

Removal of Halogens from Pyrolysis Oils Produced by Plastics Containing Flame Retardants

Takaaki Wajima, Zar Zar Hlaing, Akiko Saito, Hideki Nakagome

Abstract—Plastics containing brominated flame retardants are commonly used in electrical and electronic products, and disposal or recycle of these products is difficult because of their halogen content. In this study, brominated acrylonitrile butadiene styrene (Br-ABS) was pyrolyzed at 450 °C. The halogen content in the product oil was reduced by addition of sodium hydroxide (NaOH) and pine charcoal. The mass fraction of bromine in the oil obtained without the NaOH or charcoal was 3.2 %, whereas those in the oils obtained with NaOH and charcoal were 1.74 % and 1.25 %, respectively. Using both NaOH and charcoal, the bromine mass fraction in the oil was reduced to 0.6 %. Combustion tests were used to determine the calorific values of pyrolysis oils with various bromine contents, and any corrosion that could limit their use as an alternative fuel was evaluated after these tests. Pyrolysis oil with a bromine content of less than 2000 mg/L could be used as fuel without corrosion.

Index Terms—charcoal, halogen, pyrolysis oil, sodium hydroxide,

I. INTRODUCTION

Most plastics used in electrical and electronic equipment contain various flame-retardant substances. The main components of plastics in waste electrical and electronic equipment are high impact polystyrene and acrylonitrile butadiene styrene (ABS). These polymers are widely used in TV casings, computers, printers and other office electrical and electronic equipment. Brominated flame-retardants (BFRs), such as polybrominated biphenyls, polybrominated diphenyl ethers, tetrabromo bisphenol-A (TBBA) and polybrominated epoxy resins, are used in these plastics and contribute to their toxicity, which makes it difficult to dispose of or recycle these plastics. Plastics containing BFRs need careful processing to either destroy or remove the flame retardant [1].

By 2030, it is predicted that developing countries will produce at least twice as much WEEE as developed countries [2]. In computers, BFRs are used in four main applications, including in printed circuit boards, connectors, plastic covers, and cables [1]. At present, there are around 150 million

computers purchased each year globally, and about 100 million of these are purchased in developed countries [2]. Therefore, methods for recycling plastics containing BFRs are important.

Pyrolysis is a feasible method for recycling WEEE waste. It has been investigated for thermal degradation of toxic BFRs and production of fuels or chemical feedstocks for the petrochemical industry. Various pyrolysis processes for plastics containing BFRs have been tested, including fluidized bed pyrolysis [3], two-stage pyrolysis [4], long residence time pyrolysis, and pyrolysis in the presence of iron and calcium based catalysts [5]. Recently, it was reported that the bromine content in pyrolysis oil obtained from Br-ABS in a fixed bed reactor at 440 °C can be reduced using ZSM-5 and Y-Zeolite [6]. The mass fraction of bromine in pyrolysis oil was 2.7 % without the zeolites, and it was 2.6 % with the zeolites. The bromine content in pyrolysis oil from high impact polystyrene has also been reduced using calcium-based additives (CaO, Ca(OH)₂, oyster shell) in a bench-scale system equipped with a fluidized bed reactor at 460 °C [7]. In this case, the mass fraction of bromine in the oil was 5 % without any additives, and 1.6, 1.3, and 2.7 % with CaO, Ca(OH)₂, and shell, respectively.

In the present study, we attempted to reduce the halogen content of pyrolysis oil using NaOH as an additive and pine charcoal as an absorbent. NaOH was used to trap the halogens in inorganic compounds (e.g. NaBr) in the pyrolysis reactor. Pine charcoal, which shows excellent absorption of atmospheric moisture and decomposes of formaldehyde, ethylene gas, dioxin, ammonia and chemical odors [8], was used to absorb halogen from the gas generated during pyrolysis. We also evaluated the effect of the bromine content in the pyrolysis oil on the calorific value. Corrosion caused by the various oils was also investigated as it could limit the use of oil as an alternative fuel.

II. EXPERIMENTAL

A. Materials

ABS containing a BFR was obtained from Asahi Kasei (Tokyo, Japan). The resin contained 65 % ABS, 30 % BFR, and 5 % other compounds. The elemental composition of the ABS is shown in Table I. NaOH was obtained from Wako Pure Chemical Industries (Osaka, Japan). Pine charcoal was prepared by pyrolysis under nitrogen at 550 °C for 4 h in a bed reactor.

