Environmental Science & Technology

Article

pubs.acs.org/est

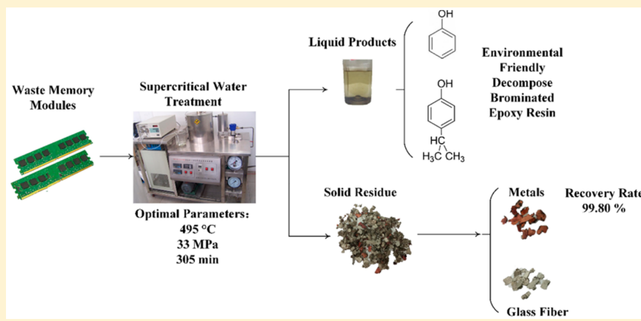
Application of Supercritical Water To Decompose Brominated Epoxy Resin and Environmental Friendly Recovery of Metals from Waste Memory Module

Kuo Li and Zhenming Xu*

School of Environmental Science and Engineering, Shanghai Jiao Tong University, 800 Dongchuan Road, Shanghai 200240, People's Republic of China

Ⓢ *Supporting Information*

ABSTRACT: Waste Memory Modules (WMMs), a particular kind of waste printed circuit board (WPCB), contain a high amount of brominated epoxy resin (BER), which may bring a series of environmental and health problems. On the other hand, metals like gold and copper are very valuable and are important to recover from WMMs. In the present study, an effective and environmental friendly method using supercritical water (SCW) to decompose BER and recover metals from WMMs was developed instead of hydrometallurgy or pyrometallurgy simultaneously. Experiments were conducted under external-catalyst-free conditions with temperatures ranging from 350 to 550 °C, pressures from 25 to 40 MPa, and reaction times from 120 to 360 min in a semibatch-type reactor. The results showed that BER could be quickly and efficiently decomposed under SCW condition, and the mechanism was possibly free radical reaction. After the SCW treatments, the glass fibers and metal foils in the solid residue could be easily liberated and recovered, respectively. The metal recovery rate reached 99.80%. The optimal parameters were determined as 495 °C, 33 MPa, and 305 min on the basis of response surface methodology (RSM). This study provides an efficient and environmental friendly approach for WMMs recycling compared with electrolysis, pyrometallurgy, and hydrometallurgy.



■ INTRODUCTION

Recently, the upgrade and replacement of electrical and electronic equipment has been increased rapidly with the rapid development of electronic manufacturing technologies. Upgrade and replacement resulted in a large quantity of waste printed circuit boards (WPCBs).[1] The most common WPCBs use glass fibers and brominated epoxy resin (BER) as the framework materials, with metals used as the electric circuits.[2] Serious pollution could be generated if WPCBs were not properly disposed of, because the brominated flame retardants (BFRs) therein may cause the formation of toxic compounds. Their special physical and chemical characteristics make them difficult to recycle.[3,4]

The common processing methods for WPCBs are landfill and incineration, which can produce a wide diffusion of BFRs. As for landfill and incineration, BFRs can be easily converted into some extremely hazardous compounds, such as polybrominated dibenzo-*p*-dioxins (PBDD), tetrabromobisphenol (TBBPA), and polybrominated dibenzofurans (PBDF).[5]

Meanwhile, WPCBs are attracting more and more attention due to the valuable metals therein. From every ton of WPCBs can be extracted more than 300 g of gold, 2 kg of silver, 25 kg of tin, and 130 kg of copper.[6]

Waste Memory Modules (WMMs), a particular kind of WPCB, draw the most attention because of its golden fingers with a higher and purer metal content (copper 10 wt %, gold 0.7 wt %).[7] Therefore, the recycling of WMMs has a great practical significance for sustainable development of the human living environment and resources recycling.

Nowadays, metal recovery from WPCBs mostly depends on pyrometallurgy and hydrometallurgy. However, these methods create considerable toxicity risks worldwide. There is a notorious destination for improper WPCBs recycling in Guiyu, China. Using aqua regia, cyanidation, and blast furnace to recover metals from WPCBs brought serious air and water pollution there.[8] The official processing method is fusing WPCBs into metal ingots under the high temperature as the pretreatment and recovering metal separately by hydrometallurgy or electrolysis as the aftertreatment. As a consequence, effluent and off-gas must be dealt with properly during fusing, pickling, cyanidation, or electrolysis.[9]

Physical methods were also mostly used to recover metals and nonmetallic materials from WPCBs according to their different physical properties. Physical methods had developed rapidly, these methods could be divided into three steps:

Received: September 22, 2014
Revised: January 7, 2015
Accepted: January 12, 2015
Published: January 12, 2015

DOI: 10.1021/es504644b
Environ. Sci. Technol. 2015, 49, 1761−1767

dismantling, crushing, and sorting. Vortex separation, magnetic separation, and electrostatic separation processes had been widely used in the industry with high efficiency and no secondary pollution.[10] However, physical methods generally achieved only preliminary separation of metals and nonmetals, with relatively high loss ratio of precious metals.

