REMOVAL OF ORGANOBROMINE COMPOUNDS FROM THE PYROLYSIS OILS OF FLAME RETARDED PLASTICS USING ZEOLITE CATALYSTS

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ABSTRACT

Two flame retarded plastics have been pyrolysed in the presence of two Zeolite catalysts to remove the organobromine compounds from the derived pyrolysis oil. The flame retarded plastics were, acrylonitrile – butadiene – styrene (ABS) that was flame retarded with tetrabromobisphenol A and high-impact-polystyrene (HIPS) that was flame retarded with decabromodiphenyl ether. The two catalysts investigated were Zeolite ZSM-5 and Y-Zeolite. Pyrolysis was carried out in a fixed bed reactor at a final pyrolysis temperature of 440 ºC. The pyrolysis gases were passed immediately to a fixed bed of the catalyst bed. It was found that the presence of Zeolite catalysts increased the amount of gaseous hydrocarbons produced during pyrolysis but decreased the amount of pyrolysis oil produced. In addition, significant quantities of coke were formed on the surface of the catalysts during pyrolysis. The Zeolite catalysts were found to reduce the formation of some valuable pyrolysis products such as styrene and cumene, but other products such as naphthalene were formed instead. The Zeolite catalysts, especially Y-Zeolite, were found to be very effective at removing volatile organobromine compounds. However, they were less effective at removing antimony bromide from the volatile pyrolysis products, although some antimony bromide was found on the surfaces of the spent catalysts.

Keywords: - flame retarded plastics, brominated polystyrene, brominated ABS, Zeolite, catalyst.

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1. INTRODUCTION

In recent years there has been a growing interest in using pyrolysis to process scrap plastics from waste electrical and electronic equipment (WEEE). In the European Union the disposal of WEEE is closely controlled by the European Commission's WEEE Directive, which requires that WEEE is collected separately and each type of material (e.g. plastics, metals) is separated and recycled [1]. However, the plastic fraction of WEEE is particularly problematic to recycle because it often contains brominated flame retardant (BFR) additives such as polybrominated diphenyl ethers (PBDE's) or tetrabromobisphenol A (TBBPA). Many BFRs are considered to be extremely toxic and plastics which contain BFRs need careful processing to either destroy or remove the flame retardant additives [2]. Therefore, the use of pyrolysis for processing WEEE plastics has been intensively investigated as a means of thermally degrading the toxic flame retardants and producing fuels or chemical feedstock that can be used by the petrochemical industry.

Various pyrolysis processes have been tested for processing plastics which contain BFR's including fluidised bed pyrolysis [3], two-stage pyrolysis [4], long residence time pyrolysis [5], and pyrolysis in the presence of iron and calcium based catalysts [6]. Another possible method of processing plastics which contain BFR's would be to use pyrolysis in conjunction with a Zeolite catalyst. Recently, Blazso and Czegeny [7] have investigated the destruction of TBBPA over several catalysts, including Zeolite, which proved to be among the most effective catalysts. They used pyrolysis-GC/MS to investigate the decomposition of pure TBBPA. Blazso [8] investigated the pyrolysis of brominated epoxy resin using pyrolysis-GC/MS and reported reduced concentrations of brominated compounds when Zeolite was present in the pyrolysis process. In an earlier study, Blazso et al [9] used pyrolysis-GC/MS to investigate the pyrolysis of flame retarded printed circuit boards and phthalic polyester that was flame retarded with brominated polystyrene, they reported decreased concentrations of organobromines during the pyrolysis of both plastics in the presence of Zeolites.

In addition to their potential for destroying toxic brominated flame retardants, Zeolites could also upgrade the pyrolysis products of WEEE plastics. Zeolites have been used on numerous occasions to upgrade the products of plastic pyrolysis [10, 11], with the intention of generating more pyrolysis gas and upgrading the composition of the pyrolysis oil to give more valuable components. Therefore, Zeolite catalysts could not only help efficiently destroy toxic brominated flame retardants during pyrolysis of WEEE plastics, but could also help generate more valuable and useful pyrolysis products.

There has been some initial work on the use of Zeolite catalysts to remove organobromine compounds from pyrolysis oils using pyrolysis/catalysis however, there is a further need to fully characterise the products of such systems. In this work, a fixed bed reactor has been used to investigate the pyrolysis of two flame retarded plastics. The first plastic was high impact polystyrene (HIPS) that was flame retarded with decabromodiphenyl ether (deca-BDE) and the second plastic was acrylonitrile – butadiene – styrene (ABS) co-polymer that was flame retarded with TBBPA. The volatile pyrolysis products from each plastic were passed over either Y-Zeolite or ZSM-5 Zeolite catalyst. The pyrolysis products were characterised using GC/MS, GC-FID/ECD, and FT-IR.

2. EXPERIMENTAL

2.1 Materials

HIPS that was flame retarded with deca-BDE and antimony trioxide was supplied by Atofina (UK) Ltd and the ABS that was flame retarded with TBBPA and antimony trioxide was supplied by Vamptech (Italy). The elemental composition of both the plastics are shown in table 1. The elemental analysis of the plastics was determined using a CE Instruments Flash EA 1112 elemental analyser. The system combusts the sample at 1000 °C and analyses the combustion gases of the sample to determine, carbon, hydrogen, nitrogen and sulphur composition. Oxygen is analysed separately by the instrument. The halogen content of the plastics was determined using bomb calorimetery according to EPA method 5050. The bomb was loaded with 1g of sample and a small volume of alkali solution before being charged with pure oxygen. Upon combustion of the sample, the halogens are released and are dissolved in the alkali solution. Once the bomb had cooled it was thoroughly rinsed with more alkali solution. The halogen content of the alkali solution was then determined using a Dionex DX100 ion chromatograph fitted with a Dionex AS4A column. The efficiency of the system was checked by combusting materials with known chlorine and bromine contents.

Two pure Zeolites were used in this study, Y-Zeolite with a SiO_2 / Al_2O_3 molar ratio of 80 and a surface area of 780 m^2/g and ZSM-5 Zeolite with a SiO_2 / Al_2O_3 molar ratio of 80 and a surface area of 425 m^2/g. Both the Zeolites were supplied by Zeolyst International (USA) and were used as received in the pellet form. The zeolite pellets were cylindrical and measured approximately 1mm in diameter by 5mm in length. The Zeolites were prepared by heating them up to 550 ℃ in a furnace and then cooling them in a desiccator, the cooled Zeolite was then loaded into the fixed bed reactor.

2.2 Fixed Bed Reactor

Each plastic was pyrolysed in a fixed bed reactor (FBR), the reactor measured 260mm in length by an internal diameter of 45 mm and was externally heated by a 1.5kW tube furnace (figure 1). At the start of each experiment, a crucible that contained 10g of plastic sample and 10g of activated Zeolite was placed in the reactor. The Zeolite was supported on wire gauze above the plastic samples so that when the plastic pyrolysed the volatile pyrolysis gases passed over the catalyst. The catalyst bed was at the same reaction temperature as the plastic sample.

