

# Effects of Adding Hydrotalcite with Different Compositional Ratios in the Pyrolysis Treatment of Brominated Plastics

Kimi Hanazawa, Moemi Toritsuka, and Naoyuki Morita

**Abstract**—In recent years, chemical recycling technologies related to the pyrolysis of plastics into fuels have received increasing attention under the circular economy agenda with respect to resource depletion. Herein, a method is presented to reduce halogen compounds in the product oil derived from the pyrolysis of polystyrene with tetrabromobisphenol A. Analysis was undertaken to identify the bromine compounds present in the residue after the pyrolysis treatment. Pyrolysis was conducted in the presence of hydrotalcites as a function of the Mg and Al additive composition ratio (type 1; KW-1000 and type 2; K W-2000). The bromine compounds identified in the oil after pyrolysis at 400 °C were determined as 2-bromophenol, 4-bromophenol, 2,4-dibromophenol, 1-bromomethylbenzene, 2-bromomethylbenzene, and 3,6-dibromo-2,5-xylidine. In the absence of hydrotalcite, bromine compounds were still detected in the product oil, residue and gas, whereas the addition of KW-2000 reduced the concentration of bromine compounds in the product oil. The reduced concentration of the bromine compounds in the product oil is suggested to be related to the trapping of bromine by the added hydrotalcite during the pyrolysis of the plastic.

**Index Terms**—Brominated flame retardants, hydrotalcite, polystyrene, pyrolysis.

## I. INTRODUCTION

Because plastics are used across numerous sectors, their demand and production have increased worldwide over the years. However, the majority of plastic waste is sent to landfill or dumped into the ocean, resulting in numerous environmental problems, such as marine pollution [1]–[4]. Additionally, fossil fuels, which are the raw materials for plastics, are limited non-renewable energy sources; therefore, plastic recycling is essential if plastic demand continues to increase [5]–[7]. Technologies to convert plastics into oil (the raw material) are receiving increasing attention, especially in EU countries, and particularly pyrolysis technologies as a means for chemical recycling [8]. Of particular concern is the electrical and electronic waste (WEEE) emitted from the disposal of engineered plastics used in household appliances. Waste plastics that do not contain brominated flame retardants can be categorized as product oils, residues, or

gases after being subjected to pyrolysis.

However, because brominated flame retardants are added to WEEE, the resulting oil after pyrolysis contains bromine compounds, which increases the difficulties in plastic recycling. Furthermore, such processes also lead to the formation of dioxins, environmental pollutants, when reused [9]. Therefore, proper treatment of WEEE is required. Although there are numerous reports on the recycling and pyrolysis of plastics [10]–[21], we previously reported the use of hydrotalcite (HT), which is an aluminum-magnesium hydroxide complex, for the pyrolysis of brominated plastics to recover the contained bromine compounds as residues. The concentration of bromine compounds in the oil was reported to be reduced [22]–[24]. Additionally, HT (compositional formula:  $\text{Mg}_6\text{Al}_2(\text{OH})_{16}\text{CO}_3 \cdot m\text{H}_2\text{O}$ ) has an influence on the catalytic performance that allows the pyrolysis treatment temperature to be reduced to 400 °C, from typical temperatures of 600–800 °C. Herein, HT was added as a function of the Al/Mg mass ratio to polystyrene containing tetrabromobisphenol A, a typical brominated flame retardant. The polystyrene was subjected to pyrolysis at 400 °C to recover the bromine compounds as a residue and to reduce the concentration of bromine compounds in the product oil. HT comprises divalent  $\text{Mg}^{2+}$  and trivalent  $\text{Al}^{3+}$  host layers with anionic species dispersed within the inter-layered guest layers. Therefore, HT is classified as a layered double hydroxide comprising metal complex hydroxides. Furthermore, as HTs exhibit catalytic properties, a wealth of interdependent research has recently focused on HTs as ion exchange materials and as materials for gas removal. The high anion exchange capacity of HT, which is comparable to that of organic ion exchange resins, has attracted particular attention as an adsorbent for the removal of various contaminants from aqueous solutions. Furthermore, the adsorption properties of inorganic anions onto HT including borates, nitrates, fluorides, phosphates, sulfates, chromates, and arsenate have been examined. The anion adsorption mechanism onto HT is believed to result from the formation of inter-layered extrasphere complexes through anion exchange reactions. Recently, the molar ratio of the HT divalent  $\text{Mg}^{2+}$  and trivalent  $\text{Al}^{3+}$  has been reported to improve catalytic performance [25]–[28]. Herein, varying aluminum and magnesium ratios were employed as additives to investigate the influence of pyrolysis on brominated polystyrene.

