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The products characteristics of calcium-basic compounds pyrolysis with waste printed circuit boards (PCB)

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Abstract

The co-pyrolysis of PCB and calcium-basic compounds was investigated in this paper. The yield of liquid products of simple PCB pyrolysis was the highest and it reached 10.51%. After adding various calcium based waste, the copper foil was basically not corroded during pyrolysis as the calcium based waste adsorbed HBr. After pyrolysis, the organic substances were carbonized and became brittle. Thus, it was quite easy to separate metal from glass fiber cloth and strip off and remove the carbon black on the glass cloth. The Pyro-gas wasn't so seriously influenced by additives. The content of CH_4 was 67-70% while other contents were mainly small molecules such as C_2H_6, C_2H_4, C_3H_8, and C_3H_6.

Keywords: WEEE; PCB; pyrolysis; recycling; calcium-basic waste

1. Introduction

Waste Electrical and Electronic Equipment (WEEE) is increasing at a rate three times that of average municipal waste and posed to be a significant contributor to future environmental contamination. The increase in disposal of WEEE is associated with the increase in use of electronic and electrical equipment, the frequent upgrading of equipment and, in some cases, the relatively high cost of repair compared to the purchase of new equipment.

PCB is the important part in WEEE. The basic material of PCB is glass-fibre polymer sheet moulding compound (SMC), which is thermoset composite material. Thermoset polymers have been traditionally considered to be non-recyclable plastic materials, as they are not fusible and therefore cannot be

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remoulded into other shapes. While the organic part in PCB is mainly thermoplastic with contents of flame-retardants. Additionally, thermoplastics contain flame retardants like bromide and antimony [1]. The inorganic part mainly includes metals and ceramics [2]. It usually contains a variety of metals such as Cu, Fe, Pb, Zn, and noble metals like Au, Ag, Pt, Pd and even rare elements such as Ta. The distribution of these two material groups in different PCB varies.

The high Br (Brominated Flame Retardants, BFR) contents in PCB not only are the major emission source of PBDD/Fs [4], but also release acid gas (HBr) as well as brominates that corrodes equipment under thermal treatment. As calorific value of PCBs calorific value is very low, and even worse it can produce Dioxin (PCDD) or Furan (PBDD) when burning, consequently incineration is not an appropriate method for disposal of this type of wastes. Pyrolysis can be considered as an alternative method of recycling PCBs, in the pyrolysis process (heating without oxygen), the organic part of the PCBs is decomposed to low molecular weight products, liquids or gases, which can be useful as fuel or chemical source, and the PCBs itself changes brittle, delamination, easily for crushing, while the inorganic such as glass-fibre keep fairly intensity can be recycled into other composites or any other plastic materials.

The pyrolysis process is not new; it has been applied over the years to carbonaceous materials such as coal or biomass. At present it is being considered as a non-conventional method of recycling of polymeric materials. However, there is little published information about pyrolysis of SMC, even less to offer guidance for the possibilities of recovery of PCBs.

The pyro-oil could not be directly used because it contains Br such as brominated phenols [3]. Numerous studies show that [5-7] during the pyrolysis of PCB, Br is distributed in all three phase products, which undoubtedly increases the difficulty to reuse it. So the paper devotes to add calcium-basic waste to investigate the product change for easy PCB recycling.

2. Materials and Methods

PCB used in this study was heterogeneous and came from obsolete PCs. Also the as-received samples were reshredded by a laboratory hammermill to homogenize the samples and were subsequently riffled. PCB is crushed to about 5.0 cm × 5.0 cm (Fig 1.) and the ultimate and proximate results were shown in table 1. In a typical run 20g PCB and 10g calcium-basic additive is used. The calcium-basic additive used in the experiment is form calcium wastes (Fig 2.)

Fig 1. PCB experimental material

Table 1. Ultimate analysis and proximate analysis of samples.

Ultimate analysis,%					Proximate analysis, %				
Cad	Had	Oad	Nad	St	Mad	Vad	Aad	FCad	Qb.ad/KJ.Kg-1
18.62	1.75	9.86	0.61	0.0472	0.28	27.47	68.83	3.42	9.8892×104

Note: M-moisture; V-volatile; A-ash; FC-fixed carbon

Fig 2. Calcium-basic wastes

Pyrolysis of PCB and calcium-basic waste was carried out in a tubular oven (Fig 3). A schematic diagram of experimental pyrolysis system was shown in Figure 4. A quartz tubular reactor (1.2 m in length and 0.06 m in diameter) was fixed in the oven; the oven was controlled by a programmable temperature controller. The carrier gas nitrogen metered with automated flow meter controllers and the rate is 1.5 L/min, was fed to the reactor to sweep the evolved products from the reaction zone and thereby prevented secondary reactions of the pyrolysis vapours. The sample was heated at 10 ˚C/min to the final temperature, and held for 30 min. The vapour passed a series of gas-liquid separators. Liquid was trapped in a glass at low temperature with ice/ water. The non-condensed gas passed through an active carbon tube and was collected by a gas bag. The main objective of the use of this simple degradation apparatus was to determine the qualitative composition of the pyrolysis reactor effluents, both gases and liquids.