After the sample and catalyst had been loaded, the reactor was sealed and purged with nitrogen before being heated to 440°C at a rate of 10°C min^{-1} and then held at temperature for 45 minutes. Upon pyrolysis of the plastics sample, the volatile pyrolysis products passed over the Zeolite catalyst and then exited the reactor and were collected by a train of water-cooled and dry-ice cooled condensers. Any hydrogen bromide and bromine gas was collected by a bubbler system that was loaded with an alkaline solvent, the insoluble gases were collected in a Teflon gas bag and analysed off-line. Each plastic was pyrolysed in the fixed bed reactor in the presence of either Y-Zeolite or ZSM-5 and additionally in the absence of any catalyst; each test was carried out at least twice to ensure that the results were repeatable.

The pyrolysis gases were analysed using two Varian 3380 gas chromatographs and a Dionex ion chromatograph. Hydrocarbons from C_1 to C_4 were analysed using a second Varian CP-3380 gas chromatograph with a Flame Ionisation Detector (GC/FID). The column used was 2 m long with 2 mm diameter packed with 80-100 mesh Hysesp. Nitrogen was used as the carrier gas. The temperature was programmed to start at 60 °C for 3 minutes, ramped at 10 °C min^{-1} to 100 °C, held for 3 minutes, finally ramped to 120 °C at 20 °C min^{-1} and held for 9 minutes at 120 °C. The injector was held at 150 °C while the detector temperature was 200 °C. The permanent gases were analysed by the second Varian CP-3380 gas chromatograph with two packed columns and with two thermal conductivity detectors (GC/TCD) was used for the analysis of the permanent gases. Hydrogen, carbon monoxide, methane and nitrogen were analysed on a 2 m length by 2 mm diameter column, packed with 60-80 mesh molecular sieve. Argon was used as the carrier gas. The amount of oxygen in the sample was evaluated using the GC/TCD and the result was used to calculate the amount of dilution of the sample by air, which often occurs during GC analysis of gases. Carbon dioxide was analysed on a 2 m length by 2mm diameter column with Haysep 80-100 mesh packing material. The gas chromatograph oven was held isothermally at 40 °C for the analysis; the injector oven was at 120 °C. The detector oven operated at 120 °C with filament temperature of 160 °C. The total mass of gas evolved was calculated from the measured concentrations and molecular masses of the gases rather than calculated by difference. The halogens collected by the fixed bed reactor's alkaline bubbler system were analysed using a Dionex DX100 ion chromatograph fitted with a Dionex AS4A column.

The pyrolysis oils were analysed by gas chromatography mass spectrometry (GC-MS), a gas chromatograph fitted with flame ionisation and electron capture detectors (GC-FID/ECD), and by Fourier Transform Infra-Red Spectrometry (FT-IR). The GC-MS was a CE Instruments 2000 series GC fitted with a 30m RTX-5 column. The injector temperature was 300°C and the oven was held at 40°C for 15 minutes, then ramped to 280°C at 5° C/min, and then held for 15 minutes. The mass spectrometer electron energy was 70eV and the ion source and coupling temperatures were 220°C and 300°C respectively. The GC-FID/ECD was a Varian 3380 fitted with a 30m ZB-5 column that was split so the analytes passed through both detectors simultaneously. The oven programme was the same as for the GC-MS and the injector was heated to 290ºC and the FID and ECD were heated to 300ºC and 310ºC respectively. Standard solutions were used to calibrate the GC-FID/ECD. Functional group, compositional analysis of the oils was carried out using a Nicolet Magna 560IR FT-ir spectrometer with spectral library search facility. Weighed samples of oil were thinly coated onto a potassium bromide disk. The spectrometer scanned the sample from 450 cm^{-1} to 4000 cm^{-1} wavelength and spectral peak heights normalised to the major C-H peak.

The halogen content of the oils was determined using bomb calorimetery and ion chromatography according to EPA method 5050, as described above.

3. RESULTS AND DISCUSSION

3.1 Materials balance

When Br-ABS and Br-HIPS were pyrolysed in the fixed bed reactor they decomposed to form char, oil, and gas. In addition, when a Zeolite catalyst was added to the reaction system a significant quantity of coke formed on the surface of the catalyst. The formation of coke led to a decrease in the yield of pyrolysis oil but an increase in the yield of gas.

During Br-ABS pyrolysis in the absence of a catalyst, the oil yield was 47.5 wt% but this decreased significantly to 35.4 wt% when ZSM-5 was the catalyst and 23.8 wt% when Y-Zeolite was the catalyst. At the same time, the yield of gas increased from 1.8 wt% when no catalyst was present to 4.2 and 4.4 wt% when the catalyst was ZSM-5 and Y-Zeolite respectively. Coke formation accounted for 7.5 and 22.0 wt% of the plastic feedstock during the use of ZSM-5 and Y-Zeolite respectively.

Brebu et al [12] investigated the pyrolysis of ABS in a fixed bed reactor using similar reaction conditions to those used in this work and reported that the mass balance was 7.8 wt% gas, 63.5 wt% oil, and 28.7 wt% char. In a separate piece of work, Brebu et al [13] reported that in a fixed bed reactor, Br-ABS that contained a brominated epoxy type flame retardant pyrolysed to form 5 wt% gas, 34 wt% oil, and 61 wt% residue.

In the absence of a catalyst, Br-HIPS pyrolysed to form 75.6 wt% oil. However, when ZSM-5 was present, the yield of pyrolysis oil decreased to 49.9 wt% and when Y-Zeolite was the catalyst the oil yield was just 41.2 wt%. At the same time, ZSM-5 increased the gas yield from 0.4 to 3.5 wt% and Y-Zeolite increased the gas yield even further to 6.7 wt%. The coke formed on the surface of the ZSM-5 catalyst accounted for 9.2 wt% of the plastic and the Y-Zeolite caused the formation of 21.1 wt% of coke.

Bhaskar et al [14] studied the pyrolysis Br-HIPS that was flame retarded with deca-BDE and antimony trioxide and found that the mass balance was 72 wt% oil, 4 wt% gas, and 23 wt% residue. Williams and Bagri [15] have reported that when polystyrene was pyrolysed in a fixed bed reactor, the presence of ZSM-5 reduced the mass of oil to 91.6 wt% from 96.6 wt%; Y-Zeolite reduced the mass of oil even further to 70.6 wt%. They also reported that the pyrolysis gases were increased from 0.1 wt% to 1.6 wt% by ZSM-5 and 4.1 wt% by Y-Zeolite and that 9.2 wt% and 23.9 wt% coke was found on the surface of ZSM-5 and Y-Zeolite respectively.

