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PYROLYSIS OF BROMINATED FEEDSTOCK PLASTIC IN A FLUIDISED BED REACTOR

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ABSTRACT

Fire retarded high impact polystyrene has been pyrolysed using a fluidised bed reactor with a sand bed. The yield and composition of the products have been investigated in relation to fluidised bed temperature. The bromine distribution between the products and a detailed analysis of the oils using GC-FID/ECD, GC-MS, FT-ir, and size exclusion chromatography has been carried out. It was found that the majority of the bromine transfers to the pyrolysis oil and the antimony was detected in both the oil and the char. Oil made up over 89.9% of the pyrolysis products. Over 30% of the oil consisted of benzene, toluene, ethylbenzene, styrene and cumene. The pyrolysis gases were mainly hydrocarbons in the C_1-C_4 range but some HBr and Br_2 was detected.

KEYWORDS : Flash pyrolysis, fire retarded plastic, bromine recycling

1. INTRODUCTION

A significant and increasing proportion of plastic waste is contained in consumer products such as television casing materials, computer equipment, photocopiers, washing machines and printed circuit boards. Total electrical and electronic equipment waste generated in Europe is estimated at 4.4 million tonnes annually and of that tonnage, it is estimated that 0.73 million tonnes of the waste is plastic material and this is predicted to grow by 20% over the next 5 years [1]. Waste Electrical and Electronic Equipment (WEEE) has been classified as a priority waste stream and is subject to recent EU legislation, via the Waste Electrical and Electronic Equipment Directive which includes ambitious recycling and recovery targets. Over 95 % of such waste is currently landfilled, since it represents a difficult waste to recycle. The EU Directive calls for, among other things, the recovery of the major plastic components of WEEE [2].

High impact polystyrene (HIPS) makes up a significant proportion of WEEE plastics and is often fire retarded with decabromodiphenyl ether (deca-BDE) and diantimony trioxide to decrease the flammability of the plastic. Deca-BDE is added to HIPS because the bromine radicals quench combustion reactions while diantimony trioxide is added as a synergist because it increases the rate of bromine release by forming antimony bromides and antimony oxybromides [3]. The flame retardant content of WEEE represents a major hindrance to the development of recycling technologies, particularly the presence of bromine and antimony

Pyrolysis has been extensively researched as a technique for the recycling of waste polystyrenes [4-6]. It is thought that the products of waste plastic pyrolysis can potentially be used either as fuels, raw materials or as feedstock for the petrochemical industry [7]. Although the slow pyrolysis of brominated HIPS has been investigated previously using a small scale reactor [5], investigations into the flash pyrolysis of brominated HIPS in a laboratory scale reactor are scarce. The flash pyrolysis of polystyrene in the absence of flame retardants has been investigated before and results in the breakdown of the polymer into gases and oils, which mainly contain styrene monomers, dimers, and trimers. However, brominated HIPS appears to decompose differently to polystyrene [8]. The pyrolysis of brominated HIPS occurs in two stages, firstly by the emission of volatile brominated compounds and secondly by the emission of polymer degradation products, although the two stages do overlap [8].

In this work, a fluidised bed reactor measuring 1m in height by 120mm in diameter has been used to pyrolyse brominated HIPS at temperatures between 450-550°C. The aim of this work was to investigate the flash pyrolysis of brominated HIPS and to characterise the pyrolysis products, particularly the distribution of bromine and antimony between the reaction products and the brominated compounds formed in the product oil.

2. EXPERIMENTAL

2.1 Materials

High impact polystyrene (HIPS) that was flame retarded with decabromodiphenyl ether (deca-BDE) and diantimony trioxide was supplied by Atofina Ltd (UK). The elemental analysis of the HIPS was determined using a CE Instruments CHNS-O analyser and the results are shown in table 1.

The bromine content of the plastic was determined using a Gallenkamp Autobomb bomb calorimeter (EPA method 5050). Briefly, 50mL of $Na_2CO_3/NaHCO_3$ solution was placed in the bottom of the bomb calorimeter and a known mass of plastic was then combusted. The bomb was left sealed for 30 minutes 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 efficiency of the system was checked by combusting materials with known bromine contents. The volume of alkali solution placed in the bomb calorimeter was increased from the EPA standard method because of the high bromine content of the plastic.

The antimony content of the plastic was determined by atomic absorption spectrometry (AA) after acid digestion of the plastic. An aliquot of the plastic was refluxed in a mixture of 10mL of hot sulphuric acid and 1mL of hot nitric acid for 1 hour and then allowed to cool. A further 3mL of nitric acid was then added to the solution and the digestion flask was returned to the hotplate for another twenty minutes before being cooled; this step was repeated until the digestion was complete.

2.2 Fluidised bed reactor

The brominated HIPS was pyrolysed in a fluidised bed reactor at bed temperatures of 450-550 °C, a range recommended for the monomer recovery from waste polystyrene pyrolysis [9]. The fluidised bed reactor (figure 1) was electrically heated to the required final temperature before each 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 1mm diameter apertures. A small amount of nitrogen gas 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 HBr and Br_2 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 the second scrubber 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. After passing through the scrubbers the wash solutions returned to the reservoirs.

2.3 Analysis of the pyrolysis products

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. The bromine content of the char could not be determined using the bomb calorimeter because the char could not be readily separated from the sand in sufficient quantity for the bromine determination. Instead, a portion of the fluidised bed was placed in a stainless steel tube that was then heated by a muffle furnace to 700°C. 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 which 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 or antimony was present. The system used was a Cambridge Scanning Co. Camscan Series III SEM coupled with EDX and had a full computer based data handling and imaging. Because the quantity of char was very small compared to the quantity of sand, it was not possible to analyse the antimony content of the chars by acid digestion and atomic absorption (AA) spectrometry.

The bromine content of the pyrolysis oil was determined using the bomb calorimeter methodology followed by ion chromatography. The presence of antimony was conducted on a qualitative basis via acid digestion followed by atomic absorption spectrometry.

A Nicolet 560 FT-ir with data processing and spectral library facilities was used to analyse the functional groups present in the oil. A small amount of pyrolysis oil was coated on a KBr disk and the spectrometer scanned the sample from 450-4000cm^{-1}. The molecular weight distribution of the oils was determined by size exclusion chromatography. The system consisted of a 30-cm long by 0.78-cm ID column from Phenomenex, with a silica bead packing of 50-Å average pore size, connected to a Merk-Hitachi UV detector tuned to detect aromatic compounds and a Varian RI detector capable of detecting all hydrocarbons.

