Polycyclic Aromatic Hydrocarbon (PAH) formation in thermal degradation of Styrene Butadiene Copolymer (SBR)

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ABSTRACT
This study has been initiated to quantify the release of the Polycyclic Aromatic Hydrocarbon (PAH) from Styrene Butadiene Copolymer (SBR), which is the main constituent of tires. The identification and quantification has been determined experimentally using Gas Chromatography/Mass Spectroscopy (GC/MS) coupled to Thermo-Gravimetric Analysis (TGA) unit. SBR samples were pyrolysed in a TGA unit in a N₂ atmosphere. The identities and absolute concentrations of over 32 major and minor species have been established, including a large number of aromatics, substituted aromatics, and PAHs. The light hydrocarbon species also have been determined simultaneously and identified as H₂, C₂H₂, CH₄, C₂H₆, and C₄H₁₀ with lower concentrations of other hydrocarbon gases. Significant amounts of ethyl benzene, toluene, and styrene were observed between 330°C and 500°C. The largest PAH detected was the family of C₂₄H₁₄ (molecular weight 302), benzo[ghi]perylene with peak concentrations reaching 0.19 ppmv. The effluent species detected suggest that formation of PAH’s occurs either through hydrocarbon addition reactions or benzene ring combination reactions. In addition, the chemical structure of SBR lends itself gas phase release of benzene molecules or radicals, thus facilitating the PAH production route. Preliminary calculations done using MOPAC provided some insight into the energy required to break the benzene ligand bond from the butadiene structure. The measurements supply information on the identities and levels of hazardous air pollutants, and provide useful new data for the development and validation of detailed reaction mechanisms describing their origin and fate.

INTRODUCTION
The disposal of used automobile tires has caused many environmental and economical problems. In the US, 750 million to 2 billion used tires have been stockpiled, which are increasing at a rate of 280 million per year[1]. Around 2,600,000 metric tons of used tire were produced in the European Union in 2001. A low percentage is re-capped or reused for second-quality rubber but around 80% of these tires are accumulated in dumps, posing hazards such as disease and accidental fires and adversely impacting the environment[2].

Tire disposal requires special solid waste management because of their particular properties. The durability and strength of tires make their disposal and reprocessing extremely difficult.
Furthermore, tires are not very amenable to biodegradation. That reason alone suggests landfilling of tires is not an option.

The high energy content of waste tires has been recognized by other industries looking for cheap energy alternatives. Cement kilns already have sufficient capacity to consume the entire annual U.S waste tire generation. Energy recovery should be the desired end use for scrap tires. For example, Tire-Derived Fuel (TDF – whole or shredded tires) is utilized as a supplemental or dedicated fuel by some cement kilns, pulp and paper mills, electric utilities and dedicated tire-to-energy facilities. TDF contains 32,600 to 37,300 KJ/Kg, which is a higher energy content than most types of coal. Moreover, more facilities are looking at gasification of waste tires to produce synthesis gas for other uses.

Tires are composed of various rubbers, such as natural rubber (NR), butyl rubber (BR), or styrene butadiene rubber (SBR). The most commonly used tire rubber is styrene-butadiene copolymer (SBR), containing 25 wt% styrene. In addition to the rubber compounds, tires contain reinforcing fillers, fiber, extenders, and vulcanizing agents. This leads to a very complicated reaction system that leads to long burnout times which can result in particulate matter and PAH generation.

As a result of legislative action, such as the 1990 Clean Air Act Amendment on Air Toxics, there is a growing need to establish the identities and levels of trace byproducts that are formed in the combustion of tires. Of particular concern are the formation of aromatics and polycyclic aromatic hydrocarbon (PAH), because of their potential adverse health effects. Many PAHs are known to be toxic, mutagenic and carcinogenic, and their release is of great environmental concern. PAHs also have been shown to be a factor on DNA damage, cause single strand DNA breakage in human T-and B-lymphocytes and granulocytes. Other case studies have shown a connection between PAH exposure in the manufacturing industry and skin cancer incidents.

