STUDY ON LOW-TEMPERATURE PYROLYSIS OF LARGE-SIZE PRINTED CIRCUIT BOARDS

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ABSTRACT

A pyrolysis experiment of FR4-type Printed Circuit Board (PCB) was conducted in a fixed-bed experimental apparatus with lower pyrolysis temperature (500°C) and large-size PCB sample (16-20cm²). The properties of pyrolytic gas and tar were compared to the pyrolysis results of a high temperature (800°C) and small-size PCB (1.5-2cm² or powder). Endothermic heat of PCB pyrolysis reaction was calculated based on the experimental data collected. The results showed that: (1) PCB pyrolysis produced 10.17wt% of gas, 18.23wt% of tar and 71.60wt% of solid particle. (2) Similar to previous studies, CO, CO₂, and 2-methyl propene were the main components in pyrolysis gas and the pyrolysis tar consisted of phenol and alkyl aromatics. However, the propylene, bromomethane, and bromine content of this pyrolysis gas study were significantly different. (3) It was easier in this experiment to separate the metals and fibre glass compared to the regular pyrolysis with a crushed PCB and a final temperature of 800°C. (4) The endothermic heat of PCB pyrolysis is about 19.692MJ/kg, the calorific capacity of pyrolytic gas produced by one kilogram of PCB is about 2.386MJ, and is 4.502MJ for tar. The overall calorific capacity of pyrolytic gas and tar accounts for 35% of required pyrolysis heat.

INTRODUCTION

Fast development of electronic technology and new technological innovations has lead to an increase of waste printed circuit boards (PCB) worldwide (Lee et al., 2007). PCB usually contains fiberglass reinforced resins, flame retardants and metals. The purity of precious metals in PCB is about 10 times more than that of rich ores (Li et al., 2008). Recycling of rare metals in PCB like gold, or nickel can bring commercial profit. However, considering environmental protection and business sustainability, the simple recycling processes currently in practice are usually unacceptable due to the brominated flame-retardants and heavy metals in PCB, which can produce secondary pollution.

It has been proven that pyrolysis is a possible way to dispose of waste PCBs, in which the organic resin is converted to flammable gases and tar, which is then used as fuel for the process itself. The fibreglass and metals then remain as residue of the pyrolytic reaction (Hall & Williams, 2007). The advantage of pyrolysis is that different components in PCB can be separated safely and all the useful materials can be reclaimed. Although a lot of research on the pyrolysis of waste PCB have been reported, most of them focused on thoroughly pyrolyzing the PCB, production analyses of organic resins (Vasile et al., 2007; Hall & Williams, 2006; Chien et al., 2000) in PCB, as well as debromination methods [Hornung et al., 2003; Blazsó et al., 2002], while the fate of the metals in PCB...
were often overlooked. Moreover, these studies used crushed samples in the range of 1.5-2cm², for pyrolyzing with the final temperature usually up to 800°C, in order to fully decompose the organic components (Hall & Williams, 2007; Sun, 2004). The process therefore requires high mechanical energy for breaking down the PCB and high thermal energy for PCB pyrolysis.

In the current research, the focus was to use samples in the size range of 20cm² or larger, at a lower final pyrolysis temperature of around 500°C in order to reduce the process energy demand. In previous studies, the pyrolysis temperature zone of FR-4 PCB was 303.27~342.83°C at the rate of 10°C/min and 313.32~364.86°C at the rate of 20°C/min (Guo, 2008). The solid residue, especially metals and fibreglass were collected and analyzed with the SEM. The compositions of pyrolysis gas and tar were analyzed with GC-MS, FID-IR. The calorific capacities of pyrolysis gas and tar were calculated and measured as well. This process demonstrates simpler and more energy saving characteristics.

MATERIALS AND METHODS

Samples
The PCB experimental samples were provided by Yantat Printed Circuit Boards CO., LTD (Shen Zhen City). The substrate materials were fibreglass-reinforced epoxy-resin, brominated epoxy-resin flame retardant and a copper cladding laminate on top. The type of the sample is FR-4.

