Waste Management xxx (2018) xxx–xxx

Contents lists available at ScienceDirect

Waste Management

journal homepage: www.elsevier.com/locate/wasman

Effect of chemical pretreatment on pyrolysis of non-metallic fraction recycled from waste printed circuit boards

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A R T I C L E I N F O

Article history:
Received 31 August 2017
Revised 13 February 2018
Accepted 15 February 2018
Available online xxxx

Keywords:
Non-metallic fraction
Waste printed circuit boards
Pyrolysis
Chemical pretreatment
Char characterization

A B S T R A C T

The non-metallic fraction from waste printed circuit boards (NMF-WPCB) generally consists of plastics with high content of Br, glass fibers and metals (e.g. Cu), which are normally difficult to dispose. This work aims to study the chemical pretreatments by using alkalis, acids and alkali-earth-metal salts on pyrolysis of NMF-WPCB. Char (60–79%) and volatile matter (21–40%) can be produced via the pyrolysis process. In particular, the ash content can reach up to 42–56%, which was attributed to the high content of glass fibers and other minerals. Copper (Cu, 2.5%), calcium (Ca, 28.7%), and aluminum (Al, 6.9%) were the main metal constituents. Meanwhile, silicon (Si, 28.3%) and bromine (Br, 26.4%) were the predominant non-metallic constituents. The heavy metals such as Cu were significantly reduced by 92.4% with the acid (i.e. HCl) pretreatment. It has been proved that the organic Br in the plastics (e.g. BFR) can be transformed into HBr via the pyrolysis process at relatively high temperature. It was noteworthy that the alkali pretreatment was more benefit for the Br fixation in the solid char. Particularly, the Br fixation efficiency can reach up to 53.6% by the sodium hydroxide (NaOH) pretreatment with the pyrolysis process. The formed HBr can react with NaOH to generate NaBr.

1. Introduction

Printed circuit boards (PCB) are the integral component of any electronic equipment (Ghosh et al., 2015). Their basic structures are the copper-clad laminate consisting of glass-reinforced epoxy resin and a number of metallic materials including precious metals (Ghosh et al., 2015; Zhang et al., 2017a). Waste PCB (WPCB) are known as one of the largest amounts of E-wastes (Cucchiella et al., 2015). However, WPCB with rich resources are referred to as “urban mines” (Zhan and Xu, 2016). In general, WPCB contain two parts of metal fractions (MF) and non-metallic fractions (NMF). The MF account for nearly 30 wt% in WPCB, mainly including Cu, Sn, Fe, Ni, and Zn (Chen et al., 2013; Rubin et al., 2014). Additionally, various precious metals such as Au, Ag, and Pb (Chehade et al. 2012) could be used as contact materials or plating layers because of their conductivity and chemical stability present in WPCB (Chen et al., 2013). Up to now, many researches have been conducted to recover and reuse the valuable materials of E-waste. Most of researchers focus on the recycle of MF (Li and Xu, 2010; Ma et al., 2012; Xue et al., 2012; Zhan and Xu, 2009; Wang et al., 2017), because the recovery of metals brings resource-efficient economy. The disposal of NMF taking up 70 wt% of WPCB has drawn more and more attention (Zhang et al., 2017a). However, the recycle of NMF-WPCB is a difficult process (Duan et al., 2016), because it still consists of toxic heavy metals, brominated flame retardants (BFRs), glass, plastics and other hazardous substances (Zhang et al., 2017a; Zhang et al., 2017b). In the past, the NMF-WPCB had been commonly disposed by combustion or landfill (Rocchetti et al., 2018). Combustion of the NMF-WPCB can produce toxic polybrominated dibenzodioxins and dibenzofurans (PBDD/Fs), while the landfill leads to the pollution of groundwater due to BFRs and heavy metals (Guo and Xu, 2009; Xiao et al., 2017; Soler et al., 2018). In addition, the pyrolysis process can reduce the secondary environmental pollution caused by the combustion process. Pyrolysis as an efficient waste valorization method can not only recycle all the valuable metals, but also deal with organic matters in WPCB (Moltó, et al., 2009; Yamane, et al., 2011). The products of liquid and solid from pyrolysis of WCPCB could be used as industrial materials, fuels and carbons materials with the aim of fulfilling the better resources utilization of the NMF-WPCB.

So far, the effect of the chemical pretreatment on pyrolysis of NMF-WPCB has been rarely reported (Yousef et al., 2017). In this work, the NMF-WPCB was pretreated by acid, alkali and alkali-earth-metal salts prior to the pyrolysis process. Therefore, the

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https://doi.org/10.1016/j.wasman.2018.02.036
0956-053X/

Please cite this article in press as: Shen, Y. Effect of chemical pretreatment on pyrolysis of non-metallic fraction recycled from waste printed circuit boards. Waste Management (2018), https://doi.org/10.1016/j.wasman.2018.02.036

physicochemical properties of pyrolysis char were characterized to assess the effects of chemical pretreatment on disposal of the NMF-WPCB environmentally friendly.

2. Materials and methods

2.1. Raw feedstocks

The feedstock of the NMF-WPCB was collected from a WEEE disposal company in Changzhou, China. The raw feedstock was initially ground and sieved to obtain the solid particles with uniform sizes (<0.07 mm). The properties of the NMF-WPCB are shown Table 1. It could be found that raw feedstock are mainly composed of volatile matter (25.67 wt%), fixed carbon (21.29 wt%) and ash with high-content (53.24 wt%). Carbon (C) is about 19.83 wt%. And hydrogen (H) and nitrogen (N) are about 2.53 wt%. In addition, chemical constitutes mainly include metals (e.g. Al, Cu, Ca, Sn) and bromine (Br). These results were consistent with the reported works (de Marco et al., 2008; Tatariants et al., 2018). The high-content of Br (26 wt%) was attributed to the presence of BFRs plastics in the NMF-PCB.

