Journal of CO_2 Utilization 20 (2017) 66–72

Contents lists available at ScienceDirect

Journal of CO_2 Utilization

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

Using CO_2 to mitigate evolution of harmful chemical compounds during thermal degradation of printed circuit boards

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ARTICLE INFO

Keywords:
E-waste
Pyrolysis
Waste disposal
Polycyclic aromatic hydrocarbons (PAHs)
Brominated compounds

ABSTRACT

In this study, CO_2 was used as a reaction medium in the pyrolysis of printed circuit boards (PCBs), thus providing a novel route to mitigate the evolution of harmful chemical species during the thermal degradation of PCBs. For example, this study showed that CO_2 acts as an effective carbon scavenger during the pyrolysis of PCBs. CO_2 facilitated the thermal cracking of volatile organic compounds (VOCs) that evolved from the thermal degradation of PCBs. As a result, CO_2 mitigated the evolution of various harmful pollutants such as phenol and benzene derivatives, PAHs and brominated pollutants, which resulted in the increased generation of syngas (H_2 and CO). This study indicates that using CO_2 as a reaction medium could lead to the development of a more environmentally benign process for the thermal treatment of PCBs and other harmful and/or refractory wastes.

1. Introduction

Electronic waste (e-waste) can be defined as obsolete and discarded electronics and their component parts. This includes a wide range of products such as household appliances and business devices. E-waste can be classified into six categories: (1) temperature exchange equipment (such as air conditioners and refrigerators); (2) screens (for example, monitors, televisions and laptops); and (3) lamps (including fluorescent and LED lamps); (4) small telecommunication and IT equipment (such as mobile phones, modems/routers and GPS); (5) small equipment (for example, vacuum cleaners, microwaves and electrical tools); and (6) large equipment (such as dryers, washing machines, and photocopiers) [1]. Rapid changes in technology, and policies such as planned obsolescence, have caused a rapid increase in the global production of e-waste, from 3.38×10^7 tons in 2010 to 4.18×10^7 tons in 2014 [1]. Only 10–40% of discarded e-waste is currently recycled. The remaining e-waste is either sent for landfill or is thermally treated (for example, by incineration) [2]. However, these are not environmentally benign options, since e-waste contains potentially harmful substances that pose a threat to human health and the environment. For instance, heavy metals (such as lead, mercury, copper, nickel, zinc, arsenic, antimony, selenium, cadmium, and chromium) are used in the manufacture of electronic goods [3]. It has been reported that 5000 tons of copper are emitted annually into the environment, rather than being recycled [4]. In oxidative environments (such as incineration), a large amount of polycyclic aromatic hydrocarbons (PAHs) can be generated from e-waste [3]. In addition to PAHs, a range of dioxins can be also emitted during incineration. Dioxins are known to be lipophilic carcinogens and endocrine disrupters, which accumulate in living organisms and in food chains [5]. For example, the detection of polychlorinated dibenzo-*p*-dioxins/dibenzofurans (PCDD/Fs) and polybrominated dibenzo-*p*-dioxins/dibenzofurans (PBDD/Fs) in e-waste dismantling and recycling centres has been recently reported [6–11]. Polybrominated diphenyl ethers (PBDEs) are known to leach from the surfaces of e-waste into the environment, because they are widely used as flame-retardants in electrical devices [12–17].

Printed circuit boards (PCBs) are commonly used in electrical/electronic equipment. Thus, e-waste contains a large quantity of PCBs. PCBs consist of silicon, various metals (such as aluminium, iron, lead, gold, nickel and silver), glass fibres, resins and fire retardants (such as halogenated compounds) [18]. PCBs can be recycled in several ways, including mechanical recycling, physical and magnetic separation, and smelting and scraping methods [18,19]. However, all these recovery processes require the proper disposal of brominated epoxy resins [20]. In addition, toxic gases and particulate matter containing a wide-range of PAHs and dioxins are emitted during the crushing and separation processes involved in PCB recycling [21]. Therefore, it is highly desirable to develop an environmentally benign PCB disposal process.

Among the various PCB disposal technologies available, thermochemical processes, such as pyrolysis, are promising candidates devel-

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http://dx.doi.org/10.1016/j.jcou.2017.05.009
Received 18 April 2017; Received in revised form 4 May 2017; Accepted 11 May 2017

oping an environmentally benign disposal method [22–24]. The pyrolysis of PCBs has advantages over methods such as landfill and incineration, because most of the macromolecular organic substances in PCBs can be decomposed into synthetic gas (syngas; H_2 and CO) and volatile organic compounds (VOCs) [25–30]. In addition, the yield and/or composition of the pyrolytic products can be modified by altering the pyrolytic conditions in the presence of suitable catalysts [27]. However, halogenated additives used as flame retardant in PCBs provide favourable conditions for the generation of halogenated chemical species, due to their high reactivities. Dehalogenation of the pyrolytic products is desirable, because most halogenated compounds exhibit high environmental toxicity. In addition, previously used thermal treatments of such compounds produce aromatic hydrocarbons and polycyclic aromatic hydrocarbons (PAHs) that are toxic, carcinogenic and mutagenic organic compounds that are highly stable in the environment [31,32], and thereby very hazardous to human health. Especially, PAHs are inevitable by-products of incomplete combustion and pyrolysis processes [33]. Ideally, a method that performs the thermal destruction of PCBs and mitigation of the harmful products in a single process should be developed.

