

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/225077623>

Carbon Distribution from Pyrolysis of Tire Derived Fuels

ARTICLE *in* INDUSTRIAL & ENGINEERING CHEMISTRY RESEARCH · DECEMBER 2006

Impact Factor: 2.59 · DOI: 10.1021/ie051397o

CITATIONS

18

READS

86

3 AUTHORS, INCLUDING:



Mingming Lu

University of Cincinnati

43 PUBLICATIONS 454 CITATIONS

SEE PROFILE



Tim C. Keener

University of Cincinnati

196 PUBLICATIONS 1,174 CITATIONS

SEE PROFILE

Carbon Distribution from the Pyrolysis of Tire-Derived Fuels

Kessinee Unapumnuk, Mingming Lu,* and Tim C. Keener

Department of Civil and Environmental Engineering, University of Cincinnati, Cincinnati, Ohio 45221-0071

Products from the pyrolysis of tire-derived fuels (TDFs) were investigated with various analytical techniques and under various final pyrolysis temperatures and heating rates. The pyrolytic products are classified as char (solid product), pyrolysis oil (liquid), and gas. Principal functional groups of the TDF and pyrolysis oil were confirmed by a Fourier transform infrared spectrometer, coupled with attenuated total reflectance (FT-IR/ATR). The byproducts in the pyrolysis oil fraction were individually quantified using gas chromatography coupled with mass spectrometry (GC-MS). The major products are one- and two-ring methyl-substituted aromatic isomers. Byproduct formation mechanisms of TDF pyrolysis were hypothesized based on the products identified. The mechanisms for aromatic hydrocarbons formation were found to be associated with polymer degradation, methyl displacement, and the Diels–Alder reactions. Our study indicated that GC-MS coupled with FT-IR is sufficient to investigate the semivolatile and volatile organic species from the decomposition of complex polymeric materials such as tires.

Introduction

Scrap tires have heating values comparable to that of coal with significant quantities generated every year. They are low cost, and the physical and chemical properties are also relatively consistent. The potential as a fuel has been recognized especially recently with the rising costs of fossil fuels and the increased problems with landfill and storage. Legitimate markets for scrap tires are growing, and significant interest has been expressed by several industries concerning the use of tires, or tire-derived fuel (TDF), for fuel purposes.¹ Public concerns over the use of scrap tires as a fuel are mainly related to their impact on air emissions, in particular, the possibility of producing carcinogenic compounds such as polycyclic aromatic hydrocarbons (PAHs) during combustion.^{2–5} Sooting or byproducts from an incomplete combustion is the primary source of not only health problems but also reduced fuel efficiency in combustion.

Various studies have been performed on TDF combustion, and the conclusions vary significantly because of the different experimental approaches used. Lemieux² indicated that volatile organic emissions such as chloromethane, benzene, and styrene from TDF combustion were comparable to those from pulverized coal and oil combustion, although no significant quantities of semivolatile organic compounds were reported in his work. Atal et al.⁴ studied the survivability of semivolatile PAH from the combustion of pulverized bituminous coal and ground automobile tires. They reported none of the deuterated PAH, adsorbed on the surface of mixed fuels, existed after the combustion process. Small amounts of the overall labeled PAH standards were recovered in other deuterated components under high temperature ~1150 °C in the pyrolysis. Atal et al.⁴ and Levendis et al.⁵ measured PAH emissions from dry-injected cylindrical streams of coal and waste tire crumb particles in a sealed laminar flow furnace. They claimed that total amounts of PAH remained unchanged, though a slight change in the distribution between the gas and the condensed PAH phases were observed.

Pyrolysis reactions can occur in any combustion system when the oxygen level is less than stoichiometric conditions. Pyrolysis has been recognized as an important investigative method to

understand combustion byproduct formation and is known to be a major pathway in the combustion process that generates aromatic hydrocarbons.^{6–11} Kaminsky et al.⁶ reported <5% (by weight of tires) of benzene and toluene in the pyrolysis oil at 750 °C from a fluidized-bed reactor. Tire pyrolysis in rotary kilns has been investigated by several studies. The study of pyrolysis temperature effects on product composition of shredded tires was conducted in a rotary kiln incinerator from 500 to 800 °C, which resulted in 35–50% (by weight of tires) of charcoal, 40–42% of oil, and 10–23% of gas.⁶ The pyrolysis of whole tires in a rotary kiln reactor resulted in 18–25% (by weight of tires) of gas, 25–30% of oil, 35–45% of carbon black and filler material, and 8–12% of steel cord.¹² Pyrolysis of scrap tires has also been performed to produce various byproducts in gaseous, liquid, and solid forms to generate economic value, and the operating conditions can be varied to generate targeted byproducts. The potential applications of oils, solid char, and gas yielded from the pyrolysis of TDFs have been explored in several studies.^{6–10,13} The derived gases are useful as a fuel, and the solid chars can be used as a smokeless fuel, carbon black, and activated carbon.^{6–8,13} The derived oils from TDF pyrolysis have a high calorific value, similar to that of a medium heating oil, and may be used for substitution of conventional fuels or be added to petroleum refinery feedstocks.^{6,7,9,10} The derived oils have been recognized as the most valuable products, particularly by the chemical industry, and there is rising interest to use it as an alternative fuel. Although the derived oils probably have the most economic value out of the three byproducts from the pyrolysis of TDF, its market potential may be affected by the composition of the pyrolytic byproducts, which can vary widely with operating parameters. Various chemical composition of the derived oils have been identified by different studies.^{6,7,9,11,13–16} Limonene was found to be a major component in pyrolysis oil.^{6,9,11,14,16} Significant quantities of light aromatic compounds such as benzene, toluene, xylene, and styrene were recovered in those studies. Cypress and Bettens⁷ suggested that the concentrations of naphthalene at 3.8% and phenanthrene at 1.6% (by weight of tires) were generated via a two-stage pyrolysis process. Williams and Taylor¹¹ analyzed the molecular-weight distribution of pyrolysis oil from a static-batch fixed-bed reactor. They concluded that >10% of the total mass of tire-derived oil was contributed to

* Author to whom correspondence should be addressed. E-mail: mingming.lu@uc.edu.

Table 1. Chemical Composition of TDF from the Material and Safety Data Sheet

chemical	percentage
carbon black	16–36
clay	<1
titanium dioxide	<1.5
zinc dioxide	<2.0
sulfur	<2.0
petroleum hydrocarbons	5–13
rubber compounds	40–48

the concentration of PAH. Some carcinogenic PAHs such as benzo[a]pyrene, benzo[e]pyrene, chrysene, and fluoranthene were present in significant concentrations. Cunliffe and Williams⁹ used a nitrogen-purged static-bed batch reactor to batch pyrolyze 3 kg of shredded scrap tires at temperatures between 450 and 600 °C. The results of the gas analysis support the decomposition mechanisms of dehydrogenation of alkanes to alkenes, followed by cyclization and aromatization. The chemical reaction pathways for the formation of aromatic compounds are similar to those of fossil fuels, such as coal and diesel, as evidenced by the studies on the cofiring of coal and TDF.^{4,5}

The purposes of this study were to (1) generate a temperature profile of aromatic hydrocarbons and isomers using a laboratory-scale pyrolysis unit; (2) render, where possible, fundamental knowledge related to aromatic ring formation from the controlled pyrolysis of shredded tires; and (3) to obtain comprehensive data on the chemical properties of these oils, in order to utilize the pyrolysis oils as a refining feedstock. Our experiments were designed to study changes in the pyrolysis temperature and heating rates, the resultant changes in the composition of the aromatic compounds in pyrolysis oils, and the overall mass balance on a carbon basis.

