Influence and Effect of The Hydrotalcite Added in The Pyrolysis of The Bromine-Based Plastic

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（千葉大学審査学位論文）

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Chapter1

General Introduction

1.1. Introduction

1.1.1. Status of plastic recycling

Plastic materials have long been used in society because plastic is lightweight, easily molded, durable, and can be relatively cheap [1]. Plastics are used to produce a wide range of products, including bags, bottles, accessories, furniture, chemical products, and the casings for electronic devices. As the consumption of plastic has grown, its inability to degrade in waste facilities has meant it has often been sent to landfill, decreasing the capacity of remaining landfill sites. Also, because plastic is a waste, there are serious environmental concerns attached to its disposal, such as the potential for soil and water pollution [2]. When not landfilled, waste plastic may be incinerated, but this is likely to release toxic substances, such as dioxins and furans [3]. On the other hand, it is possible to thermally decompose plastic at high temperatures to recycle the waste for it to be used as chemical feedstocks in place of those derived from fossil fuels.

In Europe, the law on the recovery and recycling of waste electrical and electronic equipment (WEEE) was introduced in 2002 [4]. This placed the responsibility for recovery and recycling of waste with the product manufacturer (extended producer responsibility, EPR). Now, when consumers visit retail stores to buy new products that are not usually reused, the old product is recycled there at the same time. This legislation was introduced to counter the alarming rise in WEEE in developed countries, reaching approximately 50 million tons annually around the world. As well as plastic, WEEE contains a number of useful resources including copper, aluminum, and even more valuable metals such as gold. Despite this, the proportion of WEEE that is recycled globally is very low. Further, a large portion of WEEE produced in developed countries is exported to developing countries for processing [5].

1.1.2. Chemical recycling and WEEE in China

In 2008 China implemented a law to restrict WEEE (The People's Republic of China Economic Circulation Promotion Law) with environmental regulations that tighten every 5 to 10 years. Following this, in 2009, China implemented an EPR and established a government-run collection and recycling system for WEEE.

In China, the majority of WEEE is dismantled in disposal plants before being sold as recycled parts and raw materials. Relatively little WEEE is repaired and resold as usable electric and electronic equipment because of difficulties in ensuring the safety of repaired products. Environmental protection has often been overlooked, which has led to high levels of pollution. Even in recycling facilities that are managed by the government, only a handful operate in an environmentally appropriate manner.

The rapid development of technology over the last 30 years has changed the structure of society through the introduction of computers, mobile phones, digital cameras, and an emerging range of smart appliances. Because plastic plays an important role in these consumer goods, addressing the impact of WEEE is an important social issue.

1.1.3. Case Study: Tirafushi Island

Floating in the Indian Ocean, Tirafushi, an island in the Maldives known as the "island of garbage" (Fig. 1) has caused serious environmental problems and is facing a serious waste problem.

Fig. 1 Landfill on Tirafushi [6]

Every day, 200 tons of refuse is brought to the island. This is in part from tourists, who produce, on average, 2.8 kg of waste, and in part from Maldives residents (who produce, on average, 7.2 kg). Because there is no incineration plant in the Maldives, materials such as glass, metal, and paper are recovered by hand and exported to countries such as India. Here, WEEE that is overlooked by the hand-sorting is incinerated with other materials, producing toxic fumes.

1.1.4. The WEEE Directive

In the EU, two relevant directives were enacted in 2003. One limits the use of hazardous substances in electrical and electronic equipment (Directive 2002/95/EC) while the other promotes the recovery from and recycling of materials from such equipment when it is discarded (Directive 2002/96/EC) (Fig. 2). One purpose of these laws is to increase the recycling and reuse of used consumer electrical and electronic equipment. The laws also aim to decrease the impact of releasing polybrominated biphenyls (PBBs), polybrominated diphenyl (PBDE ethers), lead, mercury, cadmium, chromium, and heavy metals by increasing their recovery from older WEEE and decreasing their use going forward.

However, despite these directives and the EPR, only a third of WEEE produced in the EU is reported to be properly processed within the EU; the rest is sent abroad where concerns over improper processing lead to fears of environmental and health problems.

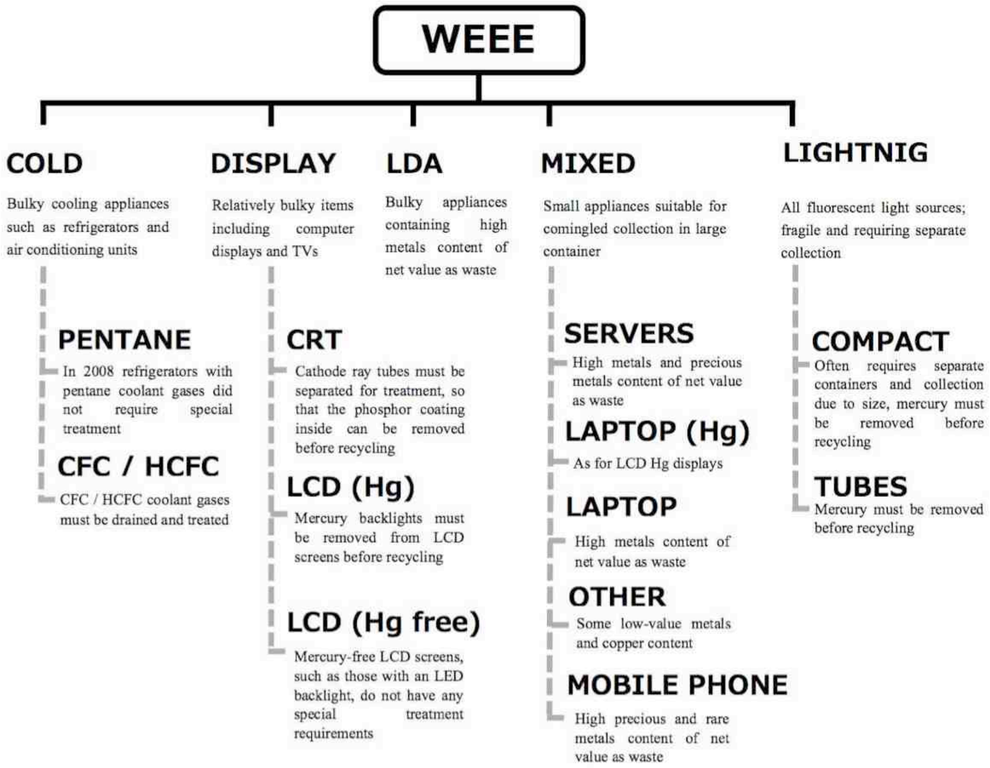

Fig. 2 Categories of WEEE [7]

1.2. Purpose of this study

1.2.1. Bromine compounds in WEEE pyrolysis product oil

The plastic used in products that become WEEE often includes a metal or a bromine compound (represented here by tetrabromobisphenol A (TBBA)) as a flame-retardant. When recycled, TBBA-containing plastics form oils that also include bromine compounds, which makes reuse of these products difficult. The problems arise because the use of bromine-containing oils releases dioxins and furan compounds, which are hazardous to humans and the environment. Therefore, urgent measures for the removal of bromine from such plastics during the recycling process are important for the recycling of WEEE.

1.2.2. Developments to date

Many studies have been carried out on the thermal decomposition of plastics. The zeolite ZSM-5 and a molecular sieve made from Red Mud have been shown to increase the yield of oil that is produced during pyrolysis of waste plastics [8,9]. However, when the plastics contain brominated flame-retardants, as in the case of WEEE, the toxicity of this oil has been found to be a particular problem [10–14]. For example, during thermal decomposition at temperatures of 300–500 °C, brominated dibenzo-dioxins and brominated furan compounds are formed [15]. Because recycling rates are currently limited by the generation of toxic by-products, the potential use of catalysts to prevent the release of halogen compounds into the oil and gas phases during the thermal decomposition of plastics has been studied [16]. For example, polypropylene, polyethylene, polystyrene, and poly-brominated compounds have been mixed with polyvinyl chloride and decomposed using calcium carbonate (calcium-C) [17]. In other work, the quality of the pyrolysis oil was improved by using a commercial hydrogenation catalyst, DHC-8 [18]. Furthermore, using two zeolite catalysts (H-USY and H-Beta) in a vapor-contact method increased the yield of oil from the thermal decomposition from 93% to 96% [19].

Given the magnitude of the yield, this work focused on decreasing the amount of bromine in the product oil and containing it instead in the residue. The following chapters center on the adsorption of plastic components onto an active carbon catalyst, and on the role of the catalyst in transforming the plastic to product oil.

1.2.3. Hydrotalcite

Although the use of activated carbon can improve the product yield and quality, it is usually mixed in with the product oil, decreasing the ease with which the oil can be used. Therefore, this work investigates hydrotalcite (HT), which has anion-adsorbing properties. HT's high capacity for anion-exchange, which is comparable to that of organic ion-exchange resins, has received much attention and has promoted HT's use as an adsorbent for the removal of various contaminants from aqueous solutions. Indeed, the adsorption properties have been studied for a wide range of inorganic anions, including borate, nitrate, fluoride, phosphate, sulfate, chromate, arsenate and selenate. HT, which is more commonly known for its use as a stomach and headache medicine, adsorbs anions according to an anion-exchange reaction [20]. HT is a layered double hydroxide with divalent Mg^{2+} and trivalent Al^{3+} anions, and a weakly bound intermediate carbonate layer that provides the anion-exchange ability (Fig.3) [21] [22]. The addition of HT to the production process has been reported to boost the yield of biodiesel from 62 to 77% [23] [24] and to be useful in the aerobic oxidation of benzyl alcohol [25].

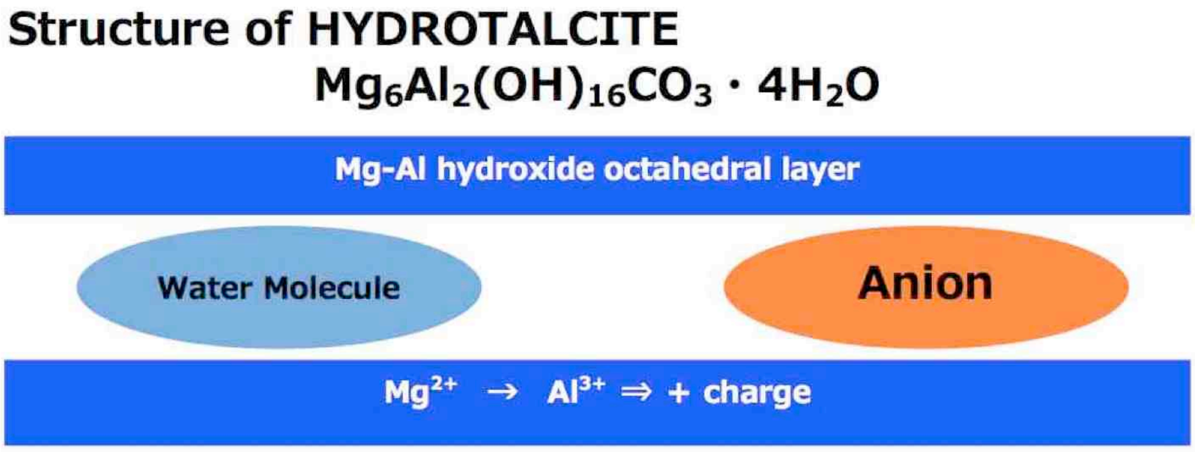

Fig. 3 Structure of hydrotalcite

1.2.4. Outline of this study

In this study, plastics are thermally decomposed in the presence of HT to produce a product oil that is free of bromine compounds, which were instead collected in the residue.

Section 2 investigates the thermal decomposition of polystyrene with added TBBA to examine the behavior of the bromine compound in the presence of zeolites and an inert material (sand).

Section 3 investigates the thermal decomposition of polystyrene, polypropylene, and polyethylene (all with added TBBA) in the presence of HT to examine the distribution of bromine compounds in the product oil.

Section 4 introduced a further additive—acrylo-nitrile-butadiene-styrene (ABS)—to examine the impact on HT and bromine compounds.

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Chapter2

2.1. Introduction

Plastics are widely used in various products, such as electrical equipment. Such products constitute large amounts of waste at the end of their lives. In recent years, the recycling technology of plastics has developed to the level that a recycling society has emerged. A variety of recycling techniques have been used in recycling waste plastic, of which pyrolysis is one of the most promising. In pyrolysis, plastic polymers are converted into gas, oil, and carbon residue for uses such as chemical feedstock and fuel [1]. There is abundant literature on the chemical recycling of waste plastics and basic research on thermal decomposition, especially using catalyst [2]–[13]; e.g., the yield of product oil via plastic pyrolysis can be increased using ZSM-5 zeolite, red mud and mesoporous molecular sieves [14], [15]. However, plastics from electrical waste contain toxic brominated flame retardants, which pose a problem particularly for recycling [16]–[20]. For example, the treatment of brominated compounds from 300 to 500 °C results in the possible formation of brominated dibenzodioxins and furans [21]. This should be avoided because of the carcinogenic character of these products. Moreover, the production of hazardous byproducts reduces the acceptance of recycling processes by society. There has been research into the preventing the release of halogen gas into oil and gas phases by pyrolysis [22], especially using additives as catalyst. For example, it was reported that polybrominated compounds mixed with polypropylene, polyethylene, polystyrene, and polyvinyl chloride can be thermally decomposed using a carbon composite of calcium carbonate (calcium-C) [23]. It was also reported that the quality of the pyrolysis oil was improved using commercial hydrogenation catalyst DHC-8 [24]. In the present study, polystyrene containing bromine compounds was pyrolyzed at 400 °C using hydrotalcite (HT) as an additive. The HT is classified as a layered double hydroxide composed of metal complex hydroxide: $[M^{2+}{}_{1-x}M^{3+}{}_{x}(OH)_2]^{x+}[(A^{n-})_{x/n} \cdot nH_2O]^{x-}$ (x = 0.2–0.33), where M^{2+} and M^{3+} are divalent Mg^{2+} and trivalent Al^{3+} metal ions, respectively, and A^{n-} is an anionic species [25]. The structure of HT is a positively charged brucite-like octahedral layer and a negatively charged interlayer containing anions and water molecules [26]. HT has received increasing attention in recent years as an ion exchanger [27]–[29], catalyst [30], [31] and a material for gas removal [32], [33]. However, there have been no studies on the pyrolysis of waste plastics with bromine compound using hydrotalcite. Additionally, for comparison, plastics with bromine compounds were pyrolyzed using sea sand and molecular sieves, which are popular additives in the pyrolysis of plastics. We investigated the effect of hydrotalcite on the pyrolysis of plastics with bromine compound.

2.2. Experimental

2.2.1. Materials

Plastic samples containing bromine (BR-PS) were prepared by mixing 20 g of PSJ polystyrene (PS) (Asahi Kasei Chemicals Corporation Co., Ltd.) and 2 g of tetrabromobisphenol A (TBBA) (Tokyo Chemical Industry Co., Ltd., Tokyo, Japan). The elemental composition of the BR-PS, which was calculated from chemical compositions of each reagent, is given in Table I.

To reduce bromine compounds in the product oil, synthetic hydrotalcite, KW-1000, (Kyowa Chemical Industry Co., Ltd.), sea sand (Wako Pure Chemical Industries, Ltd.), molecular sieve 4A (Wako Pure Chemical Industries, Ltd.) and molecular sieve 13X (Wako Pure Chemical Industries, Ltd.) were used as additives. The experimental conditions are listed in Table II.

Table I: Elemental composition of the BR-PS.

Elemental composition (wt. %)	
Carbon	85.9
Hydrogen	10.8
Bromine	3.0
Oxygen	0.28
Silicon	0.02

Table II: Experimental conditions in the study

	Experimental condition
I	PS + TBBA
II	PS + TBBA + Sea sand
III	PS + TBBA + Molecular sieve 4A
IV	PS + TBBA + Molecular sieve 13X
V	PS + TBBA + Hydrotalcite

2.2.2. Experimental apparatus and procedures

The experimental apparatus used in this study is shown in Figure 1.