Experimental Devices
Fig.1 shows the experimental apparatus of pyrolysis, which is a horizontal cylinder fixed-bed reactor 120mm in length and 100mm in internal diameter. It was externally heated using a 4kW furnace, equipped with a programmable temperature controller. In order to acquire pyrolysis energy consumption information, a Watt-hour meter was used.

![Fig. 1: Schematic diagram of the experimental apparatus on pyrolysis](image)

1—temperature controlled furnace; 2—cylindrical pyrolysis reactor; 3—thermocouple; 4—temperature control system; 5—condenser; 6—pyrolysis tar collector; 7—gas bag; 8,9 — valve; 10—Watt-hour meter

Fig. 1: Schematic diagram of the experimental apparatus on pyrolysis

Pyrolysis products collection and analysis
The experiment procedures were as follows:
(1) A full size uncrushed FR4-PCB (weight of 60 gram) with size of app 20cm² was put into the reactor;

(2) The furnace temperature controller was programmed in two stages:
   The first stage: Temperature range: 30°C~500°C; time: 47min, leading to an end-
   temperature of 500°C at a heating rate of 10°C/min.
   The second stage: to be programmed to keep the furnace at a constant temperature
   of 500°C for 1 hour.

   The pyrolysis temperature zone for the FR4-type PCB was 300-500°C [Guo, 2008];
   the pyrolytic temperature and time used were considered to meet a compromise of
   proper degree of pyrolysis and low energy consumption.

(3) The reactor was sealed; valve 8 was closed and valve 9 was opened; nitrogen
   gas was blown into the reactor for 20 minutes to ensure an anaerobic pyrolysis
   environment; the initial Watt-hour meter reading P1 was recorded and the reactor
   was switched on.

(4) When the temperature reached the pyrolysis zone, according to the information
   from TG analysis [Guo, 2008], valve 9 was closed and valve 8 was opened to allow
   the pyrolysis gas to pass through, while the pyrolysis tar liquidized in the condenser
   and dripped into collector 6. After the system cooled and the program complete, we
   recorded Watt-hour meter reading P2, and the solid residue was taken out for analysis.

   Liquid and gas products were examined by GC-MS and FT-IR method. The GC-MS
   instrument was VG ZAB-HS fitted with a SE capillary column (50m×0.2mm×0.3µm),
   with high purity helium as the carrier gas, with a split ratio of 30:1, and 2ml injector.
   The injector temperature was 240°C. The mass spectrometer electron energy reading
   was 70eV with an emission current of 200µA. The ion source temperature was 200°C
   and scanning rate was 1 time per second, mass range was 20-350a.m.u and Nist atlas data
   base was for components identification. Solid product was analyzed by a PHILIPS
   XL30W/TMP SEM. The Calorific capacity of the pyrolysis gas was calculated
   according to the components individual calorific capacity and content. Pyrolysis tar was
   measured by an oxygen bomb calorimeter.

**Pyrolysis energy consumption**

The energy consumption of heating the reactor itself was measured by completing the
experiment without placing a sample inside. The actual energy consumption of the
pyrolysis includes the calorific capacity of PCB pyrolysis reaction and heat loss during
reaction. Therefore the required net endothermic value, ΔH, of PCB pyrolysis reaction is:

\[ \Delta H = \frac{(P_2 - P_1) - (p_2 - p_1)}{m} \]

where P1, P2 are the initial and the final readings of the Watt-hour meter in pyrolysis of
the PCB. p1, p2 are the initial and the final readings of the Watt-hour meter for heating
the empty reactor using the same programme. Here m is the weight of the sample.

