Pollution control mechanism analysis of thermal degradation of decabromodiphenyl ether by zinc oxide

Lan Gao
Hebei University
Yuan Lei
Hebei University
Zhansheng Li
Hebei University
Peng Yan Liu (hbupyliu@163.com)
College of Chemistry and Environmental Science https://orcid.org/0000-0001-5695-3001

Research Article

Keywords: Zinc oxide, Decabromodiphenyl ether, Thermal degradation, Mechanism, Brominated dioxins, Activation energy

Posted Date: April 19th, 2021

DOI: https://doi.org/10.21203/rs.3.rs-262596/v1

Abstract

Low brominated diphenyl ethers and brominated dioxins with high toxicity were easily produced in the pyrolysis process of decabromodiphenyl ethers, Based on this, the pyrolysis process of BDE-209 and ZnO was studied by differential thermal gravimetric analysis (DTA-TG), X-ray diffraction (XRD), GC and GC / MS. The results showed that the addition of zinc oxide reduced the activation energy of BDE-209 thermal degradation reaction, thus reducing the thermal degradation temperature of BDE-209; after the addition of zinc oxide, BDE-209 pyrolysis produced more brominated dioxins at 400 ℃ When BDE-209 and ZnO were degraded at 400 ℃ at 2.4:1 (w / W), the degradation rate reached 100% at 2 h. At this time, the relative content of hexabromo- and heptabromo- dioxins was lower, and the relative content of hexabromobenzene and pentabromobenzene was the highest. Combined with Arrhenius formula calculation, soft and hard acid-base theory and XRD product analysis of pyrolysis residue, the mixed pyrolysis mechanism of BDE-209 and zinc oxide was deeply discussed, which provided a theoretical basis for pollution prevention and control of waste printed circuit boards in heat treatment.

Introduction

Polybrominated diphenyl ethers (PBDEs) are a kind of flame retardants widely used(Rahman et al. 2001). Commercial decabromodiphenyl ethers (BDE-209) containing 97% decabromodiphenyl ethers and 3% nonabromodiphenyl ethers have the largest application in the market due to their low price and superior performance(Luo et al. 2007; Sun et al. 2020), accounting for more than 75% of the total flame retardants (Sakai et al. 2001). BDE-209 is usually used in circuit boards, textiles and other products as additive flame retardants (Talsness.2008; Oloruntoba et al. 2019).

Due to the addition mode of PBDEs and the characteristics of semi-volatility(Yao et al. 2021; Hites et al. 2020; Zhang et al. 2021) at room temperature, PBDEs are released into the environment during their production and during the use, waste and subsequent treatment of added commodities. PBDEs entering the environment carry out multi-medium migration, transformation and degradation through physical, chemical and biological channels(Xu et al. 2020; Luo et al. 2020; Pan et al. 2016); when the content of PBDEs in the environment reaches a certain level, it will produce toxicity to organisms (Gu et al. 2012; Dunnick et al. 2012); Lin Haitao et al. (Lin et al.2016) found that when the concentration of BDE-209 in PM (particulate matter) is high in Guangzhou, it will seriously endanger human health; however, the memory ability of T-exploration maze in zebrafish exposed to low concentration of 2,2',4,4'-tetrabromodiphenyl ether (BDE-47) for a long time has been decreased due to neuron damage(Zheng et al.2017). Therefore, it is of theoretical and practical significance to find a degradation method that is fast and effective for PBDEs and avoids or reduces secondary pollution.

Currently, the disassembled and simply recycled printed circuit board, it is often disposed of by pyrolysis or incineration. One of the main applications of BDE-209 is added into printed circuit board. The printed circuit board(Bilesan et al.2020) contains a plurality of metal elements such as zinc. When the circuit board is treated by pyrolysis, these metals and their compounds have an effect on the degradation of

BDE-209(Liu et al.2020). Cozzani (Federica et al.2006) found that during the pyrolysis of waste circuit boards containing brominated diphenyl ethers, some of the bromine is released in the form of hydrogen bromide, forming brominated compounds such as lower brominated diphenyl ethers with higher toxicity than BDE-209. It also contains more toxic polychlorinated dibenzo-p-dioxin, and improper treatment will produce secondary pollution, which will cause serious harm to the ecological environment and organisms. Zinc, iron and other metal elements are easy to be oxidized to form metal oxides during the pyrolysis process. Meanwhile, these metal oxides can be used to catalyze the pyrolysis of PBDEs, which can not only save resources, but also reduce the environmental risks in the treatment of PBDEs.