3.2 Pyrolysis gases

When Br-ABS copolymer was pyrolysed on its own, significant concentrations of $C_1 - C_4$ gases were produced as well as some hydrogen. In general, alkanes were more abundant than alkenes, with the exception of butane which was outnumbered by butene/butadiene, presumably because of the presence of butadiene monomer from the ABS. When a catalyst was added to the reaction system, some significant changes were noted in the type and quantity of pyrolysis gas produced (table 2). The presence of Y-Zeolite doubled the quantity of hydrogen produced by ABS pyrolysis, although ZSM-5 had no effect. The presence of both catalysts caused an increase in the production of all the $C_1 - C_4$ gases during Br-ABS pyrolysis. It is interesting that over the range $C_1 - C_3$, Y-Zeolite was more effective at generating alkane gases and ZSM-5 was more effective at producing alkene gases. The situation was reversed for C_4, however, with Y-Zeolite being more effective at generating butene/butadiene and ZSM-5 being more effective at generating butane. During Br-ABS pyrolysis, the catalysts had the most impact on the production of C_3 gases, ZSM-5 increased propene production by over 1100% and Y-Zeolite increased propane production by 720%. Overall, ZSM-5 increased gas production by 135% and Y-Zeolite increased gas production by 145% during Br-ABS pyrolysis.

The pyrolysis of Br-HIPS in the absence of a catalyst resulted in much lower gas production than the pyrolysis of Br-ABS. However, when a Zeolite catalyst was used the amount of pyrolysis gas generated increased dramatically. During Br-HIPS pyrolysis the use of ZSM-5 led to a 1500% and Y-Zeolite to an 1100% increase in the amount of hydrogen generated. By far the most dramatic increase was in the amount of propane generated, with Y-Zeolite increasing the propane generation by 7750% and ZSM-5 by 3300%. Other large increases were seen for ethane, which increased by 1600% in the presence of ZSM-5 and butane/butadiene, which increased by 2500% in the presence of Y-Zeolite. Overall, Y-Zeolite increased gas production by 1650% and ZSM-5 by 800% during the pyrolysis of Br-HIPS.

Williams and Bagri [15] found that when they pyrolysed polystyrene in a fixed bed reactor with ZSM-5, ethene and propene were the major gaseous products where as Y-Zeolite led to an even distribution of C_1 to C_4 products. In this work, propane and ethane were the most abundant gaseous products when Br-HIPS was pyrolysed in the presence of ZSM-5 and butene/butadiene and ethane when Y-Zeolite was the catalyst.

Although the presence of a ZSM-5 or Y-Zeolite catalyst caused an increase in the amount of gas generated during Br-ABS and Br-HIPS pyrolysis, the actual amount of gas was still quite a small percentage of the total decomposition products. For example, propane production from Br-HIPS in the presence of Y-Zeolite was the largest of any $C_1 - C_4$ component, but still only accounted for 2.3% of the plastic feedstock. Therefore, while the use of Zeolite catalysts

certainly increases gas production during Br-ABS and Br-HIPS pyrolysis, it is unlikely that Zeolites can be used to generate large concentrations of $C_1 - C_4$ gases in a fixed bed reactor.

3.3 Pyrolysis oils

The pyrolysis oils where characterised by GC-MS, GC-FID, and FT-IR. The GC-MS was used to identify the components that were present in the oil and the GC-FID was used to quantify these components. The FT-IR was used to further investigate the functional groups that were present in the oil. The GC-FID results are presented in table 2 as mg / $g_{plastic}$ because this is the most accurate way of representing the changes in the pyrolysis products when the different catalysts are used. If the results were presented as the percentage composition of the pyrolysis oil they could be misleading because the amount of pyrolysis oil produced altered depending on which catalyst was used. For example, the mass of ethylbenzene produced during pyrolysis could remain the same no matter which catalyst is used, but its concentration in the pyrolysis oil might increase or decrease because the total mass of pyrolysis oil produced increases or decreases. It should also be noted that our experimental system prohibits us from analysing C_5 and C_6 compounds effectively and therefore they are excluded from this analysis. An example of the GC-FID chromatograms is shown in figure 2.

When Br-ABS was pyrolysed in the absence of a catalyst the main pyrolysis products (table 2) were toluene, ethylbenzene, styrene, cumene, alpha-methylstyrene, phenol, 4-isopropylphenol, benzenebutanenitrile, and 1,3-diphenylpropane. Phenol and 4-isopropylphenol were present due to the decomposition of the TBBPA flame retardant and benzenebutanenitrile is a pyrolysis product of styrene-acrylonitrile, the other major products are all common pyrolysis products of styrene. The major compounds found in the pyrolysis oil of Br-ABS are very similar to those reported in the literature [13, 16].

When the pyrolysis products of Br-ABS were passed over ZSM-5 or Y-Zeolite, the amount of toluene and ethylbenzene produced remained about the same, although Y-Zeolite did decrease the amount of toluene slightly, from 71.1 to 51.4 mg / $g_{plastic}$. However, the amounts of the other major products from the pyrolysis of the styrene portion of Br-ABS (styrene, cumene, alpha-methylstyrene, and 1,3-diphenylpropane) were all dramatically reduced in the presence of Zeolite catalysts, with Y-Zeolite being the most active. For example, 28.2 mg / $g_{plastic}$ of alpha-methylstyrene was produced during Br-ABS pyrolysis in the absence of a catalyst, but only 9.6 mg / $g_{plastic}$ was produced when ZSM-5 was present and Y-Zeolite reduced this further to just 0.3 mg / $g_{plastic}$.

As well as altering the amount of common styrene products produced during the pyrolysis of Br-ABS, the Zeolite catalysts also affected the amount of products produced from the pyrolysis of the TBBPA flame retardant. ZSM-5 and Y-Zeolite both reduced the amounts of phenol, 4-isopropylphenol, 2,4-dibromophenol, bisphenol A, and TBBPA produced, with Y-Zeolite being the most active catalyst in all cases. In fact, both the Zeolite catalysts removed 2,4-dibromophenol and bisphenol A completely and Y-Zeolite also completely stopped the production of TBBPA. Both Zeolite catalysts were also very effective at removing benzenebutanenitrile from the pyrolysis products, with ZSM-5 reducing the quantity produced from 47.0 to 12.4 mg / $g_{plastic}$ and Y-Zeolite reducing the amount even further to 1.6 mg / $g_{plastic}$. The presence of ZSM-5 and Y-Zeolite also completely stopped the production of 1-(bromoethyl)benzene, which is a common product of brominated styrene-based polymers.