The major sources of PAH emission are the processes of incomplete combustion. Over the past years, there has been great interest in mechanism of PAH and soot formation in combustion, and considerable progress has been made in our understanding of these processes. As legislation moves to control smaller particulate matter, such as PM2.5, there will be an increased need to understand the growth mechanisms for various combustion and gasification processes.

PAH formation mechanisms have been extensively studied in the past for a range of hydrocarbon fuels, leading to a few well known reaction pathways. Frenklach and co-workers studied acetylene combustion and developed the C2 reaction sequence toward PAH formation. Bittner and Howard also developed a similar hydrogen abstraction-acetylene addition (HACA) scheme looking at C2 and C3 fuels. Marinov has postulated propargyl consumption by H atoms as an important reaction step that limits aromatic and PAH growth. While there has been considerable progress, most of the mechanistic work done was for the combustion of gaseous hydrocarbon fuels.

In terms of solid fuels, there has been
little experimental work and no mechanistic work to our knowledge that attempts to quantify and understand the mechanistic routes to PAH formation. There has been some previous work done using waste tires that show PAH identities measured from combustion systems[1, 20, 21, 22, 23, 24]. However, those studies do not explore the possible sources and routes that lead to PAH formation.

This study is to quantify the release of the PAH from SBR and to gain insight into the reaction mechanism that leads to PAH production and growth. The identification and quantification has been determined experimentally using GC/MS coupled to TGA unit. The absolute concentrations of 32 major and minor species also have been determined simultaneously. Moreover, these measurements can supply information on the identities and levels of hazardous air pollutants, and provide useful new data for the development and validation of detailed reaction mechanisms describing PAH origin and fate.

EXPERIMENTAL

All experiments were done using a Netzsch STA 409 PC/4/H thermo-gravimetric Analysis unit capable of TG and differential thermal analysis (DTA) measurements. The apparatus is computer controlled using Netzsch software for continuous data acquisition and control. The temperature ramp rates were provided as input to the software which then controlled a furnace to achieve the heating rates used for these tests. Those heating rates were 20K/min over a temperature range from ambient to 773K. In addition, all data is digitally recorded and S-type thermocouple readings are compared to target temperature and time.

The gases used for the experiments were ultra high purity and purchased through T.W. Smith (New York). The flow rates were set using calibrated Gimont (02911-02930) flow meters properly scaled for the experimental ranges. The TGA apparatus has two inlet ports, one for a protective gas of pure nitrogen that shrouds the balance mechanism from any heat or effluent gases and was set at a flow rate of 20ml/min. The second port was used for introducing the gas mixture of interest to provide the desired atmosphere during the experiment. The flow rate of the atmosphere inlet was 80ml/min; this combined with 20ml/min protective gas flow to yield a 100ml/min total flow past the test sample that was maintained for all experiments done. In addition to flow meter calibration for each gas, once GC sample were taken to ensure the proper gas ratio were obtained and matched the flow meters. Typically the GC measurements matched the flow meter settings within a few percent. The effluent of the TGA was sent to either a micro-GC (Agilent 4000) or a GC/MS (Agilent 9890/5973) for identifications and quantification of chemical species from TGA. The sampling system, which including transfer lines, was maintained over 300°C using Omega heat tape to minimize the condensation and/or adsorption of PAHs on surfaces[25].

The GC was equipped with a capillary column (0.25mm × 30m HP-5MS) which was directly interfaced to a quadrupole mass spectrometer. Identification of species were accomplished by matching both the gas
chromatographic retention times to pure components and mass spectral fragmentation patterns to standard MS libraries. Species concentrations were determined by multi-level calibrations using Restek PAHs (31264/610 PAH Calibration Mix A) standard and Sigma Aldrich aromatic standard (Supelco 44587).

The high-purity SBR test sample was purchased from Sigma-Aldrich Chemicals (St. Louis) in a granular form ranging in sizes between 180 and 200 mesh. Initial test sample weights were typically between 10mg as samples came from that same batch. Prior to each test, a baseline run was done for each sample mixture. This baseline is then used to subtract the changes of sample carrier system due to the buoyancy changes of the gas mixture as temperatures were changed.