The pyrolysis oils were characterised using gas chromatography (GC) with dual flame ionisation and electron capture detection (GC-FID/ECD); the flame ionisation detector (FID) detecting all hydrocarbons and the electron capture detector (ECD) detecting halogenated hydrocarbons. The GC was a Varian 3380 fitted with a ZB-5MS column (30m x 0.32mm i.d. x 0.25µm film thickness) that was split so that the analytes passed through the FID and ECD detectors simultaneously. The GC was programmed to hold at 40 °C for 15 minutes and then heat to 280 °C at 5 °C min^{-1} and hold for a further 15 minutes. The injector was heated to 300 °C and the FID and ECD were heated to 300 °C and 310 °C respectively. The results from the GC-FID/ECD were compared with those from a coupled gas chromatograph-mass spectrometer that used the same type of column and GC programme.

GC-ECD analysis of PBDE's in the pyrolysis oil was carried out using a Varian 3380 GC fitted with a Varian CP-SIL 5CB column (15m x 0.25mm i.d. x 0.25µm film thickness). The GC was calibrated using a Cambridge Isotope Laboratories predominant congener mixture. The GC oven was programmed to hold at 100 °C for 1.2 minutes, ramp to 140 °C at 2 °C min^{-1}, ramp to 220 °C at 4 °C min^{-1}, ramp to 280 °C at 8 °C min^{-1}, hold for 31.5min.

A syringe was used to take gas samples from the fluidised bed reactor using a port between the second condenser and the scrubber unit; these gas samples were analysed off-line for hydrocarbon and permanent gases using gas chromatography. Alkanes and alkenes from C_1 to C_4 were analysed using a Varian CP-3380 GC fitted with a FID. Nitrogen carrier gas flowed through a stainless steel 2m by 8mm column packed with n-octane Porasil C of 80-100 mesh size. CO_2, CO, H_2, and O_2 were analysed on a second Varian CP-3380 that was fitted with two columns and two thermal conductivity detectors (TCD). Three gas samples were taken at pre-arranged intervals throughout each test on the fluidised bed and the average result was calculated to be the pyrolysis gas composition.

3. RESULTS AND DISCUSSION

3.1 Product Yield

The mass balances of oil, char and gas and the bromine mass balance in relation to the flash pyrolysis of brominated high impact polystyrene (HIPS) at 450 °C, 500 °C, and 550 °C are shown in table 2. During flash pyrolysis, at least 89.9% of the plastic was converted to oil, which was collected in the condensers. As the flash pyrolysis temperature increased the amount of gas produced increased. Increased gas yields with increasing temperature would be expected because the higher temperature thermally degrades molecules down faster and the higher energy input allows more secondary reactions to occur [10].

Bhaskar et al [5] reported that when HIPS that contains deca-BDE and diantimony trioxide is subjected to slow pyrolysis to 430 °C, 72% of the plastic converts to pyrolysis oil, 23% to char, and 4% to gas [5]. This would suggest that the flash pyrolysis of brominated HIPS leads to the formation of greater amounts of pyrolysis oil and less char than slow pyrolysis, but it should be noted that the final pyrolysis temperature in the work of Bhaskar et al was only 430 °C [5], whereas in this work, the temperatures were higher. The flash pyrolysis of polystyrene with no flame inhibitors present has been reported to produce about 90-95% wax/oil and 2% gas, with little or no char being produced [6, 11].

The antimony content of the pyrolysis oil on a qualitative basis was measured by atomic absorption (AA) spectrometric analysis following acid digestion of the oils. The presence of antimony was confirmed in significant concentrations at more than 50 wt% antimony in the oils. The scrubber wash solutions were also analysed by AA but no antimony was recorded. It was not possible to quantitatively measure the antimony content of the char by AA but it was confirmed that antimony was present in the char by using EDX (figure 2).

3.2 Bromine balance

Table 2 shows the fate of the bromine during the flash pyrolysis of brominated HIPS. Regardless of the pyrolysis temperature, over 98% of the bromine fed into the fluidised bed reactor was present in the pyrolysis oil. The bomb calorimeter was used to determine the bromine content of the oil but a larger combustion chamber was needed to determine the bromine in the char. The char was therefore burnt in a muffle furnace but no bromine was detected. EDX analysis was used to confirm that no bromine was present in the char (figure 2).

The gas phase bromine was captured by two wet scrubbers; the first scrubber was washed with deionised water and the second scrubber was washed with an alkali solution. Hydrogen bromide is very soluble in water and was therefore most likely to have been captured in the first scrubber. Bromine gas is only slightly soluble in water so is more likely to have been captured in the second scrubber unit. Figure 3 shows the proportion of bromine captured by each scrubber. Up to a temperature of 500 °C, 85-90% of the gas phase bromine was captured by the first, pH neutral, scrubber with the remainder being captured by the alkali scrubber. At a temperature of 550 °C, only 50% of the gas phase bromine was captured by the pH neutral scrubber; this change in capture efficiency coincided with a drop in the total amount of gas phase bromine. That decrease was in fact due to a decrease in hydrogen bromide capture in the first scrubber rather than a decrease in the total hydrogen bromide and bromine produced (table 2).

Bhaskar et al [5] found that slow pyrolysis to 430 °C, at 3°C min^{-1}, of a plastic very similar to that used in this work led to 76% of the bromine input being present in the pyrolysis oil and 5% of the bromine being in the char. It would therefore appear that the flash pyrolysis of brominated HIPS leads to more bromine being present in the oil than the slow pyrolysis of brominated HIPS. At pyrolysis temperatures of 450 °C and 500 °C, the majority of gas phase bromine was probably hydrogen bromide as it was captured in the first scrubber, this reflects the fact that hydrogen bromide elimination is favoured over bromine elimination during the debromination of PBDE's [4]. It is not clear why hydrogen bromide elimination should decrease once the flash pyrolysis temperature reaches 550 °C.

3.3 Pyrolysis oil

Flash pyrolysis of brominated HIPS in the fluidised bed reactor resulted in at least 89.9% of the plastic being converted to pyrolysis oil. The organic constituents of the pyrolysis oil were examined using GC-FID/ECD and, on average, 257 peaks were recorded by the FID with 110 of those peaks also giving a response on the ECD. ECD detectors only respond to electronegative elements such as bromine, chlorine, and some forms of oxygen and nitrogen.

