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Evolution of Products in the Combustion of Scrap Tires in a Horizontal, Laboratory Scale Reactor

A. FULLANA,* R. FONT,
J. A. CONESA, AND P. BLASCO

Department of Chemical Engineering, University of Alicante,
Apartado 99, Alicante, Spain

A horizontal laboratory reactor was used to study the evolution of byproducts from the combustion of scrap tires at five nominal temperatures (ranging from 650 to 1050 °C) and different oxygen:sample ratios. A model was used to calculate the bulk air ratio (λ), and the oxygen consumption was discussed considering this ratio λ . More than 100 volatile and semivolatile compounds were identified and quantified by gas chromatography mass spectrometry, plotting their yields vs the bulk air ratio and temperature. Five different behaviors considering the bulk air ratio and the temperature were identified.

Introduction

As a result of the great increase in the use of automobiles, the destination of scrap tires has been converted into a social problem of great importance. The production of scrap tires is valued at 2.5 million tons a year in the U.S.A., 2.0 millions tons in the European Union, and 0.5 millions tons in Japan (1).

Disposing of scrap tires in landfills is the most common solution for this type of waste. The major problem of using this method is that the scrap tires take up considerable space because they are not easily compacted, and furthermore the openings expose the landfills to insects, rodents, and birds (2). On the other hand, the holes between pieces of tires permit rainwater to pass that may produce an important leaching of wastes. Another problem of landfills with scrap tires is the high risk of fire. Uncontrolled fire may produce large amounts of toxic (3) and mutagenicity compounds (4).

Recycling tires has been extended to use in asphalt, fuel, and pyrolysis. The high net calorific power (about 8500 kcal/kg) converts the tires in appropriate waste for obtaining fuel by pyrolysis. Pyrolysis of scrap tires is an expensive process and markets are limited. Another possibility of utilization of the high net calorific power of tires is the use of the whole tires as fuel.

Several authors have studied the pyrolysis of tires: (1) Teng et al. (5) studied the pyrolysis of scrap tires from the point of view of manufacturing active carbon. (2) Conesa et al. (6) studied the primary decomposition by thermogravimetric analysis. They found that a tire is composed of three decomposable fractions from the point of view of pyrolytic decomposition. The same authors checked that the first fraction could be a mineral oil, the second natural rubber, and the third synthetic rubber (styrene-butadiene). (3) Conesa et al. (7) also studied the composition of the gas obtained from the pyrolysis of scrap tires in a fluidized bed reactor.

TABLE 1. Ultimate Analysis of the Tire Used in This Work

	% wt		% wt
C	83.5	O (by diff)	6.8
H	7.8	volatile matter	61.2 ^a
N	0.39	fixed carbon	31.5 ^a
S	1.5	ash	7.3 ^a

^a Calculated by Conesa et al. 1998 (18).

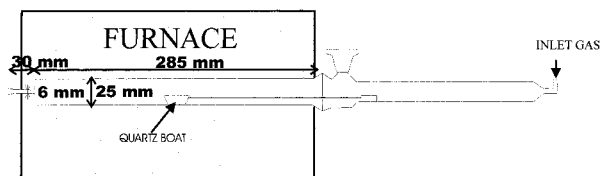


FIGURE 1. Diagram of the furnace used in combustion experiments.

They analyzed several volatile hydrocarbon compounds and discussed the evolution of their yields with cracking severity.

Now the use of scrap tires for fuel offers the best alternative for reusing rubber. Several industries use this waste to replace traditional fuels. Thus, in 1996, 27 cements kilns and 12 paper mills used tire-derived fuel (TDF) as a supplement fuel (8). On the other hand, TDF was used in a dedicated tire-to-energy plant.

The main problem of using TDF is the air contamination effects. Although there are not many papers on the subject, some have studied scrap tire combustion where the pollutants are analyzed in great detail.

In this paper, the pollutants resulting from the combustion of scrap tires have been analyzed at different conditions. More than 100 compounds have been identified and quantified including light hydrocarbons (methane, acetylene, ...), monoaromatic compounds (benzene, toluene, xylene, ...), polyaromatic hydrocarbons (naphthalene, phenanthrene, pyrene, ...), partially oxygenated compounds (dibenzofuran, naphthol, ...) and other heterocyclic compounds.

Equipment and Experimental Procedures

Material. The original tire (DUNLOP SP LE MANS) was shredded into small pieces with a mean diameter of 5 mm. These pieces were then immersed in liquid nitrogen and were ground in a grinder to a diameter less than 1 mm.

