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An investigation of the thermal degradation mechanisms of a waste tire through chemical analysis including hydrocarbons, benzene derivatives, and Polycyclic Aromatic Hydrocarbons (PAHs) at high temperature

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ABSTRACT

Previous work has focused on a series of fundamental Thermal Gravimetric Analysis (TGA) studies using representative atmospheres found in Waste-to-Energy (WtE) boilers. Those studies were done for waste tires and their major constituents, such as Styrene-Butadiene Copolymer (SBR) and Poly-Isoprene (IR). The outcome has been the elucidation of the likely mechanism responsible for initial decomposition, final product and byproduct formation. To extend that understanding to a more practical level, a flow through apparatus has been used to test waste tire samples in the temperature range of 500°C-800°C. A chemical analysis in this temperature range has been performed to compare the thermal degradation mechanism and air pollutant generation in low temperature regimes. The release of chemicals from a tubular quartz reactor containing a tire sample has been determined experimentally using a GC/MS. Significant Volatile Organic Carbons (VOCs) including benzene derivatives, PAHs, and Hetero-N containing PAHs were observed. This study identifies and quantifies the concentration levels of various hazardous air pollutants, and provides new data for the overall development and validation of detailed reaction mechanisms that can describe the thermal degradation of waste tires. This information will enable the development of mitigation strategies that can address those levels of pollutant species.

KEYWORDS: Thermal degradation, Waste tire, Styrene Butadiene Rubber (SBR), Polyisoprene (IR (Natural Rubber: NR)), Waste-to-Energy, Volatile Organic Carbons (VOCs), Polycyclic Aromatic Hydrocarbons (PAHs), Hetero-N containing PAH

INTRODUCTION

A range of specialized components are used in a tire that serve to ensure the tire meets its intended design and performance requirements. Thus, direct reuse is limited without some form of chemical or thermal processing[1]. Considering a tire generation rate of 280 million per year in the U.S., waste tires can serve as a source of high quality fuel, having a high calorific value that is roughly similar to that of coal[2, 3]. However, their heterogeneity creates issues with regard to complete burnout and emissions. To accommodate these alternative feedstocks, various processes have been resurrected and modified, such as gasification and oxy-fuel combustion.

Considerable study has been done investigating the overall gasification process behavior in reactors [4-9] and studying the thermal and kinetic behavior of tire particle via the TGA tests[10-14]. Experimental work done by TGA shows much more precise and reliable data due to its ability to tightly control temperature and monitor mass change. However, the TGA test has intrinsic drawbacks due to limited heating rates, thus complimentary studies via more realistic reactor conditions need to be done. Despite this, the TGA is an excellent apparatus to

understand thermal degradation and air pollutant generation mechanisms of tires due to their heterogeneous constituents; constituents like reinforcing filler, fiber, and extenders with various rubbers, such as NR, Butyl Rubber (BR), and SBR[11, 15, 16].

Previous work related to utilizing waste tires to recover energy and useful chemicals has been focused on pyrolysis/gasification and combustion at various oxygen concentrations at relatively low temperatures between 300°C and 500°C [17-23]. Previous work shows that most bond cleavage on monomers of main constituents is followed by hydrogenation/dehydrogenation. The substituted aromatics appear to have been formed by gas phase addition reactions and this confirmation has been carried out with structural isomers to elucidate hierarchical growing steps of substituted aromatics. Tire samples already contain a benzene ligand monomer and are a very likely precursor of PAH formation. This molecular structure likely accelerates the PAH formation during thermal conversion of tires.

To extend that understanding to a more practical level, a flow through apparatus has been used to test waste tire samples in the temperature range of

500°C-800°C. The chemical release from a tubular quartz reactor containing a tire sample has been determined experimentally using a GC/MS in a nitrogen atmosphere. The absolute concentrations of 50 major and minor species also have been determined during the thermal conversion process of tire samples. Significant VOCs including benzene derivatives, PAHs, and Hetero-N containing PAHs were observed.

