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Interactions of three municipal solid waste components during *co*-pyrolysis

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ABSTRACT

The interactions of three MSW components (orange peel, tissue paper and PVC) during *co*-pyrolysis were investigated using thermogravimetric analyzer coupled with Fourier transform infrared spectrometer (TGA–FTIR). The overlap ratio of TG curves was introduced to evaluate the interaction quantitatively. The interaction of orange peel and tissue paper was slight, with the overlap ratio of 0.9936. The interaction of orange peel and PVC inhibited the production of alkyls and alkenes, and weakened the peaks of HCl and C_6H_6. The interaction of tissue paper and PVC was significant with the overlap ratio 0.9296. The interaction of tissue paper and PVC promoted pyrolysis at low temperature (below 300 °C) and suppressed the pyrolysis at high temperature. Meanwhile, the residue was increased. The generation of CO_2, alkyls, alkenes, and carboxyls was intensively influenced by interaction of tissue paper and PVC. The second and third peak of HCl disappeared, because of the reaction of HCl with other organic compounds.

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1. Introduction

Large amount of municipal solid waste (MSW) are produced year by year. It is certain that the use of landfills is not a long-term solution, which causes many problems, such as land occupation, underground water pollution, and air pollution [1]. Pyrolysis is regarded to be a potential option for MSW disposal, because it can reduce the MSW volume, and produce oil and gases that can be further utilized [2,3]. In addition, due to the low temperature and oxygen content in the process of MSW pyrolysis, toxic carcinogenic compounds e.g. dioxins are largely reduced compared with MSW incineration, which is strongly opposed by publics particularly in China [4].

MSW is a complicated mixture of components such as food residue, paper, and plastics. The MSW components in Chinese cities are shown in Fig. 1. The content of food residue, plastics, paper, textiles, wood waste and rubber, in decreasing order, were 55.86%, 11.15%, 8.52%, 3.16%, 2.94%, and 0.84% [5].

Due to the complex of MSW, most of research has studied the pyrolysis of single components [6,7]. However, the components do not act independently during pyrolysis [8,9]. Pine cone and synthetic polymers (PE, PP and PS) were *co*-pyrolyzed at 500 °C by Brebu et al. Due to the synergistic effect in the pyrolysis of the biomass/polymer mixtures, higher amounts of liquid products were obtained, compared to theoretical ones. The *co*-pyrolysis of pure cellulose and polymers showed that, in the presence of cellulose, degradation reaction leading to more gas formation and less char yield was more advanced than in the case of *co*-pyrolysis with pine cone [10]. Caglar and Aydinli investigated the *co*-pyrolysis of hazelnut shell and ultra-high molecular weight polyethylene (UHMWPE) mixtures. It could be definitely stated that there were interactions between components. *Co*-existence of hazelnut shell and UHMWPE rendered gas products in expense of liquid at all temperature and composition conditions [11]. The mixtures of PVC and straw were pyrolyzed in a tube furnace at the heating rate of 10 K min^{-1}, which was reported by McGhee et al. [12]. It showed that during the pyrolysis of straw with PVC, yield of bio-char from straw was increased, and also the bio-char become less reactive, compared with the pyrolysis of pure straw. However, the effect of interactions on thermogravimetric characteristics in previous research were only discussed qualitatively, and the gas products from interactions were rarely reported.

As shown in Fig. 1, food residue, paper and plastics are the most abundant combustible fractions of MSW. In this paper, the interactions among orange peel, tissue paper and PVC were studied. Orange peel, tissue paper and PVC were the representative of food residue, paper and plastics, respectively. The technology of thermogravimetric analyzer coupled with Fourier transform infrared

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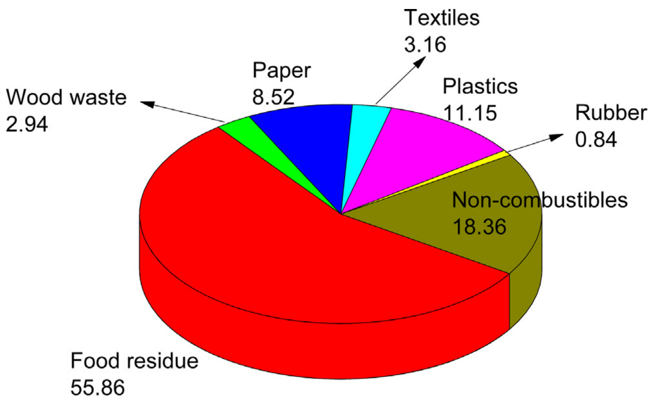

Fig. 1. The mean physical composition of MSW in China.

spectrometer (TG–FTIR) [13,14] is applied here to record the mass loss data and predict the product-evolution patterns. The effect of the interactions on mass loss characteristics were analyzed quantitatively and the gas products with or without interactions were discussed.

2. Material and methods

2.1. Materials

The proximate and ultimate analyses of the samples were shown in Table 1. The fixed carbon content of orange peel is very high (20.60%), while the volatiles of tissue paper and PVC are very high. Orange peel and tissue paper have similar elemental compositions and PVC has a chlorine content of 56.35 wt.%, which was also reported by Li et al. [15]. Before pyrolysis, the samples were dried at 105 °C to constant weight to eliminate the moisture. Samples were ground to less than 500 μm, which is small enough to prevent heat transfer effect in isothermal and dynamic experiments [16].