2.2. Experimental procedure

2.2.1. Chemical pretreatment

Raw feedstock (10 g) of the NMF-WPCB powder was initially pretreated by chemical reagents (i.e. KOH, NaOH, K_2CO_3, Na_2CO_3, HCl), respectively. The mass ratio of raw feedstock and chemicals was about 5–1. Then, the solid mixture was fed into the distilled water (300 ml) and stirred for 2 h. Furthermore, all of the mixtures were dried in an oven at 105 °C for 10 h. Finally, the pretreated feedstocks could be dry stored and used for the further pyrolysis process (as illustrated in Fig. 1).

2.2.2. Pyrolysis process

The pyrolysis process was conducted in a fixed-bed reactor (dimension: length 1.0 m × inner width 0.1 m) as illustrated in Fig. 1, mainly including a pyrolysis furnace, an electrical controller, a cooling system, a liquid collector and a gas collection system. The dry feedstock (5 g) was initially fed into the furnace. Before heating, nitrogen (N_2) was continuously led into the reactor with a flow rate of 0.5 L/min to blow away the air. The final temperature was controlled at 500 °C (the heating rate: 50 °C/min) with a retention time of 1 h to ensure the complete pyrolysis. After the whole experiment finished, the pyrolysis products of char, oil and gas could be collected, respectively.

2.3. Analytical methods

The proximate analysis was performed by the thermogravimetric analysis (*TGA-4000, PerkinElmer, USA*) and the ultimate analysis was conducted by an elemental analyzer (*EA, VARIO EL III, Element, Germany*). The chemical constitutes were determined by using an X-ray fluorescence (*XRF, Olympus Innovex X-5000, Canada*). The organic functional groups on the surfaces were characterized by using a fourier transform infrared spectrometer (*FT-IR, IS5, Japan*). The surface microstructures were analyzed by using a scanning electron microscope (*SEM, SU1510, Hitachi, Japan*). The crystal structures were characterized by the X-ray diffraction analysis (*XRD-6100, Shimadzu, Japan*). The X-ray diffraction (XRD) pattern was obtained at 20–60 kV and 2–80 mA, using the Cu Kα radiation (λ = 0.154 nm), in range of 10–80° (2θ) with a step width of 0.002°.

3. Results and discussion

3.1. TGA analysis

The thermal stability of raw feedstock was indispensable for pyrolysis process. Fig. 2 shows the TG and DTG curves. The thermal decomposition can be divided into three stages of <300 °C, 300–450 °C, and 400–800 °C, respectively. It can be found that the mass loss in stage I was not remarkable compared with the other two stages. It may be caused by water evaporation and trace amount of organics decomposition. In the stage II, it can be found that weight of the feedstock decreased significantly by 25%, corresponding to the DTG curve with the mass loss peak at 300 to 450 °C, which can be attributed to the decomposition of volatile matter (reported as a lower molecular weight aliphatic hydrocarbons and aromatic hydrocarbons) (Grause et al., 2008). As shown in Fig. 2, it can be found that it has only one peak in the temperature range from 300 to 450 °C. Obviously, the volatile matter appears in the temperature range of 300 to 450 °C (similar to HBr), which is consistent with the results in the reported work (Hadi et al., 2015). In the stage III, the tendency of weight loss became slow in the temperature range of 450–800 °C. It suggests that nearly 72% of the solid residue was not decomposed by the complete pyrolysis process, which might be attributed to a large amount of inorganic matters (e.g. glass, Ca, Cu).

In general, the products from the pyrolysis of the dry-based feedstock are composed of volatile matter, fixed carbon and ash. As shown in Fig. S1, the contents of volatile matter, fixed carbon and ash changed after chemical pretreatment. For instance, the ash content increased slightly by the alkali pretreatment, while it decreased by the acid or alkali-earth-metal salt pretreatment (e.g. K_2CO_3, ~20%). It shows that the appropriate chemical pretreatment could also improve the properties of NMF-WPCB as a fuel by increasing the volatile matter and decreasing the ash content.

3.2. Characteristics of the pyrolysis char

3.2.1. Elemental analysis

The elements of feedstocks and the pyrolysis chars are shown in Table S1. It is found that the contents of C and H were significantly reduced after the pyrolysis process, which was caused by the decomposition of organics (e.g. plastics). Meanwhile, the nitrogen

Table 1
Proximate analysis, ultimate analysis and chemical constitutes of the raw feedstocks.

Proximate analysis (wt.%, dry-basis)			Ultimate analysis (wt.%, dry-basis)					
Volatile	Fixed carbon^a	Ash	C	H	N	O^b	H/C	O/C
25.47	21.29	53.24	19.83	1.84	0.69	77.64	1.12	3.91
Chemical constitutes (wt.%)								
Al	Ba	Br	Ca	Cr	Cu	Fe	I	K
6.8623	0.7904	26.4331	28.6569	0.0868	2.5084	0.9528	0.2478	0.2405
Mg	Na	P	Pb	S	Si	Sn	Sr	Ti
0.2925	2.3573	0.0815	0.3535	0.1476	28.2566	0.5384	0.6895	0.504

Note: [Fixed-carbon]^a = 100 − [volatiles] − [ash]; [O]^b = 100 − [C] − [H] − [N].