The thermodynamic calculation of Gibbs energy change for selective bromination reaction shows that HBr can be formed during the thermal degradation of brominated flame retardants (BFRs), which can be used as a brominating agent (Shibata et al. 2006) for metal oxides (Ding et al.2018; Miller et al. 2017) (such as ZnO, PbO, CuO and Fe2O3). Therefore, based on the DTA-TG (Differential Thermal/Thermo-gravimetric Analyzer) analysis on the mixture of BDE-209 and ZnO, as well as the analysis on pyrolysis products and efficiency at different temperatures, time, and different mass ratios of BDE-209 and ZnO, the conditions for effective prevention and control of pollution in the thermal degradation process of BDE-209 were found in this experiment. Combined with X-ray diffraction analysis of pyrolysis residues, Arrhenius formula calculation of activation energy and hard and soft acids and bases theory (HSAB), the mechanism of thermal degradation of BDE-209 and ZnO mixture was discussed, and the distribution of thermal degradation products was used to analyze the pollution prevention and control conditions of thermal degradation of BDE-209, so as to provide theoretical support for the safe treatment and disposal of printed circuit boards and other wastes containing BDE-209.

Materials And Methods

Laboratory Instruments and Reagents

Gas Chromatography-Mass Spectrometry, 7890A-5975C, Agilent, USA; Gas Chromatograph, 7890B, Agilent Company, USA; Open vacuum atmosphere tubular electric furnace, SK-1200°series, Tianjin Zhonghuan Experimental Electric Furnace Co., Ltd.; Thermogravimetric Analyzer, STA449C, German NETZSCH Company; Electronic Analytical Balance, AB135-S, METTLER TOLEDO, USA; Ultrasonic Instrument, KQ-250B, Kunshan Ultrasonic Instrument Co., Ltd.; Vortex Oscillator, WH-861, Taicang Hualida Laboratory Equipment Co., Ltd.; Pure water machine, Purelab Classic UV, ELGA, UK.

Toluene (chromatographic pure, J.T. Baker), BDE-209 (standard, purity > 98%, Tokyo Chemical Industry Co., Ltd., Japan), PBDEs 12 mixed standards (tribromo to decabromo, CIL, USA), PBDEs 39 mixed standards (monobrominated to heptabrominated diphenyl ether, AccuStandard, USA), octabrominated dibenzo-p-dioxin, heptabrominated dibenzo-p-dioxin, hexabrominated dibenzo-p-dioxin, hexabromobenzene, pentabromobenzene standard (purity > 98%, Beijing J&K Technology Co., Ltd.).

Instrumental Analysis Conditions

Gas chromatography conditions: DB-5HT capillary column; Injection port temperature: 300 ℃; Detector: μ-ECD, temperature: 340 ℃; Injection mode: no shunt; Carrier gas: high purity nitrogen (purity ≥ 99. 999%), flow rate: 1.0 mL/min; Make-up flow rate: 30.0 mL/min; Injection volume: 1 L; Heating procedure: after keeping at 90 ℃ for 1min, it rises to 150 ℃ at 25 ℃/min for 1min, and then rises to 320 ℃ at 10 ℃/min for 3 min.

Gas chromatography-mass spectrometry conditions: DB-5HT capillary column; Ion source: EI source, source energy 70 eV, ion source temperature: 230 ℃; Temperature of quadrupole: 150 ℃; Auxiliary heating temperature: 280 ℃; Injection port temperature: 300 ℃; Carrier gas: high purity helium (purity ≥ 99. 999%); Scanning mode: full scanning and selective ion scanning; Solvent delay: 4min. The heating procedure is the same as that of gas chromatography.

Experimental Methods

Thermogravimetric analysis

The sample was put into an open alumina dry pot and heated at a set heating rate of 5 ℃/min. Thermal analysis was carried out in nitrogen atmosphere with a nitrogen flow rate of 150 mL/min. Each sample was analyzed three times in parallel.

