Removal of Bromine from Pyrolysis Oil with NaOH in a Reflux Condenser System

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***Abstract*—ABS resin containing a brominated flame retardant was pyrolyzed with NaOH at 450 °C in a system equipped with a reflux condenser. This produced a pyrolysis oil with a low bromine content. As the quantity of NaOH was increased, the yield of the oil decreased, and the yields of solid residue and gas increased. Bromine compounds present in the oil included 2-bromophenol, 3-bromophenol and 2,4-bromophenol, with 2-bromophenol present at the highest levels and 3-bromophenol at the lowest. The bromine content in the pyrolysis oil obtained with NaOH was lower than that in the oil obtained without NaOH. The results indicate that the addition of NaOH were effective for reducing the bromine content in the oil using the reflux condenser apparatus. The bromine was captured in the solid residue and not discharged as waste gas.**

Keywords—ABS; bromine; pyrolysis oil; sodium hydroxide; reflux condenser

I. INTRODUCTION

Plastics are inexpensive, light and durable materials with low thermal and electrical conductivity. Because of these properties and the fact they are simple to manufacture, plastics are widely used in many applications. With increasing plastic consumption, plastic waste volumes have also increased and resulted in serious environmental problems because of the persistence of plastic in landfills. Plastic waste has a high organic content and energy, and these resources are either totally lost if the plastic is disposed in a landfill or only partially recovered if the plastic is incinerated. Because the world has limited reserves of coal, crude oil and natural gases, preservation of existing non-renewable materials and discovery of new carbon sources for feedstock materials and fuels are important. Pyrolysis is one of the best methods available for recovery of materials and energy from polymer waste. About 10 % of the energy content of waste plastic is used to convert scrap into valuable hydrocarbon products in pyrolysis [1]. These hydrocarbon products are obtained by breaking down polymers at high temperatures into their original petrochemical feedstock components, while any additives (e.g. metals, inorganic fillers and supports) remain in the pyrolysis residue.

Waste plastics can be divided into the following two hydrocarbon groups: polyethylene, polypropylene and polystyrene; and, hydrocarbons containing heteroatoms, such as polyvinylchloride, acrylonitrile-styrene-butadiene resin (ABS) and polyethylene terephthalate.

One of the major components of waste from electric and electronic equipment is ABS, which usually contains brominated flame retardants (BFRs), tetrabromobisphenol A (TBBPA) and brominated epoxy oligomers. ABS are widely used as flame retardants in plastics in the electronics industry and in textiles. Plastics that contain BFRs include epoxy and polycarbonate resins, ABS, high impact polystyrene, and phenolic resins. Brominated ABS (Br-ABS) and brominated high impact polystyrene are commonly found in waste from electric and electronic equipment. The presence of bromine in ABS can result in dioxin and/or benzofuran formation during pyrolysis because of the reactions of organic halogen compounds in the pyrolysis oil [2,3]. Therefore, it is necessary to remove halogens from pyrolysis oils.

Various pyrolysis processes have been tested for processing plastics that contain BFRs, including fluidized bed pyrolysis [4], two-stage pyrolysis [5], long residence time pyrolysis [6], and pyrolysis in the presence of iron and calcium based catalysts [7]. Recently, William et al. [8] reported the removal of bromine from Br-ABS using zeolite ZSM-5 and zeolite Y in a fixed bed reactor at 440 °C. The mass fraction of bromine in the pyrolysis oil produced without the zeolites was 2.7 %, while the mass fraction of bromine in the pyrolysis oil produced with the zeolites was 2.6 %. Kim et al. [9] also reported the removal of bromine from high impact polystyrene using Ca-based additives, including CaO, $Ca(OH)_2$, and oyster shell, in a bench-scale system equipped with a fluidized bed reactor at 460 °C. The mass fraction of bromine in pyrolysis oil produced without an additive was 5 %, and the mass fractions in pyrolysis oil produced with CaO, $Ca(OH)_2$, and shell were 1.6, 1.3, and 2.7 %, respectively.

In the present study, virgin Br-ABS was pyrolyzed at 450 °C with or without NaOH in a system equipped with a reflux condenser. This is expected to reduce the quantity of bromine in the pyrolysis oil to trace levels. The main objective of this study was to determine the influence of NaOH on the debromination of pyrolysis oil.

II. MATERIALS AND METHODS

A. *Samples*

ABS containing a BFR was obtained from Asahi Kasei Chemicals Co. Ltd. (Tokyo, Japan). This virgin material contained 65 % ABS, 30 % BFR, 3.8 % antimony trioxide, and 1.2 % other compounds. NaOH was obtained from Wako Pure Chemical Industries, Ltd (Osaka, Japan).

B. *Experimental Procedure*

Pyrolysis was performed in a glass reactor (length 130 mm, i.d. 50 mm) connected to a glass reflux condenser (length 350 mm, i.d. 12 mm) as shown in Fig. 1. Pyrolysis was performed under nitrogen. Approximately 60 g of the ABS was loaded into the reactor with NaOH (1 % to 5 % of the ABS mass). In a typical run, nitrogen gas was passed through the reactor at 50 mL/min for 60 min to remove oxygen. The reactor temperature was then increased to the decomposition temperature (450 °C) at a rate of 5 °C/min, and held at 450 °C for 30 min. The temperature of the plastic in the bottom of the reactor was measured using a thermocouple and recorded as the decomposition temperature.