RESULT AND DISCUSSION

The first experiments were carried out in a pure nitrogen atmosphere to determine the thermal degradation and ascertain whether any residual remained in the crucible. The residual mass was measured electromechanically. The thermal degradation rate and final masses were in agreement with Oh et al[7, 26] and Chen et al.[27] who investigated SBR in inert atmospheres using TGA.

As seen in Figure 1, slower temperature rates led to more mass loss at any given temperature due to longer reaction time. However, all final mass conversion reached 99.9% or greater. Post test inspection of the crucible did not show any sign of residual material. It can therefore be concluded that the SBR samples were pure and only contained the one co-polymer.

![Fig.1. TG and DTG curves for the SBR sample in N₂ atmosphere at various heating rates](image)

As can be seen in the figure there is a lateral shift in thermograms with respect to the heating rates. The temperature where the maximum rate of weight loss occurs, as evidenced by a peak in the DTA curves, shifts toward higher values as the heating rate is increased. This lateral shift is caused by the combination of time and temperature[28]. The higher heating rates provide less time for the sample to react thus causing a shift in maximum weight loss. This effect is commonly observed when using TGA. The slight asymmetry can be explained by a possible change in reaction order during experimentation, which likely indicates a change in mechanistic behavior. Previous work done by the authors have attempted to explain the change in mechanism occurring at various oxygen reaction atmospheres and hydrogen spiked atmospheres[29].

The structure of the SBR molecule has been assembled using the SPARTAN® interface to the MOPAC® program. The simulation has been carried out to get preliminary information including electron density, LUMO(Lowest Unoccupied Molecular Orbit), and
HOMO (Highest Occupied Molecular Orbit) using equilibrium geometry based on Hartree-Fock approximations using the 3-21G method. The results of the calculations enable generation of electron densities along the molecule, thus identifying likely reaction sites. The shapes and locations of the orbitals can be used to provide information about bonding within the molecule. Often, the HOMO and LUMO are used to help understand reactivity, and the energy difference between these two orbitals is often used as an approximation of the ease with which the molecule might be exited. For example, the HOMO is the orbital that could act as an electron donor, since it is the outermost (highest energy) orbital containing electrons. The LUMO is the orbital that could act as the electron acceptor, since it is the innermost (lowest energy) orbital that has room to accept electrons.

Figure 2. Chemical structure of SBR; 25% styrene, 75% butadiene linked co-polymer

Figure 2 shows the chemical structure of a unit of the SBR polymer molecule, with an optimized equilibrium state geometry showing the LUMO and HOMO electron densities. Characterizing the SBR structure as having a butadiene base with an aromatic ligand, one can use the electron density calculations as a guide to the likely first reactions that will occur. In addition, relative bond dissociation energies indicate that the likely first scission reactions are between the aromatic ligand carbon and the butadiene base carbon. This suggests that the first reactions during the thermal breakdown of SBR will be the release of an aromatic radical.

Evidence of this mechanism is found in the gas phase measurements taken during the temperature programmed reactions occurring in a nitrogen atmosphere. Figure 3 shows the concentrations (reported as ppmv including figure below) of methane, ethylene, hydrogen and n-butane. It should be noted that the observed concentrations are after dilution of the purge gas from the TGA. It is clear that the evolution of n-butane is produced from cleavage of the SBR base followed by hydrogenation.

Figure 3. Effluent concentration versus temperature in N₂ atmosphere

The concentration of hydrogen is significantly lower and begins to form after the n-butane concentration begins to decline. This is consistent with the hydrogenation mechanism (i.e. Hydrogenation is a chemical reaction in which unsaturated bonds between carbon atoms are reduced by attachment of a hydrogen atom to each carbon), that is, as less butane is formed...
there is more free hydrogen produced during the thermal breakdown of SBR. Other evidence of the initial scission that occurs is other light species, such as acetylene, methyl acetylene, hexane, were observed, at significantly lower levels.

Additional observations show the production and evolution of substituted aromatic and fused aromatic ring species. Substituted aromatics provide evidence of aromatic ligand scission (i.e. bond breakage between the aliphatic backbone and the substituted aromatic. In this case, the substituted aromatic is considered the ligand) followed by gas phase addition reactions. This is further corroborated by the detection of multiple fused ring PAH species, which can only occur in the gas phase after the aromatic ligand from the butadiene base has been released.

