



Conversion of bromine during thermal decomposition of printed circuit boards at high temperature

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ABSTRACT

The conversion of bromine during the thermal decomposition of printed circuit boards (PCBs) was investigated at isothermal temperatures ranging from 800 °C to 1100 °C by using a quartz tube furnace. The influence of temperature, oxygen concentrations (0%, 10% and 21% in the nitrogen–oxygen atmosphere) and content of steam on conversion of bromine was studied. With the increment of temperature, the conversion from organic bromine in the PCBs to inorganic bromine in the gaseous fraction increased from 69.0% to 96.4%. The bromine was mainly evolved as HBr and Br₂ in oxidizing condition and the Br₂/HBr mass ratio increased at stronger oxidizing atmosphere. The experimental results also indicated that the existence of steam can reduce the formation of Br₂. Furthermore, co-combustion of PCBs with S and CaO, both as addition agents, was investigated, respectively. In the presence of SO₂, Br₂/HBr mass ratio obviously decreased. Moreover, the utilization of calcium oxide can efficiently promote the conversion of organic bromine to inorganic bromine. According to the experimental results, incinerating PCBs at high temperature can efficiently destroy the organobrominated compounds that are considered to be possible precursors of polybrominated dibenzo-p-dioxins and dibenzofurans (PBDD/Fs), but the Br₂ and HBr in flue gas should be efficiently controlled.

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1. Introduction

In recent years, the development of modern science and technology accelerates the obsolescence of electronic and electrical equipments (EEEs) that have become one of the fastest growing waste streams around the world [1]. Such worldwidely growing waste stream has naturally increased the number of waste printed circuit boards (PCBs) that serve as one of the main component in all EEEs. The average rate of worldwide PCBs manufacture increased by 8.7%, and this figure is much higher in Southeast Asia (10.8%) and Mainland China (14.4%) [2]. Brominated flame retardants (BFRs) are widely used in the PCBs to reduce the possibility of fire under the thermal stress. But the utilization of them would also results in the formation of dangerous compounds during the recovery of waste PCBs [3]. However, in some areas of China, because of the unawareness of potential hazards from BFRs, a large number of waste PCBs were simply burnt for recovery of metals and thus it generated toxic persistent organic pollutants (POPs) such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), polybrominated diphenyl ethers (PBDEs) and halogenated dioxin-like compounds, which caused severe damages to the local environment and human health [4–7]. For that reason,

many researchers have dedicated to find safe and efficient methods for the disposal of waste PCBs.

Pyrolysis is considered to be a feasible method. Former studies mainly investigated the kinetic of thermal decomposition [8–10] and the characteristics of pyrolysis products [11–15]. During the pyrolysis process, the amount of oil is usually variable due to the contents of PCBs and experimental conditions, and the main composition is phenol and phenolic derivatives [12,13]. Approximately more than half of bromine evolved as HBr in the gaseous fraction and the remainder mainly formed brominated compounds such as brominated phenol in the oil [11,14]. However, the results obtained also evidenced the formation of extremely hazardous PBDD/Fs during pyrolysis of PCBs. Moreover, several investigations were dedicated to finding an optimal processing and addition agent for the inhibition of formation of hazardous compounds in the flue gas and the dehalogenation of brominated organic compounds in the pyrolysis oil [16–21]. Pyrolysis can effectively recover the most valuable parts of PCBs but the products need to be refined by petrochemical companies before practical usage that will increase the cost [2] and may limit the capacity of the disposal of waste because of excessive processes.

Incineration has been well recognized as the most available technology for thermal disposal of municipal solid wastes (MSWs), which can efficiently recover energy for heating and electricity. Thus, incineration should be a feasible method for the disposal of waste PCBs, which specially have higher heating value than

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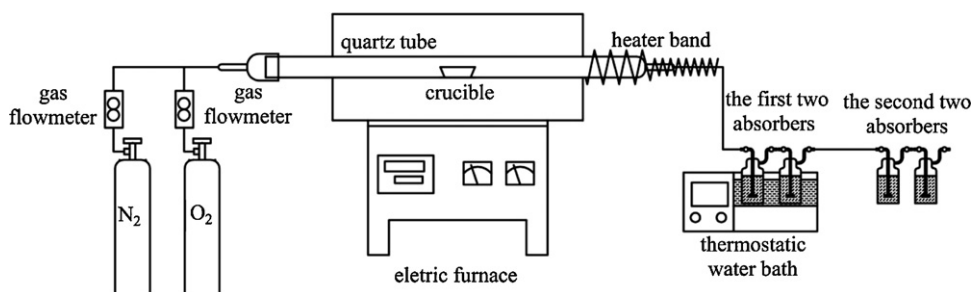


Fig. 1. Schematic diagram of quartz tube furnace.