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Table I Elemental composition of the ABS used in this study

Elemental composition (%)					
C	H	N	Br	Sb	Cl
71.87	6.64	3.94	10.70	3.50	1.00

B. Experimental Apparatus and Procedure

The experimental apparatus is shown in Fig. 1. Pyrolysis of ABS was performed in a glass reactor (length 300 mm, i.d. 50 mm) under nitrogen. A sample of ABS (60 g) was placed in the reactor, and allowed to equilibrate under nitrogen. Then, NaOH (3 g, 5 % of the ABS mass) was added to the reactor. The tubular electric furnace was heated to 300 °C at 5 °C/min, and then to 450 °C at 3 °C/min. The sample was heated for 2 h at 450 °C, which resulted in decomposition to oil, wax, char and gas. An air-cooled tube was installed to prevent blockages occurring in the condenser with rapid cooling. Residual impurities and wax were collected in the tube, and this trapped bromine and chlorine that would have otherwise gone into the pyrolysis oil. The pine charcoal was placed inside the upper part of the reactor and in the air-cooled tube. The product oil was passed through the pine charcoal. Wax was collected by the air-cooled tube and condenser. The product yields of oil, wax and char were analyzed after the experiments, and mass balances of the oil, wax, char and gas were calculated. The mass of the pine charcoal was recorded before and after the experiments.

C. Analysis

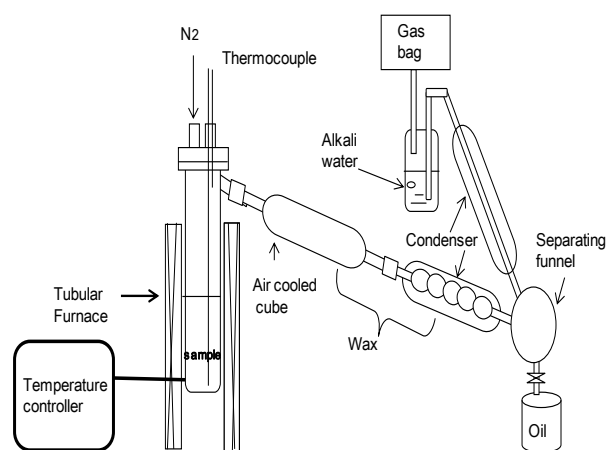
Thermogravimetry (TG) and differential thermal analysis of the ABS were conducted using a DTG-60 (Shimadzu, Kyoto, JP) under standard pressure and a nitrogen atmosphere. The temperature was increased from 25 to 550 °C at 5 °C/min.

Oil and wax were analyzed by gas chromatography/mass spectrometry (GC/MS). GC/MS was performed with a Hewlett-Packard 5890-II gas chromatograph interfaced with a HP 5972 mass selective detector. Separation was carried out on a fused-silica column (60 m × 0.25 mm i.d.) coated with SPB-5 (1.0 μm film thickness). The temperature was increased from 40 °C to 250 °C at 3.5 °C/min. Helium was used as the carrier gas (linear velocity = 20 cm/s). Electron ionization mass spectra were obtained by automatic scanning in the range 35–400 *m/z*. The sample was diluted with methanol before injection. The main compounds were identified by comparison to the GC/MS spectral library data (match quality >90 %).

The elemental bromine contents of the products (oil, wax and char) were determined using an automatic sample combustion device (AQF-2100H, Mitsubishi Chemical Analytical Tech Co. Ltd., Kanagawa, JP) and ion chromatograph (ICS-1600, Dionex, Sunnyvale, CA). In this method, the samples (oil, wax and char) were combusted in the AQF -2100H, and the gaseous bromine species were captured into an alkaline solution containing H₂O₂. The bromine content of the solution was then determined using the ion chromatograph.

A combustion experiment was conducted using the pyrolysis oil to determine its calorific value and its potential

for corrosion. ABS pyrolysis oil, which contains no bromide compounds, and Br-ABS pyrolysis oil were mixed, and the Br concentration was adjusted to 5 mg/L, 20 mg/L, 200 mg/L, 2000 mg/L and 20000 mg/L. Combustion tests were performed on 0.5 g samples in a stainless steel vessel under oxygen at 3 MPa, and the calorific values were recorded. After the combustion tests, the stainless steel plate was washed with isopropyl alcohol, under ultrasonication for 5 min, and then the level of corrosion on the surface was observed.