Experimental Method

The TDF samples were supplied by Central Ohio Contractors, Inc., and Cinergy, Inc. The supplied TDF samples were shredded and sieved to the selected sample sizes in the range of 1.00–2.00 mm. The heating value of the representative TDF samples was found to be ~37 209 kJ/kg (16 000 Btu/lb), which is ~25–40% greater than most coals. Chemical composition of the TDF samples as reported in the material safety data sheets is shown in Table 1.

Carbon contents in the pyrolysis products were measured. The carbon contents in the TDF materials and the pyrolysis char were determined using ultimate and proximate analysis. Along with the proximate and ultimate analysis of the pyrolysis char, the pyrolysis oil samples were also instrumentally examined for organic hydrocarbons and other compounds.

Experimental Setup

A laboratory-scale pyrolysis reactor was developed at the University of Cincinnati for this investigation. The schematic diagram of the pyrolysis reactor is shown in Figure 1. The reactor was designed to perform the pyrolysis of the heterogeneous TDF samples. A representative amount of materials for this study was found to be 3–4 g of TDF on a steel wire free basis.¹⁷

Pyrolysis Experiment

Details of experimental system and design of the lab-scale pyrolysis reactor have been reported elsewhere^{17,18} and are briefly described here. A pyrolysis reactor consists of a mullite ceramic reactor tube, an electrical heater (Lindberg Ltd.), and

a temperature controller (Eurotherm Ltd.). Approximately 3–4 g of TDF sample were placed in a ceramic crucible, which is hung from the closed reactor top into the ceramic tube. Nitrogen carrier gas was supplied into the reactor tube from top to bottom at a flow rate of 0.47 L/min, which was found to be an optimum flow rate for this system.¹⁷ Nitrogen flow was started 30 min before the heater was turned on to remove any remaining oxygen inside the reactor.

Three heating rates, 1, 5, and 10 °C/min, were investigated to study heat transfer effects. The final pyrolysis temperatures of 500, 600, 800, and 1000 °C were used to study the decomposition temperature effects on product distribution. The system was held for at least 1 h at the set temperature to ensure complete pyrolysis at this temperature. The carrier gas (nitrogen) was kept flowing until the temperature cooled to room temperature.

The pyrolytic volatile products were trapped at the bottom of the reactor tube by an oil condensation unit. The temperature of the oil condenser was maintained at approximately –40 °C by dry ice (frozen carbon dioxide). The condenser unit was followed by a glass fiber filter (Whatman type GF/F filter, diameter 47 mm), which was maintained at a temperature of 100 °C. The filter holder was followed by a vacuum pump, which was used to provide the flow rate of 0.47 L/min. After each set of experiments, the inside of the reactor tube was cleaned by dichloromethane (DCM) to remove any deposited soot. The overall material balance was determined after each run of experiments. The density of the condensed oil was measured and recorded.

Carbon Contents Analysis of Pyrolysis Char and TDF

The residual pyrolysis char was removed from the sample basket after each experiment. The char was kept inside a desiccator for at least 24 h and then sent for analysis of the principle fuel properties: proximate and ultimate analysis.² The fuel-property analysis of the pyrolysis char was performed by a certified commercial laboratory in Cincinnati. The following analytical methods have been used: ASTM D3172, Standard Practice for Proximate Analysis of Coal and Coke; ASTM D5865, Standard Test Method for Gross Calorific Value of Coal & Coke; and ASTM D3176–89, Standard Practice for Ultimate Analysis of Coal and Coke. Figure 2 shows the typical composition of the TDF on a steel free basis.

Principal Functional Structures Analysis of TDF and the Pyrolysis Oil

Organic functional groups in the TDF sample were obtained by a Fourier transform infrared spectrometer (FT-IR, Nicolet Magna 760), coupled with attenuated total reflectance (ATR). FT-IR measures vibrational excitation of atoms around the bonds that connect them. Characteristic peaks were absorbed for specific functional groups as a result of stretching, bending, and other modes of vibration and their combination.^{19–22} The ATR technique has been known for obtaining qualitative spectra of solid materials regardless of thickness. The absorption spectrum was generated when light was passed through the sample sheet to the depth of a few micrometers.²² A small, smooth, thin flat sheet of TDF was used. The specially designed solid sample holders held the TDF sheet against the reflecting surface of the prism. The infrared radiation penetrated and reflected with attenuation from the back surface of the sample.²¹ IR vibration frequencies characterized the presence or absence of functional groups for the hydrocarbons in TDF.

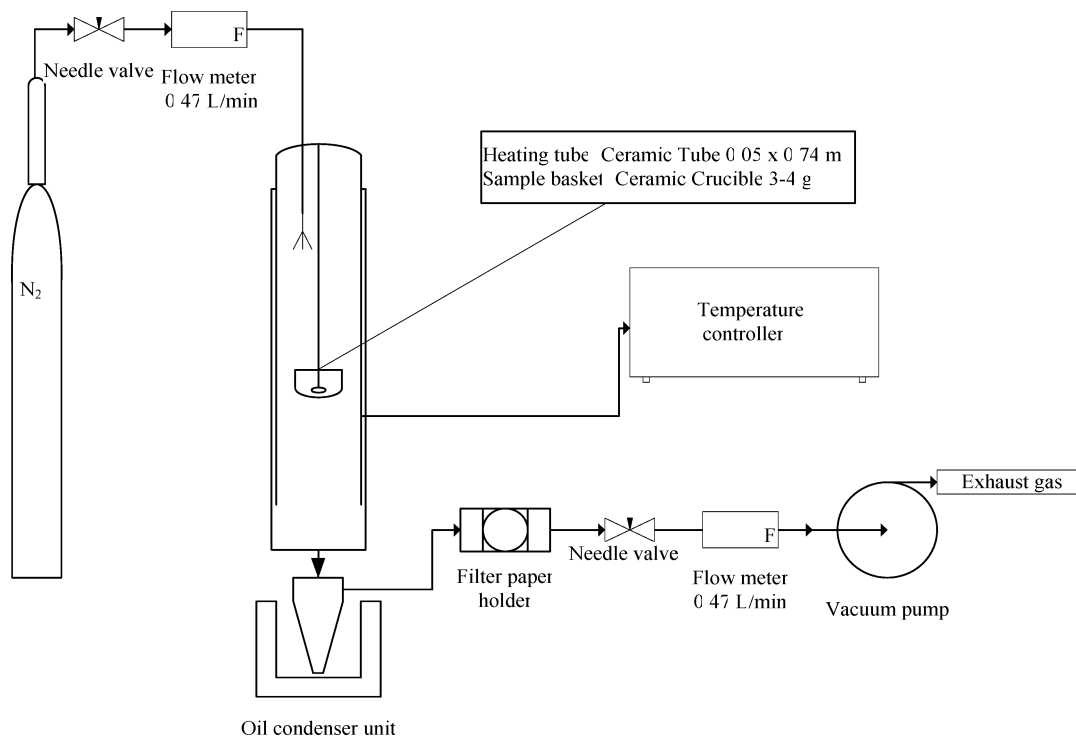


Figure 1. Schematic diagram of the pyrolysis reactor.

