THE CO-PYROLYSIS OF FLAME RETARDED HIGH IMPACT POLYSTYRENE AND POLYOLEFINS

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ABSTRACT

The co-pyrolysis of brominated high impact polystyrene (Br-HIPS) with polyolefins using a fixed bed reactor has been investigated, in particular, the effect that different types brominated aryl compounds and antimony trioxide have on the pyrolysis products. The pyrolysis products were analysed using FT-IR, GC-FID, GC-MS, and GC-ECD. Liquid chromatography was used to separate the oils/waxes so that a more detailed analysis of the aliphatic, aromatic, and polar fractions could be carried out. It was found that interaction occurs between Br-HIPS and polyolefins during co-pyrolysis and that the presence of antimony trioxide influences the pyrolysis mass balance. Analysis of the Br-HIPS + polyolefin co-pyrolysis products showed that the presence of polyolefins led to an increase in the concentration of alkyl and vinyl mono-substituted benzene rings in the pyrolysis oil/wax resulting from Br-HIPS pyrolysis. The presence of Br-HIPS also had an impact on the oil/wax products of polyolefin pyrolysis, particularly on the polyethylene oil/wax composition which converted from being a mixture of 1-alkenes and n-alkanes to mostly n-alkanes. Antimony trioxide had very little impact on the polyolefin wax/oil composition but it did suppress the formation of styrene and alpha-methyl styrene and increase the formation of ethylbenzene and cumene during the pyrolysis of the Br-HIPS.

1. INTRODUCTION

In recent years, much attention has been paid to the possibility of recycling plastics by pyrolysis and the introduction of the Waste Electronic and Electrical Equipment (WEEE) Directive [1] by the European Commission has inspired an increasing amount of research into using pyrolysis to recycle WEEE plastics. The WEEE Directive requires that Member States of the European Union meet certain targets for recycling each fraction of WEEE, including the plastic fraction. Unfortunately, WEEE plastics often contain toxic brominated flame retardants, which makes them particularly problematic to recycle [2].

Pyrolysis of plastic wastes is a proven process whereby polymers are converted into gas, oil, and char products that can then either be used as chemical feedstocks or as fuels. Previous work at our laboratories has shown that pyrolysis can be successfully used to process WEEE plastics using either a fluidised bed reactor or by batch pyrolysis [3-5]. The bromine can be safely removed from the pyrolysis products either by using an adsorbing medium to capture the bromine [6-8] or by using two-stage pyrolysis to remove the toxic brominated organics before pyrolysis of the main polymer material [9].

As well as brominated fire retardants, many WEEE plastics also contain antimony trioxide, which is added to the polymers as a synergist to increase the flame retardant properties of the brominated additives [10]. Antimony trioxide is used as a synergist in combination with polybromodiphenyl oxides (commonly referred to as polybrominated diphenyl ethers or PBDE's) and decabromodiphenyl ethane, both of which are used as fire retardants in polystyrene based polymers and co-polymers. Antimony trioxide acts as a synergist by promoting the release of bromine radicals during combustion via the formation of volatile antimony bromides, the bromine radicals then quench the combustion process by aggressively scavenging other radicals which are required for the propagation of a flame [10]. Water is a secondary product of the conversion of antimony trioxide to antimony bromide and it is thought that the hydrogen necessary for this reaction is obtained from the polymer chains [11]. Therefore, antimony trioxide is thought to have a significant impact on the pyrolysis of flame retarded polymers.

Several investigations have been carried out into the effect that antimony trioxide has on both the pyrolysis products and the fate of the bromine content of plastics during pyrolysis [11,12]. However, there is no work investigating the effect of antimony trioxide on the pyrolysis products when brominated plastics are mixed with polypropylene and polyethylene. Several investigations have been carried out into the co-pyrolysis of polystyrene and polyolefins and although there is agreement that some interaction occurs, there is some dispute about the level of interaction between the pyrolysing polymers [8, 13-17]. It is therefore possible that the co-pyrolysis of brominated styrenic polymers and polyolefins will produce not only interactions between the flame retardant additives, but also the polymer chains, which could lead to important changes in the composition of the pyrolysis products.

This work investigated the effect antimony trioxide has on the co-pyrolysis products of brominated high impact polystyrene mixed with polypropylene and brominated high impact polystyrene mixed with polyethylene. The pyrolysis of the plastic mixtures was carried out in a fixed bed reactor at a final pyrolysis temperature of 430°C and the products were analysed by GC-FID, GC-MS, GC-ECD, and FT-IR.

2. EXPERIMENTAL

2.1 MATERIALS

High impact polystyrene (HIPS) was chosen as the flame retarded plastic because it is one of the most commonly used plastics in electrical and electronic equipment and is usually flame retarded by aryl bromines with antimony trioxide as a synergist. The HIPS contained either decabromodiphenyl oxide or decabromodiphenyl ethane flame retardant and either 5% or 0% antimony trioxide. Each of the four flame retardant combinations was mixed with polyethylene or polypropylene, the composition of each sample that was investigated is shown in table 1.

Toluene, ethylbenzene, styrene, cumene, alpha-methylstyrene, (1-bromoethyl)benzene, 1-phenylnaphthalene, and 1,3,5-triphenylbenzene were supplied by Sigma-Aldrich (UK) and Alfa-Aesar (UK) and made into standards for calibration of the gas chromatographs. $C_8 - C_{20}$ and $C_{21} - C_{40}$ n-alkane standards were supplied by Sigma-Aldrich (UK).

2.2 FIXED BED REACTOR

Each sample listed in table 1 was pyrolysed in a Pyrex glass reactor (length: 35 cm; id: 3 cm) under atmospheric pressure by batch operation using the experimental setup shown in figure 1. At the start of the experiment, 10 g of plastic was loaded into the reactor, which was then heated to 120°C at 5°C min^{-1} and held for 1 hour to remove any moisture and oxygen from the reactor. Once the reactor had been purged, the temperature was increased to 430°C at a rate of 5°C min^{-1}, the temperature was then maintained until the pyrolysis was complete. The temperature of the plastic bed was measured with a thermocouple and this was taken to be the pyrolysis temperature. The pyrolysis oils were condensed to liquid products using a cold water condenser that was graduated so that the volume of oil collected could be measured as the experiment progressed. The hydrogen bromide which was evolved during pyrolysis of the plastics was trapped in a flask containing ion-exchanged water. The amount of gaseous inorganic Br trapped in the water flask was determined by an ion chromatograph (DIONEX, DX-120). The hydrocarbon gases were trapped in a gas bag and analysed at the end of the pyrolysis experiment using GC-TCD.

The pyrolysis oils were initially characterised using a Nicolet 560 FT-IR. A small aliquot of each pyrolysis oil was coated between two KBr disks and then analysed over the range 4000 – 400 cm^{-1}. The type of compounds present in the oils was determined by the FT-IR's spectral interpretation software and the functional groups were determined by comparison of each oil's spectra to correlation charts.

A more detailed characterisation of the pyrolysis oils was carried out using a Shimadzu QP2010 GC-MS fitted with a 30 m RTX-5 column. The injector temperature was 285 °C and the oven was held at 40°C for 15 minutes, ramped to 280 °C at 5 °C min^{-1}, 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 derived ion mass spectra were automatically compared to spectral libraries. The MS was not switched on until five minutes into the run, meaning that benzene and toluene could not be analyzed.

The concentration of toluene, ethylbenzene, styrene, cumene, alpha-methylstyrene, (1-bromoethyl)benzene, 1-phenylnaphthalene, and 1,3,5-triphenylbenzene in the pyrolysis oils was determined using a Varian 3380 GC-FID fitted with a 30m ZB-5 column. The GC was also fitted with an electron capture detector (ECD), so the column was split so that the analytes passed through both detectors at the same time. The injector temperature was 300°C and the FID and ECD temperatures were 300°C and 310°C respectively. The GC oven used the same programme as the GC-MS.

