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

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ABSTRACT

The pyrolysis characteristics of municipal solid waste (MSW), paper sludge (PS) and their blends were studied through a thermogravimetric simultaneous thermal analyzer from room temperature to 1000 °C. Meanwhile their kinetics were studied by Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–S unose (KAS) methods. The mass proportions of PS in the blends were 10%, 30%, 50%, 70%, 90%, respectively and the experiments were carried out at different heating rates (30, 40 and 50 °C/min). The initial temperature of MSW was lower than that of PS and the terminated temperature was higher than PS. The comprehensive characteristic index decreased progressively along with the decrease of the MSW proportion. The values of average activation energies calculated by FWO and KAS methods were highly consistent. The average activation energy reached the minimum number, 96.7 kJ/mol by KAS and 11.56 kJ/mol by FWO, with the proportion of PS was 50%.

1. Introduction

Large amount of municipal solid waste (MSW) and paper sludge (PS) are produced year by year. By 2012, the national amount of MSW clean-up reached 1.71Gt/a and dry PS production was 0.26Gt/a [1]. MSW is a complicated mixture of components and contains many flammable materials. Waste paper, kitchen garbage, trees and branches, cotton and leather, plastic, rubber and fabric are contained in MSW [2]. MSW contributed to this environmental impact issue, yet it actually was a potential energy source for energy recovery [3]. The main component of PS is lower organic matter, such as amino acid, humic acid, polycyclic aromatic hydrocarbon, heterocyclic compounds and organofluorine compounds [4]. The disposal of PS brought difficulties that if improper handled, it would make the soil contaminated with heavy metals and pesticides, air polluted by NO_X, SO_X, hydrocarbon and suspension dust, resulting in the atmosphere, surface water and groundwater contamination. The generated MSW and PS in urban areas are predominantly managed by landfill because of its low cost management option [5]. There are also other treatments such as composting, dumping into the sea, recycling in agriculture, and thermal treatment [6]. In the thermochemical treatment methods, pyrolysis and gasification are regarded as two of efficient and valid ways to recycle [7].

Pyrolysis is defined as the thermal destruction of organic materials in the absence of oxygen [8]. A pyrolysis process can be considered not only as an independent process to produce various chemical compounds and fuels, but also as the initial stage of thermal conversion process of carbonaceous materials, including combustion and gasification [9]. Co-pyrolysis is deeply influenced by a lot of factors such as heating rate, and terminated temperature. Recently, a number of studies have reported the co-pyrolysis characteristics [2,10–13]. Ren et al. [14] studied the co-pyrolysis of MSW and cotton stalk through TG-FTIR (thermogravimetric analyzer coupled with a Fourier-transform infrared spectrometer). It reported that the total weight loss of the blends increased when the mass proportion of stalk increased. Lin et al. [15] studied the thermochemical behavior of co-pyrolysis oil-palm solid wastes and paper sludge. It showed that there was a synergistic interaction at low temperature during co-pyrolysis and the lowest average activation energy was achieved when the percentage of oil-palm solid wastes was 70%.

So far the co-pyrolysis technology is still in development. The reports on the co-pyrolysis of MSW or PS with other solid fuels or biomass pyrolysis respectively can be seen repeatedly, while less work on co-pyrolysis behavior between MSW and PS was found. Therefore, under N_2 atmosphere at three different heating rates (30, 40 and 50 °C/min) via thermogravimetric analyzer, the

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main task of this work was to research the co-pyrolysis thermal behaviors and the kinetic behaviors of MSW, PS and their blends. According to Idris et al., peak height and temperature of maximum weight loss increased with the increasing heating rates during the pyrolysis [16]. At higher heating rates, the decomposition process was slower at higher temperature since the heat transfer was not as effective as they were at lower heating rates [17]. The increasing of the heating rate would delay the decomposition of sample and involve a lower weight loss. As a matter of facts, higher heating rates involve, mainly for biomass, an irregular weight reduction [18]. Therefore, the previous conclusions suggest us to choose the heating rate of 30 °C/min to analysis the pyrolysis characteristics. Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS) methods were used in this work to obtain the apparent activation energy. The result could provide a detailed observation between the blends and an optional mix proportion. Furthermore, this work will be expanded in the future to create a database of Chinese MSW and PS thermochemical prediction models.

2. Experiments and materials

2.1. Experimental facility and method

The METTLER TOLEDO TGA/DSC1 thermogravimetric simultaneous thermal analyzer whose temperature precision is ±0.5 °C and microbalance sensitivity is less than ±0.1 μg was used in this study for co-pyrolysis experiments. The samples for non-isothermal co-pyrolysis experiment were heated from room temperature to 1000 °C at heating rates of 30, 40, and 50 °C/min, with a flow rate of 80 ml/min at N_2 atmosphere which could make sure that the samples were in an inert atmosphere during the co-pyrolysis run. The initial quality of the samples was 5 ± 0.5 mg to minimize the probability of error. Before the experiment started, several blank experiments without samples were carried out to gain the baselines to use as corrections. To ensure the accuracy of the experimental results, all the experiments were conducted twice and the reproducibility was satisfied.

