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Study on the comprehensive combustion kinetics of MSW*

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Abstract: The combustion behavior of typical components of MSW was examined with a thermal gravimetric analyzer (TGA). The experiments were done over the temperature range of room temperature to 1000 °C at a heating rate of 10 °C/min and in an oxidizing atmosphere. The results indicated that the entire weight loss process of each typical component of MSW consists of one to three distinct combustion stages. The combustion of typical components of MSW could be modeled by one to three independent reactions. The corresponding parameters of typical components of MSW such as activation energy, pre-exponential factor, and reaction order were determined. The calculated results using the comprehensive kinetic model composed of one to three independent and consecutive reactions, agreed well with experimental results.

Key words: Municipal solid waste (MSW), Kinetics, Combustion, Thermal gravimetric analysis
Document code: A **CLC number:** TK16

INTRODUCTION

With the rapid development of the economy, the amount of municipal solid waste (MSW) increased at a rate of 8%−10% annually in China. The cities of China generated approximately 150 million tons of MSW in 2000 (Du, 2000; Xu *et al.*, 2001). MSW has become a serious environmental problem troubling many cities. Because of its advantage of maximum volume/quantity reduction and energy recovery, MSW incineration has been resorted to in more and more cities in China. Consequently study of the combustion characteristics of MSW is interesting. Thermogravimetric analysis is one of the most used techniques to study the combustion kinetics of fuel. Most kinetic studies use simple reaction models in different temperature range, which inevitably led to a breakpoint in the calculation in order to obtain satisfactory fits to the experimental results and usually could not yield good results for complex and diverse MSW (Li *et al.*, 1998; Cozzani *et al.*, 1995; Fritsky *et al.*, 1994; Narukawa *et al.*, 1997). A new consecutive kinetic model for the combustion of MSW is proposed in this paper based on the hypothesis that each stage of weight loss stands for a reaction of a component of the sample and that the kinetic parameters of each reaction remains constant over the whole temperature range of the experiment. This model was used to determine the corresponding parameters of typical components of MSW such as activation energy, pre-exponential factor, and reaction order. The results obtained with the kinetic model, composed of one to three independent and consecutive reactions, agreed well with experimental results.

EXPERIMENTAL DETAILS

Typical combustible components of MSW (including wood, paper, food, PE and PVC) were

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taken as samples. Samples were dried at 100 °C for 2−8 hours, and then ground to less than 0.2 mm. The initial mass of each sample was about 5 mg, thereby reducing the effects of mass- and heat-transfer resistance. Their proximate analyses are listed in Table 1.

The thermogravimetric data were obtained with SINKU RIKO TGD (made in Japan) by recording TG, DTG and DTA, under conditions of linear temperature increase (10 K/min) from room temperature to 1000 °C. The air flow rate was 100 ml/min.

TG: thermogravimetry, the sample mass change with the program-controlled temperature, %.

DTG: differential thermogravimetry, the sample mass change rate with the program-controlled temperature, $^{\circ}C^{-1}$.

DTA: differential thermal analysis, relative temperature difference between the sample and the referenced material with the program-controlled temperature, μV.

RESULTS AND DISCUSSION

Thermogravimetric results of typical components are shown in Fig.1 (in the next page). Although each sample was dried before test, waste wood and food still contain a little inherent water, which is evaporated before 160 °C, and has little weight loss of most components appears before 520 °C, effect on devolatilization and combustion. The PVC is an exception (weight loss continues until more than 700 °C). The DTG curve of each sample consists of one to three distinct stages, two stages for bio-waste (waste paper, wood, food), one stage for waste plastic (PE) and three stages for PVC. The first stage of biowaste involves volatile release and combustion; the second stage involves char combustion. Because plastic does not contain fixed carbon (Table 1), it has only one stage. The weight loss of PVC is more complicated, the first stage mainly involves release of HCl; the second stage involves release of benzene, toluene and other hydrocarbons (Wu *et al.*, 1994); the third stage may involve char combustion and decomposition of inorganic material. The analysis of thermogravimetric results is shown in Table 2.

