Journal of Hazardous Materials 264 (2014) 545–551

Contents lists available at ScienceDirect

Journal of Hazardous Materials

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

Exhaust constituent emission factors of printed circuit board pyrolysis processes and its exhaust control

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HIGHLIGHTS

- Recycling of waste printed circuit boards is an important issue.
- Pyrolysis is an emerging technology for PCB treatment.
- Emission factors of VOCs are determined for PCB pyrolysis exhaust.
- Iron-Al_2O_3 catalyst was employed for the exhaust control.

ARTICLE INFO

Article history:
Received 26 May 2013
Received in revised form
18 September 2013
Accepted 22 October 2013
Available online 30 October 2013

Keywords:
Waste printed circuit board (WPCB)
Pyrolysis
Volatile organic compounds
Iron impregnated Al_2O_3

ABSTRACT

The printed circuit board (PCB) is an important part of electrical and electronic equipment, and its disposal and the recovery of useful materials from waste PCBs (WPCBs) are key issues for waste electrical and electronic equipment. Waste PCB compositions and their pyrolysis characteristics were analyzed in this study. In addition, the volatile organic compound (VOC) exhaust was controlled by an iron-impregnated alumina oxide catalyst. Results indicated that carbon and oxygen were the dominant components (hundreds mg/g) of the raw materials, and other elements such as nitrogen, bromine, and copper were several decades mg/g. Exhaust constituents of CO, H_2, CH_4, CO_2, and NOx, were 60–115, 0.4–4.0, 1.1–10, 30–95, and 0–0.7 mg/g, corresponding to temperatures ranging from 200 to 500 °C. When the pyrolysis temperature was lower than 300 °C, aromatics and paraffins were the major species, contributing 90% of ozone precursor VOCs, and an increase in the pyrolysis temperature corresponded to a decrease in the fraction of aromatic emission factors. Methanol, ethylacetate, acetone, dichloromethane, tetrachloromethane and acrylonitrile were the main species of oxygenated and chlorinated VOCs. The emission factors of some brominated compounds, i.e., bromoform, bromophenol, and dibromophenol, were higher at temperatures over 400 °C. When VOC exhaust was flowed through the bed of Fe-impregnated Al_2O_3, the emission of ozone precursor VOCs could be reduced by 70–80%.

1. Introduction

Due to rapid economic growth and urbanization, the demand for and sale of new electrical and electronic equipment are increasing rapidly. Consequently, the ever-increasing quantity of waste electrical and electronic equipment (WEEE) has become a serious threat to the environment. Waste printed circuit boards (WPCBs) come primarily from electrical and electronic equipment such as computers, mobile phones and televisions. The United Nations Environment Program (UNEP) reported that e-waste could total as much as 40–60 million tons every year [1,2], with a 5–10% annual increase predicted, and PCBs account for approximately 3% of total e-wastes [3]. Generally, there are two main types of PCBs in WEEE: paper-based phenolic resin PCBs and fiberglass-based epoxy PCBs. Fiberglass-based epoxy PCBs are made of epoxy, glass fiber and other additives such as brominated flame retardants, accounting for about 70% of PCBs, while the remaining 30% comprises metals such as copper, tin, lead, iron, nickel and noble metals (gold, silver and palladium are also present in small quantities) [4]. The European Commission (EC) directive, 2002/96/EC, on WEEE became law in the UK in January 2007, setting targets to recover up to 80% of all WEEE generated. Therefore, the development of recycling technology is critical for PCB applications.

Many methods, including physical and magnetic separation (crushing, grinding, separation by magnetic and eddy-current and vacuum process), smelting, scraping, hydrothermal and pyrolysis technologies, are used to recycle PCBs [5–11]. Pyrolysis is an emerging method to recover useful products from WEEE, including

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http://dx.doi.org/10.1016/j.jhazmat.2013.10.049

precious metals, carbon, fuel and chemicals. However, some contaminated constituents, including crude oil, exhaust gas and residues, can be released during pyrolysis procedures. Therefore, an understanding of pyrolytic and derived pollutant characteristics is critical to the recycling and disposal of PCBs.

Most of the work investigating pyrolysis of WPCBs has concentrated on the compositions of the organic products obtained [12–17], pyrolytic kinetics [14,18–20], and brominated compound formation and fate [18,21]. A significant amount of research into the pyrolysis of WPCBs has been reported, most of which has been carried out under nitrogen atmosphere using analytical pyrolysis techniques or laboratory-scale reactors [12,21,22]. Results indicate that low-temperature (180–390 °C) processes could recycle the materials of WPCBs [6,23]. However, few studies have focused on the exhaust constituents during WPCB pyrolysis or on VOC exhaust control. Generally, some noble metals such as platinum and palladium and metal oxides such as chromium oxide, cobalt oxide and copper oxide/manganese oxide were employed as catalysts to oxidize the VOCs [24,25]. However, as most of them are expensive, an Al_2O_3 supported-iron catalyst was selected for the deconstruction of VOCs during WPCB pyrolysis.

The element composition of WPCB raw material and emission factors of pyrolytic mass distribution, residue constituents, and the exhaust from this process were determined in this study. Furthermore, the pyrolytic kinetics of WPCB were studied using a thermogravimetric (TG) analyzer to understand the thermal characteristics of WPCB. These data could be useful for the development of recycling processes and an air pollution control system for WPCB reuse by a pyrolysis process.