Preparation of Sealed Tube

The glass tube with an inner diameter of 5.0 mm was cut into several sections with an inner diameter of 5.0 cm, washed with clear water, then soaked in chromic acid solution for 30 minutes to remove possible organic matters, and finally washed with ultra-pure water, dried for later use. One end of the glass tube was sealed with an alcohol blowtorch. After adding the sample, the other end was sealed to make the sealed glass tube used for pyrolysis.

Pyrolysis experiment

2mg (± 0. 2mg) of BDE-209 sample was weighed with an analytical balance and added into a glass tube with one end sealed, and metal oxide ZnO powder was added according to the corresponding mass ratio, and the other end of the glass tube was sealed. After sealing, it was put into a tubular furnace raised to a set temperature for pyrolysis.

Pretreatment of pyrolysis products

After pyrolysis was completed, the glass tube was taken out from the tube furnace, cooled to room temperature, then the glass tube was wrapped with aluminum foil and smashed, the glass tube crushed slag and the sample were extracted together with toluene solution by ultrasonic assistance, and the extracted solution was analyzed by GC and GC-MS.

Qualitative and semi-quantitative analysis of products

The GC and GC-MS instruments and chromatographic columns used in the experiment are identical. Therefore, the peak sequence of each substance in the product was similar. The peak time of pyrolysis products was compared with the peak time of standard samples in GC, the pyrolysis products were identified as heptabrominated dibenzo-p-dioxin, hexabromobenzene, pentabromobenzene, octabrominated diphenyl ether, nonabrominated diphenyl ether and BDE-209 according to the characteristic mass spectra of the substances. The peak area on GC was used for quantification, and the relative content of the degradation products was compared and analyzed to clarify the pyrolysis trend and the change of product content.

Results And Discussion

Differential Thermal/Thermo-gravimetric Analyzer (TG - DTA) analysis

TG-DTA curves can reflect the mass and energy changes of reactants with temperature programmed temperature, so the change process from reactant to product can be inferred, so as to provide a basis for the reaction process, and determine a suitable degradation temperature for a mixture of BDE-209 and ZnO. Figure 1 shows that BDE-209 and ZnO in a mas ratio of 2.4: 1 is used as a reactant to obtain the TG-DTA curve at a heating rate of 5 ℃/min in nitrogen environment. From TG curve, it can be seen that the mixture begins to lose weight at 306 ℃. Until 357.0 ℃, the mass of the residue becomes 95% of the original mass. From 450℃ to 800℃, the change of residual mass is not obvious. Through the DTA curves, it can be seen that when the temperature is lower than 306 ℃, which is an endothermic process. There is a narrow exothermic peak between 306 ℃ and 357.0 ℃, and the overall trend from 357.0 ℃ to 450 ℃ is an endothermic process. However, there is a wide exothermic peak near 450 ℃. A wide endothermic peak occurs between 450 ℃ and 800 ℃. According to the analysis of TG-DTA curves of tetrabromobisphenol A (TBBPA) and ZnO by Oleszek(Oleszek et al. 2012), the melting process, degradation process and evaporation process of TBBPA need to absorb heat. However, the reaction between ZnO and HBr produced by degradation will release heat. By analogy, it can be judged that BDE-209 will degrade and evaporate with melting after heating up. Therefore, the overall trend is an endothermic process, and the narrow exothermic peak in the range of 306 ℃-357.0 ℃ and the wide exothermic peak near 450 ℃ may be due to the degradation of BDE-209 to produce HBr. HBr will react with ZnO to release heat. There is a wide endothermic peak between 450 ℃ and 800 ℃, which may be due to the gasification of the resulting solid $ZnBr_2$. The reaction residue was analyzed by XRD, Zinc bromide was found, as shown in Fig. 2, which also proved the formation of $ZnBr_2$ during the reaction. According to DTG curve, it can be seen that the degradation rate is very fast from 326 ℃ to 442.1 ℃, and the larger the contact area is during the combined reaction, the higher the reaction efficiency is. Therefore, combined with the melting point of BDE-209 and the melting point of ZnO, the thermal degradation temperature range of BDE-209 and ZnO is roughly determined to be 300 ~ 450 ℃.

