Investigation of Thermo-Gravimetric Analysis (TGA) on Waste Tires and Chemical Analysis Including Light Hydrocarbons, Substituted Aromatics, and Polycyclic Aromatic Hydrocarbon (PAH)

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ABSTRACT
This investigation has been initiated to characterize the thermal decomposition of waste tires with Thermo-Gravimetric Analysis (TGA) in various atmospheres ranging in oxygen content; 100% N₂, 7%, 21% (air) and 30% O₂. Chemical analysis focusing on light hydrocarbons, substituted aromatics, and polycyclic aromatic hydrocarbon has been done qualitatively and quantitatively to understand the mechanism of thermal degradation of scrap tires and hazardous air pollutants such as PAH. The release of chemicals from scrap tires has been determined experimentally using Gas Chromatography/Mass Spectroscopy (GC/MS) coupled to TGA unit. The identities and absolute concentrations of over 50 major and minor species have been established. Significant volatile organic carbons (VOC) including substituted aromatics and PAH were observed between 300°C and 500°C. In addition, significant black carbon residual was observed in most environments except air and oxygen enhanced atmospheres and suggested not only the potential recovery of black carbon out of feedstock, but also the possibility of combined thermal treatment between combustion and gasification. These 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. Finally, while high contents of VOC show significant potential to be utilized as an unconventional solid fuel, they also tend to generate hazardous pollutants.


INTRODUCTION
Based on an Environmental Protection Agency (EPA) report at the end of 2003, the U.S. yielded roughly 290 million waste tires. The estimated number of waste tires in stockpiles in U.S. was 700 to 800 million. Since that time, millions of tires have been removed from stockpiles, primarily due to aggressive cleanup through state scrap tire management programs. For example, Minnesota, Wisconsin, and Maryland are three states, which report having cleaned up all scrap tire stockpiles, however a significant amount remains. In view of the push to find alternative energy sources to reduce dependence on fossil fuels, waste tires serve as a source of high quality fuel, having a high caloric value that is roughly similar to that of coal, yet their heterogeneity poses issues with regard to complete burnout and emissions [1].

Tires contain reinforcing filler, fiber, and extenders with various rubbers, such as natural rubber (Poly-Isoprene: IR), Butyl Rubber, and Styrene-Butadiene Rubber (SBR) [2, 3] to improve the physicochemical properties leading to long operational life, high performance and safety. However, it is this same mix of constituents which impedes the direct reuse in other applications and lead to complex conditions during thermal conversion. Moreover, the different content in mineral matter and sulfur which tire shows is lower than that of coal, making this fuel more desirable from a direct emission of SOx standpoint. In addition, their low moisture and fuel-bound nitrogen content positions waste tires well for recovering energy as an end use [4-9].

Previous work related to utilizing waste tires to recover energy has been focused on pyrolysis/gasification, and limited research on tire combustion has been carried out due to its heterogeneity which gives rise to a poor understanding of the decomposition mechanisms and the ultimate production and rate of emissions during the combustion. A considerable amount of work has been done to understand the degradation process of waste tires both fundamentally and at an overall process level [10]. Several investigations have been done using isothermal and non-isothermal methods to obtain the necessary kinetic parameters that are needed for combustor development [11-17]. Most of
the work to date has attempted to model the thermal breakdown of the constituents of tires by using an overall rate expression which is usually first order [13, 18]. That work enables good general models to be developed for combustor design and process development.

Of particular concern are the formations of substituted aromatics and Polycyclic Aromatic Hydrocarbons (PAHs) due to their adverse health effects. Many PAHs are known to be toxic, mutagenic and carcinogenic, and their release is of great environmental concern. The interest in the mechanism of PAH and soot formation has made considerable progress recently in the gas phase combustion arena. For example, PAH and soot growth occur via acetylene addition as the principal reaction pathway leading to naphthalene[19-21]. A similar hydrogen abstraction-acetylene addition (HACA) scheme was introduced by Bittner and Howard [22-25] with the difference that a second acetylene molecule adds to the first one, and then the formation of the additional ring takes place by ring closure reaction of the second acetylene with existed ring. Another finding that PAH and soot growth can exploit either a C2 or C3 mechanistic route has been shown for single carbon fuels and single carbon fuel fragments[26-28].