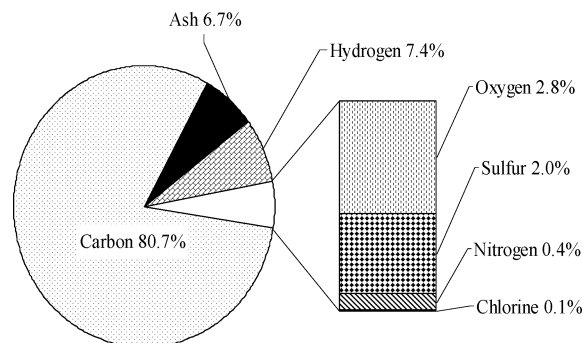


Figure 2. Proximate and ultimate analysis of TDF.

Principal functional structures of the pyrolysis oil were confirmed using the same technique and were found to be less complex than that of the TDF materials. In this analysis mode, a crystal prism with a high refractive index physically contacted the surface layer of the specimen. Absorption bands were detected from those corresponding vibrational modes within the surface of the materials contacting the prism.¹⁹ In this study, a small droplet of the pyrolysis oil was deposited on a potassium bromide (KBr) pressed microdisk, and the spectrum was acquired via transmission infrared spectroscopy (IR). The microdisk technique permits examination of sample weights as small as 1 μg .²² A pure spectrum of the pyrolysis oil was obtained since KBr contains no absorption band in the IR region. In our study, <1 μL of pyrolysis oil was dropped on the KBr pellet and analyzed by the FT-IR/ATR.

Chemical Composition Analysis of Pyrolysis Oil

The pyrolysis oil was collected from the oil condenser unit after each experiment, and 2 μL of the pyrolysis oil were dissolved in 10 mL of DCM. The diluted oil was then filtered through a poly(tetrafluoroethylene) (PTFE) pre-cut membrane filter. The filtered solvent was concentrated to the final volume of 10 mL by slowly flowing nitrogen gas onto the solvent

surface. The soluble organic fragments in the pyrolysis oil were analyzed via gas chromatography coupled with mass spectrometry (GC-MS). The system consisted of a GC (Varian model CP-3800) with a capillary column (CP-Sil 8 CB Low Bleed/MS), an autosampler (CP-8400), and a mass spectrometer (Saturn 2200).

EPA standard analytical method 525 was slightly modified for our analysis. The initial analytical temperature was set at 40 $^{\circ}\text{C}$ and held for 2 min, followed by a ramp rate of 10 $^{\circ}\text{C}/\text{min}$ to 200 $^{\circ}\text{C}$, a ramp rate of 5 $^{\circ}\text{C}/\text{min}$ to 270 $^{\circ}\text{C}$, a ramp rate of 10 $^{\circ}\text{C}/\text{min}$ to 300 $^{\circ}\text{C}$, and finally being held at 300 $^{\circ}\text{C}$ for 10 min. The injection temperature was 280 $^{\circ}\text{C}$ in splitless mode. The carrier gas was ultrahigh-purity helium, and the flow rate was 1.2 mL/min. The MS was operated in the electron-ionization (EI), full-scan mode ranging from 100 to 300 u at a scan rate of 1 s/scan. Structural identification was qualified partially by using pure chemical standards and partially by the spectral interpretation of the National Institute of Standards and Technology (NIST) library database. To identify the compounds of interest more effectively, the MS was operated at the selected ion monitoring (SIM) mode.

Results and Discussion

All product quantities are reported herein on the mass basis of the TDF carbon input for consistency and ease of comparison.

Carbon Balance from Pyrolysis Products

Figure 3 shows the carbon balance of the pyrolysis products over the temperature range of 500–1000 $^{\circ}\text{C}$. This temperature range was studied because the TDF was reported to maintain constant weight at temperatures above 500 $^{\circ}\text{C}$. Although detailed analysis and discussion on the decomposition behavior of the TDF has been reported elsewhere,¹⁸ the carbon distributions in the char and oil are essential to this study and still presented. The total carbon content in the pyrolysis gas was determined by the difference of total carbon content in the pyrolysis char

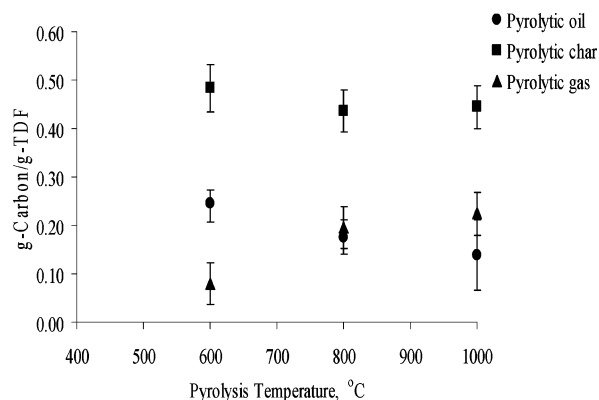


Figure 3. Carbon contents in pyrolysis products heated at 5 °C/min.

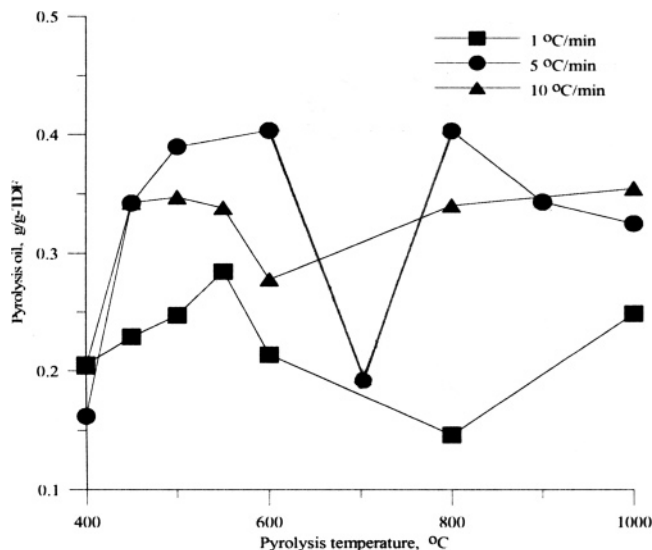


Figure 4. Pyrolysis oil mass distributions. The pyrolysis conditions were as follows: the heating rate of 1, 5, and 10 °C/min to a final pyrolysis temperature of 400, 500, 600, 700, 800, and 1000 °C, with a nitrogen flow rate of 0.47 L/min.

and the pyrolysis oil to the total carbon in the TDF. Regardless of the difference in heating rates, the carbon content in the oil tends to decrease as the temperature increases from 600 to 1000 °C. The carbon content in the solid char is the highest among the three pyrolysis products, which remains almost constant with temperature. The change in carbon content at other heating rates, such as 1 and 10 °C/min, has also been studied, and the results are similar to those in Figure 3.