Fig 3. Experimental equipment

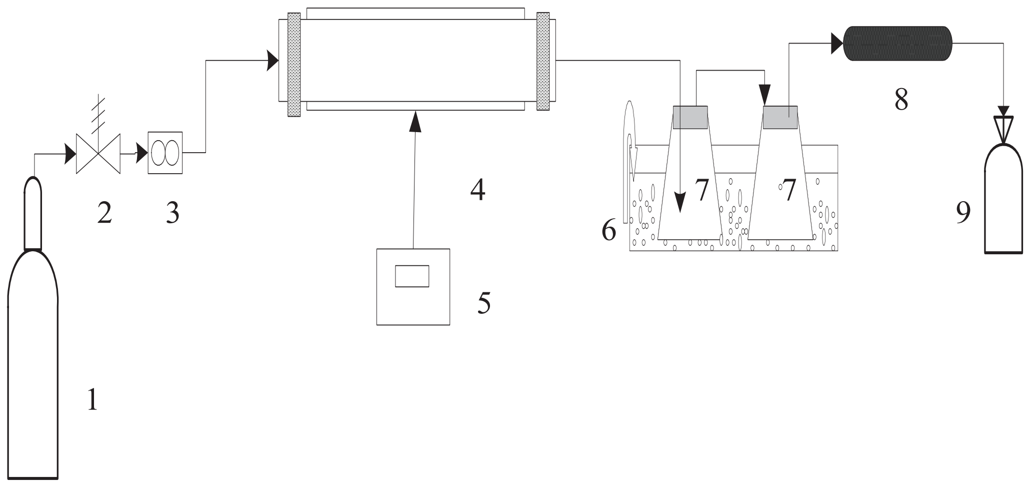

Figure 4. Experimental apparatus for pyrolysis.(1-nitrogen cylinder; 2-valve; 3-gas flow meter; 4-electric furnace; 5-temperature controller; 6-ice/water; 7-collecting flask; 8-active carbon tube; 9-gas bag)

3. Results and discussion

Solid and liquid pyrolysis yields were determined in each experiment by weighing the amount of each obtained, the pyro-gas calculated by difference. The experiment results were shown in table 2.

It was found in the experiment that the mass of condensed liquid in the first section was higher than the products in the second section and it reached 10.51%. After adding different calcium based waste, the yield rate declined in different degrees. It was also found in the experiment that the liquid product produced by sintering red mud and Bayer red mud was less than calcium carbide dust.

From the perspective of appearance, pyrolysis oil is similar to coal tar. It is a kind of black and organic liquid with water, strong smell of tar and high calorific value, the properties of which is just like those of crude oil. Hence, pyrolysis oil is usually used as power fuel. This is the simplest method that the pyrolysis oil is applied. If the valuable composition of pyrolysis oil can be made full use of, resuscitation utilizing of waste printed circuit board (PCB) and the economic benefit of pyrolysis technique can be effectively improved.

Sun Lu-shi [8] has studied that the major products from the thermal decomposition of the brominated part of the epoxy resin were mono-and di-brominated phenols and aromatic/aliphatic ethers containing one or two brominates atoms on the aliphatic chain, indicating that the cleavage of both the C-Br, C-C, N-NH2 and O-CH2 bonds takes place.

The copper foil emerging outside the solid residue of PCB after co-pyrolysis of plate-like circuit board and calcium based waste could be clearly seen (figure 5). Basically, the copper foil wasn't eroded during pyrolysis, as calcium based waste adsorbed HBr. The PCB after pyrolysis was carbonized and became brittle. Thus, it was quite easy to separate metal from glass fiber cloth. After stripping off and removing the carbon black on the glass cloth, the glass fiber cloth could be obtained. It was also founded that the powdered PCB was relatively more seriously bound with the reactor during pyrolysis and the coking was aroused. Therefore, it is inappropriate to use fixed-bed pyrolysis to recycle and process powdered PCB.

