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Quantification of polybrominated diphenyl ethers in oil produced by pyrolysis of flame retarded plastic

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In recent years, there has been extensive research into using pyrolysis to convert toxic brominated plastics into safe, bromine free fuels. However, there has been little investigation of the polybrominated diphenyl ethers (PBDE) that are present in the pyrolysis oils. PBDEs are brominated flame retardants that are extremely toxic and are difficult to analyse owing to the existence of 209 different congeners. In this work, the authors have investigated the PBDEs present in the pyrolysis oil of high impact polystyrene which contained decabromodiphenyl ether as a flame retardant. The plastic was pyrolysed in a fluidised bed reactor and the resulting oil was subjected to a rigorous clean-up procedure to remove interfering compounds before the PBDEs were quantified using gas chromatography–mass spectrometry. It was found that the most prominent PBDEs in the oil were 3-monoBDE, 4-monoBDE, 3,4′-diBDE, 3,3′,4-triBDE and 2,2′,4,4′,5,6′-hexaBDE. The lesser brominated PBDEs were more prevalent than the more heavily brominated PBDEs.

Keywords: Pyrolysis, Bromine, Plastics, Flame retardants, PBDE

Introduction

In recent years, there has been an intensive amount of research into the recycling of toxic brominated plastics by pyrolysis with the aim of producing non-toxic fuels. Pyrolysis is an established process whereby an organic material is heated in an inert atmosphere to produce char, oil and gas, which can then be combusted as fuel to generate heat. Pyrolysis of waste materials has often been promoted as a method of converting high volume waste material into low volume fuels with a high energy density. With the development of pyrolysis of brominated plastics, pyrolysis can be considered as a method of converting toxic plastics into safe fuels.

In Europe, the intensity of research into the recycling of brominated plastics has been driven by the implications of the European Commission's Waste Electrical and Electronic Equipment Directive,[1] which requires that each member state of the European Union separately collects and reuses or recycles all WEEE, including the plastic fraction. It has been reported that 2·5% of WEEE plastics contain brominated flame retardants (BFR),[2,3] although some reports have claimed that up to 12% of WEEE plastics contain some type of brominated flame retardant.[4,5] The toxic nature of a few BFRs, particularly the polybrominated diphenyl ether (PBDE) class of flame retardants,[6] means that particular care has to be taken when recycling or otherwise processing WEEE plastics.

Mechanical recycling of plastics that contain BFRs is expensive due to the complex and intermingled nature of the material[7] and therefore, mechanical recycling would only be economical for high value polymers.[8] Energy from waste is a viable option for processing WEEE plastics, but incineration suffers from problems with public relations that are unlikely to allow the combustion of more halogenated material and in any case, incineration does not allow for recovery of valuable resources. Landfilling of WEEE plastics is not an option due to both the WEEE Directive[1] and the Landfill Directive.[9] However, both the BSEF[4] and Plastic Europe (formerly APME)[8] concur that thermal recycling will have to play a major role in the future processing of WEEE plastics and hence, the interest in using pyrolysis.

The main driver in processing brominated plastics by pyrolysis is to convert the toxic polymers into a non-toxic product, i.e. fuel. Many research groups have investigated the pyrolysis of brominated plastics and most researchers are now concentrating on methods of entirely eliminating the toxic organobromines during the pyrolysis process so as to provide totally 'clean' fuels. At our laboratories, the authors have been involved in research into destroying organobromines by two stage pyrolysis,[10] fast pyrolysis[11] and pyrolysis in the presence of zeolite catalysts.[12] Other authors have investigated the possibility of destroying organobromines by using ammonia treatment,[13] molecular sieves,[14] alkali

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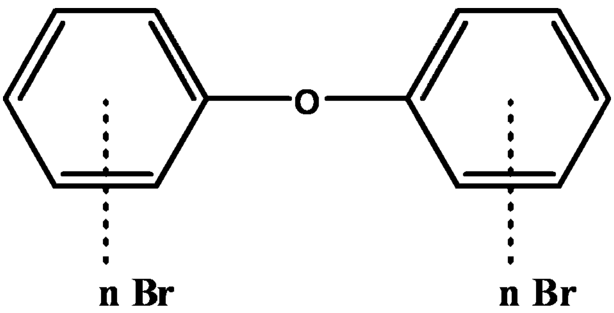