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The presence of Zeolite catalysts also increased the formation of some compounds during Br-ABS pyrolysis, most notably substituted benzenes and naphthalenes. The presence of ZSM-5 and Y-Zeolite led to increased formation of p-xylene, o-xylene, 4-ethyltoluene, 2-ethyltoluene, and diethylbenzenes, with Y-Zeolite being the most active catalyst in all cases. The amount of naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene produced during the pyrolysis of Br-ABS all increased when a Zeolite catalyst was present, with Y-Zeolite again being the most active catalyst. The most dramatic increase was for naphthalene, which increased from 0.7 to 21.8 mg / $g_{plastic}$ when the pyrolysis products were passed over Y-Zeolite. Various ethyl and dimethyl naphthalenes were also quantified and it was found that their formation was increased in the presence of a Zeolite catalyst, with the exception of 1,2-dimethylnaphthalene, which was produced in lower amounts when the Zeolite catalysts were present. The production of 1-phenylnaphthalene also decreased when Zeolite catalysts were present during the pyrolysis of Br-ABS.

FT-IR analysis of the Br-ABS pyrolysis oils (figure 3) showed a large O-H stretch at 3400 cm^{-1} in all of the oils which presumably related to the presence of phenols. The proportional size of the O-H stretch decreased when the catalysts were used to generate the oils, confirming the GC-FID analysis which suggested that the generation of phenols decreased when Zeolite catalysts were used. In addition, FT-IR analysis of the Br-ABS pyrolysis oils showed stretches at 1264 and 831 cm^{-1}, which can be related to 4-monosubstituted phenols, presumably in this case 4-isopropylphenol. The stretches relating to 4-isopropylphenol decreased in size when the Zeolite catalysts were present, confirming the GC-FID analysis which suggested that the Zeolites reduced the production of 4-isopropylphenol.

FT-IR analysis of the Br-ABS pyrolysis oils (figure 3) also confirmed the reduction in benzenebutanenitrile production when the pyrolysis products were passed over Zeolite catalysts. The FT-IR band at 2249 cm^{-1} suggests the presence of aliphatic nitrile groups and there is an additional nitrile band at 1520 cm^{-1}, both of these bands reduced in size when the catalysts were used. When the catalyst was used to generate the Br-ABS pyrolysis oils, there was a large FT-IR stretch at 1400 cm^{-1} which can be associated with naphthalenes, it was not present when the catalysts were not used and reflects the increased naphthalene production in the presence of the Zeolite catalysts noted by the GC-FID analysis of the pyrolysis oils.

FT-IR analysis of the Br-ABS oils (figure 3) showed three stretches at 3027, 3061, and 3083 cm^{-1} relating to C-H bonds in aromatic rings, the overtone and combination bands for aromatic rings are also clearly visible between 1660 and 2000 cm^{-1}. The Br-ABS oil produced in the absence of a catalyst showed C-H out-of-plane deformation bands relating to mono-substituted benzene derivatives at 698 and 752 cm^{-1}, which reflects the production of toluene, styrene, cumene, and ethylbenzene. The Br-ABS oil produced in the presence of ZSM-5 and Y-Zeolite gave much more complex C-H out-of-plane deformation bands which could not be properly identified, this reflects the more complex nature of these oils which GC-FID analysis has shown contained large amounts of various disubstituted benzenes. FT-IR analysis of all the Br-ABS pyrolysis oils confirmed the presence of methyl and methylene groups (2869, 2928, and 2961 cm^{-1}).

The results of the GC-FID analysis of the Br-HIPS pyrolysis oils are shown in table 2. In the absence of a catalyst, the most abundant pyrolysis products were toluene, ethylbenzene, styrene, cumene, and 1,3-diphenylpropane, which has previously been reported in the literature [3, 17]. It is interesting to note that alpha-methylstyrene is absent, even though it was present when Br-ABS was pyrolysed, which means that the formation of alpha-

methylstyrene during Br-ABS pyrolysis must be caused by the presence of either acrylonitrile, butadiene, or TBBPA.

ZSM-5 had very little impact on the amount of toluene produced during Br-HIPS pyrolysis but it did significantly reduce the amount of ethylbenzene produced, from 280.1 to 94.2 mg / $g_{plastic}$. Y-Zeolite slightly increased the amount of toluene and slightly decreased the amount of ethylbenzene produced during Br-HIPS pyrolysis. Both Zeolite catalysts significantly reduced the amounts of styrene, cumene, and 1,3-diphenylpropane produced during Br-HIPS pyrolysis. For example, styrene production in the absence of a catalyst was 127.8 mg / $g_{plastic}$ but this was reduced to just 3.3 mg / $g_{plastic}$ by ZSM-5 and 2.3 mg / $g_{plastic}$ by Y-Zeolite. Interestingly, the presence of ZSM-5 led to the generation of small amounts (2.1 mg / $g_{plastic}$) of alpha-methylstyrene. Puente and Sedran [18] investigated the pyrolysis of polystyrene in the presence of ZSM-5 and reported reduced concentrations of styrene, although the reductions were not as significant as in this work. Williams et al [19] also reported that ZSM-5 reduced the formation of styrene during the pyrolysis of polystyrene.

The presence of Zeolite catalysts during Br-HIPS pyrolysis led to the formation of xylenes, ethyltoluenes, and diethylbenzenes, with Y-Zeolite being the most active catalyst in all cases. Interestingly, no meta-xylene or meta-ethyltoluene was produced and para-xylene and para-ethyltoluene were the most abundant xylene and ethyltoluene isomers. The amount of propylbenzene increased when the Zeolites were present but the production of allylbenzene was stopped completely, as was 1-(bromoethyl)benzene. Indan was produced in the presence of a catalyst during Br-HIPS pyrolysis, with ZSM-5 being the most active catalyst.

When Br-HIPS was pyrolysed in the absence of a catalyst, only very low yields of naphthalene, 2-methylnaphthalene, and 1-methylnaphthalene were produced, however, the presence of a Zeolite catalyst increased their yield significantly. For example, naphthalene increased from 0.3 to 44.4 mg / $g_{plastic}$ when ZSM-5 was the catalyst and 10.9 mg / $g_{plastic}$ when Y-Zeolite was the catalyst. ZSM-5 was the more active of the two catalysts in the case of naphthalene and methylnaphthalenes. ZSM-5 was also the more effective at catalysing the production of ethylnaphthalenes and dimethylnaphthalenes, the most abundant of which was 1,7-dimethylnaphthalene (10.7 mg / $g_{plastic}$). The production of 1-phenylnaphthalene and 1,3,5-triphenylbenzene was reduced by the presence of the Zeolite catalyst, with Y-Zeolite being more active than ZSM-5.

Williams et al [19] investigated the concentration of a large number of polycyclic aromatic hydrocarbons (PAH) in the pyrolysis oil of polystyrene that had been pyrolysed in the presence of ZSM-5. They reported very high concentrations of naphthalene (18.9 wt% in the oil) and also found significant quantities of 2-methylnaphthalene, 1-methylnaphthalene, ethylnaphthalenes, and dimethylnaphthalenes, as well as a number of PAH that were not investigated in this work. Williams et al [19] proposed that the formation of PAH in polystyrene pyrolysis oil was due to the Diels-Alder reaction, a reaction mechanism that was also proposed by Koo et al [20].