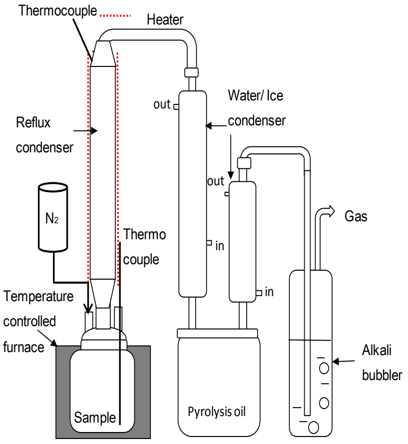

Fig. 1. Diagram of the pyrolysis reactor equipped with the reflux condenser.

The reflux condenser was heated to 200 °C. The reflux condenser was used to separate larger molecules from smaller molecules with heating. Hydrocarbon gases with low boiling points condensed before passing into the reflux condenser, and then remained in the reactor. The uncondensed fractions passed through the reflux condenser and a cold water condenser, and were collected with a separating funnel. Gases that did not condense in the cold water condenser were collected in an aluminum bag after bubbling through an alkaline solution. All the pyrolysis tests were carried out for a fixed time. After pyrolysis, the solid residue that remained in the reactor was weighed, and the mass balances of the pyrolysis products (oil, gas and solid residue) were calculated.

The halogen contents of the char and oil were determined by ion chromatography. First, about 1 g of the char or oil was combusted in a combustion flask, and then the product was washed with ion-exchanged water to dissolve any gaseous products. The anion content in the obtained solution was analyzed using an ion chromatograph (DX-120, Dionex, Sunnyvale, CA). The solid char was also analyzed by scanning electron microscopy with energy dispersive X-ray spectroscopy (JSM-6510A, JEOL, Tokyo, JP) to determine the elemental content, including bromine, chlorine, antimony and sodium.

The pyrolysis oils were analyzed by gas chromatography/mass spectrometry (GC/MS) on a Hewlett-Packard 5890-II gas chromatograph interfaced with a HP 5972 mass selective detector (Hewlett-Packard, Palo Alto, CA). Each pyrolysis oil sample was diluted with methanol before injection into the GC/MS. Sample 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 column temperature was increased from 40 °C to 250 °C at 3.5 °C/min. Helium was used as the carrier gas at a flow rate of 20 cm/s. Electron ionization mass spectra were obtained by automatic scanning in the range from 35–400 *m*/*z*. All the oils were analyzed quantitatively and qualitatively by comparing the peak sizes in the GC/MS results. The main compounds were identified by comparison with libraries of GC/MS spectral data (match quality >90 %).

III. RESULTS AND DISCUSSION

A. *Mass Balance of the Products*

The effect of NaOH addition on the yields of the pyrolysis products was investigated for pyrolysis of Br-ABS at 450 °C. The quantitative results for the decomposition of Br-ABS with addition of NaOH are shown in Fig. 2. The mass fractions of the pyrolysis oil, solid residue, and gaseous products were 56 to 63 %, 27 to 34 %, and 4 to 8 %, respectively. The yield of the pyrolysis oil decreased as the quantity of NaOH added increased, and at the same time, the yields of solid residue (char) and gaseous products increased.

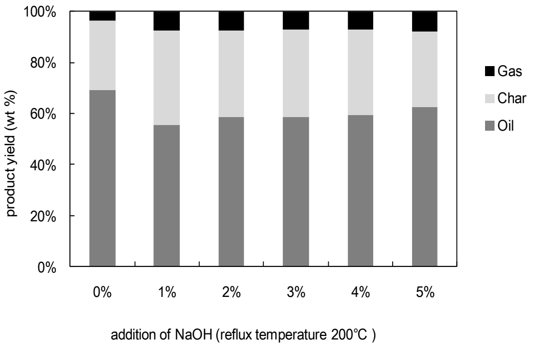

Fig. 2. Product yields from pyrolysis of Br-ABS with NaOH.

B. *Analysis of the Product*

The components in the pyrolysis oil were identified by GC/MS (Fig. 3). The major compounds were similar to those in commercial heavy oil fuel. The major components in the pyrolysis oil were isopropyl alcohol, toluene, ethylbenzene, styrene, cumene, propylbenzene, α-methylstyrene, and butylbenzene, and the minor components were isopropylphenol, 2-phenylpropan-2-ol, benzenebutanenitrile, 1,3-diphenylpropane, 1,3-diphenylbutane, α-methylstyrene dimer, 1,2-diphenylcyclopropane, 4-cumylphenol, hexadecane- nitrile, and octadecanenitrile. The bromine compounds present were 2-bromophenol, 3-bromophenol, and 2,4-dibromophenol.