Over a third of the oil was composed of benzene, toluene, ethylbenzene, styrene, and cumene (figure 4). These chemicals can be considered highly decomposed pyrolysis products as the polystyrene molecule has broken down to one mono-substituted benzene ring. A flash pyrolysis temperature of 550 °C gave increased yields of the most common pyrolysis products, with the exception of benzene, which was reduced in yield at 550 °C. It would be expected that increased yields of single benzene ring compounds would be seen at higher temperatures because there is more energy in the pyrolysis process to break down the large polystyrene molecules. The pyrolysis oil also contained significant quantities of compounds that were made up of two or more benzene rings; naphthalene, diphenylmethane, 1,2,-diphenylethane, 1-phenylnaphthalene, and 1,3,5-triphenylbenzene are examples of these molecules.

Jakab et al [3] reported that brominated HIPS decomposes to form more ethylbenzene, toluene, and cumene than when polystyrene is pyrolysed and that less styrene monomer, dimer, and trimer are produced. It was also reported that H-abstraction by diantimony trioxide and hydrogen-bromine substitution during the pyrolysis of brominated HIPS leads to the formation of condensed aromatics and triphenylbenzene products [3]. The formation of PAH's such as naphthalene from polystyrene is also well documented and understood [10].

A large number of complex molecules were present in the pyrolysis oils and gas chromatography-mass spectrometry (GC-MS) was used to try to identify some of them. The GC-MS total ion chromatogram (figure 5) was similar in appearance to the FID chromatogram. Table 3 shows the identifications and relative retention times of the compounds identified by the GC-MS and whether the identification was certain, probable, or tentative. Many more peaks on the total ion chromatograph of the pyrolysis oils could not be identified at all.

Analysis of the peak areas produced by the GC-MS showed that there was a reduction in the concentration of styrene dimer like molecules, such as 1,3-diphenylpropane, as the flash pyrolysis temperature increased. The flash pyrolysis of brominated HIPS proceeds via thermal degradation of the polystyrene polymer into styrene dimers and trimers and that, with more energy input, these molecules are further broken down into mono substituted benzene rings. According to the GC-MS analysis, the pyrolysis oils contained a significant number of oxygen and nitrogen containing compounds (table 3). The oxygen might have become available for reaction due to the decomposition of deca-BDE to bromobenzenes or through the conversion of diantimony trioxide to antimony bromide, although it has been reported that oxygen released from diantimony trioxide forms water [3]. The brominated HIPS plastic contained nitrogen containing compounds, confirmed by the elemental analysis of the plastic (table 1).

From the gas chromatographic analysis with electron capture detection, it was clear that there were large numbers of brominated organic compounds in the pyrolysis oil. The break down of deca-BDE will most likely lead to the formation of other PBDE's, bromophenols, bromobenzenes, and polybrominated dioxins and furans, as well as other brominated organics where the bromine is not attached to the benzene ring [8]. The oils from the flash pyrolysis of brominated HIPS were found to contain 1,2-dibromobenzene, 4-bromophenol, and (1-bromoethyl) benzene as examples of the type of brominated organics in the oil.

It has been reported that antimony bromide is formed during the pyrolysis of fire retarded HIPS [5]. The presence of antimony bromide in the oil produced by the flash pyrolysis of brominated HIPS has been previously observed on the GC-FID/ECD and it is probable that all the antimony in the pyrolysis oil was antimony bromide as diantimony trioxide is not volatile until a temperature of 1425 °C. If it is assumed that all the antimony in the pyrolysis oil was antimony bromide and based on the measured bromine and antimony contents of the pyrolysis oil, then at a flash pyrolysis temperature of 500 °C and 550 °C, approximately 32-33% of the bromine present in the oil could be attributed to antimony bromide. At a pyrolysis temperature of 450 °C, approximately 59% of the bromine present in the oil could be attributed to antimony bromide. Bhaskar et al [5] reported that during the slow pyrolysis of brominated HIPS, 92% of the bromine present in the pyrolysis oil was in the form of antimony bromide.

Fourier transform infra-red (FT-ir) analysis of the pyrolysis oils (figure 6) showed that there were bond vibrations that are typical of mono-substituted aromatic hydrocarbons and aliphatic hydrocarbons. The FT-ir spectra showed a small bond vibration peak at 650 cm^{-1} that is typical of an aliphatic C-Br bond and a large vibration at 1050 cm^{-1} that is typical of aryl-bromines. These vibrations could also have been caused by unbrominated hydrocarbons.

The large bond vibration peak at a 3500 cm^{-1} was probably caused by OH groups. These OH groups could be in the form of phenols from the decomposition of deca-BDE. More complex phenols and alcohols could also have been formed using the oxygen released by the transformation of diantimony trioxide to antimony bromide.

The bond vibration peaks at 2850-2950 cm^{-1} are typical of CH_3, CH_2 and CH groups, which suggest the presence of alkanes and alkenes. The vibration peaks at 3000-3100 cm^{-1} are typical of aromatic rings and the four vibration peaks between 1650-2000 cm^{-1} could be benzene ring substitution patterns. The remaining vibration peaks between 500-1700 cm^{-1} can all be related to vibrations caused by alkane, alkene, and aromatic C-H bonds.

Size exclusion chromatography (figure 7) showed some subtle differences between the three pyrolysis oils. As the flash pyrolysis temperature increased, the abundance of molecules with a molecular mass below 125 Daltons (Da) increased, this correlates with the GC-FID/ECD results that showed an increase in concentration of mono-substituted aromatics as the pyrolysis temperature increased. In all three oils, there was a significant concentration of molecules with a molecular mass of 125-140 Da. Above 140 Da, the abundance of molecules increased with decreasing pyrolysis temperature.

3.4 PBDE's in the pyrolysis oils

GC-ECD was used to detect the presence of any PBDE's in the pyrolysis oils. The GC was calibrated using a Cambridge Isotopes Laboratories (USA) predominant congener mixture that contained the congeners listed in table 4.