FT-IR analysis of the Br-HIPS oils (figure 4) shows that there were both aromatic (3082, 3061, and 3026 cm^{-1}) and aliphatic (2963, 2928, and 2869 cm^{-1}) components to the pyrolysis oil. However, there was no band at 1400 cm^{-1} relating to naphthalenes when either of the catalysts was used during Br-HIPS pyrolysis, despite a wide variety of naphthalenes being identified by the GC-MS and GC-FID.

Analysis of the C-H out-of-plane deformations in the FT-IR spectra of the Br-HIPS oils showed that when no catalyst was present only monosubstituted benzene derivatives were present, this corroborates the GC-FID results. However, when ZSM-5 or Y-Zeolite was used as a catalyst, a band was present at 813 cm^{-1}, which might indicate the presence of para-substituted benzene derivatives, this would corroborate the GC-FID analysis that found significant quantities of para-xylene and 4-ethyltoluene present in the pyrolysis oils. Comparison of the FT-IR spectra also showed that when a catalyst was used the C-H deformation bands at 991 and 909 cm^{-1} were much weaker than when no catalyst was used, these bands can be related to vinyl groups and reflect the decreased production of styrene and cumene when a Zeolite catalyst is used during Br-HIPS pyrolysis.

3.4 Bromine content of the pyrolysis oil

The main aim of using the Zeolite catalysts was to destroy the organobromine compounds and remove the bromine from the pyrolysis oils and gases. The bromine content of the pyrolysis gases was almost zero, regardless of the presence or absence of either Zeolite catalyst. However, the bromine content of the pyrolysis oils was significant. The total bromine in the pyrolysis oils was measured using a bomb calorimeter and an ion chromatograph (EPA 5050) and the organobromine content of the oils was investigated using a GC-ECD that only responds to halogenated compounds, in this case brominated compounds.

The total bromine content of the pyrolysis oils is presented in table 3 where it can be seen that when no catalyst was used the Br-ABS and Br-HIPS pyrolysis oil contained 2.7 wt% and 5.7 wt% bromine respectively. It has been reported in the literature that Br-ABS pyrolyses to form an oil that contains 0.71 wt% bromine [21] while Br-HIPS pyrolyses to form an oil that contains 11.5 wt% bromine [14], although it should be noted that the bromine content of pyrolysis oils also depends on the reaction conditions during pyrolysis.

When Br-ABS was pyrolysed in the presence of ZSM-5, the bromine concentration in the pyrolysis oil remained the same, but when Y-Zeolite was the catalyst the bromine concentration in the oil increased to 3.6 wt%. The increased concentration of bromine in the pyrolysis oil when Y-Zeolite was the catalyst was caused by a decrease in the yield of oil rather than an increase in the amount of brominated compounds in the oil. The evidence for this is presented in table 3, where it is shown that the mass of bromine in the pyrolysis oil per gram of plastic feedstock decreases as ZSM-5 or Y-Zeolite catalysts are used during the pyrolysis of Br-ABS. Therefore, it can be concluded that Zeolite catalysts were removing volatile brominated compounds from the pyrolysis products of Br-ABS and that Y-Zeolite was more active in this respect than ZSM-5.

The effect of Zeolite catalysts on the volatile brominated compounds produced by Br-HIPS pyrolysis was even more significant than for Br-ABS. Again, Y-Zeolite was the most active catalyst but ZSM-5 also significantly reduced the bromine content of Br-HIPS pyrolysis oil (table 3). The mass of bromine found in the pyrolysis oil of Br-HIPS fell dramatically from 43.1 to 17.5 and 3.3 mg / g$_{plastic}$ when ZSM-5 and Y-Zeolite were the catalysts respectively. When no catalyst was used during Br-HIPS pyrolysis, 60.7 wt% of the bromine in the plastic feedstock was contained in the pyrolysis oil, however, when Y-Zeolite was the catalyst this figure fell to 4.6%. It can therefore be concluded that the Zeolite catalysts were removing the brominated compounds from the Br-HIPS pyrolysis oils and that the relatively high bromine content of the pyrolysis oils when the catalysts were present is due to the reduced volume of oil.

It is well known that the pyrolysis oil of plastics which contain antimony trioxide as well as brominated flame contains both organobromine compounds and antimony bromide [3, 14, 16]. The results presented in table 3 refer to the total bromine content of the pyrolysis oil and to investigate the effect of Zeolite catalysts on the organobromines a GC-ECD was used.

The results of the GC-ECD analysis of the Br-ABS pyrolysis oils are presented in figure 5, each chromatogram was adjusted for the concentration of pyrolysis oil in the GC solvent so the results can be compared with each other. It can be seen in figure 5 that when Br-ABS is pyrolysed in the absence of a catalyst, the oil contains some organobromines, including 2,4-dibromophenol and 2,6-dibromophenol. However, when ZSM-5 catalyst is used during the pyrolysis process the number and concentration of organobromines decreases and when Y-Zeolite catalyst is used virtually no organobromines are present in the pyrolysis oil at all. This reinforces the GC-FID results which showed that 2,4-dibromophenol and TBBPA were removed by both Zeolite catalysts.

Similarly, figure 6 shows the organobromines present in the pyrolysis oil of Br-HIPS, where the effect of the Zeolites was even more significant than for Br-ABS. Figure 6 shows that when Br-HIPS was pyrolysed without a catalyst the pyrolysis oil contained a large number of organobromines, these are some of the 209 congeners of PBDE's which form during the pyrolysis of deca-BDE [3]. When the Br-HIPS pyrolysis products were passed over ZSM-5 catalyst the majority of the organobromine compounds were still present in the pyrolysis oil. However, when Y-Zeolite was the catalyst, virtually all the organobromine compounds were removed from the pyrolysis oil (figure 6).

Despite Y-Zeolite's effectiveness at removing organobromines from Br-ABS and Br-HIPS pyrolysis products, there was still a high concentration of bromine in the pyrolysis oil (table 3). It must therefore be concluded that Y-Zeolite was not completely effective at removing antimony bromide from the volatile pyrolysis products, although some antimony bromide was captured by the Zeolites. Figure 7 shows an EDX spectrum of ZSM-5 after it had been exposed to Br-ABS pyrolysis products and it is clear that both antimony and bromine have been captured by the catalyst. The antimony on the surface of the catalyst must be due to the presence of antimony bromide because antimony trioxide, the compound which was present in the plastic feedstock, is not volatile at the temperatures used in this work.