The pyrolysis oil was an oily liquid and yellowish in color. Figure 4 shows the mass distribution of the pyrolysis oil yields over the temperature range of 400–1000 °C under different heating rates. Multiple runs have been performed at each experimental condition, and the standard deviations are in the range of 0.15–0.4. The measurements suggest that the pyrolysis oil yielded the maximum weight at ~550–600 °C at 5 °C/min. Increasing the temperature from 350 to 600 °C increased the oil yield from 0.15 to 0.4 g/(g of initial TDF weight) at 5 °C/min. From the pyrolysis experiments, more than 50% (by weight) of the initial TDF was converted to products, 30–40% as oil and 15–25% as gas. These results are mostly consistent with the other studies on the overall yield change with pyrolysis temperature and heating rate increase.^{12–14} However, the TDF sample sizes used in this study were ~99% less than those amount used in other studies;^{12,14,16} therefore, the recovery yields of byproducts were lower than those studies. The maximum oil yields were found at the heating rate of 5 °C/min, so the

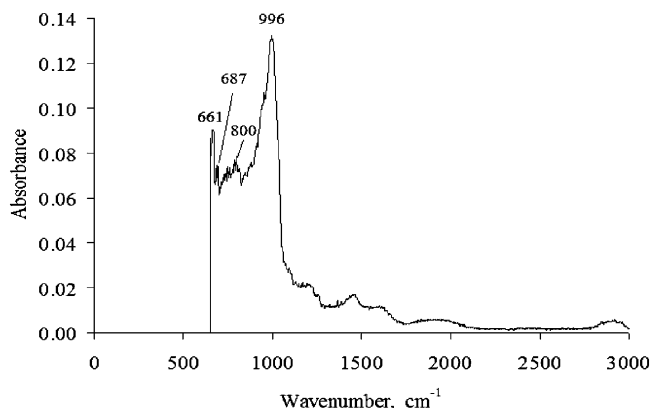


Figure 5. IR spectrum of TDF.

pyrolysis temperature series was performed at that specific heating rate. Figure 4 has also indicated a minimum oil yield for all the heating rates. The corresponding temperature ranges from 600 to 800 °C and decreases with the heating rates. This may correspond to the reaction mechanism change, which may be studied in the future.

Principal Functional Structures of TDF

Tires nowadays are made from a mixture of natural rubber (NR), which is polyisoprene²³ and synthetic rubber, which mostly is styrene–butadiene rubber (SBR), while butyl rubbers are generally used as liners because of their impermeability to air.²⁴ Tires are insoluble in organic solvents, and therefore, the individual components cannot be identified with our experimental setup. Only the principal functional groups can be obtained from FT-IR. Figure 5 shows an IR spectra of the TDF materials using FT-IR/ATR. Analysis of Figure 5 indicates that the main component of TDF is a combination of hydrocarbons at the fingerprint region from 650 to 1600 cm⁻¹. A medium absorption peak in the region 675–730 revealed a –CH=CH– (cis) structure, and a medium absorption peak in the region 960–970 indicates a –CH=CH– (trans) ring structure.²⁰ A variable absorption peak in the region 1000–675 confirmed a C–H bond type for alkenes.¹⁹ The FT-IR results are consistent with the raw material composition.

Principal Functional Structures of the Pyrolysis Oil

Parts a and b of Figure 6 show an example of IR spectra of the pyrolysis oil obtained at 500 and 800 °C at a heating rate of 5 °C/min. Parts c and d of Figure 6 show an example of IR spectra of the pyrolysis oil obtained at 500 °C at 1 °C/min and 10 °C/min, respectively. Analysis of the pyrolysis oils by FT-IR shows that the final pyrolysis temperatures and the heating rates have no significant effect on the main functional structures of pyrolysis oil in this study. Figure 6 indicates that the main component of pyrolysis oil is a combination of the olefinic groups and the aromatic rings, which are represented by the C=C bond, the C–H stretching vibration, and the C–H bending vibration. The approximate frequencies for hydrocarbon-substitute olefins and hydrocarbon-substitute heteroaromatic rings are given in Table 2.

The observation of the weak absorption peaks at 965 cm⁻¹ revealed a strong –CH=CH– (trans) in conjugation to polyenes.²⁶ A strong absorption peak in the region of 2960–2850 cm⁻¹ and an absorption peak in the region of 1470–1350 cm⁻¹ revealed the C–H stretching vibration and the C–H bending vibration, respectively.²² A medium absorption peak in the

