PYROLYSIS BEHAVIOR OF ABS WITH BROMINATED FLAME RETARDANTS

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Abstract

Pyrolysis of acrylonitrile-butadiene-styrene (ABS) resin containing brominated flame retardants was carried out using a batch processing system. The pyrolysis products were classified into four groups; liquid, gas, residue and reddish-yellow precipitate, which accumulated in the bifurcation area from the reactor to condenser tube. We investigated the bromine content in liquid, residue and precipitate samples. The effect of pyrolysis temperature on the bromine content in the liquid sample was also evaluated. The majority of the bromine was found to be concentrated in the precipitate. The bromine content in the liquid sample was around 2~3 %; the maximum at pyrolysis temperature of 400~450 ˚C. Stainless steel mesh and glass wool were placed at the upper space of the reactor to promote precipitation of Br-rich compounds on the glass wool, which would prevent condenser tube blocking. Under this pyrolysis condition, the bromine content in the liquid sample was found to reduce to about one-half.

Keywords: *pyrolysis, acrylonitrile-butadiene-styrene(ABS), brominated flame retardant, bromine content*

1. Introduction

Electronic equipment and devices have become indispensable in our daily life, and enormous amount of personal computers, printers, displays and mobile phones are being returned to our recycling centers. The quantity of the plastics separated from electric equipment is significantly increasing, and therefore, a well established recycling technology for plastic waste is required.

The pyrolysis of waste plastics into fuel oil is well known today, and some industrial plants are already in operation. However, major plastic materials processed in these plants are found to be polyethylene (PE), poly-propylene (PP) and polystyrene (PS). On the other hand, the plastics used in electric equipment are mainly acrylonitrile-butadiene-styrene (ABS), polycarbonate(PC), high impact polystyrene (HIPS) and their blends. Also, they often contain brominated flame retardant materials.

Several lab-scale studies have been reported on the pyrolysis of ABS and HIPS containing brominated flame retardants (ABS-Br, HIPS-Br) [1-3]. However, there are still many problems that prevent the pyrolized products put it into practical use. In this study, we investigated the pyrolysis behavior of ABS-Br resins, aiming to reduce bromine content in the pyrolized oil products.

2. Materials and Methods

2-1. Materials

Here, commercially available virgin ABS-Br pellets (VW-800 from UMGABS company) were used for pyrolysis. They contain a brominated flame retardant (< 25 wt%) and antimony trioxide (5 wt%) as a synergist. The grain size was 1 x 1.5 x 3 mm^3. 300 g of resin pellets was employed for each pyrolysis experiment.

2-2. Pyrolysis system and procedure

Figure 1 shows a schematic diagram of the pyrolysis system. A separable glass flask (1000 ml) was used as the reactor, and an electric furnace was used for heating. The temperature was monitored and controlled using a digital controller (Chino, DZ3000). Condition 1 was set as given in fig.1, and condition 2 was set with stainless steel mesh and glass wool placed at the upper space of the reactor.

After the sample was set in the flask, the reactor and all the connecting tubes were purged with nitrogen gas. The heater temperature was increased to 540 ˚C with heating rate of 5 ˚C/min. The temperatures of the plastic sample and released gas were monitored by thermo-couples placed at the bottom of the flask and bifurcation area. As

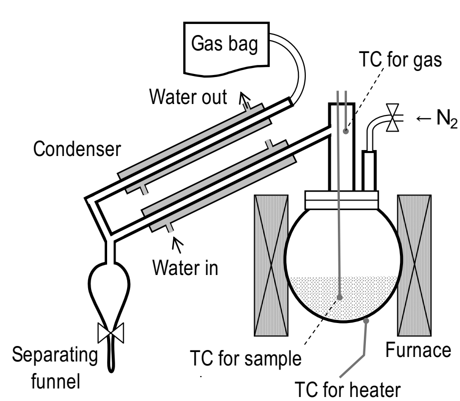

Fig 1. Schematic diagram of pyrolysis system

pyrolysis starts, the gas temperature begins to increase, and the condensable gaseous product was collected as a liquid product through the cold water condenser into the separating funnel. Pyrolysis product sampling was done at 5 min intervals.

