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# A Study on Combustion Characteristics and Kinetic Model of Municipal Solid Wastes

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In this paper, our work is focused on the fundamental combustion characteristics of the combustibles in MSW and its kinetic model. The combustion reactivity of the different combustibles in MSW and their mixtures such as TG and DTA profiles were studied by thermogravimetry (TG) and differential thermal analysis (DTA). On the basis of the investigations of combustion and pyrolysis characters of the combustibles in MSW, kinetic parameters such as activation energy and preexponential factor of each combustible were determined. A kinetic model describing the combustion reactive processes of the combustibles in MSW was proposed. From the study, it can be concluded that: (1) The combustibles in MSW can mainly be divided into two types of matters—one is fibrous matter, and the other is polymer matter. (2) The combustion process of combustibles in MSW mainly consists of two stages. At the first stage, the volatile contained in fibrous matter was released, and then the released volatile matter was combusted continuously; at the second stage, the fixed carbon of fibrous matter was burned, and pyrolysis and combustion of the polymer matter happened at the same time. (3) The combustion rate of the combustibles in MSW can be expressed by a weighted sum of rates of each combustible, and the complex combustion processes of combustibles in MSW can be described by simple kinetic model. The computed results of the kinetic model can mostly fit experimental data.

# Introduction

The amount of municipal solid wastes (MSW) is increasing dramatically in the world. And disposal of MSW has become an important global environmental issue. Thermal disposal methods such as combustion, pyrolysis, and gasification offer considerable benefits over conventional landfills: energy can be recovered, and the quantity of waste can be reduced greatly. In China, the current production of MSW is about 1,500 million tons per year and increases by 8-10% every year. Since the heating value of MSW in some area of China (especially in Southern China) increases as the proportion of combustibles in the MSW is increased due to the improving standard of living, thermal disposal of MSW and utilizing MSW as a new energy resource are feasible. The combustible in the MSW is complex, composed by many components, and each component has a different combustibility. As a result, the design and control of the MSW combustion process are more difficult than those of other single solid fuels such as coal. Therefore, it is necessary to study the combustion characteristics of MSW for designing suitable municipal incinerators and also for controlling combustion conditions to achieve higher efficiency and reduce air pollution.

Unlike single material such as coal and wood, the fundamental study of MSW has received less attention due to its complexity. Some studies<sup>1–4</sup> on single materials such as plastic, cellulose, and paper have been reported. Some of the pervious studies mostly focus on the larger devices and the processing for thermochemical treatment of MSW.<sup>5,6</sup> Only few studies were carried out on the fundamental thermochemical reaction and kinetic parameters.<sup>7,8</sup>

In this paper, the fundamental combustion characteristics of each combustible in MSW such as paper, textile, food, wood, and plastic and their mixture in

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Table 1. Proximate Analysis of Samples (Dry Basis, wt %)

sample	ash	volatile matter	fixed carbon	calorific value (kJ/g)
paper	2.28	77.35	20.37	14.87
textile	1.21	80.80	17.99	18.66
wood	4.20	80.50	15.30	14.79
food	15.38	70.80	13.72	10.71
plastic	1.00	81.23	17.77	40.06

Table 2. Ultimate Analysis of Samples (dry basis, wt %)

sample	С	Н	O	S	N
paper textile wood food plastic	40.68 44.89 42.39 32.96 80.73	6.06 6.49 5.98 4.86 13.32	46.45 44.83 41.65 36.18	0.28 0.20 0.26 0.36 0.22	0.35 1.33 0.91 1.85

different ratio were carried out by thermogravimetric study, and a kinetic model of the combustibles in MSW was developed. On the basis of the studies of pyrolysis and combustion of combustibles in MSW using TG (thermogravimetry) and DTA (differential thermal analysis), the combustion mode and process of different combustibles in MSW were discussed. Then the kinetic parameters such as activation energy and preexponential factor of each combustible were determined. Finally, a kinetic model describing the combustibles in MSW combustion processes was proposed. And the results computed by the kinetic model were compared with experimental data.