Additionally, the oils and waxes were separated into aliphatic, aromatic, and polar fractions to provide a more detailed analysis of the type of compounds present. The liquid chromatography was primarily carried out because it was difficult to analyse the aliphatic products of polyolefin decomposition when the GC-FID chromatogram was dominated by the much more prevalent aromatic compounds resulting from the pyrolysis of the Br-HIPS. The separation was carried out using 3g of silica gel that had been activated for 2 hours at 105°C. The silica gel was loaded into a 8 cm glass column and washed with hexane. A small aliquot of pyrolysis oil/wax was dissolved in 2mL of hexane and placed in an ultra-sonic bath for 15 minutes before being transferred to the top of the silica gel column. The column was left to stand for 5 minutes and then eluted with 20mL of hexane, 15mL of toluene, and 15mL of methanol. The aliphatic fraction was contained in the hexane, the aromatics in the toluene, and the polar compounds were contained in the methanol. The aliphatic, aromatic, and polar fractions were analysed using the Varian 3380 GC-FID/ECD, the aromatic and polar compounds were analysed using the same programme as mentioned above but the aliphatic fraction was analysed using an FID and injector temperature of 345°C and the oven was held at 40°C for 15 minutes, then heated to 340°C at 5°C/min, and then held for 15 minutes. Each fraction was also analysed by the ECD, although the results were influenced by the fact that many brominated aromatics, such as polybrominated diphenyl ethers, are very soluble in hexane.

3. RESULTS AND DISCUSSION

3.1 FIXED BED REACTOR

Each of the plastic samples was pyrolysed in a fixed bed reactor at 430°C and the mass balances are shown in table 2. The majority of the pyrolysis products from the pyrolysis of Br-HIPS + polypropylene was oil and wax (~79%) and the presence of antimony trioxide did have some impact on the mass balance. When antimony trioxide was present, the pyrolysis of Br-HIPS + polypropylene led to the formation of greater amounts of char and less oil/wax and gas compared to when antimony trioxide was absent from the plastic mixture. It is already known from previous studies that Br-HIPS that does not contain antimony trioxide produces large volumes

of hydrogen bromide, and therefore an increase in the proportion of gas; whereas the presence of antimony trioxide leads to the formation of antimony bromide and, therefore, an increase in the proportion of oil [12]. However, in this work, less oil was produced when antimony trioxide was present in the plastic mix than when it is absent, this suggests that antimony trioxide reacts with the polypropylene and leads to increased gas and reduced oil formation during pyrolysis. This could be due to the process of hydrogen abstraction from the polymer chains as antimony trioxide converts to antimony bromide and water. The increased char yield when antimony trioxide is present is most probably due to the presence of un-reacted antimony trioxide and increased char formation in the presence of antimony trioxide, something that has also been reported to occur by Jakab et al. [11]. Antimony trioxide is known to promote the formation of a highly cross-linked carbonaceous char under combustion conditions [10]. A similar trend to that seen in the Br-HIPS + polypropylene mixture was seen in the Br-HIPS + polyethylene mixture but the impact of antimony trioxide on the mass balances was less significant. Table 2 also shows the density of the pyrolysis oils/waxes, which have a higher density when antimony trioxide was present in the plastic due to the formation of antimony bromide.

Table 2 also shows the comparison between the predicted mass balances if the Br-HIPS and polyolefins were pyrolysed without any interaction and the actual mass balances achieved in the fixed bed reactor. During the pyrolysis of Br-HIPS + polypropylene without any antimony trioxide, less gas and char and more oil was produced than was predicted. When antimony trioxide was present in the Br-HIPS + polypropylene mixture, more gas and oil and less char was produced than predicted. When Br-HIPS + polyethylene was pyrolysed without any antimony trioxide, less gas and more oil and char was produced than predicted. When antimony trioxide was present in the Br-HIPS + polyethylene mixture, slightly less gas and oil and more char was produced than predicted. Although the type of brominated flame retardant had an impact on the mass balances, they had no effect on the trends described above. From the data presented in table 2 it is obvious that there is interaction between Br-HIPS and polyolefins during their co-pyrolysis, but it should also be noted that it is possible that antimony trioxide influenced the pyrolysis of the polyolefins as well as the Br-HIPS in which it was contained, because the presence of antimony trioxide altered the relationship between the actual and predicted mass balances. It is also clear form the data in table 2 that Br-HIPS interacted differently with polypropylene and polyethylene.

When Miskolczi et al [13] pyrolysed a mixture of HDPE and polystyrene at 430°C they found that that the plastic mixture converted to 45% residue and 50% oil, possibly because they used a shorter residence time than we have used in this work. Williams and Williams [15] reported that mixtures of HDPE/PS produced 31.5% gas, 67.3% oil/wax, and 1.2% char, LDPE/PS produced 33.8% gas, 64.0% oil/wax, and 2.2% char, and PP/PS produced 16.0% gas, 83.6% oil/wax, and 0.4% char when the heating rate was 25°C min^{-1} and the final temperature was 700°C. The high gas concentrations reported by Williams and Williams can be explained by the higher final pyrolysis temperature, but the authors also discussed the impact that mixing polystyrene with polyolefins had on the mass balance. Williams and Williams reporting that when polystyrene was mixed with polyethylene higher than predicted gas yields and lower than predicted oil/wax yields were produced. Also, when

polystyrene was mixed with polypropylene higher than predicted gas yields and lower than predicted char yields were produced. It has also been reported that the co-pyrolysis of brominated acrylonitrile-butadiene-styrene (Br-ABS) with polyethylene led to lower than predicted oil yields and higher than predicted char yields.

As well as influencing the mass balance, antimony trioxide also influenced the temperature and rate at which pyrolysis commenced. Figure 2 shows the cumulative volume of oil and wax as the pyrolysis of Br-HIPS + polypropylene and Br-HIPS + polyethylene proceeded. The presence of antimony trioxide lowered the temperature at which pyrolysis of the samples began in the fixed bed reactor from 370°C to 335°C. Jakab et al [11] also noted that antimony trioxide lowered the temperature at which pyrolysis began in polystyrene plastics and suggested that it was due to antimony trioxide causing hydrogen abstraction from the polymer chain, which allowed the chains to break down at a lower temperature than normal.

Figure 2 also shows some differences between the pyrolysis of the Br-HIPS + polypropylene and the Br-HIPS + polyethylene samples. The pyrolysis of Br-HIPS + polypropylene was very fast, occurred in a single stage, and was complete after 160 minutes, while the pyrolysis of Br-HIPS + polyethylene was much slower, after an initial period of rapid decomposition, and was not complete until after 300 minutes in the case of DDO(5) + PE and 280 minutes in the case of DDO(0) + PE. The differing decomposition profile of Br-HIPS + polypropylene and Br-HIPS + polyethylene can be explained by the structure of polypropylene and polyethylene. The branched nature of polypropylene means that the C-C bond dissociation energy in polypropylene is less than in polyethylene, so polypropylene decomposes at a lower temperature and more rapidly than polyethylene [18,19]. It is thought that polypropylene decomposition begins at 300°C [19] while polyethylene decomposition does not begin until 410-425°C [16,20]. The decomposition temperature of polypropylene means that it will be decomposing at the same time as the Br-HIPS so the pyrolysis products of each polymer will be able to interact, which will not be the case for the Br-HIPS + polyethylene mixture where the pyrolysis of the Br-HIPS will be well advanced by the time decomposition of the polyethylene begins. Therefore, it can by suggested that polypropylene had a greater impact on the mass balance of co-pyrolysed Br-HIPS + polyolefins than polyethylene (table 2), because polypropylene was able to interact with the Br-HIPS to a much greater extent than polyethylene. Faravelli [16] reported that low diffusivity and solubility between polystyrene and polyethylene meant that radicals from one polymer can not easily diffuse into the other polymer during pyrolysis and the same can be assumed for polystyrene and polypropylene. However, once in the gas phase in the a fixed bed reactor, where the residence times are relatively long, the decomposition products of each polymer will be free to react with any other pyrolysis products, no matter what their origin.

3.2 PYROLYSIS GASES

The hydrocarbon pyrolysis gases were analysed using a GC-TCD and the results are presented in figures 3 and 4. When Br-HIPS was mixed with polypropylene the presence of antimony trioxide had a significant impact on the type of pyrolysis gases produced (figure 3). The presence of antimony trioxide led to an increased proportion of ethene, ethane, and propene in the pyrolysis gas but completely suppressed the formation of butane and pentane. The type of brominated flame retardant also had an

impact on the pyrolysis gases, when decabromodiphenyl oxide (DDO) was the flame retardant in the absence of antimony trioxide, a large proportion of the pyrolysis gas was butene, however, when decabromodiphenyl ethane was the flame retardant the proportion of butene was suppressed and replaced by a large proportion of pentane (figure 3).