As evidenced in Figure 4-A, B, several substituted aromatic compounds were formed as a function of temperature. Among the substituted aromatics, concentrations of toluene and ethyl benzene are dominant. These are probably formed from a gas phase addition reaction, since they are not observed until nearly 400°C, where there is enough energy to also decompose the butadiene base. Also of interest is the comparison of the temperatures where the maximum concentrations occur between Figure 3 and Figure 4. For instance, the substituted aromatic concentration reached their maximum at a higher temperature than light hydrocarbons do. Again indicating gas phase addition reactions occurring where light hydrocarbons are combining with the aromatic ligand released from the SBR base. This shift in maximum concentration with temperature is also observed in the formation of higher order PAH species seen in Figure 5.

Even though Figure 4 shows major species among the substituted aromatic compound, other minor substitute aromatic compound also were observed but a clear trend could not be currently discerned. These species are reported in Table 1. To put the measurements of the TGA into context the concentrations were normalized to the amount of test sample used (approx. 3 mg). GC/MS measurements provide concentration values based on the volume of sample taken. In the current setup that sample includes a large amount of dilution gas. Therefore to better indicate the level of PAH production the concentrations were normalized based on the sample mass. Since the dilution gas and test gas were constant, any change in initial sample mass would lead to a commensurate change in product species.
concentration to allow comparisons to be made all.
All measurements were normalized for the amount of initial sample used. The first column shows the normalized concentration, and the second column shows a projected amount that each compound could be found in a gasification plant or the pyrolysis section of a combustor that would process 1.5 metric tons of waste tires per hour. While it is unlikely that the amounts calculated would persist through a combustion chamber unchanged, it is very possible that a significant fraction would not be oxidized completely, thus leading to emissions of PAH species or possible formation of dioxins.

**Table 1. Summary of substituted aromatic concentration**

<table>
<thead>
<tr>
<th>Substituted Aromatic Species</th>
<th>concentration [ppmv/mg sample]</th>
<th>Pyrolysis [g/hr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Toluene</td>
<td>11.54</td>
<td>1593</td>
</tr>
<tr>
<td>Ethyl-Benzene</td>
<td>9.69</td>
<td>1541</td>
</tr>
<tr>
<td>Propyl-Benzene</td>
<td>2.43</td>
<td>437</td>
</tr>
<tr>
<td>1-ethyl-4-methyl-Benzene</td>
<td>0.07</td>
<td>13</td>
</tr>
<tr>
<td>1-methyl-1-methyl-Benzene</td>
<td>0.11</td>
<td>20</td>
</tr>
<tr>
<td>1-methyl-2-propyl-Benzene</td>
<td>0.04</td>
<td>8</td>
</tr>
<tr>
<td>Butyl-Benzene</td>
<td>0.21</td>
<td>42</td>
</tr>
<tr>
<td>1,2-diethyl-Benzene</td>
<td>0.11</td>
<td>22</td>
</tr>
<tr>
<td>1-methyl-4-propyl-Benzene</td>
<td>0.12</td>
<td>24</td>
</tr>
<tr>
<td>4-ethyl-1,2-diethyl-Benzene</td>
<td>0.11</td>
<td>22</td>
</tr>
<tr>
<td>2-methylbutyl-Benzene</td>
<td>0.31</td>
<td>69</td>
</tr>
<tr>
<td>Pentyl-Benzene</td>
<td>0.28</td>
<td>62</td>
</tr>
<tr>
<td>1,3,5-triethyl-Benzene</td>
<td>0.05</td>
<td>13</td>
</tr>
<tr>
<td>1,2,4-triethyl-Benzene</td>
<td>0.16</td>
<td>40</td>
</tr>
</tbody>
</table>

**Figure 5.** PAHs concentration versus temperature

The concentration profiles as a function of temperature of PAHs from 2 rings to 6 rings, such as naphthalene, anthracene, pyrene, and benzo[g,h,i]perylene, are shown in Figure 5. Such a short residence time in the TGA reaction regime, the most probable growth mechanism for the higher PAHs is aromatic combustion reactions. This provides further evidence of gas phase addition reactions where the SBR ligands as well as the butadiene fragments combine to produce higher order PAHs.