2-3. Analytical procedure

The weight of the liquid product was measured, and then the yield was calculated for each pyrolysis temperature. The analysis of the constituents of the liquid products was carried out by gas chromatography mass spectroscopy (GC-MS). The bromine contents of all the products were measured by combustion ion chromatography (Combustion-IC).

3. Results and Discussion

The temperature profile of a typical process (condition 1) was shown in figure 2. When the sample temperature was around 350 ˚C, the sample started to melt, and the temperature rising rate became slow. Then, the gas temperature increased rapidly, and the oil release started. The liquid production rate was found to be maximum around 400~450 ˚C.

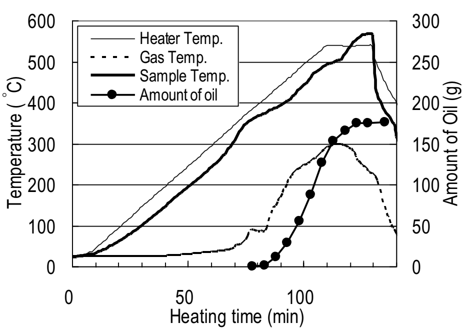

Fig.2. Temperature profile of condition 1

As Bhaskar et al. already reported [1], reddish-yellow precipitate, which they called wax residue, appeared at the bifurcation area from reactor to the condenser tube around 350 ˚C. And then, this wax completely blocked the condenser tubes. The bromine content of this precipitate was found to be 52.5 wt%, and it was confirmed that bromine is mostly condensed in the precipitate. The treatment of these brominated compounds is an important issue in the pyrolysis technology of engineering plastics, if these products are to be put into practical use.

In the present study, in order to promote precipitation of brominated compounds in the reactor, stainless steel mesh and glass wool were placed at the upper space of the reactor (condition 2), thus to prevent the condenser tube blocking. This method brought us impressive results. There was a drastic reduction in the amount of precipitate in the condenser tube of setting condition 2 compared with that of the condition 1. The yields of the liquid product of condition 1 and 2 were 40.6 % and 42.2 %, respectively.

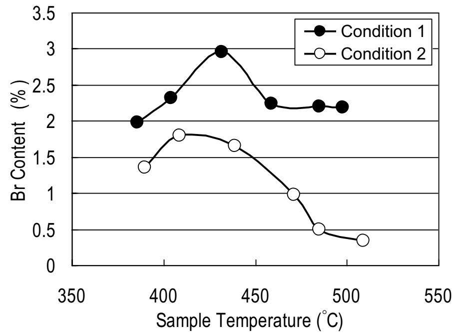

Fig.3. Bromine content of the liquid products

The bromine contents of the liquid product collected at various temperatures were evaluated by Combustion-IC, and the result is summarized in figure 3. The bromine content was found to be maximum at the temperature of 400~450 ˚C. This result suggests that keeping away the Br-rich precipitate from the liquid is effective to reduce the bromine content in the collected liquid products.

From the GC-MS data, it was found that the major constituents of the liquid products were ethyl benzene, isopropyl benzene, and styrene. A slight amount of brominated compounds were also detected, even though their chemical structures were yet to be identified. This result suggests that only precipitate separation is not enough to remove bromine completely from the liquid products, if the products are to be used as fuel. Some catalytic reactions through chemical treatments may be necessary in the pyrolysis process for the production of oil for commercial applications.

4. Conclusions

Pyrolysis of ABS-Br was carried out under two conditions. In the pyrolysis product, Br-rich precipitate was confirmed, and keeping it away from the liquid was found to be effective to reduce the bromine content in the liquid. However, from the GC-MS analysis of the liquid samples collected in our experiments with Br elimination methods, a slight amount of brominated compounds was detected in the liquid samples. Therefore, further studies for complete removal of bromine will be needed.

References

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