Removal of Bromine from Waste Plastics by Pyrolysis with Hydrotalcite

N. Morita1, M. Nakayasu2, Y. Kawabata3, and H. Nakagome4

1Manuscript received January 20, 2017; revised January 20, 2017.
2N. Morita is with the Department of Urban Environment Systems, Graduate School of Engineering, Chiba University, Japan. (E-mail: Naoyuki_Morita@chiba-u.ne.jp).
3M. Nakayasu is with the Department of Urban Environment Systems, Graduate School of Engineering, Chiba University, Japan. (E-mail: Masami_1_Nakayasu@education.metro.tokyo.jp).
4Y. Kawabata is with the Department of Urban Environment Systems, Graduate School of Engineering, Chiba University, Japan. (E-mail: tanoshimokita@gmail.com).
5H. Nakagome is a Professor at Chiba University, Japan. (E-mail: nakagome@tu.chiba-u.ne.jp).

Abstract. In recent years, there has been increasing interest in the pyrolysis of waste plastics to fuels as a form of recycling. One associated challenge is the frequent presence of halogen-based flame retardants in various consumer plastics. In this study, waste polyethylene mixed with tetrabromobisphenol A was subjected to thermal decomposition, using hydrotalcite (HT) to reduce the halogen concentration in the product oil. Samples with and without HT or with various inert additives were pyrolyzed at 450 °C under nitrogen in a glass reactor and the product oils, solid residues, and gaseous products were investigated. The addition of HT was found to increase the yield of the product oil. As well, no brominated compounds were detected in the oil when using HT. Scanning electron microscopy provided evidence that brominated compounds are captured by HT in the solid residue during thermal decomposition, thus eliminating bromine from the product oil and gases.

Keywords: pyrolysis, chemical products, hydrotalcite, brominated flame retardants.

1. Introduction

Plastics have numerous uses in various products, especially in the electrical and electronic equipment (EEE) that is so widely distributed in our society. As these devices are replaced with newer models, their lifetimes become increasingly short and significant amounts of waste are generated. This is particularly true because EEE include not only computers and mobile phones, but also hair dryers, refrigerators, and cathode ray tubes [1]. After use, these EEE become waste (WEEE) that requires significant processing [2]. In the European Union alone, 17 kg of WEEE is produced per person annually, with an estimated total of 8.3 to 9.1 million tons generated in 2005 [3]. Recently, the EU has introduced laws that aim to promote the reuse, recycling, and reduction of EEE while limiting the landfill and incineration of WEEE. These products are made of materials that can already be reused, such as glass and metals, but also contain more than 15 different types of engineering plastics, making recycling difficult [4], [5]. Waste plastics can undergo thermal, chemical or physical recycling, although the removal of flame retardant materials added to these products is an important issue in these recycling processes. The recycling of plastics via the thermal decomposition of WEEE has attracted attention as a promising technology. During pyrolysis, the polymers are converted into gaseous compounds that can be used as fuels, along with residual carbon [6]. There has been much research regarding the treatment of waste plastics using thermal decomposition with catalysts [7].
However, WEEE plastics are often treated with halogenated flame retardants, such as potentially harmful polybromines, and so require special treatment. Examples include polybrominated dibenzoparadioxins (PBDDs) and polybrominated dibenzofurans (PBDFs) [19]. Many of the plastics used for EEE also contain antimony trioxide as a synergistic component in conjunction with bromine compounds. A number of techniques have been studied for the recycling of plastics in WEEE, keeping in mind the health hazards of these compounds, including thermal decomposition [20]-[24], catalytic processes [25]-[30] and reduction with ammonia-containing polymers. The use of various other decomposition agents has also been investigated [31], [32]. Our own group has previously reported that bromine compounds in plastics can be eliminated by adding hydrotalcite (HT) during the pyrolysis process [33]-[36]. HT is a layered double metal complex hydroxide, consisting of divalent Mg2+ and trivalent Al3+ host layers with anion species contained in the interlayer guest layers [37]. HT has received increasing attention in recent years as an ion exchange material [37]-[40] with applications in catalytic gas removal [41]-[44]. The high anion exchange capacity of HT has been of significant interest and this material has been used as an adsorbent for the removal of various contaminants from aqueous solutions. The adsorption of inorganic anions such as borate, nitrate, fluoride, phosphate, sulfate, chromate, arsenate, and selenate has been studied [45]. The adsorption of anions by HT is thought to result from the formation of an interlayer outer spherical complex following an anion exchange reaction [46]. HT has also been considered as a catalyst, and there have been reports that the use of HT can improve biodiesel yields from 62% to 77% [47], [48]. In addition, the catalytic activity of HT during the aerobic oxidation of benzyl alcohol has been demonstrated [49]. The present study investigated the effects of adding HT on the elimination of bromine compounds during the thermal decomposition of polyethylene (PE). Specifically, a model polymer was pyrolyzed at 450 °C in the presence of HT, and the level of bromine in the resulting oil was assessed.