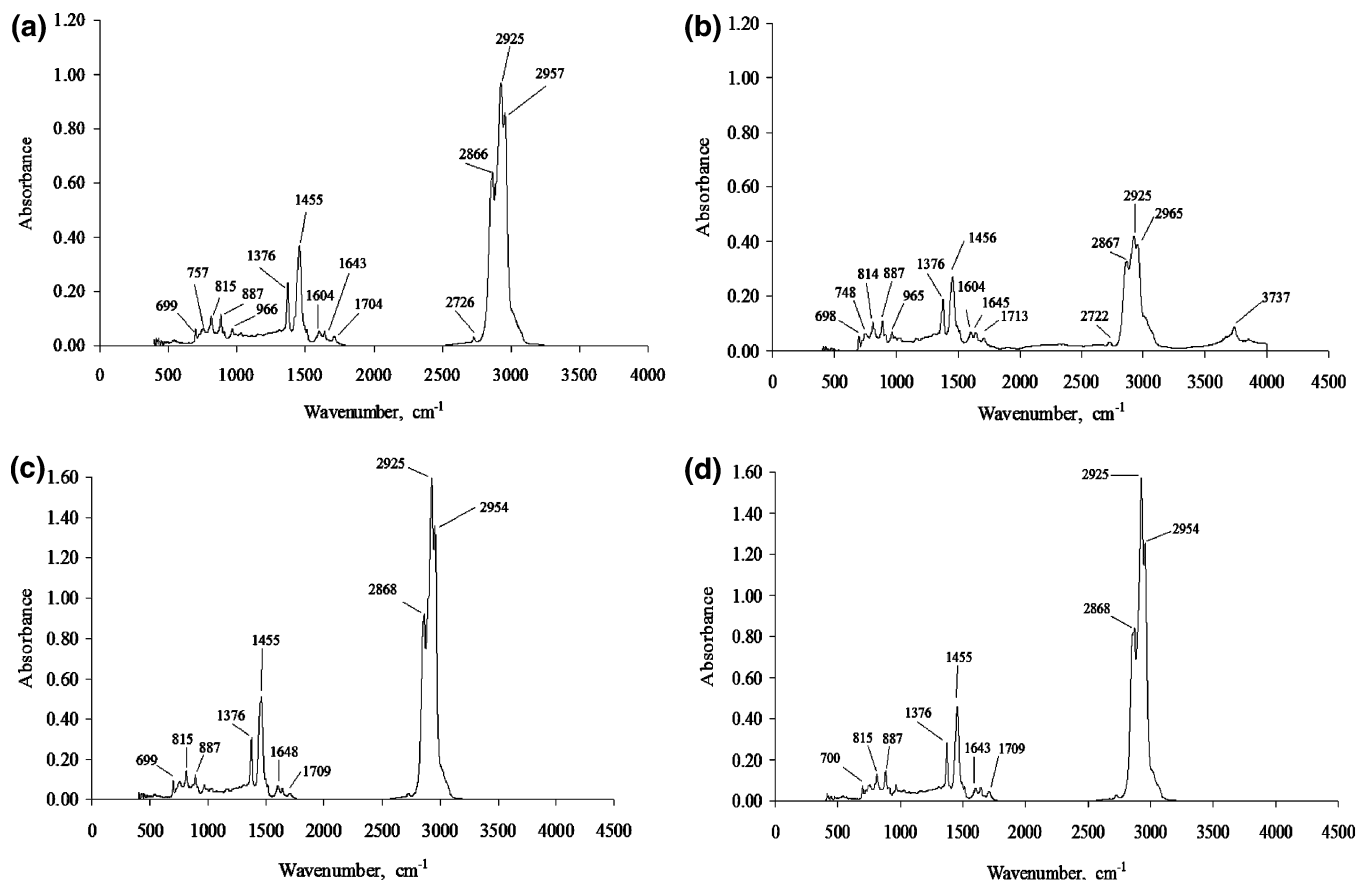


Figure 6. IR spectrum of pyrolysis oils: (a) final pyrolysis temperature 500 °C, 5 °C/min; (b) final pyrolysis temperature 800 °C, 5 °C/min; (c) pyrolysis temperature at 500 °C, 1 °C/min; (d) pyrolysis temperature at 500 °C, 10 °C/min.

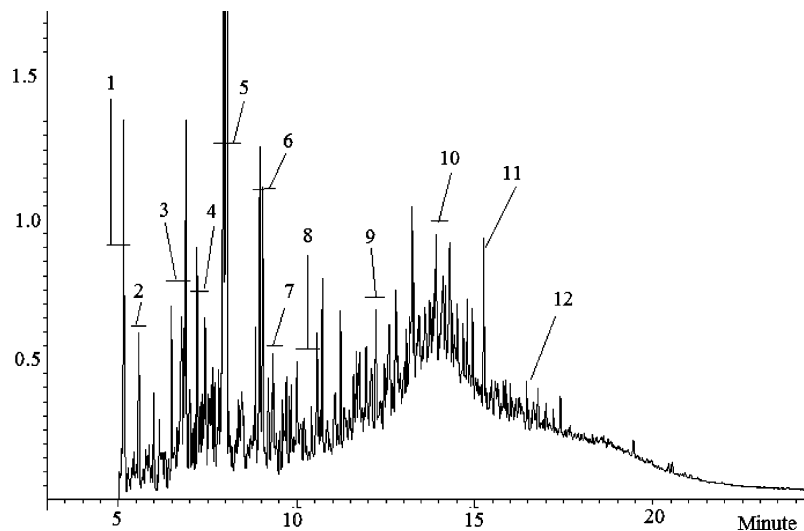


Figure 7. Total ion chromatogram of pyrolysis oils at pyrolysis condition of 5 °C/min and the maximum temperature of 500 °C. The chemical structures of the numbered group(s) are further identified by GC-MS in Table 3.



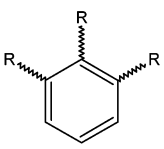
region of 1600–1450 cm^{-1} indicated a C=C in an aromatic ring.²⁰ In addition, a weak or absent absorption peak in the region of 1678–1668 cm^{-1} indicated a C=C stretch in IR.²² A variable absorption peak in the region 1000–675 cm^{-1} confirmed a C–H alkenes bond type.¹⁹ However, the presence of a weak absorption peak in the region of 1600–1700 and 3737 cm^{-1} in Figure 6b may have resulted from either the OH impurity in the sample or the KBr.²¹

The IR analysis of the pyrolysis oil has identified many more functional groups than the TDF, and it clearly suggested the existence of the aromatic structures. The individual compounds of the pyrolysis oil are identified by GC-MS.

Individual Compounds of the Pyrolysis Oil

The total ion chromatogram (TIC) of pyrolysis oil is shown in Figure 7. The identified individual compounds and isomers are numbered and the chemical structures are listed in Table 3. The compounds listed were classified based on molecular weight and functional groups. For example, C2-benzene referred to benzene with two carbon substitution (molecular weight = 106), which included three possible isomers: *o*-xylene, *p*-xylene, and ethylbenzene. Pure chemical compounds were acquired to obtain calibration curves. Whenever the pure standard is not available, the response factor of the isomer or a compound with a similar

Table 2. Approximate FT-IR Frequencies for Hydrocarbon-Substituted Olefins and Heteroaromatic Rings

Functional group	Bond Type	Wave range cm ⁻¹
CH-CH	C-H stretch alkanes	2960-2850 (<i>s</i>) ¹⁹
C=C	C=C stretch alkenes	1680-1620 (<i>v</i>) ¹⁹
	C=C	
Aromatic	C-H	1600-1450(<i>v</i>) 1470-1350 (<i>s</i>) ¹⁹
C-H	CH ₃ or CH ₂ bend alkanes	1380-1370 (<i>v</i>) ²²
	CH stretch	3050-3000 (<i>m</i>)
	C=C stretch	1678-1668 (<i>w</i>)
	<i>trans</i> CH	980-965(<i>s</i>) ²¹
	CH stretch	3050-3000 (<i>m</i>)
	C=C stretch	1662-1631 (<i>m</i>)
	CH bend	1429-1397(<i>m</i>)
	<i>cis</i> CH	650-730(<i>m,s</i>) ²¹
C=C-H	out of plane bend alkenes	790-840 (<i>s</i>) ²⁵
		1604±3
	<i>mono, ortho, and meta</i> benzene	1510-1470
		770-730
		710-690 ²¹

s = Strong absorption. *w* = Weak absorption. *m* = Medium absorption.
v = Variable absorption.

