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Theoretical and Experimental Investigations on the Combustion Characteristics of Three Components Mixed Municipal Solid Waste

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Abstract
The combustion characteristics of Mixed Municipal Solid Waste (MMSW) play a vital role in dictating the efficiency of the incineration process. At present, few studies on combustion characteristics of three components MMSW and the establishment of corresponding comprehensive kinetic model of single component waste have been reported. In the present study, based on the law of mass action and Badzioch's relation, the mathematical expressions for describing the TG (Thermogravimetric) curves and the DT (Differential thermal) curves of single component MMSW are derived. A comprehensive kinetic model for the combustion characteristics of single component MMSW is developed and the appropriateness of the model is confirmed by the experimental results. The calculated TG curves closely agree with the experimental curves; the maximum deviation between the experimental and calculated curves is within 5%. Based on the principle of mixture experiments, the co-combustion characteristics of MMSW composed of food bag, disposable chopstick and cotton cloth are studied by using TGA (Thermogravimetric Analysis) and DTA (Differential Thermal Analysis). It has been found that the activation energy of three components MMSW is lower than that of single component. Finally, based on multiple regression analysis for the design of mixture experiments and the corresponding data, an empirical formula for calculating activation energy of three components MMSW is obtained. The experimental and calculated values match closely; the maximum deviations between them is within 7%. The empirical formula provides a robust way to calculate activation energy of three components MMSW.

Keywords: Mixed Municipal Solid Waste; Combustion Characteristics; Kinetic Model; Thermogravimetric Analysis; Differential Thermal Analysis.

1. Introduction

With the increasing population and the continuous improvement in human living standard, the production of Mixed Municipal Solid Waste (MSW) and the energy consumption depicts a growing trend [1-3]. About 1.3 billion tons of solid waste was produced in the world in 2012, and it is expected to increase to 5.9 billion tons by 2025 [4]. Landfill is the traditional method of MMSW disposal [5]. Due to land occupation and underground water pollution, it has been gradually replaced by incineration process [6]. The incineration process can produce energy while eliminating MMSW and has become the most popular way of waste disposal [7-9]. For example, about 28 million tons of MMSW is burned every year to produce 2720 Megawatts of electricity in United States, and 27.3% of the energy comes from MMSW incineration in European Union [10]. Therefore, there is an urgent demand for study of the combustion characteristics of MMSW due to its role in dictating the efficiency of the incineration process.

Most of the published literature in this field of study focuses on the combustion characteristics of single component and two components MMSW [11-14]. Limited information is available in the literature concerning those of three components MMSW. MMSW is made up of a wide variety of materials, including metals, cloth, plastics, paper, wood, food, and other waste. It is necessary though to thoroughly carry out investigations on the kinetic characteristics of three components MMSW. This is the purpose of the present study and will be discussed in detail. It can be said that MMSW is a biomass waste resource, accompanying low calorific value and high-volatile content [14-16]. A study has pointed out that the volatile matter accounts for almost 80% in the combustible components of waste, and the waste burning depends mainly on volatiles combustion [17], which is a gas phase combustion (extremely fast reaction). Thus, the combustion process of MMSW is mainly based on pyrolysis and combustion of volatiles. Studies have shown that the combustion process of single component and two components waste consist of several separated stages. After ignition, solid combustible waste first undergoes a pyrolysis and volatilization combustion stage (200-400℃), followed by a fixed carbon combustion stage (above 500℃) [18-23]. Finally, the burnout stage is at temperatures between 500℃ and 600℃ [19, 21, 23]. For different types of solid combustible wastes, there are different combustion characteristics in different combustion stages. These studies analyze the theory of thermal decomposition process for solid combustible waste and confirm that pyrolysis and volatilization combustion stages are the most important ones. However, an equation which can describe the combustion process of solid combustible waste is not developed. The mathematical model based on this equation will be quite beneficial in reducing the workload of the waste combustion experiment.

As early as 1970, Badzioch's relation was proposed to analyze the pyrolysis process of coal [24], and it suggests that the rate of pyrolysis is proportional to the concentration of volatile matter released from coal. However, the effect of the heating rate is not taken into account in Badzioch's relation. Therefore, many researchers try to make improvements in Badzioch's relation. An equation of the variation of the solid conversion with time has been proposed for the thermal decomposition of biomass waste [25]. Based on this equation, Sørum et al. [26] have investigated the kinetic characteristics of eleven different components of MMSW. Detailed information on the chemical kinetics of the 11 important components in MMSW is obtained. Li et al. [27] have obtained different objective functions by using nonlinear least-square algorithms and these functions are mainly applicable to a single component MMSW. For MMSW, Guo et al. [28] have proposed that the combustion rate of MMSW can be expressed by a weighted sum of rates of each combustible component, and more complex combustion process of MMSW can be described by a simple model. However, some research results show that co-pyrolysis characteristic of MMSW is more complicated than that of the single component waste, which exhibits a lower apparent activation energy [29]. This means expressing the whole combustion process of MMSW by a weighted sum of the combustion process of each combustible component may not be appropriate. Therefore, how to obtain a new relation which can properly describe the combustion process of solid combustible waste is one of the focuses of this research.

Thermogravimetric analysis (TGA) has been widely used to analyze the kinetic characteristics of solid combustibles such as coal, wood and plastic [30-33]. TGA has been chosen by many researchers to further study the combustion characteristics of single component and two components MMSW. TGA can also be applied to study the thermal decomposition process of mixed combustible solids [34]. In recent years, TGA has been more frequently used to determine combustion parameters of single component and two components MMSW. A lot of research has been carried out about the combustion characteristics of single component MMSW. Zhou [1] has classified the combustible MMSW and drawn the DTG curves of 26 types of single component MMSW through TGA. According to the proximate and ultimate analysis and heating value results, as well as TG characteristics, MMSW components are classified into eleven groups. Chen [35] has analyzed the pyrolysis and gasification characteristics of 8 different types of combustible solid wastes by using TGA. The results show that pyrolysis characteristics of 8 different kinds of materials are similar to their gasification with the temperature less than 600°C, and the pyrolysis temperature is slight above 600°C. Luo et al. [36] have investigated the combustion characteristics of nine typical components of MMSW by TGA analyzer. The results indicate that combustion is related to not only proximate analysis, but also the chemical structure and specific chemical reactions. Similarly, as for two components MMSW, a lot of research work has already been carried out. Emmanuel et al. [37] have investigated the thermogravimetric and calorimetric characteristics during pyrolysis of wood, paper, textile and polyethylene terephthalate plastic in MMSW, and co-pyrolysis of biomass-derived and plastic components with and without torrefaction. The results show that there is a significant interaction between biomass and PET plastic during co-pyrolysis if the biomass fraction is dominant. Anjireddy et al. [38] have investigated the co-pyrolysis characteristics of MMSW and agricultural residues by using non-isothermal TGA at different heating rates. The result shows that the activation energy of MMSW significantly decreases with addition of agriculture residues. Zhou et al. [39] have investigated the interactions of nine typical MMSW fractions during pyrolysis by using TGA. The results indicate that there are strong interactions of rice/orange peel, rice/poplar wood, PVC and other components. Fan [40] has observed the interaction of the thermal characteristics when oil shale and MMSW are mixed in the combustion process, using TGA. According to the data analysis, combustion characteristic index increases progressively with the increase of the proportion of municipal solid waste. It suggests that there is a certain interaction in the combustion process of oil shale and municipal solid waste.