All the problems above should be solved properly. In recent years, supercritical water (SCW, $T \geq 374$ °C, $P \geq 22.1$ MPa) is introduced as an environmentally friendly method to decompose organic polymers due to its extraordinary properties, such as low viscosities, high mass transport coefficient, high diffusivity, and high solubility for organics.[11−13] Utilization of green solvents in chemical reactions is quite significant. As one of the nontoxic and nonflammable solvents, water has been considered to be an ideal solvent in chemical reactions compare with traditional organic solvents.[14−16] Water in SCW conditions can act not only as a solvent but also as a reactant, catalyst, or product due to the different properties, which are mainly dependent on temperature and pressure. The dissociation constant (K_w) for water is about 3 orders of magnitude higher than it is for ambient liquid water, as it approaches the critical point.[17] Supercritical water can provide abundant H^+ and OH^- and can be an efficient acid or base catalyst for organic reactions.[15]

Accordingly, in the present study, SCW was used for decomposition of organic polymers and recovery of metals in WMMs. The aims of this study were examining the organics decomposition efficiency and metal recovery efficiency from WMMs after SCW treatments, and optimizing the operation parameters for WMMs treatments by SCW.

■ MATERIALS AND METHODS

Materials and Chemicals. The WMMs used in this work were provided by Yangzhou Ningda Noble Metal Co., Ltd. (China) and Shanghai Xin Jinqiao Environmental Protection Co., Ltd. (China). The WMMs were mainly disassembled from discarded desktop computers. The parts with electronic components, such as capacitors and relays, were removed first. Then the parts with gold fingers were crushed into small pieces (10−15 mm) to obtain the mixture as raw material. Subsequently, the WMMs particle mixtures were dry at 105 °C for 24 h. The major composition of WMMs are listed in Table 1. Chemical reagents used in the experiments were all analytical reagents unless otherwise mentioned.

Table 1. Composition of the WMMs Employed in This Work (wt %)

Cu	Al	Au	organics	glass fiber
10.6051	6.9644	0.7364	31.2504	46.3215

Apparatus. Figure 1 shows the schematic diagram. The SCW treatments were carried out by using a 100 mL high-pressure semibatch-type reactor made of Hastelloy alloy whose designed temperature and pressure were 600 °C and 40 MPa, respectively (Nantong Huaxing Oil Equipment Co., Ltd., China).

About 3 g of WMMs was used in each experiment. The pressure inside the reactor was monitored by a pressure gauge attached to the reactor. The system pressure was mainly dependent on the reaction temperature and the constant-flux pump (Nantong Huaxing Oil Equipment Co., Ltd., China). During the heating process, the system pressure kept on increasing with the increase of temperature and the amount of water. When the system temperature reached the set temperature, the heater stopped temporarily and started the heat preservation process. The examined temperatures were 400, 450, and 500 °C, respectively. The system pressure was controlled by a counterbalance valve and stabilized at a certain value. The examined pressures were 25, 30, and 35 MPa. Once the reactor reached the set temperature and pressure, it was held at the condition for 120, 240, and 360 min, respectively. After the treatment, counterbalance valve was released, and the system pressure would be equal to the atmosphere. The liquid products outflowed and were gathered. Then the reactor was cooled to room temperature naturally. Once the autoclave cooled to room temperature, the reactor was opened, and the solid residue was removed from the autoclave. Afterward, the inwall of the reactor and pipes were all washed by deionized water. All the liquid products were filtrated to obtain a powdery solid residue. Two parts of residue together were dried to a constant weight to obtain the mass of solid residue.

Products Analysis. The liquid products were qualitative and quantitative analyzed by chromatograph−mass spectrum (GC-MS, TurboMass, PerkinElmer Corporation, U.S.A.). The raw materials and solid products were qualitative and quantitative analyzed by inductively coupled plasma-mass spectrometry (ICP-MS, Agilent 7500a, Agilent Corporation, U.S.A.) and X-ray fluorescence (XRF, EDX-720, Shimadzu Corporation, Japan). All the experiments were repeated three times, and only the mean values were reported.

Statistical Analysis. The response surface methodology (RSM) was used to analyze the interaction of several independent factors by the Design-Expert software (version 8.0.6, Stat-Ease, Inc., Minneapolis, MN). The experiments were conducted in a standard RSM design called Box-Behnken design (BBD) for the optimization. Temperature, pressure, and reaction time were selected as the factors with the coded values at 3 levels (−1, 0, and +1). The yields of residue and metal recovery rate were chosen as the responses of these factors. The ranges and levels of variables are given in Table 2.

■ RESULTS AND DISCUSSION

The experiments were conducted in the order shown in Table 3, and each response is also represented.

Decomposition of Brominated Epoxy Resin. Organic polymers in the WMMs, like brominated epoxy resin, could be decomposed during the SCW treatment. In this study, the solid residue was proved to be metals, glass fibers, and char. Therefore, the yield of residue could be used to present decomposition efficiency of BER in WMMs. The lower yield of solid residue represented the higher BER decomposition efficiency. Yield of residue could be calculated by eq 1. The series results in this study were shown in Table 3.

$$R1 = \frac{m}{M} \times 100\% \tag{1}$$

where $R1$ is the yield of residue; M is the weight of original material; m is the weight of solid residue after SCW treatment.

The results showed that yields of residue could be below 70 wt %, meaning more than 90% brominated epoxy resin was decomposed by the SCW treatment. The results indicated that BER in WMMs could be handled effectively under the proper SCW condition.

It was reported that SCW is an excellent reaction medium for decomposition of organic polymers, which acted as reactant as

DOI: 10.1021/es504644b
Environ. Sci. Technol. 2015, 49, 1761−1767