When Br-HIPS was mixed with polyethylene, the presence of antimony trioxide led to a significant increase in the proportions of ethene and a decrease in the proportions of butane in the pyrolysis gas (figure 4). Antimony trioxide also caused a slight increase in the proportion of butene and ethane and a slight decrease in the proportion of propane. The type of brominated flame retardant also had an impact on the type of pyrolysis gases produced by the pyrolysis of Br-HIPS + polyethylene. When DDO was the flame retardant, a slightly increased proportion of the pyrolysis gases were ethane and a slightly decreased proportion were butene compared to when DDE was the flame retardant.

There is some dispute in the literature about the composition of the pyrolysis gas resulting from the decomposition of polyolefins, with some claiming that the alkane gases outnumber the alkenes [21] and some claiming the reverse case [15, 22]. When Miskolczi et al [13] co-pyrolysed polystyrene and HDPE they found that the alkane gases significantly outnumbered the alkene gases, but when Williams and Williams co-pyrolysed polystyrene and LDPE, the alkene gases significantly outnumbered the alkane gases [15]. In this work, no pattern could be determined regarding the concentration of alkane and alkene gases in the Br-HIPS + polypropylene mixture but in the Br-HIPS + polyethylene mixture ethane outnumbered ethene and butane outnumbered butene, although the concentrations of propane and propene were roughly equal, Brebu et al noticed a similar trend to this in their work into the co-pyrolysis of Br-ABS + polyethylene [8]. One explanation for the lack of a trend in the composition of the pyrolysis gases is that only 20% of the plastic mixtures was composed of polyolefins and therefore the composition of the pyrolysis gases was mostly determined by the decomposition of the Br-HIPS.

3.2 PYROLYSIS OILS

The pyrolysis oils were initially characterised using a FT-IR spectrometer, the results for the oils/waxes resulting from the pyrolysis of the DDO flame retarded plastic mixtures are shown in figure 5 The plastics that were flame retarded with DDE gave identical FT-IR spectra to their equivalent DDO plastics and so are not shown. All of the pyrolysis oils/waxes contained both aliphatic and aromatic bonds. The three peaks between 3010 and 3110 cm^{-1} are typical of C-H stretches in aromatic rings, the series of small peaks between 1660 and 2000 cm^{-1} are benzene ring overtone bands, the two peaks at 1601 and 1493 cm^{-1} can be associated with C=C stretches in benzene rings, and the two large peaks at 758 and 698 cm^{-1} are typical of monosubstituted aromatics. The three peaks between 2850 and 2970 cm^{-1} are typical of methyl and methylene group C-H stretches and the large band at 1453 cm^{-1} indicates the presence of large numbers of -CH_2- groups. The band at 1377 cm^{-1} is typical of C-CH_3 groups where there is a single methyl group attached to a carbon atom and the two bands at 966 and 905 cm^{-1} can be associated with CH=CH_2 groups.

Although the FT-IR spectrum for each of the oils were similar, there are some small but important differences between each of the oils. The presence of antimony trioxide in the pyrolysis oil led to a decrease in the strength of the two $CH=CH_2$ bands (966 and 905 cm^{-1}) suggesting that there is a suppression of either alkene groups in the aliphatic products of polypropylene and polyethylene pyrolysis or vinyl groups in the substituted aromatic products of polystyrene pyrolysis. The C-CH$_3$ band (1377 cm^{-1}) was much more prominent in the pyrolysis oils derived from the Br-HIPS + polypropylene than the pyrolysis oil derived from the Br-HIPS + polyethylene, suggesting that a greater number of branched alkanes and alkenes are present in the Br-HIPS + polypropylene oils.

3.2.1 Analysis of the Br-HIPS pyrolysis oils and waxes

The oils were characterised using a GC-MS and a GC-FID to determine the identity and concentration of some of the components of the pyrolysis oils. The GC-MS chromatograms of the oils resulting from the pyrolysis of the plastics which were flame retarded with DDE are shown in figure 6, many of the aliphatic products of polyolefin pyrolysis are masked by the aromatic products of Br-HIPS pyrolysis. It is obvious from figure 6 that the presence of antimony trioxide has a significant impact on the pyrolysis of Br-HIPS + polypropylene and Br-HIPS + polyethylene because when antimony trioxide was present in the plastic mixture, styrene and alpha-methyl styrene were completely absent from the pyrolysis oils.

Figure 7 shows the concentration of each of the major components in the oil produced from the pyrolysis of Br-HIPS + polypropylene as measured on the GC-FID. Again it is obvious that styrene and alpha-methylstyrene are absent from the pyrolysis oils when antimony trioxide was present in the plastic mixture. However, it is also clear that the presence of antimony trioxide leads to increased yields of ethylbenzene and cumene in the pyrolysis oil. For example, the DDO(5) + polypropylene sample pyrolysed to form an oil that contained 26.8% ethylbenzene, 10.0% cumene, and no styrene or alpha-methylstyrene. However, the DDO(0) + polypropylene sample pyrolysed to form an oil which contained just 15.3% ethylbenzene and 3.6% cumene but also contained 27.6% styrene and 5.6% alpha-methylstyrene. The absence of styrene and alpha-methylstyrene can perhaps be explained by the saturation of the alkene bonds with the hydrogen formed by the dehydrogenation that must have preceded the increase in the yield of char during the pyrolysis of the plastic mixtures which contained antimony trioxide. The saturation of the alkene bond in styrene and alpha-methyl styrene would lead to the formation of ethylbenzene and cumene. The type of fire retardant also had an impact on the composition of the pyrolysis oil when Br-HIPS + polypropylene was pyrolysed. When DDO, rather than DDE, was the fire retardant, increased yields of ethylbenzene and cumene and decreased yields of styrene and alpha-methylstyrene were observed.

When Br-HIPS + polyethylene was pyrolysed in the fixed bed reactor the presence of antinomy trioxide led to the absence of styrene and alpha-methylstyrene in the pyrolysis oils and instead increased concentrations of ethylbenzene and cumene were present, presumably for the same reasons as for Br-HIPS + polypropylene. The absence of styrene and alpha-methylstyrene goes some way to explaining the reduced peak size on the FT-IR spectra at the wavelengths corresponding to $CH=CH_2$ bonds. A greater proportion of the Br-HIPS + polyethylene pyrolysis oils than the Br-HIPS +

polypropylene oils was identified by the GC-FID, suggesting that Br-HIPS decomposed more effectively in the presence of polyethylene than in the presence of polypropylene. The type of flame retardant had a significant impact on the composition of the Br-HIPS + polyethylene oils. When DDE, rather than DDO, was the flame retardant then greater concentrations of toluene, styrene, and alpha-methyl styrene were present in the pyrolysis oil.

Comparison of the results presented in this paper with those we have published previously into the pyrolysis of Br-HIPS on its own would suggest that the presence of polyolefins increases the yield of aromatic compounds [23]. The suggested mechanism for this is that the radicals created by the random scission of the polyolefins leads to the transfer of a hydrogen atom from the polystyrene chain, which in turn leads to beta-scission of the polystyrene chain creating the radical which causes depolymerization to occur.

Previous studies into the co-pyrolysis of polystyrene and polyolefins have noted increased concentrations of benzene, toluene, and xylenes [15]. Bockhorn et al. [17] suggested that hydrogen transfer from polyethylene to polystyrene causes an increase in the concentration of ethylbenzene, in effect the reverse of the mechanism suggested in this work. Bockhorn et al. also noted that there was a decrease in saturated aliphatic products in the pyrolysis oil, supporting their theory that hydrogen was transferred from polyethylene to the polystyrene pyrolysis products [17]. However, in this work, as will be discussed in a later section, the pyrolysis products of polyethylene were almost completely saturated when Br-HIPS was present in the pyrolysis mixture, suggesting that hydrogen was transferred from the polystyrene to polyethylene. Additionally, it was not only ethylbenzene that increased in concentration when polyolefins were present, but also unsaturated vinyl aromatics, which suggests that the increased concentrations of mono substituted aromatics was not due simply to hydrogen transfer from the polyolefin to the polystyrene as suggested by Bockhorn et al [17].

The GC-FID was also calibrated to determine the concentration of (1-bromoethyl) benzene in the pyrolysis oils. (1-bromoethyl)benzene was only present in the pyrolysis oils when antimony trioxide was absent from the plastic mixture and occurred in greater concentration in the oil when DDO, rather than DDE, was the flame retardant additive. There are two possible routes for the formation of (1-bromoethyl) benzene, either a Br free radical attaching itself to the radical resulting from beta-scission of a polystyrene chain or through Markovnikov addition of HBr to the alkene group of styrene.

