

## Initial studies on possibility of simultaneous recycling BFR-containing waste plastics with EAF dust

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### Introduction

Tetrabromobisphenol A (TBBPA) is the largest volume brominated flame retardant (BFR) in production today, used in more than 70 % of the world's electronic and electric (E&E) appliances as well as in many plastics, textiles and so forth. There is constant growth in the production of such products and they become obsolete quickly, this generates huge amounts of BFR-containing wastes and causes significant problems for their safe disposal and recycling. The most common way to use them is in thermal processing, as it allows recycling and recovery of both the organic and inorganic fractions of the waste. TBBPA easily decomposes during this process, generating significant amounts of gaseous HBr (Barontini et al. 2006). Our studies (Grabda et al. 2009) indicate that hydrogen bromide (HBr), generated during thermal decomposition of tetrabromobisphenol A (TBBPA), can be utilized as a reagent for bromination and evaporation of zinc oxide. The bromination-evaporation process could be advantageous for the simultaneous recycling of the waste plastics with solid wastes containing heavy metals such as plating sludge, and also metallurgical dusts, especially zinc and lead-rich electric arc furnace dust (EAFD), a significant amount of which (30% in Japan) is to be landfilled because of recovery difficulties (Hiroyuki et al. 2005).

EAFD is a valuable secondary raw material in the production of zinc as it contains up to 35 % Zn, mainly in the form of zincite (ZnO) and frankonite (ZnFe<sub>2</sub>O<sub>4</sub>). The worldwide generation of EAFD represents a possible recovery of approximately 1.4 million tones of zinc (Antrekowitsch, 2001). Recently, an alternative method for pyrometallurgical treatment of EAFD has been proposed. Chlorine was sourced from waste polyvinyl chloride (PVC) for selective chlorination and evaporation of zinc (Zhang et. Al, 2000). The potential advantages of selective bromination-evaporation process could be similar to selective chlorination: a) efficient separation of zinc from EAFD, providing resources of recovered zinc and separated iron oxide residues for iron- and steel-manufacturing; b) recycling of the bromine reagent, and c) simultaneous recycling of waste plastics containing BFR with EAFD.

Large-scale application, however, requires a good understanding of the reactivity of the main zinc bearing compounds in EAFD with the TBBPA thermal decomposition products (namely HBr), the reaction mechanism and kinetics. In this research we focus on the reactivity of ZnO and investigation of the dependency of the bromination reaction on time at selected temperatures.

### Materials and Methods

*Materials:* Tetrabromobisphenol A (97.0 %) and ZnO (99.9 %) were manually mixed at a mass ratio of 3.34:1 (TBBPA:ZnO), which was determined from the stoichiometric relationship assuming all bromine present in TBBPA was released and reacts with zinc to form zinc bromide (ZnBr<sub>2</sub>).

**Methods:** The sample (approximately 2 g) was placed on a combustion boat located inside a cooler part (jutting out beyond the furnace) of a quartz tube reactor heated by a small furnace (Fig. 1). When the temperature of the furnace was stabilized at the desired temperature, the combustion boat with sample was moved inside the furnace, where it was thermally treated at isothermal conditions under an Ar (99.9 %) flow of 50 mL/min. Investigation of the isothermal treatment of TBBPA:ZnO was performed in two series of independent experimental runs. In the first series, the sample was heated for 40 min within a temperature range from 230–310 °C (every 10 °C) then at 340 °C and 420 °C. The results allowed selection of temperatures for the second series of experiment. In this series, detailed studies on heating time and efficiency of bromination of ZnO were performed at 250 °C, 270 °C, 290 °C and 310 °C. After treatment, the sample was rapidly cooled to prevent any secondary reactions. A quartz wool filter was placed inside the reaction tube, positioned where the temperature of the outgoing gases dropped to about 100 °C, to catch condensable phase vaporized from the sample. Two traps consisting of distilled water and hexane were used for the inorganic and organic gaseous products, respectively. Additionally, the effect of oxidizing conditions (Ar + 5 vol % O<sub>2</sub>) on the bromination reaction was studied at 250 °C (for 10, 40 and 140 min) and 310 °C (for 10 and 60 min).