MSWs. Vehlou et al. [22] investigated the co-combustion waste EEs with MSWs. The author concluded that burnout of the bottom ashes was improved because of higher heating value of PCBs and the emission quality was not deteriorated. However, there were still several hundred mg/m^3 HBr in the flue gas. Due to the similar chemical properties of chlorine and bromine, Weber and Kuch [23] deduced that brominated dioxin-like compounds have similar formation mechanisms to the chlorinated dioxin-like compounds, thus the PBDD/F are formed in incineration system primarily by fly ash catalyzed de novo synthesis because the precursors can be efficiently destroyed under controlled combustion conditions. Sakai et al. [24] investigated the behavior of halogenated dioxin-like compounds during the combustion of waste EEs. The results indicated that the 89–99.7% of the input amount of brominated dioxin-like compounds from the waste EEs was destroyed. Moreover, the higher temperature of the cooling duct exit and a mixture with metals tend to promote formation of PBDD/Fs due to the de novo synthesis. These investigations primarily shed some light on the formation of extremely hazardous PBDD/Fs during the combustion of waste EEs, but the emission characteristics of inorganic bromine in flue gas still should be fully studied. Wichmann et al. [25] once documented the formation of PBDD/Fs by combustion of Polyethylene, Polystyrene, Phenolic resin and Epoxy resin in an atmosphere consisting of synthetic air and HBr, which indicated the terrible potential hazard of HBr. Moreover, Söderström and Marklund [26] also confirmed the formation of molecular bromine during incineration of waste-containing brominated flame retardants. Hence, the aim of this paper is to investigate the influence of temperature, oxygen concentrations, and content of steam on the conversion of bromine. Furthermore, co-combustion of waste PCBs with calcium oxide and sulfur for removing acid gaseous pollutants were also performed to investigate the removal efficiency and influence on bromine conversion.

2. Experimental

2.1. Material

The waste printed circuit boards used in this experiment were cut and smashed into powder. After classification, the ones with the size between 0.150 mm and 0.250 mm were selected as experiment sample. Proximate analysis and ultimate analysis of the PCBs sample were shown in Table 1. The waste PCBs are mainly constituted of a cross-linked organic matrix on a support of glass fibers and some metals. The organic matrix contains epoxy resin and brominated epoxy resin. The nitrogen and oxygen used in this experiment were supplied by a local manufacturer and their concentrations were both 99.99%.

2.2. Method

This experiment mainly aimed at the quantitative determinations of HBr and Br_2 in flue gas. The schematic diagram of the

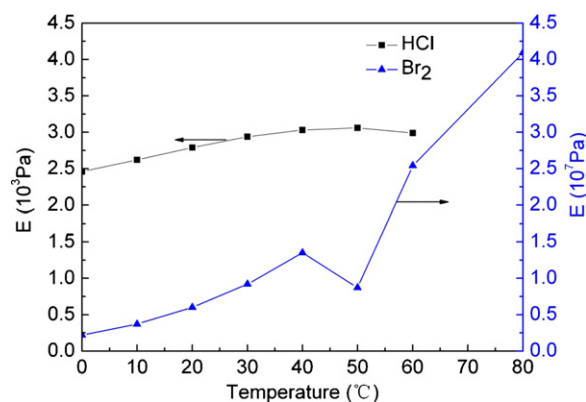


Fig. 2. Henry coefficient of Br_2 and HCl.

quartz tube furnace is shown in Fig. 1. The diameter of the quartz tube is 30 mm and the length of isothermal region is about 60 cm. About 200 mg sample, covered with some quartz sand to prevent deflagration, was quickly placed in the middle of isothermal region, then 800 mL/min of gases was introduced. The gases with different oxygen concentrations (0%, 10%, and 21%) were mixed with nitrogen and oxygen. Then the flue gas exited from the quartz tube to absorption system. Each run lasts 30 min.