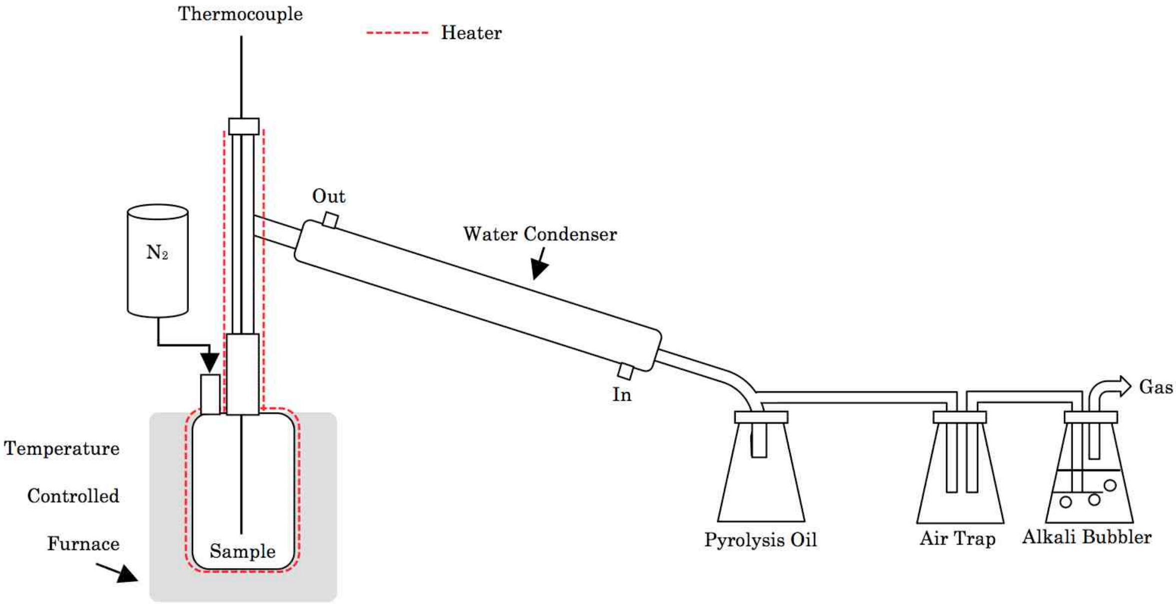

Fig.1. Experimental apparatus.

A 22-g quantity of BR-PS or a mixture of BR-PS (22 g) and additive (20 g) was added to a glass reactor. The reactor was purged with nitrogen gas at a flow rate of 50 mL/min for 60 min to remove oxygen. After oxygen substitution, the flow of nitrogen gas was stopped and the pyrolysis experiment was performed. The temperature of the plastic bed was measured as the decomposition temperature and the reactor temperature was increased to the decomposition temperature (400 °C) at a heating rate of 5 °C/min. The gases produced by pyrolysis were condensed through a cooling pipe and recovered. Non-condensable gases, which pass through the condenser, were collected in a gas pack via bubbling of alkaline aqueous solution. Residue remained in the reactor after pyrolysis. The mass balance of the pyrolysis products (oil, gas, and residue) was calculated after the experiment. The pyrolysis products obtained after experiments under each condition were analyzed.

2.2.3. Analysis

The oils were analyzed by gas chromatography/mass spectrometry (GC/MS) (Shimadzu, GC-MS-QP2010ultr) using an RTX-624 column (having thickness of 1.8μm, an inner diameter of 60 mm and a length of 0.32 mm) with pure helium as the carrier gas, and the main compounds in the oil were identified using a GC/MS spectral library. The analyses were performed at a temperature of 40 °C for 30 minutes, which was then increased to 230 °C at a rate of 5 °C/min. The structural change of the sample before and after the experiment was determined by X-ray diffraction analysis (Bruker, D2PHASER), and the morphologies of the sample before and after the experiment were observed with a scanning electron micrograph (SEM) (Hitachi High-Tech, TM3030). The alkaline aqueous solution in the bubbler trapped bromine in non-condensed gases, and bromine trapped in the bubbling solution was analyzed by ion chromatography (Shimadzu, HIP-SP). The product gas that passed through the alkaline aqueous solution was recovered by a gas pack and then analyzed using a Shim-pack column (150 mm (length) × 4.6 mm (inner diameter)) and a CDD-10Asp detector as part of a high-performance liquid-chromatography ion chromatography system.

2.3. Result and Discussion

2.3.1. Mass Balance of the Product

The product yields under each experimental condition are given in Table III. Without an additive, the yields of product oil, residue and gas were 71.0, 28.8 and 0.2%, respectively. When applying an additive, the yield of oil was the highest and that of residue was the lowest in the case of hydrotalcite. It is noted that the gas yields were lower than 1.1% under all conditions, revealing that gas was hardly generated in the pyrolysis of BR-PS.

Table III: Product yields (wt.%) under each experimental condition.

	Oil	Residue	Gas
I	71.0	28.8	0.2
II	54.1	45.2	0.7
III	68.6	31.4	0.0
IV	70.9	29.1	0.0
V	83.9	15.0	1.1

2.3.2. Analysis of the Oil Product

Components of the product oil are given in Table IV. All oil products mainly contain toluene and benzene. Components of the product oil obtained under condition I are mainly aromatic compounds, such as benzene, 1-heptene, heptane, 1-methyl-2-methylene-cyclopentane, 3-methyl-cyclooctene, 2,4-dimethyl-hexene, dimethyloctene, 2-methyloctane, 3-methylheptane, 6-methyl-2-heptane, 1-methylcyclohexene, 3-methyl-2-cyclohexen-1-ol, 2-methyl-1-heptene and toluene, and two bromine compounds, 2-bromo-2-methylpropane and 3-bromo-pentane were detected.

The results in Table IV show that bromine compounds were not detected in the oil produced under condition V. It is noted that the oils produced under conditions II, IV and V had lower molecular weight than those under conditions I and III, which means that the addition of sea sand, molecular sieves 13X and hydrotalcite promotes the decomposition of compounds with high molecular weight into compounds with low molecular weight.

2.3.3. Bromine Compounds of Residue

Bromine contents of the residue obtained under each condition are given in Figure 2. The bromine content in the residue was 2.6% without an additive and 0.5% using sea sand. With the addition of molecular sieves, the bromine content in the residue was 35–45%, which was higher than the contents under conditions I and II. Furthermore, the bromine content in the residue obtained using hydrotalcite was 90.2%, which was the highest achieved in this experiment. It is considered that bromine was trapped in the residue by the hydrotalcite, and the bromine compound was not included in the produced oil, as shown in Table IV.

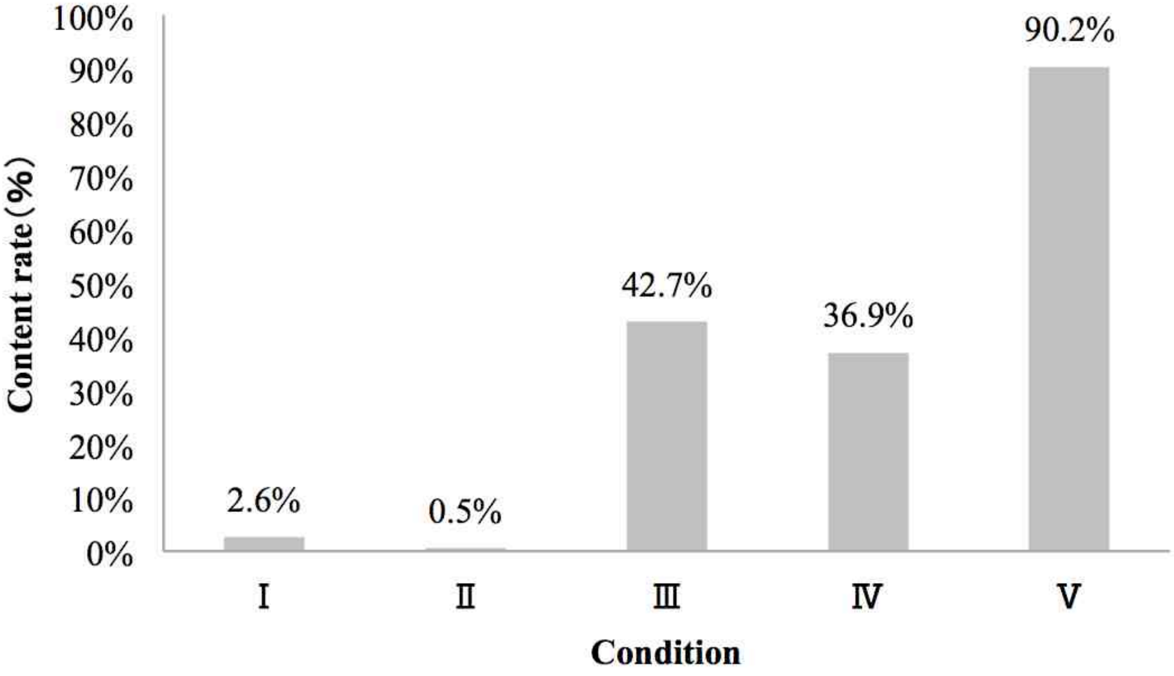

Fig. 2 Bromine contents of the residues under each condition.

Table IV: Components of product oils obtained under each experimental condition.

Compound	Formula	Condition				
		Ⅰ	Ⅱ	Ⅲ	Ⅳ	Ⅴ
3-methyl pentane	C_6H_{14}	nd	○	○	○	○
3-methyl-2-pentene	C_6H_{12}	○	○	○	○	○
2,3-dimethyl-butene	C_6H_{12}	○	○	nd	○	nd
4-methyl-1,3-pentadiene	C_6H_{10}	nd	nd	nd	nd	○
2-bromo-2-methylpropane	C_4H_9Br	○	○	○	○	nd
3,4-dimethyl-2-pentene	C_7H_{14}	nd	○	○	○	○
1-methylcyclopentene	C_6H_{10}	○	○	○	○	○
3-heptene	C_7H_{14}	nd	○	○	○	○
3-methylhexane	C_7H_{16}	○	○	○	○	○
Benzene	C_6H_6	○	○	○	○	○
1-heptene	C_7H_{14}	○	nd	○	nd	nd
Heptane	C_7H_{16}	○	nd	○	nd	nd
3-methyl-2-hexene	C_7H_{14}	○	nd	○	nd	nd
4-methyl-2-hexene	C_7H_{14}	○	nd	○	nd	nd
2-heptene	C_7H_{14}	○	nd	○	nd	nd
Methylcyclohexane	C_7H_{14}	○	nd	○	nd	nd
Ethylcyclopentane	C_7H_{14}	○	nd	○	nd	nd
2-methylheptane	C_8H_{18}	○	nd	○	nd	nd
3-bromopentane	$C_5H_{11}Br$	○	nd	○	nd	nd
1-methylcyclohexene	C_7H_{12}	○	nd	○	nd	nd
2-methyl-1-heptene	C_6H_{12}	○	nd	○	nd	nd
Toluene	C_7H_8	○	nd	○	nd	nd

○: detected, nd: not detected

X-ray diffraction patterns before and after the experiment conducted under condition V are shown in Figure 3. Before the experiment, peaks of hydrotalcite, TBBR and PS were identified. After the experiment, these peaks disappeared, and new peaks corresponding to the oxides $MgAl_2O_4$ and $MgAlSi_4O_{10}(OH)\cdot4H_2O$ appeared, owing to the formation of these oxides from hydrotalcite and silica in PS.

(a)

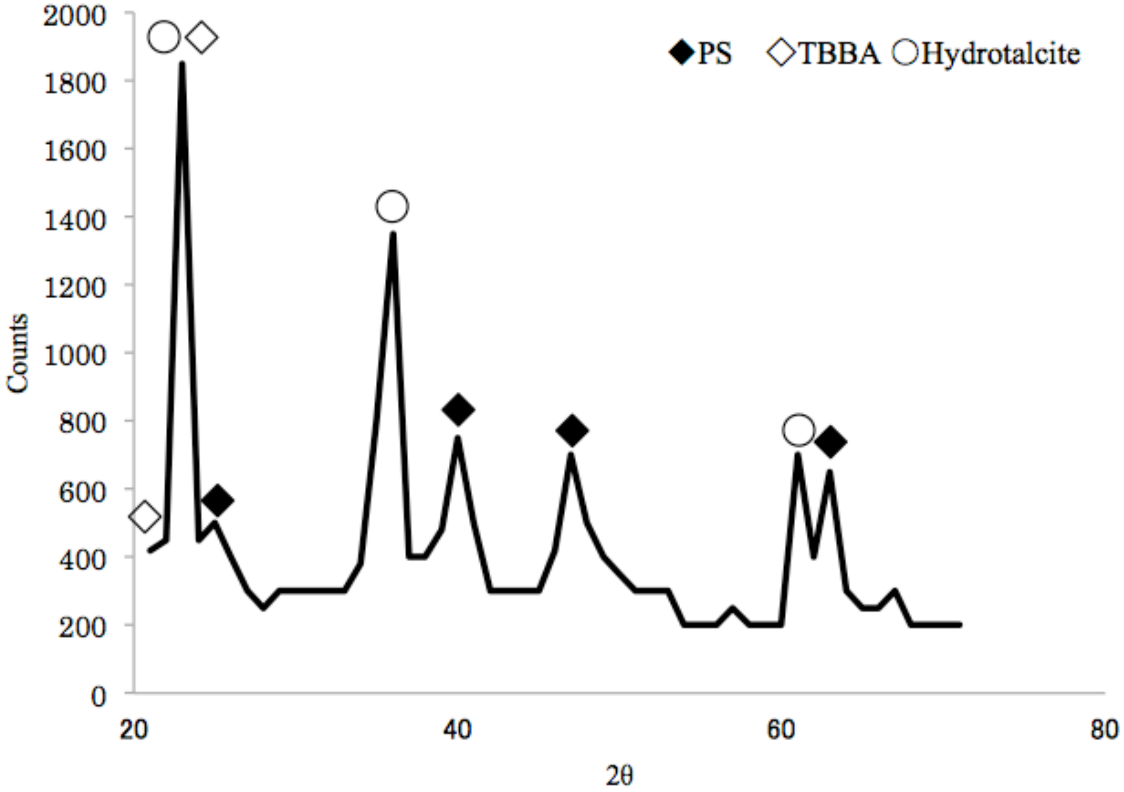

Fig. 3 (a) X-ray diffraction patterns of the samples before the experiment conducted under condition V.

(b)

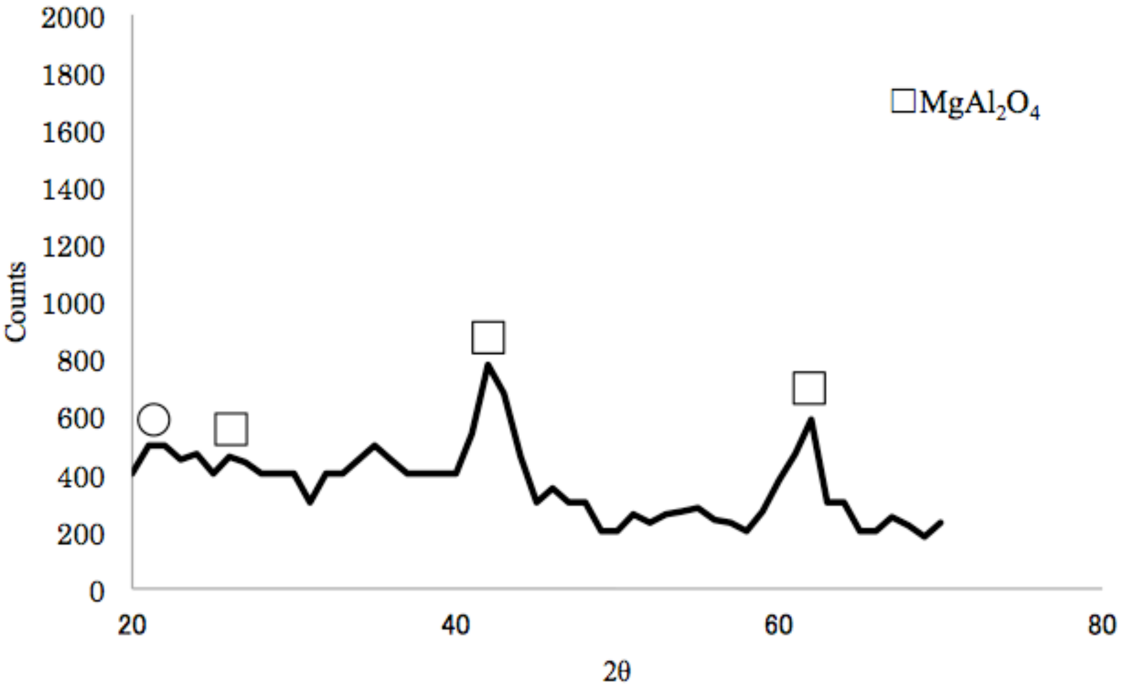

Fig. 3 (b) X-ray diffraction patterns of the samples after the experiment conducted under condition V.