Table 3. Major Products in the Pyrolysis Oil Identified by GC-MS

peak no. ^a	functional group	concentration of carbon, $\mu\text{gC/gTDF}$				
		400 °C	500 °C	600 °C	800 °C	1000 °C
1	C2-benzene (3)	39	0	6 663	4 791	1 149
2	C0-styrene (1)	0	3 473	841	896	326
3	C3-benzene (8)	35	15 241	4 549	5 653	2 627
4	C4-benzene (4)	473	54 045	20 952	22 237	12 255
5	C4-cyclohexene (7)	1576	230 405	76 490	81 606	47 871
6	C2-styrene (5)	67	19 915	9 077	8 668	5 571
7	C5-benzene (6)	0	2 028	958	972	675
8	C2-indan (5)	104	16 828	7 865	7 226	4 918
9	C3-indene (3)	0	4 410	9 350	7 747	5 685
10	C2-naphthalene (3)	0	1 166	757	558	407
11	C3-naphthalene (1)	52	7 965	7 341	5 340	3 709
12	C4-naphthalene (1)	13	1 707	2 416	1 779	1 617
total		2 359	357 183	147 260	147 473	86 809

^a The peak numbers denote compound(s) marked in Figure 7, and the numbers in parentheses refer to the number of isomers identified.

structure is used. The relative mass of the individual compounds (on a carbon basis) was calculated and divided by the mass of TDF input to become relative quantities that are comparable throughout the temperature range.

Styrene and benzene isomers mainly eluted during the first 10 min of the chromatogram (m/z 78 is the characteristic fragment ion peak) followed by C2-, C3-, and C4-substituted benzenes (m/z 91, 105, and 119, respectively), cyclohexene isomers (m/z 121 and 136), indan (m/z 131), and finally naphthalene derivatives (m/z 156, 170, and 189). Isomers of

Table 4. Most Abundant Isomeric Structure Identified by GC-MS

peak no. ^a	most abundant isomer	contribution % of all the possible isomers ^b
1	benzene, 1,4-dimethyl	79
2	styrene	NA
3	benzene, 1-ethyl-2-methyl	34
4	benzene, 1-isopropyl-2-methyl	82
5	cyclohexene-4-isopropenyl-1-methyl	87
6	styrene, α -2-dimethyl	69
7	benzene, 1-methyl-4-(1-methylpropyl)	53
8	indan, 4,7-dimethyl	48
9	indene, trimethyl	58
10	naphthalene, 1,3-dimethyl	67
11	naphthalene, 2,3,5-trimethyl	NA
12	naphthalene, tetramethyl	NA

^a The peak numbers denote compound(s) marked in Figure 7. ^b NA: Not applicable, one isomer is identified.

substituted aromatic hydrocarbons usually have similar mass spectra and can be easily grouped by the selective ion search method. The mass spectra of trimethylbenzene and ethylmethylbenzene are shown in Figure 8 as an example.

The complexity of the pyrolysis oil is suggested by the many isomers identified. Oftentimes the pattern is one prominent isomer peak followed by several smaller peaks. Table 4 lists the most abundant isomers for all the temperatures and their relative fractions. The most abundant isomers contributed on average 64% for all of the functional groups with the exception of 1-ethyl-2-methylbenzene, with 34% contribution. The C4-cyclohexene isomers are shown in Figure 9 as an example of this pattern. More than 80% of the C4-cyclohexene isomers is identified as 4-isopropenyl-1-methylcyclohexene (also known as limonene), which was the most abundant for all. One of the isomers was identified as trimethyl-methylene-cyclohexene, which may be formed by the addition reaction of alkene during pyrolysis.²⁷

Quantitatively, the total identified products in the derived oils (as shown in Table 3) increased from 0.24 wt % at 400 °C to 35.7 wt % at 500 °C, decreased drastically to ~15 wt % at 600–800 °C, then further reduced to <10 wt % at 1000 °C. The GC-MS results have indicated that the majority of compounds were found to be methyl-substituted aromatic hydrocarbons with a number of isomers. All of the compounds reached their maximum quantity at 500 °C and tended to decrease with temperature increases. Cyclohexene (~58%) and benzene (~26%) were the most abundant functional groups in the pyrolysis oil.

The most abundant group of isomers is the seven C4-cyclohexene isomers, as quantified in Table 4 and Figure 9, which contributes to >50% of the total identified products. 4-Isopropenyl-1-methyl-1-cyclohexene (limonene) is the most abundant of all. Limonene and other cyclohexene isomers suggest the depolymerization of the natural rubber, which is mainly polyisoprene, followed by the Diels–Alder reaction to form the ring structure from aliphatic components.^{16,28,29} The decomposition of the natural rubber also provides a pool of methyl radicals that can add to other aromatic byproducts to result in a series of methylated isomers. The methyl radicals may be first formed through bond scission and then from hydrogen displacement of the methyl group from the base compound as the pool of hydrogen builds up from the pyrolytic process.

The second most abundant product at 500 °C was the C4-benzene isomers. C4-benzene isomers were formed in high concentration at 500 °C and decreased with temperature increase. Similar trends have been obtained for C2-benzenes