### **Experimental Section**

**Samples.** The MSW used in this study were collected from the MSW landfill site of Guangzhou City (Guangdong Province, P. R. China). The combustibles in MSW were selected out and divided into five parts: paper, textile, wood, food, and plastic as the experimental samples. And different ratios of them were mixed to study the fundamental thermochemical reaction characteristics.

Considering that the large particles suffer from nonisothermal temperature distributions owing to the low thermal conductivity of MSW, prior to the experiments, these samples were cleaned and dried in a drier at 393 K for 8 h and then ground to less than 80  $\mu m$ . The ultimate and proximate analysis data of these samples are shown in Tables 1 and 2. From the tables, it can be found that the contents of sulfur and nitrogen of each combustible in MSW are very low and the volatile content is high.

**Experimental Conditions.** The pyrolysis and combustion experiments of the combustibles in MSW samples were carried out using a TG-DTA system (WCT-2, made by Beijing Optical Instrument Factory, China). The reaction atmospheres are nitrogen and air for combustion and pyrolysis, respectively, and the gas flow rate is 30 mL/min. About 10 mg of sample particles is loaded on the sample holder, then the sample is heated at constant heating rate of 10K/min, and the final temperature is raised to 1173 K. At the same time, the computer records the TG and DTA profiles.

#### **Results and Discussion**

**Combustion Process.** Figure 1a—e shows the TG-DTA curves of pyrolysis and combustion for each combustible. In general, it can be seen that the TG-DTA profiles of five combustibles shown in Figure 1a-e exhibit similar behavior. The profiles of DTA in Figure 1a-d show that there are two exothermic peaks in the combustion process and, correspondingly, there are two weight-loss stages on their combustion profiles. Compared with the pyrolysis profiles shown in Figure 1a-e it can be suggested that the first exothermic peak is led by released volatile matter combustion, and the second exothermic peak is due to the fixed carbon combustion. From Figure 1, it also can be seen that the second exothermic area is significantly bigger than that of the first one. There are two possible reasons for this. One is that the pyrolysis reaction takes place in first stage and it is an endothermic reaction. Another reason is that the fixed carbon has a high heating value.

As shown in Figure 1d, the profile of plastic combustion is slightly different from the other combustibles. That is, the weight loss of the first stage is much larger than that of the second stage. There is a significantly weight loss rate at the first stage in the TG profile. And a relatively small rate of weight loss appears at the second stage.

From the profiles of TG and DTA of food shown in Figure 1e, it can be seen that there is a weight loss and endothermic peak at the temperature of about 1073 K. The possible reason is that some inorganic matters in the food such as calciferous compounds in the bone are decomposed at higher temperature, which is an endothermic reaction.

On the basis of the above results, it can be concluded that the combustibles in MSW can be divided as two types of matters: one is fibrous matter, and the other is polymer matter. The combustion process mainly consists of two stages. At the first stage, the volatile contained in fibrous matter was released, and then the released volatile matter was combusted continuously. At the second stage, the fixed carbon of fibrous matter was burned, and pyrolysis and combustion of the polymer matter were started at the same time.

**Combustion Kinetic Parameters of the Different Combustibles.** The combustion reaction of the combustibles in MSW likes that of coal and can be expressed in this way:

$$A+O_2 \rightarrow B+C(g)$$

Heat and mass transfer limitations due to transfer phenomena within the sample were not considered because of the low heating rate and the small sample size used in our experimental runs. Since the concentration of  $O_2$  is excessive, the rate for the disappearance of reactant A from the mixture can be expressed as follows:

$$\frac{\mathrm{d}a}{\mathrm{d}t} = k(1-a)^n \tag{1}$$

where  $\alpha$  is the conversion of combustion reaction, k is the reaction rate constant, n is the reaction order, and t is reaction time. Insertion of the Arrhenius expression