Fig. 1 Experimental setup for pyrolysis of ABS at 450 °C

III. RESULTS AND DISCUSSION

A. Thermogravimetric Analysis of ABS

The decomposition of ABS occurs in two separate steps, as shown in Fig. 2. The mass loss in the first decomposition step (308 °C) was 16 %, and in the second decomposition step (402 °C) was 69 %. Fig. 3 shows the halogen concentrations in the pyrolysis oil produced at various decomposition temperatures. The chlorine concentration in the oil was almost constant at all decomposition temperatures from 360 °C to 450 °C. By contrast, bromine was not detected in the oil produced at a decomposition temperature of 360 °C, but was present at constant levels in the oils obtained at decomposition temperatures from 375 °C to 450 °C. The rapid mass loss between 375 °C to 450 °C shown in the TG and DTG curves (Fig. 2) was correlated with the increase in the bromine concentration at decomposition temperatures over 375 °C. Most of the halogen compounds in the ABS were decomposed and released at 375 °C. The first dip in DTG curve (at 308 °C) can be attributed to the decomposition of some of the halogens and antimony trioxide (Sb₂O₃), which is present in the BRF as a synergistic flame retardant. During the thermal decomposition of the BRF, Sb₂O₃ increases the rate of halogen release via the formation of compounds such as SbBr₃ (288 °C) [9]–[11]. A large mass decrease is observed at around 400 °C because of thermal decomposition of the resin.

In the first stage of decomposition (268–338 °C), some of the Br-ABS decomposes and chlorine from the BFR is decomposed by Sb_2O_3 and released to the gas phase. In the second stage of decomposition (338–447 °C), most of the rest of the Br-ABS decomposes, and all halogens (chlorine and bromine) from the BFRs are decomposed by Sb_2O_3 and released into the gas phase. Decomposition also results in formation of the pyrolysis oil.

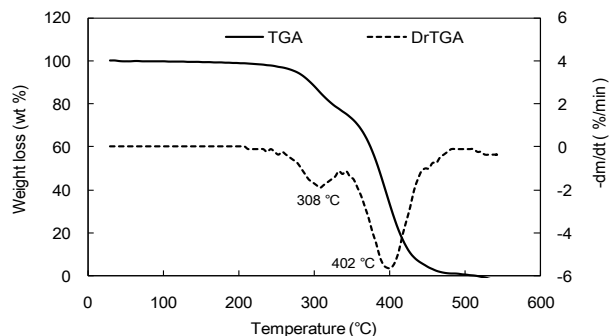


Fig. 2 TG and DTG curves of ABS decomposition

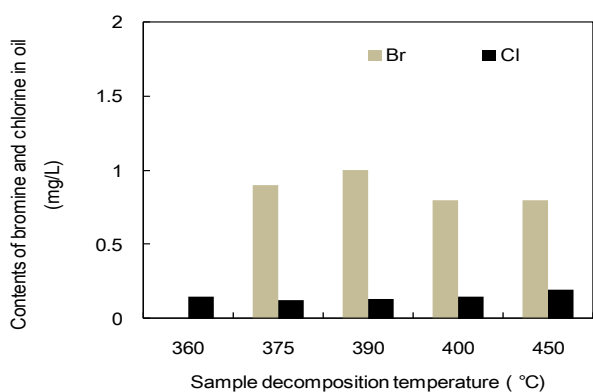


Fig. 3 Halogen concentration in the pyrolysis oil produced at various sample decomposition temperatures

B. Product Distribution

The effect of the NaOH additive and charcoal absorbent on the yields of the pyrolysis products at 450 °C was investigated. The mass balances for all experiments are shown in Table II. Decomposition of Br-ABS alone at 450 °C produced pyrolysis oil (32.36 %, mass fraction), wax (22.76 %, mass fraction), gas (4.44 %, mass fraction), and char (40.44 %, mass fraction). It has been reported that slow pyrolysis of brominated ABS, with the temperature increased to 450 °C at 10 °C/min, produces pyrolysis oil (34 %, mass fraction), gas (5 %, mass fraction), and char (61 %, mass fraction) [12]. The yield of pyrolysis oil was similar in the present study. When the NaOH additive and charcoal absorbent were added, the yields of pyrolysis oil increased to 36 % (mass fraction), and the yield of char decreased. Therefore, addition of NaOH and charcoal promotes the production of pyrolysis oil. Both with and without the additives, the main products of pyrolysis of Br-ABS were pyrolysis oil (Fig. 4 (a)) and wax (Fig. 4 (b)), then char, and then gases. With addition of pine charcoal, the wax yield decreased and the capture yield increased. These results suggest that addition of NaOH and charcoal and increase the yield of pyrolysis oil and reduce wax production.