KINETICS

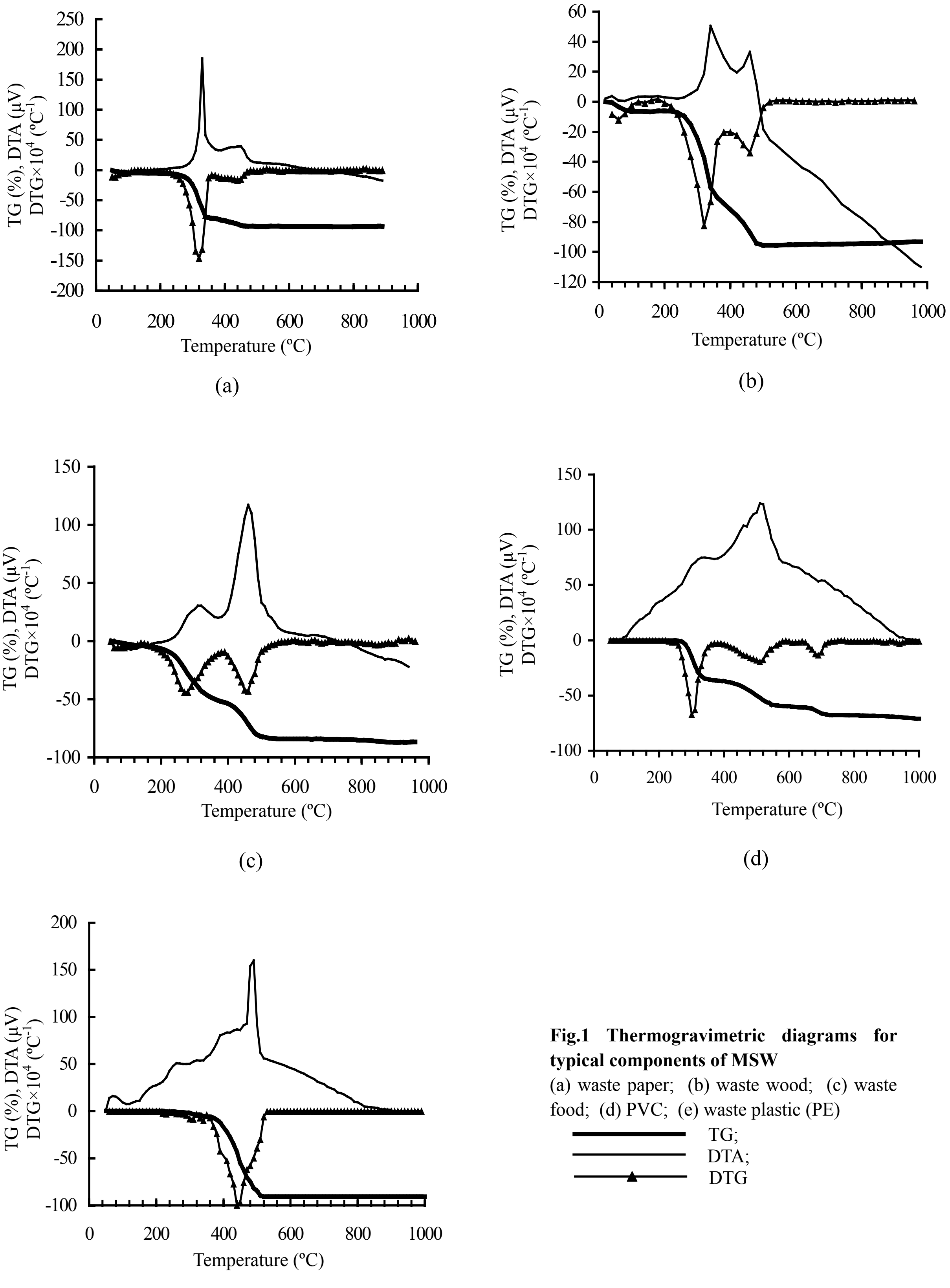
A new consecutive kinetic model for the combustion of MSW is proposed in this paper based on the hypothesis that each stage of weight loss stands for a reaction of one pseudo-part of the sample and that the kinetic parameters of each reaction keeps constant over the whole temperature range of the experiment. That means the number of weight loss stages equals the number of main reactions. In this model the evaporation of water and the residue of combustion are ruled out, and the conver-

Table 1 Proximate analyses of typical components of MSW(%)

	W (water)	*A* (ash)	*VM* (volatile matter)	*FC* (fixed carbon)
Waste wood	7.12	1.58	75.60	15.70
Waste plastic (PE)	0.57	2.58	96.85	ND
Waste paper	2.64	6.13	83.20	8.03
Waste food	14.55	4.00	60.14	21.31
PVC	0.24	24.20	69.29	6.27

Table 2 Analysis of thermogravimetric results

	Waste paper	Waste wood	PVC	Waste food	Waste plastic
Weight loss range(°C)	190−500	200−500	230−750	180−520	230−520
Number of stages	2	2	3	2	1
Weight loss peak(°C)	320/440	280/450	300/500/690	280/460	450



(a)

(b)

(c)

(d)

(e)

Fig.1 Thermogravimetric diagrams for typical components of MSW

(a) waste paper; (b) waste wood; (c) waste food; (d) PVC; (e) waste plastic (PE) sion rate is adopted to indicate the reacting degree.