1 Structure of polybrominated diphenyl ethers where n Br signifies 1–5 bromine atoms

sorbents,[15] co-treatment with polypropylene,[16] calcium and iron based catalysts,[17] sodium hydroxide and basic zeolites,[18] and strong bases such as potassium hydroxide.[19]

The above methods have had varying levels of success in destroying organobromines, but if pyrolysis is to be used to process WEEE plastics on a commercial scale, then some knowledge of the organobromines that are present in the pyrolysis oils will be required. For most BFRs, this will be relatively straightforward; however, if PBDEs are the flame retardant, then the situation is much more complex because they can decompose to form 209 different congeners (Fig. 1). The concentration of PBDEs in pyrolysis oil would be particularly important in a commercial environment because of the extremely toxic nature of some of the congeners.[6] Therefore, it is necessary to investigate the likely distribution of PBDE congeners in pyrolysis oil.

The number of PBDE congers presents some difficult analytical challenges, not least the fact that if gas chromatography–mass spectrometry (GC–MS) is to be used for analysis, the PBDE peaks can be masked by other more prevalent compounds. Additionally, some of the PBDE congeners are thermally labile, so care must be taken during the analysis to preserve the original congeners. In this work, the authors have built on previous work into using a fluidised bed to pyrolyse high impact polystyrene (HIPS) that was flame retarded with decabromodiphenyl ether[20] by investigating the PBDE congeners that are present in the pyrolysis oil. Acid and basic silica gels have been used to remove interfering compounds from the pyrolysis oil before analysing the PBDEs using GC–MS.

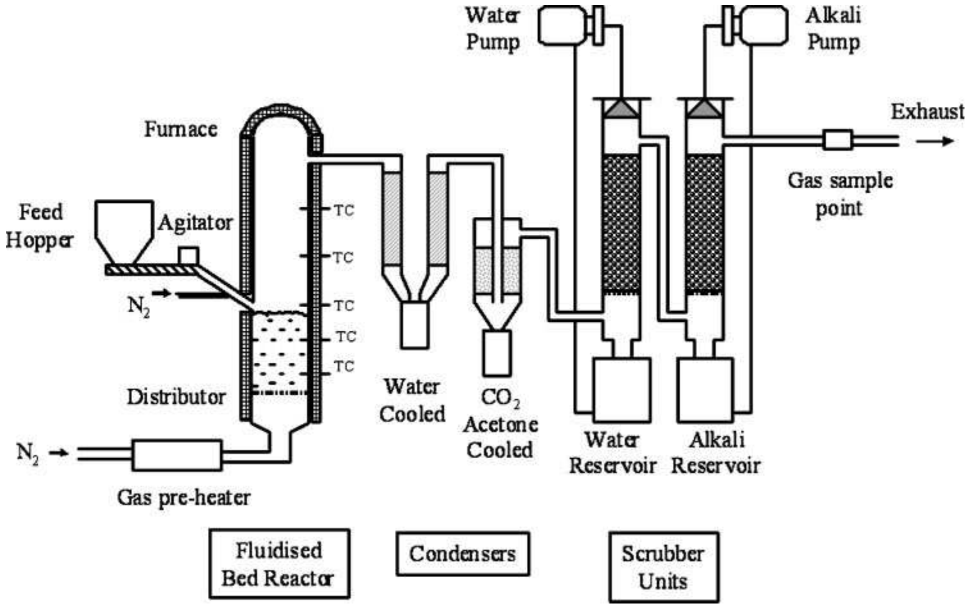
Experimental

Fluidised bed reactor

Flame retarded HIPS, which contained 8·6% decabromodiphenyl ether and 5·5% antimony trioxide,[20] was pyrolysed in a fluidised bed reactor at a bed temperature of 500°C. The fluidised bed reactor (Fig. 2) was electrically heated to the required final temperature before the test began. Once thermal equilibrium had been reached, 35 g of the plastic was fed into the reactor at a rate of 1·5 g min^{-1} using a screw feeder that was fed with the polymer material from a hopper. The port through which the plastic was fed into the furnace was water cooled and agitated to prevent the plastic melting and sticking to the port before it entered the furnace.