Only recently has work been done using waste tires which shows PAH identities, yet has little information on pathways that lead to the PAH detected[2, 29-33]. Tire samples already contain a benzene ligand monomer and are a very likely precursor of PAH formation. Butadiene is another constituent on the monomer and due to its stability becomes a significant intermediate during hydrocarbon combustion and undergoes continued reaction in the gas phase. This molecular structure likely accelerates the PAH formation during thermal conversion of tires[34, 35].

Experimental work has been carried out to characterize the thermal decomposition of the actual tire felling using Thermo-Gravimetric Analysis (TGA) coupled to Gas Chromatography/Mass Spectroscopy (GC/MS) in various atmospheres; 100% N2, air and oxygen-lean (7% O2) and rich (30% O2) air. The absolute concentrations of 50 major and minor species also have been determined during the thermal conversion process of tire samples.

**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 simultaneously. 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 that then controlled a furnace to achieve the heating rates used for these tests. Those heating rates were 10K/min over a temperature range from ambient to 500°C. In addition, all data is digitally recorded and S-type thermocouple readings are compared simultaneously to target temperature and time.

The gases used for the experiments were ultra high purity and purchased through Tech Air (New York). The flow rates were set using calibrated Gimont (02911-02930) flow meters properly scaled for the experimental ranges and Aalborg thermal mass flow controller (GFC5-010378) certified by Aalborg® Inc. 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 mass flow controllers. 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) using a valving system for identification and quantification of chemical species from TGA. The injection block of the GC/MS contains 10 port valve and 6 port valves (Valco Custom Valves Houston. TX.) The sampling system, which including transfer lines coupled to vacuum pump, was maintained over 300°C using Omega heat tape to mitigate the condensation and/or adsorption of PAHs on surfaces.

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 was 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 standard and Sigma Aldrich aromatic standard.

Topographical and structural information of the residuals was done using a Hitachi S4700 high resolution Scanning Electron Microscope Energy with dispersive X-ray spectroscopy in plane or cross sectional view. Used in conjunction with SEM, Energy Dispersive X-Ray Spectroscopy (EDX or EDS) detects the element present in a selected area of the SEM image providing qualitative and quantitative information.

The tire sample has been filed into small pieces. 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. Since the protective and purge gas flows were constant for all tests, differences in sample starting weight will yield different gas phase concentrations. Therefore, measured concentrations were normalized to a standard starting weight of solid sample to enable better comparisons.

**RESULTS & DISCUSSIONS**

The thermo-gram depicted in Figure 1 shows the representative data obtained from TGA experiments with a waste tire in pure nitrogen, air oxygen lean (7% O2) and oxygen rich (30% O2) atmospheres. These conditions were chosen to simulate real combustor conditions and explore the impacts of oxygen enhancement of the combustor.

As shown in Figure 1, four experiments were done at 10°C/min heating rate over a temperature range from ambient to 1000°C which corresponded to a range of weight changes. More complete mass loss was observed as the amount of
oxygen increased. Based on the weight change shown in Figure 1, temperatures below 300°C was not enough to initiate any observed thermal degradation reactions. In addition, the thermal decomposition rates in terms of slopes shown in the middle of Figure 1 were roughly the same for all atmospheres, thus independent of oxygen concentration. During this initial decomposition there is not only volatilization occurring but decomposition of the polymers is also occurring to a large extent as evidenced by the onset of PAH detection. More detailed information will be discussed later.

Figure 1. Thermo-gram of a waste tire in various atmospheres

A significant amount of unreacted residual was observed in the pure nitrogen atmosphere with less residual as the oxygen concentration increased. As shown in figure 2, SEM images of the residual in the air atmosphere were recorded. The size of and density of the residual is inversely proportional to temperature. This indicates that only at high temperatures can the oxygen react sufficiently with the solids.