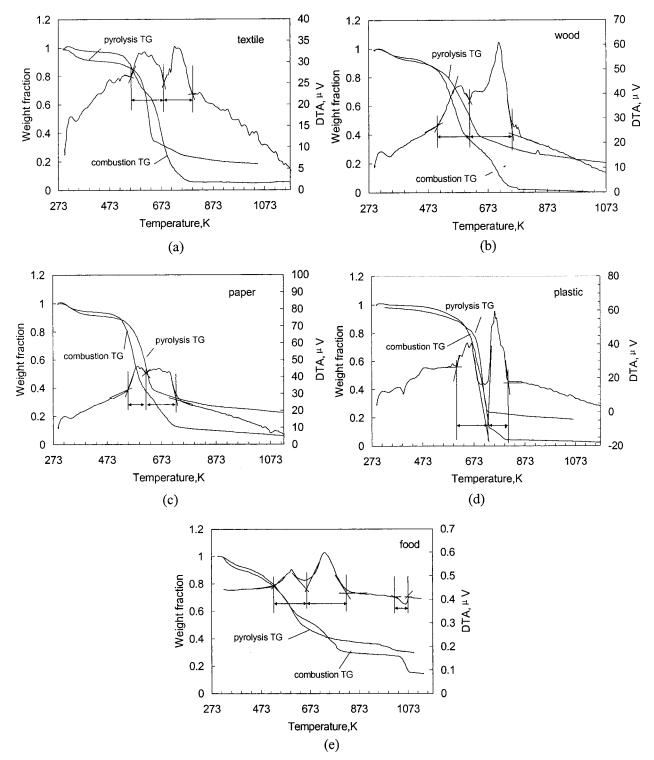


Figure 1. Profiles of TG and DTA of each combustible.

for the reaction constant and the relation between temperature and heating rate leads to

$$k = Ae^{-E/RT} (2)$$

$$\phi = \frac{\mathrm{d}T}{\mathrm{d}t} \tag{3}$$

$$\frac{\mathrm{d}\alpha}{\mathrm{d}T} = \frac{A}{\phi} \mathrm{e}^{-E/RT} (1 - \alpha)^n \tag{4}$$

E is the apparent activation energy, A is the preexponential factor, and  $\Phi$  is the heating rate.

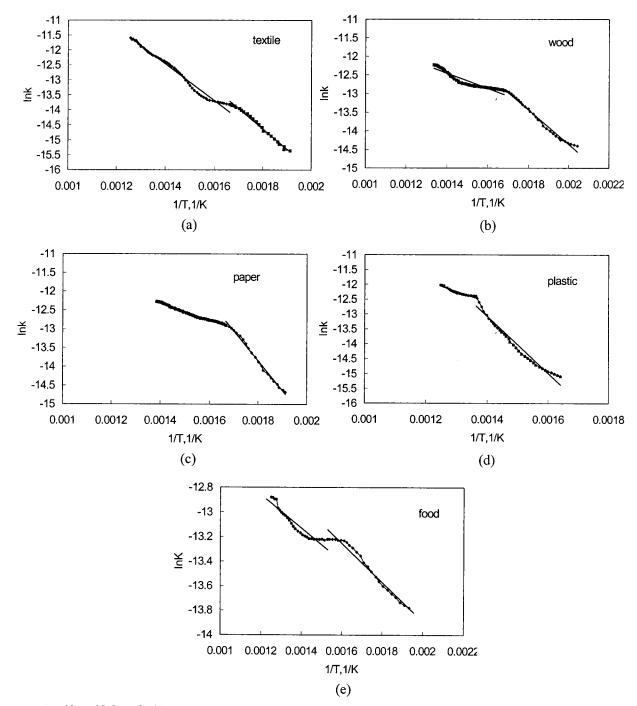
In the determination of the kinetic parameters by means of the above equations, various analysis methods  $^{9-14}$  have been suggested. In the present study, the nonisothermal analysis method proposed by Ito et al.  $^{14}$  was used.

<sup>(9)</sup> Haykiri-Açma, H.; Ersoy-Meriçboyu, A.; Küçükbayrak, S. *Proceedings of ICCS'97, 9<sup>th</sup> International Conference on Coal Science*; Essen, Germany, Sept. 7–12, 1997; DGMK: Hamburg; pp 915–918. (10) Freeman, E. S.; Carroll, B. *Fuel* **1958**, *62*, 394–401.

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**Figure 2.** Profiles of lnk and 1/T.