The objectives of this work are to identify and quantify the concentration levels of various hazardous air pollutants released from the combustion of waste tires. Additionally, the high temperature and low temperature thermal degradation mechanisms are compared. Thus, this work provides new data for the overall development and validation of detailed reaction mechanisms that can describe the thermal degradation of waste tires.

EXPERIMENTAL

All of the experiments were done using a vertical tubular reactor shown in Figure 1, made of ¼ inch OD quartz tubing (Chemglass ® CGQ-0800T-13); ¼ inch Stainless Ultra-Torr® Vacuum Fitting (Swagelok SS-4-UT-6-400) was used in order to maintain airtight connections. Experimental temperature was achieved using a split-hinged furnace (Multiple Unit, Hevi Duty Electric Company) over a temperature range from 500°C to 900°C and the temperature was simultaneously compared with a K-type thermocouple to ensure the target temperature was met.

The tire sample was filed into small pieces. Initial test sample weights were 10mg and all samples were loaded into the center of the tubular reactor. In order to hold the filed tire sample, a quartz-fritted disk (Chemglass ® CGQ-0207-03) was used.

The gases used for the experiments were ultra high purity, purchased from TechAir and flow rates were set using a Aalborg thermal mass flow controller (GFCS-010378). The purge gas (N₂) flow rate was maintained at 100ml/min for all experiments. The effluent from the tubular reactor was sent to the GC/MS (Agilent 9890/5973) for identification and quantification of chemical species. The injection block of the GC/MS contains a 10 port valve system and a 6 valve system (Valco Custom Valves Houston TX.) The sampling system, which includes the transfer lines coupled to a vacuum pump, was maintained over 300°C using Omega heating tape (STR-101 series) to mitigate the condensation and/or adsorption of PAHs onto the surface.

The GC was equipped with a capillary column (0.25mm×30m HP-5MS), which directly interfaced to a quadrupole mass spectrometer. Identification of species was accomplished by matching species retention times to those of the pure components. Multi-level calibrations were completed using Restek PAH standard (Lot #A03448), Supelco Alphagaz PIANO calibration standard (Lot #2102), and Supelco Japanese Indoor gas standard (Lot #4M7537-U).

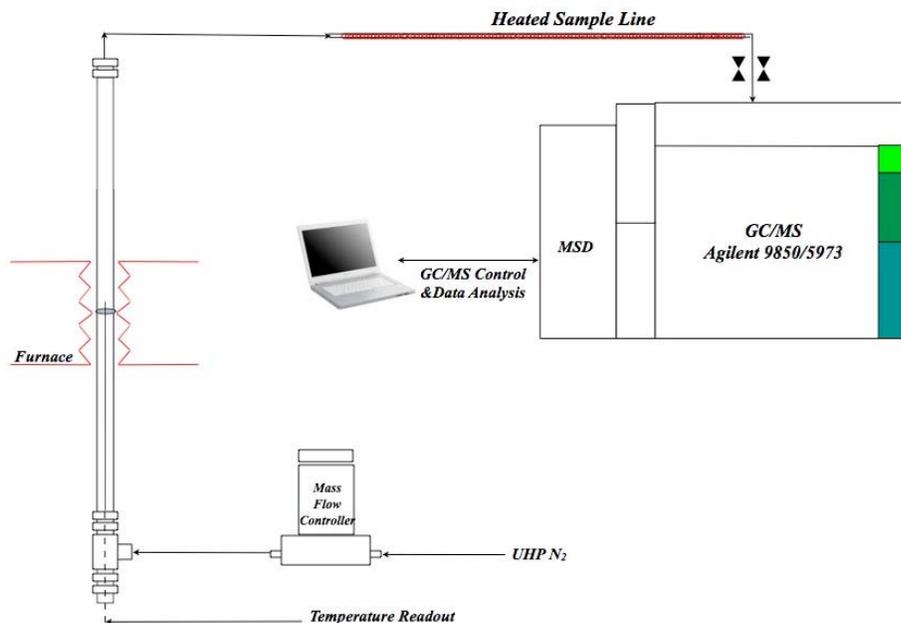


Figure 1. Entire experiment setup for high temperature thermal degradation

RESULTS AND DISCUSSION

The representative data from a series of the TGA tests with waste tires under the condition of 10°C/min heating rate over a temperature range from ambient to 1000°C in various atmospheres were shown in Figure 2.