There are significant number of research studies carried out on the combustion characteristics of single component MMSW and coal, while the studies on the co-thermal characteristics of mixed waste mainly focus on the two components MMSW. Limited number of studies can be found regarding the kinetic characteristics, such as TG and DT curves, frequency factor and activation energy, of three components MMSW. Moreover, there are only a few references about the development of the mathematic model, which can describe the whole combustion process of single component MMSW. To the best of the authors' knowledge, there are almost no publications about the establishment of comprehensive kinetic model for single component MMSW and empirical formula for calculating the activation energy of MMSW composed of three components. Furthermore, as MMSW consists of various components, the research on its kinetic characteristics is very complicated. Due to the strong interaction between the components of MMSW, it is not satisfying to use kinetic characteristics of single component to study those of MMSW by using quality weighted-average method. Therefore, there is a great demand for a thorough investigation of the combustion characteristics of three components MMSW.

In this study, we mainly focus on the co-thermal characteristics of three components MMSW. Based on the law of mass action and Badzioch's relation, the mathematical calculation models of TG and DT curves for single component MMSW are derived. The models can reasonably describe the combustion process of single component MMSW. Meanwhile, the kinetic equations for three components MMSW are established. Furthermore, 7 experimental conditions are designed by using three typical MMSW (cotton cloth, disposable chopstick, and food bag) components, on the basis of the principle of mixture experiment, to obtain TG and DT curves of single component, two components and three components MMSW through TGA and DTA. Then, the analysis of the co-thermal characteristics of the three components MMSW is carried out to judge whether it is stepwise. Based on the experimental results, an empirical formula for calculating activation energy of three components MMSW composed of cotton cloth, disposable chopstick, and food bag is obtained, and the other three experiments are carried out to verify it. The results obtained are helpful to comprehensively understand the kinetic characteristics of combustion of three components MMSW.

2. Development of a Comprehensive Kinetic Model for Waste Combustion

2.1 Derivation of Mathematical Model for Waste Combustion Reaction

According to the law of mass action, the reaction rate of solid fuel combustion at constant oxygen concentration can be expressed as [23]:

$$\frac{d\alpha}{d\tau} = k_0 \times e^{-\frac{E}{RT}} \times (1-\alpha)^n \tag{1}$$

where τ is the reaction time, α is the conversion rate during the reaction, n is the reaction order (n=1, according to [41]), E is the activation energy, T is the reaction temperature, k_0 is the frequency factor and R is the general gas constant. According to [27]:

$$\alpha = \frac{w_0 - w}{w_0 - w_\infty} \tag{2}$$

where w_0 and w_∞ are value of initial and final mass, and w is the instantaneous mass. The experiment is conducted at constant heating rate. With the definition of the heating rate as $\Phi = dT/d\tau$ [27], equation (1) can be re-written as:

$$\frac{d\alpha}{d\tau} = \frac{d\alpha}{dT} \cdot \frac{dT}{d\tau} = \frac{d\alpha}{dT} \cdot \phi = k_0 \times e^{-\frac{E}{RT}} \times (1-\alpha) \tag{3}$$

Thus, equation (1) can be re-written as:

$$\frac{d\alpha}{dT} \cdot \phi = k_0 \times e^{-\frac{E}{RT}} \times (1-\alpha) \tag{4}$$

Dividing both sides of equation (5) by Φ, the following equation is obtained:

$$\frac{d\alpha}{dT} = \frac{k_0}{\phi} e^{-E/RT} (1-\alpha) \tag{5}$$

By integrating equation (5) from 0 (corresponding to $T=T_0$) to α (corresponding to T), the following equation is obtained:

$$\int_0^{\alpha} \frac{1}{(1-\alpha)} d\alpha = \frac{k_0}{\phi} \int_{T_0}^{T} e^{-\frac{E}{RT}} dT \tag{6}$$

As the value of $\frac{E}{RT}$ is very large [41], $\int_{T_0}^{T} e^{-\frac{E}{RT}} dT \approx \frac{RT^2}{E} e^{-\frac{E}{RT}}$ is assumed. Re-arranging and integrating equation (6), the following equation can be obtained:

$$-\frac{\ln(1-\alpha)}{T^2} = \left(\frac{k_0 R}{\phi E}\right) \cdot e^{-\frac{E}{RT}} \tag{7}$$

Equation (7) can be expressed in logarithmic form as:

$$\ln\left[\frac{-\ln(1-\alpha)}{T^2}\right] = \ln\left(\frac{k_0 R}{\phi E}\right) - \frac{E}{RT} \tag{8}$$

Assuming $\ln(-\ln(1-\alpha)/T^2)=Y$, $1/T=X$, $-E/R=c$ and $\ln(k_0R/\phi E)=a$, equation (8) can be expressed in the following form:

$$Y = A + CX \tag{9}$$

The constants A and C in equation (9) can be predicted by regression according to TG curve, then the frequency factor (k_0) and activation energy (E) are obtained. Obviously, lower the activation energy, higher the reaction rate of combustion, and easier the fuel is on fire.

2.2 Derivation of mathematical expression of TG curve

Badzioch [24] proposed a pyrolysis kinetic equation for coal in 1970, suggesting that the pyrolysis rate is proportional to the concentration of precipitated volatiles. Volatile matter accounts for almost 80% in the combustible components of waste, and waste burning depends mainly on volatile matter combustion [17], which is a gas phase combustion. Therefore, combustion of waste can be approximately regarded as a one-step reaction. This makes it possible to use the Badzioch's relation to describe the entire combustion process of waste. Thus, the following equation is obtained:

$$\frac{dw}{d\tau} = k_0 \cdot \exp\left(-\frac{E}{RT}\right) \cdot (w_\infty - w) \tag{10}$$

The Badzioch's relation does not take into account the effect of the heating rate which is clearly related to weight loss rate of fuel and should be considered in waste combustion model. According to the related knowledge of calculus, weight loss rate of fuel can be expressed in the following form:

$$\frac{dw}{d\tau} = \frac{dw}{dT} \cdot \frac{dT}{d\tau} = \frac{dw}{dT} \cdot \phi \tag{11}$$

Combining equations (10) and (11), the following equation can be obtained:

$$\frac{dw}{dT} = -\frac{1}{\phi} k_0 \cdot \exp\left(-\frac{E}{RT}\right) \cdot (w - w_\infty) \tag{12}$$

Equation (12) not only modifies the Badzioch's relation (considering the effect of the heating rate), but also substitutes τ (time) in the Badzioch's relation with the T (temperature), which greatly facilitates the numerical calculation of the combustion process. The reason is that T (temperature) is always chosen as abscissa in TG and DT curves. By integrating equation (12) from w_0 (corresponding to $T = T_0$) to w (corresponding to $T = T$), the following equation is obtained:

$$\int_{w_0}^{w} \frac{1}{w-w_\infty} dw = -\frac{1}{\phi} k_0 \int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right) dT \quad (13)$$

The integral term on the right-hand side of equation (13) can be transformed to the following equation by step-by-step integration:

$$\int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right) dT = \int_{T_0}^{T} \frac{RT^2}{E} d\left[\exp\left(-\frac{E}{RT}\right)\right] = \frac{RT^2}{E} \exp\left(-\frac{E}{RT}\right)\Big|_{T_0}^{T} - \int_{T_0}^{T} \frac{2RT}{E} \exp\left(-\frac{E}{RT}\right) dT \quad (14)$$

Moving $\int_{T_0}^{T} \frac{2RT}{E} \exp\left(-\frac{E}{RT}\right) dT$ to the left side of equation (14), the following equation is obtained:

$$\int_{T_0}^{T} \left(1+\frac{2RT}{E}\right) \exp\left(-\frac{E}{RT}\right) dT = \frac{RT^2}{E} \exp\left(-\frac{E}{RT}\right)\Big|_{T_0}^{T} = \frac{RT^2}{E} \exp\left(-\frac{E}{RT}\right) - \frac{RT_0^2}{E} \exp\left(-\frac{E}{RT_0}\right) \quad (15)$$