4. CONCLUSIONS

In this work we have shown that Zeolite catalysts (Y-Zeolite and ZSM-5) can be used to remove brominated compounds from the volatile pyrolysis products of Br-ABS and Br-HIPS. Y-Zeolite was found to be capable of removing all of the organobromine pyrolysis products of TBBPA and deca-BDE. However, the use of Zeolites can have a detrimental effect on the value of the pyrolysis products. The use of both Zeolites, but especially Y-Zeolite, led to a reduction in the mass of oil produced during pyrolysis due to coke formation on the surface of the catalysts. The Zeolite catalysts also reduced the amount of valuable chemicals such as styrene that were produced during pyrolysis, although other valuable chemicals such as naphthalene were produced in greater quantities as well as increased gas yields. Therefore, the ability of Zeolites to remove brominated compounds from the pyrolysis products must be balanced with their tendency to reduce the quantities of valuable pyrolysis products. The use of Zeolite catalysts during the pyrolysis of flame retarded plastics would also raise questions about the most appropriate way to process the spent catalyst.

Y-Zeolite was the more effective of the two Zeolites tested in this work, especially when deca-BDE was the flame retardant. However, when Y-Zeolite was used the yields of valuable products such as styrene tended to be lower than when ZSM-5 was the catalyst. Neither Y-Zeolite nor ZSM-5 was able to completely capture the antimony bromide from the volatile pyrolysis products, although this might change if increased catalyst to plastic ratios were employed. In addition, an investigation into the effectiveness of the zeolite catalysts after they have been reactivated will also be required if the technique described in this paper is to be used to process brominated plastics on a commercial scale.

ACKNOWLEDGEMENTS

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Table 1 Elemental composition of the plastic samples

	ABS	HIPS
C	72.6	80.2
H	6.8	7.2
N	3.3	0.2
O	3.2	0.8
Br	10.9	7.1
Sb	3.2	4.6

Table 2 **The volatile pyrolysis products of Br-ABS and Br-HIPS in the presence of ZSM-5 and Y-Zeolite and also in the absence of a catalyst**

mg / g$_{plastic}$	ABS only	ABS + ZSM-5	ABS + Y-Zeolite	HIPS only	HIPS + ZSM-5	HIPS + Y-Zeolite
H$_2$	1.0	0.9	2.1	0.1	2.1	1.6
Methane	2.6	3.5	4.6	0.7	1.7	4.2
Ethene	1.2	3.8	1.9	0.4	4.9	4.0
Ethane	2.1	2.9	3.8	0.4	6.9	5.8
Propene	0.8	9.5	3.7	0.3	3.8	3.3
Propane	1.1	5.8	9.2	0.3	10.0	23.3
Butene / butadiene	4.9	7.2	13.8	0.8	2.6	19.5
Butane	1.0	4.3	2.3	0.4	2.8	3.5
toluene	71.1	74.7	51.4	124.7	122.0	157.7
ethylbenzene	115.0	112.9	112.8	280.1	94.2	211.0
m-xylene	nd	nd	nd	nd	nd	nd
p-xylene	0.1	3.5	5.6	nd	11.9	19.0
styrene	36.2	10.7	1.3	127.8	3.3	2.3
o-xylene	nd	0.9	2.1	nd	3.8	6.4
cumene	37.4	3.8	5.8	59.3	1.7	8.6
allylbenzene	nd	nd	nd	0.6	nd	nd
propylbenzene	nd	1.6	3.0	1.0	2.9	3.4
3-ethyltoluene	nd	nd	nd	nd	nd	nd
4-ethyltoluene	nd	3.0	6.2	nd	10.3	15.7
2-ethyltoluene	nd	nd	1.3	nd	1.6	2.9
alpha-methylstyrene	28.2	9.6	0.3	nd	2.1	nd
phenol	39.9	27.9	10.4	nd	nd	nd
indan	nd	2.6	3.8	nd	17.0	7.3
1,3-diethylbenzene	nd	1.1	1.6	nd	4.6	4.6
1,4-diethylbenzene	nd	0.8	1.2	nd	2.2	2.3
1,2-diethylbenzene	nd	nd	0.4	nd	0.7	1.1
1-(bromoethyl)benzene	0.1	nd	nd	0.2	nd	nd
naphthalene	0.7	7.4	21.8	0.3	44.4	10.9
4-isopropylphenol	41.5	0.5	0.1	nd	nd	nd
2-methylnaphthalene	0.6	5.3	10.4	0.3	33.4	5.9
1-methylnaphthalene	0.8	1.0	4.2	0.4	8.9	2.4
benzenebutanenitrile	47.0	12.4	1.6	nd	nd	nd
2,4-dibromophenol	0.4	nd	nd	nd	nd	nd
2-ethylnaphthalene	0.1	1.5	1.2	nd	8.6	0.9
1-ethylnaphthalene	nd	0.1	0.4	nd	2.2	0.3
2,6-dimethylnaphthalene	nd	0.6	1.2	nd	4.4	0.8
1,7-dimethylnaphthalene	1.3	1.5	4.4	nd	10.7	2.5
1,4-dimethylnaphthalene	0.2	0.5	0.5	0.7	1.3	nd
1,2-dimethylnaphthalene	0.5	0.1	0.2	nd	0.4	nd
1,3-diphenylpropane	17.6	11.5	0.8	74.2	6.8	1.5
1-phenylnaphthalene	0.7	0.3	0.1	6.8	3.0	0.2
Bisphenol A	0.3	nd	nd	nd	nd	nd
1,3,5-triphenylbenzene	nd	nd	0.1	2.4	1.4	0.4
TBBPA	0.2	0.1	nd	nd	nd	nd

Table 3 The bromine concentration in the pyrolysis oils and the mass and yield of bromine found in each pyrolysis oil