The ultimate analysis of the tires is presented in Table 1. The equipment used for this analysis was a Perkin-Elmer 2400 oven with a temperature of 1020 °C. (The combustion was carried out in a pure oxygen atmosphere. Organic compounds were totally decomposed to CO₂, SO₂, N₂, and water by a flash combustion and post catalytic oxidation. The amounts of these compounds were determined by gas chromatography; the standard used was sulfanilamide, and the sample size was 2 mg.)

Details on the pyrolytic decomposition can be found elsewhere (6, 7).

Pyrolysis Furnace. A horizontal quartz reactor was used (Figure 1), where the sample was introduced inside a boat that moved toward the inside of the reactor. The volatiles evolved were cracked and burnt inside the reactor at the second part of the reactor. The sample in the small boat was introduced at constant velocity (0.5 mm/s) into the furnace, whose temperature profile was previously determined. Figure 2 shows the temperature profile corresponding to the nominal temperature 850 °C.

* Corresponding author phone: +34-965903400 ext. 3003; fax: +34-965903828; e-mail: andres.fullana@ua.es.

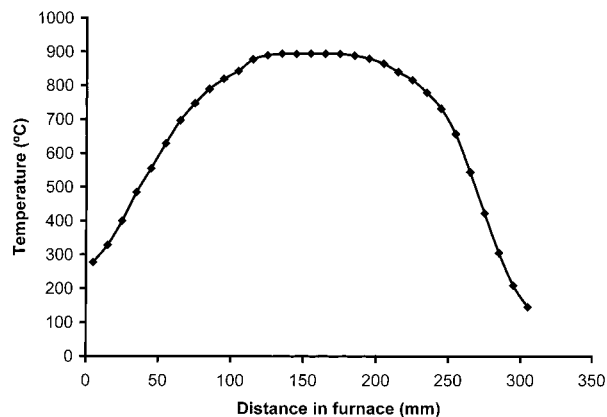


FIGURE 2. Temperature profile in furnace (nominal temperature 850 °C).

The volatiles evolved were collected in a Tedlar bag for analysis of light hydrocarbon compounds and a small tube containing the resin (XAD-2) was used for collecting the semivolatile compounds.

Analytical Method. The gases collected in the Tedlar bag were analyzed by gas chromatography. The capillary Alumina-KCL PLOT column with the FID detector was used to analyze the light hydrocarbon compounds: methane, ethane, ethylene, propylene, butane, acetylene, benzene, toluene, etc. On the other hand, the Carbosieve S2 and Mol Sieve 5 columns with TCD were used for the analysis of O₂, N₂, CO₂, and CO.

The semivolatiles adsorbed in the XAD-2 resin (around 3 g) were extracted with 100 mL of dichloromethane, following the EPA 3540c method. An internal deuterate standard (1,4-dichlorobenzene-*d*₄, naphthalene-*d*₈, acenaphthene-*d*₁₀, phenanthrene-*d*₁₀, chrysene-*d*₁₂, and pyrene-*d*₁₂) was added before the extraction. The deuterate compounds were used to estimate the evolution yields of the byproducts, and then the extract was concentrated to 2 mL with a micro-Kuderna-Danish equipment.

Semivolatile organic compounds were analyzed by gas chromatography/mass spectrometry (GC/MS). The capillary column DB-5 MS was used, and the compounds were identified by MS (15–450 amu, 70 eV). The qualitative identification of compounds was performed comparing the mass spectrums with those of the NIST database. The index from Lee and Kovad (9, 10) was also used to identify compounds with a similar spectrum. A semiquantitative estimation of the yields was obtained using factors obtained for the deuterate internal standards (EPA method 8270c section 7.7.3). Note that the software of GC/MS equipment suggests a list of the possible compounds. In the identification of the peaks of the chromatogram, the most probable compound is taken except when the other indicators (Lee and Kovad index, boiling point, and logical correlation in chromatograms of different runs) also indicate that another compound is the most probable. For a precise identification and quantification of every single compound using the EPA method 8270c, a standard for each compound would have been required. This level of work was however considered to be beyond the scope of this research.

Index annotations with the method used in the quantification and identification have been included in the tables where the compounds are shown.