Therefore, for each pseudo-part (Coats and Redfern, 1964)

$$\frac{\mathrm{d}\alpha_i}{\mathrm{d}\tau}=A_i\exp(-\frac{E_i}{RT})(1-\alpha_i)^{n_i} \tag{1}$$

For PVC, i=1, 2, 3; for biowaste, i=1, 2; for waste plastic (PE), i=1. The variable α_i is the degree of transformation of the pseudo-part i.

$$\alpha_i=\frac{w_{i0}-w_i}{w_{i0}-w_{i\infty}} \tag{2}$$

w_{i0} is the initial weight of pseudo-part i; w_i is the weight of pseudo-part i at time τ; $w_{i\infty}$ is the residual weight of pseudo-part i in the end, based on the hypothesis, $w_{i\infty}=0$; E_i is apparent activation energy of pseudo-part i (J/mol); n_i is the reaction order of pseudo-part i; A_i is the pre-exponential factor of pseudo-part i (min^{-1}); R is the gas constant (J/molK); T is heating temperature (K).

Heating rate β is a constant since the temperature is raised linearly.

$$\beta=\frac{\mathrm{d}T}{\mathrm{d}\tau} \tag{3}$$

Combining Eq.(3) with Eq.(1) we can write

$$\frac{\mathrm{d}\alpha_i}{\mathrm{d}T}=\frac{A_i}{\beta}\exp(-\frac{E_i}{RT})(1-\alpha_i)^{n_i} \tag{4}$$

The combustion of each sample can be written as follows:

$$\alpha=\sum_{i=1}^{I}z_{i0}\alpha_i \tag{5}$$

$$z_{i0}=\frac{w_{i0}-w_{i\infty}}{w_0-w_\infty} \tag{6}$$

$$\alpha=\frac{w_0-w}{w_0-w_\infty} \tag{7}$$

α is the general conversion rate of the sample at time τ; I is the number of pseudo-parts; w_0 is the initial weight of the sample; w is the weight of the sample at time τ; w_∞ is the residual weight of the sample in the end; z_{i0} is the ratio of the weight of pseudo-part i to the global loss weight of the sample .

Differentiating Eq.(5), we get

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T}=\sum_{i=1}^{I}z_{i0}\frac{\mathrm{d}\alpha_i}{\mathrm{d}T} \tag{8}$$

Therefore, once the kinetic parameters E_i, n_i, A_i and z_{i0} are solved, the global kinetic equation of the sample can be calculated. These parameters are determined by the least square method by minimizing the following function:

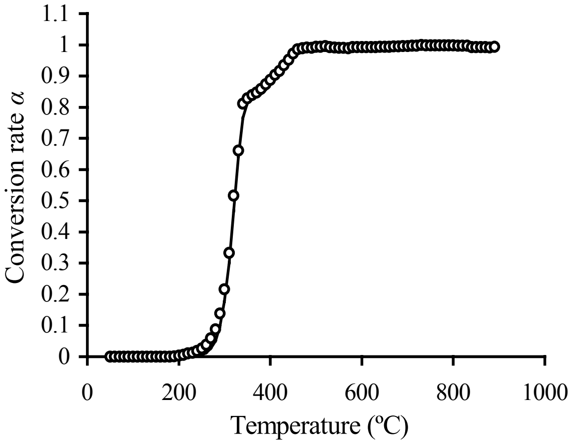
$$S=\sum_{j=1}^{N}[(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_j^{\mathrm{exp}}-(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_j^{\mathrm{calc}}]^2 \tag{9}$$

The subscript j refers to the data points used; N is the number of data points; $(\mathrm{d}\alpha/\mathrm{d}T)^{\mathrm{exp}}$ represents the observed value and $(\mathrm{d}\alpha/\mathrm{d}T)^{\mathrm{calc}}$ represents the calculated value. The average deviation σ is used to describe the accuracy of the calculation result.