EDX analysis was done on the residuals to determine the amount of carbon and Zn. Other minerals were detected at low levels and a trend could not be discerned. As tabulated in Table 1, main tire residual was a black carbon and one interesting feature of the residual in 100% N₂ atmosphere was to only have 19.03% zinc content remaining even though the boiling point of zinc based on NIST Web-Book database is 907°C[36].

As shown in Figure 1 and Table 1, the thermal decomposition of a waste tire has two main steps. First, the thermal decomposition of waste tires before 500°C gave off a miscellaneous volatile organic product and its reaction mechanism is quite complex. Second, the thermal degradation after 500°C showed mainly combustion behavior, and its reaction is relatively simple compared to first step of the thermal degradation of a waste tire.

To characterize and investigate more detailed thermal decomposition information GC/MS measurements were used to quantify the effluent of the TGA experiments. Major species have been reported[34, 35], there the focus here is on higher order hydrocarbons, specifically aromatics. The chemical species identified from GC/MS measurement in various atmospheres including N₂, air, and lean and rich air are summarized in Table 2. Due to the low concentrations as a result of significant amounts of dilution atmosphere and the sensitivity of the GC/MS concentration profiles could not be well characterized.

Table 1. EDX quantitative result of element of a tire residual

<table>
<thead>
<tr>
<th>ATMOSPHERE</th>
<th>TEMPERATURE</th>
<th>C wt%</th>
<th>Zn wt%</th>
</tr>
</thead>
<tbody>
<tr>
<td>100% N₂</td>
<td>1000°C</td>
<td>78.47%</td>
<td>19.03%</td>
</tr>
<tr>
<td>Lean Air</td>
<td>500°C</td>
<td>93.48%</td>
<td>NA</td>
</tr>
<tr>
<td>Lean Air</td>
<td>700°C</td>
<td>88.15%</td>
<td>NA</td>
</tr>
<tr>
<td>Lean Air</td>
<td>1000°C</td>
<td>31.42%</td>
<td>NA</td>
</tr>
</tbody>
</table>

Table 2. Summary of light hydrocarbon

<table>
<thead>
<tr>
<th>Chemical Species (M.W)</th>
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</thead>
<tbody>
<tr>
<td>Methane (16)</td>
</tr>
<tr>
<td>Acetylene (26)</td>
</tr>
<tr>
<td>Ethane (30)</td>
</tr>
<tr>
<td>Propane (44)</td>
</tr>
<tr>
<td>n-Butane (58)</td>
</tr>
<tr>
<td>But-1-ene (56)</td>
</tr>
<tr>
<td>1,3-butadiene (54)</td>
</tr>
<tr>
<td>Pentane (72)</td>
</tr>
</tbody>
</table>
As shown in Table 2, several alcohol species were observed along with CO and CO₂ when oxygen was present. However, there are a significant amount of unreacted hydrocarbons indicating that volatilization and combustion occur simultaneously. This shows that even in the presence of significant excess air, these chemical species could persist for an extended period in the combustor. Besides these reactions, the gas phase addition reaction also can be expected. For example, Acetone shown in Table 2 is likely formed from the oxidation of the secondary alcohol by the gas phase addition. Aldehydes or carboxyl acids are probably formed during oxidation or the observed alcohols. In addition, Table 2 implies that there are hydrogenation reactions (i.e. unsaturated bonds between carbon atoms are reduced by attachment of hydrogen atoms to each carbon.) For example, n-pentane, pentene and 1,4-pentadiene may be generated from hydrogenation reaction of released aromatic ligands. Previous work with Styrene Butadiene Rubber (SBR) done by the authors showed that the concentration of hydrogen is significantly lower than observed here and begins to form after n-butane concentration begins to decline[35].

As shown in Table 2, thiophene also was observed and its observation regime is roughly from 300°C to 400°C. This chemical species likely comes from vulcanization agent. It is expected that upon complete oxidation in the combustor the sulfur species will convert to SOx.

