal and appeared in the fixed carbon combustion stage but with a lower $(dm/dt)_{max}$. These results may have occurred because the $(dm/dt)_{max}$ appeared in the fixed carbon combustion stage, decreasing the MSW content in the mix and increasing the fixed carbon content, which burned intensely, leading to $(dm/dt)_{max}$ increasing . It can be observed that the burning of the MSW-coal mix essentially exhibited the combustion features of the respective materials. It (Figure 3) also shows that with increasing MSW content in the mix (from 0% to 75%), the T_{max} of the mixes tended to decrease, indicating that the MSW in the mix could improve the combustion characteristics of coal to a certain extent.

The T_F reflects the burning speed of the material. The T_F of MSW was 520 ℃ and that of coal was 705 ℃, indicating that it was easier for MSW to burn out than coal. As the MSW content in the mix increased from 25% to 75%, the T_F decreased by 75 ℃, and the time to reach burnout was shortened by 7.5 min. Moreover, after adding MSW to coal, the T_F of all of the mixes significantly decreased compared to coal, indicating that the MSW in the mix promoted the combustion of coal.

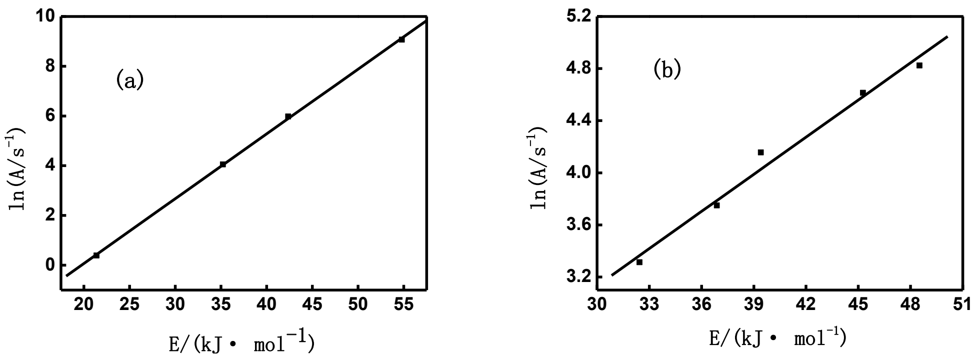

Figure 3. Relationships between activation energy and pre-exponential factor ((a) Volatile precipitation and combustion phase; (b) Fixed carbon combustion phase)

Index of Comprehensive Combustion Characteristics (SN)

The index of comprehensive combustion characteristics (S_N) of a MSW-coal mix can be used to represent the combustion performance of the mix: the greater the S_N, the better the combustion performance. The S_N is calculated by equation (1) (Lu et al., 2012; Wang et al., 2012; Zhang et al., 2005).

$$S_N = \frac{\left(dm/dt\right)_{\max} ?\left(dm \quad dt\right)_{mean}}{T_i^2 T_F} \tag{1}$$

In the equation, $(dm/dt)_{mean}$ represents the average burnrate (% min^{-1}): The greater $(dm/dt)_{mean}$, the more easily the material burns, and the better the combustion performance. The calculation results are shown in Table 4.

The $(dm/dt)_{mean}$ and the S_N of MSW were the highest, while the values for coal were the lowest (Table 4), indicating that MSW performed the best in combustion while coal performed the worst. In addition, as the MSW content in the mix increased, the $(dm/dt)_{mean}$ and the S_N of the mixes all increased gradually, indicating that MSW could improve the combustion properties of coal, e.g., by speeding up the burn rate of coal.

Table 4. Comprehensive behavior indexes of living garbage and coal blends.

Sample	Ti/ ℃	TF/ ℃	(dm/dt) max/(% ·min-1)	(dm/dt) mean/(% ·min-1)	SN
Garbage	268.6	520	6.86	3.12	9.19×10^{-8}
75% Garbage	269.7	595	5.48	2.52	5.40×10^{-8}
50% Garbage	270.8	635	4.27	2.20	3.50×10^{-8}
25% Garbage	271.5	670	3.64	2.13	2.77×10^{-8}
Coal	419.4	705	3.71	2.04	1.59×10^{-8}

Combustion Kinetics Analysis

The purpose of combustion kinetics analysis is primarily to determine the “kinetic triplet”, i.e., the mechanism function f(α), activation energy E_a and frequency factor A, which define the combustion reaction mechanism that can be used to explain the principles of the thermal kinetics reactions obtained in the experiments (Jiang et al., 2013). The combustion kinetics of the MSW-coal mix were analyzed using the Coats-Red fern integral method (Hu et al., 2008; Sait et al., 2012) in this study.

According to the law of conservation of mass, Arrhenius equation and gas-solid reaction function in the chemical reaction process, the following burn rate equation can be deduced:

$$\frac{d\alpha}{dt} = Ae^{\left(-\frac{E}{RT}\right)}(1-\alpha)^n \tag{2}$$

In this equation, α is the conversion rate (%): $\alpha = \frac{W_0 - W_t}{W_{0-}W_\infty} \times 100\%$; in which w_0 and w_∞ are the sample initial weight and sample final weight(mg); w_t is the sample weight at the temperature point of T (mg); t is the combustion reaction time (s); E is the activation energy (kJ ·mol^{-1}); A is the pre-exponential factor (s^{-1}); R is the gas constant(8.314J (mol ·K)$^{-1}$); T is the combustion temperature(K); and n is the reaction order.