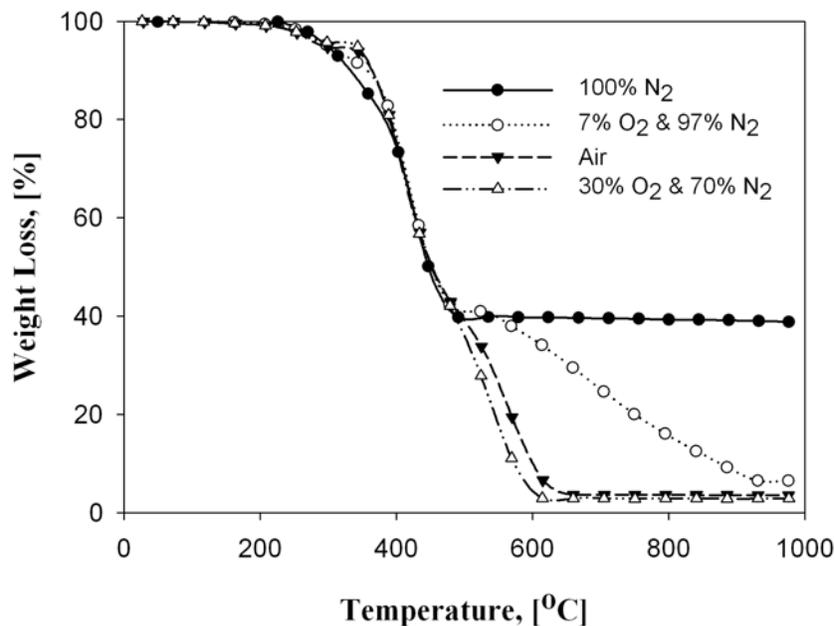


Figure 2. Thermograms of a waste tire in various atmospheres

The previous work confirmed that the thermal decomposition of a waste tire has two main steps when oxygen is present. First, the thermal decomposition of waste tires below 500°C gives off volatile organic products. Second, the thermal degradation above 500°C shows mainly combustion behavior (i.e. CO₂ and H₂O as main products), and its reaction is relatively simple compared to the first step of the thermal degradation of a waste tire. Thus, the thermal degradation mechanisms of waste tires have been investigated over the temperature range from 300°C to 500°C in various atmospheres with GC/MS analysis, which confirmed the bond scission on each monomer followed by hydrogenation/dehydrogenation and some chemical species recombined by gas phase reactions.

As shown in Figure 2, more complete mass loss is observed as the amount of oxygen is increased and a significant amount of unreacted residual was observed in the pure N₂ atmosphere. In the previous work done by author, EDX analysis was done on the residuals to determine the amount of carbon that remained. In addition, low levels of other elements, such as Zn and Fe, were detected yet a trend could not be discerned.

The experimental work done with the TGA unit in Figure 2 did not reflect a real condition for gasification or combustion process in that an actual combustor is usually operated at high temperature gradients. It is imperative that the experimental work at high temperature should be done to simulate real thermal processes such as gasification and combustion process. Consequently, the thermal degradation of waste tires between 500°C and 800°C has been investigated with a vertical tubular reactor in N₂ atmosphere.

To investigate more detailed thermal decomposition at high temperatures, the GC/MS measurement has been carried out with effluent from a tubular reactor. A representative chromatogram from a tire at 600°C in a nitrogen atmosphere is shown in Figure 3 and identified chemical species have been labeled with numbers. All of the chemical species labeled in Figure 3 are summarized in Table 1.