	Br concentration in the oil (%)	Mass of Br in the oil (mg/g$_{plastic}$)	Yield of bromine in the oil (%)
ABS only	2.7	12.8	11.8
ABS + ZSM-5	2.6	9.2	8.4
ABS + Y-Zeolite	3.6	8.6	7.9
HIPS only	5.7	43.1	60.7
HIPS + ZSM-5	3.5	17.5	24.6
HIPS + Y-Zeolite	0.8	3.3	4.6
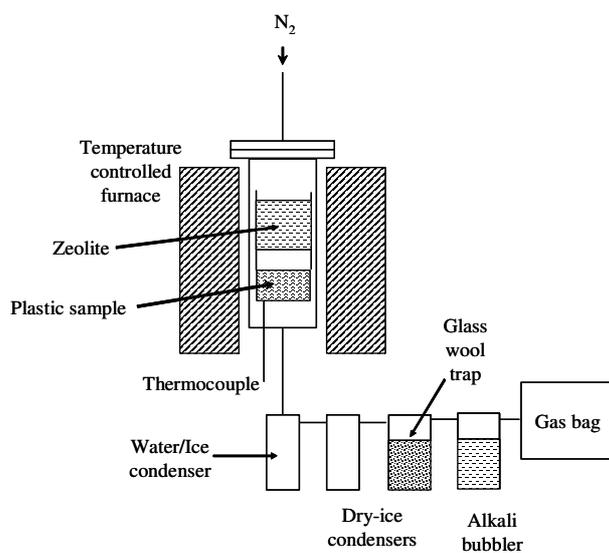
Figure 1. Schematic diagram of the fixed bed reactor
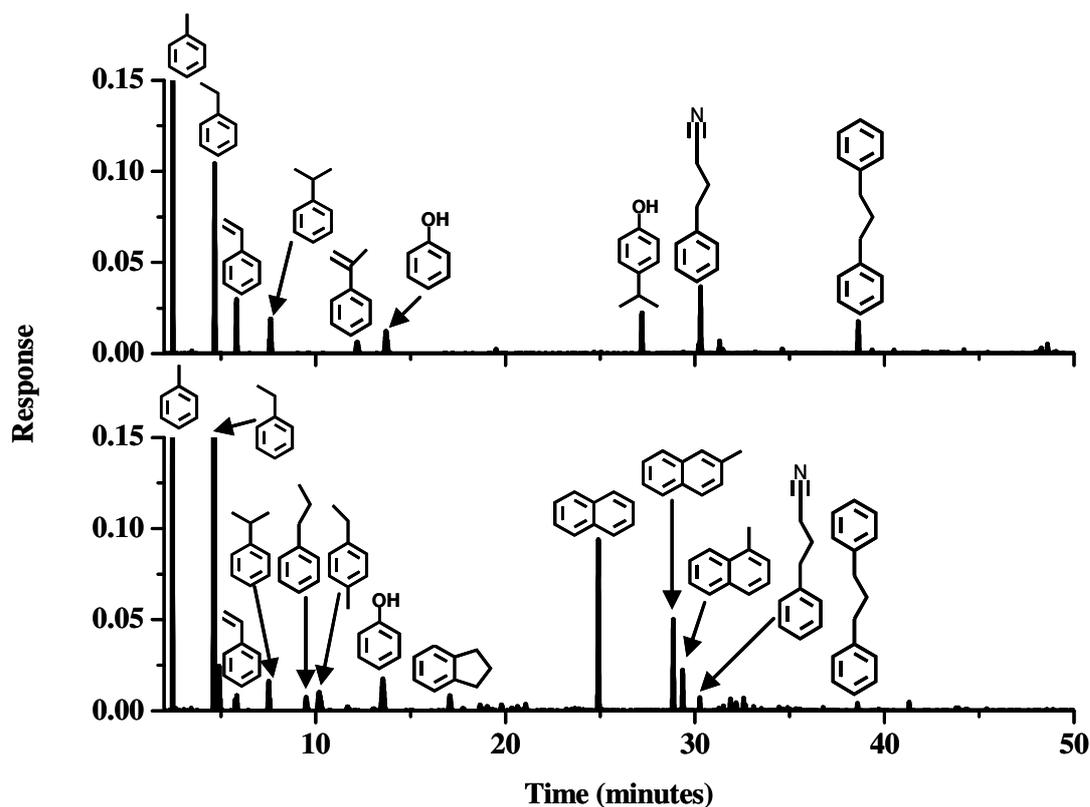
Figure 2. GC-FID chromatograms of the oil produced by Br-ABS pyrolysis without a catalyst (top) and with a Y-Zeolite catalyst (bottom).
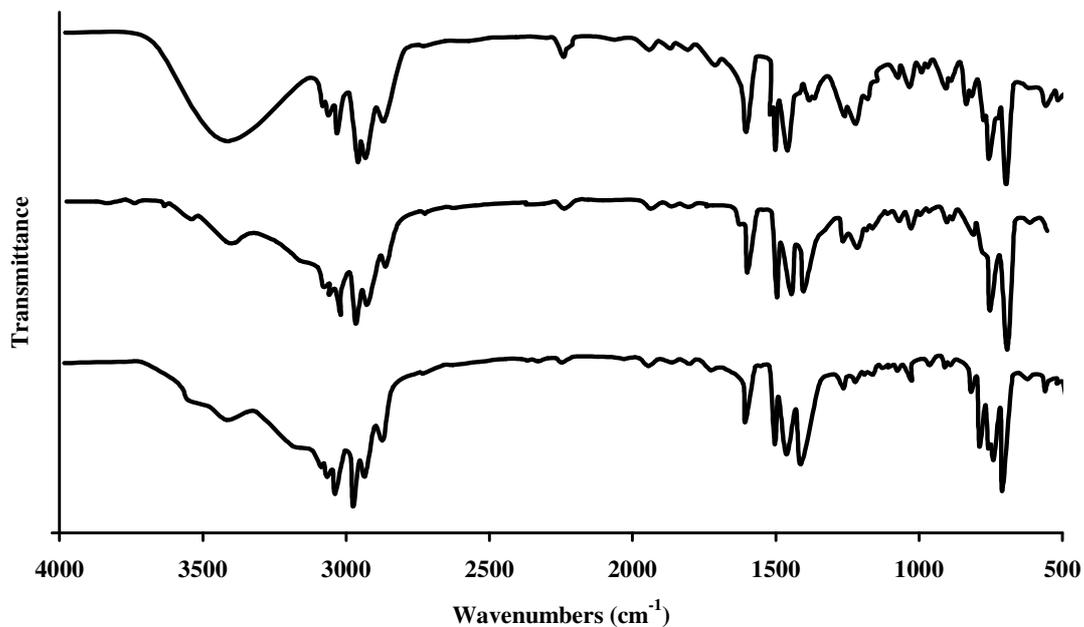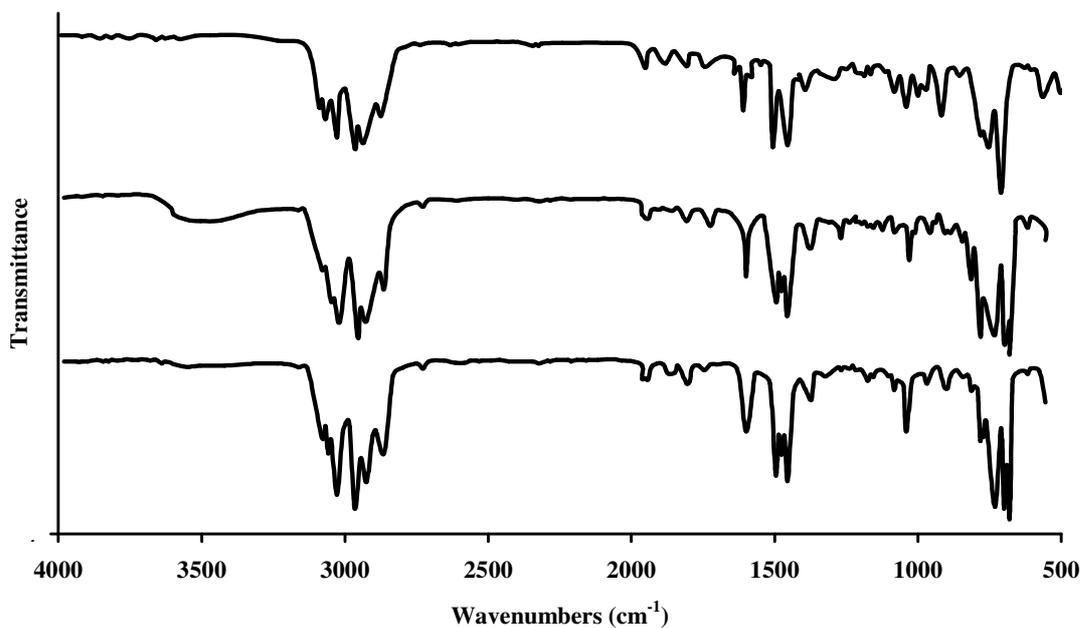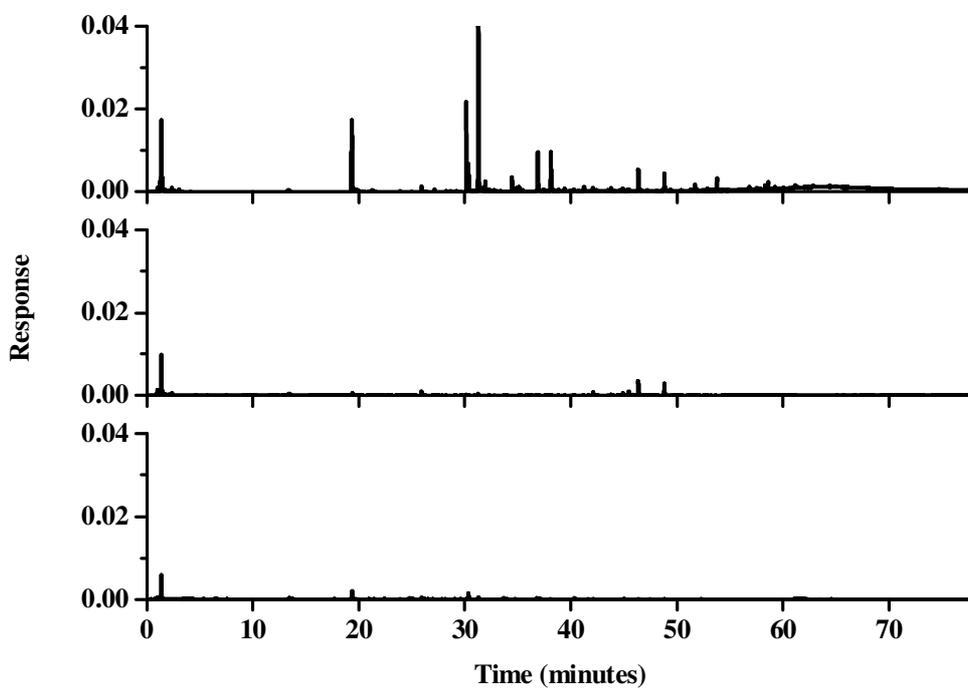