According to [41], the value of $\frac{RT}{E}$ is very small and it can be neglected, thus:

$$1+\frac{2RT}{E} \approx 1, \frac{RT_0}{E} \approx 0, \frac{RT_0{}^2}{E} \approx 0, \ \exp\left(-\frac{E}{RT_0}\right) \approx 0 \ \text{and} \ \frac{RT_0{}^2}{E} \exp\left(-\frac{E}{RT_0}\right) \approx 0 \quad (16)$$

Therefore, equation (15) can be rewritten as:

$$\int_{T_0}^{T} \exp\left(-\frac{E}{RT}\right) dT \approx \frac{RT^2}{E} \exp\left(-\frac{E}{RT}\right) \quad (16)$$

Thus, equation (13) can be simplified as:

$$\int_{w_0}^{w} \frac{1}{w-w_\infty} dw = \ln \frac{w-w_\infty}{w_0-w_\infty} = -\frac{1}{\phi} k_0 \frac{RT^2}{E} \exp\left(-\frac{E}{RT}\right) \quad (17)$$

By integrating the above equation from w_0 (corresponding to $T = T_0$) to w (corresponding to $T = T$), the following equation is obtained:

$$\frac{w-w_\infty}{w_0-w_\infty} = \exp\left[-\frac{1}{\phi} k_0 \frac{RT^2}{E} \exp\left(-\frac{E}{RT}\right)\right] \quad (18)$$

Inserting $\alpha = \frac{w_0-w}{w_0-w_\infty}$ into equation (18), the following equation is obtained:

$$1-\alpha = \exp\left[-\frac{1}{\phi} k_0 \frac{RT^2}{E} \exp\left(-\frac{E}{RT}\right)\right] \quad (19)$$

Equation (19) is the derived mathematical expression of the TG curve of single component waste. Corresponding TG curve can be predicted according to this equation, which greatly reduces the test workload and saves cost. The experimental verification of this equation will be described in detail below.

2.3 Derivation of mathematical expression of DT curve

Corresponding DT curve can be easily obtained according to equation (19). When the temperature is T_1 and the sample weight is w_1, thus, the following equation is obtained:

$$w_1 = (w_0 - w_\infty) \cdot \exp\left[-\frac{1}{\phi} k_0 \frac{R{T_1}^2}{E} \exp\left(-\frac{E}{RT_1}\right)\right] + w_\infty \tag{20}$$

When the temperature is T_2 and the sample weight is w_2, the following expression can be obtained:

$$w_2 = (w_0 - w_\infty) \cdot \exp\left[-\frac{1}{\phi} k_0 \frac{R{T_2}^2}{E} \exp\left(-\frac{E}{RT_2}\right)\right] + w_\infty \tag{21}$$

Subtracting equation (21) from equation (20), the following equation is obtained:

$$w_1 - w_2 = (w_0 - w_\infty) \cdot \left\{\exp\left[-\frac{1}{\phi} k_0 \frac{R{T_1}^2}{E} \exp\left(-\frac{E}{RT_1}\right)\right] - \exp\left[-\frac{1}{\phi} k_0 \frac{R{T_2}^2}{E} \exp\left(-\frac{E}{RT_2}\right)\right]\right\} \tag{22}$$

According to equation (12), the following equation is derived:

$$\frac{dw}{d\tau} = \frac{dw}{dT}\frac{dT}{d\tau} = \frac{dw}{dT}\phi = \frac{w_1 - w_2}{T_1 - T_2}\phi \tag{23}$$

Since the expression of $w_1 - w_2$ has been given in equation (22), combining equation (22) with equation (23), the following equation is acquired:

$$\frac{dw}{d\tau} = \frac{w_0 - w_\infty}{T_1 - T_2} \cdot \phi \cdot \left\{\exp\left[-\frac{1}{\phi} k_0 \frac{R{T_1}^2}{E} \exp\left(-\frac{E}{RT_1}\right)\right] - \exp\left[-\frac{1}{\phi} k_0 \frac{R{T_2}^2}{E} \exp\left(-\frac{E}{RT_2}\right)\right]\right\} \tag{24}$$

Equation (24) is the derived mathematical expression of the DT curve of single component waste. Corresponding DT curve can be obtained according to this equation. It should be noted that, in order to ensure sufficient calculation accuracy, time period of weight loss of fuel sample should be as short as possible, that is to say T_1 and T_2 should be as close as possible. The experimental verification of this equation will also be described in detail below.

2.4 Establishment of Empirical Formula for Calculating Activation Energy of Three Components MMSW

MMSW is a mixture composed of a variety of typical components. In order to further understand the combustion characteristics of MMSW, it is necessary to carry out investigations on the combustion characteristics of MMSW by using TGA. Due to the limited crucible capacity of TG analyzer, only the combustion characteristics of three components MMSW composed of cotton cloth, disposable chopstick, and food bag are analyzed in this paper. In order to minimize the experimental workload, mathematical methods must be used to optimize the experimental program. In mathematics, the research method on various performance of the blend is called mixture design. Mixture experiments are commonly encountered in industrial product formulations (e.g., food processing, chemical formulations and pharmaceutical drugs) but the application in research of combustion of MMSW is limited. According to the principle of mixture design, the constraint of a mixture experiment is to set the sum of the components to 1 (100%). For the design of three components mixture used, the minimum number of experiments to be carried out is N and $N = 2^3-1 = 7$ [42]. The detailed designs of the seven experiments are listed in table 1, which will be described in detail in the next section. Based on the experimental data, empirical formula for calculating activation energy of three components waste can be obtained by using regression analysis. On the basis of the principle of mixture experiments described in reference [42], we assume that the empirical formula for calculating activation energy of three components MMSW can be expressed as follows:

$$y = a_1 \cdot y_1 \cdot x_1 + a_2 \cdot y_2 \cdot x_2 + a_3 \cdot y_3 \cdot x_3 + b_{12} \cdot y_{12} \cdot x_1 \cdot x_2 + b_{13} \cdot y_{13} \cdot x_1 \cdot x_3 + b_{23} \cdot y_{23} \cdot x_2 \cdot x_3 + c \cdot y_{123} \cdot x_1 \cdot x_2 \cdot x_3 \quad (25)$$

here x_1, x_2 and x_3 are proportions of the components of MMSW, y_1, y_2 and y_3 are the corresponding activation energy of each component, y_{12}, y_{13} and y_{23} are the activation energy of mixtures composed of any two components (each component accounts for 1/2), y_{123} is the activation energy of three components mixture (each component accounts for 1/3), y is the average activation energy of three components MMSW with different mixing ratios and a_1, a_2, a_3, b_{12}, b_{13}, b_{23} and c are coefficients. The values of the coefficients can be obtained (see section 4.3.2 for details) by adopting multiple regression analysis [43]. The detailed descriptions of multiple regression analysis can be found in [43], and hence, is not repeated here. The validation of the empirical formula will be carefully depicted in section 4.3.2. Equation (25) is a simple and practical empirical formula for calculating the activation energy of MMSW composed of three components mixed in different proportions. This work is of much practical value and will be discussed in detail below.

3. Experimental Methodology

Due to the limited capacity of the crucible of the test equipment, we only carry out the experiments on MMSW composed of three components. The equipment used in this study is the TG analyzer (STA-409 PC) manufactured by Netzsch company in Germany. With this analyzer, the TG and DT curves can be simultaneously obtained and the sample is heated from ambient temperature to 900°C. The experimental errors in the weight loss and temperature measurements are ±0.5% and ±2℃ respectively. The three types of waste components investigated in this study are cotton cloth, disposable chopstick, and food bag. The moisture content of cotton cloth and food bag is negligible. Although the disposable chopsticks are produced from fresh wood, and have a certain amount of water, as time goes by, in this study, the moisture content of the disposable chopsticks becomes negligible, due to evaporation of water. Hence, the effect of moisture is difficult to see from the TG and DTA curves. According to the principle of mixture design, there are seven experimental conditions, shown in table 1 [42].