Major chemical species identified in the previous work, done between 300°C and 500°C, were C₄₋₅ hydrocarbons (n-Butane, But-1-ene, 1,3-Butadiene, Pentane, 1-Pentene, 1,3-Pentadiene, and Isoprene.) In the high temperature experiments, n-Butane, But-1-ene, 1,3-Butadiene and Isoprene were not observed. This observation was explained by a

certain reaction, such as the *Diels-Alder reaction*, that used up saturated and unsaturated C₄ hydrocarbons and Isoprene; thus, this may lead to more favorable condition for generating chemical species having a benzene ring.

Similar to the previous low temperature work, chemical species summarized in Table 1 indicate that there were hydrogenation or dehydrogenation reactions. For example, hydrocarbons having a C₅₋₆ backbone summarized in Table 1 showed all possible bonds in terms of unsaturated and saturated carbon.

Significant sulfur in a tire is mostly observed as a form of heterocyclic compounds such as Thiophene or Benzothiazole. One interesting feature is the observation of Pentyl-Thiophene in that this chemical species was not detected in the previous

work and the bond scission pattern was different at high temperature. For example, the bond scission pattern at high temperature pyrolysis may occur more irregularly. One interesting feature in the high temperature pyrolysis is the presence of hetero-N containing PAHs, chemical species not observed in the low temperature work. The detailed information on heterocyclic compounds will be discussed later.

Bond scission followed by hydrogenation/dehydrogenation and gas phase additions can cause various gas phase precursors that lead to favorable conditions for generating air pollutants such as VOCs and PAHs. Methyl addition through gas phase reaction, caused by more complex bond scission, provides more chances to generate various chemical species.

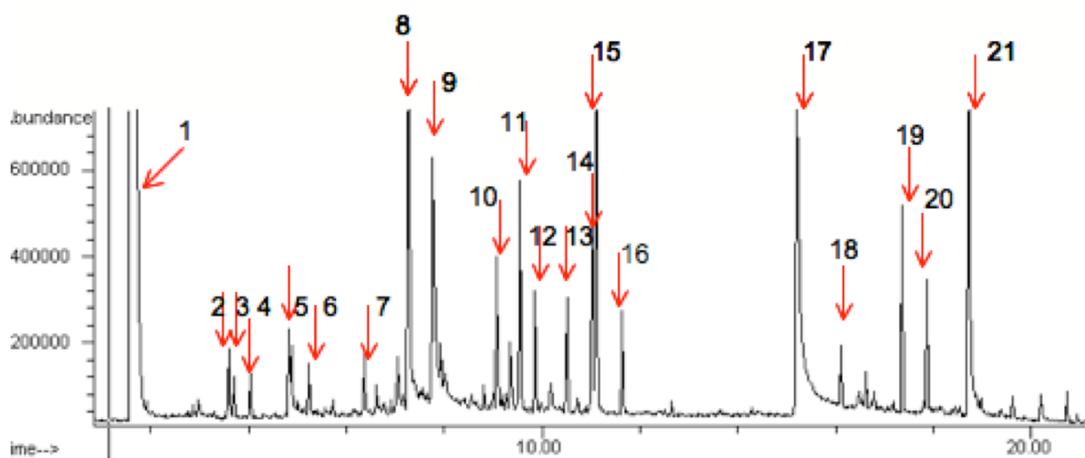


Figure 3. Chromatogram of pyrolysis of a tire sample at 600°C

Table 1. Identified chemical species in the chromatogram from the pyrolysis of a tire at 600°C