Discussion on pyrolysis conditions

Temperature Analysis of Pyrolysis Products of BDE-209 and ZnO Mixture

According to the thermal degradation temperature range determined by DTA-TG analysis of BDE-209 and ZnO mixture, 300 ℃, 400 ℃ and 450 ℃ were preliminarily selected as the thermal degradation temperatures of BDE-209 and ZnO (2.4: 1, w/w). As shown in Fig. 3, it can be found from the figure that at 300 ℃, BDE-209 mainly undergo reductive debromination reaction, and products include nonabrominated diphenyl ether and octabrominated diphenyl ether. The relative content of BDE-209 in the product was 47.82%, showing that it is not completely degraded. Therefore, the degradation efficiency of BDE-209 is low at low temperature. After raising the pyrolysis temperature of mixture to 400 ℃, the variety of products increased. In addition to PBDEs, products also include dioxin and bromobenzenes. Among them, the relative percentage of low-brominated dioxin such as heptabrominated dibenzo-p-dioxin, hexabrominated dibenzo-p-dioxin and pentabrominated dibenzo-p-dioxin was higher, accounting for 20%, 13% and 5%, respectively. With the pyrolysis temperature increasing to 450 ℃, the variety of products changed little. However, the relative percentage of low brominated dioxin is reduced, the relative percentage content of bromobenzene products increased. Stanmore (Stanmore 2004) found that dioxin were easy to undergo homogeneous reaction between 500 ℃ and 800 ℃. However, according to Fig. 3, it can be seen that after ZnO is added to BDE-209, the temperature of dioxin generation is reduced. Therefore, when the waste printed circuit board is pyrolyzed, as well as it is determined to contain metal zinc, the temperature of thermal degradation should be controlled to prevent the generation of low brominated dioxin during thermal degradation, thus preventing and controlling environmental pollution.

Pyrolysis Analysis of BDE-209 and ZnO Mixtures with Different Ratios

Because BDE-209 and ZnO are rich in mixed thermal degradation products at 400 ℃, and the relative content of low brominated dibenzo-p-dioxin is high, 400 ℃ is selected as the temperature research condition for mixed thermal degradation to facilitate research. BDE-209 and ZnO are mixed at the ratio of 1: 0, 5: 1, 2.4: 1, 1: 1 and 1: 2 (w/w), and thermally degraded at 400 ℃ for 120 min. The types of degradation products are shown in Fig. 4. It can be observed that with the increase of ZnO addition, the degradation rates of BDE-209 gradually increase, which are 63.2%, 73.2%, 100%, 100% and 100%, respectively. At the same time, it is found that when the ratio of BDE-209 to ZnO is 2.4: 1, BDE-209 has been thermally degraded completely. According to theoretical calculations, 1mol of BDE-209 needs 5mol ZnO after complete debromination. According to the mass ratio, the ratio of BDE-209 to ZnO can be calculated to be 2.37: 1, which is about 2.4: 1. It can be seen that when the ZnO content in the mixture exceeds the theoretical mass ratio, the degradation rate of BDE-209 has no obvious change. With the increase of ZnO content, the relative percentage of low-brominated diphenyl ethers in thermal degradation products showed a decreasing trend, while the relative percentage of dioxin showed an increasing trend, but the change trend was not obvious when the mass ratio of the two exceeded 2.4: 1. However, the relative percentage of different brominated products has obvious changes. As shown in Fig. 5, with the increase of ZnO addition amount, the relative percentage of low bromination products gradually increases, which is due to the reduction and debromination of ZnO. ZnO exceeding the theoretical ratio will react with brominated diphenyl ethers and dioxin in thermal degradation products, resulting in reduction and debromination reaction, resulting in an increase in the relative percentage of low brominated products. Studies have found that the toxicity of low brominated products is higher than

that of high brominated products (Zeng et al.2008; Lagalante et al. 2011). Therefore, the addition amount of ZnO should be appropriate during the degradation of BDE-209, so as to prevent the production of low brominated products with stronger toxicity during thermal degradation and pollute the environment.