Table 1 Experimental program of MMSW combustion characteristics

Experiment	Cotton Cloth	Disposable Chopstick	Food Bag
1	1	0	0
2	0	1	0
3	0	0	1
4	0.5	0.5	0
5	0.5	0	0.5
6	0	0.5	0.5
7	1/3	1/3	1/3

Test conditions must first be determined when combustion characteristics of waste are studied using TGA. Combustion curves with different shapes will be obtained under different test conditions. The experimental conditions are as follows:

i. Weigh 10mg sample according to the proportion in table 1.
ii. The normal heating rate (20ºC/min) is used and the temperature is raised from ambient temperature to 900ºC until the sample is burnout.

iii. The paper speed of 15mm/min is selected.
iv. Air flow of 80ml/minute is blown into the burning chamber for combustion of waste sample.
v. Each test is run three times and the mean value is recorded.

4. Results and Discussions

4.1 Combustion characteristics of single component MMSW

Figure 1 shows the TG curves of single component MMSW, for disposable chopstick (A), food bag (B) and cotton cloth (C).

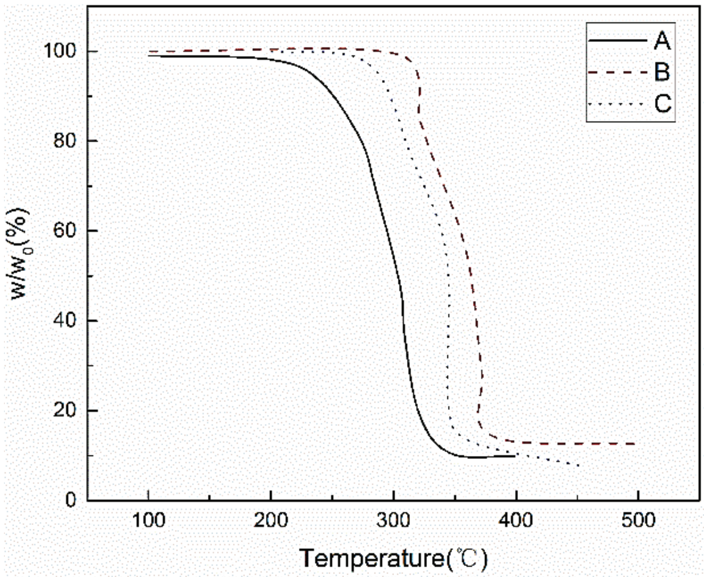

Figure 1 TG curves of single component MMSW

It can be seen from in the figure that there is a weight loss at the temperature range of 275-350°C in case of the disposable chopstick, 330-400°C in case of food bag and 290-360°C in case of cotton cloth. It means that the disposable chopstick exhibits good ignition performance compared to the food bag and the cotton cloth. Based on the values of temperature where the TG curves drop sharply, it can be concluded that the disposable chopstick is most easy to catch fire, followed by cotton cloth and finally food bag. Thus, the food bag has relatively poor ignition characteristics. Therefore, in order to ensure stable combustion of waste, the temperature of the main combustion zone in MMSW incinerator should not be lower than 500°C. Figure 2 shows the DT curves of single component MMSW, for disposable chopstick (A), food bag (B) and cotton cloth (C).

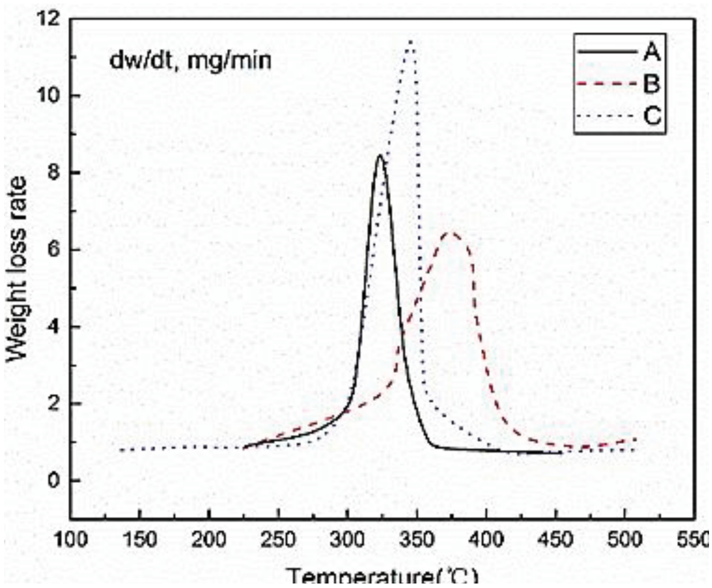

Figure 2 DT curves of single component MMSW

It can be seen from the figure that each curve shows a single peak which corresponds to the combustion stage of volatile. The reason is that volatile accounts for 80% of the combustible components of waste [32], while waste burning depends mainly on volatile combustion. Due to the volatile, waste burns much faster than fixed carbon, which implies that the combustion of waste is very different from coal. Based on the values of temperature where the maximum weight loss rates of several samples locate, the temperature of the food bag is the highest (373°C), followed by cotton (343°C) and finally the chopstick (314°C), which also shows that food bags have relatively poor combustion performance. In order to ensure smooth ignition of plastic, the furnace temperature should be maintained at a high level (not less than 500°C) in the incineration equipment. From the average height of the combustion peaks on the DT curves of waste samples, the highest value corresponds to cotton cloth (11.3mg/min), followed by disposable chopstick (8.5mg/min) and finally food bag (6.2mg/min).

In terms of material composition, the thermal degradation mechanism of fractions is explicated as follows. Disposable chopsticks are made of wood, while the composition of the wood is lignocellulose with low ignition point, high volatile content and fast burning rate. Therefore, seen in figure 2, the temperature associated with the maximum weight loss rates of the disposable chopsticks is the lowest and the burning performance is excellent. However, the food bag is made of plastic. The composition of plastic is Polyethylene, which is difficult to burn because of its high ignition temperature, low combustion rate and long burnout time. Therefore, the temperature associated with the maximum weight loss rates of the food bag is high and the peak weight loss rate is low. The composition of cotton is natural fiber with low ignition temperature, easy to burn, and fast burning rate. Therefore, the temperature associated with the maximum weight loss rate of cotton is lower, and the peak of weight loss rate is much larger than that of disposable chopsticks and food bag, as shown in figure 2. Therefore, when there is more cotton cloth in the MMSW, sufficient air should be supplied to meet the needs of combustion at its early stage. Since food bag is a kind of plastic, air supply should be appropriately delayed ensuring stable combustion and burnout, when there is more plastic in MMSW.

In addition to above mentioned parameters (like maximum weight loss rate), the activation energy and the frequency factor of single component waste are important characteristic parameters to determine difficulty and rate of combustion reaction. Therefore, determining their values by TGA is of great importance for the study on combustion characteristics of fuels. The values of constants a and a in equation (9) can be obtained by regression, according to TG curves. The frequency factor and activation energy can then be obtained. The calculation results of the kinetic parameters of typical waste components are shown in table 2.