Our previous study reported that using CO_2 as a reaction medium in the pyrolysis of styrene-butadiene copolymer (one of the main constituents of waste tires) led to a substantial reduction in PAHs, because CO_2 inhibited cyclization and expedited the thermal cracking of VOCs [24]. Thus, in this study we investigated the application of CO_2 to mitigate the formation of harmful chemical species evolved from the pyrolysis of PCBs. Specifically, we sought to determine the mechanism of CO_2 as a carbon scavenger in the pyrolysis of PCBs. Systematic experimental work was conducted, including: (1) characterization of the thermal degradation of PCBs in N_2 and CO_2; (2) determining the mass balance of the pyrolytic products, and (3) characterization of pyrolytic gases and oils.

2. Experimental

2.1. Materials

PCBs were obtained from a recycling company in Seoul, Korea. The PCBs were ground, sieved (particle size < 1 mm), and then stored at 25 °C in a desiccator. Table 1 shows the elemental composition of the ground PCBs used as the feedstock in this study. The PCBs were characterized using a Hitachi S-4700 field emission-scanning electron microscope/energy dispersive X-ray spectroscope (FE-SEM/EDX). Ultra-high-purity air and N_2 were purchased from Kuk-Je Industrial Gases Inc. (Anyang, Gyeonggi, Korea). Ultra-high-purity CO_2 was purchased from Green Gas (Gwangju, Gyeonggi, Korea). Dichloromethane (≥99.9%) was purchased from Sigma-Aldrich (St. Louis, MO, USA).

2.2. Thermogravimetric analysis of PCBs

Thermal characterization of PCBs was conducted by thermogravimetric analysis (TGA) using a Mettler Toledo TGA unit. TGA experiments were conducted using 3 ± 0.01 mg of ground PCBs from 30 to 900 °C at a heating rate of 10 °C/min in N_2 or CO_2.

Table 1
Elemental composition of the PCBs used in this study.

Element	wt.%
C	55.2
O	27.9
Mg	1.1
Al	2.5
Si	5.3
Ca	3.9
Fe	0.6
Br	3.6
Total	100.0

2.3. Pyrolysis of PCBs and characterization of pyrolytic products

A laboratory-scale quartz tubular reactor (OD: 25 mm, ID: 22 mm, L: 0.6 m) with a batch-type sample loading in an alumina boat was chosen for conducting pyrolysis of PCBs in N_2 or CO_2. A 3.3 ± 0.01 g PCB sample was loaded for each experiment. The gas flow rate was maintained at 600 mL/min using mass flow controllers (MFCs). The reactor was heated (10 °C/min) using a temperature-programmable tubular furnace (DAIHAN Scientific, Korea). The temperature inside the reactor was monitored with a K-type thermocouple. Pyrolytic gases were qualified and quantified using an INFICON 3000A micro-GC. A standard gas mixture (RIGAS, Korea) was used for calibration of the micro-GC. Quality assurance (QA) and quality control (QC) in the micro-GC are given in Supporting information (Table S1). To identify the chemical species in the pyrolytic oil, the liquid was analysed using an Agilent 7890B GC/TOF-MS (ALMSCO, UK) equipped with an Agilent DB-Wax column. Detailed operating conditions of the GC/TOF-MS analyses are shown in the Supporting information (Table S2).

3. Results and discussion

3.1. Characterization of thermal degradation of PCBs in N_2 and CO_2

To investigate the thermal degradation of PCBs in N_2 and CO_2, TGA tests were conducted from 25 to 900 °C. The representative mass decay (thermogravimetry; TG), differential thermogravimetry (DTG) and differential scanning calorimetry (DSC) curves are shown in Fig. 1. As shown in Fig. 1a, the TG and DTG curves from 25 to 780 °C with N_2 and CO_2 are almost identical, which suggests that the physical aspects of the process (onset and end temperatures of thermal degradation) are not affected by CO_2. The DSC curve between 25 and 780 °C confirms these results (Fig. 1b); the DSC curves for N_2 and CO_2 are almost identical. Hence, the thermal energy required for the thermal degradation of PCBs in N_2 and CO_2 is not significantly different. As illustrated in Fig. 1a and b, major thermal degradation (~24 wt.% of the original mass of PCBs) occurred from 280 to 460 °C, which was likely due to devolatilization, particularly of brominated epoxy resins in the PCBs. This is consistent with the elemental analysis results shown in Table 1. A further mass loss (~7 wt.%) was observed between 460 and 780 °C in N_2 and CO_2.

However, a final mass conversion (mass decay) of PCBs occurred in CO_2 at temperatures higher than 780 °C, which was attributed to the Boudouard reaction ($C(s) + CO_2(g) \rightleftharpoons 2CO(g)$). Although the Boudouard reaction is thermodynamically favourable at temperatures higher than 720 °C [34], in these PCB experiments the Boudouard reaction was initiated at 780 °C. This suggests that more energy is required to initiate the Boudouard reaction in PCBs under these conditions than is theoretically required. However, the thermal degradation of PCBs at > 780 °C in CO_2 cannot be solely explained by the Boudouard reaction, because a mass decay of PCBs was also observed in N_2 at > 780 °C. The rate of the Boudouard reaction is known to be very slow because it is a heterogeneous reaction between solid carbon and gaseous CO_2 [35]. Thus, the mass decay of PCBs in CO_2 resulting from the Boudouard reaction may be not too substantial. Moreover, the experimental data in Fig. 1 suggests that the energy requirement to conduct pyrolysis of PCBs in CO_2 at temperatures lower than 780 °C is equivalent to that in N_2.

3.2. Pyrolysis of PCBs in CO_2

To determine the effect of CO_2 on the composition of the pyrolytic products of PCBs, the pyrolytic products were analysed. The analysis