3.2.2 Analysis of the polyolefin pyrolysis oils and waxes

As well as analysing the pyrolysis oil/wax by GC-FID, liquid chromatography was also used to separate the oil/wax components into aliphatic, aromatic, and polar fractions. Each of the liquid chromatography fractions was analysed by GC-FID and the chromatograms of the aliphatic fraction are presented in figure 9 and 10, the longest aliphatic chain that could analysed using the GC-FID was C_{46} and all the samples analysed contained chains of this length. The chromatograms of the aromatic fraction looked very similar to the GC-MS and GC-FID chromatograms of the whole oil/wax and only very low concentrations of polar compounds were identified, so

these results are not presented in this work. To complement the analysis of the aliphatic fraction, polypropylene and polyethylene were pyrolysed individually, in the absence of Br-HIPS, so that the influence of Br-HIPS on the aliphatics could be properly assessed.

Figure 9 shows the effect that Br-HIPS and Br-HIPS with antimony trioxide has on the pyrolysis products of polypropylene. When polypropylene was pyrolysed on its own the GC-FID chromatogram contained several groups of six to eight peaks between C_{10} and C_{30}, above C_{30} only the n-alkane, n-alkene, and n-alkadiene peaks were present in any significant concentration. The groups of peaks were fairly random in their composition and probably consisted of alkenes, alkadienes, and various combinations of branched aliphatics. Previous authors have also noted a similar peak pattern and suggested that the peaks for C_9, for example, are 2-methyl-4-octene, 2-methyl-2-octene, 2,6-dimethyl-2,4,-heptadiene, 2,4-dimethyl-1-heptene, and 2-methyl-1-octene [19]. When polypropylene was co-pyrolysed with Br-HIPS, the GC-FID chromatogram of the aliphatic fraction showed that there were uniform groups of peaks centred around the odd-numbered n-alkanes between C_{11} and C_{39} (figure 9), from C_{40} to C_{46} only n-alkane peaks were detected. When antimony trioxide was added to the Br-HIPS + polypropylene mix, then an increase in the heavier compounds of each group of peaks was observed, suggesting that a greater number of saturated compounds were being formed.

Figure 10 shows the products of pyrolysis of polyethylene in the presence of Br-HIPS and antimony trioxide. It is obvious from figure 10 that Br-HIPS had a significant impact on the pyrolysis products of polyethylene. When polyethylene was pyrolysed on its own, the oil/wax was made up of both 1-alkenes and n-alkanes, which has been reported to occur by other authors [21,24]. However, when polyethylene was mixed with Br-HIPS, the oil/wax was made-up almost exclusively of n-alkanes, which could be the result of the transfer of hydrogen from the polystyrene chains to the radicals that resulted from the random scission of polyethylene. This hydrogen transfer resulted in the formation of increased concentrations of alkyl and vinyl benzenes, as discussed in the above section. Evidence of the low concentration of alkenes in the Br-HIPS + polyethylene pyrolysis oil/wax can also be seen in the FT-IR analysis (figure 5), where it can be seen that the $CH=CH_2$ stretch at 905 cm^{-1} is much smaller in the Br-HIPS + polyethylene oil/wax than the Br-HIPS + polypropylene oil/wax. When antimony trioxide was present in the plastic mixture, a greater number and intensity of peaks occurred slightly after the elution of the n-alkane (figure 10).

Other authors who have investigated the co-pyrolysis of polystyrene and polyethylene have reported conflicting results regarding the effect of polystyrene on the pyrolysis products of polyethylene. Miskolczi et al [13] and Bockhorn et al [17] reported that the co-pyrolysis oil/wax of polystyrene / HDPE consisted of n-alkanes and 1-alkenes, but Williams and Williams [15] reported that the oils and waxes of polystyrene / HDPE and polystyrene / LDPE consisted of mainly 1-alkenes. Bockhorn also reported that the greater the fraction of polystyrene in the polystyrene / polyethylene mixture, the greater the proportion of alkenes would be present in the oil/wax. However, in this work, a mixture of 80% polystyrene / 20% polyethylene was used and the pyrolysis oil/wax was mostly alkanes. It is possible that the behaviour of Br-HIPS is different enough from polystyrene to cause these differences or that the

heating rate and final pyrolysis temperature are crucial factors in determining the composition of the aliphatic co-pyrolysis products of polystyrene and polyethylene.

3.2.3 GC-ECD analysis of the pyrolysis oils and waxes

As well as analysing the pyrolysis oil/wax by GC-MS and GC-FID it was also analysed by GC-ECD to determine the distribution of halogenated compounds. The results of the GC-ECD analysis of the oil/wax from the co-pyrolysis of Br-HIPS and polypropylene are shown in figure 11, the results from the co-pyrolysis of Br-HIPS + polyethylene were very similar to those from the co-pyrolysis of Br-HIPS + polypropylene and so are not presented here. When decabromodiphenyl oxide (DDO) was the flame retardant, the presence of antimony trioxide led to the formation of a large number of brominated compounds in the pyrolysis oil but the absence of antimony trioxide led to an even greater number of heavier brominated compounds as well as (1-bromoethyl) benzene. When decabromodiphenyl ethane was the flame retardant there were many fewer compounds detected by the GC-ECD, especially when antimony trioxide was present in the plastic mixture. The GC-ECD chromatograms for the co-pyrolysis of Br-HIPS and polyolefins were very similar to the chromatograms when Br-HIPS was pyrolysed on its own in our other work [23].

GC-ECD analysis of the fractionated oil/waxes showed that there were some differences between the aliphatic, aromatic, and polar fractions. The aliphatic fraction contained a number of medium boiling point halogenated compounds that might be polybrominated diphenyl ethers or other halogenated compounds that are very soluble in hexane; the peak pattern suggested that they were not halogenated aliphatics. The aromatic fractions contained a large number of medium and high boiling-point compounds which could be associated with non-polar polybrominated diphenyl oxides and ethanes that are likely to form when decabromodiphenyl oxide or decabromodiphenyl ethane partially decomposes. The polar fractions tended to contain less brominated compounds and the peaks that were present could probably be associated with bromophenols, bromobenzenes, and polar polybrominated diphenyl oxides and ethanes.

CONCLUSIONS

The presence of antimony trioxide in the Br-HIPS + polyolefin mixture led to decreased oil/wax yields, the reverse of what would be expected, as during Br-HIPS pyrolysis the presence of antimony trioxide leads to increased oil formation. Evidence that interaction occurred between Br-HIPS and polypropylene and Br-HIPS and polyethylene was found in the materials mass balances which showed differences from the predicted values. It was also suggested that antimony trioxide may have interacted with the polyolefins, despite being contained within the Br-HIPS polymer.

The co-pyrolysis of Br-HIPS + polyolefins led to increased concentrations of vinyl and alkyl aromatics in the pyrolysis oil/wax compared to the pyrolysis of Br-HIPS on it own. Br-HIPS also influenced the pyrolysis products of the polyolefins, especially polyethylene by converting the unsaturated compounds to saturated compounds. The presence of antimony trioxide appeared to have very little impact on the polyolefin pyrolysis products but it did suppress the formation of styrene and alpha-methylstyrene during the decomposition of the Br-HIPS.

ACKNOWLEDGEMENTS

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Table 1 Description and composition of the samples pyrolysed in the fixed bed reactor

Code	Description	Br content (wt%)	Sb$_2$O$_3$ (wt%)
DDO(5) + PP	8g HIPS with DDO and Sb2O$_3$ + 2g PP	8.6	4.0
DDO(0) + PP	8g HIPS with DDO + 2g PP	8.6	0.0
DDE(5) + PP	8g HIPS with DDE and Sb2O$_3$ + 2g PP	8.6	4.0
DDE(0) + PP	8g HIPS with DDE + 2g PP	8.6	0.0
DD0(5) + PE	8g HIPS with DDO and Sb2O$_3$ + 2g PE	8.6	4.0
DD0(0) + PE	8g HIPS with DDO + 2g PE	8.6	0.0
DDE(5) + PE	8g HIPS with DDE and Sb2O$_3$ + 2g PE	8.6	4.0
DDE(0) + PE	8g HIPS with DDE + 2g PE	8.6	0.0

Table 2   The effect of antimony trioxide on the mass balance during the co-pyrolysis of Br-HIPS + PP and Br-HIPS + PE in a fixed bed reactor at 430°C