Figure 8 shows the gas chromatography with electron capture detection chromatogram for the oil resulting from pyrolysis of brominated HIPS at 450 °C. Peaks were present on the chromatogram at the same relative retention time as all of the PBDE congeners listed in table 4, suggesting that the PBDE congeners listed in table 4 might be present in the pyrolysis oils of brominated HIPS. Deca-BDE (PBDE number 209) eluted from the column a considerable time after any other analytes. Figure 9 shows the concentration of deca-BDE in the pyrolysis oil. It is clear from figure 9 that as the pyrolysis temperature was increased the concentration of deca-

BDE in the pyrolysis oils decreased, such that at a flash pyrolysis temperature of 550 °C no deca-BDE was detected in the pyrolysis oil. At a pyrolysis temperature of 450 °C, <0.10% of the deca-BDE input into the fluidised bed reactor was present in the pyrolysis oil.

3.5 Pyrolysis gases

The amount of gas produced by the flash pyrolysis of brominated HIPS increased as the pyrolysis temperature increased (table 2). An example of the composition of the pyrolysis gases is shown in figure 10. It should be noted that butene and butadiene co-eluted on the gas chromatograph and are therefore reported together. HIPS consists of a polystyrene phase and a dispersed polybutadiene phase [3] so butadiene should be present in the pyrolysis gas. Hydrogen gas was only present when the pyrolysis temperature was 550 °C.

As the pyrolysis temperature increased, the quantity of all the hydrocarbon gases also increased with the exception of propane and butane. The proportion of hydrogen bromide in the pyrolysis gases decreased rapidly with increasing temperature due to a combination of reduced bromine in the gas phase and increased production of hydrocarbon gases. The proportion of bromine in the gases also decreased with increasing pyrolysis temperature. Uemura et al [11] reported that, during the flash pyrolysis of polystyrene, methane, ethane, and H_2 gases were produced but no ethene, propene, CO, or CO_2 was detected.

In terms of the composition of the hydrocarbon gases released by the flash pyrolysis of brominated HIPS, the proportion of butene/butadiene released decreased with increasing temperature and the proportion of methane and propene increased with increasing temperature. No particular trend could be determined for the remaining hydrocarbon gases. The pyrolysis gases were also analysed for CO_2 and CO but the concentration of both was found to be below the detection limit of the GC. Williams and Williams [6] reported that for the flash pyrolysis of polystyrene containing no flame retardants, as the flash pyrolysis temperature of polystyrene increased from 500 °C to 550 °C the production of methane, ethene, and hydrogen increased but the production of ethane, propane, propene, butane, and butene decreased [6]. They also reported that the alkene gases were present in higher concentration than the alkane gases [6].

4. CONCLUSIONS

High impact polystyrene that was fire retarded with decabromodiphenyl ether and diantimony trioxide was successfully flash pyrolysed in a fluidised bed reactor at temperatures between 450 °C and 550 °C. The plastic decomposed to form at least 89.9% oil with a small amount of char and pyrolysis gas. The pyrolysis char contained over half the antimony and none of the bromine. Most of the bromine was present in the pyrolysis oil with less than 2% of the bromine in the pyrolysis gas. The most abundant products in the pyrolysis oil were benzene, toluene, ethylbenzene, and styrene. The pyrolysis oil also contained antimony bromide and brominated organics such as 1,2-dibromobenzene, 4-bromophenol, and (1-bromoethyl) benzene. The pyrolysis gases contained hydrocarbon gases from C_1 to C_4 as well as small amounts of hydrogen bromide and bromine. Increasing the pyrolysis temperature from 450 °C to 550 °C had only subtle impacts on the pyrolysis products. As the temperature increased the quantity of gas produced also increased but the amount of hydrogen bromide and bromine decreased. The increased pyrolysis temperature led to an increase in the concentration of light organic compounds such as ethylbenzene and styrene in the pyrolysis oil.

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Table 1 Elemental composition of the brominated HIPS

Element	Wt%
Carbon	80.0
Hydrogen	7.2
Nitrogen	0.2
Oxygen	0.9
Bromine	7.2
Antimony	4.6

Table 2 Total mass balance and bromine balance during the flash pyrolysis of brominated HIPS

	Temp. °C	450	500	550
Mass (%)	Char	5.6	8.7	5.2
	Oil	94.0	89.9	93.0
	Gas	0.4	1.5	1.9
Bromine (%)	Char	0.0	0.0	0.0
	Oil	98.6	98.0	99.5
	Gas	1.4	2.0	0.5

Table 3 Compounds identified by GC-MS in the pyrolysis oil of brominated HIPS flash pyrolysed at 500 °C

Name	RT	Certainty	Peak No.
Ethyl benzene	7.7	***	1
Styrene	9.0	***	2
Cumene	11.9	***	3
Naphthalene	27.9	***	4
1,4-dihydro-1,4-methanonaphthalene	32.1	***	5
2-methylnaphthalene	32.1	***	
Diphenylmethane	35.5	**	6
1,2-diphenylethane	37.7	***	7
1,3-diphenylpropane	40.8	***	8
1,2-diphenylcylcopropane	41.2	***	
(1-Phenyl-1-butenyl)benzene	41.3	***	
1,3-Diphenyl-1-butene	41.4	**	
1,1,3-Trimethyl-3-phenylindane	42.2	***	
(1-Phenylcyclopropyl)benzene	42.6	***	
Anisyl butyrate	42.7	**	9
1,4-Diphenylbutane	43.0	**	
1-Phenyltetralin	43.4	***	
1,3-Diphenyl-1-butene	43.5	***	
1,4-Diphenylbutadiene	44.3	***	
Isoquinoline	44.5	*	10
1-phenylnaphthalene	45.2	***	
9-(1-methylethyl) anthracene	45.3	**	
4,4'-Dimethyldibenzyl	46.4	**	11
2-phenylnaphthalene	47.4	***	
9-(2-propenyl)-anthracene	47.8	**	
2-(phenylmethyl)-naphthalene	49.8	**	
Methyl isoheptadecanoate	50.1	**	
a-Methylbenzyl methyl ether	55.3	**	
2,5-dimethyl benzenamine	55.5	**	12
2-Amino-1,4-dimethylbenzene	55.9	**	
2-Bromo-4'-methylacetophenone	56.2	*	
2,6-dimethylbenzenamine	56.4	*	
1-Ethyl-3,5-dimethylbenzene	57.7	*	
1-Isopropyl-3-methylbenzene	59.2	*	
1,3,5-Triphenylbenzene	62.9	**	
1,3-Cyclohexadiene	65.3	*	
2-Phenyl-1,2-propanediol	65.4	**	
3,3,6,6-Tetramethyl-1,4-cyclohexadiene	66.1	**	

