Polycyclic Aromatic Hydrocarbon (PAH) Formation in Thermal Degradation of Styrene Butadiene Copolymer (SBR)

Elilhann Kwon & Marco J. Castaldi
Department of Earth and Environmental Engineering.
Henry Krumb School of Mines, Columbia University

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 Spectrometry (GC/MS) coupled to Thermo-Gra-dimetric Analysis (TGA) units. SBR samples were pyrolyzed 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, CH₄, C₂H₆, C₃H₈, 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 CoH₄s (molecular weight 362), benzol[ghi]pentylene, with peak concentrations reaching 0.19 ppmv. The effluent samples 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 hazards at air pollutants, and provide useful new data for the development and validation of detailed reaction mechanisms describing their origin and fate.

Experimental Setup

Effluent concentration versus temperature in N₂ atmosphere

Results & Discussions

Concentration profiles as a function of temperature of PAHs

Summary of Substituted Aromatics and PAH Concentration

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 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. 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. 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.

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 benzol[ghi]perylen, are shown in Figure. 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 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 substituted aromatic compounds is responsible 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.