As can be seen from Fig. 6, with the increase of ZnO addition, the number of low brominated dibenzo-p-dioxin gradually increases. When the ratio of BDE-209 to ZnO is 1: 2, the relative percentage of heptabrominated dibenzo-p-dioxin is 15%, and the relative percentage of hexabrominated dibenzo-p-dioxin is 30%; When the ratio of BDE-209 to ZnO is 1: 1, the relative percentage of heptabrominated dibenzo-p-dioxin is 30%, and the relative percentage of hexabrominated dibenzo-p-dioxin is 15%; When the ratio of BDE-209 to ZnO is 2.4: 1, the relative percentage of heptabrominated dibenzo-p-dioxin is 20%, and the relative percentage of hexabrominated dibenzo-p-dioxin is 13%; And the ratio of the two is 5: 1 or ZnO is not added, the proportion of both heptabrominated dibenzo-p-dioxin and hexabrominated dibenzo-p-dioxin does not exceed 13%. From the above data, it is found that with the increase of ZnO content, the relative percentage of heptabrominated dibenzo-p-dioxin and hexabrominated dibenzo-p-dioxin increased, However, when the ZnO content is low, the degradation rate of BDE-209 is low. Therefore, the mixed mass ratio of BDE-209 and ZnO should be properly controlled, which can not only efficiently degrade BDE-209 but also prevent the production of low brominated products with high toxicity. In this experiment, the ratio of BDE-209 and ZnO is 2.4: 1 for further research. At this time, the thermal degradation products of BDE-209 are rich and the degradation rate is high, which has certain research value for the prevention and control of thermal degradation pollution of waste printed circuit boards.

Time Analysis of Pyrolysis Products of BDE-209 and ZnO Mixtures

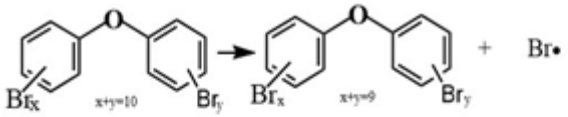
BDE-209 and ZnO mixture have a mass ratio of 2.4: 1 (w/w) and the thermal degradation temperature is 400 ℃, The products with different thermal degradation time were analyzed. As shown in Fig. 7, with the extension of the degradation time, the relative percentage content of BDE-209 gradually decreases, from 83.97% at 30min to 29.44% at 90min, and has been completely degraded at 120min. At the same time, compared with the degradation of BDE-209 without ZnO, it is found that the degradation time of BDE-209 after ZnO is added is shortened. According to the research of Altarawneh et al. (Altarawneh et al. 2019), it is because ZnO changes the degradation pathway of BDE-209 and reduces the activation energy of the reaction.

The analysis of degradation products showed that with the extension of degradation time, the content of hexabromobenzene gradually increased, and the relative percentage gradually changed from 3.25–34.95%. However, the relative percentage of octabrominated dibenzo-p-dioxin was 3.86% at 30min, and increased to 8.69% at 60min. However, with the change of time, the relative percentage of octabrominated dibenzo-p-dioxin gradually decreased to 3.97% after 120min. The relative percentage of hexabrominated dibenzo-p-dioxin increased gradually, and the relative percentage was 12.61% at 120min. Therefore, from the whole product distribution, it can be seen that there are two main ways to degrade BDE-209, one is ether bond cleavage and recombination, and the other is debromination and hydrogenation reduction. After adding ZnO, the thermal degradation products of BDE-209 are mainly bromobenzenes and low

brominated dibenzo-p-dioxin at 120min, which just shows that ZnO plays a role in debromination and reduction of BDE-209 and its thermal degradation products, and also promotes the cleavage of ether bonds. Therefore, the metal zinc contained in the waste printed circuit board produces ZnO during the thermal degradation process, which not only shortens the thermal degradation time of BDE-209, but also reduces the temperature of producing low brominated dioxin, which provides a theoretical basis for the heat treatment of waste printed circuit boards.

Discussion on the Mechanism of Mixed Pyrolysis of BDE-209 and ZnO

The thermal degradation of the mixture of BDE-209 and ZnO conforms to the first-order kinetic equation, and its reaction rate constant is shown in the data in Table 1. With the increase of thermal degradation temperature, the degradation rate constant gradually increases. According to Arrhenius formula, the activation energy value of BDE-209 thermal degradation under the action of ZnO is 38.3 kJ/mol, which is lower than the activation energy value of BDE-209 thermal degradation obtained by He Siying(He 2019)and others (52.4 kJ/mol), which just shows that the addition of ZnO changes the thermal degradation process of BDE-209 and reduces its reaction activation energy. Therefore, the thermal degradation rate of BDE-209 is increased. Combined with Ralph Pearson's soft and hard acid-base theory, they are divided into hard base, soft base and boundary base according to the electronegativity, radius, electron loss ability and deformability of anions. According to the charge number, radius and polarizability of cations, they are divided into hard acid, soft acid and boundary acid and other parameters. Bromine ion belongs to boundary base, zinc ion belongs to boundary acid, and oxygen ion belongs to hard base. Combined with the rule of "hard acid preferentially combines with hard base, soft acid preferentially combines with soft base", bromide ion and zinc ion are easier to combine. The XRD pattern of FIG. 2 shows the presence of ZnBr2 in the product. Therefore, it is inferred that the thermal degradation process of BDE-209 and ZnO is as follows:



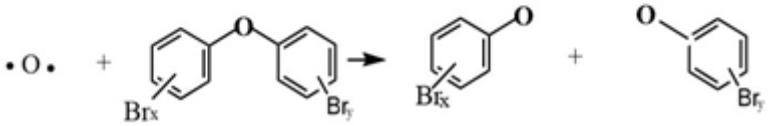


Table 1
First order kinetics and thermodynamics data of BDE-209 pyrolysis at different temperatures with ZnO ratio of 2.4:1 (w / w)

t/℃	k/min^{-1}	Lgk	1/T	Ea/(KJ/mol)
300	0.00349	-2.46	0.00174	38.3
400	0.00615	-2.21	0.00149	
450	0.03285	-1.48	0.00138	

By discussing the thermal degradation mechanism of BDE-209 and ZnO and analyzing the thermal degradation conditions, it was found that after ZnO was added in the pyrolysis process, when BDE-209 was thermally degraded at 400 ℃-450 ℃, the species of low brominated dioxin in the degradation products increased. In addition, with the increase of temperature, the relative percentage of bromobenzene substances decreased, and with the extension of reaction time, the relative percentage of bromobenzene substances gradually increased. Therefore, when heat treating waste printed circuit boards, it is necessary to strictly control the thermal degradation conditions and do a good job in environmental pollution prevention and control.

Conclusion

TG - DTA analysis and X-ray diffraction patterns of thermogravimetric residues show that the addition of ZnO to BDE-209 can increase its thermal degradation rate and reduce its thermal degradation temperature range.

The mixed thermal degradation of BDE-209 and ZnO mixture can shorten the degradation time of BDE-209, but it is easy to produce low brominated dioxin. Therefore, the thermal degradation conditions should be effectively controlled when heat treating waste printed circuit boards.

Combined with Arrhenius formula and soft-hard acid-base theory, the thermal degradation mechanism of BDE-209 and ZnO mixture was speculated.

Declarations

Ethics approval and consent to participate Not applicable.

Consent for publication Not applicable.

Author contributions Lan Gao, Yuan Lei and Pengyan Liu designed the study, developed the method and wrote the manuscript. Zhansheng Li contributed methods for the TG-DTA analysis. All the authors edited the manuscript.

Funding This research was supported by the National Natural Science Foundation of China (No.21377033), the Natural Science Foundation of Hebei Province (No. B2018201224), Scientific and Technological Research Guidance Projects in Institutions of Higher Learning of Hebei Province(ZC2016148), Transformational Development Research Fund Project of Baoding University (2015Z06).

Data availability Data sharing is not applicable to this article as no datasets were generated or analysed during the current study.

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Figures

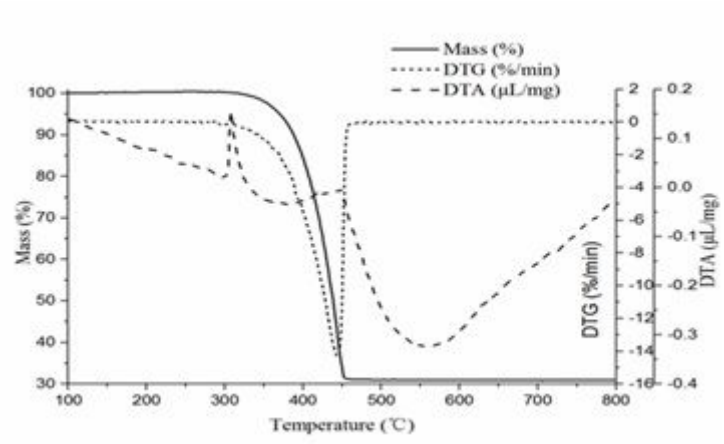

Figure 1

TG/DTG and DTA recordings for mixture of BDE-209/ZnO (2.4:1,w/w) at 5 °C/min under N2