*** certain, ** probable, * tentative

Table 4. PBDE congeners present in the calibration standard

Compound name	PBDE Number	Retention Time	Peak Number
2,2',4-Tribromodiphenyl ether	17	31.5	1
2,4,4'-Tribromodiphenyl ether	28	32.4	2
2,3',4',6-Tetrabromodiphenyl ether	71	37.2	3
2,2',4,4'-Tetrabromodiphenyl ether	47	37.9	4
2,3',4,4'-Tetrabromodiphenyl ether	66	38.7	5
2,2',4,4',6-Pentabromodiphenyl ether	100	41.8	6
2,2',4,4',5-Pentabromodiphenyl ether	99	43	7
2,2’,3,4,4’-Pentabromodiphenyl ether	85	44	8
2,2',4,4',5,6'-Hexabromodiphenyl ether	154	44.9	9
2,2',3,4,4',5'-Hexabromodiphenyl ether	138	46.9	10
2,2',3,4,4',5',6-Heptabromodiphenyl ether	183	48.3	11
2,3,3',4,4',5,6-Heptabromodiphenyl ether	190	49.7	12
Decabromodiphenyl ether	209	71.8	13

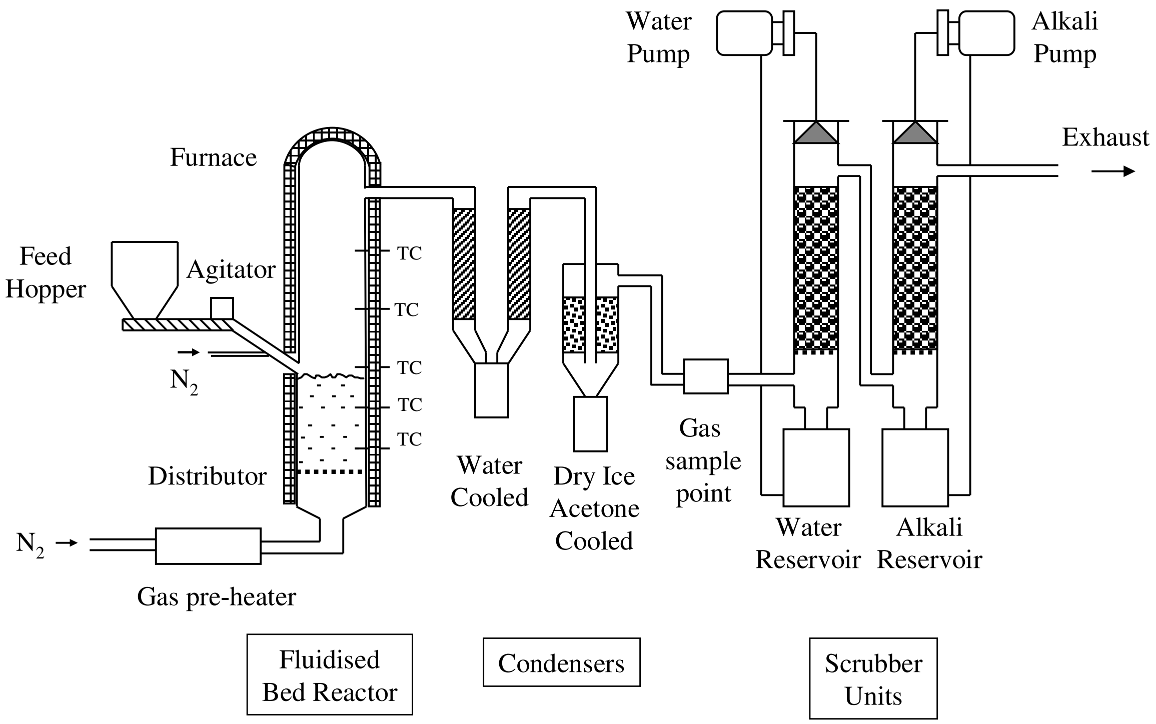

Fig. 1. Schematic diagram of the fluidised bed reactor and absorption scrubber system.

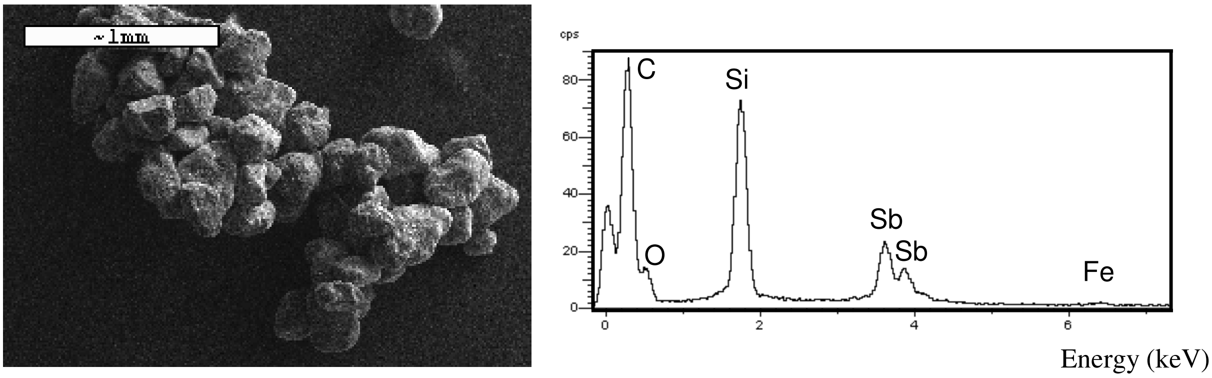

Fig. 2. Scanning electron microscopy microgram and energy dispersive X-ray analysis of the residual sand particles coated with pyrolysis char derived from the fluidised bed pyrolysis of brominated HIPS at 550 °C.