Table 2 Combustion kinetic parameters of typical waste components

Waste Name	Temperature Range (°C)	Regression Equation	Correlation Coefficient	Frequency Factor (1/s)	Activation Energy (kJ/mol)
Disposable chopstick	275～314 314～350	Y = 9.2-12.77X Y=12.08-14.43X	0.907 0.917	0.42e8 0.85e9	106.17 119.97
Food bag	330～373 373～400	Y = 6.56-12.6X Y = 10.28-14.8X	0.916 0.966	0.3e7 0.34e9	104.76 123.05
Cotton cloth	290～343 343～360	Y = 8.68-13.37X Y = 12.6-15.55X	0.947 0.904	0.26e8 1.54e9	111.16 129.28

Table 2 shows that the values of the activation energy of the disposable chopstick, food bag and the cotton cloth are all high. This implies that the design of incinerating section should first be considered to ensure high furnace temperature, when waste with high content of the food bag, cotton cloth and the disposable chopstick are incinerated. This shows that TGA has an important role in deciding the incineration process efficiency.

Based on the mathematical model of single component waste TG and DT curves, and by taking the measured value of activation energy and frequency factor (from table 3) into the numerical calculation method, the corresponding TG and DT curves can be obtained, which can significantly reduce the experimental workload and saves manpower and capital costs. Because the residual carbon burning section is ignored in this model, calculated results have to be compared with the experimental results to determine the appropriateness of this model. The comparisons between the experimental values and the calculated values are shown in figures 3 and 4, for disposable chopstick (A), food bag (B) and cotton cloth (C).

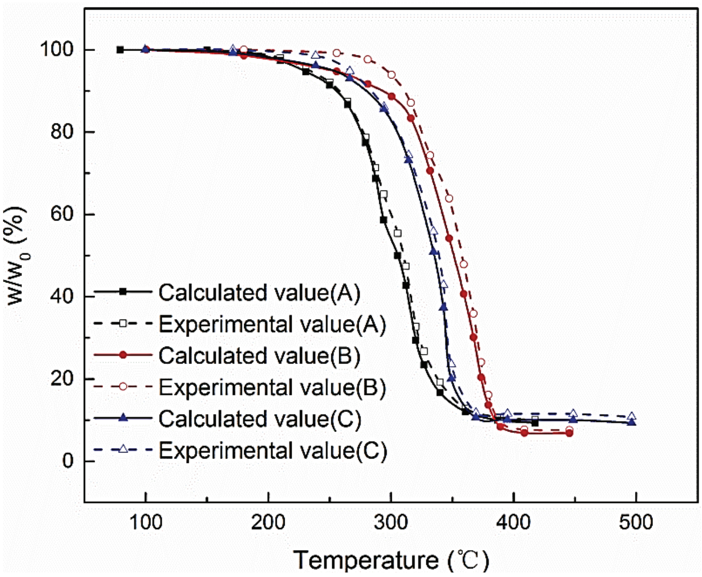

Figure 3 Comparison between experimental and calculated TG curves

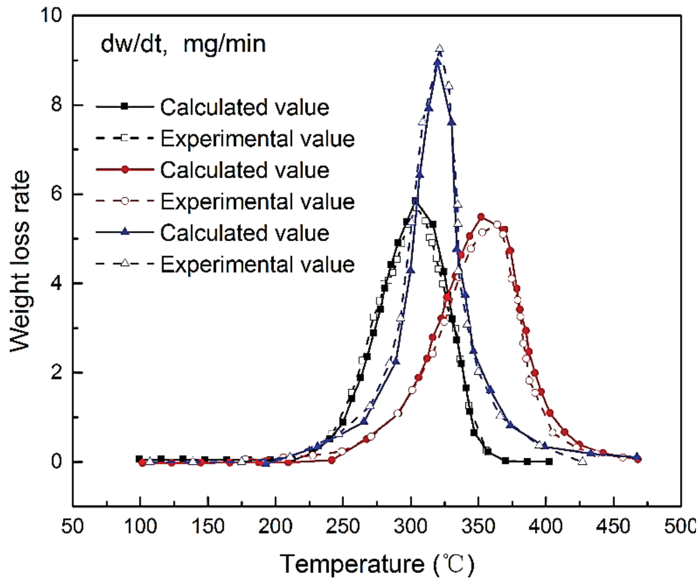

Figure 4 Comparison between experimental and calculated DT curves

It can be seen from figure 3 that the calculated TG curves fit well with the experimental ones, while the degree of fitness of calculated and experimental DT curves is slightly worse, according to figure 4. Moreover, it can be clearly seen that the results of comparison are very satisfying. In order to make a further quantitative analysis of the comparison results, it is very appropriate to use relative deviation as follows:

$$\text{Relative deviation} = \text{ABS}\left(\frac{\text{Value}_{\text{exp}} - \text{Valeu}_{\text{cal}}}{\text{Value}_{\text{exp}}}\right) \tag{26}$$

Figure 5 depicts the relative deviations of TG curves.

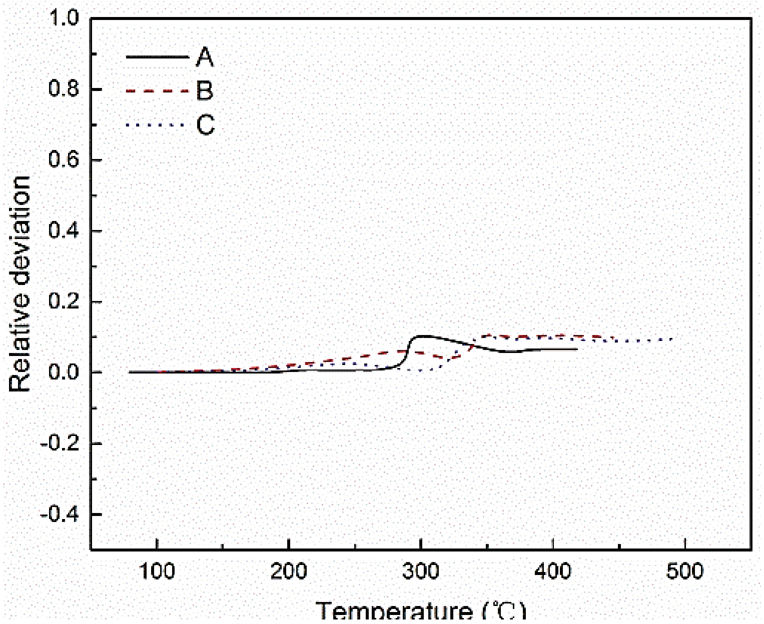

Figure 5 Relative deviation of TG curves

It can be seen from figure 5 that the calculated TG curves fit well with the experimental ones and the maximum deviation between the experimental and calculated curves does not exceed 0.1 (10%). This confirms the appropriateness of the mathematical models for TG curves. As for DT curves**,** we are more interested in the values of the temperature and the weightlessness rate of curve peak because they are of significant importance to the incineration process efficiency. The relative deviations between the calculated and experimental results of peak temperature and peak weightlessness rate are summarized in table 3.

Table 3 Comparisons between experimental and calculation results of DT curves

	Temperature peak of A component	Weightlessness rate peak of A component	Temperature peak of B component	Weightlessness rate peak of B component	Temperature peak of C component	Weightlessness rate peak of C component
Calculated results	303.472	5.85283	352.036	5.48803	319.849	8.94737
Experimental results	304.587	5.72848	363.853	5.31468	321.386	9.24775
Relative deviation	0.003661	0.02170733	0.032477	0.0326172	0.004782	0.032481414

It can be seen in table 3 that the degree of compliance of calculated and experimental results is also excellent. Moreover, the maximum deviation between the experimental and calculated curves does not exceed 5%. This means that the comparison results are very satisfying.