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## II. EXPERIMENTAL

## A. Materials

Plastic samples containing bromine were prepared by mixing 20 g of polystyrene (Asahi Kasei Chemicals Co., Ltd.) with 2 g of tetrabromobisphenol A (Tokyo Chemical Industry Co., Ltd.). To reduce the bromine compounds in the product oil, synthetic HTs, KW-1000 and KW-2000 (Kyowa Chemical Industry Co., Ltd.), and sea sand (Wako Pure Chemical Industry Co., Ltd.) were used as additives. The compositional ratios of the HTs used in the experiments are presented in Table I.

TABLE I: HYDROTALCITE COMPOSITION

	Al <sub>2</sub> O <sub>3</sub> (wt %)	MgO (wt %)	Mg/Al <sub>2</sub> O <sub>3</sub>	Na (wt %)
KW-1000	19.3	35.1	4.60	0.02
KW-2000	32.9	59.6	4.58	—

KW-1000 is a synthetic HT comprising a Mg/Al<sub>2</sub> ratio = 4.5. KW-1000 is sintered to yield KW-2000. KW-2000 is KW-1000 with the inter-layer water, inter-layer anions and OH groups coordinating to Mg and Al removed in HT. KW-2000 typically reverts back to the HT structure when suspended in water.

## B. Experimental Apparatus and Procedure

Samples were converted into a simulated brominated plastic by mixing 20 g of polystyrene (Asahi Kasei Chemicals Co., Ltd.) with tetrabromobisphenol A (Tokyo Chemical Industry Co., Ltd.) as an additive. Synthetic HTs (KW-1000 and KW-2000 Kyowa Chemical Industry Co., Ltd.) were used as additives within the samples. A mixture of 20 g of the sample with the prescribed amount of HT was used. Sea sand (methanol wash, 425–850 µm, Wako Pure Chemical Industries, Ltd.) was added as a comparison. The experimental conditions are presented in Table II.

TABLE II: EXPERIMENTAL CONDITIONS

Conditions	Sample Contents	Additive ratios
I	Br-PS	—
II	Br-PS + KW-1000	1 : 1
III	Br-PS + KW-1000	2 : 1
IV	Br-PS + KW-2000	1 : 1
V	Br-PS + KW-2000	2 : 1
VI	Br-PS + Sea Sand	1 : 1

Br-PS; PS+TBBA.

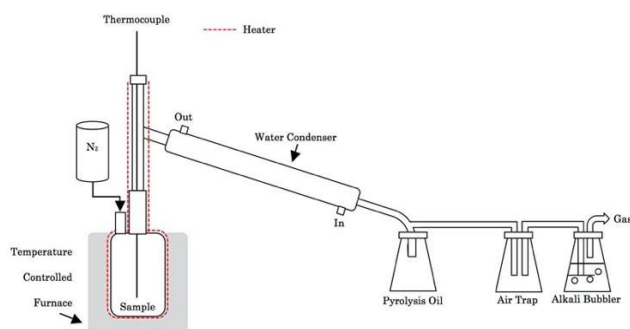


Fig. 1. Experimental apparatus.

The experimental apparatus used herein is shown in Fig. 1. A mixed sample was placed in a metal reactor under a nitrogen atmosphere (flow rate = 50 mL/min, 1 hr) to remove oxygen from the reactor. The pyrolysis experiments were performed after finishing the nitrogen displacement. The decomposition temperature of the sample was measured using a thermocouple. The temperature of the sample was raised to 400 °C at a rate of 5 °C/min. After reaching 400 °C, the sample was maintained at the temperature set-point for 30 min before allowing to cool naturally. The gas generated during the pyrolysis was condensed through the cooling pipes and collected as product oil in a collection vessel. The non-condensable gas product was collected in a gas pack after bubbling through an alkaline solution and the composition measured.

## C. Analysis

The product oil was diluted 100 times in hexane and analyzed by comparing the peaks obtained by gas chromatography-mass spectrometry (GC-MS). The main compounds were identified from a GC-MS spectral library. Pure helium was used as the carrier gas. Analysis was undertaken using a Rtx-1 column (30 m, length; 0.25 mm, internal diameter; 0.25 µm, film thickness) on a Shimadzu GC-MS-QP2010ultr instrument. The bubbled alkaline solution was diluted 100 times with ultrapure water and analyzed qualitatively by ion chromatography (IC) using a Shim-pack column coupled to a CDD-10Asp detector using a high-performance liquid chromatography Shimadzu IC system. The HT residue was observed for structural changes by x-ray diffraction (XRD, MiniFlex, Rigaku).

## III. RESULTS AND DISCUSSION

## A. Yield and Residue Analyses of the Produced Oils

The product oil yields are shown in Fig. 2, where yield is observed to increase as a function of HT, suggested to be as a result of the HT catalytic performance. However, when the same amount of KW-2000 was added, as in condition IV, the yield was observed to be extremely low, however, because the mass of KW-2000 is light, the volume of KW-2000 is assumed to be greater than that of KW-1000, which inhibits the thermal decomposition. The reason for the higher yields observed in conditions II and III (KW-1000) relates to the tendency of polystyrene to degrade in the presence of water. Additionally, KW-1000 comprises inter-layer water, which is presumed to have a degree of influence on the degradation reaction.