The plastic was flash pyrolysed in a fluidised bed that was made up of sand that had been sieved to 300–425 μm in diameter. The fluidised bed was supported on a distributor plate where nitrogen gas flowed through 1 mm diameter apertures. A small amount of nitrogen gas was also purged into the furnace through the screw feeder to prevent the pyrolysis products flowing up into the plastic feeding system.

The pyrolysis gases and oils exited from the top of the furnace and entered a series of condensers to recover the oil. Most of the oil was recovered by the first condenser, which was water cooled. The second, dry ice/acetone cooled condenser was packed with steel pall rings and glass wool to help remove all the pyrolysis oil from the gas stream. After the condensers, the pyrolysis gases flowed through a wet scrubber system that was designed to remove inorganic halogens from the pyrolysis gas. The two scrubbers operated in a counter flow mode with the gas flowing upwards. Each scrubber was constructed from glass and was packed with plastic pall rings. The first scrubber unit was washed with deionised water and



2 Schematic diagram of fluidised bed reactor

the second scrubber unit was washed with an alkali solution of Na_2CO_3 and $NaHCO_3$. The scrubber units were supplied with liquid from two reservoirs at a rate of 9 L min^{-1}. After passing through the scrubbers, the wash solutions returned to the reservoirs.

At the end of the experiment, the oil was recovered from the condensers and stored in amber glass bottles until analysis of the PBDEs took place. The solutions from the scrubber unit were analysed for their bromine contents using a Dionex DX100 ion chromatograph fitted with a Dionex AS4A column.

The bromine content of the oil was determined using a Gallenkamp Autobomb bomb calorimeter (EPA method 5050). Briefly, 10 mL of $Na_2CO_3/NaHCO_3$ solution was placed in the bottom of the bomb calorimeter and a known mass of oil was then combusted. The bomb was left sealed for 30 min and was then opened and thoroughly rinsed with the alkali solution. The resulting brominated solution was then analysed by ion chromatography using a Dionex DX100 ion chromatograph fitted with a Dionex AS4A column.

The pyrolysis char was retained by the sand that made up the fluidised bed. Once the bed had been removed from the furnace, three 20 g samples of sand were combusted at 700°C in a furnace to determine the quantity of char. Air was passed over the sample and exited from the stainless steel tube into a Dreschel bottle that contained an alkali solution to capture any bromine. The bromine content of the alkali was then analysed by the Dionex ion chromatography system described earlier. The chars were also examined by scanning electron microscopy with energy dispersive X-ray analysis (SEM–EDX) to establish whether any bromine was present. The system used was a Cambridge Scanning Co. Camscan Series III SEM coupled with EDX and had full computer based data handling and imaging.

Sample clean-up and analysis

The sample clean-up was carried out using a packed column which consisted of (from top to bottom) 2 g sodium sulphate, 1 g silica gel, 4 g acid silica gel, 0·5 g silica gel, 2 g basic silica gel and 0·5 g silica gel. The packed columns were conditioned with 100 mL of hexane (HPLC grade). The basic silica gel was coated with 2% KOH and the acid silica gel was coated with 44%H_2SO_4, all of the silica gels and the sodium sulphate were supplied by Supelco (UK) and were of dioxin grade.

The pyrolysis oil was made into a stock solution of 0·1251 g of pyrolysis oil in 100 mL of hexane and for each clean-up, 2·5 mL of the stock solution was diluted to 25 mL of hexane. The 25 mL of hexane solution was spiked with 250 μL of 4-chlorobiphenyl as an internal standard and was then loaded onto the column and eluted; 4-chlorobiphenyl was chosen as an internal standard because PCBs are known to exhibit similar properties to PBDEs. The column was washed with a further 25 mL of hexane and the resulting solution was blown down under nitrogen at 40°C to a volume of 20 μL. Six separate clean-ups were carried out simultaneously using the same clean-up method to give an insight into the repeatability of the clean-up procedure and provide an average result of the PBDE content of the sample.

The cleaned oil samples were analysed using a Shimadzu QP 2010 fitted with an AOC 20i autosampler; a 2·5 μL injection volume was used and the column was a SLB – 5 ms (30 m × 0·25 mm × 0·25 μm film thickness). The GC was programmed to hold at 100°C for 5 min and then ramp at 2°C min^{-1} to 140°C, ramp at 4°C min^{-1} to 220°C, ramp at 8°C min^{-1} to 310°C and then, hold for 40 min. The GC programme was designed to provide good separation of the PBDEs and also preserve the decaBDE, which can thermally decompose on the GC and is generally considered difficult to analyse. The GC–MS was operated in selective ion mode (SIM), two ions were monitored for each class of PBDE (e.g. monoBDE, triBDE) and the identification of each congener was confirmed by comparing the ion abundance ratios as well as by comparing the mass spectra.

