PYROLYSIS OF A WASTE FRACTION OF ACRYLONITRILE BUTADIENE STYRENE (ABS) CONTAINING BROMINATED FLAME RETARDANTS IN A FLUIDIZED BED REACTOR: EFFECT OF VARIOUS Ca-BASED ADDITIVES (CaO, $Ca(OH)_2$ AND OYSTER SHELLS) ON THE PYROLYSIS OIL CHARACTERISTICS

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Abstract

A waste fraction of acrylonitrile butadiene styrene (ABS) containing brominated flame retardant and antimony trioxide (Sb_2O_3) as synergist was pyrolyzed in a bench-scale plant equipped with a fluidized bed and char separation system. Experiments were carried out to find out the effect of the three additives (CaO, $Ca(OH)_2$, oyster shells) on the characteristics of pyrolysis oil. The oil and gas fraction were quantitatively and qualitatively analyzed by GC-FID/TCD and a GC-MS and the content of bromine and chlorine in the oil fraction was determined by EPA 5050 method. The antimony content of pyrolysis products was analyzed by an ICP-AES. Analysis of the pyrolysis oil obtained in the absence of additive that was mainly composed of toluene, ethylbenzene, styrene, cumene, α-methylstyrene, phenol, benzenebutanenitrile and (1-chloroethyl)-benzene. The contents of bromine and chlorine in the pyrolysis oil produced at 484 °C without any additive were about 2000 and 2700 ppm, respectively. The bromine and chlorine contents of the pyrolysis oil produced in the presence of $Ca(OH)_2$, decreased down to 500 and 600 ppm, respectively.

Keyword: *Pyrolysis, Fluidized bed, Acrylonitrile butadiene styrene, Halogen compounds, Additive*

1. Introduction

The management and treatment of waste electrical and electronic waste (WEEE), which is generating about 50 million tons worldwide, is becoming a major topic [1]. WEEE is continuously increasing and consequently gives rise to environmental problems. Among the WEEE materials, plastics are difficult to be recycled mainly due to the flame retardants in them. According to the EU directive, however, the fraction of major plastics of WEEE demands for recovery [2]. To convert WEEE plastics containing brominated flame retardants into either fuel oil or useful chemicals, pyrolysis, which is one of the promising techniques, has been widely investigated by many researchers. Pyrolysis of ABS containing brominated flame retardant has been mostly carried out in the fixed bed reactor, and the research using a fluidized bed reactor was rare.

In this work, a waste fraction of acrylonitrile butadiene styrene containing flame retardants was pyrolyzed in a pyrolysis plant equipped with a fluidized bed and char separation system. The goal of this study was to find out the influence of various additives (CaO, $Ca(OH)_2$, oyster shells) on the characteristics of pyrolysis oil

2. Materials and Methods

Material. Waste acrylonitrile butadiene styrene containing brominated flame retardant was provided by local recycling center in Korea. First, the feed material was grounded and sieved to reduce the particle size with a diameter of 2~3.35 mm. It contained brominated flame retardants with synergist (Sb_2O_3). The bromine, chlorine and antimony content of feed material were about 3.2, 0.4 and 3.8 wt.%, respectively. The additives (CaO, $Ca(OH)_2$, and oyster shells) were powder type and were mixed the feed material before pyrolysis experiment.

Pyrolysis plant and procedure. Fig.1 shows the pyrolysis plant.

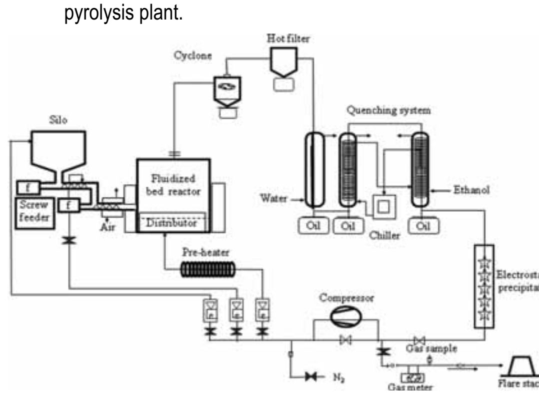

Fig. 1 Pyrolysis plant

It consisted mainly of feeding system, fluidized bed reactor, char separation system, quenching system and product gas circulating system. The fluidized bed reactor, which was indirectly heated by electricity, was made of a sus-316 steel tube with a height of 390 mm and an inner diameter of 110 mm. The char separation system was composed of a cyclone and a hot ceramic filter, which could designed to capture the particle size bigger than 10 and 2 μm, respectively. The quenching system was consisted of one steel condenser which was water-cooled at 20 °C and two glass condensers which were ethanol-cooled at -25 °C. The latter part of the quenching system was electrostatic precipitator that can capture an aerosol phase in the pyrolysis gas. The non-condensable gas was circulated into the fluidized bed reactor through the pre-heater by a compressor.

Reaction conditions. All the experiments were carried out around 485 °C, with feed rates of around 3.8 g/min and at fluidizing flow rates of about 64 NL/min. Table 1 shows the other experimental parameters.

Table 1. Reaction conditions

Parameters	Run									
	1	2	3	4	5	6	7	8	9	10
Additive	x		CaO			$Ca(OH)_2$			Oyster shell	
Amount of additive (g)	0	15	30	60	15	30	60	15	30	60

In each experiment, the input of the feed material was 0.3 kg, and 3.8 kg quartz sand was used as the fluidized bed material. The experiments (R2-R4: CaO, R5-R7: $Ca(OH)_2$ and R8-R10: oyster shells) were performed to find out the effect of the calcium based additives on the characteristics of the pyrolysis oils. The weight ratio of the feed material to an additive was 1:0.05 (CaO), 1:0.1($Ca(OH)_2$) and 1:0.2 (oyster shells), respectively.