To confirm whether the HT recovered bromine, the residues after pyrolysis (conditions III and V) were observed by energy dispersive x-ray spectroscopy (EDS, S2RANGER, BRUKER), and bromine, which was not present prior to pyrolysis, was observed after pyrolysis (Fig. 3). Therefore, the EDS data infer that bromine can be recovered as a residue during pyrolysis in the presence of a HT additive.

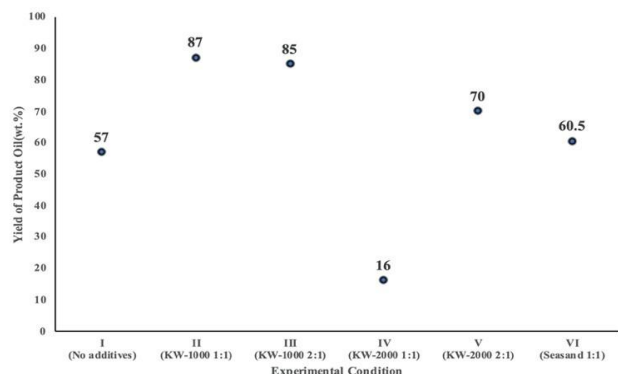


Fig. 2. Yields of the produced oils.

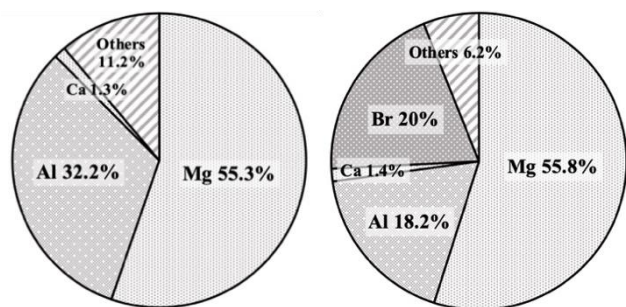


Fig. 3(a). Changes to the residue composition (condition III) before and after pyrolysis.

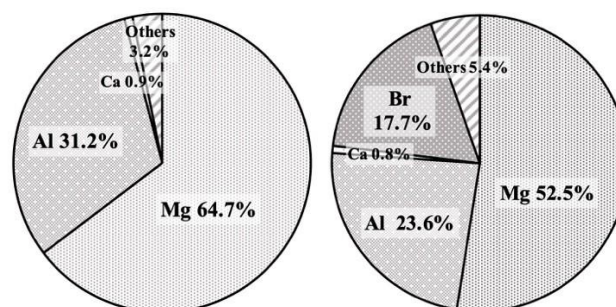


Fig. 3(b). Changes to the residue compositional (condition V) before and after pyrolysis.

### B. Qualitative and Quantitative Analyses of the Generated Oils

Benzene and toluene have previously been reported as the main constituents of the oils produced by the pyrolysis of polystyrene [25]. Thus, qualitative and quantitative analysis of the bromine compounds were conducted herein with the amount of bromine compounds obtained in condition I normalized to 100%. The results are shown in Table III.

TABLE III: BROMINE COMPOUND TYPES PRESENT IN THE PRODUCED OILS

Bromine Compound	Molecular formula	Experimental conditions					
		I	II	III	IV	V	VI
2-Bromophenol	C <sub>6</sub> H <sub>5</sub> BrO	100.0	31.9	31.2	2.4	20.7	108.2
4-Bromophenol	C <sub>6</sub> H <sub>5</sub> BrO	100.0	N.D.	N.D.	N.D.	0.4	68.1
2,4-Dibromophenol	C <sub>6</sub> H <sub>4</sub> Br <sub>2</sub> O	100.0	N.D.	N.D.	N.D.	N.D.	340.5
1-Bromomethylbenzene	C <sub>8</sub> H <sub>9</sub> Br	100.0	2.5	2.5	N.D.	0.9	45.8
2-Bromomethylbenzene	C <sub>8</sub> H <sub>9</sub> Br	100.0	191.7	200.0	N.D.	30.1	54.1
3,6-Dibromo-2,5-xylidine	C <sub>8</sub> H <sub>9</sub> Br <sub>2</sub> N	100.0	38.9	38.9	N.D.	N.D.	20.4

N.D. = Not detected.

### C. Qualitative and Quantitative Analyses of the Generated Oils

The volume of gas obtained under all conditions was <2 L, and the sample composition was considered to be distributed to either residual carbon or the product oil. The obtained gases were analyzed by GC (Shimadzu GC 2014) (Fig. 4).