The GC–MS was calibrated using two standard solutions, EO 5113 and EO 5103, which were obtained from LGC Promochem (UK) and manufactured by Cambridge Isotopes Laboratories Inc. (USA). EO 5113 is a PBDE unlabelled PAR solution which contains all the PBDEs for which standards are available with the exception of decaBDE. EO 5103 is a PBDE predominant congener mixture that does contain decaBDE as well as a selection of the other congeners present in EO 5113. EO 5103 was used to confirm the identification of the analytes in EO 5113. EO 5113 contains 39 PBDE congeners which when the decaBDE congener is added from EO 5103, means that only 40 of the 209 PBDE congeners could be identified and quantified. The structure of PBDEs means that congeners that have the same number of bromine atoms do not necessarily have the same mass spectra, as the bromine atoms can be distributed differently between the two benzene rings, this made it impossible to even identify with a significant degree of confidence any congeners that were not in the standards. Therefore, although many more PBDE congers were undoubtedly present in the pyrolysis oil than in the standard mixtures, the authors have been restricted to only reporting on the congeners for which standards are available.

Results and discussion

Product yield

The pyrolysis of the brominated high impact polystyrene produced a mainly oil product and much lower yields of a char and gas product. The oil yield was 89·9 wt-%, the gas yield was 1·5 wt-% and the char yield was 8·7 wt-%. The products of pyrolysis were analysed for their bromine content. The scrubber unit solutions were analysed to determine the content of HBr and Br_2 present in the gases by ion chromatography, which was found to be 2 wt-% of the bromine content of the original HIPS plastic. The char was analysed for its bromine content by combustion in a muffle furnace followed by trapping of the off gases in solution and analysis using ion chromatography. However, no bromine was detected. Energy dispersive X-ray analysis of the char sample was also used to confirm that no bromine was present in the char. Therefore, the fast pyrolysis of the brominated HIPS produced a mainly oil product which contained 98% of the bromine fed into the fluidised bed reactor as brominated HIPS. This was confirmed by combusting an aliquot of oil in a bomb calorimeter and then washing the bomb with an alkali solution. The alkali solution was then analysed by ion chromatography to determine its bromine content and hence the bromine content of the oil.

Oil analysis for PBDEs

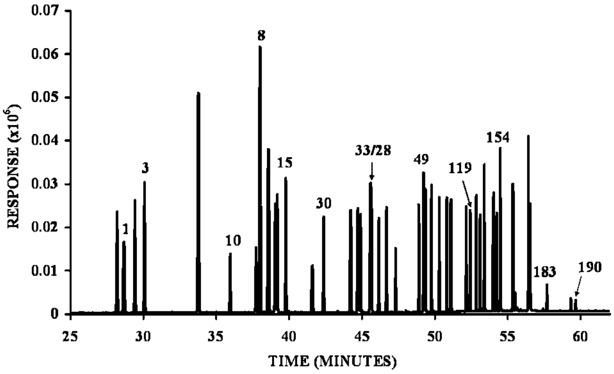
The oils were analysed to determine the concentration of PBDEs using a series of steps which involved calibration of the GC–MS system, clean-up of the pyrolysis oil to remove interfering compounds and quantification of the PBDEs.

Calibration of GC–MS

The retention times and relative retention times of each analyte in the PBDE standards are shown in Table 1, as well as the component ID (the IUPAC number assigned to each PBDE congener). Co-elution of some analytes was observed, but complete separation of all the PBDE congeners is very difficult to achieve. The chromatograms of both the PBDE standards are shown in Figs. 3 and 4, where it can be seen that good separation of the analytes and good resolution of decaBDE (PBDE #209) has been achieved.