The absorption system is the crucial part of this experiment. The temperature of the first two absorbers, containing 0.05 mol/L sulphuric acid, was kept at 60 °C and the temperature of the last two absorbers, containing 0.06 mol/L potassium iodide solution, was kept at room temperature. When the flue gas pass through the first two absorbers, HBr was absorbed by sulphuric acid solution, but Br_2 escaped and entered into the second two absorbers in which Br_2 reacted with KI to form KBr. Then wash the absorbers by deionised water and detected Br^- by ion chromatography. The quantitative data of Br_2 and HBr can be attained according to the concentration of Br^- .

Table 1

Ultimate and proximate analysis of the waste PCBs sample.

	Concentration (wt %)
Ultimate analysis	
C	26.36
H	2.8
O	15.58
N	1.00
S	0.02
Br	7.25
Proximate analysis	
Moisture	1.23
Ash	53.01
Volatiles	37.17
Fixed carbon	8.59
High heating value HHV (MJ/kg)	11.368

Table 2
Distribution of bromine between first two and last two absorbers.

Simulation object	First two absorbers (%)	Last two absorbers (%)
HBr	99.39	0.61
Br ₂	0.65	99.35

The method of separating Br₂ and HBr bases on the principle of chromatography: different materials can be separated by their different distribution coefficient between stationary phase and mobile phase [27]. In our experiment, the flue gas can be view as mobile phase and the solution in the first two absorbers can be view as stationary phase. Thus, HBr and Br₂ with different Henry coefficient (shown in Fig. 2 [29]) can be efficiently separated. This method has been already used by Hall and Williams [28] for qualitative determinations. Because the data of HBr is not available now, we assume that it is similar to HCl because of the similar chemical properties between them. With temperature increasing, the Henry coefficient of Br₂ increases obviously but that of HCl is very slow. At 60 °C the value of the former is 8000-plus times than that of the latter. Therefore HBr with lower Henry coefficient tends to be captured by the first two absorbers, but Br₂ with higher Henry coefficient can easily escape and is captured by potassium iodide solution.

To demonstrate this assumption, a simulation test of absorption was carried out. HBr or Br₂ was put into the first absorber, and then hot air was introduced into the absorber and passed through all absorbers. HBr was still in first two absorbers but Br₂ was carried by the hot air and then absorbed by potassium iodide solution. After 30 min, the bromine ions in the absorbers were detected by ion chromatography. The results are shown in Table 2. Because it is difficult to control Br₂ vapor to simulate the flue gas, the simulation test is a little different from the practical combustion. But the influence can be neglected.

3. Results and discussion

3.1. Bromine conversion during thermal decomposition under different atmospheres

Combustion and pyrolysis of waste PCBs were carried out at temperature ranging from 800 °C to 1100 °C. Moreover, sodium bicarbonate was added into the potassium iodide solution to prevent the oxidization of iodide ions by oxygen which is a strong oxidant in acidic solution. As a matter of fact, the solution remained colorless after pure oxygen was introduced. After 3 min of combustion, the color of potassium iodide solution became yellow, because iodide ions were oxidized and formed colored I₃⁻. However, the color did not change during pyrolysis. The different experiment phenomenon also suggested the existence of Br₂ in oxidizing condition at high temperature which coincided with later experiment results.

To specify the bromine conversion, three different parameters were defined: ratio of the mass of bromine converted to Br₂ and HBr to the mass of bromine in sample, namely α ; ratio of the mass of bromine converted to Br₂ to the mass of bromine converted to HBr and Br₂, namely β ; ratio of the mass of bromine converted to Br₂ to the mass of bromine in sample, namely γ .

As evident from Fig. 3, there are no significant differences in the values of α between pyrolysis and combustion. This result indicates that the presence of oxygen do not significantly affect the conversion ratio α . With the increment of temperature from 800 °C to 1100 °C, the values of α obviously increase from 69.0% to 96.4% during combustion and from 62.0% to 96.7% during pyrolysis. Most of the organobrominated compounds are destroyed at high temperature to form HBr and Br₂. But the data from Fig. 4 show an obvious difference between the two conditions. The values of γ increase

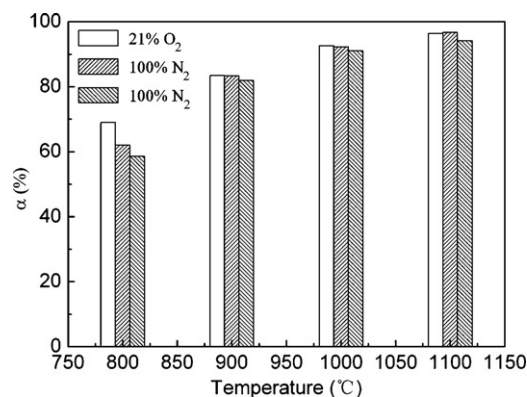


Fig. 3. Conversion of bromine α during combustion and pyrolysis of waste PCBs (α : ratio of the mass of bromine converted to Br₂ and HBr to the mass of bromine in sample).

from 30.7% to 80.4% with temperature increasing during combustion; however they keep steady at a lower level during pyrolysis, proximately 4%. A large quantity of Br₂ evolved during combustion can also be deduced from the color change of potassium iodide solution, which has been mentioned earlier in this paper.