**RESULTS AND DISCUSSIONS**

**Pyrolysis gas analysis**

The pyrolysis of FR4-type PCB produced 71.60wt% of solid residue, 18.32wt% of tar
and 10.71wt% of gas in this experiment. Fig.2 shows a chromatogram chart of the
gaseous product. The major compositions of it were CO (label 1 represented the
chromograph peak), CO\(_2\) (label 2), propylene (label 3), bromomethane (label 5). Also
significant amounts of 2-methylpronepene (label 4), bromoethane (label 7), dichloromethane (label 8), small amounts of acetone (label 6), a bit of bromocyclopopyl (label 10), bromopropane (label 9 and label 11 isomerism) were detected. This is similar to the studies reported in the literature (Hall & Williams, 2007; Sun, 2004), in which CO and CO\textsubscript{2} were the major contents, but C\textsubscript{1}~C\textsubscript{4} alkane, alkene or bromo-alkane consisted of the rest of the pyrolysis gas. Nevertheless, this is different to the studies reported by literature (Hall & Williams, 2007; Sun, 2004), where propylene and bromomethane were significant contents, as well having a high content of bromine in the pyrolysis gas. This is probably due to the component difference of the experiment samples, in which bromo-epoxy resin was one of the main compositions, and there were different additives for various reasons. Moreover, the difference in sample size may be another reason. We used uncrushed 16-20cm\textsuperscript{2} PCB, but the samples used in previous studies were crushed 1.5-2cm\textsuperscript{2} PCB.

According to component and content of the pyrolysis gas produced by 1 kg of PCB, the calorific capacity was about 2.386 MJ/kg (PCB). Thus using pyrolysis gas after debrominating to fuel the process itself is recommended for the PCB disposal.

**Pyrolysis tar products**

Pyrolysis tar consisted of 41.02wt% light tar, 44.04wt% heavy tar, and 8.30wt% water and 6.64wt% wax. The compositions of the light tar were analyzed by GC-MS method. Fig.3 shows a GC chart of light tar, in which 34 kinds of C\textsubscript{3}~C\textsubscript{17} organic compositions, with molecular weights between 58 and 240, were found. The main components of the light tar were acetone (label 1), phenol (label 2), 4-ethylphenol (label 3), 3-(1-methyl-ethyl)-phenol (label 4), pentamethylethylphenol (label 5). Also peaks between peaks 1 and 2 represented alkyl benzenes. Peaks between peaks 2 and 5 are characterized as alkyl phenols. The tar also contained residues of bromide. Only one bromide-containing compound was detected (peak 6 represent), which was 1-(3-bromo-4-hydroxyphenyl)-ethanone (molecular formula CsH\textsubscript{7}BrO\textsubscript{2}).

FT-IR analysis of the light tar and heavy tar is shown in Fig.4 (a) and Fig.4 (b), respectively, for details of pyrolytic tar. The similar spectrograms indicate that the main component of the heavy tar should be aromatics as well. In Fig.4 (a), the spectra for the large peak around 3600-3000cm\textsuperscript{-1}(around 3350cm\textsuperscript{-1} in Fig. 4(b)) that is associated with O-H stretches in phenols. The small peak at 3045cm\textsuperscript{-1}, 3090cm\textsuperscript{-1} (3069cm\textsuperscript{-1} and 3043cm\textsuperscript{-1} in Fig. 4(b)) can be associated with benzene ring C-H stretches, either in phenols or in other aromatic compounds. The peaks of 1597cm\textsuperscript{-1}, 1504cm\textsuperscript{-1}, 1471cm\textsuperscript{-1} (1601cm\textsuperscript{-1},
1508 cm\(^{-1}\), 1470 cm\(^{-1}\), 1361 cm\(^{-1}\) in Fig 4(b)) can be associated with aromatic C=C stretches. The peaks around 2000-1600 cm\(^{-1}\) (1940 cm\(^{-1}\), 1882 cm\(^{-1}\), 1837 cm\(^{-1}\), 1767 cm\(^{-1}\)) in Fig. 4(a) can be associated with frequency double of out-of-plane vibrations in benzene rings. The peaks between 1230-900 cm\(^{-1}\) (1231 cm\(^{-1}\), 1111 cm\(^{-1}\), 1071 cm\(^{-1}\), 1025 cm\(^{-1}\) in Fig 4(a); 1229 cm\(^{-1}\), 1176 cm\(^{-1}\), 1109 cm\(^{-1}\), 1072 cm\(^{-1}\) in Fig 4(b)) can be associated with in-plane bending vibration in benzene rings. The two peaks between 2962 cm\(^{-1}\) and 2870 cm\(^{-1}\) (2960 cm\(^{-1}\), 2869 cm\(^{-1}\)) in Fig 4(b)) can be associated with methyl groups and methylene groups. Strong absorption peaks around 1700 cm\(^{-1}\) (1709 cm\(^{-1}\) in Fig 4(b)) can be associated with carbonyl groups. Compared to the results in literature (Hall & Williams, 2007; Sun, 2004), the main contents of the tar were similar, which consisted of phenol and alkyl aromatics. The low calorific value was 27.183 MJ/kg for light tar and 29.240 MJ/kg for heavy tar, respectively, according to measurements with an oxygen bomb calorimeter. Both were lower than a typical 0# diesel low calorific value of 42.00 MJ/kg.