4.2 Combustion characteristics of two components MMSW

4.2.1 TGA and DTA of two components MMSW

Figure 6 shows the TG curves of the two components MMSW, where A is the disposable chopstick, B is the food bag and C is the cotton cloth.

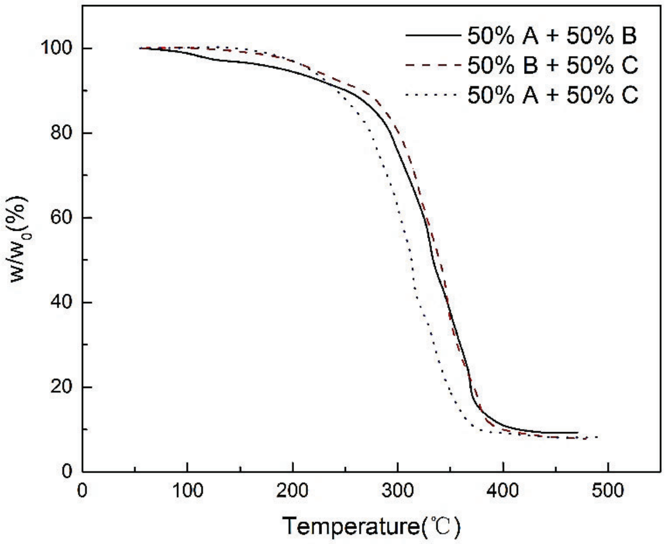

Figure 6 TG curves of two components MMSW

From the profiles of TG shown in figure 6, it can be seen that the starting temperature for weight loss of mixture of disposable chopstick (A) and cotton cloth (C) is lower than that of the other two mixtures, which testifies that the ignition performance of disposable chopsticks and cotton cloth is better than that of the food bag, which has been discussed above. In order to further study the combustion process of two components MMSW, experiments of DTA are carried out. Figure 7 shows the DT curves of the two components MMSW.

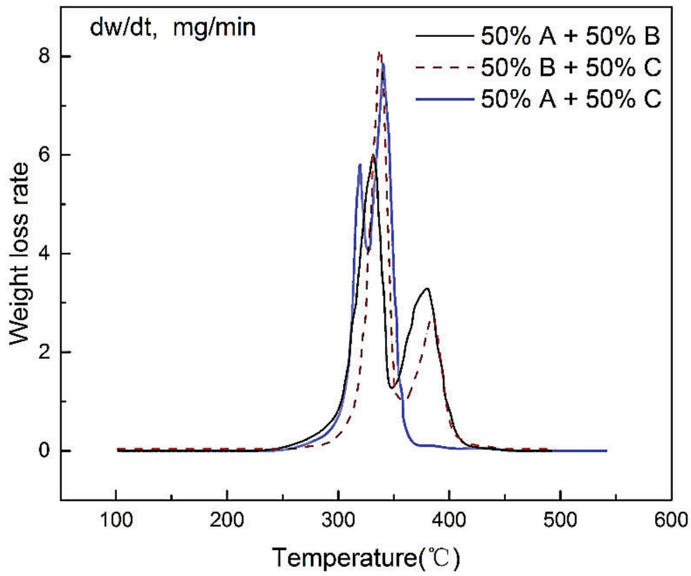

Figure 7 DT curves of two components MMSW

It can be seen from figure 7 that the combustion curves of the mixed samples exhibit characteristics of multi-peak. The mixture of disposable chopstick (A) and food bag (B) has peak temperatures of 331°C and 380°C. Meanwhile, the peak temperatures of the mixture of cotton cloth (C) and food bag (B) are 336°C and 385°C respectively, while the peak temperatures of the mixture of disposable chopstick (A) and cotton cloth (C) are 317°C and 340°C respectively. It can be concluded that combustion process of MMSW exhibits a stepwise characteristic. Each combustion peak of the samples is exhibited in the DT curves of the MMSW and the corresponding temperatures of these peaks are close. The peak temperatures of the maximum rate of weight loss of two components MMSW increase slightly compared to the single component MMSW. The reasons are as follows: as for two components MMSW, when the volatile of low ignition point component starts to burn, the first peak temperature appears. Since the quantity of volatile of low ignition point ingredient in two component MMSW is much less than that of single component at the same weight, the heat released is also far less than that of the single component waste, which inevitably leads to the peak temperature moving backward, but the maximum temperature deviation does not exceed 20°C. This conclusion is consistent with that of [29] because the combustion reaction mechanism of two-component waste is more complex than that of single-component waste, and there is an interaction between the two components of the waste. This shows that combustion time of MMSW slightly increases compared to that of single component waste, but its combustion characteristics are not significantly changed. In the absence of exact experimental data, its combustion characteristics can be approximately predicted by using those of single component MMSW. This conclusion has some guiding significance for the institutes that do not have conditions to do MMSW combustion test.

4.2.2 Activation energy of two components MMSW

Table 4 shows the kinetic parameters of the two components MMSW calculated by regression analysis, according to equation (9).

Table 4 Kinetic parameters of two-component MMSW combustion

Waste Name	Temperature range (°C)	Regression equation	Correlation coefficient	Frequency factor(1/s)	Activation energy (kJ/mol)
Disposable chopstick+ Food bag	300～331	Y=6.09-11.96X	0.862	0.18e7	99.44
	331～348	Y=4.62-11.15X	0.931	0.38e6	92.70
	348～380	Y=0.23-8.42X	0.977	0.35e4	70.00
	380～400	Y=4.55-11.22X	0.993	0.35e6	93.28
Cotton cloth +Food bag	310～336	Y=5.83-12.08X	0.915	1.37e6	100.4
	336～353	Y=8.68-13.8X	0.902	0.27e8	114.7
	353～385	Y=2.05-9.64X	0.961	0.25e5	80.2
	385～395	Y=8.7-14.04X	0.983	0.28e8	116.7
Disposable chopstick +Cotton cloth	304～317	Y=8.3-13.01X	0.915	0.19e8	108.2
	317～330	Y=7.9-12.77X	0.93	1.15e7	106.2
	330～340	Y=5.4-11.26X	0.987	0.87e6	93.62
	340～370	Y=0.23-8.073X	0.981	0.34e4	67.12

It can be seen from table 4 that the two components MMSW has lower activation energy than single component MMSW. In the first group of experiments (disposable chopsticks + food bag), a large amount of heat is required when the disposable chopsticks are ignited, so the activation energy is higher in the temperature range of 300-348°C. As time pass by, the heat released by the burning of disposable chopsticks causes the food bag to be burned in the temperature range of 348-380°C. In this stage, disposable chopsticks and food bag burn together, which makes the combustion reaction easier. Thus, the stronger interaction and chemical reaction between the disposable chopsticks and food bag result in the lowest activation energy. In the temperature range of 380-400°C, the disposable chopstick is burned out, only the food bag is left. Because the poor combustion characteristic of the food bag, the heat released by the food bag by its own combustion is not sufficient to ensure itself to be burned easily, so the activation energy is higher in this range. The second set of experiments (cotton cloth + food bag) and the third group of experiments (disposable chopsticks + cotton cloth) can be explained using the same mechanism as follows.

As temperature rises, waste component with low activation energy burns first. In fact, the released heat plays a preheating role for the component with high activation energy and improves the ignition conditions of the high activation energy component. When the high activation energy component is ignited, the low activation energy component continues to burn, which plays a critical role in supporting combustion. Therefore, it can be assumed that MMSW is more flammable than single component waste, which is beneficial to the design of the actual waste incineration equipment.

4.3 Analysis of combustion characteristics of three components MMSW

4.3.1 TGA and DTA of three component MMSW

Figure 8 depicts the TG curve of three components MMSW.