SEM images of the sample (a) before and (B) after the experiment are shown in Figure 4. Many particles were observed before the experiment and large particles with small particles on their surfaces were observed after the experiment. It may be considered that large particles are Mg-Al oxides and small particles, which may be bromine compounds, were adsorbed and precipitated on the surface of oxides.

(a)

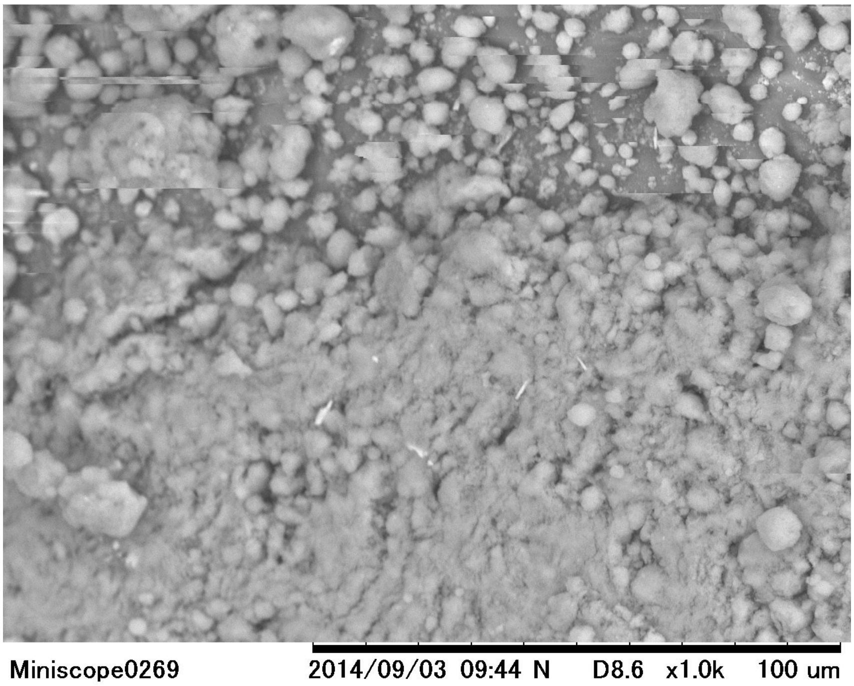

Fig. 4 (a) SEM image of the sample before the experiment conducted under condition V.

(b)

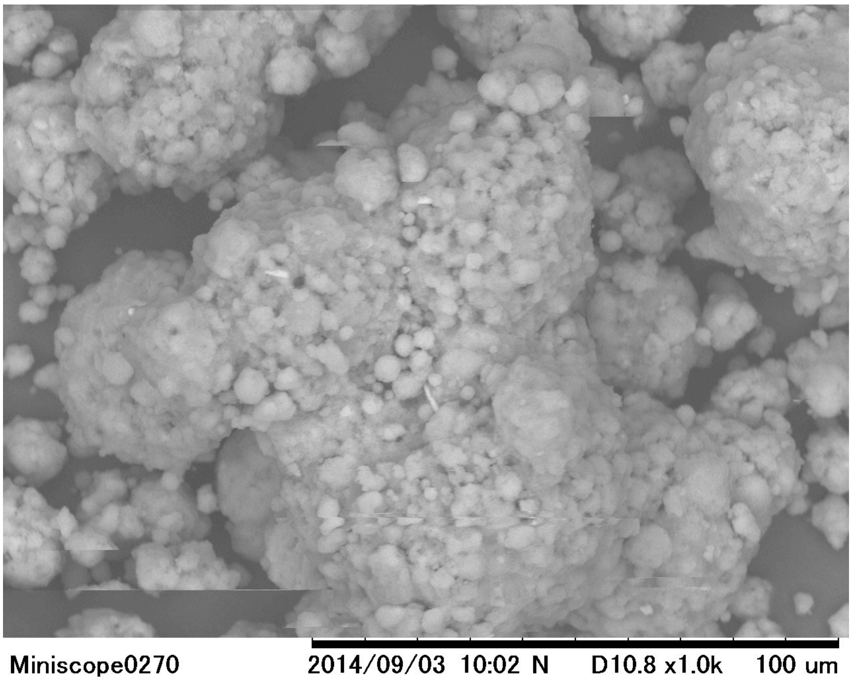

Fig. 4 (b) SEM image of the sample after the experiment conducted under condition V.

2.3.4. Gas Production

Bromine contents of the gas under each condition are given in Table V. The bromine content in 20 g of BR-PS was 1843 mg, and the content in the gas phase was 0–0.9 mg. Therefore, bromine was mainly distributed in the residue and product oil by pyrolysis in this experiment.

The amounts of CO_2, CH_4, C_3H_6 and C_3H_8 in the productive gas are given in Table VI. Gases with high molecular weight were produced without an additive but not detected with an additive. It is noted that CO_2 in the gas originated from CO_2 in the layered structure of hydrotalcite.

Table V: Bromine content in gas under each condition.

	Bromine content (mg)
I	0.3
II	0.0
III	0.7
IV	0.9
V	0.4

TABLE VI: Amounts of CO_2, CH_4, C_3H_8 and C_3H_6 in the gas (wt. %).

	CO_2	CH_4	C_3H_8	C_3H_6
I	nd	nd	37.6	53.0
II	nd	nd	nd	nd
III	nd	nd	nd	nd
IV	nd	nd	nd	nd
V	0.2	nd	nd	nd

○: detected, nd: not detected

2.4. Conclusion

We investigated methods of reducing the content of bromine compounds in product oil obtained by pyrolysis of bromine-based plastic. The oil produced from PS resin containing brominated flame retardants by pyrolysis using hydrotalcite did not contain bromine compounds. Additionally, the production yield of oil was greater and the capture of bromine in the residue was higher using hydrotalcite than using sea sand and molecular sieves. These results suggest that hydrotalcite is an excellent additive for oil production from waste plastics by pyrolysis.

2.5. Reference

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Chapter3

3.1. Introduction

Plastics derived from fossil fuels are used in a number of chemical products, leading to a large amount of waste after use. The recycling of waste plastics includes thermal or chemical recycling, but there is also material recycling. Reducing the amount of fuel using waste plastics by chemical recycling is one of the various recycling waste plastics that has been attracting attention. However, chemical products, such as a flame retardant, are added, and producing a product oil containing a halogen compound is a problem for efficient fuel utilization. By thermal decomposition, plastic is converted to a gas for use as a chemical raw material, as well as in fuels, oils, and as the residual carbon [1]. There is much literature regarding the basic research and chemical recycling on the thermal decomposition of waste plastic using a catalyst [2]-[13]. For example, ZSM-5 zeolite, the red mud mesoporous molecular sieve, was used in the thermal decomposition of plastics, and the product oil yield was increased [14][15]. However, brominated flame retardants are toxic, which is a particular problem when recycling waste plastics [16]-[20]. For example, the treatment of brominated compounds from 300 to 500 °C results in the possible formation of brominated dibenzodioxins and furans [21]. This generation of toxic by-products prevents the promotion of social recycling. Using additives as a catalyst during thermal decomposition has shown to prevent the release of halogen gas in the oil and gas phases [22]. For example, polystyrene (PS), polypropylene (PP), polyethylene (PE), and polyvinyl chloride mixed with a poly-brominated compound can be decomposed using the carbon composite of calcium carbonate (calcium–C) [23]. Moreover, the quality of pyrolysis oil can be improved using a commercial hydrogenation catalyst, DHC-8 [24]. Furthermore, the yield of product oil from thermal decomposition using a catalyst was reported to improve to 96% from 93% when using two types of zeolite catalysts, H-USY and H-Beta, in a vapor contact method [25]. We previously reported to reduce the content of bromine compounds contained in the product oil with the addition of hydrotalcite (HT) in the thermal decomposition of brominated PS [26]. HT is classified as a layered double hydroxide compound containing the metal complex hydroxide of an anionic species, Mg^{2+} and Al^{3+}, host layer and an interlayer of a guest layer [27] [28]. HT has been an increasing focus of research, including use as ion exchangers [27]-[30], and as a catalyst [31] [32] in gas removal [33] [34]. The high anion exchange capacity of HT organic ion-exchange resins has received much attention when utilized as an adsorbent for the removal of various contaminants from aqueous solutions. The adsorptions of borate, nitrate, fluoride, and phosphate have been studied as well as inorganic anions such as sulfates, chromates, arsenates, and selenates. The adsorption mechanism of anions to the HT has been shown to occur by the interlayer forming outer sphere complexes in an anion exchange reaction [35]. Moreover, HT has been attracting attention as a catalyst. For example, in biodiesel fuel production, a yield increase from 62% to 77% has been reported [36] [37]. Furthermore, the catalytic activity has been reported in the aerobic oxidation of benzyl alcohol using HT [38]. In this study, the thermal decomposition of plastics was used to investigate the effect of HT in reducing the bromine content in the product oil. The thermal decomposition at 400 °C followed the similar conditions required to convert waste plastic to fuel.

3.2. Experimental

3.2.1. Materials

PSJ PS (Asahi Kasei Chemicals Corporation), PP (Teijin Co., Ltd.), and high density PE (Asahi Kasei Chemicals Corporation) in 20 g amounts were mixed with 2 g of tetrabromobisphenol A (TBBA; Tokyo Kasei Corporation) to simulate a bromine-containing plastic resin, and the corresponding samples were denoted as BR-PS, BR-PE, and BR-PP, respectively. HT (DHT-4A; Kyowa Chemical Industry Co. Ltd.) was used an additive by mixing 20 g with a bromine-containing plastic sample (22 g). The experimental conditions are shown in TABLE I.

TABLE I Experimental conditions in this study

Sample	Experimental condition
I	PS + TBBA
II	PS + TBBA + HT
III	PP+ TBBA
IV	PP + TBBA + HT
V	PE + TBBA
VI	PE + TBBA + HT

3.2.2. Experimental apparatus and procedures

The experimental apparatus used in this study is shown in Fig.1. The sample (42 g or 22 g) was placed in a glass reactor, and oxygen was removed from the reactor by flushing with nitrogen gas at 50mL/min for 60 min. The temperature of the sample chamber of the glass reactor was measured using a thermocouple, and the decomposition temperature of 400 °C was achieved at a heating rate of 5 °C/min. At 400 °C, the apparatus was allowed to cool. Gas generated during the pyrolysis was recovered as it passed through the cooling tube and condensed as the product oil. Non-condensable gas was collected in a gas pack by bubbling through an alkaline aqueous solution. A bromine alkaline generated gas bromide ions in the solution, and the gas in the gas pack was measured as a decomposition product gas.

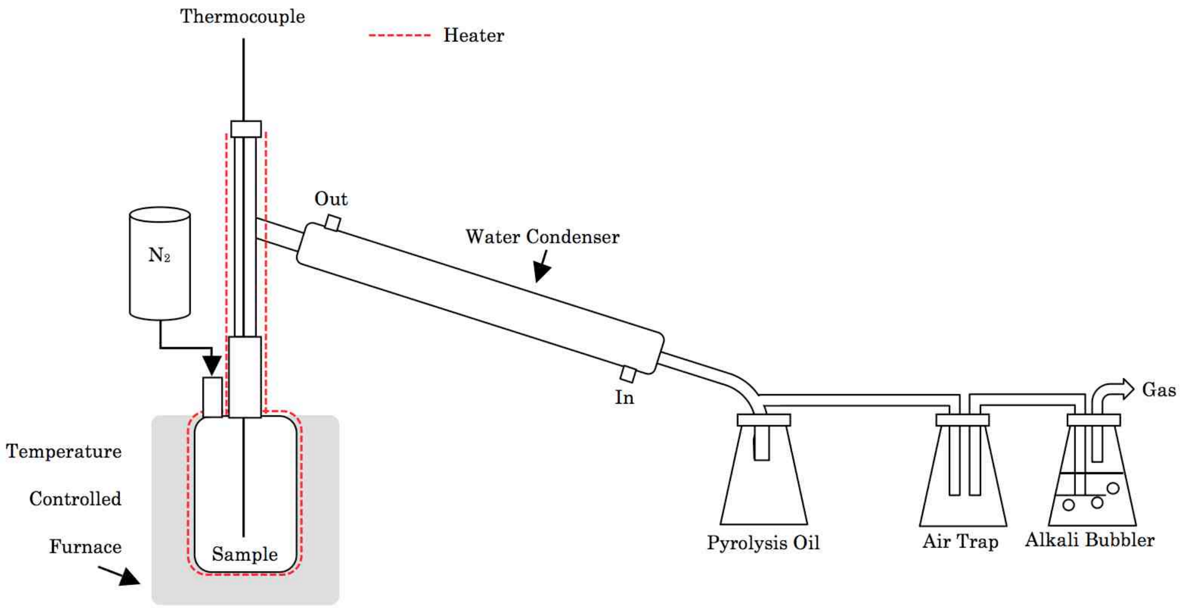

Fig.1 Experimental apparatus

3.2.3. Analysis

The product oil was diluted 100 times with hexane (Wako Pure Chemical Industries) and analyzed by comparing the peaks obtained using gas chromatography mass spectrometry (GC-MS). The main compounds were identified using the GC-MS spectral library. Pure helium was used as a carrier gas. A Rtx-1 column (inner diameter 0.25 mm and film thickness 0.25 μm) was used for analysis on a Shimadzu GCMS-QP2010ultra. Analysis was performed by increasing the temperature from 40 °C to 230 °C at a rate of 5 °C/min for 30 min. The alkaline aqueous solution that trapped any non-condensable gases were diluted 100-fold with ultrapure water and analyzed by ion chromatography. A Shim-pack column (150 L × 4.6), detector CDD-10Asp on a Shimadzu HPLC ion chromatography system was used. The residue in the sample chamber was analyzed using a Bruker QUANTAX energy-dispersive X-ray spectrometer attached to a scanning electron microscope (SEM; Hitachi High-Tech TM3030).

3.3. Results and Discussion

3.3.1. Product oil yield

The product oil yields obtained by pyrolysis are shown in Fig.2. The yield of the product oil for the plastics without HT were in the order BR-PP> BR-PS> BR-PE. In all of brominated plastics, an increase in product oil yield was observed by the addition of HT.

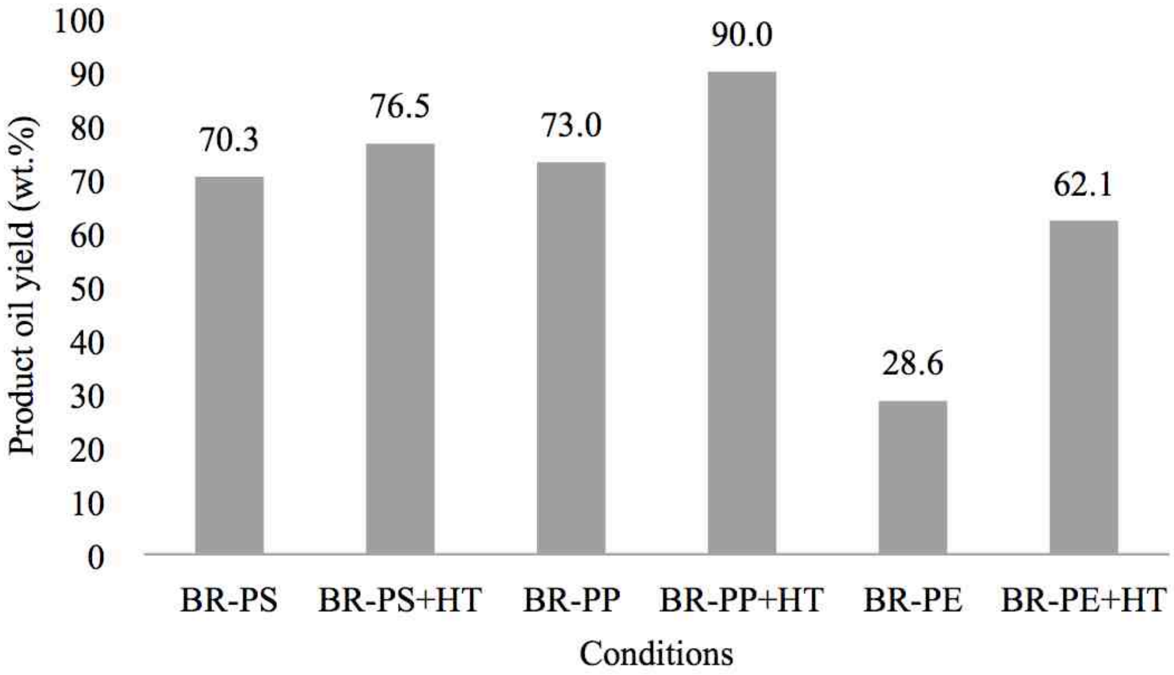

Fig. 2 Changes in product oil yield

BR-PE+HT showed a yield twice that of BR-PE, which was because of the catalytic action of HT [36] [37]. Although gas was generated in the thermal decompositions, its volume was below 1 L in all experiments.