Under thermal stress, brominated flame retardants in PCBs release HBr mainly by following three reactions [30]:



where MBr: brominated flame retardant molecule; RH: flammable molecules in gaseous fraction. Considerable HBr in combustion zone would substitute the more reactive H[•] and OH[•] radicals for less reactive Br[•] radicals to stop radical chain reaction. It is obvious that oxygen is not reactant and cannot directly change the chemical equilibrium of these reactions. However, more M–Br bonds tend to split at higher temperature to form HBr or bromine radicals. So α is mainly determined by the temperature.

However, the obviously different characteristics of Br₂ emission should be due to different fundamental mechanisms of formation. In inert condition, debromination reactions, which were considered to be a key role in the formation of PBDD/Fs during thermal decomposition of BFRs [23], were the possible source of Br₂. On the other hand, HBr evolved can be oxidized by oxygen to form Br₂ under oxidizing condition by reaction (4):

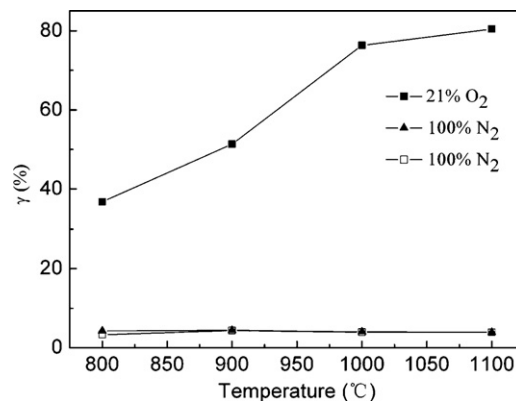


Fig. 4. Conversion of bromine γ during combustion and pyrolysis of waste PCBs (γ : ratio of the mass of bromine converted to Br₂ to the mass of bromine in sample).

Table 3
Chemical equilibrium constant of reaction (4) and reaction (7).

t (°C)	800	900	1000	1100
K				
Reaction (4)	2.96E+6	2.00E+5	2.00E+4	2.93E+3
Reaction (7)	7.30E+7	1.26E+6	4.25E+4	2.38E+3

This reaction is similar to the famous Deacon reaction. However, due to weaker oxidation of bromine, more Br_2 were generated under the same condition compared with chlorine. In order to demonstrate this reaction, further experiments with 10% oxygen in the nitrogen–oxygen atmosphere and air containing steam were carried out respectively. The result is showed in Fig. 5. A decrement of the parameter β can be observed in the presence of steam at temperature rising from 900 °C to 1100 °C. A slow increment of β occurred with temperature increasing. Under lean oxygen atmosphere, obvious decrement (18.7–41.4%) of parameter β compared with air combustion, and a slow linear increment of β with temperature were both observed which indicated the reaction (4) was mainly controlled by the oxygen concentration during combustion.

The common result that more Br_2 generated at higher temperature was observed during combustion of waste PCBs under different atmosphere. However, as a matter of fact, the reaction (4) is exothermic and their chemical equilibrium constant was calculated [31]. As evident from Table 3, although the equilibrium constant sharply decreases with temperature increasing, it is still larger than 2900 at 1100 °C. Thus, we can conclude that the reaction almost completes at all temperatures when chemical equilibrium is achieved. But our experiment results even show completely opposite tendency. However, this phenomenon may be attributed to the limitation of chemical reaction rate. The chemical reaction rate of HBr and O_2 is too slow to achieve the chemical equilibrium with relatively short residence time (approximately 5 s in isothermal region) at lower temperature which led to lower percentage of Br_2 in gaseous fraction. However, chemical reaction rate increases sharply with temperature increasing according to the Arrhenius equation, which leads to the nearly completion of chemical equilibrium and increases the formation of Br_2 at higher temperature. This hypothesis can also explain the fact that no molecular bromine was detected even in oxidizing condition in the former research [11]. It can be inferred that chemical reaction rate is the main limiting factor of reaction (4) in limited time. Thus, we can conclude that chemical equilibrium of reaction (4) was never achieved in our experiment and the change of bromine conversion could be attributed to the change of chemical reaction rate which further varies with temperature and oxygen concentration, and to the