#	Chemical Species	#	Chemical Species
1	Nitrogen (Purge Gas)	2	2,4-dimethyl-1,3-pentadiene
3	2,4,4-trimethyl-1-pentene	4	2,4,4-trimethyl-2-pentene
5	Toluene	6	2,2,4-trimethyl-hexane
7	4-methyl-1,3-heptadiene	8	4-ethenyl-cyclohexene
9	Ethylbenzene	10	2,5-dimethyl-2,4-hexadiene
11	Styrene	12	2,5,5-trimethyl-1-hexen-3-yne
13	2-pentyl-thiophene	14	2,2,4-trimethyl-pentane
15	Limonene	16	1,1-dimethyl-cyclohexane
17	Benzothiazole	18	1-methyl-1-propene
19	4-octene	20	Azomycin
21	2,4-dimethyl-quinoline		

The previous work with waste tires and their main constituents, such as SBR and IR, showed that

the most apparent chemical species identified and quantified during the pyrolysis process between 300°C

and 500°C were Styrene and Limonene, which directly derived from SBR and IR, respectively. Like the previous result, the amount of Styrene and Limonene was significant during pyrolysis process at

high temperature and the concentration of Styrene and Limonene observed at 600°C from a tire, SBR, and IR was shown in Figure 4.

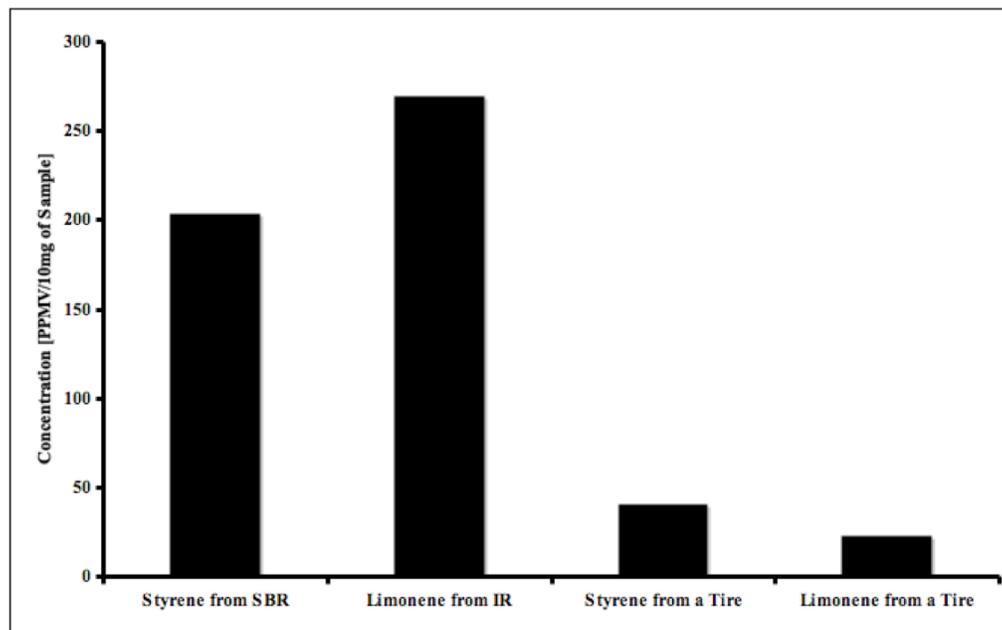


Figure 4. Concentration of Styrene and Limonene from the pyrolysis of a tire, SBR, and IR in N₂ at 600°C

As shown in Figure 4, the concentration of Styrene and Limonene from the pyrolysis process of SBR and IR reached approximately 210 and 270 PPMV/10mg of sample respectively. In addition, the concentrations of these chemical species from the pyrolysis of tires were apparently lower level due to 40% black carbon as evidenced in Figure 2 and the previous work.