3.3.2. Analysis of the product oil

The results of the obtained product oil were analyzed by GC-MS. The thermal decomposition of BR-PS produced toluene, ethylbenzene, styrene, benzene, and phenol, as well as 1-bromo ethyl benzene and 3-bromo-4-hydroxy phenyl ethanone as bromine compounds as shown in Fig.3 (a). When HT was added, the bromine compounds were not detected, and toluene, o-xylene, and styrene were the main compounds detected as shown in Fig.3 (b).

(a)

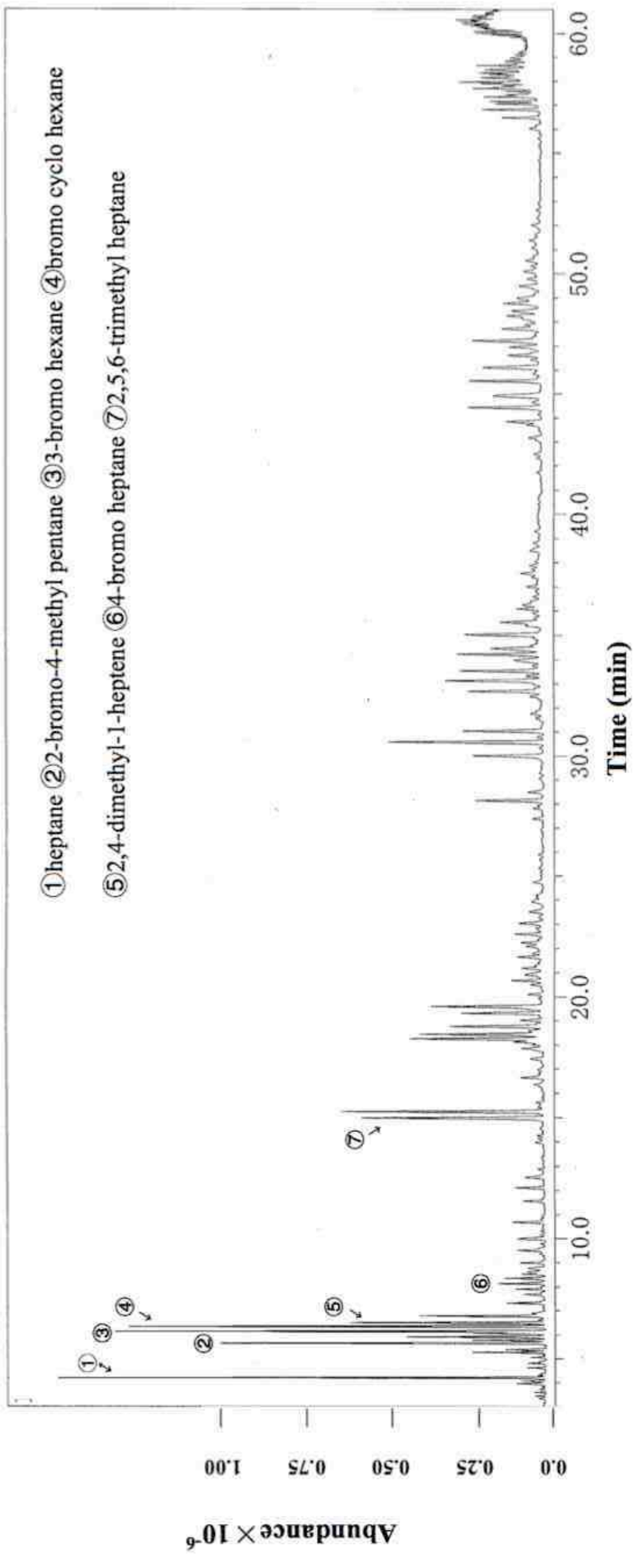

Fig. 3 (a) GC-MS chromatograms of the product oils after pyrolysis for BR-PS.

(b)

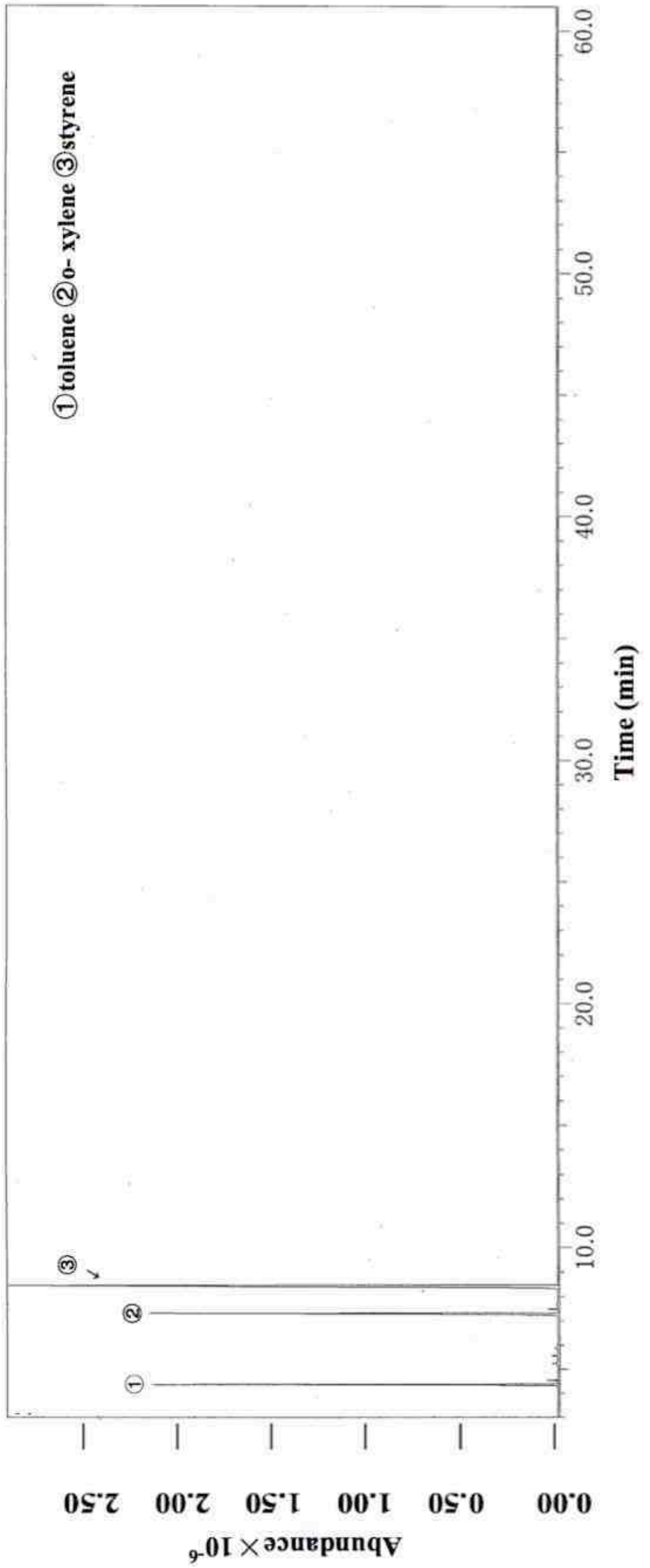

Fig. 3 (b) GC-MS chromatograms of the product oils after pyrolysis for BR-PS+HT.

From the BR-PP chromatogram, heptane, 2.5.5-trimethyl heptane, 4.6-dimethyl dodecane, propyl cyclohexane, 2,4-dimethyl-1-heptene, 2,6-dimethyl-3-heptene, and 1,3,5-trimethyl cyclohexane, as well as bromine compounds 2-bromo-4-methyl pentanone, 3-bromo hexane, bromo cyclo hexane, and 4-bromo heptene were detected as shown in Fig.4 (a). Upon addition of HT, the bromine compounds were not detected. Toluene, phenol, 2.4- dimethyl-1-heptene, and 2.5.6- trimethyl heptane were detected as the main compounds as shown in Fig.4 (b).

(a)

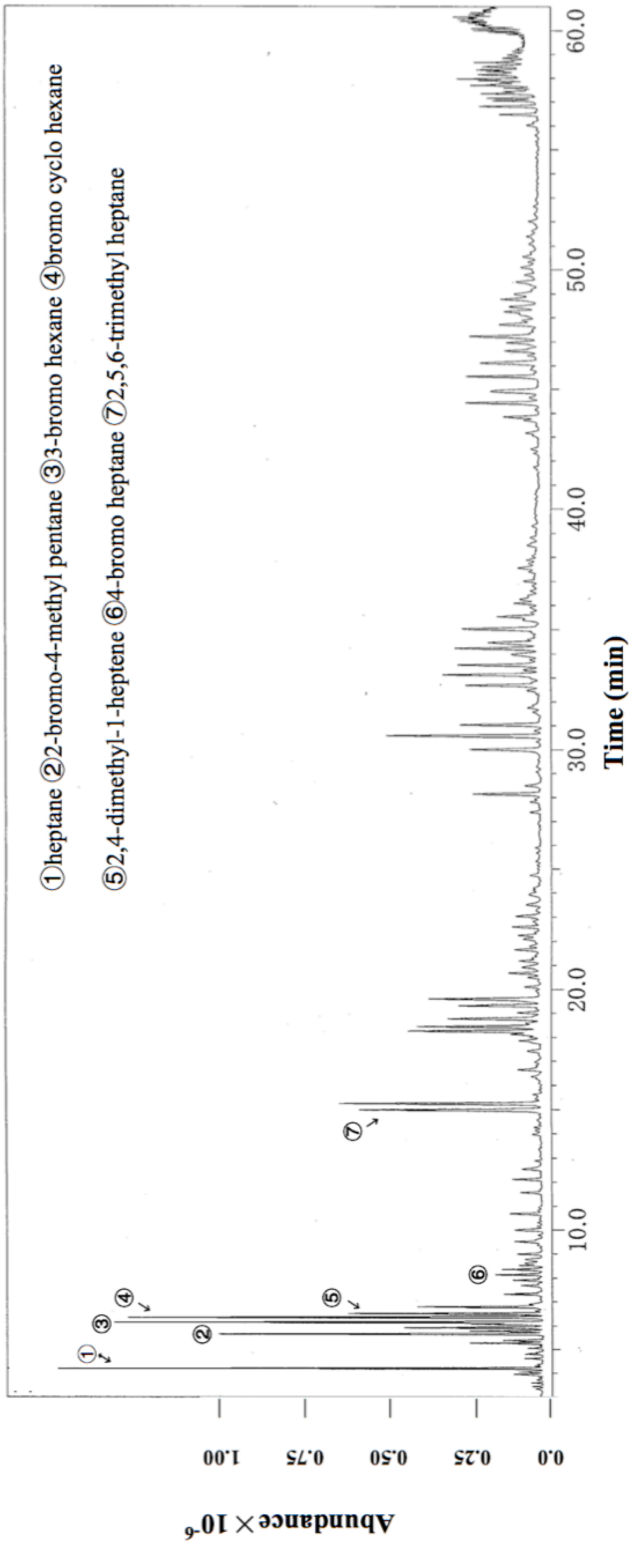

Fig. 4 (a) GC-MS chromatograms of the product oils after pyrolysis for BR-PP.

(b)

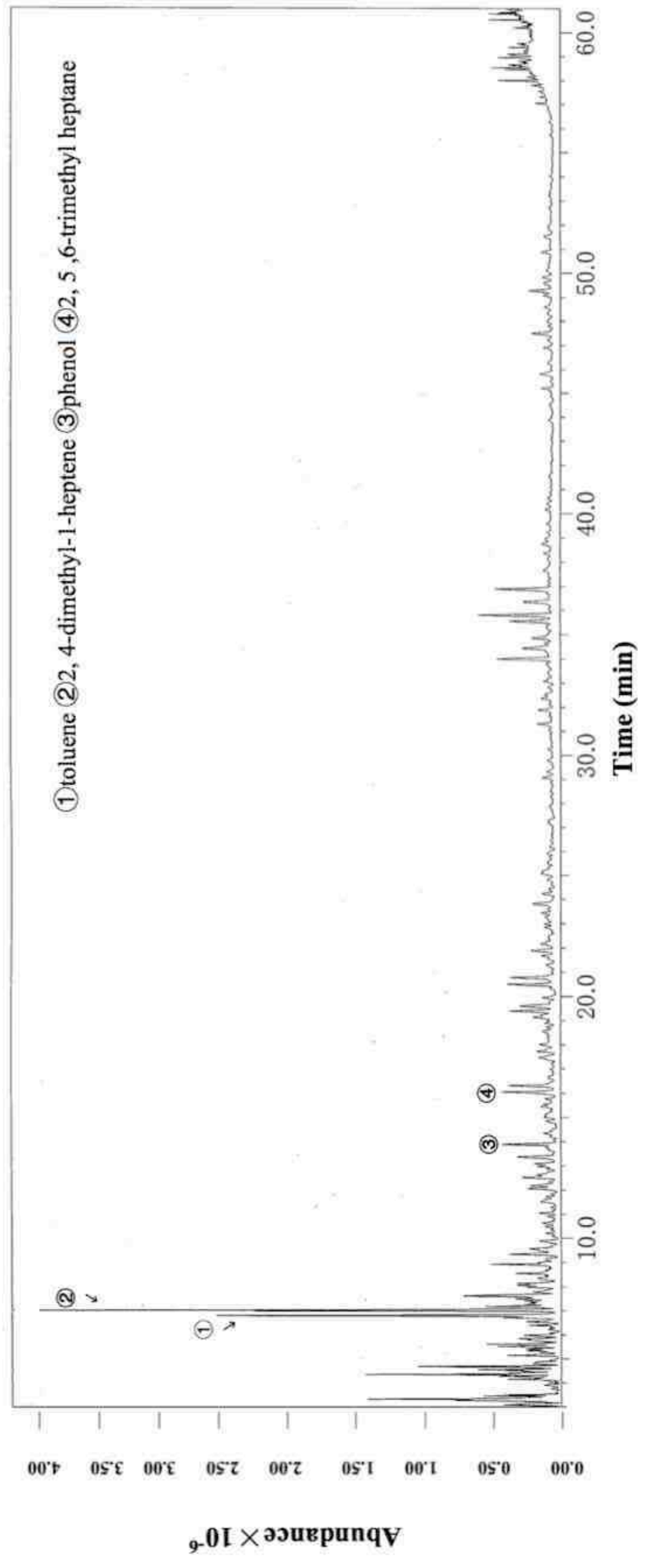

Fig. 4 (b) GC-MS chromatograms of the product oils after pyrolysis for BR-PP+HT.

From the BR-PE chromatogram, 1-octene, n-octene, 1-nonene, phenol, 1-decane, dodecane, undecane, tridecane, tetradecane, heptadecane, and hexadecane, as well as bromo cyclohexane were detected as shown in Fig. 5 (a). Upon addition of HT, no bromine compounds were detected. Toluene, n-octene, o-xylene, 1-decane, dodecane, undecane, tridecane, tetradecane, heptadecane, and hexadecane were detected as shown in Fig. 5 (b).