**Sample qualification:** The formed solid, condensed and gaseous products were analyzed by XRD, EPMA, ICP, IC and GC-MS methods.

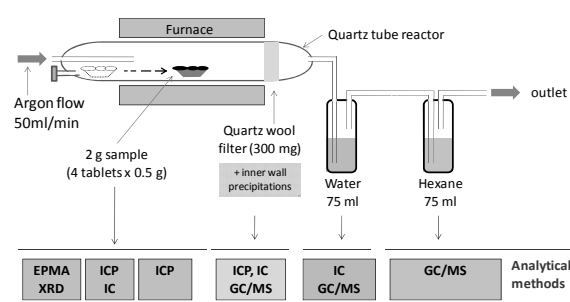


Fig. 1. Schematic of the experimental set-up for the furnace and overview of the analytical procedures used.

## Results and Discussion

**Effect of temperature on bromination of ZnO by TBBPA:** The thermal treatment of TBBPA with ZnO (3.34:1) at 230 °C essentially does not change the weight or chemical composition of the original mixture. Heating to higher temperatures reveals strong relationships between the intensity of decomposition of TBBPA and efficiency of bromination of ZnO (correlation coefficient = 0.998). Debromination of TBBPA begins at 240 °C and overlaps with the start of ZnO bromination by released bromine (Table 1, Fig. 2A). At this temperature, less than approximately 2 % of inorganic bromine is released from TBBPA, resulting in bromination of approximately 5 % of the zinc. Elevation of the temperature to 280 °C, increases the amount of released bromine and induces greater efficiency of the bromination reaction to maximum levels (63 % of Br released and 69 % of zinc brominated). Further increases in the temperature do not affect the bromination rate (Table 1, Fig. 2A). This is because all possible sources of bromine for the reaction (TBBPA and brominated products of its decomposition) are completely decomposed as indicated by GC-MS analysis of solid residue (data not shown here). Isothermal treatment of TBBPA:ZnO for 40 min reveals that bromination of ZnO begins at 240 °C and is completed at 280 °C with a maximum yield of 69 %. The process is strongly dependent on decomposition of the flame retardant, providing inorganic bromine suitable for the reaction.

*Effect of time on bromination of ZnO by TBBPA:* The results shown in (Table 2, Fig. 2B) reveal that the rate of ZnO bromination is strongly dependent on heating time at the lowest experimental temperature (250 °C), and the effect of time weakens with increasing temperature, until its complete decay at 310 °C.

Table 1. Amount of bromine released from TBBPA and the fate of zinc during isothermal treatment of TBBPA and ZnO for 40 min at various temperatures, expressed as percentages.

Temperature	Released Br	Br bounded to Zn for Br released	Brominated Zn for total Zn	Vaporized Zn for total Zn	Vaporized Zn for brominated Zn	Zn loss
°C	%	%	%	%	%	%
230	< 1	98	2	0.00	0.00	24
240	2	99	5	0.00	0.00	4
250	8	100	15	0.00	0.01	6
260	36	93	45	0.00	0.00	4
270	50	94	59	0.00	0.01	5
280	63	98	69	0.01	0.02	5
290	62	95	66	0.04	0.07	3
300	59	95	64	0.13	0.20	2
310	59	93	64	0.14	0.22	3
340	63	95	68	0.46	0.68	3
420	60	89	62	3.35	5.44	6

This is a direct consequence of progress in the decomposition of TBBPA, increasing the abundance of inorganic bromine suitable for the reaction. Zinc bromination increases with time until both the primary and secondary sources of bromine in the solid residue are used up. The process time reduces as the applied temperature increases, and appears instantaneous at temperatures of 310 °C and above. The maximum bromination yield is independent of the applied conditions and ranges from 64–70 %.