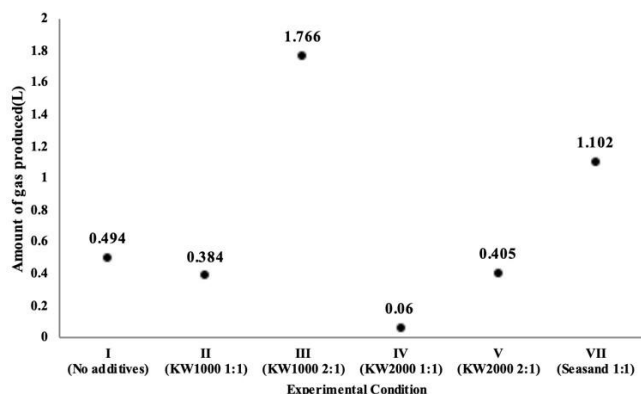


Fig. 4. Volume of gas produced as a function of the experimental conditions.

The gas components were identified as H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub>. Furthermore, bromine ions were detected in the alkaline solution from conditions I and VI. No bromine ions

were detected from the other conditions.

### D. XRD Analysis of the Residues

The HT used herein is a synthetic HT, which is structurally different from the original form. Therefore, the HT structure was verified by XRD to determine if any structural changes had been undertaken at 400 °C. The HT possesses a layered structure and the XRD pattern should present two peaks if there is a layered structure. The XRD results are shown in Fig. 5. Because two peak values were obtained in all the samples after pyrolysis, the HT structure is retained after pyrolysis.

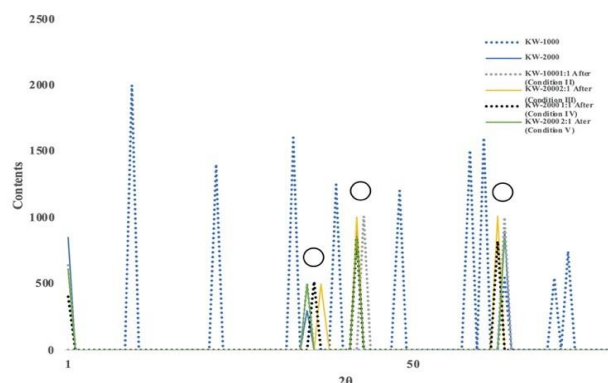


Fig. 5. X-ray diffraction patterns of the additives.

#### IV. CONCLUSION

Herein, HTs with varying Mg and Al ratios were employed as additives to examine the influence on the pyrolysis of plastics. Two different HT types were observed to recover bromine compounds and increase the product oil yield. HT is suggested to function as an alkali catalyst as a result of the exhibited basicity. Two HT types, KW-1000 and KW-2000, were studied and KW-2000 is hypothesized to be a more effective catalyst because of the enhanced basicity. However, the density of KW-2000 is lower, and hence requires larger volumes, which is considered to be a factor that inhibits thermal decomposition (Fig. 2). Hence, optimizing the HT loading is an important parameter.

The product oil yield increase is related to the HT catalytic performance; however, KW-1000 retained inter-laminar water, which accelerates both polystyrene degradation and the associated hydrolysis reactions, which increases the yields compared with the other conditions.

Halogen gas produced during the pyrolysis was observed on the HT surface. Because the ion exchanged gas is not observed on the HT surface, the halogen gas is suggested to be recovered on the surface because of the potential difference effect between the Mg and Al generated in the HT rather than the recovery of halogen ions as a result of the HT ion exchange capacity. Additionally, the neutralization reaction is understood to derive from an acid-base reaction between halogen (acidic) gas and HT (alkaline gas).

In the recovery of bromine compounds, the concentration of numerous bromine compounds was reduced when employing HT as an additive. However, the concentration of bromine compounds having large molecular weights was observed to increase in conditions II and III, which is suggested to be related to the 30 min heating dwell time after pyrolysis. Because the highly basic KW-2000 HT demonstrates a high neutralization ability, KW-2000 is considered not to be influenced by the 30 min heat retention time (Table III).

These results suggest that the addition of HT to the pyrolysis of brominated plastics reduces the concentration of bromine compounds in the resulting product oil. However, there remain problems to be circumvented, such as optimization of the HT loading and verification of the heat retention time. The observed behaviors varied depending on the Mg and Al compositional ratios and the presence or absence of inter-layer water, which suggests that the nature and loading amount of the HT are crucial parameters to the quality of the oil produced.

#### CONFLICT OF INTEREST

All authors declare that: (i) no support, financial or otherwise, has been received from any organization that may have an interest in the submitted work; and (ii) there are no other relationships or activities that could appear to have influenced the submitted work.

#### AUTHOR CONTRIBUTIONS

K. Hanazawa and M. Toritsuka performed the

experimental work and data analysis. The wording of the final paper was agreed upon by all authors.

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