(a)

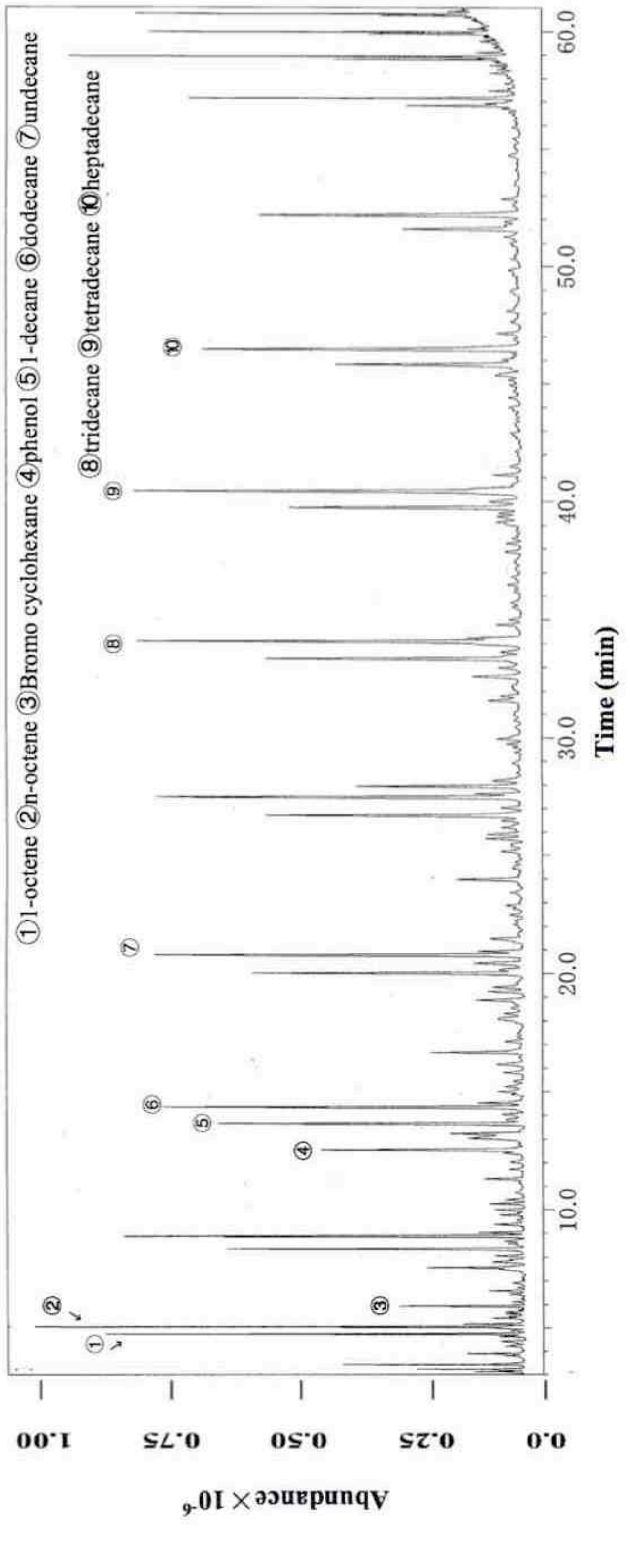

Fig. 5 (a) GC-MS chromatograms of the product oils after pyrolysis for BR-PE.

(b)

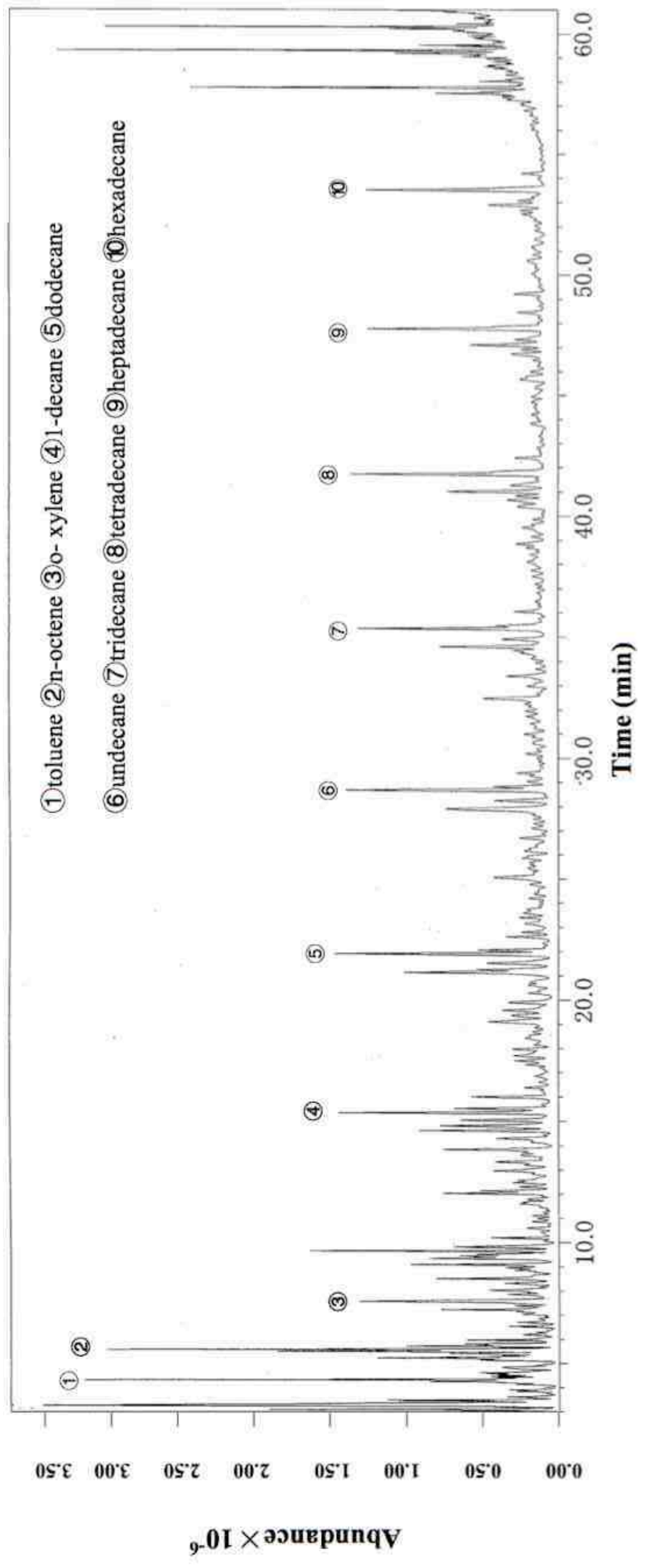

Fig. 5 (b) GC-MS chromatograms of the product oils after pyrolysis for BR-PE+HT.

3.3.3. Bromine content in the residue

The surface of each residue sample was analyzed using energy-dispersive X-ray spectroscopy coupled with SEM, which was applied to the residue after pyrolysis to examine any bromine remaining in the residue. The results are shown in the element distribution maps in Fig. 6.

(a)

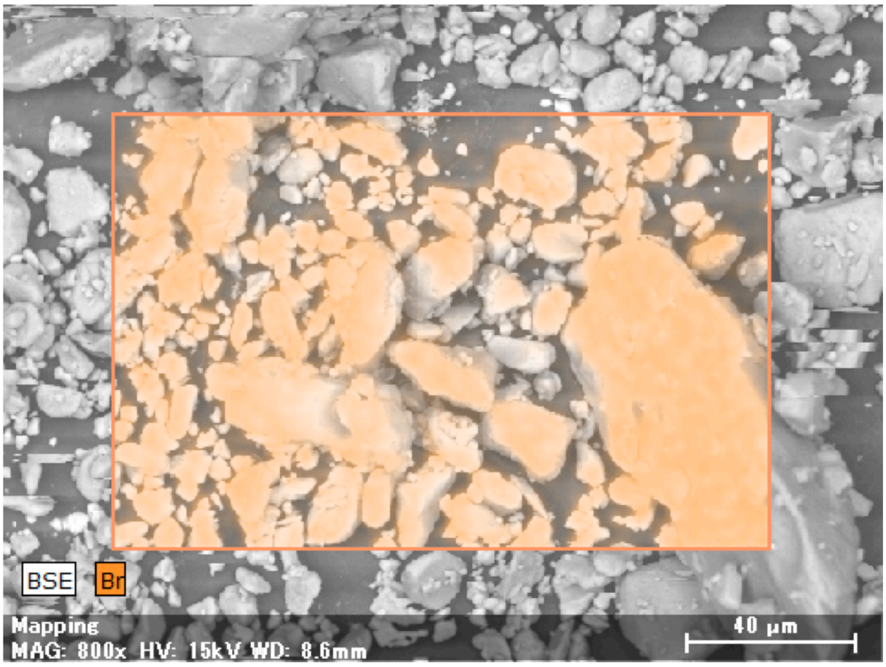

Fig. 6 (a) Energy-dispersive X-ray spectroscopy images of BR-PS.

(b)

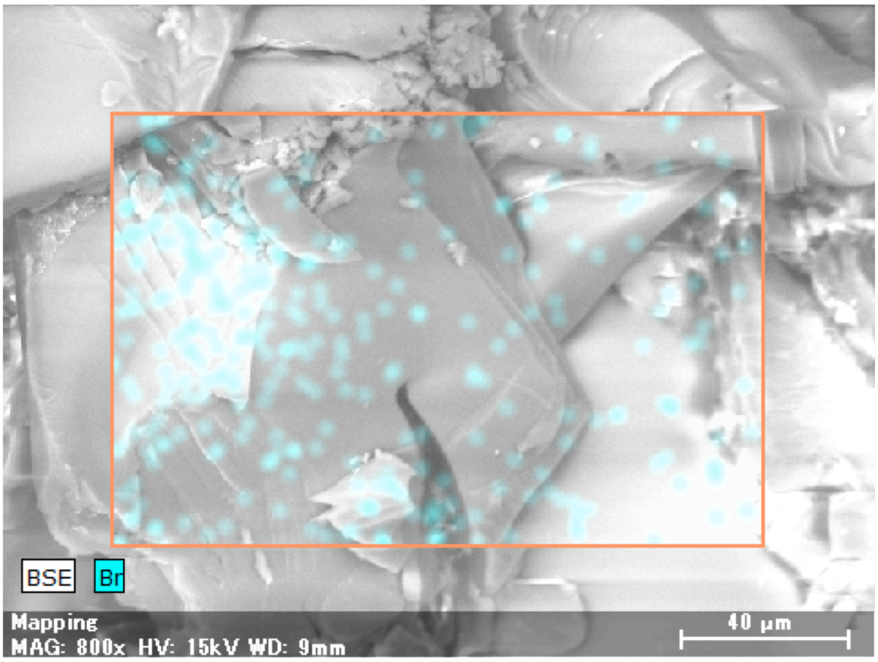

Fig. 6 (b) Energy-dispersive X-ray spectroscopy images of residue of BR-PS.

(c)

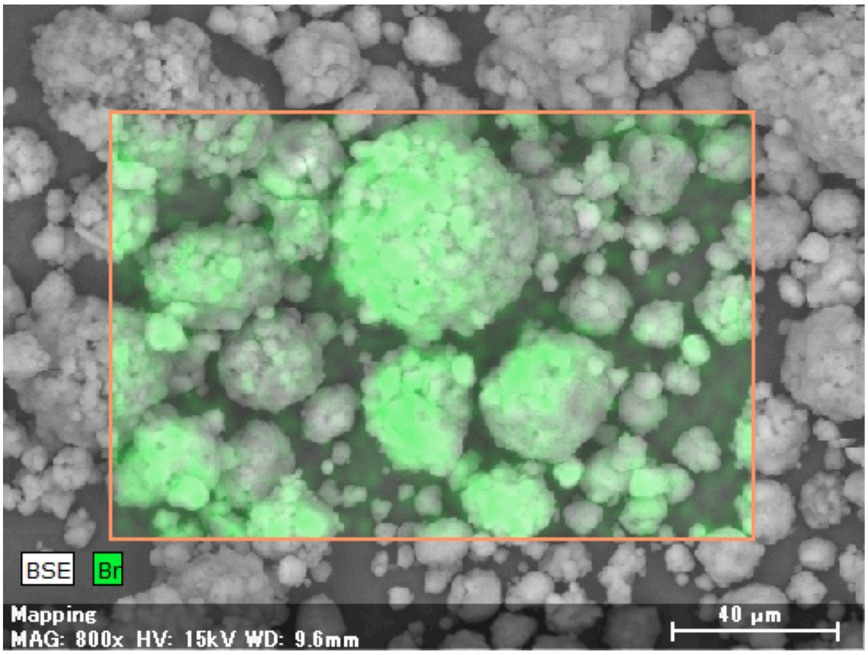

Fig. 6 (c) Energy-dispersive X-ray spectroscopy images of residue of BR-PS+HT.

(d)

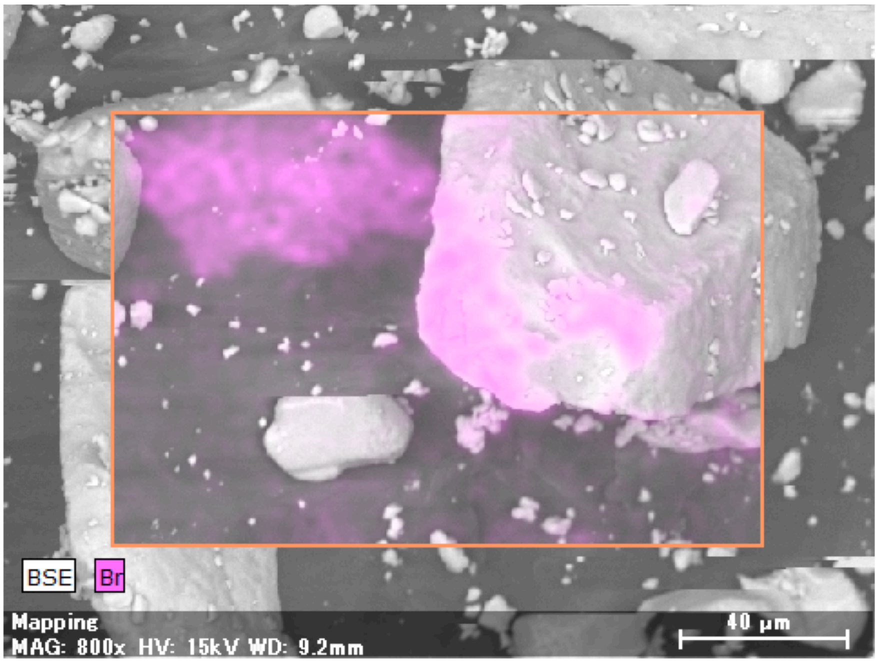

Fig. 6 (d) Energy-dispersive X-ray spectroscopy images of BR-PP.

(e)

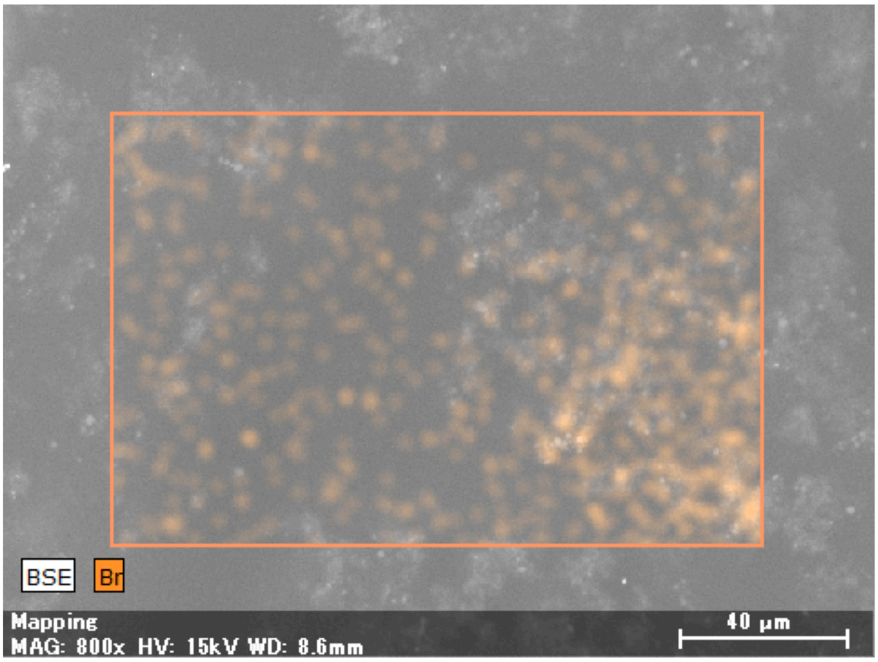

Fig. 6 (e) Energy-dispersive X-ray spectroscopy images of residue of BR-PP.