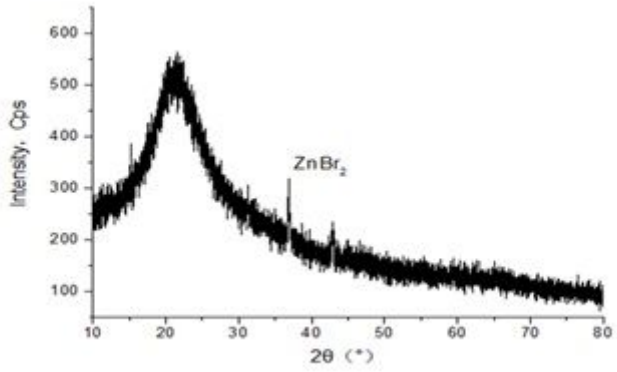

Figure 2

X-ray diffractionpatterns of reaction products in solid residue collected at 800 ℃ after thermal treatment of mixture of BDE-209/ZnO in N2

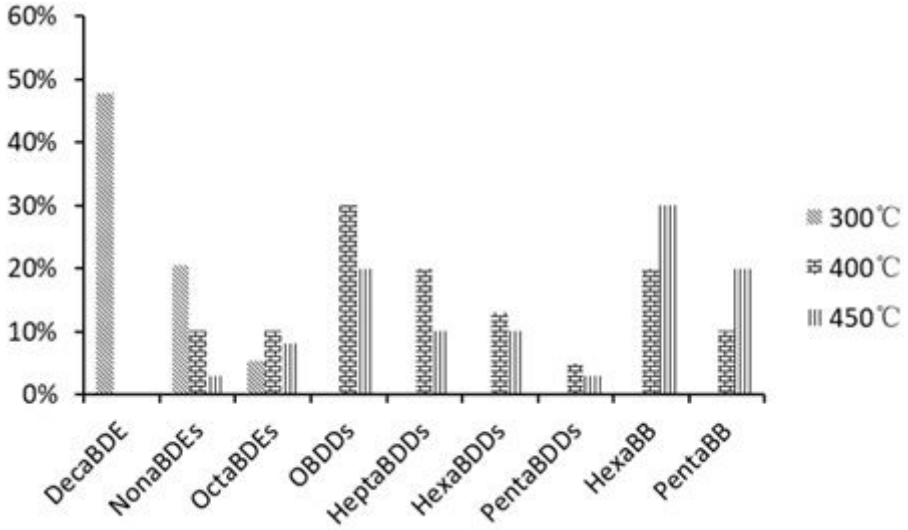

Figure 3

The proportion distribution of PBDEs and dioxins after mixed pyrolysis of BDE-209 and ZnO at different temperatures

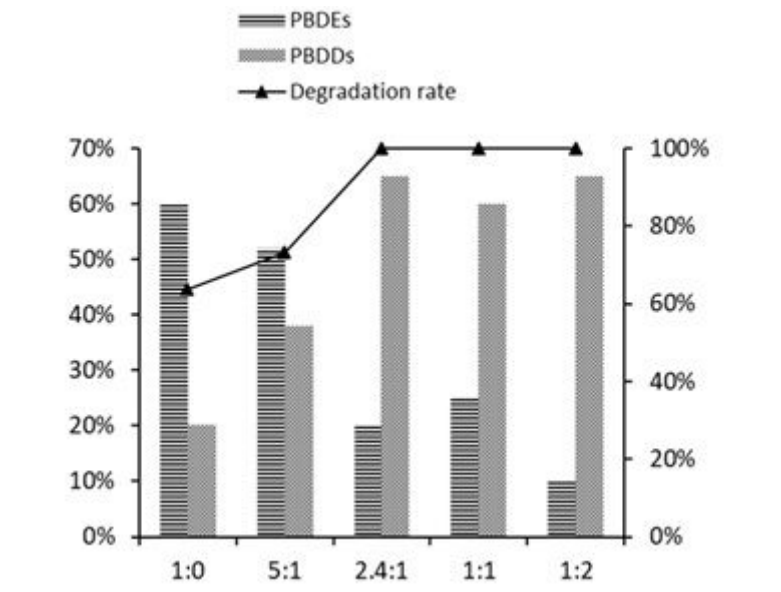

Figure 4

The proportion distribution of PBDEs and dioxins and the degradation efficiency of decabromodiphenyl ethers after mixed pyrolysis of BDE-209 and ZnO in different proportions