The chemical species, identified from the pyrolysis process with a tire, SBR, and IR at high temperature, were not much different compared to the previous work in terms of main mechanisms such as bond scission followed by hydrogenation or dehydrogenation and gas phase reaction. All chemical species observed from the previous work were also detected at high temperatures and these identified and quantified chemical species at 600°C and 800°C are shown in Figure 5. However, one interesting feature in Figure 5 is the concentrated Phenyl-C_{5,6} species; as their concentrations were not significant in the low temperature work. For example, the concentration of n-Pentyl-Benzene was more than that of Toluene. The concentrated n-Pentyl-Benzene suggests that the generation of n-Pentyl-Benzene derived not only from recombination by gas phase reaction but also from

direct bond scission from the main backbone of polymer in a tire.

As stated before, the detection of heterocyclic compounds was not observed in the previous work. As shown in Table 1, 2,4-dimethyl-Quinoline, and Benzothiazole were identified during pyrolysis process of tires at high temperature. In addition, Carbazole was also identified during the pyrolysis of a tire at high temperature.

Observation of these heterocyclic compounds could be explained in two ways: first, the sample used for experimental work contains in its matrix; second, the nitrogen source could be derived from the nitrogen purge gas. To confirm this, the chemical effluent from the pyrolysis of SBR and IR at 600°C was investigated with the GC/MS with samples comprised of only carbon and hydrocarbon.

The GC/MS measurement with chemical effluent from the pyrolysis of IR at 600°C did not show any heterocyclic compounds, but 1-Benzyl-1,2,3-triazole was identified from the effluent of the SBR sample. The observation of 1-Benzyl-1,2,3-triazole postulated that the nitrogen source for heterocyclic hydrocarbons came from the N₂ purge gas. For example, the nitrogen purge gas attributed to the reaction with radical such as C, CH, and CH₂

fragments from the pyrolysis of SBR at 600°C. All identified heterocyclic compounds are shown in Figure in 6.

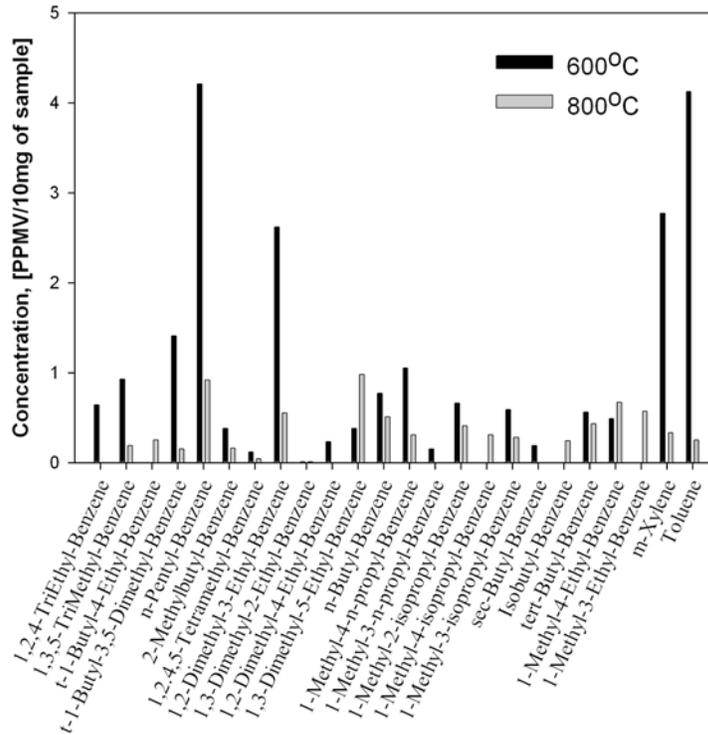


Figure 5. Identified benzene derivative from the pyrolysis process from a tire at 600°C and 800°C

Thus, other heterocyclic compounds identified during the pyrolysis of a tire were also generated by recombination between the radical fragments by bond scission and the nitrogen purge

gas. One interesting feature was that all chemical species containing nitrogen atoms in their chemical formula had benzene rings due to relative stability.