Quantification of PBDEs

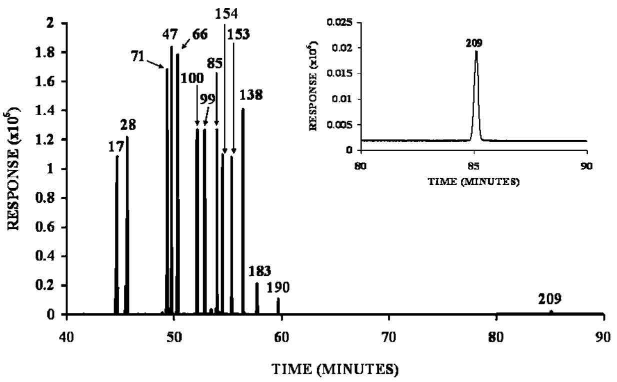
The concentration of the PBDEs in the pyrolysis oil are listed in Table 2 and an example GC–MS chromatogram of the clean pyrolysis oil is shown in Fig. 5. Table 2 also shows the standard deviation and the coefficient of variation between each of the six clean-ups. In this particular work, the best statistical test to use when comparing the data is the coefficient of variation as the large range of mean values means that comparisons of the standard deviation can be misleading. The coefficient of variation values ranged from 6·1 to 69·3% depending on the PBDE congener being investigated and the repeatability of the clean-up procedure can therefore be said to range from excellent to poor, depending on which congener is being analysed. When using a clean-up procedure as rigorous as the one used in this work, it is to be expected that the recovery of each analyte will differ from sample to sample to some extent.



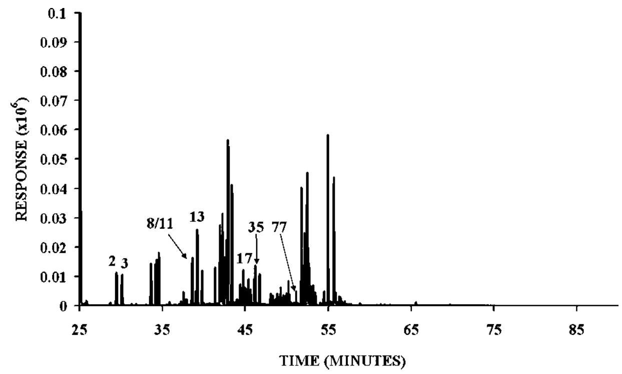
3 Gas chromatography–mass spectrometry total ion chromatogram (TIC) of EO-5113 standard

Table 1 Retention times and relative retention times of components of standard EO 5113 and EO 5103

Name	Retention time, min	RRT	Component ID
2-monoBDE	28·7	0·576	PBDE 1
3-monoBDE	29·4	0·590	PBDE 2
4-monoBDE	30·1	0·604	PBDE 3
2,6-diBDE	36·0	0·723	PBDE 10
2,4-diBDE	37·7	0·757	PBDE 7
3,3′-diBDE/2,4′-diBDE	38·6	0·775	PBDE 11/8
3,4-diBDE	39·0	0·783	PBDE 12
3,4′-diBDE	39·2	0·787	PBDE 13
4,4′-diBDE	39·8	0·799	PBDE 15
2,4,6-triBDE	42·4	0·851	PBDE 30
2,4′,6-triBDE	44·2	0·888	PBDE 32
2,2′,4-triBDE	44·7	0·898	PBDE 17
2,3′,4-triBDE	44·9	0·902	PBDE 25
2’,3,4-triBDE/2,4,4′-triBDE	45·6	0·916	PBDE 33/28
3,3′,4-triBDE	46·1	0·926	PBDE 35
3,4,4′-triBDE	46·7	0·938	PBDE 37
2,4,4′,6-tetraBDE	48·9	0·982	PBDE 75
2,2’,4,5′-tetraBDE	49·2	0·988	PBDE 49
2,3′,4′,6-tetraBDE	49·4	0·992	PBDE 71
2,2′,4,4′-tetraBDE	49·8	1·000	PBDE 47
2,3′,4,4′-tetraBDE	50·3	1·010	PBDE 66
3,3′,4,4′-tetraBDE	51·1	1·026	PBDE 77
2,2′,4,4′,6-pentaBDE	52·1	1·046	PBDE 100
2,3′,4,4′,6-pentaBDE	52·4	1·052	PBDE 119
2,2′,4,4′,5-pentaBDE	52·8	1·060	PBDE 99
2,3,4,5,6-pentaBDE	53·1	1·066	PBDE 116
2,3′,4,4’,5-pentaBDE	53·4	1·072	PBDE 118
2,2′,3,4,4′-pentaBDE	54·0	1·084	PBDE 85
2,2′,4,4′,6,6′-hexaBDE	54·1	1·086	PBDE 155
3,3′,4,4′,5-pentaBDE	54·2	1·088	PBDE 126
2,2′,4,4′,5,6′-hexaBDE	54·5	1·094	PBDE 154
2,2′,4,4′,5,5′-hexaBDE	55·3	1·110	PBDE 153
2,2′,3,4,4′,5-hexaBDE	56·4	1·133	PBDE 138
2,3,4,4′,5,6-hexaBDE	56·5	1·135	PBDE 166
2,2′,3,4,4′,5′,6-heptaBDE	57·7	1·159	PBDE 183
2,2′,3,4,4′,5,6-heptaBDE	59·3	1·191	PBDE 181
2,3,3′,4,4′,5,6-heptaBDE	59·7	1·199	PBDE 190
2,2′,3,3′,4,4′,5,5′,6,6′-decaBDE	85·1	1·710	PBDE 209