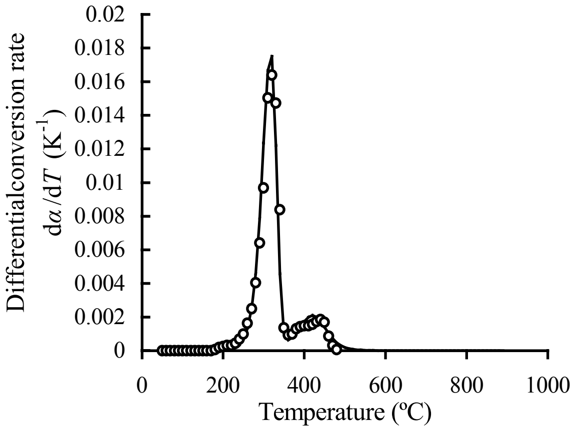
$$\sigma=\frac{\sqrt{\frac{S}{N}}}{(\frac{\mathrm{d}\alpha}{\mathrm{d}T})_{\mathrm{m}}^{\mathrm{exp}}}\times 100\% \tag{10}$$

where $(\mathrm{d}\alpha/\mathrm{d}T)_{\mathrm{m}}^{\mathrm{exp}}$ is the maximum experimental value of $\mathrm{d}\alpha/\mathrm{d}T$. The kinetic parameters for typical component of MSW are shown in Table 3. The average deviation σ varies from 3.19% to 9.48%.

Experimental and calculated normalized DTG, TG curves are shown in Fig.2. Table 3 and Fig.2 indicate that the comprehensive kinetic model composed of one to three independent and consecutive reactions, yields results agreeing well with the experimental results over the whole temperature range.


Conversion rate *α*
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
200
400
600
800
1000
Temperature (ºC)

(a)


Differentialconversion rate
d*α* /d*T* (K⁻¹)
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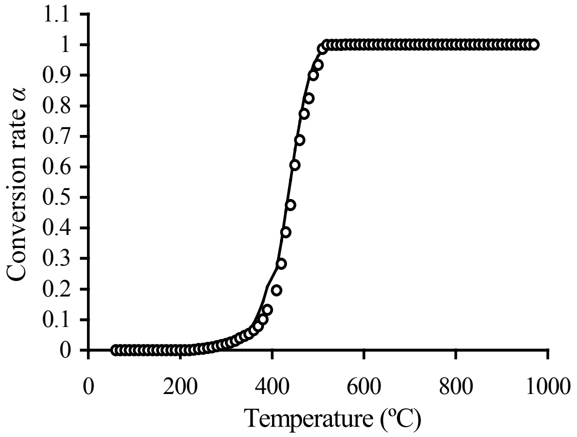
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
0
200
400
600
800
1000
Temperature (ºC)

(a)'


Conversion rate *α*
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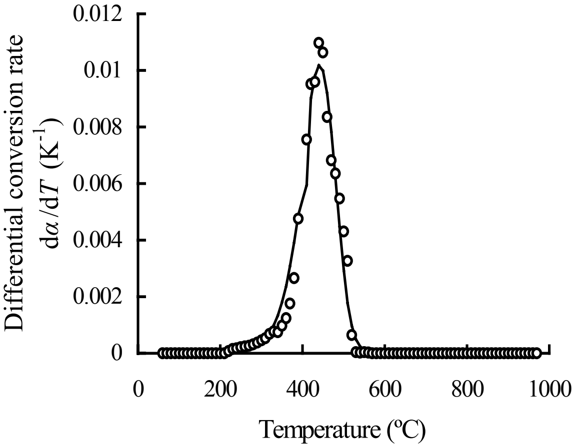
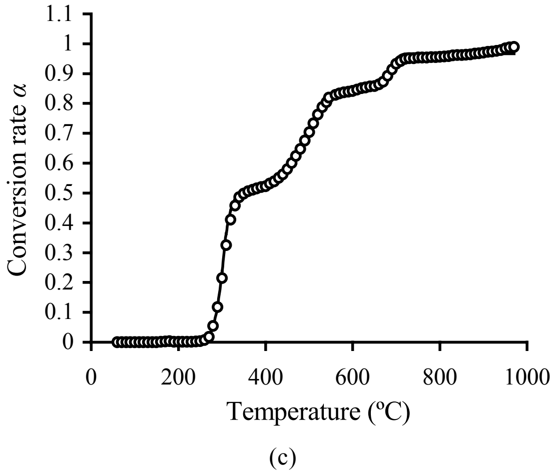
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
200
400
600
800
1000
Temperature (ºC)