	Mass (wt %)			Oil density (g/mL)
	Gas	Oil/wax	Char	
PP	18.7	80.0	1.3	0.8
DDO(5) + PP (calc.)[a]	*7.8*	*79.1*	*13.1*	
DDO(5) + PP	8.2	80.2	11.6	1.07
DDO(0) + PP (calc.)[a]	*12.4*	*77.8*	*9.8*	
DDO(0) + PP	9.6	81.4	9.0	0.95
DDE(5) + PP (calc.)[a]	*8.1*	*78.9*	*13.0*	
DDE(5) + PP	8.3	80.2	11.5	1.04
DDE(0) + PP (calc.)[a]	*13.1*	*77.4*	*9.5*	
DDE(0) + PP	9.7	82.3	8.0	0.95
PE	24.1	73.0	2.9	0.8
DDO(5) + PE (calc.)[a]	*8.9*	*77.7*	*13.4*	
DDO(5) + PE	8.5	77.6	13.9	1.02
DDO(0) + PE (calc.)[a]	*13.5*	*76.4*	*10.1*	
DDO(0) + PE	9.4	77.4	13.2	0.95
DDE(5) + PE (calc.)[a]	*9.2*	*77.5*	*13.3*	
DDE(5) + PE	9.2	76.7	14.1	1.02
DDE(0) + PE (calc.)[a]	*14.2*	*76.0*	*9.8*	
DDE(0) + PE	9.2	77.0	13.8	0.93

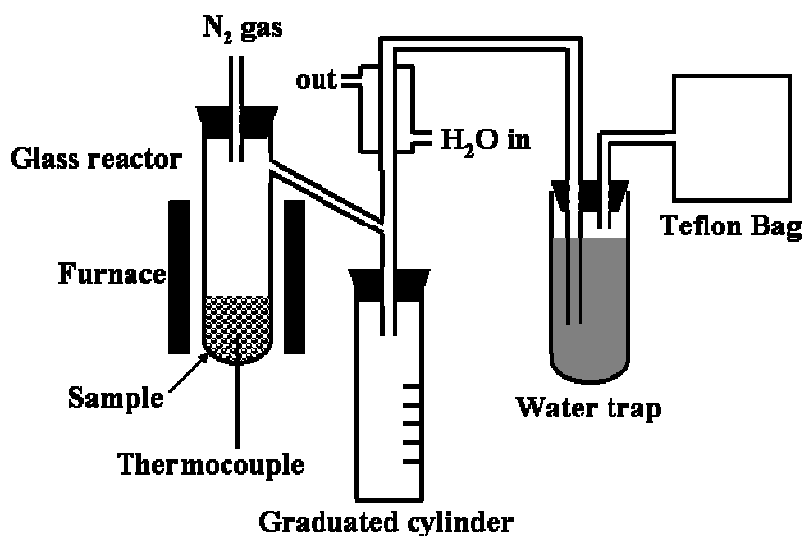a: calculated mass balance assuming no interaction between the polymers

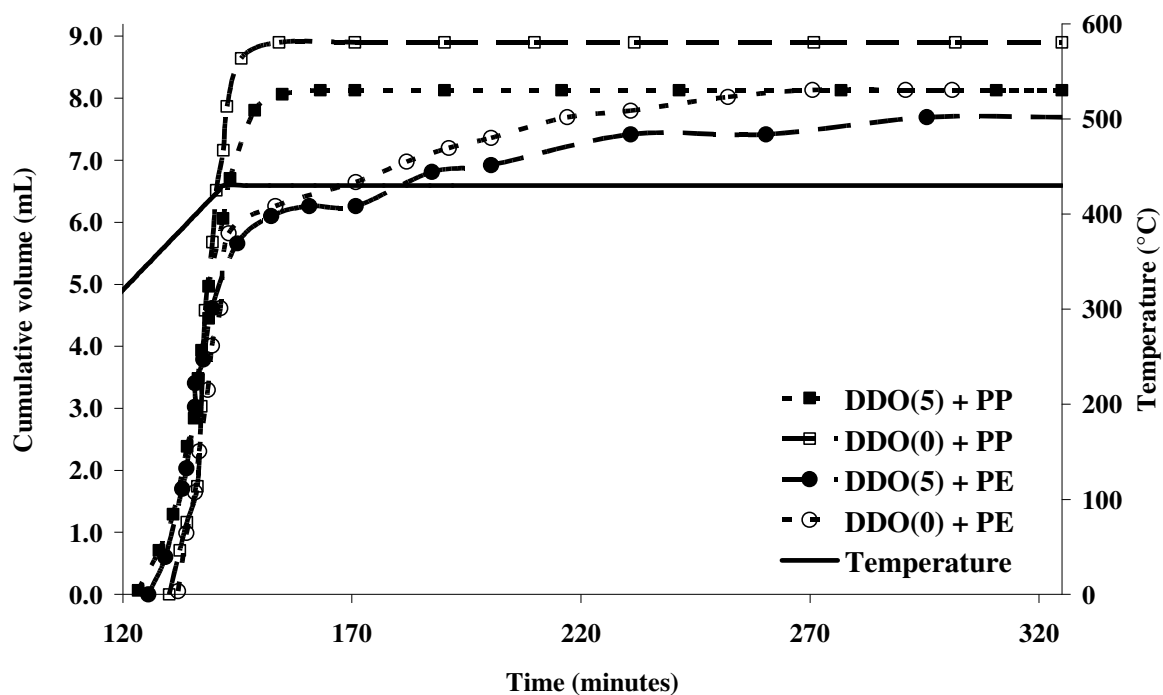**Figure 1 Schematic diagram of the fixed bed reactor used to pyrolyse the plastic samples**