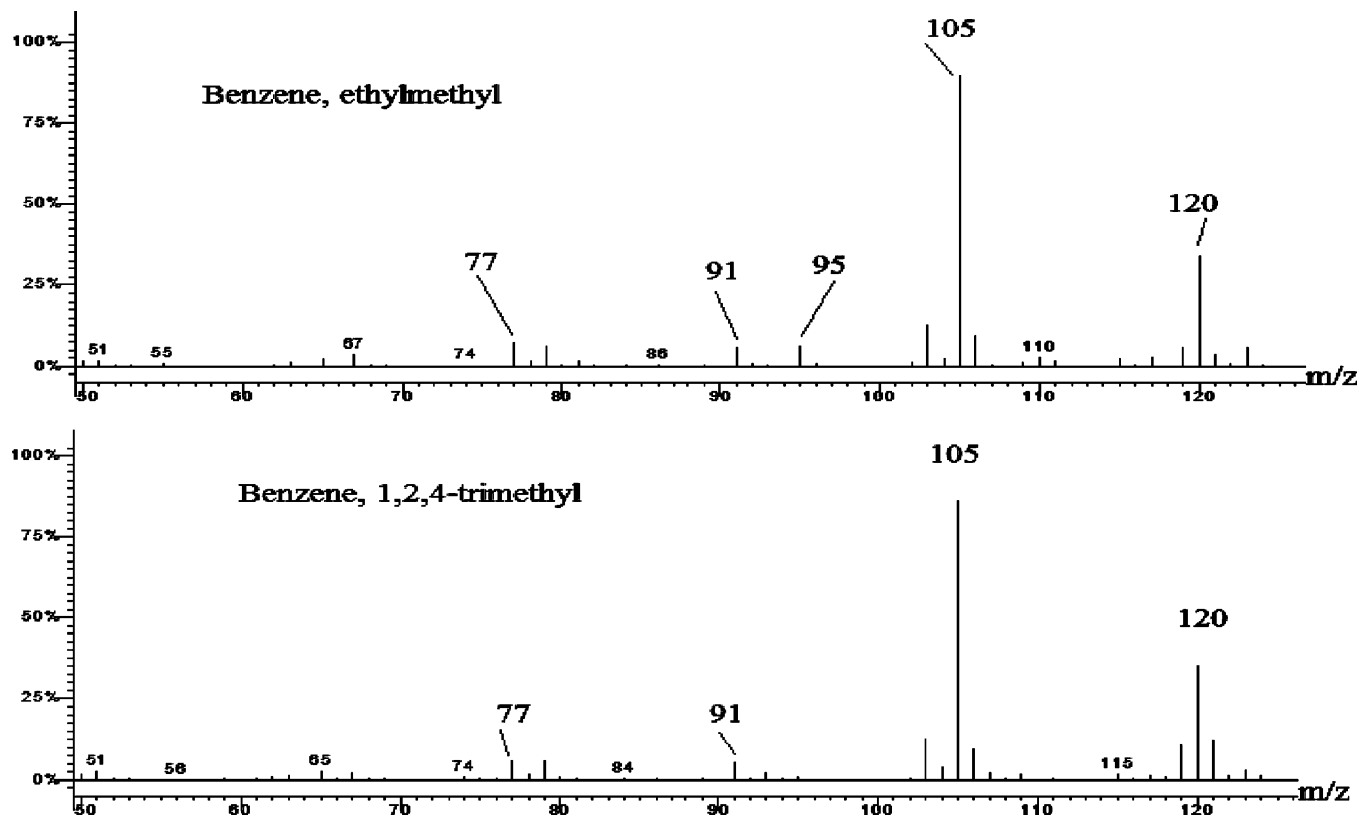


Figure 8. Isomeric mass spectrum of trimethylbenzene and ethylbenzene.

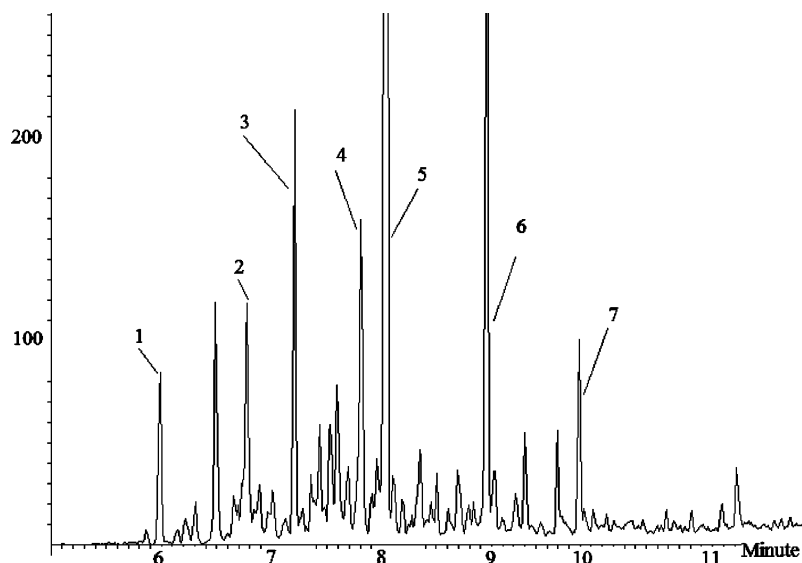


Figure 9. C4-cyclohexenes in the pyrolysis oil from selective ion chromatogram: pyrolysis condition of 5 °C/min and the maximum temperature of 500 °C: (1) 1,5,5,6-tetramethyl-1,3-cyclohexadiene; (2) 1,5,5-trimethyl-6-methylene-cyclohexene; (3) 1,3,5,5-tetramethyl-1,3-cyclohexadiene; (4) terpinolene; (5) 4-isopropenyl-1-methyl-1-cyclohexene (limonene); (6) terpinolene; (7) terpinolene.

and C3-benzenes, which can be the result of the thermal degradation of limonene in oils⁹ or the loss of methyl groups from the C4-benzenes. Styrene has been identified in minor quantities. The formation of styrene can be resultant from the depolymerization of the synthetic rubber fraction, which is mainly the styrene-butadiene polymer.

Naphthalene, indan, and indene could be produced from cyclization reactions of alkyl benzenes.³⁰ These compounds, together with the alkylbenzenes, were the principal oil products derived from the degradation of the styrene-butadiene rubber. Styrene, naphthalene, and indan contributed to ~16% of the total functional groups in the pyrolysis oils.

Different operating conditions, such as temperature, pressure, heating rate, and residence time, can result in vastly different byproduct formation. In this study, PAH compounds with more than three aromatic rings were not detectable. This may be due to several factors. As indicated by other similar studies, a low carrier gas flowrate in the pyrolysis process results in less pyrolysis byproducts,^{10,14,31} and the reduction of these monoaromatic products tends to result in lower quantities of the heavier PAH compounds. Although TDF pyrolysis has been performed at higher temperatures such as 800 and 1000 °C, the pyrolysis oil collected has been much less in quantity. It is possible that the depolymerization process at higher temperatures increasingly

results in the formation of soot (which is measured as char). As with our studies of the methylnaphthalenes, the starting material with alkylated components (such as TDF) tends to result in less of the heavier PAHs, partly because of the reactivity of the alkyl groups, such as the methyl and ethyl groups.³²

Conclusions

The pyrolysis of TDF yielded a complex mixture of hydrocarbons in the pyrolysis oil along with gaseous and char products. The principal functional groups of the oils appeared to be the olefinic groups and aromatic hydrocarbon rings, and they were fairly independent of the heating rates. Analysis of the pyrolysis oils by FT-IR shows that the final pyrolysis temperatures and the heating rates have no significant effect on the main functional structures of pyrolysis oil in this study. However, the individual composition of the oil depended quantitatively on the final pyrolysis temperature. The maximum oil yield was found at the heating rate of 5 °C/min. The quantities of the byproducts reached the maximum concentration at 500 °C and then started to decrease with temperature. The major products include alkylated isomers of cyclohexene, benzene, and naphthalene as well as indan and styrene. The alkyl groups contained in the raw material resulted in more isomers and added complexity to product formation. The most abundant groups of isomers are the C4-cyclohexene and C4-benzene isomers, which contribute to >50% of the total identified products. The byproducts suggest that depolymerization, ring structure formation by Diels–Alder reactions, and alkylation are the major reaction pathways. This study has shown that a pyrolysis reactor can be designed and operated to produce specific products from used tires under known operating conditions, such as temperature, pressure, residence time, etc. Pyrolysis conditions can be altered to maximize the quantity of the pyrolysis oil.

Acknowledgment

The authors would like to offer their thanks to Prof. F. James Boerio and Dr. Supa Wirasate from the Chemical and Material Engineering Department of the University of Cincinnati for help with the FT-IR analysis. Thanks to Ming Chai for his help with part of the experiments.