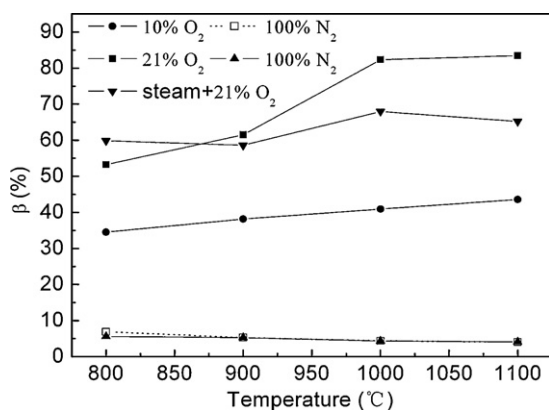


Fig. 5. Conversion of bromine during thermal decomposition of waste PCBs under different atmosphere (β : ratio of the mass of bromine converted to Br_2 to the mass of bromine converted to HBr and Br_2).

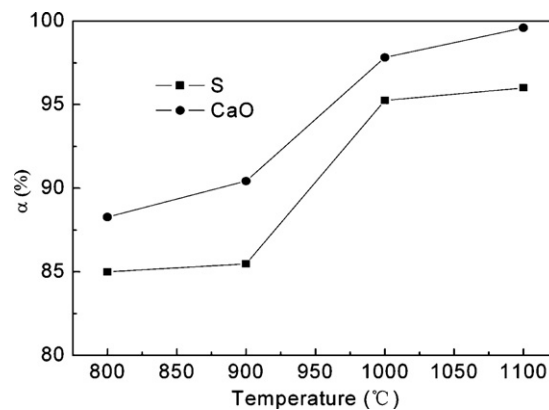


Fig. 6. Conversion ratio of bromine α during co-combustion with different addition agents (α : ratio of the mass of bromine converted to Br_2 and HBr to the mass of bromine in sample).

change of reverse reaction rate which further varies with steam concentration. However, this hypothesis should be demonstrated by further research.

3.2. Influence of addition agents on conversion of bromine

Two addition agents, calcium oxide and sulfur, were used to co-combust with waste PCBs at the temperature ranging from 800 °C to 1100 °C to investigate their influence on the conversion of bromine. The Ca/Br and S/Br mol ratio were 4.0 and 2.0, respectively. The results are illustrated in Figs. 6 and 7. As shown in Fig. 6, the value of α is 88.2–99.6% for calcium oxide and 85.0–96.0% for sulfur. The inorganic bromine in the flue gas did not reduce but obviously increase during co-combustion with CaO compared with data from Fig. 3. This result indicated that calcium oxide can obviously promote the conversion from organic bromine to inorganic bromine but cannot efficiently remove inorganic bromine at high temperature. Actually, the fact that calcium oxide did not perform well in removal efficiency at higher temperature region may be due to the low melting point (730 °C) and boiling point (806–812 °C) of CaBr_2 and the long residence time in our experiment. One the one hand, the melting CaBr_2 limited gas diffusion to interior unreacted CaO . On the other hand, the formed CaBr_2 can easily evaporate at high temperature and the captured bromine by CaO subsequently emitted in the gaseous fraction again. However, the promotion by sulfur mainly occurs at low temperature.

The relation between parameter β and temperature is shown in Fig. 7. With temperature increasing, the parameter β substantially

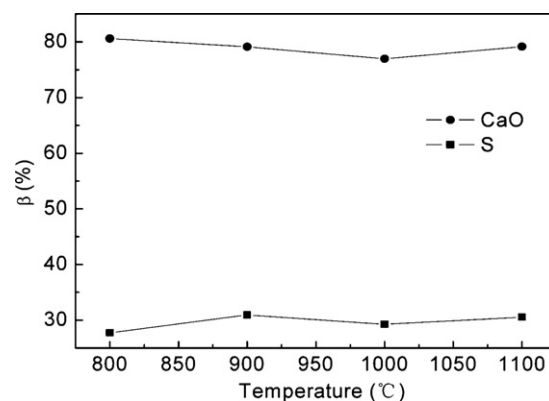


Fig. 7. Conversion ratio of bromine β during co-combustion with different addition agents (β : ratio of the mass of bromine converted to Br_2 to the mass of bromine converted to HBr and Br_2).