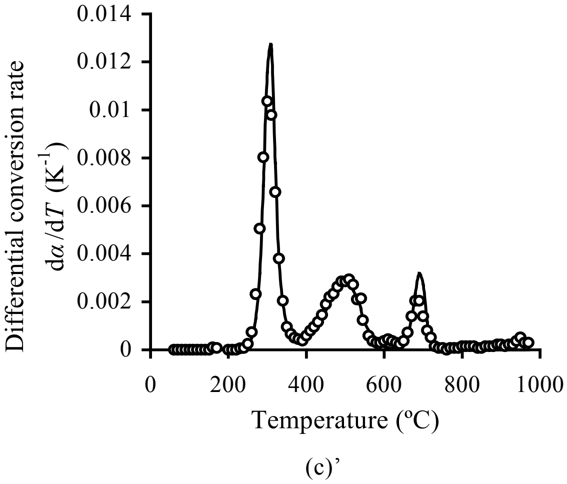
(b)


Differential conversion rate
d*α* /d*T* (K⁻¹)
0.012
0.01
0.008
0.006
0.004
0.002
0
0
200
400
600
800
1000
Temperature (ºC)

(b)'


Conversion rate *α*
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
200
400
600
800
1000
Temperature (ºC)

(c)


Differential conversion rate
d*α* /d*T* (K⁻¹)
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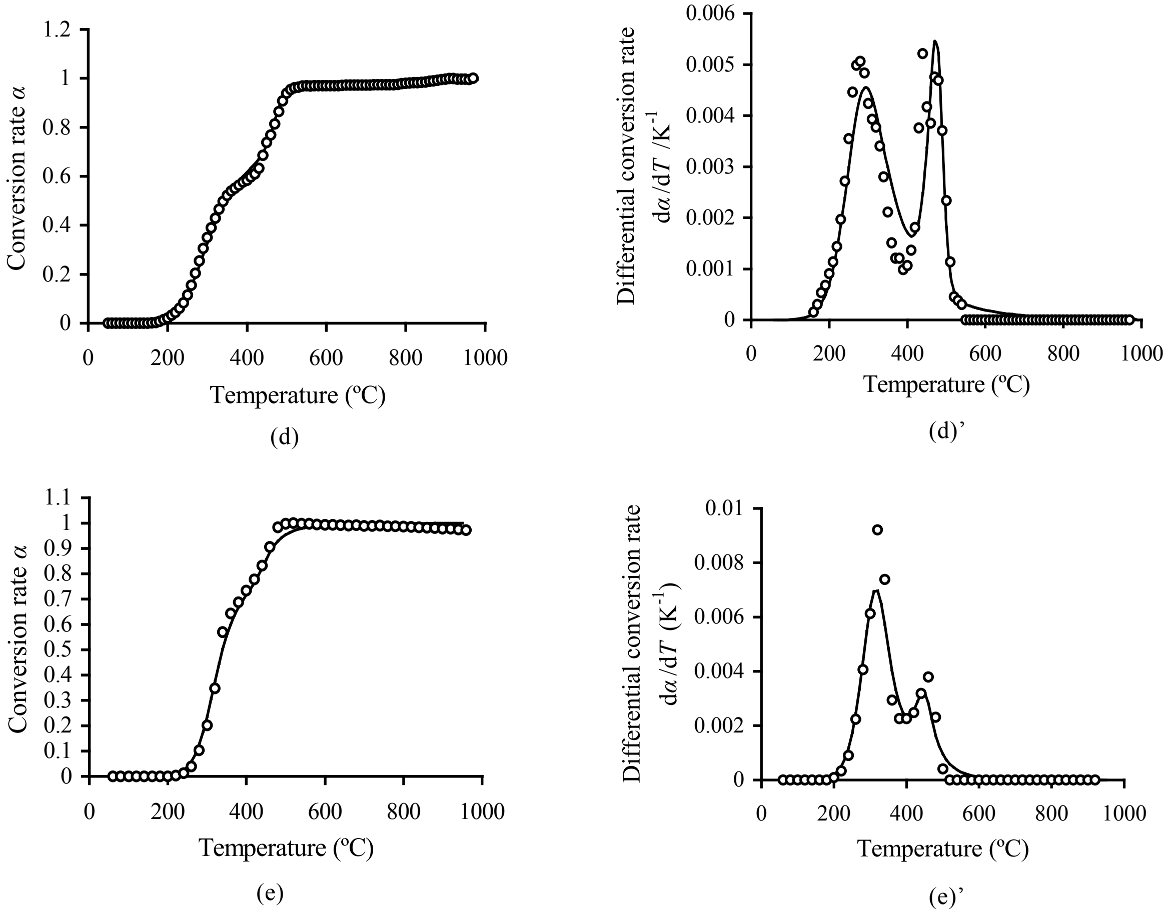
0.012
0.01
0.008
0.006
0.004
0.002
0
0
200
400
600
800
1000
Temperature (ºC)