Solid products
The solid products consisted of metals, fibreglass, and residual ash from the organic resins. Fig. 5 (a) shows the photographs of the pyrolytic residue, in which one can tell the metals and fibreglass clearly by their different morphological features. It is easy to separate the metals and fibreglass manually after the pyrolysis. Fig. 5 (b) shows the
photos after they were separated. Fig. 5(c) shows the morphology of one of the original solid products of pyrolyzed PCBs, where drillings and thin copper wires are still in place. The low pyrolysis temperature results in tough fibreglass residue. This is helpful for fibreglass recycling.

![Residue of printing ink on the surface of the PCB became brittle and distributed on the surface of the metal sheet. Having removed the residue, the copper metal sheet was found to be quite clean. The SEM charts of the metal sheet were shown in Fig.6 (a) and (b). The gold-plated surface of the metal sheet of the PCB contains copper, gold, and nickel. Thus, the pure gold, and nickel from the metal sheet may be recovered in a future study. Elements of the flakes of fibreglass were also analyzed by SEM, as shown in Fig.6(c). Carbon from the residue of resins adhered to the fibreglass. Mole ratio of Si to Ca was 2:1; while it was 3:1 for Si to Al. SEM results of metal sheet are shown in Fig.6 (d). Carbon-oxygen compounds had to be removed from the metal sheet before being able to recover the pure copper.]

**Fig. 5: Photos of solid products**

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**Fig. 6: SEM results for solid products**
Pyrolysis Reaction Energy Balance Analysis

PCB disposal via pyrolysis, the producing gas and tar are usually used as fuel to supply part of the energy needed for pyrolysis. Therefore energy balance analysis is necessary. According to experiments and data calculated, it is estimated that the endothermic value of PCB pyrolysis is about 19.69MJ/kg. The calorific capacity of pyrolysis gas and tar, according to calculation and measurement, are 2.39MJ/kg (PCB) and 4.50MJ/kg (PCB), respectively. Therefore it balances 35% of required energy for the pyrolysis; additional heat source will be needed.

CONCLUSIONS

Large-size FR-4 PCB was pyrolysed in a fixed-bed reactor at 500°C for about 1 hour. The pyrolysis products consisted of 72.76 wt% of solid residue, 8.33 wt% of tar and 18.91 wt% of gas.
The pyrolysis gases consisted mainly of CO, CO$_2$, propylene, bromomethane. Significant amounts of 2-methylpropene, bromoethane dichloromethane, small amounts of acetone, and trace amount of bromocyclopopyl and bromopropane were found in the gaseous products. Aromatic compounds were the main compositions of the pyrolysis tar, which contained high concentrations of phenol, acetone, ethylphenol, 3-(1-methyl-ethyl)-phenol, pentamethylethylphenol. Oxygen-containing organic groups were found in these compounds. Low concentrations of bromine containing compounds were detected.
The pyrolysis solid residue contained metals, fibreglass, and organic materials. Metals and fibreglass were easy to separate via manual operation. Copper was the main component in metal scraps, and small amounts of more valuable metals such as gold and nickel could be recovered. The surface of the fibreglass was covered in carbon elements. Compared to the results with crushed small-sized samples at the final pyrolysis temperature of 800°C in the earlier studies, similarly it was CO and CO$_2$ that were the main component in the pyrolysis gas; and the pyrolysis tar consisted of phenol and alkyl aromatics. The differences were that there was more bromine stay in the gas, and only a little in the tar; the metallic scraps and the fibreglass was easier to separate and recycle.
The endothermic value of PCB pyrolysis reaction is about 19.692MJ/kg. The total calorific capacity gotten from pyrolysis products accounts for 35% of required reaction heat, so additional heat source will be required.

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