(f)

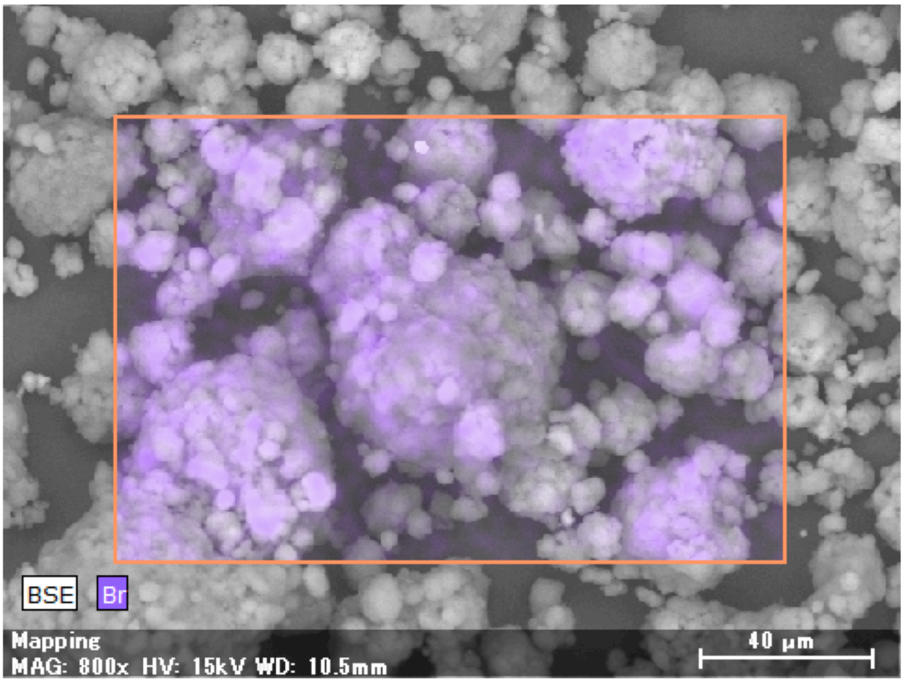

Fig. 6 (f) Energy-dispersive X-ray spectroscopy images of residue of BR-PP+HT.

(g)

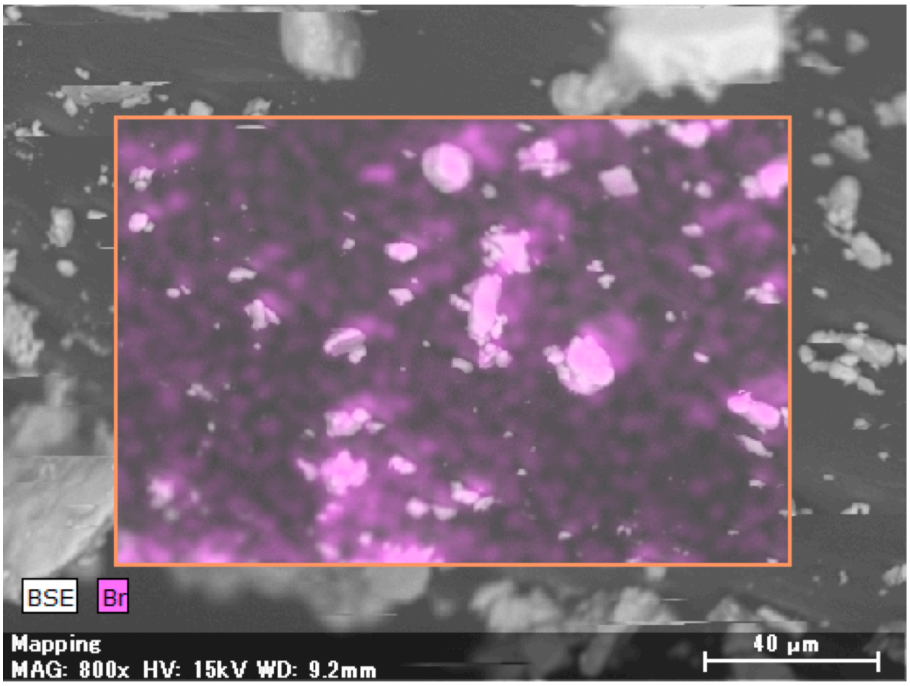

Fig. 6 (g) Energy-dispersive X-ray spectroscopy images of BR-PE.

(h)

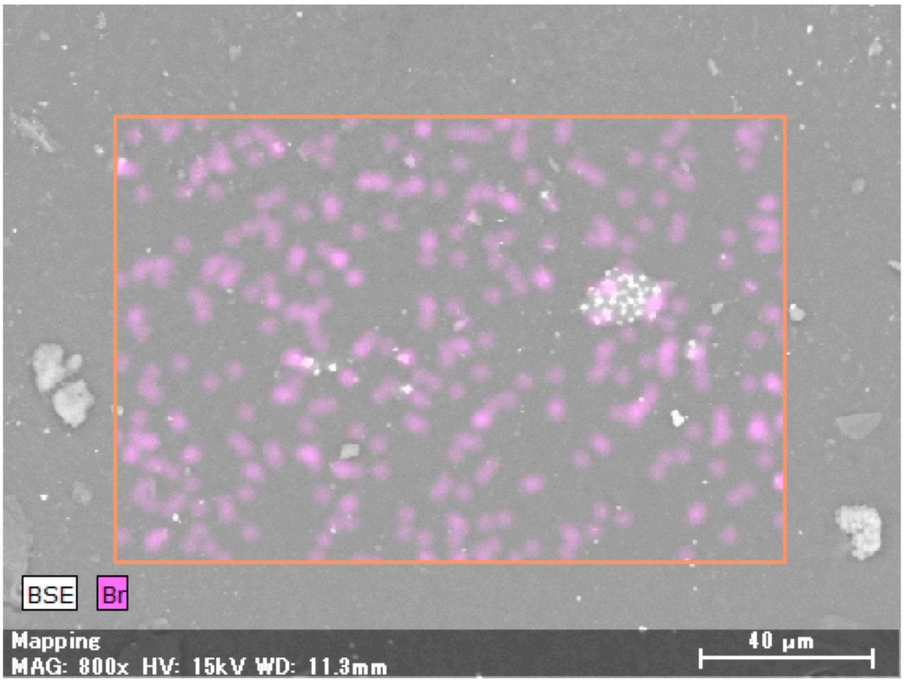

Fig. 6 (h) Energy-dispersive X-ray spectroscopy images of residue of BR-PE.

(i)

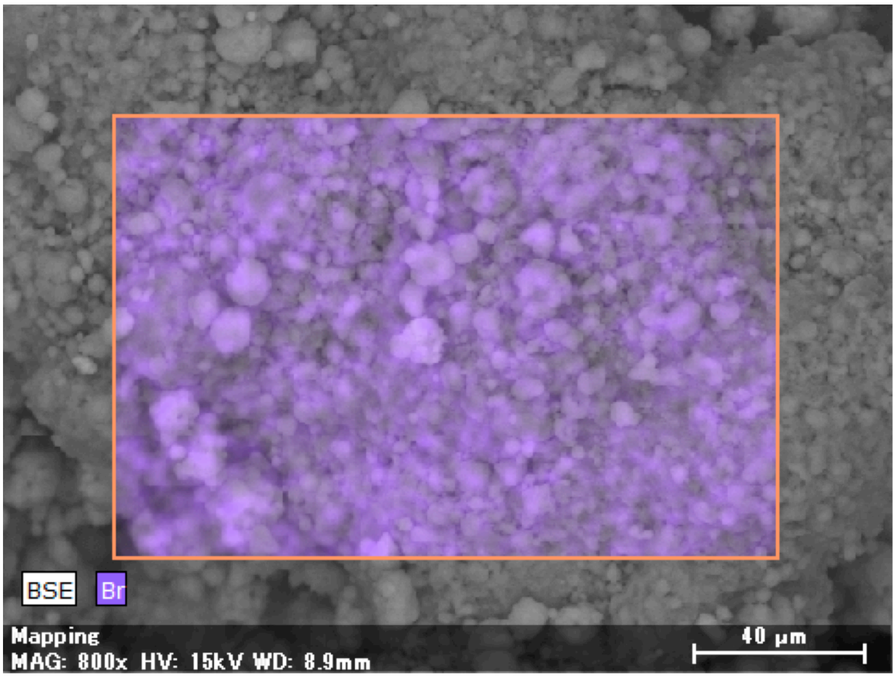

Fig. 6 (i) Energy-dispersive X-ray spectroscopy images of residue of BR-PE+HT.

The simulated bromine-containing samples before pyrolysis, BR-PS, BR-PP, and BR-PE, showed similar bromine distributions on the particle surface (Figs. 6 (a), (d), and (g)). The residue after the pyrolysis showed scattered bromine distributions at lower concentrations than those before pyrolysis (Fig. 6 (b), (e), and (h)). Upon the addition of HT to the samples and after pyrolysis, the bromine content on the particle surfaces were uniformly distributed (Fig. 6 (c), (f), and (i)). In the cases of samples without HT addition, bromine was not left in the residue, whereas in the cases of those with HT, bromine remained in the residue, indicating that bromine generated by the thermal decomposition was captured by HT.

3.3.4. Analysis of the generated gas

The analysis results of gas generated by pyrolysis are shown in Fig.7 and TABLE II. Only the generated gas of the simulated bromine-containing samples contained bromine. Although there are cases where the gas from the degradation of plastics contained other compounds, such as H_2 and CH_4, in this study, their presence in the samples without HT was not confirmed (Table II). For all of the samples with added HT, bromine was not detected in the gas, whereas as other compounds, particularly H_2 and CH_4, were detected. These result support the previous results that the bromine was captured by HT in the thermal decomposition reaction, and bromine was not released into the generated gas.

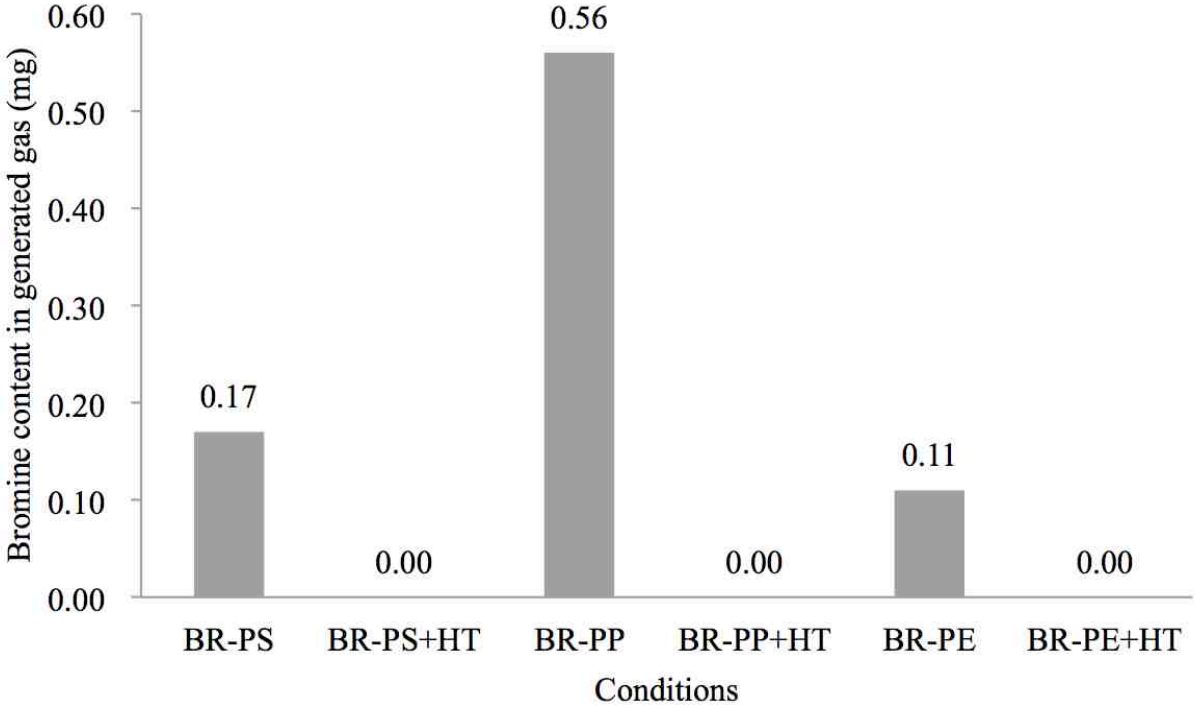

Fig. 7 Bromine content in the generated gas

TABLE II Amounts of H_2, CO_2, CH_4, C_2H_4 and C_2H_6 in the gas (wt. %)

	H_2	CO_2	CH_4	C_2H_4	C_2H_6
I	nd	nd	nd	nd	nd
II	24.6	9.9	5.1	nd	nd
III	nd	nd	nd	nd	nd
IV	32.2	8.0	18.5	2.4	6.4
V	nd	nd	nd	nd	nd
VI	67.9	2.0	19.5	3.4	5.8

○: detected, nd: not detected

3.4. Conclusion

In this study, we examined a method of reducing bromine compounds in the product oil obtained by the thermal decomposition of bromine-containing PS, PP, and PE samples using HT. We successfully obtained product oil containing no bromine compounds after the thermal decomposition of brominated plastic samples with the addition of HT. The yields of product oil obtained from samples with HT also greatly increased. Therefore, plastics containing brominated flame retardants can be thermally decomposed by the addition of HT without emitting toxic bromine compounds into the product oil or generated gas. The resolution of HT is high, which is because of its catalytic effect. The residue of samples with HT contained concentrated bromine, and the obtained product oil did not contain bromine. The thermal decomposition of PS with HT has been previously shown to reduce the bromine compound content in the product oil, and the findings in this study further develop this use of HT in waste plastic recycling.

3.5. Reference

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Chapter4

4.1. Introduction

Electrical and electronic equipments (EEEs) are ubiquitous in our society, and have increasingly shorter lifespans as they become outdated and are replaced by newer models. EEEs constitute not only of computers, mobile phones, hair dryers, or refrigerators, but also cathode ray tubes [1]. These EEEs are subsequently considered as waste electrical and electronic equipments (WEEEs) at the end of their lifespan. Hence, the treatment of WEEEs has gained considerable importance [2]. In the European Union, the amount of WEEE generated per capita in 2005 was 17 kg that corresponds to an estimated 8.3–9.1 million tons of waste [3]. The EU has recently introduced legislation aimed to encourage reuse of WEEE and recycling to reduce the amount of WEEE sent to landfills and incineration [4]. These products contain many materials that can be recycled, such as glass or metal. However, the remaining components that can constitute 15 types of plastics currently make the recycling process difficult [5]. Chemical recycling of plastics by thermal decomposition of WEEE has attracted interest as a promising technology. Upon thermal decomposition, the plastic polymer is converted into oil, residual carbon, and gases, which can be used as a chemical raw material and fuel [6]. Furthermore, there is a rich literature on basic research and chemical recycling of waste plastic based on thermal decomposition in the presence of a catalyst [7]–[18]. WEEE plastics typically consist of a flame retardant containing halogen compounds, and thus require special handling. Flame retardants can reduce the flammability of plastics, however, they represent a health hazard to humans owing to their toxic polybrominated compound components. Examples of such toxic components include polybrominated dibenzo-p-dioxins and polybrominated dibenzofurans [19]. The main plastic components in WEEE are acrylonitrile–butadiene–styrene (ABS) and high impact polystyrene (HIPS).

