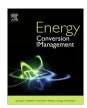


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Thermogravimetric analysis of the co-combustion of paper mill sludge and municipal solid waste



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ABSTRACT

The thermal characteristics and kinetics of paper mill sludge (PMS), municipal solid waste (MSW) and their blends in the combustion process were investigated in this study. The mass percentages of PMS in the blends were 10%, 30%, 50%, 70% and 90%, respectively. The experiments were carried out at different heating rates (10 °C/min, 20 °C/min and 30 °C/min) and the temperature ranged from room temperature to 1000 °C in a thermogravimetric simultaneous thermal analyzer. The results suggested that the ignition temperature and burnout temperature of MSW were lower than that of PMS, and the mass loss rate of MSW was larger especially at low temperatures. There were only two mass loss peaks in the differential thermogravimetry (DTG) curve, while three mass loss peaks were observed when the blending ratios of PMS were 30%, 50%, 70%. The value of the comprehensive combustion characteristic index of the blends indicated a good combustibility when the percentage of PMS (PPMS) in the blends was less than 30%. There existed certain interaction between the combustion process of PMS and MSW, especially at high temperature stage. Activation energy (*E*) value obtained by the Ozawa–Flynn–Wall (OFW) method and the Starink method were very consistent. When the mass percentage of PMS in the blends was 80%, the *E* average value attained the minimum.

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1. Introduction

With the improvement of residents' living standard and pressure of the increasing population, the output of municipal solid waste (MSW) is growing with each passing day, which poses a great pressure and threat to the environment urban inhabitants live on [1,2]. MSW generation has been increasing at an annual rate of 8–10%, with over 200 million tons of MSW being produced based on a predicted value by 2015 [3]. A large proportion composition of MSW derives from biomass, that is, waste paper, restaurant-kitchen garbage, trees and branches, cotton and leather. And plastic, rubber and fabric come from fossil fuels [3]. MSW is regarded as a kind of renewable energy by the U.S. department of energy and the United States environmental protection agency [4]. Therefore, the disposal of MSW is not only a truly serious environmental problem recovery process of energy, but also a way of the utilization of secondary recovery energy and energy conservation [5].

Four disposal methods of MSW, which are currently used, are landfilling, composting or recycling in agriculture, dumping into sea and incineration [6]. As the output and volume of MSW

increase annually, a large more places and time are needed to the disposal of MSW. Obviously, landfilling, composting or recycling in agriculture and dumping into sea cannot meet the requirement of modern society day by day. Based on the principle of reduction, recycling and harmless, incineration method is widely used as one of the main methods of Waste-to-Energy (WTE) treatments around the world, and become the main trends of the development of MSW treatments [4,7–11].

Sludge treatment is always an important problem all over the world [11–13]. According to European regulations, the management methods of sewage sludge may consequently promote the recovery of valuable raw materials, the utilization in agriculture and industry, and the recovery of heat and energy [12]. However, the construction of facilities for sludge treatment is still badly lagged behind, and the requirement of sludge disposal has become increasingly urgent. Compared with other methods, such as land-filling, composting or recycling in agriculture and dumping into sea, sludge incineration method has the advantages of reduction, harmless and recycling. Therefore, sludge incineration or co-combustion with other solid fuels is a method of sludge treatment which is widely used [13–15].

At present, with the reduction of finite reserved fossil fuel and the continual increasing requirement of fossil fuels, the energy

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shortage problem is becoming increasingly acute. The combined utilization of municipal solid waste and fossil fuels, which is attracting more and more attention and research, has become one of the best way to replace the single fossil fuels [16,17]. However, because of the characteristics of paper mill sludge (PMS) with high volatile, high ash content and low calorific value [18,19], it is necessary that auxiliary fuel is added into the sludge in the sludge combustion system to ensure the stability of combustion conditions [12]. So far there have been a lot of research reports about the co-utilization of sludge and other solid fuels [8,19–22]. The available calorific value of municipal solid waste increases gradually because of the improvement of people's living standard, so incineration method is used to be of great potential to deal with municipal solid waste. The low caloric value (LCV) of MSW was 5600 kJ/kg tested in Guangzhou in 2006, and reached 6800 kJ/kg in 2013. From the perspective of environmental protection and economy, the co-combustion of PMS and MSW will be a good method of PMS and MSW processing at the same time. Not only the pollution of PMS to the environment can be reduced, but also the heat generated by the sludge incineration process can be used effectively. Some research suggests that co-combustion of MSW and inferior coal can improve the decomposition and combustion characteristic, strengthen the reactivity of substances with a low chemical reactivity, reduce the uncombusted coke content [23]. Compared with PMS, more volatile material of MSW will be emitted at lower temperature range, which will help to reduce the reaction time required in the entire combustion reaction process.