Table II Mass balances from various pyrolysis experiments

Material	Product of yield (wt %)				
	Oil	Wax	Char	Gas	Capture
Br-ABS	32.36	22.76	40.44	4.44	-
Br-ABS + Charcoal	36.13	8.80	31.19	4.12	19.76
Br-ABS+ NaOH	36.45	24.64	34.91	4.00	-
Br-ABS+ NaOH + Charcoal	36.52	4.47	33.22	3.20	22.59



(a) Oil (b) Wax

Fig. 4 Photos of (a) the pyrolysis oil and (b) wax

C. Analysis of Pyrolysis Products

The components in the pyrolysis oil were identified by GC/MS (Fig. 5). The major compounds were toluene, ethylbenzene, styrene, cumene, α -methylstyrene, 2-bromophenol, 3-bromophenol, benzenebutanenitrile, 2,8-dimethylquinoline, 3-methylbutyl benzene, 2,4-dibromophenol, 1,3-diphenylpropane, 1,2-diphenylcyclopropane, 4-butylidiphenylmethane, hexadecanenitrile, octadecanenitrile, benzenebutanenitrile and 9-phenylacridine. Bromine was present as 2-bromophenol, 3-bromophenol and 2,4-dibromophenol. The GC/MS results indicate that the Br-ABS used in this study contains TBBA as the flame retardant, because TBBA decomposes to 2-bromophenol, 3-bromophenol and 2,4-dibromophenol (Fig. 6). When charcoal was added to the pyrolysis mixture, 4-butylidiphenylmethane, hexadecanenitrile, octadecanenitrile, benzenebutanenitrile and 9-phenylacridine were not detected in the pyrolysis oil because the charcoal captured these compounds in a similar manner to activated carbon. With addition of NaOH, the peaks of the pyrolysis oil compounds increased and those of bromine compounds (6, 7 and 11) decreased. This was because NaOH promoted ABS pyrolysis and reduction of halogens. With both NaOH and charcoal, both the number of components and quantity of bromine compounds decreased in the product oil.

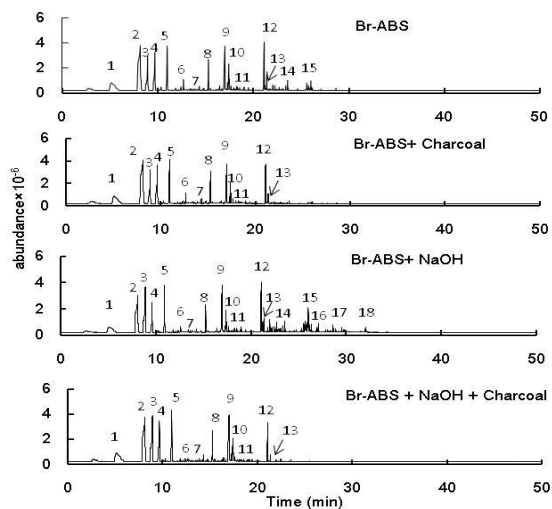


Fig. 5 GC/MS chromatograms of pyrolysis oils from Br-ABS with and without NaOH and charcoal addition. Compounds are numbered as follows: 1, toluene; 2, ethylbenzene; 3, styrene; 4, cumene; 5, α -methylstyrene; 6, 2-bromophenol; 7, 3-bromophenol; 8, benzenebutanenitrile; 9, 2,8-dimethylquinoline; 10, 3-methylbutyl benzene; 11, 2,4-dibromophenol; 12, 1,3-diphenylpropane; 13, 1,2-diphenylcyclopropane; 14, 4-butylidiphenylmethane; 15, hexadecanenitrile; 16, octadecanenitrile; 17, benzenebutanenitrile; and, 18, 9-phenylacridine.

The mass fractions of the halogen compounds in the products (oil, wax and char) are shown in Table III. The mass fractions of bromine and chlorine in the pyrolysis oil from Br-ABS alone were 3.2 and 0.2 %, respectively. With addition of charcoal, the mass fractions of bromine and chlorine decreased to 1.7 and 0.9 %, respectively. With addition of NaOH, the mass fractions of bromine and chlorine decreased to 1.3 and 0.004 %, respectively. With addition of both NaOH and charcoal, the mass fractions of bromine and chlorine decreased to 0.6 and 0.002 %, respectively, which were the lowest levels observed among the four experiments. The halogen content in the char obtained with NaOH and that obtained with charcoal were higher than in the other experiments (i.e. no additive or both additives). These results indicate that both NaOH and charcoal can trap halogen.