2. Experimental

2.1. Materials

Samples simulating a bromine-containing plastic resin (BR-PE) were prepared by mixing 20 g of waste PE obtained from crushed computer mice (Fujitsu, Ltd.) with tetrabromobisphenol A (TBBA, Tokyo Kasei Co., Ltd.). Synthetic HT (DHT-4A, Kyowa Chemical Industry Co., Ltd.) was employed, adding either 10 or 20 g of the HT to 20 g of the BR-PE. In addition, for comparison purposes, either 4Å molecular sieves (1/16, Wako Pure Chemical Industries, Ltd.), 13X molecular sieves (1/16, Wako Pure Chemical Industries, Ltd.), or sea sand (prewashed with methanol, 425 to 850 μm, Wako Pure Chemical Industries Co., Ltd.) was added to the BR-PE. A summary of the experimental samples is provided in Table I.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>I</td>
<td>Disposable Polyethylene</td>
</tr>
<tr>
<td>II</td>
<td>Disposable Polyethylene + TBBA (BR-PE)</td>
</tr>
<tr>
<td>III</td>
<td>BR-PE + Molecular sieves 4A</td>
</tr>
<tr>
<td>IV</td>
<td>BR-PE + Molecular sieves 13X</td>
</tr>
<tr>
<td>V</td>
<td>BR-PE + Sea sand</td>
</tr>
<tr>
<td>VI</td>
<td>BR-PE + HT (PE:HT=1:1)</td>
</tr>
<tr>
<td>VII</td>
<td>BR-PE + HT (PE:HT=2:1)</td>
</tr>
</tbody>
</table>

2.2. Experimental Apparatus and Procedures

The experimental apparatus used in this study is shown in Fig. 1. A sample was placed in a glass reactor and a flow of nitrogen gas at 50 mL/min was applied for 60 min to remove oxygen. After purging, the nitrogen flow was stopped and the thermal decomposition experiment was conducted. The sample temperature, as determined using a thermocouple, was raised to 450 °C at 5° C/min. After the temperature reached 450 °C, heated was ceased and the reactor was allowed to naturally cool to room temperature. The gas generated during thermal decomposition passed through a cooling pipe where it condensed into an oil
that was collected in a container. The gaseous products that did not condense were collected in a gas pack after bubbling through an alkaline aqueous solution.

Fig. 1: The experimental apparatus

2.3. Analysis

The product oil was diluted by a factor of 100 with hexane (Wako Pure Chemical Industries, special grade reagent) and subsequently analyzed by gas chromatography/mass spectrometry (GC/MS, Shimadzu GC-MS-QP2010ultr). The primary product compounds were identified using the spectral library associated with the instrument software. Pure helium was used as the carrier gas in conjunction with an Rtx-1 column (i.d. 0.25 mm, 0.25 μm film thickness). The initial column temperature was 40 °C for 30 min, after which it was raised to 230 °C at 5°C/min.

The residue remaining after the thermal decomposition was analyzed by scanning electron microscopy (SEM, Hitachi High-Tech TM 3030) in conjunction with energy dispersive X-ray spectroscopy (EDS, Bruker QUANTAX). The concentration of bromine was quantitatively determined by selecting five points in the EDS image of the sample and reporting the average value. The gaseous products were analyzed by gas chromatography (Shimadzu GC-2014) both qualitatively and quantitatively.

3. Results and Discussion

3.1. Product Oil

The yields of product oil obtained from pyrolysis are plotted in Fig. 2. These data confirm that the addition HT increased the yield of oil.

![Fig. 2: Yields of product oil](image)

Fig. 2: Yields of product oil
The chemical components of the product oils are summarized in Table II. Decane was confirmed to be the most common product, and 3-bromophenol and 2-bromotetradecane were detected as bromine compounds. These data also demonstrate that product oil containing no bromine compounds was obtained by adding HT.