2.2. Materials

The paper sludge (PS) investigated was collected from a paper mill in Guangdong Province in China. The municipal solid waste (MSW) was a complicated mixture of components such as food waste, peel and wood. According to the actual measurement for Guangzhou living garbage, the content of food waste, polyvinyl chloride (PVC), wood, fruit waste, paper and textiles, in decreasing order, were 37.16%, 23.36%, 13.90%, 10.58%, 8.50% and 6.50%, respectively. Food waste and fruit waste were collected from the supermarket or restaurant; wood was collected from trees; paper was collected from the classrooms in South China University of Technology. Textiles were collected from a shopping mall in Guangzhou. PVC was acquired from the waste classification. After air-dried at 105 °C for 24 h, crushed, grinded, the samples were sieved to the desired particle size (<178 μm). The components of MSW were listed in Table 1. The PS was added to MSW at weight ratios of 10%, 30%, 50%, 70% and 90%. All the samples were mixed for an hour in a micro rotary mixer then air-dried at 105 °C for 24 h. Finally, we acquired 50 mg mixed samples. Then 5 mg of the blends were taken as experimental samples by quartering for TGA experiments. Desiccators were used to store the final samples. The ultimate analysis and proximate analysis were tested according to GB/T212-2008, GB211-84 and ASTM D5373-08, respectively. The Vario EL cube elemental analyzer was used for the ultimate analysis. Then, the ultimate analysis and the proximate analysis of MSW and PS were listed in Table 2.

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

2.3. Kinetics model

To further study the pyrolysis characteristics of MSW, PS and their blends, kinetics analysis methods were used. The reaction process and mechanism could be deeply understood through kinetics analysis and the complexity of the reaction could also be predicted. The fundamental rate equation of heterogeneous solid phase reactions could be described as Eq. (1) [19]:

$$d\alpha/dt = k(T)f(\alpha) = A\exp(-E_\alpha/RT)f(\alpha) \quad (1)$$

where $d\alpha/dt$ stands for the rate of conversion, k for the rate constant, $f(\alpha)$ for the reaction model, α for conversion degree in the process (%), A for the pre-exponential Arrhenius factor (s^{-1}), E_α for the apparent activation energy (kJ/mol), R for the universal gas constant (kJ/mol), and T for the reaction temperature (K). The conversion rate (α) was defined as Eq. (2):

$$\alpha = (m_0 - m_t)/(m_0 - m_\infty) \quad (2)$$

where m_0 represented for the initial weight of the samples (mg), m_t and m_∞ for the time t and final mass of the samples, respectively. For the non-isothermal is conversional experiments at constant heating rate, $\beta = dT/dt$. Eqs. (1) and (2) could be written as Eq. (3):

$$d\alpha/dT = (A/\beta)\exp(-E_\alpha/RT)f(\alpha) \quad (3)$$

Flynn–Wall–Ozawa (FWO) and Kissinger–Akahira–Sunose (KAS) methods as the typical representative of multiple scanning rate method are used frequently [19–23]. So FWO and KAS methods were chosen to be used in this study to calculate the apparent activation energy. The expression of FWO method was based on the following Eq. (4) [19,23]:

$$\ln(\beta) = \ln[AE_\alpha/Rg(\alpha)] - 5.331 - E_\alpha/RT \quad (4)$$

For $\alpha = const$, and through the slope of the straight line matched by plotting $\ln(\beta)$ vs. $1/T$, E could be calculated.

The expression of KAS method was based on the following Eq. (5) [20]:

$$\ln(\beta/T_\alpha^2) = \ln[AR/E_\alpha g(\alpha)] - E_\alpha/RT_\alpha \quad (5)$$

For $\alpha = const$, E could be obtained through the slope of the straight line matched by plotting $\ln(\beta/T_\alpha{}^2)$ vs. $1/T$.

3. Results and discussion

3.1. Thermogravimetric analysis of MSW and PS

Pyrolysis is defined as the thermal destruction of organic materials in the absence of oxygen [8]. Pyrolysis is the basis of almost all

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

Samples	Ultimate analyses (wt.%)					Proximate analyses (wt.%)		
	C	H	O	N	S	Volatile	Fixed carbon	Ash
PS	16.46	1.63	20.22	0.7	1.42	39.16	1.27	59.57
MSW	48.08	6.48	36.22	1.82	0.74	75.60	17.75	6.66