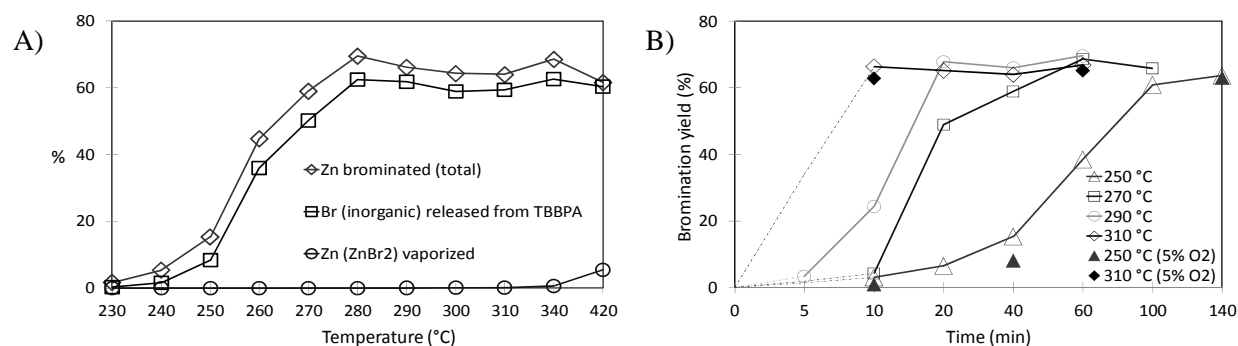


Fig.2. Effect of temperature (A) and time (B) on effectiveness of zinc bromination and amounts of inorganic bromine released from TBBPA during thermal treatment of TBBPA:ZnO (3.34:1).

The maximum quantity of inorganic bromine released during TBBPA decomposition ranges from 63–65 % (Table 2). Most of this bromine (96 % on average) is bound with zinc present in the mixture. A small amount of inorganic bromine (maximum 8 %) (Table 2) is lost from that available for reaction, because it vaporizes from the solid residue before contacting with any ZnO particles. A similar phenomenon was observed in our previous experiments with a constant heating rate (Grabda et al., 2009), in that case the unreacted bromide was thought to result from some time-dependent factor(s)

affecting the bromination reaction. However, results indicate that it could be due to reasons other than heating time, such as vaporization from the outer surface of the heated sample. Detection of unreacted bromine even at the beginning of TBBPA decomposition (Table 2) may indicate such vaporization is a real possibility. Alternatively, the portion of bromine that is lost may result from formation of a solid black residue called char (cross-linked high molecular weight compounds).

Table 2. Amount of bromine released from TBBPA and the fate of zinc during thermal treatment of TBBPA and ZnO at various temperatures, expressed as percentages.

Temp.	Time	Released Br	Br bounded to Zn for Br released	Brominated Zn for total Zn	Vaporized Zn for total Zn	Vaporized Zn for brominated Zn	Zn loss
°C	min	%	%	%	%	%	%
<b>Argon</b>							
250	10	< 1	98	3	0.00	0.00	3
	20	2	100	6	0.00	0.00	5
	40	8	100	15	0.00	0.01	6
	60	35	94	38	0.00	0.01	3
	100	60	95	61	0.00	0.01	5
	140	63	92	64	0.00	0.01	7
270	10	1	94	4	0.00	0.00	7
	20	43	96	49	0.01	0.01	5
	40	50	94	59	0.00	0.01	5
	60	65	98	69	0.01	0.01	4
	100	64	96	66	0.01	0.01	8
290	5	< 1	98	3	0.00	0.00	0
	10	18	98	24	0.00	0.01	0
	20	62	98	68	0.03	0.04	1
	40	62	95	66	0.04	0.07	3
	60	64	97	70	0.05	0.08	1
310	10	61	97	66	0.12	0.18	3
	20	60	97	65	0.07	0.11	5
	40	59	93	64	0.14	0.22	3
	60	64	98	67	0.17	0.25	1

*Oxidizing atmosphere:* The presence of oxygen (5 vol %) had no significant effect on decomposition of TBBPA, in either the amount of inorganic bromine released during decomposition or the ZnO bromination yield (Fig. 2B). A slight drop was observed in the amount of released inorganic bromine and resulting ZnO bromination during isothermal heating for 40 min under oxidizing conditions at 250 °C (Fig. 2B). However, this may result from analytical inaccuracy, as all other results obtained under oxidizing conditions show no such discrepancy.

## References

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