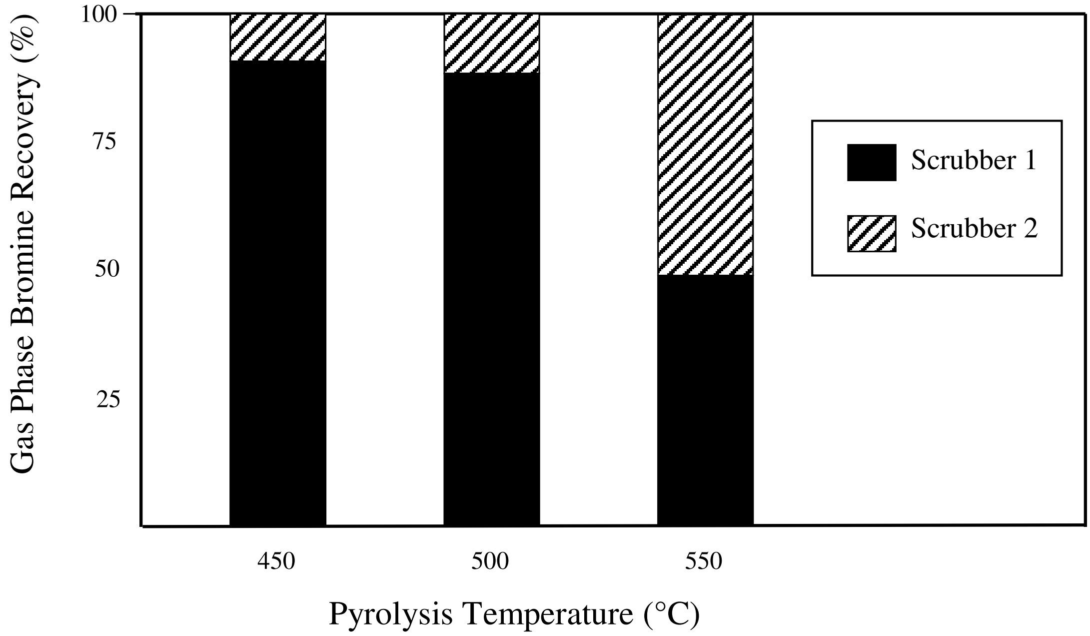

Fig. 3. Partitioning of bromine between scrubber 1 and scrubber 2 of the absorption system.

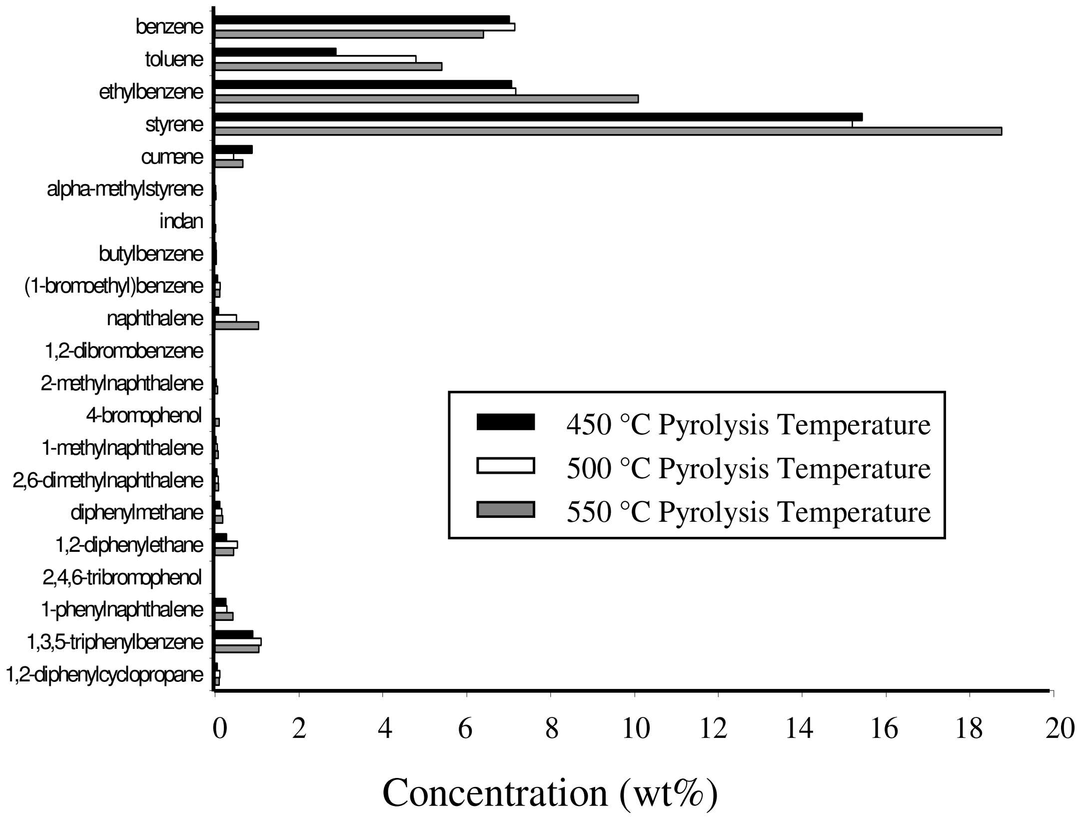

Fig. 4. Composition of the pyrolysis oils derived from the fluidised bed pyrolysis of brominated HIPS in relation to pyrolysis temperature determined by GC-FID/ECD.