Figure 2 The cumulative volume of oil/wax collected in the reactor condensers as the pyrolysis of Br-HIPS + PP and Br-HIPS + PE proceeded
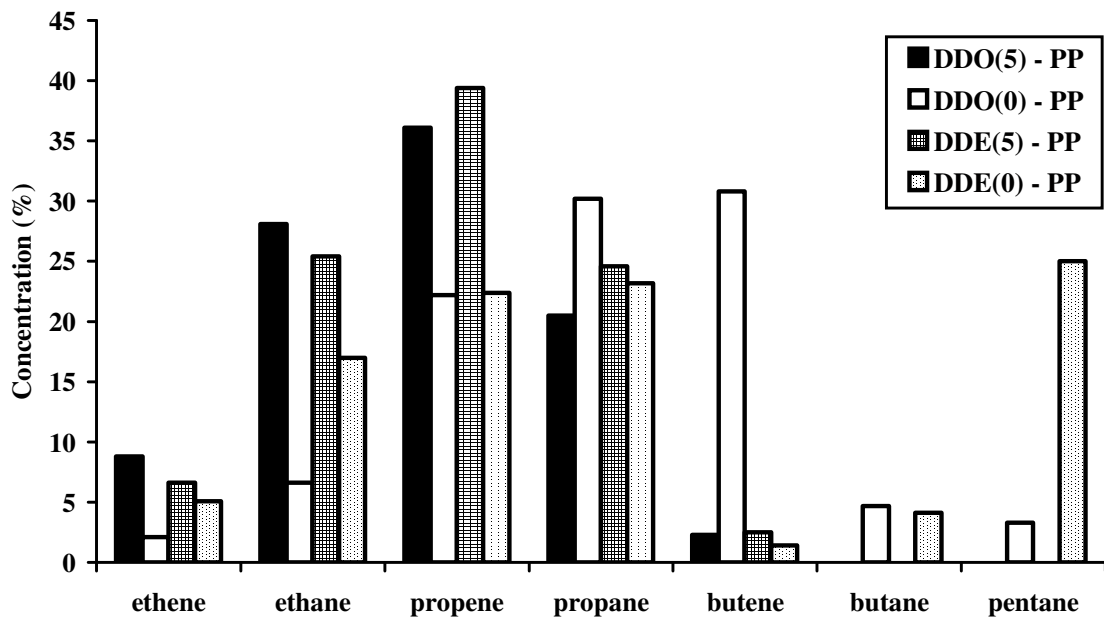
Figure 3 The composition of the organic pyrolysis gases during the pyrolysis of Br-HIPS + PP at 430°C in a fixed bed reactor
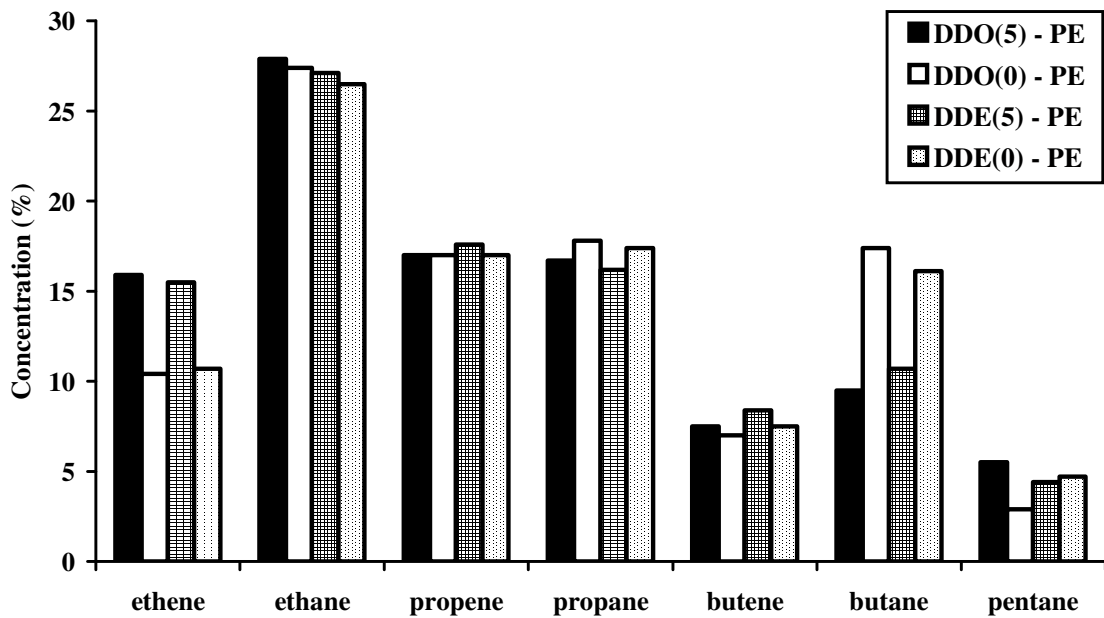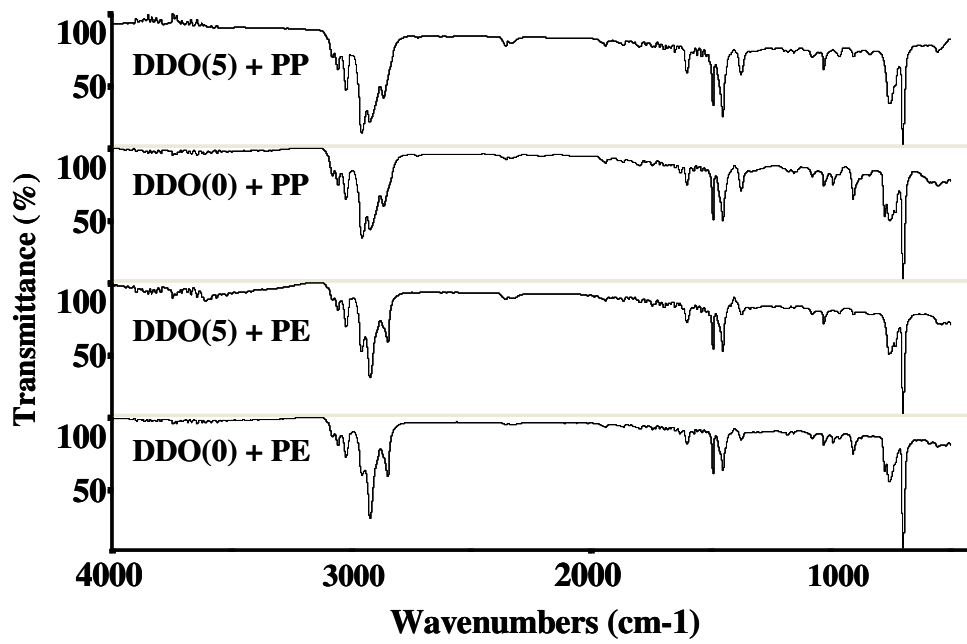

Figure 4 The composition of the organic pyrolysis gases during the pyrolysis of Br-HIPS + PE at 430°C in a fixed bed reactor