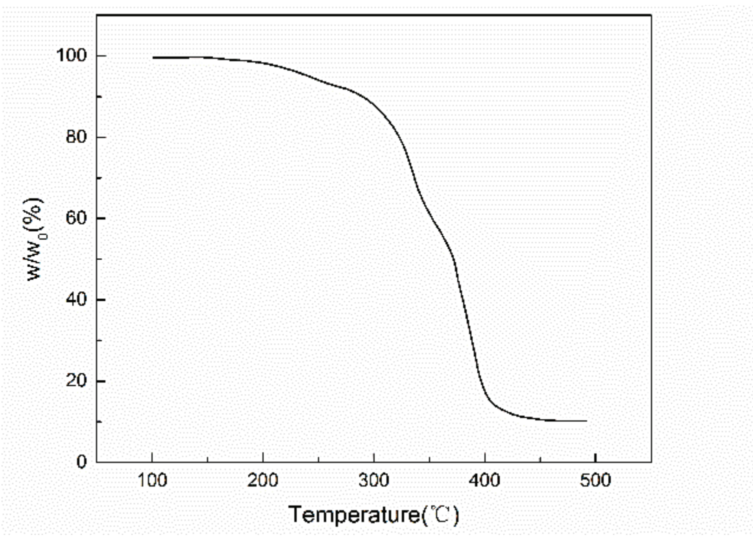

Figure 8 TG curve of three components MMSW

As shown in figure 8 it can be clearly seen that the combustion process mainly consists of three stages because the TG curve drops sharply in three sections. There is a weight loss at the temperature range of 290-330°C, 330-370°C and 370-400°C respectively. This means that the combustion process of three components MMSW exhibit stepwise characteristics and the combustion process of the individual samples can be observed in the TG curves of the three components MMSW. In order to further study the combustion characteristics of three components MMSW, the DT curve is obtained. Figure 9 depicts the DT curve of three components MMSW.

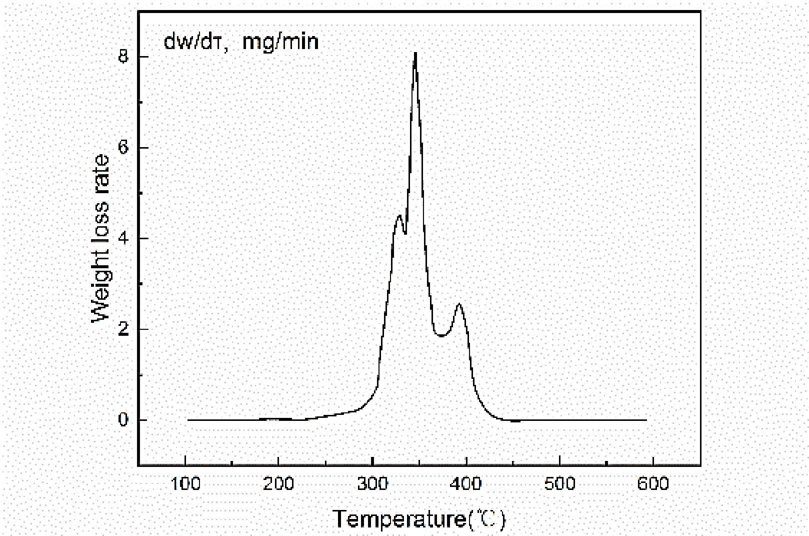

Figure 9 DTA curve of three components MMSW

Similar to combustion characteristics of two components MMSW, the DT curve of three components MMSW composed of disposable chopstick, cotton cloth and food bag also shows triple temperature peaks: 326°C (first peak), 343°C (second peak) and 390°C (third peak).

The above-mentioned results show three-stage and three-peak characteristics. The variation in curves can be explained based on material decomposition. Because the burning sample contains three kinds of waste components, the first stage (290-330°C) is dominated by the disposable chopstick decomposition. During this stage, the burning rate of chopsticks (lignose) is the largest and the weight loss rate is the highest at 326℃, so it shows the first peak. During the second stage (330-370°C), the burning rate of cotton is the largest and the weight loss rate is the highest at 343°C, so it shows the second peak. During the third stage (370-400°C), the burning rate of the food bag is the largest and the weight loss rate is the highest at 390℃, so it presents the third peak. The temperature peaks of each component in the single, two and three-component MMSW are listed in table 5.

Table 5 Temperature peaks of each component in the single, two and three-component MMSW

Items	Temperature peak of single component MMSW	Temperature peak of two components MMSW (1+2)	Temperature peak of two components MMSW (2+3)	Temperature peak of two components MMSW (1+3)	Temperature peak of three components MMSW
1.Disposable chopstick	314°C	331°C		317°C	326°C
2.Food Bag	364°C	380°C	385°C		390°C
3.Cotton cloth	321°C		336°C	340°C	343°C

As shown in table 5, each temperature peak is close to combustion peaks in DT curves of single component MMSW. However, certain deviations also exist. It implies that there are certain interactions between the components of MMSW although the combustion characteristics of MMSW can be approximately estimated by using combustion characteristics of single component waste. Moreover, the kinetic parameters of three components MMSW are listed in table 6.

Table 6 Kinetic parameters of three components MMSW

Waste Name	Temperature range (°C)	Regression equation	Correlation coefficient	Frequency factor(1/s)	Activation energy (kJ/mol)
disposable chopstick+ Cotton cloth +Food bag	300～343 343～400	Y=2.77–10.16X Y=2.25–9.93X	0.972 0.907	0.54e5 0.31e5	84.47 82.56

It can be clearly seen from table 6 that the activation energy of three components MMSW is lower than single component and two components MMSW. When waste is burned in an incinerator, disposable chopstick made from lignocellulose with a low ignition point is burnt first. When the heat released by disposable chopstick is enough to burn cotton, cotton and disposable chopstick will combust together. Both of them promote each other's combustion. Therefore, the activation energy of two-component waste is lower than that of single-component waste. As time pass by, when the heat released by disposable chopstick and cotton is enough to burn food bag, they will burn together. The mutual promotion of the three components on combustion has become more intense. At the same time, the interaction and co-combustion reaction between the three components is more complicated than two-component and single-component, so the activation energy of three components waste is much lower. This is conducive to the process efficiency of MMSW incineration equipment. This further confirms the conclusion that certain interactions exist between the components of MMSW. Therefore, it is necessary to discover a new empirical formula for calculating activation energy of three components MMSW. This will be described in detail in the next section.

4.3.2 Establishment and validation of empirical formula for calculating activation energy of three components MMSW

According to equation (25), the empirical expression for calculating the activation energy of three components MMSW composed of disposable chopstick, food bag and cotton cloth is:

$$y = a_1 \cdot y_1 \cdot x_1 + a_2 \cdot y_2 \cdot x_2 + a_3 \cdot y_3 \cdot x_3 + b_{12} \cdot y_{12} \cdot x_1 \cdot x_2 + b_{13} \cdot y_{13} \cdot x_1 \cdot x_3 + b_{23} \cdot y_{23} \cdot x_2 \cdot x_3 + c \cdot y_{123} \cdot x_1 \cdot x_2 \cdot x_3 \quad (26)$$

where x_1 is the percentage of disposable chopstick, x_2 is the percentage of food bag, x_3 is the percentage of cotton cloth, y_1, y_2 and y_3 are the corresponding average activation energy of disposable chopstick, food bag and cotton cloth respectively, y_{12} is the average activation energy of two components MMSW composed of disposable chopstick and food bag (Each component accounts for 1/2), y_{13} is the average activation energy of two components MMSW composed of disposable chopstick and cotton cloth (Each component accounts for 1/2), y_{23} is the average activation energy of two components MMSW composed of food bag and cotton cloth (Each component accounts for 1/2), y_{123} is the average activation energy of three components MMSW composed of disposable chopstick, food bag and cotton cloth (Each component accounts for 1/3) and y is average activation energy of three components MMSW with different mixing ratios. According to the values of average activation energies of single component, two components and three components MMSW given in tables 2, 4 and 6, the coefficients in the equation (26) can be obtained by using multiple regression analysis [43]. The calculation results of coefficients are listed in table 7 and the average activation energy values of the MMSW are listed in table 8.