Table 2. The quantity containing of three co-pyrolysis liquid products of PCB by different conditions (PCB:X = 2:1).

sample	source	Quantity /g	The liquid quantity /g	Liquid /%
PCB:A	a	0.88	1.059	3.53
	b	0.18		
PCB: B	a	1.98	2.0575	6.86
	b	0.08		
PCB: C	a	2.39	2.615	8.72
	b	0.23		
PCB:D	a	1.77	1.9434	6.48
	b	0.17		
PCB	a	1.44	2.1026	10.51
	b	0.67		

A: sintered red mud; B: Bayer red mud; C: calcium carbide dust ;D: CaO; a:The first section of condensing; b: the second section of condensing

Figure 5. The co-pyrolysis solid residues of PCB in a tube furnace.

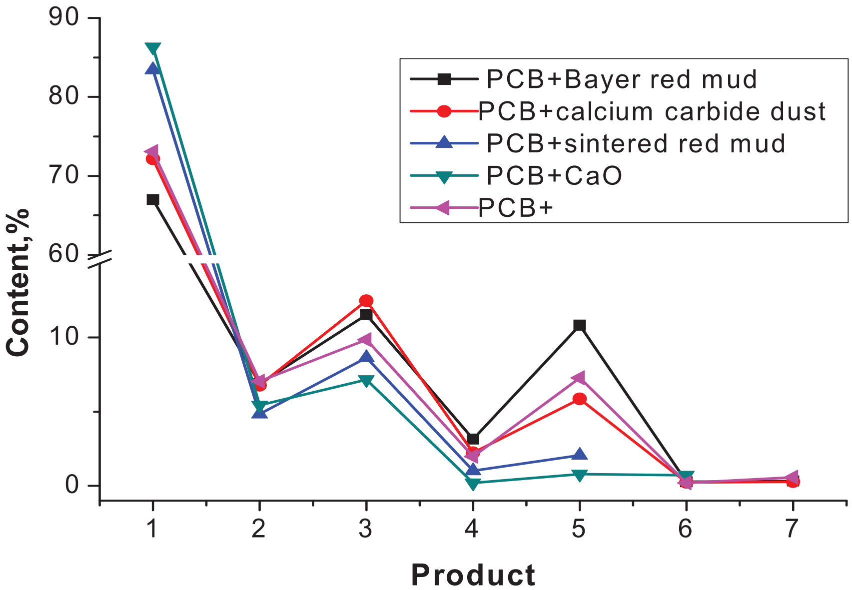

Figure 6.The pyrolytic-gas analysis by GC（PCB:X=2:1）（1-CH42-C2H6；3-C2H4；4-C3H8；5-C3H6；6-C4H10；7-C4H）

It could be seen from the yield rate that the solid products accounted for 70.14% during the pyrolysis of simple PCB (Table 3.). The proportion of solid products would be higher no matter what kind of calcium based waste was added. Perhaps both of them adsorbed volatile matters especially Br and reacted with it. In this case, the percentage of solid products rose by 8% - 9%. Meanwhile, as for Bayer red mud, the proportion of solid products increased by 7.5% or so, while that the solid products of sintering red mud accounted for a proportion with the range from 72.73% to 75.38%.

Table 3. The co-pyrolysis productivity of solid products of PCB Mixing of different additives with different ratios (PCB:X = 2:1).

sample	Solid product/%	sample	Solid product/%
PCB: A	72.7306	PCB:C	78.0667
PCB: B	77.6325	PCB:D	84.3872
PCB	70.1369	-	-

A: sintered red mud; B: Bayer red mud; C: calcium carbide dust; D:CaO

It is mainly low molecular alkanes and olefin, which is similar to other research result [4]. The composition and yield is basically the same under different reaction conditions (Figure 3). The content of CH4 was 67-70% while other contents were mainly small molecules such as C_2H_6, C_2H_4, C_3H_8, and C_3H_6. The pyrolytic gas have fairly high calorific value from the composition, which could serve as a heating gas to make the pyrolysis process self- sustained.

4. Conclusions

The yield of liquid products of simple PCB pyrolysis was the highest and it reached 10.51% or so. After adding various calcium based waste, the yield rate declined at different degrees. Meanwhile, the burnt black pyrolysis oil with similar properties of crude oil could also be processed, considering developing the function of high calorific value. From the perspective of the solid waste residues of circuit board after co-pyrolysis of PCB and calcium based waste, the copper foil was basically not corroded during pyrolysis as the calcium based waste adsorbed HBr. After pyrolysis, the organic substances were carbonized and became brittle. Thus, it was quite easy to separate metal from glass fiber cloth and strip off and remove the carbon black on the glass cloth. The pyro-gas wasn't so seriously influenced by additives. The content of CH_4 was 67% -70% while other contents were mainly small molecules such as C_2H_6, C_2H_4, C_3H_8, and C_3H_6.

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