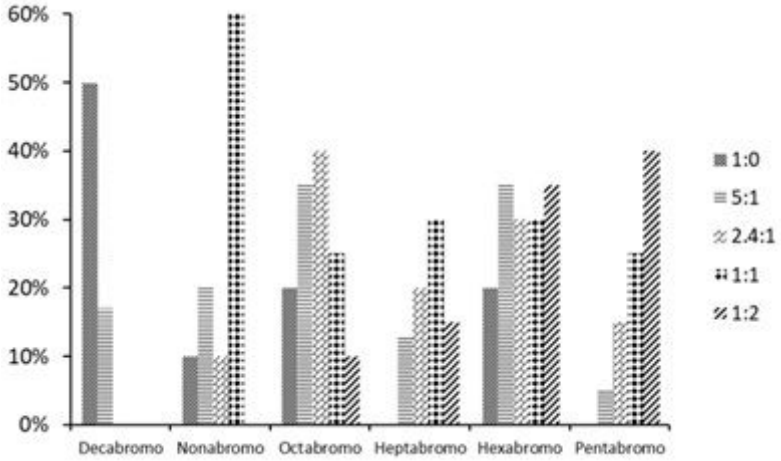

Figure 5

The content change of brominated products after mixed pyrolysis of BDE-209 and ZnO in different proportion

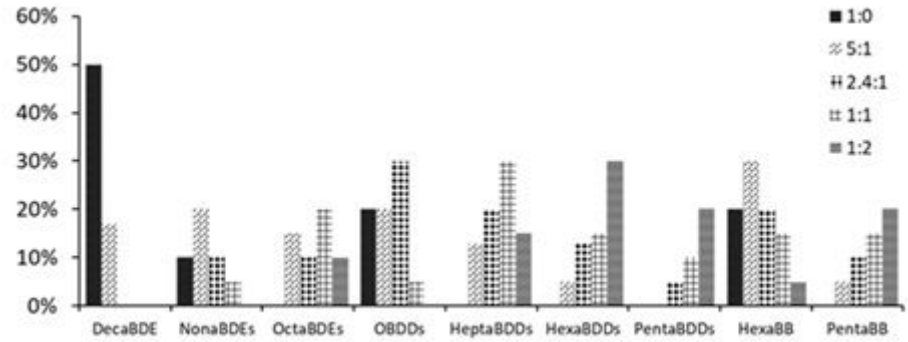

Figure 6

The relative content of pyrolysis products of BDE-209 and ZnO mixed in different proportions

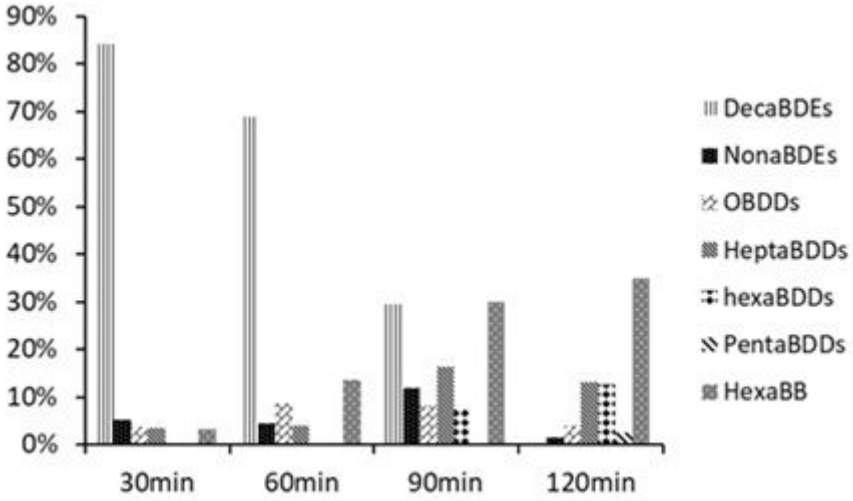

Figure 7

Effect of degradation time on the distribution of pyrolysis products at 400 ℃ when the ratio of BDE-209 to ZnO is 2.4:1 (w / w)