<table>
<thead>
<tr>
<th>Detectable substance</th>
<th>Molecular formula</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
<th>V</th>
<th>VI</th>
<th>VII</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-octane</td>
<td>C₈H₁₈</td>
<td>○</td>
<td>nd</td>
<td>Nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>2,4-Dimethylhexane</td>
<td>C₄H₁₀</td>
<td>○</td>
<td>nd</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>○</td>
<td>nd</td>
</tr>
<tr>
<td>1-nonene</td>
<td>C₅H₁₀</td>
<td>○</td>
<td>nd</td>
<td>○</td>
<td>○</td>
<td>nd</td>
<td>○</td>
<td>nd</td>
</tr>
<tr>
<td>Undecane</td>
<td>C₁₁H₂₃</td>
<td>○</td>
<td>nd</td>
<td>○</td>
<td>○</td>
<td>nd</td>
<td>○</td>
<td>○</td>
</tr>
<tr>
<td>Decane</td>
<td>C₁₀H₂₂</td>
<td>○</td>
<td>nd</td>
<td>○</td>
<td>○</td>
<td>nd</td>
<td>○</td>
<td>nd</td>
</tr>
<tr>
<td>3-Bromophenol</td>
<td>C₆H₅BrO</td>
<td>nd</td>
<td>nd</td>
<td>○</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Dodecane</td>
<td>C₁₂H₂₆</td>
<td>○</td>
<td>nd</td>
<td>○</td>
<td>○</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>Tetradecane</td>
<td>C₁₄H₃₀</td>
<td>○</td>
<td>nd</td>
<td>○</td>
<td>nd</td>
<td>nd</td>
<td>○</td>
<td>nd</td>
</tr>
<tr>
<td>2-bromotetradecane</td>
<td>C₁₄H₂₉Br</td>
<td>nd</td>
<td>○</td>
<td>Nd</td>
<td>○</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
<tr>
<td>1-heptadecane</td>
<td>C₁₇H₃₃</td>
<td>○</td>
<td>nd</td>
<td>Nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
<td>nd</td>
</tr>
</tbody>
</table>

○: Detected  nd: Not Detected

### 3.2. Residue

![Fig. 3: (a) EDS image of the residue from sample II](image)

![Fig. 3: (b) EDS image of the residue from sample VI](image)
The amount of bromine contained in each residue was quantified by surface observations in conjunction with EDS. The level of bromine in sample II, without HT addition, was 1.61%. This concentration increased to 22.4% and 20.1% in samples VI and VII, to which HT had been added, indicating that bromine was trapped in the residue when HT was included in the specimen.

The results of SEM observations of the residues are shown in Fig. 3. Both small and large particles are evident on the surface as the amount of added HT increases. It can be inferred from these images that bromine was adsorbed on the surfaces of small oxide particles, because the large particles are Mg or Al-based oxides.

### 3.3. Gas Production

The volume of gas generated by pyrolysis was less than 1 L in all experiments. From this, it can be inferred that the samples were primarily transitioned to either product oil or solid residue by thermal decomposition. Analysis of the gases recovered by the gas pack found the presence of H2, CH4 and CO2. It is assumed that the H2 and CH4 resulted from the thermal decomposition of the PE, while the CO2 came from the HT.

### 4. Conclusion

This study investigated the removal of bromine compounds from the oil obtained by the pyrolysis of waste plastics containing brominated flame retardants, using HT. The results demonstrate the possibility of obtaining oil containing no bromine compounds. In addition, a higher yield of oil was obtained in conjunction with the addition of HT. These effects are especially evident when HT is added at a ratio of 2:1. Thus, it appears that HT has a catalytic effect and there is an optimum addition amount. Qualitative analyses of the product oils from samples to which HT had been added demonstrate the absence of bromine compounds, suggesting that HT adsors these brominated species. EDS surface observations of the residues found bromine concentrations of 1.61%, 22.39% and 20.12% in the case of samples II, VI and VII, demonstrating that the HT adsors the bromine compounds. This concentration of the bromine in the residue upon the addition of HT is believed to have removed brominated compounds from the product oils. PE typically contains a wax component and, during thermal decomposition, this material often causes clogging of the cooler piping. However, in the present study, samples VI and VII did not exhibit clogged and also showed higher product oil yields. It can be inferred from these yields that the HT also serves to decompose the wax component. The residue from plastic pyrolysis is typically landfilled, and dissolution testing has demonstrated that the bromine compounds contained in the residue do not leach out. In addition, our previous work has demonstrated that the use of thermal decomposition can reduce the amount of waste going to landfill by approximately 80% [35]. In summary, this work has demonstrated that the addition of HT during the thermal decomposition of waste plastics containing brominated flame retardants substantially reduces the level of bromine compounds contained in the product oil.
5. Acknowledgments

The contributions of Ms. Nonoka Suzuki and Ms. Sonoka Hasegawa of the Tokyo Metropolitan Tama High School of Science and Technology are gratefully acknowledged. The authors also wish to acknowledge the Kyowa Chemical Industry Co., Ltd. for donating the hydrotalcite used in this work.

6. References