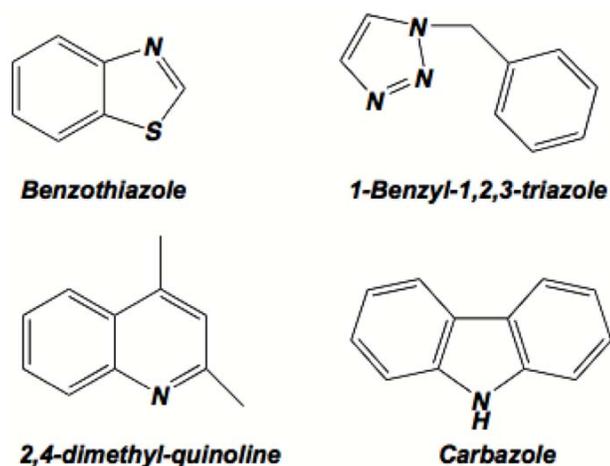


Figure 6. Identified heterocyclic aromatic compounds

As stated above, two main thermal degradation mechanisms by bond scission and gas phase reaction provide a favorable condition for PAH generation. The concentration of identified PAHs species from molecular weights of 128 to 276 from the pyrolysis of a tire, SBR, and IR at 600°C is shown in Figure 7. All PAHs shown in Figure 7 were the same as those in previous work done by the author.

The concentration profiles of PAHs were not shown due to an indiscernible trend. These particular pathways of aromatic derivatives show a robust preference for PAH generation because there are multiple routes where benzene and other substituted aromatics can be created. The mitigation of benzene derivatives is the most feasible way to prevent PAH formation.

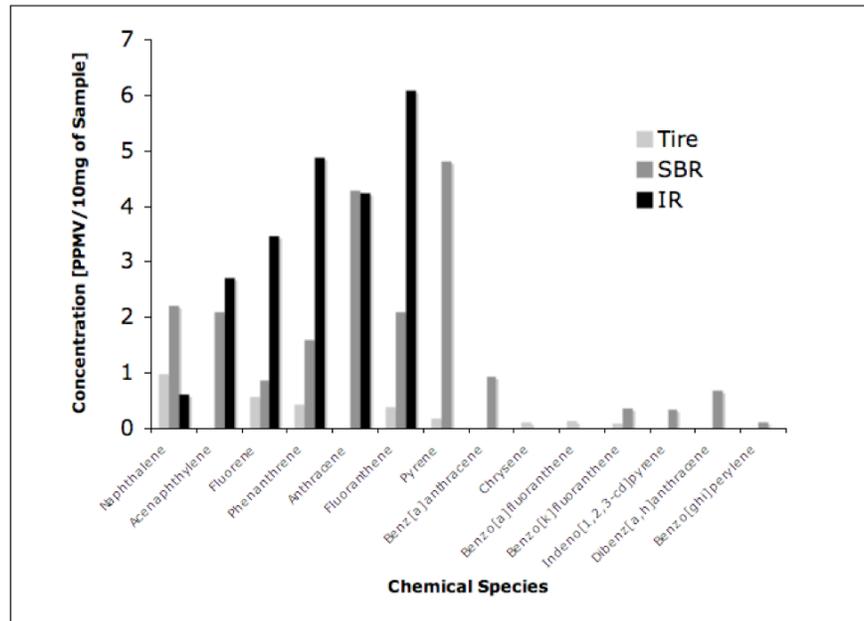


Figure 7. Concentration of PAHs at 600°C

CONCLUSION

The GC/MS measurement from a tubular reactor with waste tires has been carried out to characterize the thermal decomposition by the

pyrolysis process at high temperature. The thermal degradation mechanism of waste tires was bond scission on polymer followed by hydrogenation and recombination by gas phase reaction. However, bond

scissions on polymers of waste tires were irregular, which leads to a variety of chemical species. This triggered to formation of benzene derivatives as a precursor of PAH formation. Lastly, the radical fragments from the bond scission at high temperature reacted with a nitrogen used for a purge gas and then formed the heterocyclic aromatic compounds.

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