Additionally, antimony trioxide is typically present as a synergist for the bromine-based flame retardant compounds. Is a technology for recycling the plastic of WEEE from hazards to health of these compounds research. In particular, extensive studies on the thermal decomposition of ABS [20]–[24], the use of catalyst [25]–[30], and the use of ammonia as a reducing agent [31], [32] have been carried out. As reported in the literature, the pyrolysis of brominated flame retardants-containing ABS in tubular reactors affords the release of bromine from the middle distillate and heavy oil component [23]. Moreover, studies on the thermal degradation of ABS using semi-batch reactors showed that the brominated flame retardant components could be converted into residual carbon [21]. Another study examined the thermal decomposition of tetrabromobisphenol A, a brominated flame retardant, in the presence of a zeolite catalyst (ZSM-5 or Y-type zeolite), whereby the latter catalyst was more effective in removing the bromine compound [27]. We previously reported that it was possible to reduce the content of bromine in the oil produced upon thermal decomposition of brominated polystyrene by using hydrotalcite (HT) additive [33]. HT is a layered double hydroxide consisting of a metal complex hydroxide comprising anionic species in the divalent Mg^{2+} and trivalent Al^{3+} host layers and interlayer of the guest layer [34], [35]. HT is the catalyst [36], [37] and gas removal [38] material for the [39], as ion exchanger [34], [35], [40], [41] has received increasing attention in recent years. High anion exchange capacity comparable to HT organic ion-exchange resins has received much attention and has been used as an adsorbent for the removal of various contaminants in aqueous solutions. The adsorption properties of inorganic anions such as sulfates, chromates, arsenates, selenate, borates, nitrates, fluorides, and phosphates have been studied [42]. The adsorption of anions onto HT is known to proceed via the formation of inter-layer outer sphere complexes upon an anion exchange reaction [43]. Additionally, HT has been generating interest as a catalyst in bio-diesel fuel production, whereby a noted increased yield from 62% to 77% has been observed in the presence of HT catalyst [44],

[45]. The catalytic activity of HT has been further demonstrated in the aerobic oxidation of benzyl alcohol [46].

In this study, a method is presented to reduce the content of bromide in oil generated upon thermal decomposition of ABS at 400 °C, whereby HT was employed as an additive during the pyrolysis process (Fig.1).

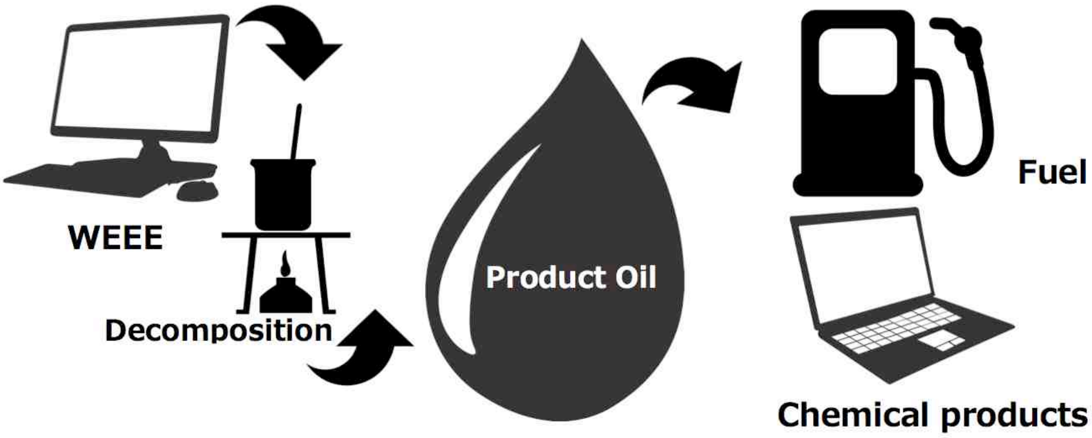

Fig.1 Image of research

4.2. Experimental

4.2.1. Materials

ABS was obtained from Asahi Kasei Chemicals Corporation. A synthetic HT was used as an additive (DHT-4A; Kyowa Chemical Industry Co., Ltd.,).

4.2.2. Experimental Apparatus and Procedures

The experimental apparatus used in this study is shown in Fig. 2. A mixture of HT and ABS (20 g) were introduced into a glass reactor. To remove oxygen from the reactor, the latter was flushed with nitrogen gas at 50 mL/min for 1 h. Pyrolysis was then initiated. The temperature of the glass reactor where the sample resided was monitored using a thermocouple. The temperature of the reactor was increased to 400 °C at a heating rate of 5 °C/min, after which it was allowed to cool naturally. The gases generated during pyrolysis were recovered in a recovery container as the product oil passed through the cooling condensation pipe. Non-condensable gases were collected in a gas pack via bubbling of an alkaline aqueous solution, a bromine alkaline generated gas bromide ions in the solution.

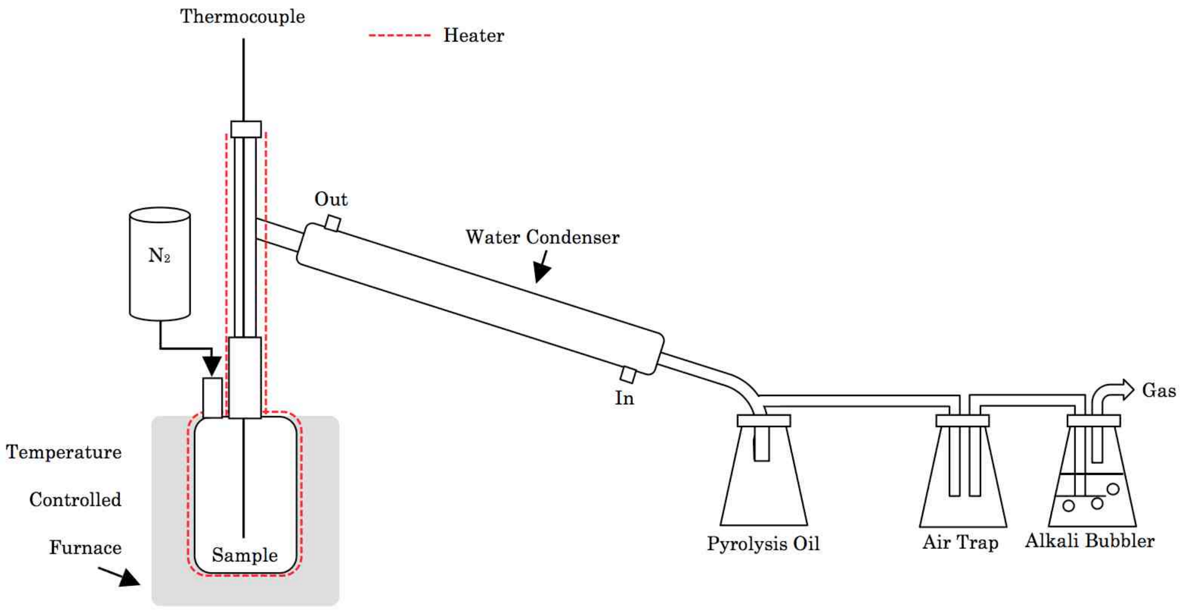

Fig. 2. Experimental apparatus.

4.2.3. Analysis

The product oil was diluted 100 times with hexane (Guaranteed Reagent grade, Wako Pure Chemical Industries), and analyzed by comparing the peaks obtained by gas chromatography–mass spectrometry (GC–MS) on a Shimadzu GCMS-QP2010 Ultra. The compounds were identified using a GC–MS spectral library. Pure helium was used as a carrier gas and a Rtx-1 column (inner diameter of 0.25 mm and film thickness of 0.25 µm) was used. For analysis, the temperature was maintained at 40°C for 30 min, and then increased to 230 °C at a heating rate of 5 °C/min.

The bubbling alkaline aqueous solution was diluted to 100-fold with ultrapure water and subjected to ion chromatography on a Shimadzu ion chromatograph to determine the bromine concentration. A Shim-pack column (150 L × 4.6) and CDD-10Asp detector were used.

The structure of the residue (following pyrolysis) was examined by X-ray diffraction (XRD; D2 PHASER, Bruker xxx). The composition of the residue was examined by scanning electron microscopy (TM3030, Hitachi) coupled with energy-dispersive X-ray spectroscopy (BURUKER QUANTAX). Elemental distribution mapping of the surface of the sample residue following thermal decomposition was conducted. Energy-dispersive X-ray spectroscopy images were collected from five different samples areas, and provided quantitative determination of the bromine contents in these areas. The obtained values were averaged accordingly to determine the representative content of bromine.

Furthermore, assuming that the landfill .The residue obtained after pyrolysis was subjected to a bromine dissolution test. The residue was mixed with distilled water at a ratio of 3: 100 of 200 times / min, and the mixture was shaken for 2 h. The supernatant liquid following centrifugation was subjected to ion chromatography to determine the content of bromine leached from the residue.

4.3. Result and Discussion

4.3.1. Product Oil

The yield of the product oil obtained upon pyrolysis of ABS is shown in Fig. 2. As the results show, the yield of the product oil varied in the range of 35–45% regardless of the amount of added HT (0–20 g).

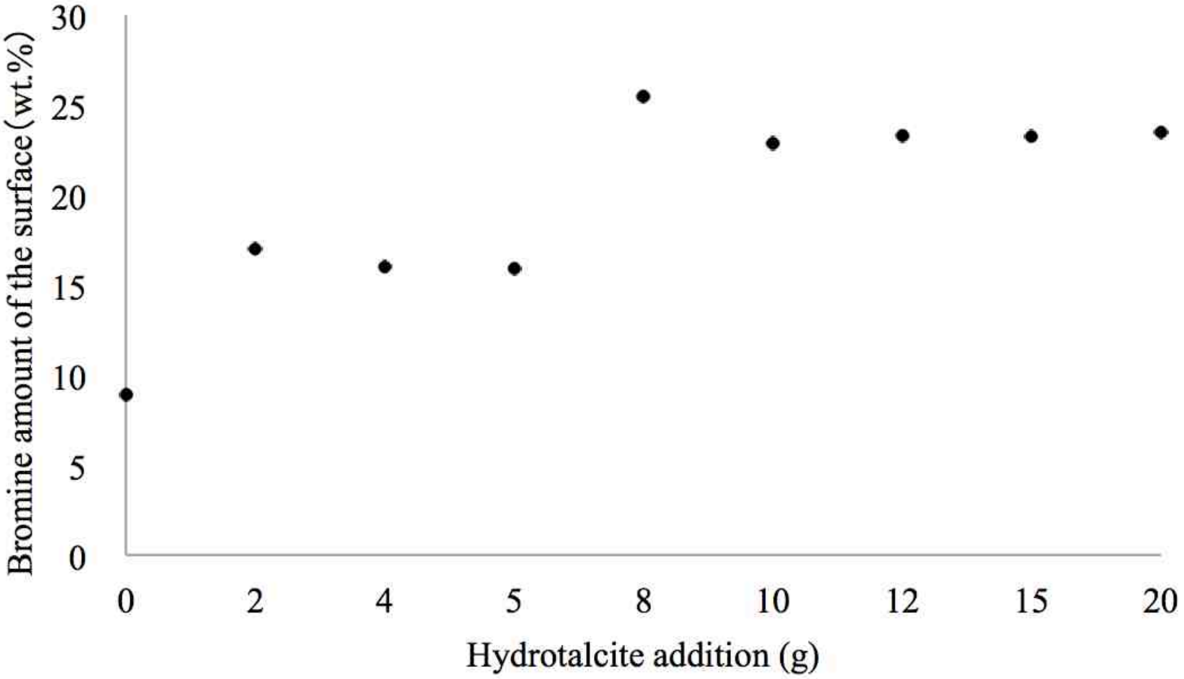

Fig. 3 Yield of product oil following pyrolysis of ABS in the presence of varying amounts of HT additive.

4.3.2. Residue

Table I lists the chemical components in the oil generated upon thermal decomposition of ABS in the presence of varying amounts of HT. Toluene, ethylbenzene, styrene, phenol, n-butyl benzene, and 1-methoxy-1-methylethylbenzene were detected along with bromine compounds 1-bromomethyl-4-methylbenzene, 2-bromophenol, 4-benzyloxy bromobenzene, 2,6-dibromophenol, and 2-bromotoluene upon thermal decomposition of ABS in the absence of HT additive. In contrast, the bromine compounds were not detected when the HT additive amount was greater than 8 g.

Fig. 3 illustrates the amount of bromine in the product oil upon thermal decomposition of ABS in the presence of varying amounts of HT additive. As the results show, in the absence of HT additive, the amount of bromine determined was 100%, which decreased upon addition of HT. Further increases to >8 g resulted in negligible detectable amounts of bromine. Hence, the results reveal that the amount of bromine in the product oil can be considerably reduced to zero upon addition of HT (>8 g).

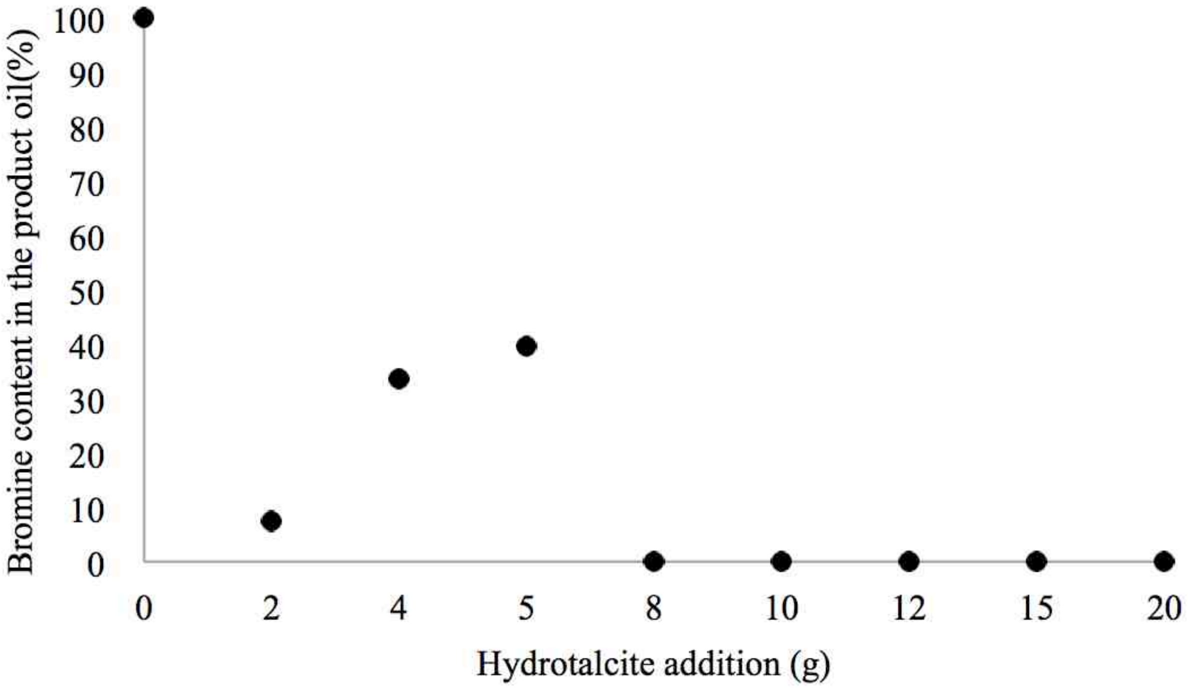

Fig. 4 Bromine content in the product oil following pyrolysis of ABS in the presence of varying amounts of HT additive.

The observation results of the residue by SEM are shown in Fig. 4. When the added amount of HT increased, the large particles and the small particles could be observed on the surface. The former can be interred to be Mg-Al oxides. And bromine can be interred to have been absorbed on the surface of the later.

The amount of bromine in the residue following pyrolysis is shown in Fig. 5. As the results show, the amount of bromine was 8.9% when HT was not added, and increased to 16% as the additive amount of HT increased (2–5 g). The amount of bromine was 23% when more than 8 g of HT was used. Thus, the results further confirmed that bromine was trapped within the residue upon addition of HT.