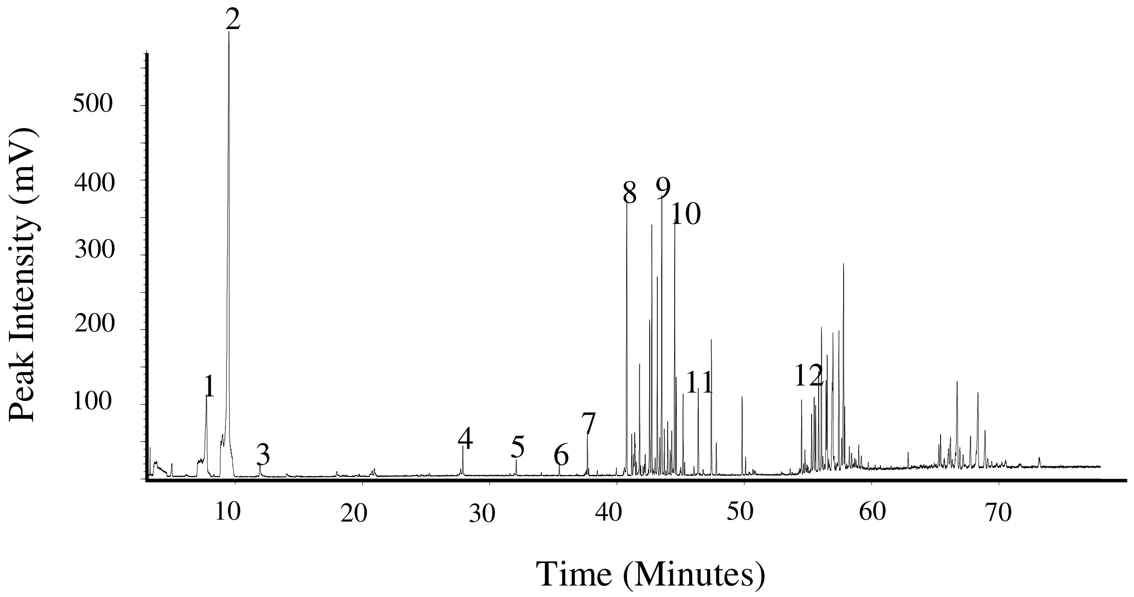

Fig. 5. Typical gas chromatography-mass spectrometry total ion chromatogram of the pyrolysis oil

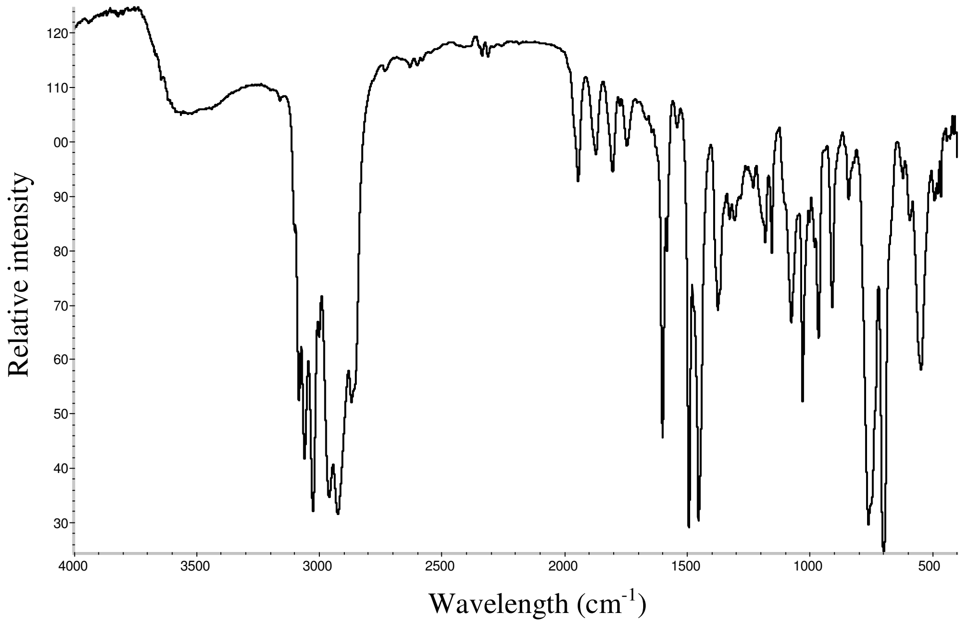

Fig. 6. A typical FT-ir spectra of oil derived from the flash pyrolysis of brominated HIPS

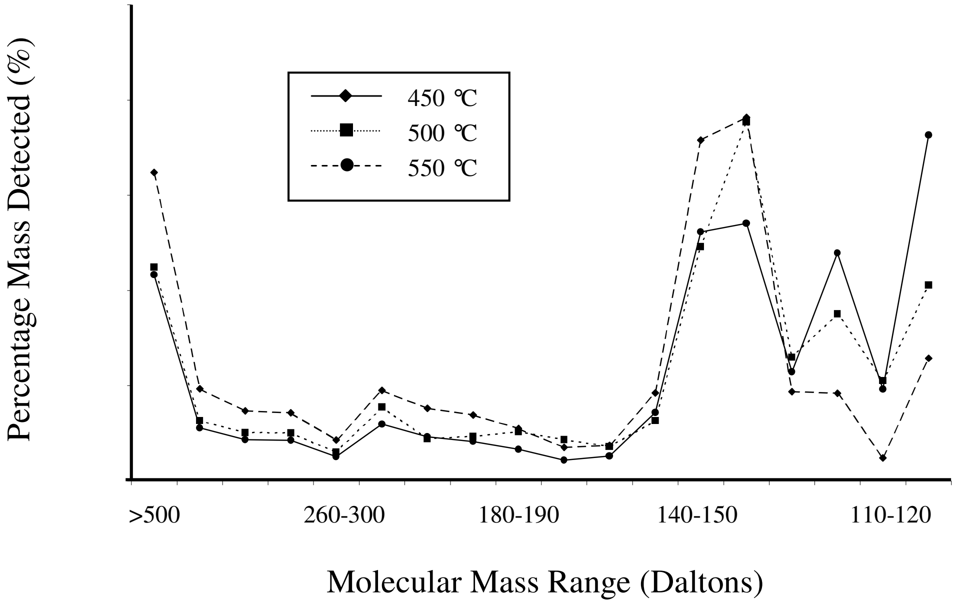

Fig. 7. Molecular mass range of the pyrolysis oils analysed by size exclusion chromatography in relation to pyrolysis temperature.