Table 7 Calculation results of regression coefficients

a_1	a_2	a_3	b_{12}	b_{13}	b_{23}	c
1.000	1.006	0.994	-1.057	-0.562	-0.981	-1.638

Table 8 Average activation energy values of the MMSW

y_1(kJ/mol)	y_2(kJ/mol)	y_3(kJ/mol)	y_{12}(kJ/mol)	y_{13}(kJ/mol)	y_{23}(kJ/mol)	y_{123}(kJ/mol)
113.07	113.905	120.22	88.855	103	93.785	83.515

Thus, equation (26) can be re-written as:

$$y = 1.000 \cdot y_1 \cdot x_1 + 1.006 \cdot y_2 \cdot x_2 + 0.994 \cdot y_3 \cdot x_3 - 1.057 \cdot y_{12} \cdot x_1 \cdot x_2 - 0.562 \cdot y_{13} \cdot x_1 \cdot x_3 - 0.981 \cdot y_{23} \cdot x_2 \cdot x_3 - 1.638 \cdot y_{123} \cdot x_1 \cdot x_2 \cdot x_3 = 113.075x_1 + 114.594x_2 + 119.526x_3 - 94.366x_1x_2 - 58.712x_1x_3 - 93.138x_2x_3 - 129.729x_1x_2x_3 \quad (27)$$

The above equation needs to be validated by experimental methods. Three typical test conditions (presented in table 9) determined by mixture design principles [42], combustion characteristics of three component MMSW are tested and the corresponding TG curves are shown in figure 10.

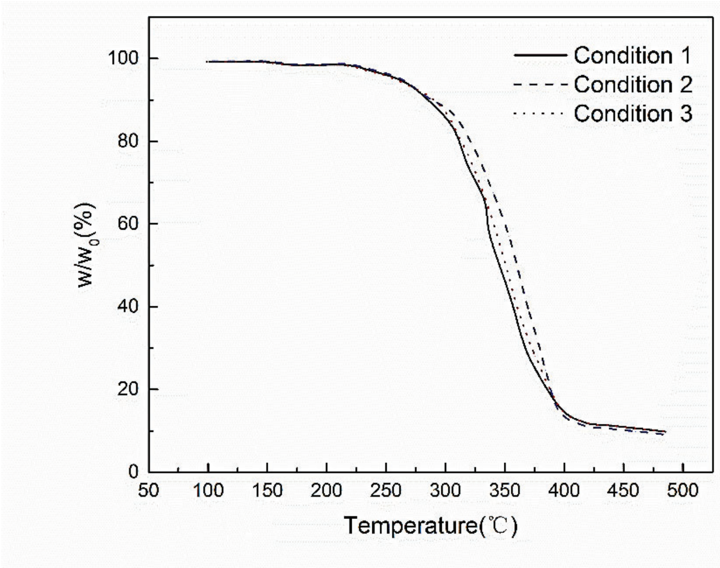

Figure 10 TG curves of verification experiment of three components MMSW

The values of activation energy of three components MMSW can be obtained by regression, according to TG curves. Then, they are compared with the values calculated by the empirical equation. Comparison between experimental values and calculated values using empirical equation is shown in table 9.

Table 9 Comparisons between experimental and calculation results

Experiment	Disposable chopstick	Food bag	Cotton cloth	Average activation energy (kJ/mol)		Relative deviation
				Experimental value	Calculated value	
Condition1	1/2	1/4	1/4	86.1	85.94	0.19%
Condition2	1/2	1/2	1/4	89.8	84.19	6.25%
Condition3	1/2	1/4	1/2	82.2	87.62	6.59%

It can be clearly seen from table 9 that the experimental values and the calculated values match well and the maximum deviations between them do not exceed 7%. Therefore, this equation can be widely applied with credibility. Since the determination of activation energy of MMSW by TGA is very complicated, it is a simple and practical way to calculate the activation energy of three components MMSW according to the activation energy of single component MMSW, which is known.

5. Conclusions

The main content of the present study is to carry out theoretical and experimental research on the kinetic combustion characteristics of MMSW. Based on the analysis of the results, it can be concluded that the entire combustion curve of single component MMSW shows a single peak which is high and sharp in DT curve, and hence it verifies the credibility of the conclusion that the burning of waste mainly depends on the combustion of volatiles and can be regarded as a gas phase combustion. This brings about a substantial simplification of the numerical calculation of the waste combustion process.

On the basis of the kinetic combustion characteristics of the MMSW which are obtained in present study, it can be observed clearly that the burning performance of plastic waste is poor compared with that of other waste. In the design of actual waste incinerator, main burning zone temperature in combustion chamber should be maintained at a high level (higher than 500°C) and the combustion air supply should be appropriately postponed. A comprehensive kinetic model for single component MMSW is established through rigorous mathematical derivation. The models provide a theoretical basis for drawing TG and DT curves of combustible ingredient in a single component solid fuel and gives a novel method for calculating activation energy and frequency factor of single component MMSW. The accuracy of the models is verified because the maximum deviations between experimental values and calculated values do not exceed 10%.

Based on the principle of mixture experiments, the combustion characteristic parameters of three components MMSW are obtained. Compared with those of single component waste, there is no significant change in the combustion characteristics of MMSW composed of two or three components. The combustion characteristics of two or three components MMSW exhibit stepwise characteristics and each combustion peak of individual samples can be observed in the DT curves of the MMSW. However, its activation energy is lower than that of single component waste and this makes it easy to burn. Meanwhile, its kinetic characteristics can be approximated by those of single component waste.

Nomenclature

α	Conversion rate for the reaction	T	Reaction temperature(K)
ϕ	Heating rate(K min^{-1})	T_i	Reaction temperature in time i(K)
τ	Reaction time(min)	w_0	Instantaneous mass of sample in initial (mg)
A	Coefficient in equation(9)		
a_j	Regression coefficient of single component MMSW (disposal chopstick j=1, food bag j=2, cotton cloth j=3)	w_i	Instantaneous mass of sample in time i(mg)
		w_∞	Instantaneous mass of sample in final(mg)
b_{hj}	Regression coefficient of two component MMSW(disposal chopstick h,j=1, food bag h,j=2, cotton cloth h,j=3)	X	Independent variable in equation(9)
C	Coefficient in equation(9)	x_j	Percentage of a component (disposal chopstick j=1, food bag j=2, cotton cloth j=3)
c	Coefficient in equation(25)		
DT	Differential thermal		
DTA	Differential thermal analysis		
E	Activation energy(J mol^{-1})	y	Dependent variable in equation(9)
k_0	Frequency factor(s^{-1})	y_j	Activation energy of single component MMSW (disposal chopstick j=1, food bag j=2, cotton cloth j=3) (kJ mol^{-1})
MSW	Municipal solid waste		
MMSW	Mixed municipal solid waste		
N	Minimum number of tests	y_{hj}	Average activation energy of two components MMSW (disposal chopstick h,j=1, food bag h,j=2, cotton cloth h,j=3) (kJ mol^{-1})
n	Reaction order		
R	General gas constant(J mol^{-1} K^{-1})		
TG	Thermogravimetric		
TGA	Thermogravimetric analysis	y_{123}	Average activation energy of three components MMSW (kJ mol^{-1})

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