If the experiments are conducted at a constant temperature and speed $\Phi = \frac{dT}{dt}$ (the heating rate of this experiment was 10K min-1), then $dt = \frac{dT}{\Phi}$ can be substituted into equation (2) to obtain

$$\frac{d\alpha}{dT} = \frac{A}{\Phi} e^{\left(-\frac{E}{RT}\right)} (1-\alpha) \tag{3}$$

After Coats-Red fern integration on equation (3) and approximation, the following equations can be generated:

when n=1,
$$\ln(-\frac{\ln(1-\alpha)}{T^2}) = \ln\left(\frac{AR}{\Phi E}\right) - \frac{E}{RT} \tag{4}$$

when n≠1,
$$\ln(\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}) = \ln\left(\frac{AR}{\Phi E}\right) - \frac{E}{RT} \tag{5}$$

Using $\ln(-\frac{\ln(1-\alpha)}{T^2})$ or $\ln(\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)})$, as the vertical axis and 1/T as the abscissa to map, a line can be obtained, and the slope and intercept of the line can be used to calculate the activation energy E and activating factor A. In this experiment, investigating combustion in two stages, i.e., the volatiles exudation and combustion stage and the fixed carbon combustion stage, with different reaction orders, conducted the combustion kinetics analysis of the mix during the combustion process. The kinetic equations with the best fit and related parameters were then calculated using the

Table 5. Kinetic parameters of combustion for living garbage, coal and their blends.

Sample	**n**	**Temperature range (℃)**	**Dynamic equation**	**E/(kJ ·mol-1)**	**ln(A/s-1)**	**R**
Garbage	2	240~380	y=-6590x-2.02	54.79	9.07	0.9943
	1	400~510	y=-3902x-7.26	32.44	3.31	0.9923
75% Garbage	2	240~400	y=-5095x-4.86	42.36	5.98	0.9905
	1	420~570	y=-4740x-6.61	39.41	4.16	0.9924
50% Garbage	2	240~400	y=-4236x-6.60	35.22	4.05	0.9925
	1	420~630	y=-4436x-6.95	36.88	3.75	0.9916
25% Garbage	2	240~400	y=-2574x-9.77	21.40	0.39	0.9901
	1	420~660	y=-5445x-6.29	45.27	4.61	0.9950
Coal	1	360~690	y=-5836x-6.15	48.52	4.82	0.9983

Coats-Red fern integral method. The results are shown in Table 5. By comparing the reaction order, it was found that the principles of the combustion reaction kinetics of MSW and the MSW-coal mix at the volatiles exudation and combustion stage and the fixed carbon combustion stage were rather different, exhibiting second-order and first-order reaction kinetics, respectively. Liu et al. (2015) studied the combustion characteristics and kinetics of kitchen waste and found that the combustion stage also exhibited second-order and first-order reaction kinetics. In comparison, the reaction of coal followed only first-order kinetics throughout the combustion process.

In the volatiles exudation and combustion stage, the activation energy decreased from 42.36 to 21.40 kJ mol^{-1}as the MSW content in the mix decreased, indicating that the reactivity gradually increased. In addition, the activation energy of the mix at this stage was always lower than the activation energy of MSW, which generated higher reactivity in the combustion of the mix than in MSW alone. The main reason is that within the temperature range of 240-400^{o}℃, the major combustion component in the mix was the volatiles in the MSW; With decreasing MSW content in the mix, the combustion from the volatiles in the mix decreased, and therefore, the energy required for combustion was lowered, and the reactivity of the combustion was enhanced.

The fixed carbon combustion stage was the main combustion stage of coal, during which the activation energy of the mixes were lower than that for coal, but the combustion reactivity of the mixes were higher than that for coal, indicating that MSW promoted the combustion of coal. When the proportion of MSW in the mix was 50%, the minimum value of the activation energy was 36.88 kJ mol^{-1}, achieved the highest reactivity. When MSW and coal are blended at a proportion of 50%, the combustion performance of coal was maximized. Hu et al. (2015) analyzed the co-combustion of paper mill sludge and municipal solid waste and found that with decreasing paper mill sludge content in the mix, the reactivity of the combustion was the trend of the increase after the first decrease. Massaro et al. (2014) studied the combustion characterization of briquetted coal fines with municipal solid waste plastic (MSW) binders and found that with the increase of MSW in the mix could decrease the reactivity of the combustion of coal.

With the increasing MSW content in the mix, during the volatiles exudation and combustion stage and fixed carbon combustion stage, the activation energy and pre-exponential factor were synchronized in their dynamics (Table 5). Linear integration on the kinetic parameters of the activation energy E_a and pre-exponential factor A at these two stages produced a well-fitted linear equation, indicating that kinetic compensation effects existed in the combustion of the mix. Guo et al. (1999) studied the combustion kinetics of MSWs and found that there existed a kinetic compensation effect.

The linear kinetic compensation effect relationship can be expressed as follows (Bai et al., 2013):

$$\ln A = aEa + b \tag{6}$$

Where a and b are the compensation coefficients. The fitting coefficients obtained through linear integration on the kinetic parameters for these two stages are shown in Table 6, and the fitting line is shown in Fig. 3.

Table 6. Fitting data of dynamic compensation line.

Combustion phase	a	b	R
Volatile precipitation and combustion phase	0.261	-5.143	0.9998
Fixed carbon combustion phase	0.095	0.283	0.9913

CONCLUSIONS

The MSW promoted the combustion of coal in the mix. The MSW-coal in the mix essentially maintained their respective combustion characteristics during the co-combustion process and MSW improved the overall combustion performance of coal in the mix. The combustion of the MSW-coal mix followed second-order kinetics in the volatiles exudation and combustion stage and followed first-order kinetics in the fixed carbon combustion stage. As the MSW content in the mix increased, there existed a kinetic compensation effect in the two stages (i.e., the volatiles exudation and combustion stage and the fixed carbon combustion stage).

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