So far, the reports on the co-combustion of MSW and PMS with other solid fuel combustion respectively are seen repeatedly, while there are few reports about the research on the co-combustion of PMS and MSW. Because of the characteristics of PMS with high volatile, high ash content and low calorific value, sludge combustion may bring about some unfavorable effects on the combustion conditions of reaction system. Therefore, further studies are necessary to study and analyze the combustion characteristics of PMS and MSW in the combustion process, and the interactions that existed possibly among co-combustion of PMS and MSW, so that combustion temperature and the stability of the combustion chamber will be guaranteed and the emissions of pollutants may reduce. Therefore, this paper studies combustion characteristics and the reaction kinetics of PMS, MSW and their blends under different heating rate and blending ratio. The kinetic parameters during the combustion process were calculated by two iso-conversional methods: the Ozawa-Flynn-Wall (OFW) method and the Starink method. Moreover, the interaction between PMS and MSW was also investigated under the different blending ratio. The results obtained will help to further understand the co-combustion process of PMS and MSW, and provide the reference and guidance for the design and operation of MSW incinerator blended with sludge.

2. Methods

2.1. Materials

The PMS used in this study was collected from a paper mill in Guangdong Province in China. According to the typical composition of MSW in Guangzhou city in China, the combustible components of food waste, peel, wood and branches, paper, PVC (one of the most common component of plastic), fabric were chosen as experiment samples of MSW, and the noncombustible components such as metal, glass and batteries were eliminated. The components of MSW on received basis were listed in Table 1. The raw materials were named PMS and MSW, and the percentage of PMS in the blends was named PPMS. PMS and all the composition of MSW were dried at 105 °C for 24 h in drying oven, after which

Table 1 Composition of MSW on as received basis (wt.%).

Component	Food waste	Fruit waste	Wood	Paper	PVC	Textiles
MSW	37.16	10.58	13.90	8.50	23.36	6.50

Table 2
The ultimate analyses and proximate analyses of PMS and MSW on dry basis.

Samples	Ultima	Ultimate analyses (wt.%)				Proximate analyses (wt.%)		
	С	Н	0	N	S	Volatile	Fixed carbon	Ash
PMS MSW	16.46 48.08	1.63 6.48	20.22 36.22	0.7 1.82	1.42 0.74	39.16 75.60	1.27 17.75	59.57 6.66

the samples were crushed, grinded and sieved to the desired particle size (less than 178 µm). All the components of MSW that had been processed before were mixed together according to the mass percentage of the MSW components. The mass percentage of PMS added to MSW were 10%, 30%, 50%, 70%, 90% (10%PMS90%MSW, 30%PMS70%MSW, 50%PMS50%MSW, 70%PMS30%MSW, 90%PMS10%MSW), respectively. All the samples of PMS and MSW were mixed respectively according to the desired proportion of blends in a micro rotary mixer for 1 h to obtain 50 mg mixed samples. Then 5 mg mixture samples were taken as experimental samples by coning quartering method. The samples obtained eventually were stored in the desiccators. The ultimate analysis and proximate analysis of PMS and MSW on dry basis were shown in Table 2.

2.2. Experimental facility and method

The experiments were conducted in METTLER TOLEDO TGA/DSC1 thermogravimetric simultaneous thermal analyzer. The temperature accuracy was ± 0.5 °C, and microbalance sensitivity was less than ± 0.1 µg. The samples of the non-isothermal co-combustion experiment were heated from room temperature to 1000 °C at different heating rates of 10, 20, 30 °C/min, in which the gas flow of air was 80 ml/min. All the initial quality of the samples were 5 ± 0.5 mg. Before the start of the experiment, several experiments without samples were carried out to obtain the baseline, which were deducted when the experiments with samples started, in order to eliminate the systematic errors of the instrument itself. To reduce the experiment error as much as possible, all the experiments were conducted at least twice, and the reproducibility was quite good.

2.3. Kinetic theory

Kinetics analysis method was used to further study the combustion characteristics of PMS, MSW and their blends. The fundamental rate equation of heterogeneous solid phase reactions could be expressed as the Arrhenius equation [18]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) = A\exp\left(-\frac{E_{\alpha}}{RT}\right)f(\alpha)$$
 (1)

where t is the time (min), A is the pre-exponential Arrhenius factor (s⁻¹), E_{α} is the apparent activation energy (kJ/mol), R is the universal gas constant (kJ/mol), T is the reaction temperature (K), $f(\alpha)$ is the reaction model function, α is conversion degree in the process, which is described as [13,19]:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_\infty} \tag{2}$$

where m_0 is the initial mass of the samples (mg), m_t is the final mass of the samples (mg), m_{∞} is the mass of the samples at the time t (mg). For the non-isothermal and heterogeneous solid phase

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