2.2. Experimental apparatus

The TGA experiments were performed by a NETZSCH STA 409C/3/F with a flow rate of 100 ml min^{-1} of N_2. Temperature rose from room temperature to 1000 °C at a heating rate of 10 K min^{-1}. Repeated experiments showed that TG curves had good reproducibility.

The FTIR measurements were performed by a Nicolet Nexus 670 spectrometer coupled to TGA to measure typical gas products. The volatiles released during pyrolysis were swept into FTIR gas cell quickly by N_2 with the flow rate of 100 ml min^{-1}. The tube and FTIR gas cell were preheated to 150 °C. The spectrum scope was set in the range of 4000–400 cm^{-1} with the resolution factor 1.00 cm^{-1}. To get gas production per mass samples, the mass of samples was divided.

3. Results and discussion

3.1. Structure of components

Fig. 2 shows overlaid FTIR spectra of orange peel, tissue paper and PVC. Several characteristic peaks of orange peel can be observed, such as 3387 cm^{-1} (OH), 2931 cm^{-1} (CH of methylene), 1646 cm^{-1} (O—H of adsorbed water), and 1019 cm^{-1} (C—O). The most intense band in the high energy zone (3000–3600 cm^{-1}) is assigned to the existence of free and intermolecular bonded hydroxyl groups, related to a large amount of OH groups from carbohydrates and those of lignin, as well as to the symmetric and asymmetric stretching vibrations associated with H_2O molecules

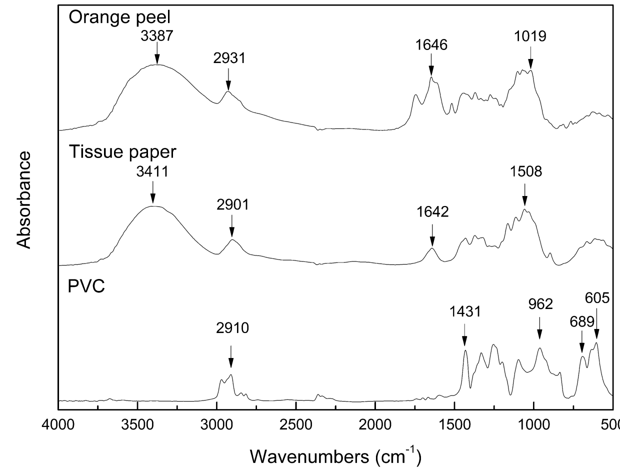

Fig. 2. FTIR spectrum of three samples.

[17]. The obvious peaks of tissue paper include 3411 cm^{-1} (OH), 2901 cm^{-1} (CH of methylene), 1642 cm^{-1} (O—H of adsorbed water), and 1058 cm^{-1} (C—O). For PVC, these peaks are found at 2910 cm^{-1} (CH of methylene), 1431 cm^{-1} (CH_2), 962 cm^{-1} (CH_2), 689 cm^{-1} (C—Cl), and 605 cm^{-1} (C—Cl).

3.2. Pyrolysis of single component

3.2.1. TG characteristics of component

The TG and derivative thermogravimetric (DTG) curves of orange peel, tissue paper and PVC are shown in Fig. 3. Orange peel began to lose weight very early (~100 °C), and the residue was highest. From the DTG curve, orange peel had two main peaks at 226 and 333 °C, respectively, which was also reported by Lopez-Velazquez et al. [17], but the intensity of peaks was not strong. Tissue paper had a small quantity of residue after pyrolysis, which was consistent with the fixed carbon and ash content in Table 1. Tissue paper had only one main peak at 353 °C. The main composition of tissue paper is cellulose. It has been reported that the peak of cellulose at the same condition was in the range of 341–354 °C [18,19], and the peak of tissue paper was in this range. The decompose of PVC could be divided into three steps, the first step was from 250 to 325 °C, which was also the main mass loss range, the second step was from 325 to 375 °C, and the last step was from 375 to 525 °C. The maximum peak of PVC was at 286 °C.

3.2.2. FTIR analysis of single component

According to the widely applied Lambert–Beer law, the absorbance at a specific wavenumber is linearly dependent on gas concentration. Thus the variation of absorbance in the whole process can reflect the tendency of product yield of the gas species [19,20]. In the FTIR plots for all three samples, the percent transmittance as a function of temperature is shown for the wavenumbers of 2384 cm^{-1}, 2180 cm^{-1}, 2917 cm^{-1}, 908 cm^{-1}, 1747 cm^{-1}, 1182 cm^{-1}, 2727 cm^{-1}, and 3085 cm^{-1} that correspond to the absorption by CO_2, CO, alkyls, alkenes, carbonyls, carboxyls, HCl, and benzene, respectively. Because of the complexity of H_2O spectrum, the peak of H_2O is not characterized.

As shown in Fig. 4(a), the gas products of orange peel pyrolysis at DTG peak temperature included CO_2, H_2O, alkyls, carboxyls, and HCN. As shown in Fig. 4(b), CO_2 and carbonyls had similar release patterns, which had two peaks, as shown by DTG curve in Fig. 3(b). While alkenes had the peak at approximate 500 °C, due to secondary reactions. The generation of alkyls had two peaks, the first peak was at approximate 225 °C, and the second peak was at 450–500 °C. The main components of orange peel include pectin,

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