Of particular interest is that the 3 and 4 ring PAHs, such as anthracene and pyrene concentration is comparable to naphthalene. Of PAHs evolution, definitely concentration of naphthalene should be dominant in lower temperature range. Our work shows that that the concentration of pyrene reaches the maximum concentration in relatively lower temperature range. Furthermore, the concentration of anthracene show higher concentration than naphthalene does. Thus, it can be postulated that highly concentrated substituted aromatic compounds recombine through another mechanism that does not include naphthalene as an intermediate species. This is likely the
cleavage of the butadiene base with the aromatic ligand still attached.

The normalized concentrations are used due to different weight samples. The other PAHs observed from experiments and the normalized concentrations were shown in Table 1. The second column value shows each PAH mass per unit hour in pyrolysis plant, which assumed 1.5ton/hr feeding rate\[30, 31\].

Table 2. summary of PAH concentration

<table>
<thead>
<tr>
<th>PAH Species</th>
<th>Concentration [ppmv/mg sa]</th>
<th>Pyrolysis [g/hr]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzo[ghij]perylene</td>
<td>0.19</td>
<td>79</td>
</tr>
<tr>
<td>Dibenz[a,h]anthracene</td>
<td>0.14</td>
<td>58</td>
</tr>
<tr>
<td>Indeno[1,2,3-cd]pyrene</td>
<td>0.16</td>
<td>66</td>
</tr>
<tr>
<td>Benzo[a]pyrene</td>
<td>0.92</td>
<td>348</td>
</tr>
<tr>
<td>Benzo[k]fluoranthene</td>
<td>0.05</td>
<td>19</td>
</tr>
<tr>
<td>Benzo[a]fluoranthene</td>
<td>0.20</td>
<td>762</td>
</tr>
<tr>
<td>Chrysene</td>
<td>0.57</td>
<td>195</td>
</tr>
<tr>
<td>Benz[a]anthracene</td>
<td>0.84</td>
<td>287</td>
</tr>
<tr>
<td>Pyrene</td>
<td>0.67</td>
<td>203</td>
</tr>
<tr>
<td>Fluoranthene</td>
<td>0.39</td>
<td>118</td>
</tr>
<tr>
<td>Anthracene</td>
<td>1.40</td>
<td>374</td>
</tr>
<tr>
<td>Phenanthrene</td>
<td>0.51</td>
<td>136</td>
</tr>
<tr>
<td>Fluorene</td>
<td>0.96</td>
<td>239</td>
</tr>
<tr>
<td>Acenaphthene</td>
<td>1.50</td>
<td>347</td>
</tr>
<tr>
<td>Acenaphthylene</td>
<td>0.84</td>
<td>192</td>
</tr>
<tr>
<td>Naphthalene</td>
<td>1.23</td>
<td>236</td>
</tr>
</tbody>
</table>

Conclusion

Measurements taken from a series of experiments simulating a waste tire gasification process or a pyrolysis section of a combustor show the potential to form significant amounts of PAH. In addition, the evolution of light hydrocarbon species, such as methane and n-butane, 14 substituted aromatic compounds, and 16 PAHs were identified and quantified. Molecular orbital energy calculations combined with species concentration profiles provide insight into a possible SBR breakdown mechanism and likely steps for PAH formation and growth.

With regard to the SBR chemical structure, PAHs formation is caused by addition of the substituted aromatic compounds. In addition, the 3 and 4 ring PAHs, such as anthracene and pyrene, had a higher concentration than naphthalene did giving further insight into the mechanism of SBR decomposition. Furthermore, the maximum concentration of the 3 and 4 ring PAHs occur at a relatively lower temperature than naphthalene did. This indicates that PAH formation from SBR has a tendency toward creating the multiple fused ring PAHs in a non-oxidizing environment.

Reference

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17. J. D. Bittner, J. B. Howard and H. B. Palmer, Chemistry of intermediate species in the rich combustion of benzene, NATO Conference