Experimental Procedure. The bulk air ratio λ ($\lambda = (m_{\text{fuel}}/m_{\text{air}})_{\text{stoichiometric}}/(m_{\text{fuel}}/m_{\text{air}})_{\text{actual}}$) is an important parameter in the combustion process, as it is an indicator of the quantity of oxygen present in the process ($\lambda = 0$ in the pyrolysis processes, $\lambda = 1$ when the oxygen present is the stoichiometric necessary one for a complete combustion, and $\lambda > 1$ for the

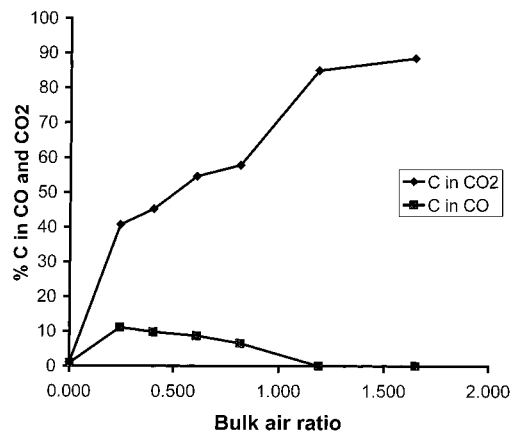


FIGURE 3. CO and CO₂ yields vs the bulk air ratio.

TABLE 2. Experimental Conditions in the Combustion Scrap Tire Using a Horizontal Laboratory Scale Reactor

run no.	nominal temp	mass of scrap tire (mg)	mass flow (mg/s)	bulk air ratio (λ)
p850–100	850	100	2.0	0
c850–100	850	100	2.0	0.24
c850–61	850	61	1.21	0.40
c850–40	850	40	0.80	0.61
c850–30	850	30	0.60	0.82
c850–21	850	21	0.41	1.19
c850–15	850	15	0.29	1.65
c650–100	650	100	2.00	0.24
c750–100	750	100	2.00	0.24
c950–100	950	100	2.00	0.24
c1050–100	1050	100	2.00	0.24

run with excess of oxygen). This relation is the inverse of bulk equivalence ratio ϕ used elsewhere (11).

Table 2 presents the operating conditions of the 11 runs performed at different temperatures and oxygen ratios.

The mass flow of waste was calculated considering that the sample, which was uniformly distributed in a short distance and burnt in a fixed front, so the rate of advance of the boat can be related with the burning rate of the sample. Under this assumption and using the ultimate analysis data, the mass flow in the combustion process can be calculated; these values are shown in Table 2.

The gas flow (air or nitrogen) used was 280 mL/min at 25 °C and 1 atm. For this flow, the residence time estimated is 5–7 s inside the central part of the furnace, where the temperature is above the nominal temperature minus 50 °C.

Results

The results are presented and discussed from two viewpoints. On one hand, runs from 1 to 7 were programmed to estimate the effect of the bulk air ratio λ . In this way, this ratio λ was varied between 0 (pyrolysis experiment) and 1.39, while the temperature was maintained at 850 °C. On the other hand, in the experiments 7–12, the temperature is the variable operating conditions, and the bulk air ratio is approximately constant ($\lambda = 0.25$).

Effect of Bulk Air Ratio (λ). Table 3 shows the yields of volatile and semivolatile organic compounds detected in the experiments at different bulk air ratio. A logical result of yields can be observed, and an estimated error around 5% can be considered as acceptable for these runs.

Glass wool in the second part of the reactor was used in runs with $\lambda \geq 0.4$ to obtain a good air mixing.

Figure 3 shows the variation of the CO₂ yield, observing that this increases progressively with λ values as far as $\lambda = 1$, whereas the CO yield increases for λ less than 0.45, while

TABLE 3. Yields and Behavior of Volatile and Semivolatile Compounds for the Runs at Different Bulk Air Ratio^e

run no.	p850-100	c850-100	c850-61	c850-40	c850-30	c850-21	c850-15	
temp (°C)	850	850	850	850	850	850	850	
sample mass (g)	0.1	0.1	0.060	0.040	0.030	0.020	0.015	
mass flow (mg/min)	120	120	73	48	36	25	18	
bulk air ratio (λ)	0	0.24	0.40	0.61	0.82	1.19	1.65	
total out bulk ratio (λ^T_{out})	0	0.559	0.633	0.734	0.768	1.01	1.04	