4 Gas chromatography–mass spectrometry total ion chromatogram of standard EO 5103 showing PBDE ID numbers and magnified area around decaBDE (PBDE #209) peak



5 Gas chromatography–mass spectrometry total ion chromatogram of pyrolysis oil after sample clean-up showing some of PBDEs present

A general observation of the coefficients of variation is that the lower brominated PBDEs have lower values and are therefore more repeatable than the higher brominated PBDEs. This would suggest that the clean-up procedure is more effective for the lower brominated PBDEs than the higher brominated ones and that in future work, there might need to be some refinement of the clean-up procedure to improve the repeatability of the quantification of the higher brominated PBDEs.

Of the three monoBDEs investigated, 3-monoBDE (PBDE #2) was the most prominent and only very small concentrations of 2-monoBDE (PBDE #1) were present in the oil. The most prominent diBDE was 3,4′-diBDE (PBDE #13) and the most prominent triBDE was 3,3′,4-triBDE (PBDE #35). Several of the triBDEs investigated were not detected in the pyrolysis oil, as were some of the tetraBDEs, the most concentrated of which was 3,3′,4,4′-tetraBDE (PBDE #77). Virtually, no pentaBDEs were detected in the pyrolysis oil; of the seven pentaBDEs investigated, only 3,3′4,4′,5-pentaBDE (PBDE #126) was detected and that was only present in very low concentrations. Several hexaBDEs were detected, by far the most prominent of which was 2,2′4,4′,5,6′-hexaBDE (PBDE #154). No heptaBDEs or decaBDE were detected in the pyrolysis oil and although they were not present in the standard mixtures, analysis of the GC–MS chromatograms suggested that very little or no octaBDE or nonaBDE were present in the pyrolysis oil.

If hexaBDE is excluded from the data set, then it is possible to see some patterns in the data. The PBDEs which have bromine atoms positioned on the 3, 3′, 4 or 4′ position seem to be much more prominent than the other congeners and PBDEs that have bromine atoms in the 2 or 2′ position appear to be the least abundant. For example, the most prominent di-, tri- and tetraBDE all contained all of their bromine atoms in the 3, 3′, 4 or 4′ positions and in the case of pentaBDE, the only congener detected was 3,3′,4,4′,5-pentaBDE. It is possible that PBDE congeners that have the bromine atoms in the 3 or 4 positions are more stable during the pyrolysis process, but caution should taken when interpreting these results because only 40 of the 209

Table 2 PBDEs detected in pyrolysis oil after six repetitions of sample clean-up procedure