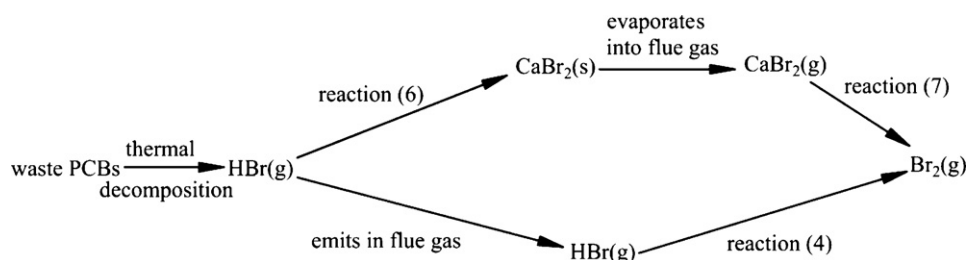
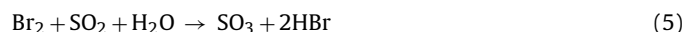


Fig. 8. Formation pathway of Br_2 when co-combustion with CaO .

keeps steady under the two conditions. However, co-combustion with sulfur can obviously decrease the percentage of Br_2 . This result can be explained by the Br_2 reduction reaction:



A similar result was found during incineration of waste-containing brominated flame retardants [26].

It could be seen by comparison between Figs. 5 and 7, the presence of CaO can efficiently increase the percentage of Br_2 at lower temperature (800°C , 900°C). The phenomenon may be explained by this hypothesis: bromine was generated in two different routes showed in Fig. 8. In one route, HBr was captured by CaO and formed less volatile CaBr_2 at first, and then it evaporated into gaseous fraction and was oxidized by oxygen. In the other route, HBr directly emitted in the gaseous fraction and reacted with oxygen. So according to Fig. 8, a part of Br_2 was generated by the reaction (7) during co-combustion with CaO but all Br_2 was generated by reaction (4) in the earlier experiment. As shown in Table 3, we can conclude that the limitation of reaction (7) is chemical reaction rate. On the one hand, due to the influence of reaction (6) and evaporation of CaBr_2 , reaction (7) occurred later than the reaction (4). At this moment, sufficient oxygen would take part in the reaction (7) to promote the formation of Br_2 because other volatile compounds have nearly burnt out. On the other hand, reverse reaction rate decreased due to the formation of solid CaO whose melting point is 2580°C . In a word, more Br_2 was generated by the reaction (7). But with temperature increasing, reaction (6) tended to be limited which has been mentioned earlier in this paper, thus reaction (7) was also limited because of the decrement of CaBr_2 . Hence, the promotion of forming Br_2 is not obviously at higher temperature. However, this hypothesis should be also demonstrated by further research.



4. Conclusions

In our experiment, the influence of temperature, oxygen concentrations, and content of steam on the bromine conversion was investigated at isothermal temperatures ranging from 800°C to 1100°C by using a quartz tube furnace. Furthermore, co-combustion of waste PCBs with calcium oxide and sulfur were also performed, respectively. As we expect, organobrominated compounds tend to be destroyed with high efficiency during complete combustion at high temperature, and the conversion from organic bromine in the PCBs to inorganic bromine in the gaseous fraction increased to 96.4%.

Both HBr and Br_2 were detected in the gaseous fraction during combustion. They can be separated well due to different Henry coefficient, and then quantitatively analyzed by ion chromatography. The quantitative data indicated that increasing temperature or oxygen concentration can promote the formation of Br_2 , which is generated by the oxidation of HBr . However, significant quantity of Br_2 existing in flue gas perhaps tends to form extremely hazardous

compounds-PBDD/Fs by fly ash catalysed de novo synthesis [23]. Thus removal of Br_2 should be seriously considered during incineration of waste PCBs. The experimental results also evidenced that sulfur oxide can efficiently limit the formation of Br_2 by reduction reaction converting Br_2 to HBr that is easy to be captured by lime compared with Br_2 . Therefore co-combustion waste PCBs with coal which is also used for co-combustion of wastes containing chlorine to inhibit PCDD/Fs [32] may be considered as a promising option.

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