TABLE I: Components of Product Oil Obtained Using Varying Amounts of HT Additive

Compound	Formula	Amount of hydrotalcite additive (g)								
		0	2	4	5	8	10	12	15	20
Toluene	C_7H_8	○	○	○	○	○	○	○	○	○
Ethylbenzene	C_8H_{10}	○	○	○	○	○	○	○	○	○
Styrene	C_8H_8	○	○	○	○	○	○	○	○	○
1-Bromomethyl-4-methylbenzene	C_8H_9Br	○	○	○	○	nd	nd	nd	nd	nd
Phenol	C_6H_5OH	○	○	○	○	nd	nd	nd	nd	nd
n-Butyl benzene	$C_{10}H_{14}$	○	○	○	○	nd	nd	nd	nd	nd
1-Methoxy-1-methylethylbenzene	$C_{10}H_{14}O$	○	○	○	○	nd	nd	nd	nd	nd
2-Bromophenol	C_6H_5BrO	○	○	○	○	nd	nd	nd	nd	nd
4-Benzyloxy bromobenzene	$C_{13}H_{11}BrO$	○	○	○	○	nd	nd	nd	nd	nd
2,6-Dibromophenol	$C_6H_4Br_2O$	○	○	○	○	nd	nd	nd	nd	nd
2-Bromotoluene	C_7H_7Br	○	○	○	○	nd	nd	nd	nd	nd

○: detected, nd: not detected

(a)

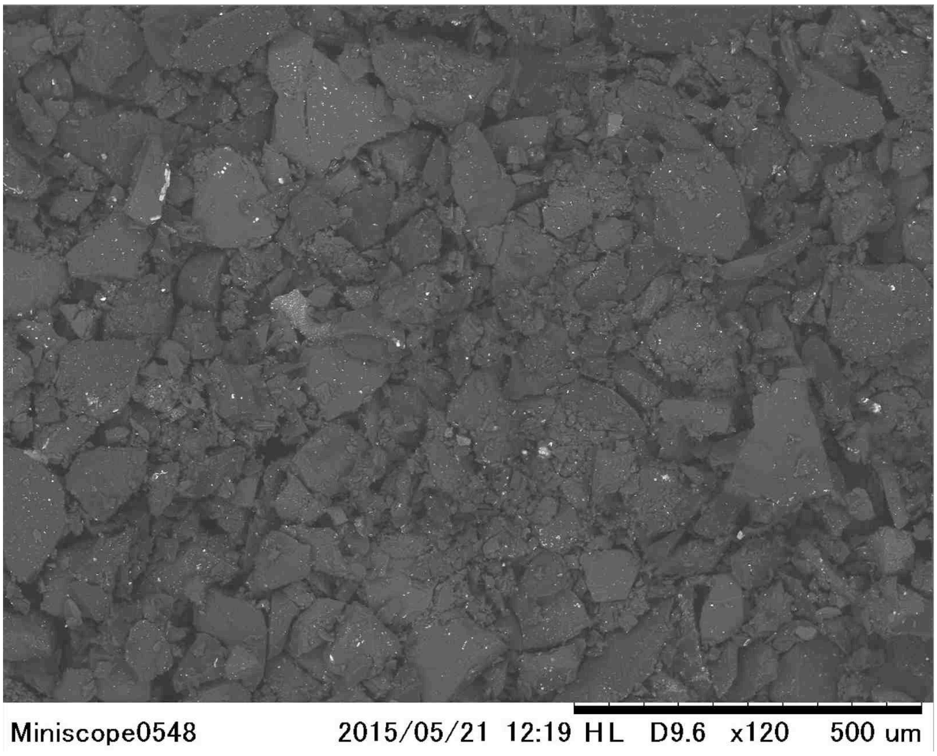

Fig. 5 (a) Residue after pyrolysis of ABS without HT.

(b)

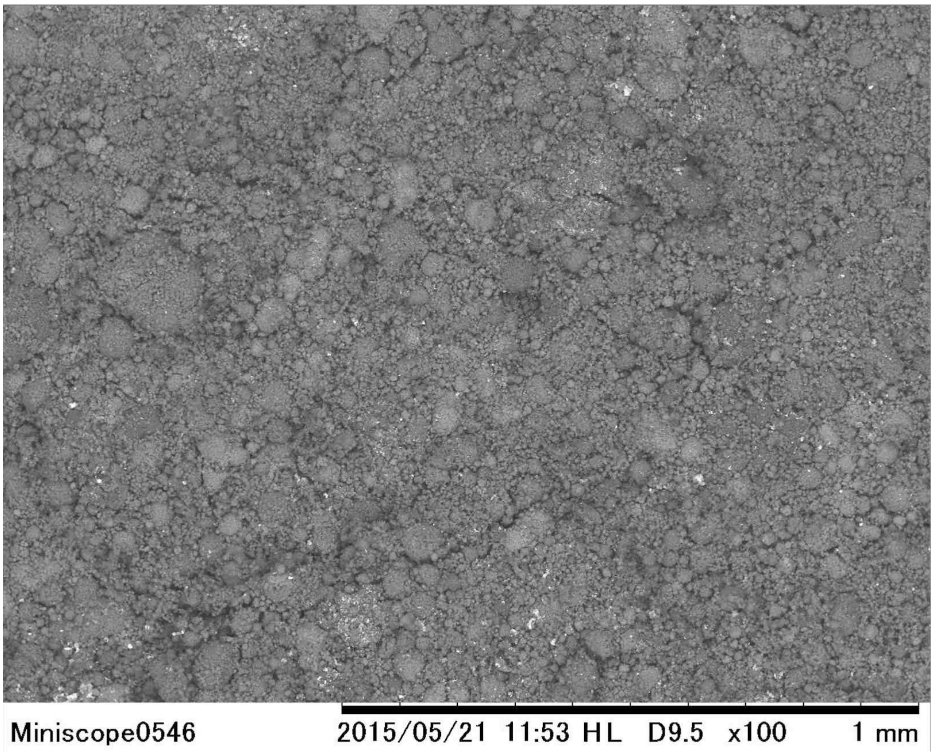

Fig. 5 (b) Residue after pyrolysis of ABS with 8g of HT.

(c)

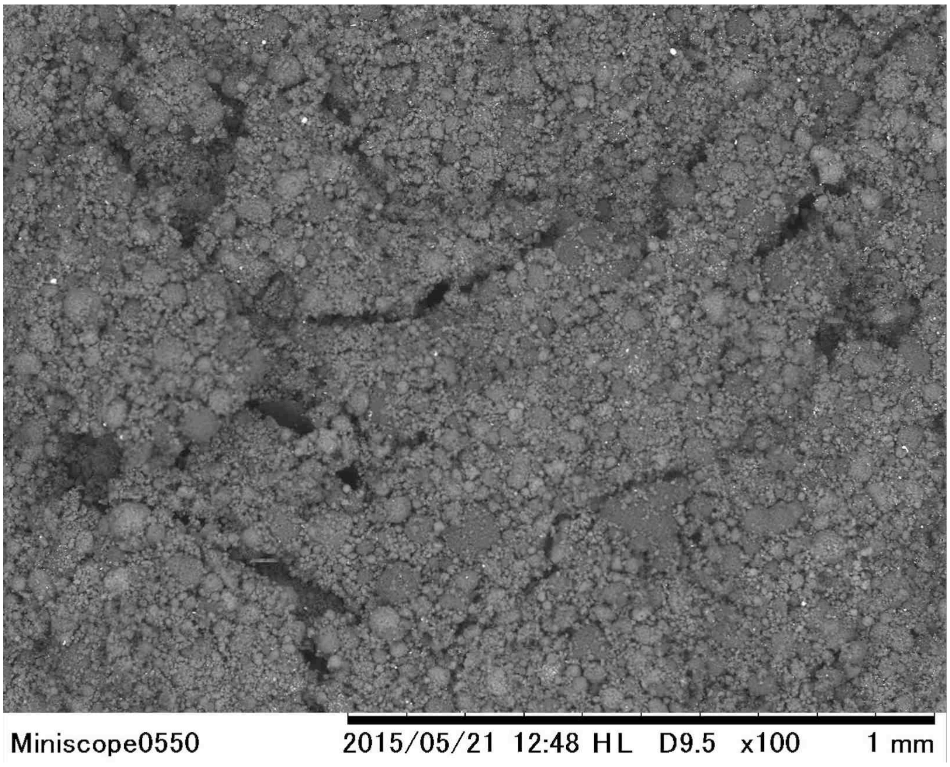

Fig. 5 (c) Residue after pyrolysis of ABS with 10g of HT.

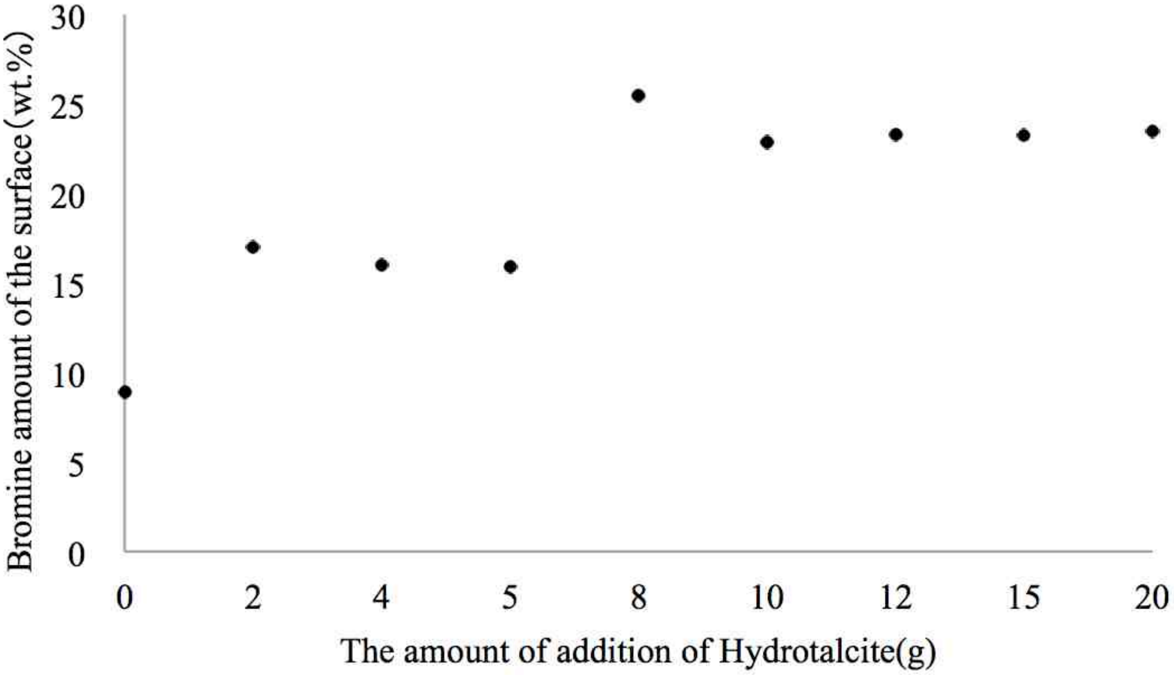

Fig. 6 Variations in the amount of bromine on the residue surface as a function of HT additive amount.

The bromine dissolution test did not show leaching of bromine from the residue under all conditions examined. Therefore, we can conclude that bromine is strongly encapsulated into hydrotalcite.

4.3.3. Content of Bromine in Gas

The gases generated upon pyrolysis of ABS were analyzed. Incidentally, the volume of gas generated by thermal decomposition was less than 1 L in all experiments conducted. The components of the water-insoluble gas include H_2, CH_4, and CO_2. H_2 and CH_4 were derived from the thermal decomposition of the plastic, whereas CO_2 was derived from the combustion of hydrotalcite.

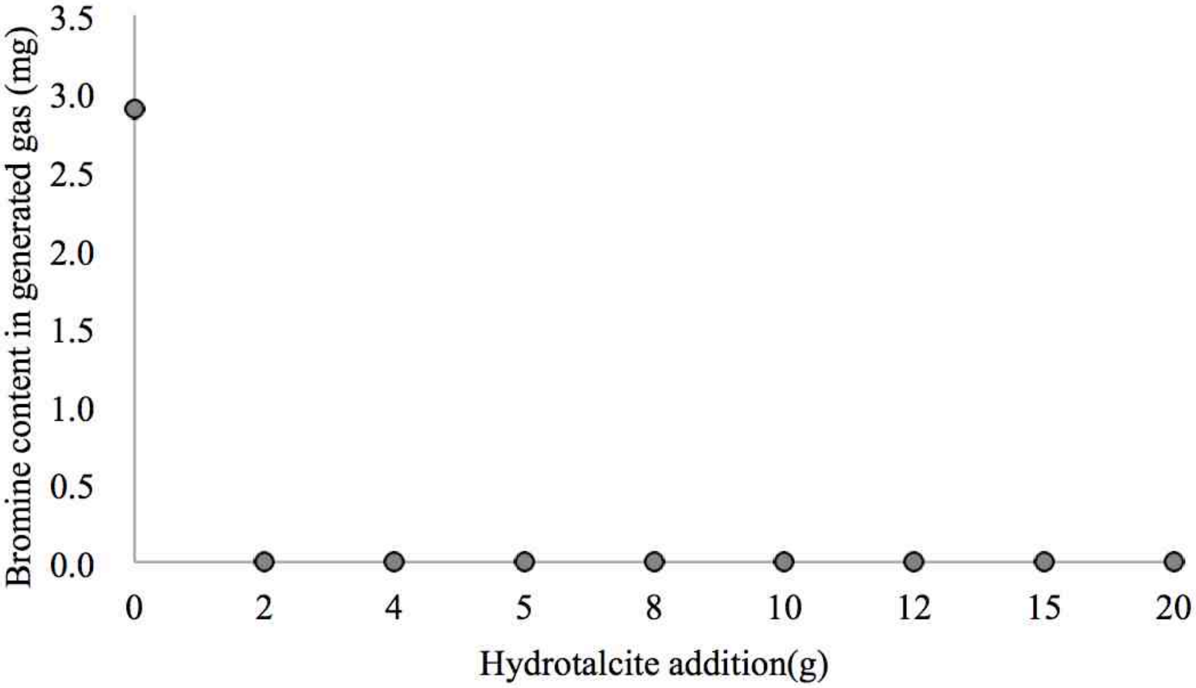

Fig. 7 Bromine content in the gas generated upon pyrolysis of ABS in the presence of HT at varying amounts.

The content of bromine in the generated water-soluble gas is shown in Fig. 6. In the absence of HT additive, bromine was detected in the generated gas. In contrast, bromine was not detected when HT additive was used within the HT amounts studied. This result further confirmed that bromine was firmly trapped within the HT matrix and thus was not released in the gases produced during pyrolysis.

4.4. Conclusion

In this study, the reduction of bromine content in the product oil obtained upon thermal decomposition of bromine-based plastic ABS was examined by introducing hydrotalcite additive. The results showed that the addition of an appropriate amount of hydrotalcite (>8 g) to ABS sample (20 g) resulted in considerable reduction of the content of bromine (to zero) detected in the product oil.

The residue was added hydrotalcite is concentrated bromine, it is believed that the reason may be obtained a product oil of bromine does not contain. Furthermore, the bromine dissolution test confirmed that bromine was efficiently encapsulated within the hydrotalcite matrix, and thus did not leach in solution.

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Chapter5

5.1. General Conclusions

This study aimed to produce a pyrolysis oil that was free of bromine compounds when using plastics that contained bromine-based fire-retardants as the starting material.

In Chapter 2, I added the fire-retardant TBBA to polystyrene (a representative plastic for WEEE) and carried out a simulation of the pyrolysis process. I added active carbon, the material with the aperture including the shell of the scallop to extract bromine by ion exchange during the pyrolysis of the plastic, but a bromine compound was detected a study in from provided generation oil at first by pyrolysis. In general adding zeolite to the pyrolysis decreased bromine levels in the oil product. In addition, the tendency that it leaked, and yield rose in molecular sieve 13X shown to be high in resolving power was provided when it leaked and used molecular sieve 4A and 13X. This led me to add HT because of its ability to adsorb bromine and catalyze the reaction. The thermal stability of HL limited the pyrolysis temperature to 400 °C.

Although HT is known to have anion-adsorption properties, this is the first time it has been used as a pyrolysis additive. Pyrolysis with HT of polystyrene with TBBA resulted in no bromine being detected in the product oil.

In Chapter 3, I investigated similar pyrolysis processes with polyethylene, and polypropylene. All results showed that the addition of HT prevented bromine appearing in the product oil. EDX element-mapping of the pyrolysis residue confirmed that the bromine was retained in that fraction.

In Chapter 4, I investigated the impact on the pyrolysis products of acrylonitrile-butadiene-styrene (ABS) of changing the amount of HT. Above a threshold value, adding more HT had no impact on the yield.

Overall the previous chapters show that adding HT during the pyrolysis of waste plastics can increase the yield of product oil and prevent its contamination by bromine compounds, which are often used in fire-retardants in plastics. Implementation of the results in this work could improve processes used to recycle WEEE around the world.

Publications

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