		Concentration in oil, ppm								
Component	**ID**	**Sample 1**	**Sample 2**	**Sample 3**	**Sample 4**	**Sample 5**	**Sample 6**	**Mean**	**Standar deviation, ppm**	**Coefficient variation, %**
2-monoBDE	BDE 1	12·3	9·0	15·0	11·4	13·3	9·5	11·7	2·1	17·8
3-monoBDE	BDE 2	121·3	114·1	125·8	98·7	102·9	91·0	109·0	12·4	11·4
4-monoBDE	BDE 3	91·9	83·4	97·3	77·2	82·7	70·7	83·9	8·8	10·5
2,4-diBDE	BDE 7	16·7	16·1	16·5	16·9	17·7	14·4	16·4	1·0	6·1
2,6-diBDE	BDE 10	1·7	1·1	1·0	1·6	1·6	1·0	1·3	0·3	21·4
3,3′-diBDE/2,4′-diBDE	BDE 11/8	73·3	75·4	69·7	75·7	69·4	58·9	70·4	5·7	8·1
3,4-diBDE	BDE 12	32·2	32·8	31·5	34·4	33·0	27·4	31·9	2·2	6·9
3,4′-diBDE	BDE 13	170·6	177·8	168·0	177·9	162·6	140·9	166·3	12·6	7·6
4,4′-diBDE	BDE 15	65·0	65·8	63·6	67·6	62·5	53·4	63·0	4·6	7·3
2,2′,4-triBDE	BDE 17	41·4	42·8	51·1	59·8	57·5	39·0	48·6	8·1	16·6
2,3′,4-triBDE	BDE 25	44·3	46·2	51·9	57·1	56·5	42·2	49·7	5·8	11·7
3,3′,4-triBDE	BDE 35	109·7	96·8	61·9	124·3	105·9	71·7	95·1	21·7	22·9
3,4,4′-triBDE	BDE 37	82·8	70·2	42·9	92·1	80·2	54·3	70·4	17·0	24·2
2,2′,4,4′-tetraBDE	BDE 47	12·2	11·8	9·9	12·2	29·3	9·9	14·2	6·8	48·1
2,2′,4,5′-tetraBDE	BDE 49	17·5	30·1	28·4	10·8	18·3	28·3	22·2	7·1	32·1
2,3′,4,4′-tetraBDE	BDE 66	19·7	27·7	18·9	25·2	18·0	16·4	21·0	4·0	19·3
3,3′,4,4′-tetraBDE	BDE 77	48·7	36·7	17·1	55·0	36·7	18·4	35·4	14·1	39·7
3,3′,4,4′,5-pentaBDE	BDE 126	4·5	4·7	3·2	16·0	11·4	2·7	7·1	4·9	69·3
2,2′,3,4,4′,5′-hexaBDE	BDE 138	17·8	16·5	11·9	17·0	11·3	6·2	13·5	4·1	30·3
2,2′,4,4′,5,5′-hexaBDE	BDE 153	14·1	13·2	3·3	14·0	9·5	5·6	10·0	4·3	42·8
2,2′,4,4′,5,6′-hexaBDE	BDE 154	102·1	90·1	28·8	113·3	63·3	36·4	72·3	32·0	44·3

possible congeners were investigated and so, the data will naturally be skewed towards these 40 congeners.

In this work, no decaBDE (PBDE #209) was detected in the pyrolysis oil. However, in the authors' previous work, it was determined that 22·4 ppm of decaBDE was present in the oil when Br–HIPS was pyrolysed at 500°C in a fluidised bed reactor.[20] Because decaBDE has such a high molecular weight, it elutes long after any other pyrolysis products on a gas chromatograph, so its concentration in pyrolysis oil can easily be measured without resorting to any pre-analysis clean-up. Therefore, it can be concluded that the clean-up procedure used in this work cannot be used for investigating decaBDE as it may be removed during the clean-up step. It is also possible that this clean-up procedure might not be suitable for hepta-, octa- and nonaBDE as none of these were observed in the cleaned pyrolysis oil.

The data presented in this work would suggest that the less brominated PBDE congeners are more prevalent in the pyrolysis oil than the PBDEs with a higher number of bromine atoms. This is of some concern as there is evidence that the lower brominated PBDEs (mono to penta) are more toxic than the higher brominated PBDEs because they can enter cells more easily, however, all of the ten PBDE congener groups are thought to exhibit health effects including neurotoxicity, thyrotoxicity, estrogenicity and carcinogenicity.[21] The almost total absence of pentaBDE from the pyrolysis oil is an advantage because it is considered to be the most bioaccumulative PBDE and therefore potentially the most dangerous when considering long term health effects.[22]

Conclusions

In recent years, there has been intensive research into converting toxic brominated plastics into clean, bromine free liquid fuels using pyrolysis. However, there has been little investigation into the presence of polybrominated diphenyl ethers in the pyrolysis oils. There are 209 PBDE congeners and they are all considered to be extremely toxic and their presence in commercial pyrolysis oils could be dangerous to human health. In this work, high impact polystyrene that was flame retarded with decabromodiphenyl ether and antimony trioxide was pyrolysed in a fluidised bed reactor and the resulting oil was analysed for PBDEs. A rigorous clean-up procedure was applied to the pyrolysis oils before quantification of the PBDEs was carried out on a GC–MS.