To investigate more detailed information on gasification/pyrolysis, combustion reaction, and the PAH formation mechanism, benzene derivatives (substituted aromatics) have been quantified with distinction between structural isomers to begin the understanding of the thermal decomposition of a waste tires. Additionally, these benzene derivatives provide valuable information into the understanding of the PAH formation mechanisms. Figure 3 shows the simple aromatic structures detected; benzene, toluene, and ethyl benzene at 10°C/min heating rate in the air atmosphere. All concentrations presented in this paper were normalized as discussed in the experimental section. Figure 3 shows that the concentration of toluene and ethyl benzene reaches roughly up to 6PPMV and a much lower benzene amount of about 1 PPMV.

The chemical species shown in Figure 3 were also observed in N₂, as well as the oxygen lean and rich atmospheres, which again is an indicator that volatilization by the thermal decomposition occurred simultaneously with oxidation (combustion) reactions. The observation that the benzene concentration remains low through the entire temperature range indicates the aromatic structures are likely released from the polymer. This is in contrast to gas phase addition reactions forming benzene or adding to a benzene molecule, where one would expect a similar concentration profile, but offset in temperature from the other species.

A significant amount of phenol was observed during the testing and is plotted in Figure 4 as a function of temperature for the oxygen containing atmospheres.

Figure 3. Concentrations of chemical release from TGA unit at 10°C/min heating rate in air atmosphere
As shown in Figure 4, the concentrations of phenol are proportional to that of oxygen and the maximum concentration achieved was the most for the aromatic species detected here. Of interest is the peak concentrations were achieved at higher temperatures compared to the aromatics in Figure 3. The concentration of phenol is increasing when concentration of toluene and ethyl benzene is decreased, which can be an evidence of a gas phase addition reaction as well. Benzaldehyde (C₆H₅CHO) is a chemical compound consisting of a benzene ring with an aldehyde substituent. Moreover, benzoic acid by oxidation of benzaldehyde was also observed. This hierarchical oxidation reaction gives an insight of oxidation by gas phase addition reaction.

Prior to discussing the PAH formation mechanism, the origin of benzene ring needs be understood, since it is typically considered a necessary chemical species to be present. The benzene ring likely comes from the surface of the SBR. In addition, a Diels-Alder reaction can be a possible mechanism to create benzene ring in the gas phase. The Diels-Alder reaction is an organic chemical reaction between a conjugated diene (1,3-butadiene) and a substituted alkene (ethane), commonly termed the dienophile. Under the condition of the thermal decomposition by volatilization along with combustion, Diels-Alder reaction can be a possible way to create additional benzene. As evidence of this, 1,3-butadiene, ethane, and cyclohexene were identified in the gas phase, thus the right compounds are present. In addition, significant concentration of cyclohexene as an intermediate was observed. For a better understanding, the Diels-Alder reaction mechanism is presented in Figure 5. However, the concentration of benzene and cyclohexene is much smaller than that of styrene which is directly comes from SBR. Thus, benzene and its derivatives are primarily formed from SBR backbone with gas phase reactions contributing to a lesser extent.

To investigate more detailed information on PAH formation mechanism from benzene derivatives, 37 aromatic species have been quantified, including structural isomers (4, 7, 16, 3, and 5 structural isomers of benzene derivatives having molecular weight of 106, 120, 134, 148, and 162 respectively). Since structural isomers provide not only evidence of a gas phase addition reaction but also elucidation of likely hierarchical growth from smaller aromatic compounds.
More detailed explanation on gas phase addition reaction under at 10°C/min of heating rate in a pure nitrogen atmosphere is present in Figure 7. The concentration of m-xylene is relatively higher and begins to form before 1-ethyl 3-methyl benzene and 1,2,4-trimethyl benzene. This is consistent with gas phase reaction. For example, m-xylene may have used up a precursor to form 1-ethyl benzene and 1,2,4-trimethyl benzene. In addition, isomers of m-xylene, such as p-xylene has relatively higher temperature by factor 10 compared to that of m-xylene.