Figure 3. FT-ir spectra of the oil resulting from the pyrolysis of Br-ABS without a catalyst (top), with ZSM-5 (middle), and with Y-Zeolite (bottom).

Figure 4. FT-IR spectra of the oil resulting from the pyrolysis of Br-HIPS without a catalyst (top), with ZSM-5 (middle), and with Y-Zeolite (bottom).

Figure 5. GC-ECD chromatograms of the oil produced by the pyrolysis of Br-ABS without a catalyst (top), with ZSM-5 (middle), and with Y-Zeolite (bottom).
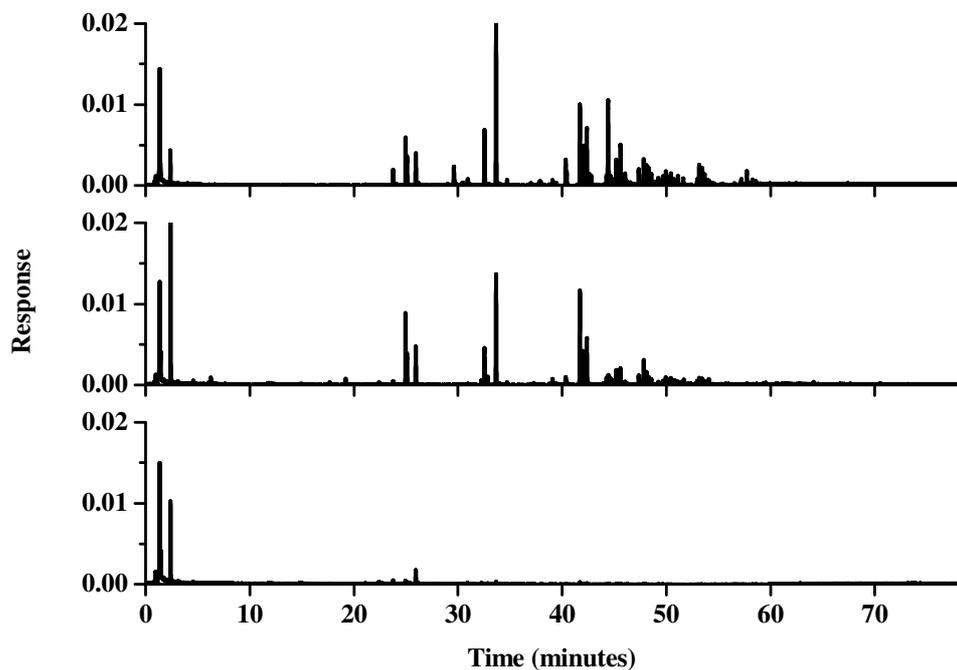
Figure 6. GC-ECD chromatograms of the oil produced by the pyrolysis of Br-HIPS without a catalyst (top), with ZSM-5 (middle), and with Y-Zeolite (bottom).
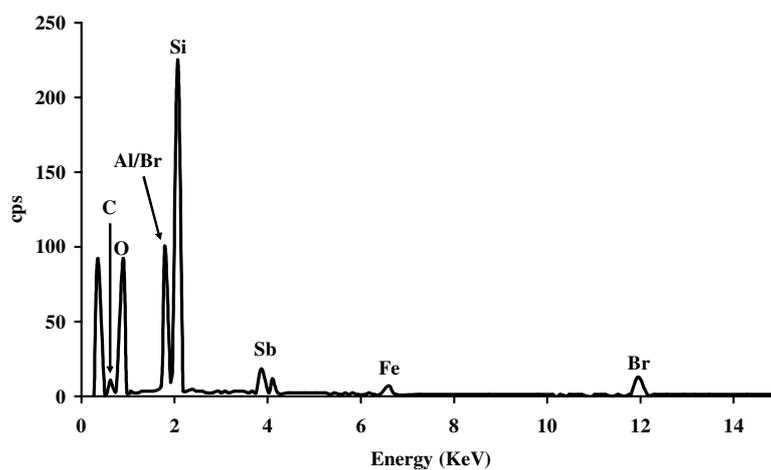
Figure 7. SEM-EDX spectra of ZSM-5 catalyst after Br-ABS pyrolysis products had been passed over it