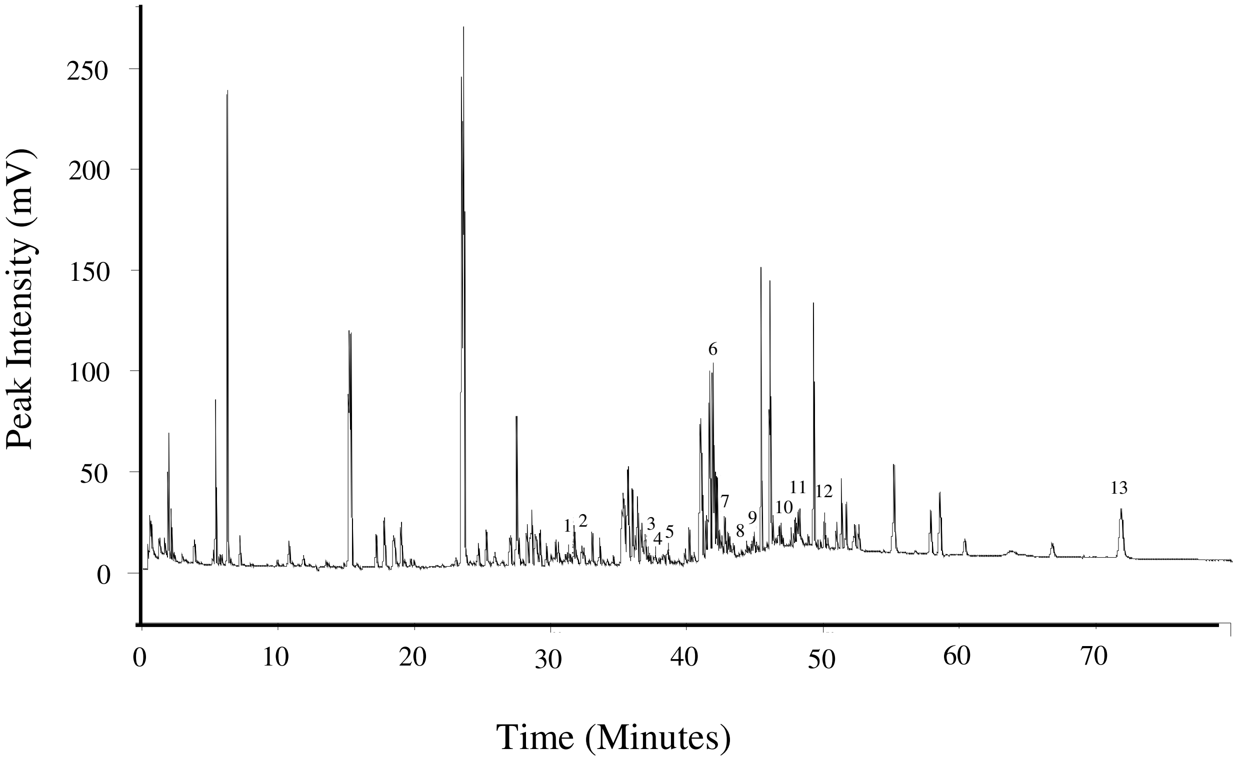

Fig. 8. Analysis of the brominated pyrolysis oil derived from the fluidised bed pyrolysis of brominated HIPS at 450 °C using gas chromatography with electron capture detection.

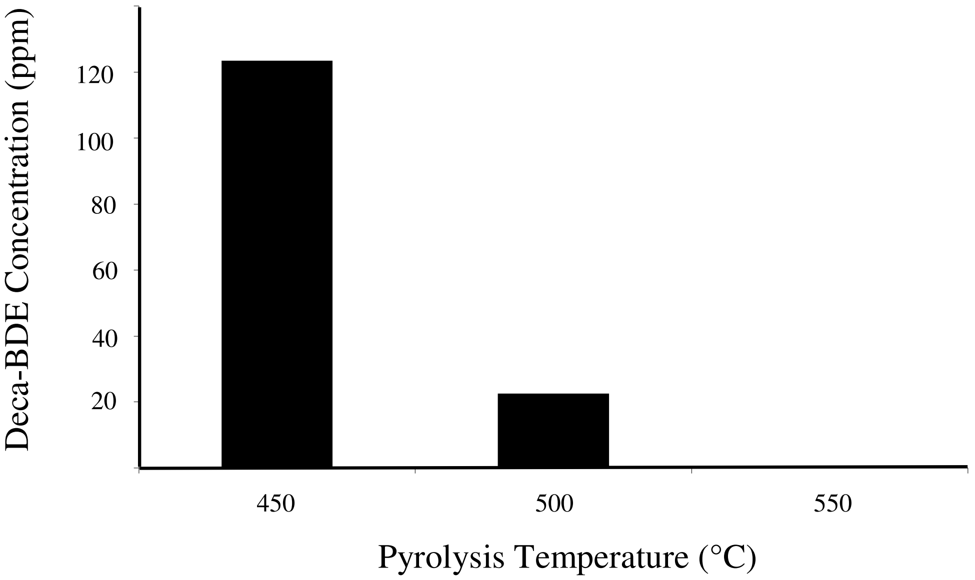

Fig. 9. Concentration of decabromodiphenyl ether (deca-BDE) in the pyrolysis oil in relation to the temperature of pyrolysis

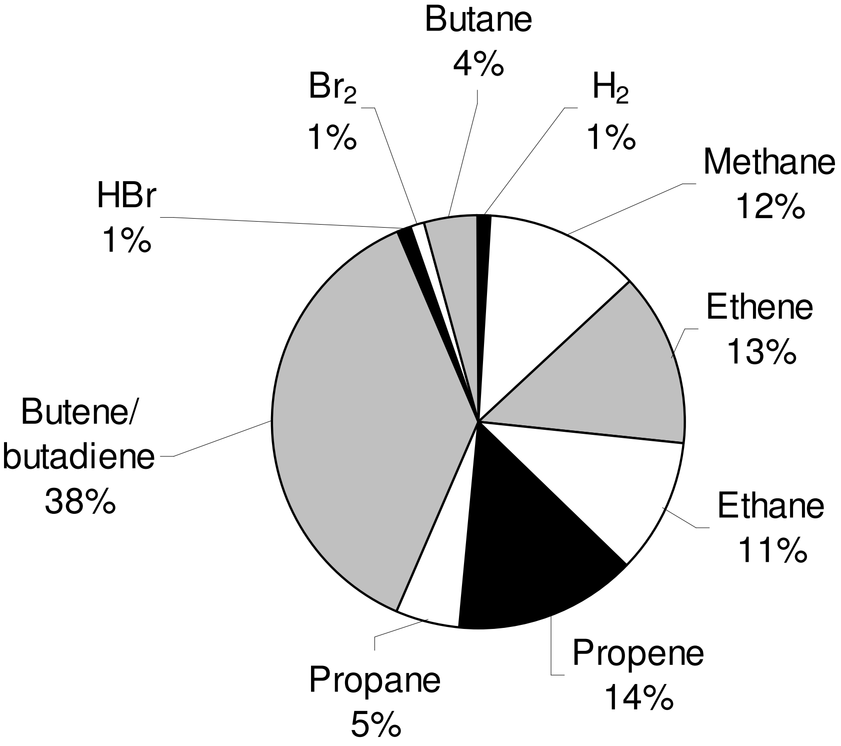

Fig. 10. The composition of the pyrolysis gases derived from the fluidised bed pyrolysis of brominated HIPS at 550 °C