As shown in Figure 7, the gas phase reaction is related to hierarchical growing steps of benzene derivatives. These growing steps of benzene derivatives were observed in air, and lean/rich air atmosphere. However, the origin and fate of pentyl benzene and hexyl benzene is ambiguous in terms of gas phase addition reaction in that these benzene derivatives have a possibility to directly breakdown from tire followed by hydrogenation. Thus, concentrations of isomers of benzene derivative in lean air atmosphere having a molecular weight of 162 such as hexyl benzene, 1,2,4-trimethyl benzene, and 1,3,5-trimethyl benzene were present in Figure 8.

All benzene derivatives presented in Figure 8 continued to increase as the temperature increased. These species are likely released from the solid residual instead of forming in the gas phase. Since a gas phase reaction doubles for every 100°C temperature increase, one would expect a very rapid oxidation reaction and thermal decomposition to occur at the higher temperatures. Indeed, hexyl benzene was observed in low temperature regime and steadily increased with the appearance of the other highly substituted aromatics. While the origin of hexyl benzene is not entirely clear, the temperature regimes where the highest concentrations are observed indicated the most plausible way it formed was from the surface of the residual.

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. Thus, compared to conventional fuels tire gasification and combustion has a high likelihood of accelerating PAH formation.

One of the smallest PAH is naphthalene which is plotted in Figure 9. An interesting feature in Figure 9, the concentration of naphthalene is proportional to oxygen concentration. Currently, it is not very why this occurs. However, more substituted PAHs such as 1,2-dimethyl and 1,3-dimethyl naphthalene were identified with GC/MS in a nitrogen atmosphere and the peak concentration of these substituted PAHs is inversely proportional to oxygen concentration.

The concentration profiles of representative 2, and 3 ring PAHs in air atmosphere such as naphthalene, acenaphthene, flourene, and anthracene is presented in figure 10. In addition, phenanthrene, pyrene, chrysene, benzo[ghi]perylene, Dibenz[a,h]anthracene, and Benzo[k]fluoranthene were also observed but discernable trends could not be established.
As evidenced before, benzene derivative generated by gas phase addition accelerates PAH formation. Thus, the mitigation of benzene derivatives is the most feasible way to prevent PAH formation. The oxidation by combustion process should be helpful to mitigate levels of benzene derivative and PAH. On the hand, combustion process occurs simultaneously with pyrolysis. Regarding gas phase addition reaction to form benzene derivatives, combustion process with secondary air addition can be possible way to control these chemical species. Based on energy recovery, combustion process as heating source will be also a desired end use.

CONCLUSION

Measurement taken from a series of experiments with a waste tire has been carried out to characterize thermal decomposition by combustion and gasification. Roughly 40% residual was observed before reaching 500°C and the residual was determined as a black carbon using SEM/EDX. The thermal degradation of waste tires has two main steps when oxygen presented. The thermal degradation by volatilization and combustion occurred simultaneously and then mainly combustion reaction was observed. This provides evidences as plausible energy recovery source by combustion process.

Along with oxidation, volatilization was occurred simultaneously, which triggered the formation of benzene derivatives as a precursor of PAH formation. Oxidation was mainly observed in α-carbon when oxygen presented. In this work, several hierarchical oxidation steps were also observed. For example, oxidized benzene derivative such as phenol reached up to 30 PPMV in enhance air atmosphere, and these concentrations were inversely proportional to oxygen concentration. The secondary oxidized chemical species derived from phenol, such as benzaldehydes were observed, which was comparable to the concentration of phenol. Thus, oxidation can be a feasible way to reduce the concentration benzene derivatives, which can induce an insight to control the levels of air pollutant including VOCs and PAHs. For instance, significantly mitigated benzene derivatives including toluene and ethyl benzene were observed up to 6PPMV in air atmosphere, which was proportional to oxygen concentration because fast oxidation triggered to block the pathway to form benzene derivatives. Indeed, significant concentration of benzene derivatives and PAHs were observed when oxygen presented. Thus, the combustion process with secondary air addition will be the feasible way to control chemical species which has adverse effect on health and energy recovery from combustion process will be desired end use.

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REFERENCES


29. Giere, R., M. Blackford, and K. Smith, *TEM study of PM2.5 emitted from coal and tire combustion in a thermal power station*. Environ Sci Technol FIELD