Analysis of products. As pyrolysis products, the three fractions, namely, oil, gas and char were obtained. A fraction of oil produced from each run was distilled in a laboratory scale apparatus under reduced pressure (210 °C, 13.3 Kpa) to obtain a light fraction. This distillation condition corresponded to the boiling point of 9H-fluorene (boiling point = 295 °C at atmospheric pressure). An analysis of each oil components was quantitatively and qualitatively analyzed using response factor of each component. The applied capillary column of both GC-FID and GC-MS was a HP-5MS and helium was used as the carrier gas. The bromine content of oil was analyzed by the EPA 5050 method which was used by a bomb calorimeter and by an Ion chromatography. The product gas produced was analyzed with GCs using a TCD and a FID, and argon was used as a carrier gas. The applied columns were a Carboxen 1000 for TCD and an HP-plot Al_2O_3/KCl for FID. The antimony content in the oil, distillation residue was analyzed by an ICP-AES.

3. Results and Discussion

Organic mass balance. In each experiment, the oil yield was determined by weighing liquid product. The gas yield was calculated by multiplying the volume, which was measured the gas meter, and the gas density. The char yield was calculated by difference. After the distillation of pyrolysis oils, we obtained the light phase, which can be analyzed by GC-MS, and the viscous phase. In this study, the light phase and the viscous phase were designated as the oil and the distillation residue, respectively. Finally, the char and the distillation residue were burnt in furnace to find out the organic content in them. The organic mass balance of each experiment is shown in Table 2.

Table 2. Total organic mass balance.

Total organic mass balance (wt.%)	Run									
	1	2	3	4	5	6	7	8	9	10
Gas	4	2.7	2.3	2.4	2.7	1.6	2.2	3.5	3.8	4.3
Oil	74.7	67	61.7	49.8	61.3	58.6	53.4	64.6	58.9	65.4
Benzene	1.1	0.2	0.2	0.1	0.2	0.3	0.2	0.2	0.3	0.2
Toluene	9.3	4.6	6.1	3.5	4.5	4.6	3.4	4.3	4.2	3.8
Ethylbenzene	18.9	6.4	6.6	3.8	6.3	5.5	3.2	11.7	10.8	7.2
m/p/o-xylene	0.2	0.3	0.1	0.1	0.1	0.1	0.1	0.3	0.1	0.1
Styrene	16	17	18.8	11.6	11.5	16.2	12	3	10.1	9.4
Cumene	4.2	2.4	2.1	1.3	2.3	1.9	0.9	3.7	3.5	2.4
α-methylstyrene	2.5	4.1	5.9	3.5	4	4.5	3.7	2.4	4.1	4.7
Phenol	3.3	4.4	5.7	2.8	4	3.8	1.8	4.3	6.2	5.8
1,3-diphenlypropane	0.3	1.7	0.3	1.7	0.5	1.6	1.9	3.2	1.2	2.7
N-compounds	9.9	12.9	7.1	10.3	11.8	10.5	11.9	14.1	8.4	13.8
Br-compounds	0.4	0.3	1.2	0.3	0.2	0.4	0.4	0.9	0.2	0.6
Cl-compounds	1.7	1.2	0.3	1.1	1.4	0.9	1.1	1.1	1.1	-
Others	4	7.5	4.9	6	9.6	5.4	7.3	10.5	6.3	11.2
Not detected	2.9	4.2	2.4	3.7	4.9	3	5.5	4.8	2.3	3.6
Char	8.4	18.5	26.4	35.6	23.7	26.6	35.3	20.8	25.8	22.7
Distillation residue	12.9	11.7	9.7	12.3	12.3	13.2	9.1	11.2	11.5	7.6

Bromine, chlorine and antimony content in pyrolysis oil. To reduce the bromine and chlorine content in the oil, calcium-based additives (CaO, $Ca(OH)_2$, and oyster shells) were applied the feed material per additive in weight ratios of 1:0.05, 1:0.1 and 1:0.2. Table 3 shows the amount of bromine and chlorine in the oil with (Run4, Run7 and Run10) and without (Run1) the additives. The antimony content of oil and distillation residue (Run7) was 0.001 and 0.002 wt.%, respectively. Most of antimony was concentrated in the char.

Table 3. Content of Bromine and Chlorine in the oils.

Run	Concentration (wt.%)	
	Bromine	Chlorine
1	0.2	0.27
4	0.17	0.07
7	0.05	0.06
10	0.2	0.04

4. Conclusions

In this study, the acrylonitrile butadiene styrene with brominated flame retardant was pyrolyzed in a fluidized bed reactor equipped with char separation system. To achieve the dehalogenation of oil, the three calcium-based additives (CaO, $Ca(OH)_2$, and oyster shell) were applied by mixing with the feed material. The pyrolysis oil obtained in the absence of additive consisted mainly of toluene, ethylbenzene, cumene, α-methylstyrene, phenol, benzenebutanenitrile and (1-chloroethyl)-benzene. In the presence of additive, especially $Ca(OH)_2$, the bromine and chlorine content in the oil decreased down to 0.05 and 0.06 wt.%, respectively. It was found that the Ca-additives were very effective for the dehalogenation of oil.

References

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