

DECABROMODIPHENYL ETHER DECOMPOSITION IN SUB-CRITICAL WATER OXIDATION - EVALUATION OF PBDD/DFS FORMATION

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Introduction

Decabromodiphenyl ether (DeBDE), which is one of brominated flame retardants (BFRs), has been used as an additive in fireproofing plastics, building materials and textiles.^{1,2} The levels of DeBDE and the other polybromodiphenyl ethers (PBDEs) are also increasing in the environment. Therefore, there is an urgent need to establish some practical management systems for the treatment of the waste containing BFRs in order to prevent environmental pollution. Development of removal method of BFRs from the waste is desired as one of the elemental technologies in these systems.

Recently, the hydrothermal reaction is being introduced as an environment-friendly method to the waste recycling system in Japan to reduce hazardous chemicals. The hydrothermal reaction using subcritical water has advantages of lower consumption of energy and cost compared to the supercritical water oxidation method.³ Moreover, this method can be used to recover chemical resources from plastics according to Dubois *et al.*⁴ They suggested the possibility of recovery of acetic acid from polystyrene or polyethylene by hydrothermal reaction. Some researchers have reported on the reduction of BFRs in resins by the hydrothermal reaction, such as PBDEs or tetrabromobisphenol-A in acrylonitrile butadiene styrene resin.⁵⁻⁷ However, details of the decomposition processes and mechanism during the reaction have not been well described. Further, attention has been paid to the impurities or by-products in BFRs such as polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/DFs)⁸, or brominated/chlorinated mixed compounds because relatively high levels of PBDD/DFs were detected in wasted television cabinets and other flame-retarded plastics.⁹

In this study, we investigated the decomposition process of DeBDE and occurrence of by-products such as PBDD/DFs by the hydrothermal reaction of DeBDE.

Materials and Methods

Hydrothermal reaction was carried out in a micro autoclave (50 ml) made of SUS 316 stainless steel filled with 40 ml of hexane-washed distilled water.¹⁰ DeBDE (1100 pmol) was dissolved in toluene at 100 mg/l and 10 μ l of toluene solution was spiked into the autoclave chamber, which was then sealed. A proportional integral derivative (PID) system controller was used to control the temperature. In the first stage defined as "Heating time", the chamber was heated for 25 min until a temperature of 300 °C and a pressure of 8 MPa were achieved. The chamber was held under these conditions for an optional period of 0, 10, 30, 60, 120, 240 or 360 min defined as "Processing time" in each experiment. The "Reaction time" was defined as the sum of "Heating time" and "Processing time". In the final stage defined as the "Cooling time", a fan was used to cool the chamber down to 100 °C, which was then was soaked into iced water for 20 min.

Results and Discussion

Decomposition rate of DeBDE and the homologue composition of PBDEs in sub-critical water

Approximately 45% of decomposition of DeBDE was confirmed after initial 12 min of hydrothermal reaction when the temperature reached 200 °C (Figure 1). When the temperature in the reactor reached 300 °C after heating time, 80% of DeBDE was decomposed. After additional 30 min heating, DeBDE was completely decomposed. With the decrease of DeBDE, NoBDEs were increased. And octa- and hepta-BDEs were increased followed by the decrease of NoBDEs. In this way, step by step debromination took place during the hydrothermal reaction. After 145 min of the reaction time, total PBDEs remained about 90 pmol as 7% of the input. They have been decomposed completely for the 265 min of the reaction.

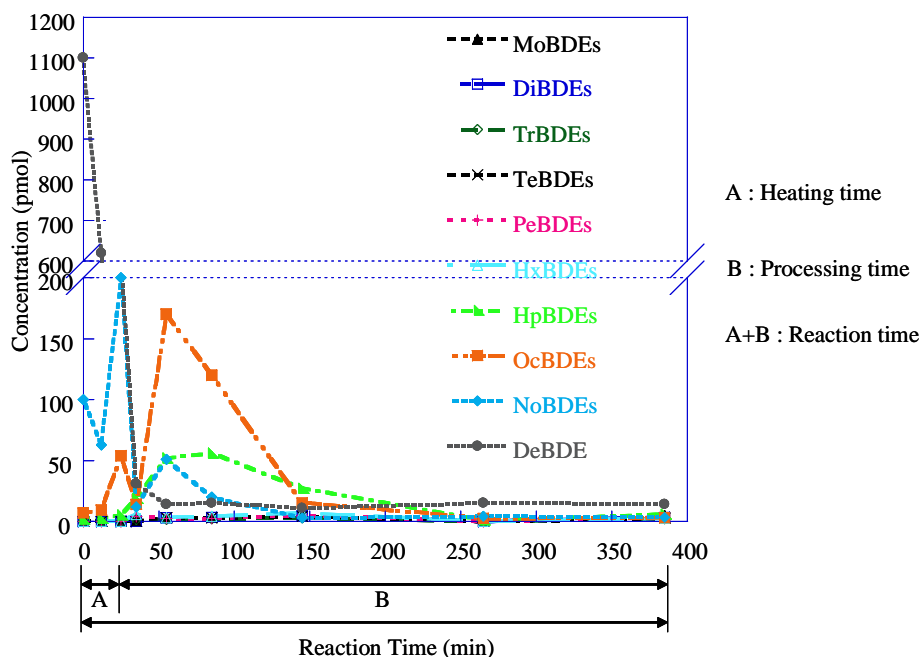


Figure 1 Time-course changes of PBDE homologues (pmol) in the sub-critical water with reaction time.