The most abundant PBDE found in the pyrolysis oil was 3,4′-diBDE (PBDE #13) and the lower brominated PBDEs appeared to be more abundant, then the higher brominated PBDEs. Virtually, no pentaBDEs, the most dangerous congener group, were detected in the pyrolysis oils. The results show that it is possible to measure PBDEs in pyrolysis oil and therefore, test the effectiveness of some of the pyrolysis techniques which are being used to eliminate organobromines from the pyrolysis oil of brominated plastics.

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References

1. Directive 2002/96/EC of the European Parliament and of the Council on Waste Electrical and Electronic Equipment, Official Journal of the European Commission, L37/24, Brussels, Belgium, 2003.
2. BSEF: 'An introduction to brominated flame retardants', BSEF, Brussels, Belgium, 19 October 2000, 28.
3. L. Tange and D. Drohmann: 'Closing the bromine cycle - bromine recovery from plastics containing brominated retardants - an option for sustainable bromine production', Geneva, Switzerland, 2002.
4. H. Boerrigter, A. B. J. Oudhuis and L. Tange: 'Bromine recovery from the plastics fraction of waste of electrical and electronic equipment (WEEE) with staged gasification', ECN Biomass, Petten, Netherlands.
5. J. Vehlow, B. Bergfeldt, H. Hunsinger, K. Jay, F. E. Mark, L. Tange, D. Drohmann and H. Fisch: 'Recycling of bromine from plastics containing brominated flame retardants in state-of-the-art combustion facilities', APME, Brussels, Belgium 2002, 18.
6. World Health Organisation: 'Brominated diphenyl ethers', Environmental Health Criteria 162, World Health Organisation, Geneva, Switzerland, 1994.
7. Plastics Europe: 'An analysis of plastic production, demand and recovery in Europe', Brussels, Belgium, 2006.
8. F. E. Mark: 'The characteristics of plastic-rich waste streams from end-of-life electrical and electronic equipment', Plastic Europe, Brussels, Belgium, 2006.
9. EC: Directive 1999/31/EC of the European Parliament and of the Council on the landfill of waste, Official Journal of the European Commission, L182/1, Brussels, Belgium, 1999.
10. T. Bhaskar, W. J. Hall, N. M. M. Mitan, A. Muto, P. T. Williams and Y. Sakata: *Polym. Degrad. Stabil.*, 2007, **92**, 211–221.
11. W. J. Hall and P. T. Williams: *Energy Fuels*, 2006, **20**, 1536–1549.
12. W. J. Hall and P. T. Williams: *J. Anal. Appl. Pyrol.*, 2008, **81**, 139–147.
13. M. Brebu, E. Jakab and Y. Sakata: *J. Anal. Appl. Pyrol.*, 2007, **79**, 346–352.
14. M. Blazso and Z. Czegeny: *J. Chromatogr. A*, 2006, **1130A**, 91–96.
15. M. P. Luda, N. Euringer, U. Moratti and M. Zanetti: *Waste Manage.*, 2005, **25**, 203–208.
16. A. Hornung, S. Donner, A. Balabanovich and H. Seifert: *J. Clean. Prod.*, 2005, **13**, 525–530.
17. M. Brebu, T. Bhaskar, K. Murai, A. Muto, Y. Sakata and M. A. Uddin: *Polym. Degrad. Stabil.*, 2005, **87**, 225–230.
18. M. Blazso, Z. Czegeny and C. Csoma: *J. Anal. Appl. Pyrol.*, 2002, **64**, 249–261.
19. M. P. Luda, G. Camino, A. I. Balabanovich and A. Hornung: *Macromol. Symp.*, 2002, **180**, 141–151.
20. W. J. Hall and P. T. Williams: *J. Anal. Appl. Pyrol.*, 2006, **77**, 75–82.
21. M. A. Siddiqi, R. H. Laessig and K. D. Reed: *Clin. Med. Res.*, 2003, **1**, 281–290.
22. M. C. Newman and M. A. Unge: 'Fundamentals of ecotoxicity', 2nd edn, 48; 2003, New York, Lewis Publishers.