Figure 5 **FT-IR spectra of the pyrolysis oils resulting from the pyrolysis of Br-HIPS + polypropylene and Br-HIPS + polyethylene with and without antimony trioxide**
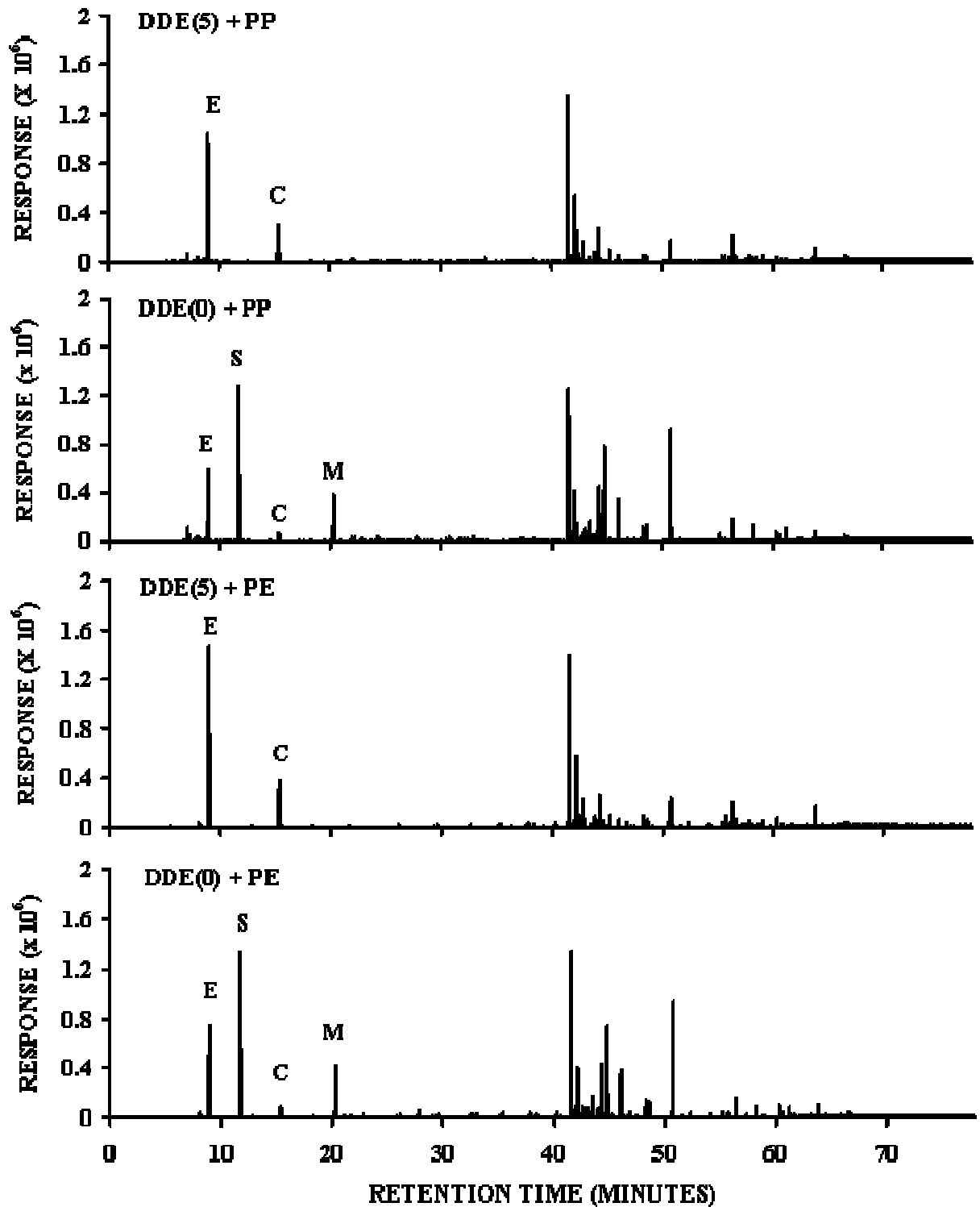
Figure 6 GC-MS analysis of the unfractionated oil/wax resulting from the pyrolysis of Br-HIPS + PP and Br-HIPS + PE at 430°C where E = ethylbenzene, S = styrene, C = cumene, and M = alpha-methylstyrene
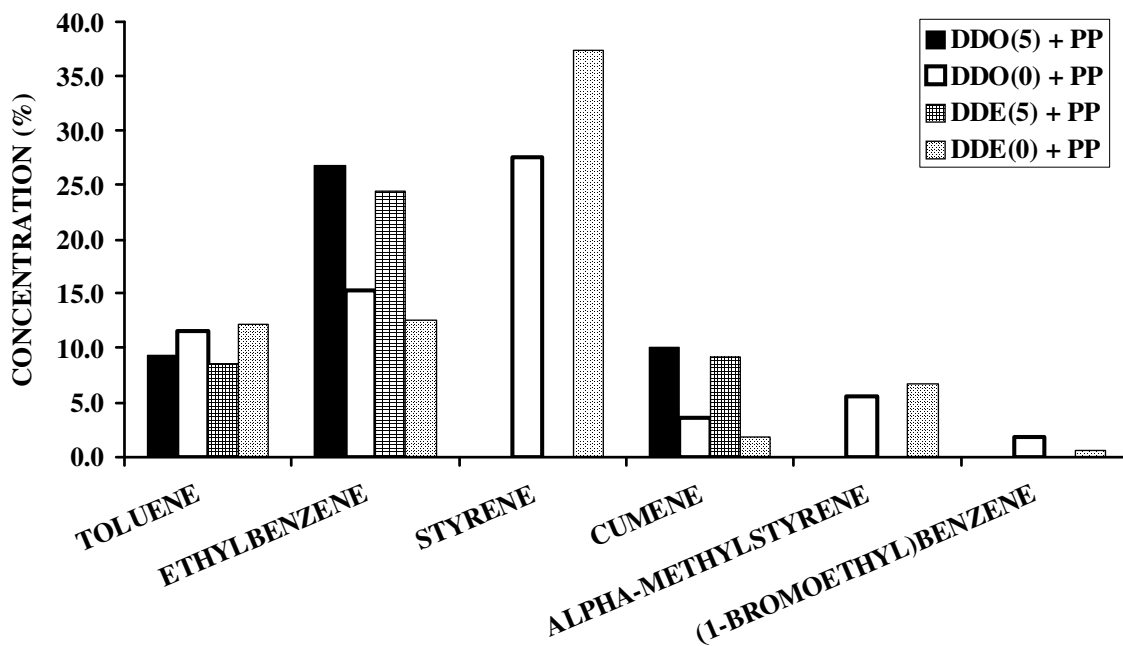
Figure 7 Concentration of the major components in the oil resulting from the pyrolysis of Br-HIPS + polypropylene at 430°C in a fixed bed reactor
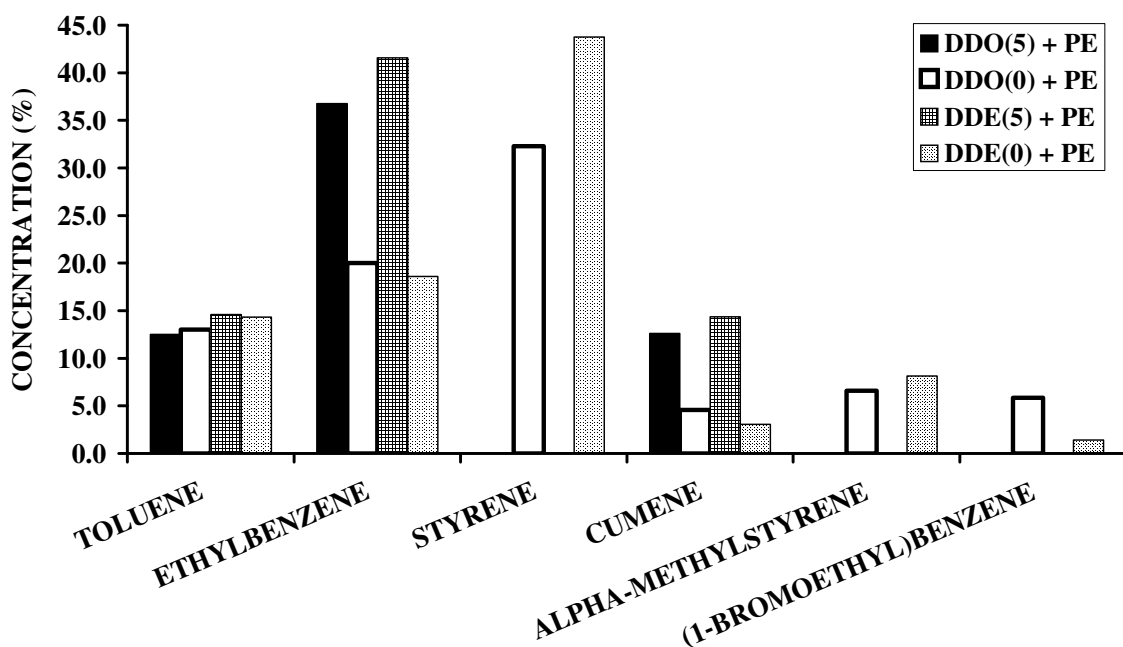