2. Experimental

2.1. Material

Fiberglass-based epoxy PCBs were obtained from scrap computers in a recycling plant in Taiwan and ground into 4.5 ± 0.3 mm pieces in the laboratory. The WPCB samples were stored in a desiccator at 25 °C and 45% relative humidity until analyzed.

Pure nitrogen (99.995%) was purged in a tube (an electrical furnace quartz tube (I.D. 30 mm and length 70 cm) for 10 min before the pyrolysis process to reduce the oxygen content. Five grams of WPCB were placed in the center of the electrical furnace under nitrogen atmosphere, and the WPCB samples were pyrolyzed for 30 min at temperatures ranging from 200 to 500 °C. Pyrolytic liquid and exhaust gas were collected, maintained at 200 °C, and then allowed to flow into a series of four glass bottles in an ice-bath cooler (less than 4 °C) to yield condensable products. The first two bottles were used to collect the liquid product, and the other two were used to ensure that the liquid was completely collected. Exhaust gas was collected in a 3-l glass bottle, and the temperature was maintained at about 200 °C to reduce the effect of exhaust condensation during the pyrolysis processes.

2.2. Pyrolysis kinetics

A computer-controlled TG system (thermobalance) that can record temperature and weight (Cahn VersaTherm TGA, Thermo Fisher Scientific, USA) was used to measure the WPCB pyrolysis. The data showing sample weight variation by temperature were used to measure the pyrolysis kinetic parameters. Heating rates of 5 °C/min were applied to samples weighing about 10 mg. Pure nitrogen (99.995%) was used as the purge gas.

The following equations of kinetics expression in Arrhenius form were derived for the WPCB conversion rate [26]:

$$\frac{d\theta}{dt} = A \cdot \exp\left(-\frac{E_a}{RT}\right) \cdot (1-\theta)^n \quad (1)$$

The natural logarithm of Eq. (1) is taken to obtain

$$\ln\left(\frac{d\theta}{dt}\right) = \ln[A \cdot (1-\theta)^n] - \frac{E_a}{RT} \quad (2a)$$

Furthermore, Eq. (2a) can be expressed as follows:

$$\ln\left(\frac{d\theta}{dt}\right) + \frac{E_a}{RT} = \ln(A) + n\ln(1-\theta) \quad (2b)$$

where θ = transformation rate ($\theta = (m_0 - m)/(m_0 - m_f)$), m_0 (g) = weight of WPCB at $t = 0$; m (g) = residual weight of WPCB after pyrolysis at $t = t$; m_f (g) = weight of WPCB residue at $t = \infty$; t = pyrolysis time (min); A = frequency factor (min^{-1}); E_a = activation energy (kcal/mol); R = gas constant; T = absolute temperature (K); and n = apparent reaction order.

2.3. Catalyst preparation

Al_2O_3 (Versal 250 from La Roche Chemicals, USA) was selected to support the Fe catalyst. The $Fe(NO_3)_3{\cdot}9H_2O$ aqueous solution immersed with Al_2O_3 particles and Fe load was adjusted to a normal 5% (w/w). The $Fe(NO_3)_3$ solution immersed Al_2O_3 particles were put into the electric furnace, dried at 105 °C in air for 24 h and then calcined at 600 °C for 6 h.

Catalysts were loaded in a U-shaped quartz reactor (18 mm O.D., 16 mm I.D.) after being reduced in a hydrogen atmosphere at a heating rate of 10 °C/min up to 600 °C, held for 1 h, and then cooled to the temperature of the reactor, 300 °C, for catalytic reaction. The pyrolysis exhaust (100 mL/min) of WPCB was fed into a reactor containing the Fe-Al_2O_3 catalyst at a flow rate of 100 mL/min. The catalyst-containing reactor was heated by an electrical furnace, and the temperature was maintained at 300 °C.

2.4. Chemical analysis

2.4.1. Element constituents

The surface composition of the pyrolytic residue samples was analyzed with an SEM (JXA-840, JEOL, Japan) equipped with an Energy Dispersive X-ray Spectrometer (EDX, AN10000/85S, Links, England). The analyzed elements included C, N, O, Mg, Si, Cl, K, Cu, and Br. Analysis was performed on five samples in duplicate for quality assurance and control.

2.4.2. Major gas pollutants

CO, CO_2, SO_2, NOx, and CH_4 were measured in the pyrolysis exhaust gas of WPCB by an infrared gas analyzer (ZSV, Fuji Electric System Co., Ltd., Japan). In addition, the H_2 was analyzed by a gas chromatograph (HP-6890 GC) equipped with a thermal conductivity detector.

2.4.3. Volatile organic compounds analysis

2.4.3.1. Oxygenated and halogenated VOCs. Twenty-five nitrogenated, oxygenated and halogenated VOCs were analyzed for WPCB pyrolysis exhaust (details of the species analyzed are shown in Table 1). VOC samples were preconcentrated by a purge-and-trap system (Varian, Inc.), then purged and analyzed by a GC/MS (Varian 3600 GC, Varian Saturn 2000 MS). The trap system was cooled to −160 °C by liquid nitrogen. The desorber was then heated to 160 °C for purging. The GC was equipped with a fused silica capillary column (60 m at 0.32 mm I.D. with 1 μm DB-1, J&W) and connected to the MS. The standard gases were prepared with pure chemicals