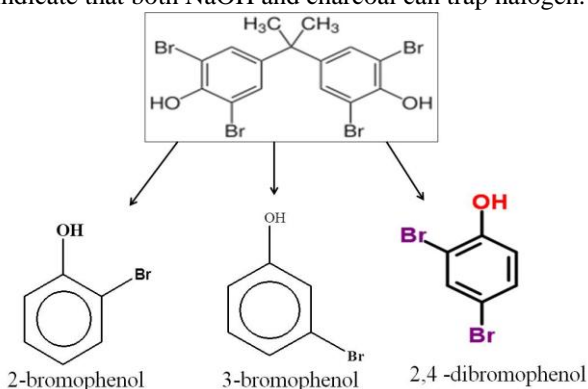


Figure 6 Decomposition of tetrabromo bisphenol-A

Table III Mass fractions of halogens in the different pyrolysis products

Material	Concentration of halogen (wt %)								
	Oil		Wax		Char		Capture		F
	Br	Cl	Br	Cl	Br	Cl	Br	Cl	
Br-ABS	3.2	0.2	41.6	7.3	10.4	2.4	0.6	0.0	0.0
Br-ABS + Charcoal	1.7	0.9	17.8	1.3	8.6	1.5	0.6	43.5	4.8
Br-ABS+ NaOH	1.3	0.0	23.1	1.0	30.2	0.2	0.3	0.0	0.0
Br-ABS+ NaOH + Charcoal	0.6	0.0	6.0	0.5	34.1	5.1	0.9	44.6	5.3

D. Calorific Value and Corrosion

The calorific value of the pyrolysis oil was investigated in a combustion test (Fig. 7). The calorific value of oil with higher bromine content was lower than that of oil with lower bromine content. The calorific values of pyrolysis oil containing 5 mg/L, 20 mg/L, 200 mg/L, 2000 mg/L and 20000 mg/L were 40.0 MJ/kg, 39.5 MJ/kg, 39.2 MJ/kg, 39.0 MJ/kg and 38.0 MJ/kg, respectively. The calorific value of heavy oil is 39.1 MJ/kg, which is similar to that of pyrolysis oil containing 2000 mg/L bromine. After the combustion test, corrosion was observed on the surface of the stainless steel in some cases (Fig. 8). Corrosion of the stainless steel occurred with the oil containing 20,000 mg/L bromine, while no corrosion was observed with oil containing less than 2000 mg/L bromine. Therefore, oil with a bromine concentration lower than 2000 mg/L could be used as an alternative fuel.

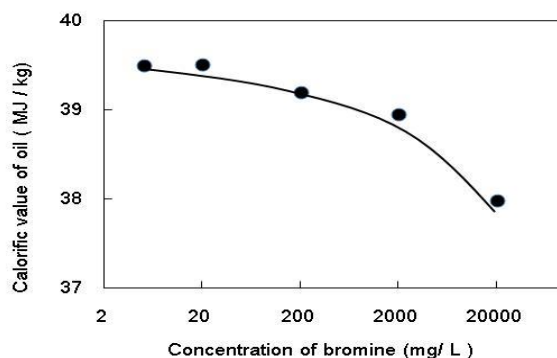


Figure 7 Calorific values obtained in combustion tests for pyrolysis oils with various bromine contents

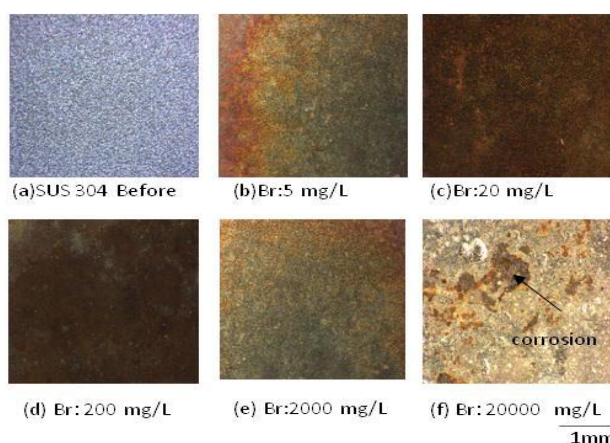


Figure 8 Corrosion on the surface of the stainless plate after the combustion test

IV. CONCLUSION

ABS resin containing a BFR was pyrolyzed at 450 °C using NaOH and charcoal. With addition of NaOH and charcoal to the pyrolysis mixture, the yield of pyrolysis oil increased and that of char decreased compared with pyrolysis without the additives. Using both NaOH and charcoal, the mass fraction of bromine in the pyrolysis oil was reduced from 3.2 % to 0.6 %. Combustion tests indicated that the pyrolysis oil with a bromine concentration of less than 2000 mg/L could be used as fuel without corrosion. These results indicate that NaOH as an additive and charcoal as an absorbent are effective for reducing the levels of bromine compounds in oil to use as fuel. However, the bromine content in the oil obtained was still high for fuel applications. Therefore, future research could look at reducing the bromine content further by altering the amount or type of additive and absorbent.

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