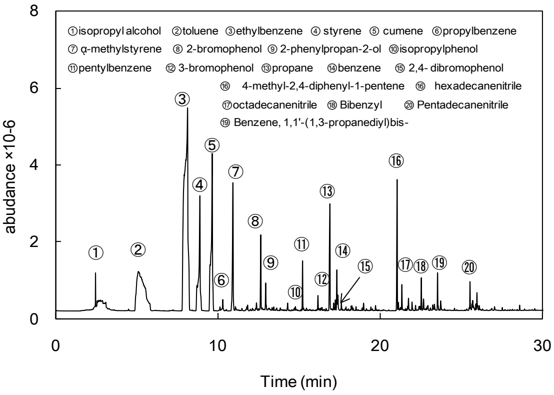

Fig. 3. GC/MS chromatogram of pyrolysis oil.

The concentrations of bromine compounds in the pyrolysis oils obtained with addition of NaOH are shown in Fig. 4. As the quantity of NaOH additive increased, the concentrations of the bromine compounds in the oil decreased. The concentration of 3-bromophenol decreased slightly, and then became almost constant above a NaOH mass fraction of 1 %. The concentration of 2-bromophenol decreased to zero, and that of 2,4-dibromophenol gradually decreased. The total concentration of 2-bromophenol, 3-bromophenol, and 2,4-dibromophenol was 296 mg/L without NaOH addition and 56 mg/L with a NaOH mass fraction of 5 %.

These results indicate that addition of NaOH reduces the level of bromine compounds in pyrolysis oil.

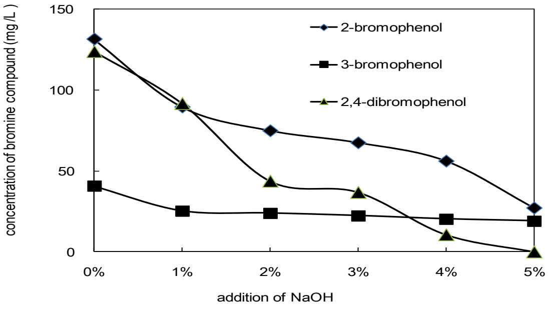

Fig. 4. Concentrations of bromine compounds in the pyrolysis oil.

The concentrations of halogens in the pyrolysis oils are shown in Table 1. As the quantity of NaOH added increased, the halogen content in the pyrolysis oil decreased. Without addition of NaOH, the concentrations of fluoride, chloride and bromine were high at 450, 1598 and 7505 mg/L, respectively. By contrast, with NaOH addition, these concentrations decreased to 155, 129 and 452 mg/L for fluoride, chloride, and bromine, respectively. These results indicate that the pyrolysis oil produced with NaOH could be used as an alternative fuel.

TABLE I. HALOGEN CONCENTRATIONS IN THE PYROLYSIS OIL FROM ABS

NaOH mass fraction (%)	**Halogen concentration (mg/L)**		
	F	***Cl***	***Br***
0	450	1598	7505
1	385	826	4582
2	370	416	2684
3	275	263	2395
4	172	232	1455
5	155	129	452

The solid residue was analyzed by SEM/EDX to determine the elemental content, including bromine, chlorine, antimony and sodium (Table 2). As the quantity of NaOH increased, the contents of sodium, fluoride, chloride and bromine increased. The bromine content was the highest among the three halogens at all levels of NaOH addition. These results indicate the NaOH reduced the halogen concentrations by capturing halogen compounds in the solid residue and stopping their transfer into the pyrolysis oil.

TABLE II. ELEMENTAL COMPOSITIONS OF RESIDUES FROM PYROLYSIS OF ABS

NaOH mass fraction (%)	**Elemental composition (mass fraction, %)[a]**								
	C	***N***	***O***	***F***	***Na***	***Cl***	***Co***	***Br***	***Sb***
0	73.0	13.5	5.7	0.3	n.d.	0.1	0.1	6.2	1.2
1	66.5	13.8	2.9	0.3	0.9	0.2	n.d.	12.0	3.4
2	65.1	13.0	3.0	0.5	1.5	0.2	n.d.	12.6	4.1
3	65.1	7.0	1.6	0.5	2.5	0.4	0.1	17.7	5.3
4	64.2	6.4	1.4	0.8	2.6	0.5	0.1	18.3	5.7
5	61.6	6.6	0.1	1.7	2.6	0.7	0.2	19.4	7.1

[a] n.d.: Not detected

CONCLUSION

ABS resin containing a BFR was pyrolyzed at 450 °C in a system equipped with a reflux condenser. NaOH was added to reduce the content of bromine compounds in the product oil. As the quantity of NaOH added increased, the yield of the oil decreased, the yield of residue increased, and the yield of bromine compounds decreased. The bromine content in oil obtained via pyrolysis with NaOH was lower than that in oil obtained via pyrolysis without NaOH. These results indicate that addition of NaOH is effective for reducing the bromine content of pyrolysis oil. The halogens were captured in the solid residue rather than discharged in gaseous products.

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