Change of PBDD/DFs with heating period

The formation of PBDD/DFs was observed during the hydrothermal reaction of DeBDE (Figure 2). In all the experiments, the yields of PBDFs were up to ten times greater than those of PBDDs. The rate of transformation from DeBDE to PBDD/DFs was calculated to be below 1.6% during "Heating time". The major homologues of brominated dioxin were hexa- and octa-BDD, and mono- through octa-BDF. The rate of transformation increased with the increase in the heating period. The highest concentration of PBDD/DFs was found in the case of 35 minute heating, where the transformation rate was 19%. OcBDD and OcBDF were completely decomposed, while mono- through hexa-BDDs and mono- through hepta-BDFs were remained at high levels.

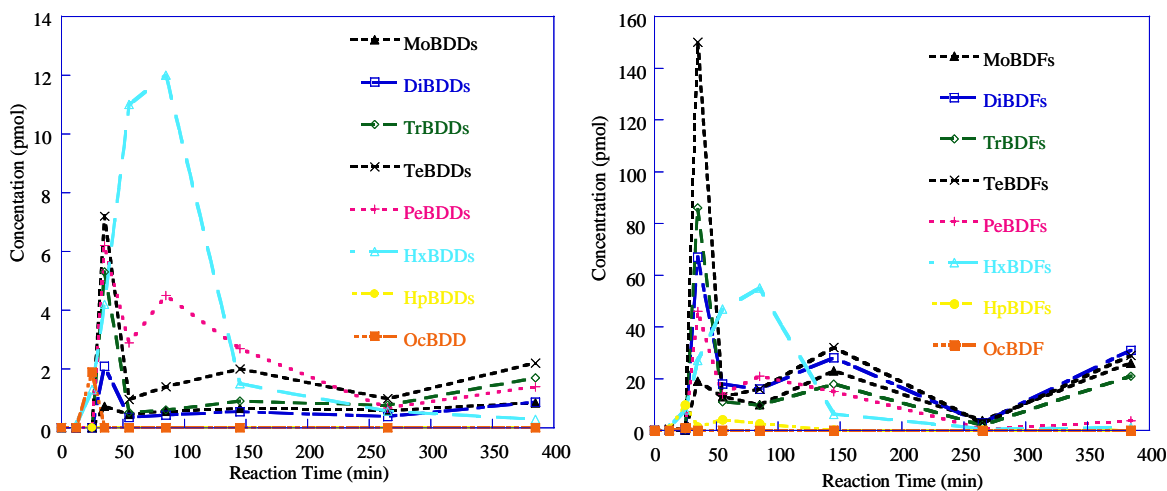


Figure 2 Time-course changes of PBDD/DF homologues (pmol) in the sub-critical water with reaction time

As the heating time was increased further to 45 min, the concentrations of PBDD/DFs decreased and the transformation rate of DeBDE to PBDDs/DFs fell below 6.9%. However, the maximum values for hexa-BDDs and BDFs recorded at 85 min heating.

Evaluation of TCDD toxicity equivalency

Dioxin-like toxicity was evaluated in order to assess the toxicity of the water solution after the hydrothermal reaction of DeBDE. In this study, we employed relative potencies (REPs) based on EC₅ (REP EC₅^{TCDD}) of several PBDD/DF and PBDE congeners obtained by the Dioxin-Responsive-Chemical Activated Luciferase gene eXpression (DR-CALUX) bioassays technology¹¹ for determination of the TCDD toxicity equivalency based on DR-CALUX-REPs (TCDD-EQs) of these by-products.

Change of the calculated TCDD-EQs PBDD/DF and PBDE congeners in the samples with extension of heating period are shown in Figure 3. TCDD-EQs was very small during the 25 min of heating period, after that, its value increased sharply and reached a maximum level of 540 pg at a time of about 40 min, and then it decreased. The TCDD-EQs contributions of PBDEs were minimal compared to PBDD/DFs after heating. Although TCDD-EQs rose temporarily, its level was very low and total transformation ratio of 2,3,7,8-substituted BDD/DFs from DeBDE was calculated to be below 0.052%, as mentioned above. Therefore, the risk of formation of PBDD/DFs in the hydrothermal reaction of DeBDE was estimated to be extremely low.

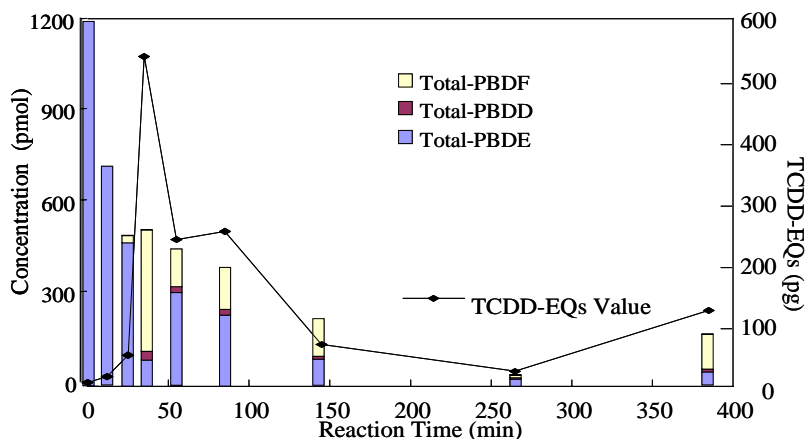


Figure 3 Time-course changes of total TCDD-EQs and the contribution rates of congeners of PBDE, PBDD/DF.

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