Literature Cited

- (1) Dodds, J.; Domenico, W. F.; Evans, D. R.; Fish, L. W.; Lassahn, P. L.; Toth, W. J. *Scrap tires a resource and technology evaluation of tire pyrolysis and other selected alternate technologies*; Report EGG-2241; Department of Energy: Idaho Falls, Idaho, 1983.
- (2) Lemieux, P. M. *Pilot-Scale Evaluation of the Potential for Emissions of Hazardous Air Pollutants from Combustion of Tire-Derived Fuel*; EPA/600/SR-94/070; U.S. Environmental Protection Agency: Washington, DC, 1994.
- (3) Leung, D. Y. C.; Wang, C. L. Kinetic study of scrap tyre pyrolysis and combustion. *J. Anal. Appl. Pyrolysis* **1998**, *45* (2), 153–169.
- (4) Atal, A.; Levendis, Y. A.; Carlson, J.; Dunayevskiy, Y.; Vouros, P. On the survivability and pyrosynthesis of PAH during combustion of pulverized coal and tire crumb. *Combust. Flame* **1997**, *110* (4), 462–478.
- (5) Levendis, Y. A.; Atal, A.; Carlson, J.; Dunayevskiy, Y.; Vouros, P. Comparative study on the combustion and emissions of waste tire crumb and pulverized coal. *Envi. Sci. Technol.* **1996**, *30* (9), 2742–2754.
- (6) Kaminsky, W.; Menzel, J.; Sinn, H. Recycling of plastics. *Conserv. Recycl.* **1976**, *1* (1), 91–110.
- (7) Cypress, R.; Bettens, B. Production of benzoles and activated carbon from waste rubber and plastics materials by means of pyrolysis with simultaneous post-cracking. In *Pyrolysis and gasification*; Ferrero, G. L.; Maniatis, K.; Buekens, A.; Bridgwater, A. V., Eds.; Elsevier Applied Science: London/New York, 1989; pp 209–229.
- (8) Williams, P. T.; Besler, S.; Taylor, D. T. The pyrolysis of scrap automotive tyres: The influence of temperature and heating rate on product composition. *Fuel* **1990**, *69* (12), 1474–1482.
- (9) Cunliffe, A. M.; Williams, P. T. Composition of oils derived from the batch pyrolysis of tyres. *J. Anal. Appl. Pyrolysis* **1998**, *44* (2), 131–152.
- (10) Pakdel, H.; Roy, C. Simultaneous gas chromatographic–Fourier transform infrared spectroscopic–mass spectrometric analysis of synthetic fuel derived from used tire vacuum pyrolysis oil, naphtha fraction. *J. Chromatogr., A* **1994**, *683* (1), 203–214.
- (11) Williams, P. T.; Taylor, D. T. Aromatization of tyre pyrolysis oil to yield polycyclic aromatic hydrocarbons. *Fuel* **1993**, *72* (11), 1469–1474.
- (12) Kaminsky, W. Thermal recycling of polymers. *J. Anal. Appl. Pyrolysis* **1985**, *8*, 439–448.
- (13) Senneca, O.; Salatino, P.; Chirone, R. A fast heating-rate thermogravimetric study of the pyrolysis of scrap tyres. *Fuel* **1999**, *78* (13), 1575–1581.
- (14) Williams, P. T.; Brindle, A. J. Temperature selective condensation of tyre pyrolysis oils to maximise the recovery of single ring aromatic compounds. *Fuel* **2003**, *82* (9), 1023–1031.
- (15) Benallal, B.; Roy, C.; Pakdel, H.; Chabot, S.; Poirier, M. A. Characterization of pyrolytic light naphtha from vacuum pyrolysis of used tyres comparison with petroleum naphtha. *Fuel* **1995**, *74* (11), 1589–1594.
- (16) Pakdel, H.; Pantea, D. M.; Roy, C. Production of dl-limonene by vacuum pyrolysis of used tires. *J. Anal. Appl. Pyrolysis* **2001**, *57* (1), 91–107.
- (17) Unapumnuak, K.; Keener, T. Kinetic Study of the Degradation Temperature vs. Weight Loss in the Pyrolysis of Tire Derived Fuels. Presented at A&WMA's 97th Annual Conference & Exhibition, Indianapolis, IN, 2004; Paper 623.
- (18) Unapumnuak, K.; Keener, T. C.; Khang, S.; Lu, M. Pyrolysis Behavior of Tire Derived Fuels at Different Temperatures and Heating Rates. *J. Air Waste Manage. Assoc.* **2006**, *56*, 618–627.
- (19) Ege, S. N. *Organic chemistry: Structure and reactivity*; D. C. Heath: Lexington, MA, 1994; pp 376–393.
- (20) Crews, P.; Rodríguez, J.; Jaspars, M. *Organic structure analysis*; Oxford University Press: New York, 1998; pp 317–347.
- (21) Colthup, N. B.; Daly, L. H.; Wiberley, S. E. *Introduction to infrared and Raman spectroscopy*; Academic Press: Boston, MA, 1990; pp 247–288.
- (22) Silverstein, R. M.; Webster, F. X.; Kiemle, D. J. *Spectrometric identification of organic compounds*; J. Wiley & Sons: Hoboken, NJ, 2005; pp 3–164.
- (23) <http://www.pslc.ws/mactest/isoprene.htm> (accessed Dec 2005).
- (24) <http://www.dnr.state.oh.us/recycling/awareness/facts/tires/thruwwi-i.htm> (accessed Dec 2005).
- (25) Arjunan, V.; Subramanian, S.; Mohan, S. Fourier transform infrared and Raman spectral analysis of *trans*-1,4-polyisoprene. *Spectrochim. Acta, Part A* **2001**, *57* (13), 2547–2554.
- (26) Colthup, N. B.; Orloff, M. K. Calculation of infrared group frequencies from molecular orbital theory. I: Out-of-plane CH₂ and CH bending vibrations in substituted ethylenes. *Spectrochim. Acta, Part A* **1971**, *27* (8), 1299–1314.
- (27) Moldoveanu, S. Analytical pyrolysis of natural organic polymers. In *Techniques and instrumentation in analytical chemistry*; Elsevier: Amsterdam/New York, 1998; Vol. 20, pp 1–31.
- (28) Groves, S.; Lehrle, R. Pyrolysis mechanisms of natural rubber deduced from the dependence of product yields on sample size. *Eur. Polym. J.* **1992**, *28* (4), 373–378.
- (29) Groves, S. A.; Lehrle, R. S.; Blazso, M.; Szekely, T. Natural rubber pyrolysis: Study of temperature-and thickness-dependence indicates dimer formation mechanism. *J. Anal. Appl. Pyrolysis* **1991**, *19*, 301–309.
- (30) Giray, E. S.; Sonmez, O. Supercritical extraction of scrap tire with different solvents and the effect of tire oil on the supercritical extraction of coal. *Fuel Process. Technol.* **2004**, *85* (4), 251–265.
- (31) Mirmiran, S.; Pakdel, H.; Roy, C. Characterization of used tire vacuum pyrolysis oil: Nitrogenous compounds from the naphtha fraction. *J. Anal. Appl. Pyrolysis* **1992**, *22* (3), 205–215.
- (32) Yang, J.; Lu, M. Thermal growth and decomposition of methyl-naphthalenes. *Envi. Sci. Technol.* **2005**, *39*, 3077–3082.

Received for review December 15, 2005
 Revised manuscript received September 1, 2006
 Accepted September 16, 2006