

# EMISSION CONTROL OF BROMINATED COMPOUNDS BY METAL OXIDES IN PYROLYSIS OF TETRABROMOBISPHENOL A AND A PRINTED CIRCUIT BOARD

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## Abstract

*Pyrolysis of tetrabromobisphenol A, a common flame retardant, has been studied under the presence of metal oxide. The formation of hydrogen bromide and brominated organic compounds is significantly suppressed by the addition of metal oxides. The bromine fixation ability of various oxides is compared and discussed. A preliminary work on thermal degradation of mixtures of a print circuit board and oxide has been also carried out. The results show that the presence of oxide is effective for the suppression of hydrogen bromide as well as brominated organic compounds.*

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**Keywords:** tetrabromobisphenol A, hydrogen bromide, brominated organic compounds, metal oxides, printed circuit board

## 1. Introduction

Pyrolysis treatment is an attractive method that enables feedstock recycling of synthetic polymers with simultaneous volume reduction of wastes. However, most of waste polymers contain various flame retardants, the influence of which should be carefully examined in the pyrolysis treatment. Tetrabromobisphenol A or 2,6,2',6'-tetrabromo-4,4'-isopropylidene-diphenol, denoted hereafter as TBBA, is commonly used as brominated flame retardant. Thermal treatment of waste resins containing TBBA results in the formation of various brominated compounds. It is known that the major degradation product of TBBA is hydrogen bromide, HBr, with some by-products of brominated phenols [1]. Uncontrolled thermal treatment of waste containing TBBA can develop polybrominated dibenzo-p-dioxins (PBDDs) and dibenzofurans (PBDFs) [2]. The emission control of such harmful compounds is becoming important in the view of the significant increase of waste electronic and electric equipment (WEEE). In the present study, we have carried out pyrolysis of TBBA in the presence of metal oxide in the view of simultaneous treatment of waste plastics and oxide wastes, such as metallurgical dust. A preliminary work has been also conducted for pyrolysis of a printed circuit board containing bromine as flame retardant.

## 2. Materials and Methods

Powder form of TBBA,  $C_{15}H_{12}Br_4O_2$  supplied from Aldrich, was used in the present study. The typical diameter was of  $\sim 50$   $\mu\text{m}$ . Pyrolysis samples were prepared by mechanical mixing of the TBBA and metal oxide powder of reagent grade ( $La_2O_3$  from Kishida Chem. Co., Ltd., and  $ZnO$ ,  $CaO$ ,  $CuO$  and  $Fe_2O_3$  from Kanto Chem. Co., Ltd.) in mortar for ca. 5 min. The mixture was consequently pelletized with the load of ca.  $2.5 \times 10^8$  Pa.

The oxides have the particle diameter of 1-10  $\mu\text{m}$ , and the BET surface area of the order of 1  $\text{m}^2/\text{g}$  [3]. It is expected that bromine released from TBBA reacts with metal oxide to form the corresponding metal bromide or oxybromide. The composition of  $[TBBA]:[Fe_2O_3] = 1:1$  and  $[TBBA]:[\text{other oxide}] = 1:2$  in molar ratio was mainly examined. This is based on the stoichiometry of the corresponding metal bromides and oxybromide, i.e.  $ZnBr_2$ ,  $CaBr_2$ ,  $CuBr_2$ ,  $FeBr_2$  and  $LaOBr$ . A printed circuit board was supplied from Hitachi Kasei Co., Ltd. (FR-4 type). The copper plate was removed by iron chloride solution. The Cu-free board was then crushed and ground down to  $< 250$   $\mu\text{m}$ . The preparation of pyrolysis sample was similar to that of TBBA – metal oxide mixtures.

Pyrolysis experiments were carried out with a horizontal type reactor (700 mm in length and 26 mm in i.d.) under helium atmosphere [4]. Detailed analytical methods of pyrolysis products are described elsewhere [4]. The formation of hydrogen bromide captured in a water trap was monitored through the amount of bromide ion,  $Br^-$ , with an ion meter (IM-40S, TOA Electronics). A bromide ion-selective electrode (TOA Br-125) was employed as the working electrode. The reference electrode (TOA HS-305DS) was a double junction-type  $Ag/AgCl$  electrode with saturated KCl solution as an inner solution and 0.1 M  $KNO_3$  solution as an outer solution adjacent to the sample solution. Gaseous and liquid products were analyzed by GC-MS.