Introducing logarithm into the above equations, the following equation is obtained:

$$\ln \left( \frac{\phi \frac{d\alpha}{dT}}{(1-\alpha)^n} \right) = \ln A - \frac{E}{RT}$$
(5)

The values of  $d\alpha/dT$ ,  $\alpha$ , and T can be obtained from Figure 1. To determine the apparent kinetic parameters in eq 5, combustion is generally analyzed as a first-order reaction. Assuming n equals 1, the calculated results of the left-hand term in eq 5 are plotted against the reciprocal of absolute temperature. It shows a straight

line in  $\ln((1-\alpha)^{-n}(d\alpha/dT)\phi)$  versus 1/T, and then the apparent activation energy E and preexponential factor A are obtained from eq 4. Figure 2a-d shows the Arrhenius curves of each component.

 $\alpha$  can be calculated from the weight-losing curve of TG using the following equation:

$$a = \frac{(w - w_0)}{(w_c - w_0)}$$

where  $w_0$ , w, and  $w_c$  are the sample weight before the combustion reaction, in the combustion reaction, and after the combustion reaction, respectively. Table 3 summarizes the kinetic parameters calculated for the combustion reactions of different combustibles. As

<sup>(14)</sup> Ito, N.; Obata, K.; Hakuta, T.; Yoshitome, H. *Kagaku Jkogaku Ronbunshu* **1983**, *9*, 434–439.

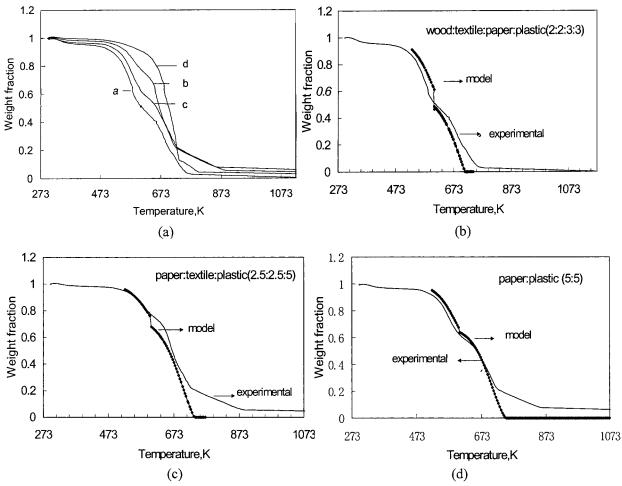


Figure 3. Comparison of kinetic model and experimental data: (a) wood:textile:plastic (2:2:3:3), (b) paper:textile:plastic (2.5: 2.5:5), (c) paper:plastic (5:5), and (d) the plastic in panel a.

**Table 3. Kinetic Parameters of Combustion Process for Different Combustibles** 

sample	range of temperature (K)	activation energy ( <i>E</i> , kJ/mol)	preexponential factor $(A, \min^{-1})$
paper	522-600	65.44	1.08E5
	600 - 722	60.36	2.28
textile	522 - 600	56.03	5.53E3
	600 - 796	50.65	1.18E3
wood	489 - 590	38.47	2.80E2
	590 - 749	16.93	1.37
plastic	635 - 733	92.37	1.40E6
	733-801	29.42	17.04
	505 - 653	4.97	0.019
food	653 - 847	15.2	0.063
	847 - 1080	16.82	0.645

shown in the combustion profiles in Figure 1, the combustion process of the fibrous matter consists of two stages, so there are two reaction constants,  $k_1$ ,  $k_2$ ;  $k_1$ and  $k_2$  are used for reactions occurring below and above 600 K, respectively. Correspondingly, there are two values of E and A.

**Combustion Kinetic Model of the Combustibles** in MSW. On the basis of the above analysis of the combustion process and the kinetic parameters, the combustibles can be divided mainly as fibrous matter and polymer matter, and the combustion process consists of two stages, though the reaction kinetic constants are different in each fibrous matter or the polymer matter. Therefore, the more complex combustion process of MSW can be described by means of a simplified reaction pathway, and the approach used herein is to consider the combustion rate of combustibles in MSW as the sum of rates of each combustible. Furthermore, the combustion reaction at the first stage is mainly from the fibrous matter; at the second stage, the polymer matter begins to burn at the second stage, and the fibrous matter simultaneously continues burning. Considering that food can be used in composting, the combustibles used for the model are paper, wood, textile, and plastic, which both frequently appeared in MSW and are easily used as energy resource. These combustible matters were mixed as samples in different ratio as shown in Figure 3, which is used to evaluate the kinetic model. For the mixture of different combustibles with different ratios, the combustion model can be expressed as the following equations:

The first stage: ≤ 600 K

$$\frac{\mathrm{d}\xi_{11}}{\mathrm{d}t} = A_{11}\mathrm{e}^{-E_{11}/RT}(1 - \xi_{11}) \tag{6}$$

$$\frac{\mathrm{d}\xi_{21}}{\mathrm{d}t} = A_{21}\mathrm{e}^{-E_{21}/RT}(1 - \xi_{21}) \tag{7}$$

$$\frac{\mathrm{d}\xi_{31}}{\mathrm{d}t} = A_{31}\mathrm{e}^{-E_{31}/RT}(1 - \xi_{31}) \tag{8}$$

$$\frac{d\xi_1}{dt} = \frac{d\xi_{11}}{dt} x_1 + \frac{d\xi_{21}}{dt} x_2 + \frac{d\xi_{31}}{dt} x_3$$
 (9)

The second stage: > 600 K

$$\frac{\mathrm{d}\xi_{42}}{\mathrm{d}t} = A_4 \mathrm{e}^{-E_4/RT} (1 - \xi_{42}) \tag{10}$$

$$\frac{\mathrm{d}\xi_{12}}{\mathrm{d}t} = A_{12}^{-E_{12}/RT} (1 - \xi_{12}) \tag{11}$$

$$\frac{\mathrm{d}\xi_{22}}{\mathrm{d}t} = A_{22}\mathrm{e}^{-E_{22}/RT}(1 - \xi_{22}) \tag{12}$$

$$\frac{\mathrm{d}\xi_{32}}{\mathrm{d}t} = A_{32}\mathrm{e}^{-E_{32}/RT}(1 - \xi_{32}) \tag{13}$$

$$\frac{d\xi_2}{dt} = \frac{d\xi_{12}}{dt}y_1 + \frac{d\xi_{22}}{dt}y_2 + \frac{d\xi_{32}}{dt}y_3 + \frac{d\xi_4}{dt}y_4$$
 (14)

where  $\zeta_1$  and  $\zeta_2$  are the conversion of the samples at the first and the second stage, respectively, x is the weight fraction of each combustible in the samples at the first stage, and y is the weight fraction of each combustible in the remained samples at the second stage.  $\zeta_{I1}$  and  $\zeta_{I2}$  are each combustible conversion at the first and the second stage, respectively, and i is equal to 1, 2, 3, or 4, with 1 being paper, 2 textile, 3 wood, and 4 plastic. E is the activation energy; E is the preexponential factor. Each E and E are the samples at the second stage, respectively, E and E are the samples at the second stage, respectively, E and E are the samples at the second stage, respectively, E and E are the samples at the second stage, respectively, E and E are the samples at the second stage, respectively, E and E are the samples at the second stage, respectively, E and E are the samples at the second stage, respectively, E and E are the samples at the second stage, E and E are the samples at the sam

The values of the kinetic model for the mixtures of the combustibles with different ratio shown in Figure 3 are calculated by the above expressions. Comparison between experimental data and the combustion model is shown in Figure 3. The experiments were carried out at constant heating rate of 10 K/min, and the heating temperature is raised to 1173 K. It can be seen from Figure 3 that the model shows a good agreement with the experimental data for the mixtures in different ratios.

#### Conclusion

On the basis of the results of the fundamental study on the characteristics of the combustibles in MSW and the kinetic model, the following can be concluded:

- (1) The combustibles in the MSW can be divided as two types: one is fibrous matter, another is polymer matter. (2) The combustion process mainly consists of two stages. At the first stage, the volatile contained in fibrous matter is released, and then the released volatile matter is combusted continuously; at the second stage, the fixed carbon of fibrous matter is burned, and pyrolysis and combustion of the polymer matter happened at the same time.
- (3) The combustion rate of MSW can be expressed by a weighted sum of rates of each combustible, and more complex combustion process of MSW can be described by simple model.

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