(c)'



(d) (d)'

(e) (e)'

Fig.2 Experimental and calculated normalized TG, DTG curves

(a), (b), (c), (d), (e) : normalized TG curve for waste paper, waste plastic(PE), PVC, waste food and waste wood respectively;

(a)', (b)', (c)', (d)', (e)': normalized DTG curve for waste paper, waste plastic(PE), PVC, waste food and waste wood respectively

○ Exp.; ——— Model

Table 3 The comprehensive kinetic parameters value for the combustion of typical component of MSW

	Parameter	Value (%)	Parameter (min^{-1})	Value	Parameter (kJ/mol)	Value	Parameter	Value	σ (%)
Plastic	z_{10}	100	A_1	2.68×10^6	E_1	95.6	n_1	1.2	3.90
Paper	z_{10}	85	A_1	5.58×10^{13}	E_1	157.1	n_1	2.6	4.00
	z_{20}	15	A_2	2.65×10^{11}	E_2	128.4	n_2	1.4	
Wood	z_{10}	81	A_1	3.80×10^{12}	E_1	92.2	n_1	2.5	5.89
	z_{20}	19	A_2	7.50×10^{13}	E_2	187.8	n_2	2.5	
Food	z_{10}	76	A_1	1.97×10^6	E_1	68.6	n_1	3.0	9.48
	z_{20}	24	A_2	1.73×10^{18}	E_2	256.8	n_2	1.5	
PVC	z_{10}	52.0	A_1	9.50×10^{21}	E_1	234.4	n_1	2.2	4.82
	z_{20}	32.3	A_2	1.20×10^7	E_2	112.8	n_2	1.3	
	z_{30}	15.7	A_3	1.29×10^{31}	E_3	571.6	n_3	1.0	

CONCLUSION

The entire weight loss process of typical MSW components consists of one to three distinct combustion stages, two stages for biowaste (waste paper, wood, food), one stage for waste plastic (PE) and three stages for PVC.

The combustion of typical components of MSW could be modeled by one to three independent reactions. Then the corresponding parameters of typical components of MSW such as activation energy, pre-exponential factor, and reaction order could be determined based on the experiments. The comprehensive kinetic model composed of one to three independent and consecutive reactions, gives results agreeing well with the experimental results.

Application of this consecutive kinetic model could avoid a breakpoint and conveniently predict the combustion rate of municipal solid waste under certain work conditions.

References

Coats, A.W., Redfern, J.P., 1964. Kinetic parameters from thermogravimetric data. *Nature*, **201**(4914):68-69.

Cozzani, V., Petarca, L., Tognotti, L., 1995. Devolatilization and pyrolysis of refuse derived fuels: characterization and kinetic modeling by a thermogravimetric and calorimetric approach. *Fuel*, **74**:903-912.

Du, Y., 2000. Advances in MSW incineration technology. *New Energy*, **22**(1):24-29.

Fritsky, K.J., Miller, D.L., Cernansky, N.P., 1994. Methodology for modeling the devolatilization of refuse-derived fuel from thermogravimetric analysis of municipal solid waste components. *J. Air & Waste Manage. Assoc.*, **44**:1116-1123.

Li, B., Yan, J.H., Shang, N., Chi, Y., Cen, K.F., 1998. Study on the combustion characteristics of MSW. *Journal of Fuel Chemistry and Technology*, **26**(6):564-568.

Narukawa, K., Goto, H., Chen, Y., Yamazaki, R., Mori, S., 1997. Japanese RDF-Fired Power Generation System and Fundamental Research on RDF Combustion. Proc. 14th Fluidized Bed Combustion, **1**:633-639.

Wu, C.H., Chang, C.Y., Hor, J.L., Shih, S.M., Chen, L.W., 1994. Two-stage pyrolysis model of PVC. *Can J Chem Eng*, **72**(4):644-650.

Xu, X., Li, X.D., Yan, J.H., Lu, S.Y., Gu, Y.L., Chi, Y., Cen, K.F., 2001. PCDD/Fs emission in a 150 t/d MSW and coal co-firing fluidized bed incinerator. *Journal of Zhejiang University SCIENCE*, **2**(3):278-283.