Figure 8 Concentration of the major components in the oil resulting from the pyrolysis of Br-HIPS + polyethylene at 430°C in a fixed bed reactor
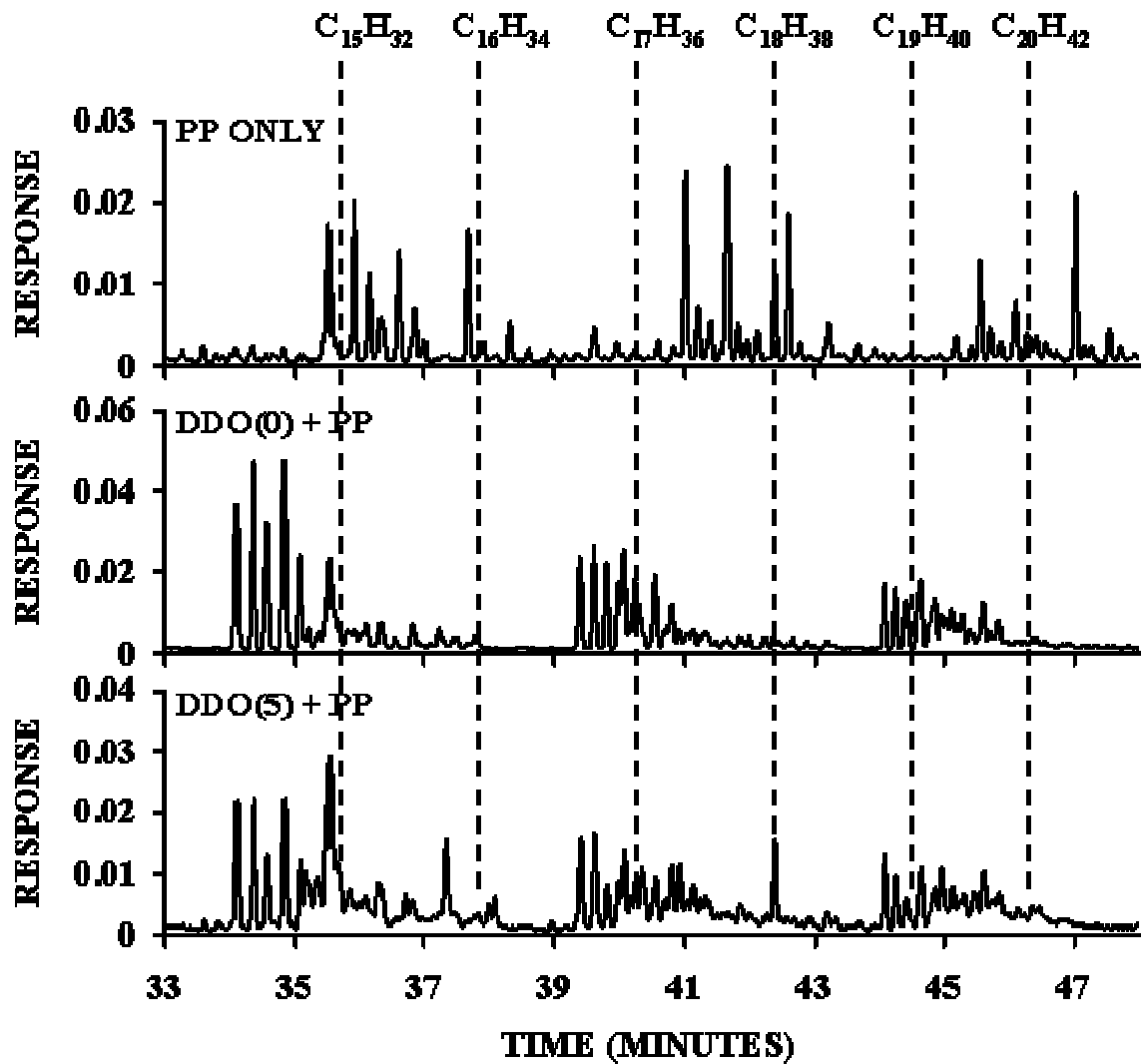
Figure 9 GC-FID chromatograms of the hexane fraction of the fractionated HIPS + polypropylene oil/wax produced by pyrolysis at 430°C in a fixed bed reactor
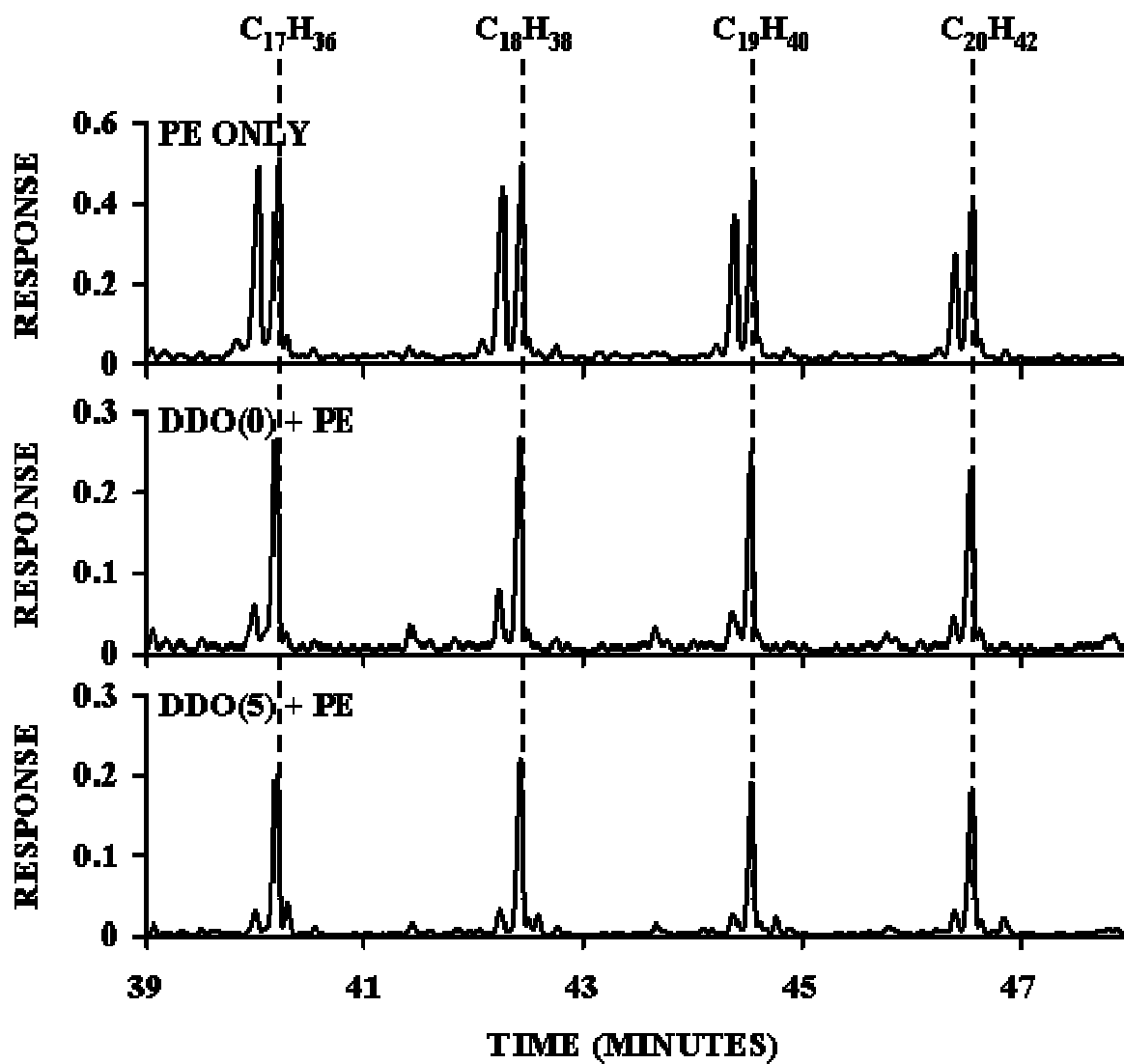
Figure 10 GC-FID chromatograms of the hexane fraction of the fractionated HIPS + polyethylene oil/wax produced by pyrolysis at 430°C in a fixed bed reactor
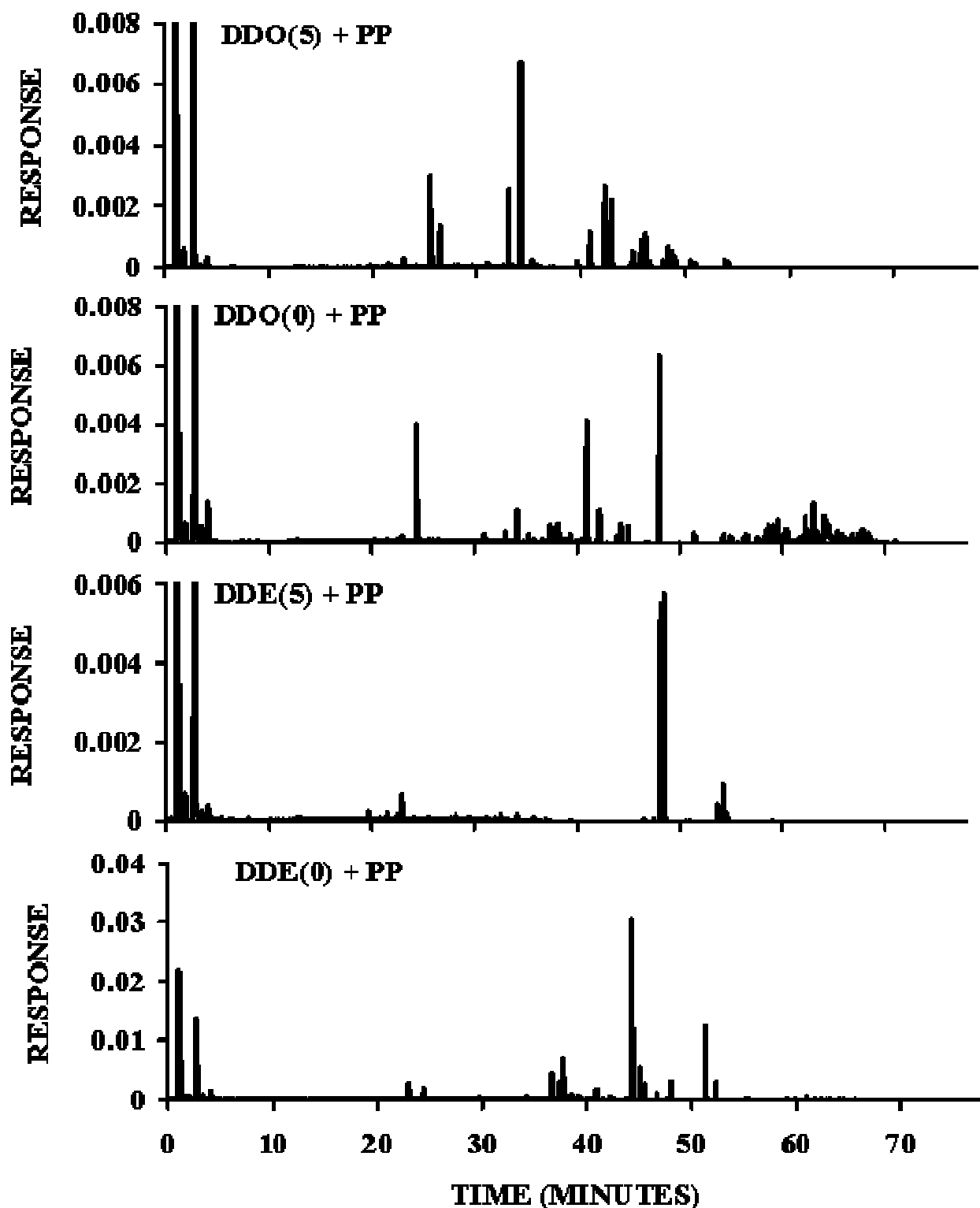
Figure 11 GC-ECD analysis of the unfractionated oil/wax resulting from the pyrolysis of Br-HIPS + polypropylene at 430°C in a fixed bed reactor