## 3. Results and Discussion

The formation of hydrogen bromide and brominated organic compounds is observed in pyrolysis of TBBA. As seen in Table 1, the addition of metal oxide gives rise to considerable suppression of HBr. In the case of the addition of lanthanum oxide with the composition of 1:2,

the formation of HBr is almost insignificant. As summarized in Table 2, the formation of the brominated organic compounds is substantially reduced by the addition of calcium oxide and  $\text{La}_2\text{O}_3$ . Thus, these oxides can be applied for the emission control of harmful brominated organic compounds.

Table 1. The ratio of trapped Br- in water trap and the initial bromine at 800 °C (in %). The composition of TBBA – oxide mixture denotes [TBBA] : [oxide] in molar ratio.

TBBA		Trapped Br (wt.%)
TBBA		92
TBBA-ZnO	1:1	38
	1:2	23
	1:3	4.0
TBBA- $\text{Fe}_2\text{O}_3$	1:1	42
	1:2	35
	1:3	17
TBBA-CaO	1:1	46
	1:2	13
	1:3	9.1
TBBA- $\text{La}_2\text{O}_3$	1:1	30
	1:2	0.5

Table 2 Product yield for pyrolysis at 800 °C,  $100 \times (\text{mass of product}) / (\text{initial mass of TBBA})$ . The sample composition is [TBBA] : [ $\text{Fe}_2\text{O}_3$ ] = 1:1 and [TBBA] : [other oxide] = 1:2.

	TBBA	+ZnO	+ $\text{Fe}_2\text{O}_3$	+ $\text{La}_2\text{O}_3$	+CaO
Phenol	0.019	2.4	2.8	0.26	0.21
p-bromophenol	6.8	0.74	0.94	0.10	0.095
m-cresol	0.057	0.019	0.027	0.0024	0.018
2-bromo-4methylphenol	0.20	0.053	0.027	0.023	0.051
3,5-dibromotoluene	0.0026	0.0011	0.0064	0.0010	0.0024
2,6-dibromophenol	2.15	0.41	0.36	0.078	0.25
2,4,6-tribromophenol	2.48	0.16	0.20	0.0071	0.10

Similar effect is observed in the pyrolysis treatment of a printed circuit board, containing bromine as flame retardants. Fig. 1 shows the product yield of bromophenols in pyrolysis of the board material at 800 °C. It is clearly seen that the formation of brominated compounds is substantially reduced by the addition of metal oxide. In comparison of the present results with those of the TBBA-oxide mixtures, it is obvious that calcium oxide plays a different role in the fixation of the

bromine. Further studies are needed in order to clarify the detailed role of the oxides in the fixation of bromine in the pyrolysis treatment.

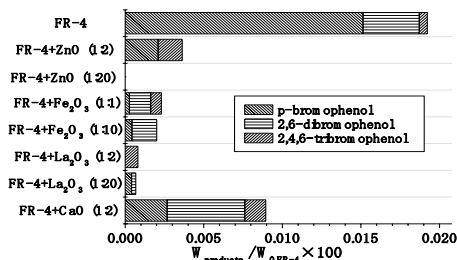


Fig. 1. Comparison of the yield of bromophenols in thermal degradation of printed circuit board, FR-4, at 800 degrees celsius. The composition in molar ratio is indicated in the parenthesis, where the mole of the corresponding TBBA in the board and that of each oxide is shown.

#### 4. Conclusions

The addition of some metal oxides reduces the formation of HBr and brominated organic compounds in thermal degradation of TBBA. Lanthanum oxide is especially effective for the suppression of HBr, and the formation of the brominated organic compounds are substantially reduced by the addition of  $\text{La}_2\text{O}_3$  and CaO. Similar suppression is observed in pyrolysis of a printed circuit board under the presence of metal oxide, though a slight difference in the role of oxides is observed. The influence of polymer matrix may not be negligible, so that further studies on thermal decomposition of various polymers containing TBBA should be carried out.

#### References

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