	pyrolysis			combustion				behavior type
	p850-100	c850-100	c850-61	c850-40	c850-30	c850-21	c850-15	
Yields of Volatile Compounds (mg/100 mg Scrap Tire)								
CO ₂ ^a	3.7	150	170	200	210	310	320	
CO ^a	1.9	25.8	22.8	20.3	15.2	nd	nd	
methane ^a	8.3	6.6	3.8	2.5	1.6	0.005	0.008	I
ethane ^a	0.28	0.032	0.012	0.002	0.003	nd	nd	I
ethylene ^a	6.3	4.2	2.4	1.16	0.89	0.002	0.007	I
propane ^a	0.10	0.045	0.021	0.010	0.006	nd	nd	I
acetylene ^a	1.07	0.84	0.73	0.54	0.38	0.005	0.002	I
CS ₂ ^a	nd	0.007	0.005	0.003	nd	nd	nd	I
butane ^a	0.012	nd	nd	nd	nd	nd	nd	I
pentane ^a	nd	0.022	nd	0.012	nd	0.0000	0.0000	I
propine ^a	0.155	0.061	0.042	0.012	0.016	0.001	0.001	I
butine ^a	0.037	0.001	0.024	0.019	0.014	nd	0.001	I
hexane ^a	0.040	0.042	0.020	0.014	0.009	nd	nd	I
benzene ^a	15	8.2	4.9	2.6	1.93	0.170	0.42	I
toluene ^a	0.92	0.40	0.19	0.084	0.062	0.010	0.064	I
total light hydrocarbons	32.5	20.5	12.2	6.9	4.9	0.18	0.56	
Yields of Semivolatile Organic Compounds (mg/kg Scrap Tire)								
phenylethyne ^b	940	250	260	300	63	nd	nd	I
styrene ^b	4700	1400	910	650	170	110	190	I
2,3-butanediol ^c	nd	nd	nd	5	250	nd	64	II
benzaldehyde ^c	nd	nd	8	36	20	17	49	
benzonitrile ^b	420	420	100	110	75	nd	nd	I
benzene, ethenylmethyl- ^b	290	240	60	52	59	15	nd	I
octane, 2,4,6-trimethyl- ^b	nd	nd	nd	88	560	480	250	II
1-hexanol, 2-ethyl ^b	18	36	14	82	81	270	550	III
benzene, 1-propynyl- ^b	3000	1800	350	550	80	21	nd	I
acetophenone ^c	nd	nd	13	33	22	120	7	II
O-isopropenyltoluene ^b	32	32	13	63	64	150	140	III
benzofuran, 2-methyl- ^c	nd	nd	12	29	nd	nd	nd	II
benzene, 1,3-diethenyl- ^b	87	24	9	6	nd	nd	nd	I
heptanoic acid, 2-ethyl ^c	nd	nd	nd	nd	nd	120	50	II
1H-indene, 1-methylene ^c	nd	nd	16	19	18	16	18	
benzaldehyde, ethyl ^b	56	37	16	49	62	73	106	III
naphthalene ^{a,d}	5600	3900	4600	4000	1200	6	19	I
benzo[b]thiophene ^{b,d}	1600	500	320	180	77	nd	nd	I
decanal ^c	nd	17	18	29	33	64	67	III
isoquinoline ^{b,d}	110	50	13	nd	nd	nd	nd	I
benzo[b]thiophene, 6-methyl- ^{b,d}	68	39	140	100	22	nd	nd	II
decanoic acid, methyl ester ^{c,d}	nd	nd	nd	nd	nd	5100	nd	II
naphthalene, methyl ^{b,d}	1100	400	250	100	nd	nd	nd	I
biphenyl ^{b,d}	5600	1300	450	310	90	nd	nd	I
acenaphthylene ^{b,d}	250	130	43	40	3	nd	nd	I
acenaphthene ^{a,d}	490	160	100	77	18	3	5	I
naphthalene, ethenyl ^{b,d}	2700	630	170	95	21	nd	nd	I
biphenylene ^b	12000	2600	1300	1100	390	nd	4	I
2-naphthalenol ^{c,d}	nd	6	nd	nd	nd	41	17	II
dibenzofuran ^{b,d}	nd	310	210	280	170	nd	nd	II
naphthalene, 1,4,5-trimethyl ^{b,d}	120	59	21	13	7	nd	nd	I
phenalene ^{b,d}	260	59	22	18	nd	nd	nd	I
fluorene ^{b,d}	3600	1000	370	290	67	nd	nd	I
aliphatic hydrocarbon <20C ^d	250	110	31	76	150	230	230	
phenol, 4-allyl-2,6-dimethoxy- ^c	nd	nd	nd	5	3	22	nd	II
biphenyl, 4-vinyl- ^{b,d}	260	60	nd	nd	nd	nd	nd	I
benzophenone ^b	220	160	nd	nd	nd	nd	30	I
1H-phenalene ^{b,d}	260	nd	6	9	nd	nd	nd	I
1,2-dihydrophenanthrene ^{b,d}	250	66	16	12	nd	nd	nd	I
fluoren-9-one ^{b,d}	nd	nd	14	16	nd	nd	nd	II
dibenzothiophene ^{b,d}	1200	340	170	88	49	nd	nd	I
phenanthrene ^a	4000	2900	1900	1300	440	6	23	I
anthracene ^c	4700	890	420	260	85	11	19	I
naphthalene, 1-phenyl- ^{b,d}	2100	440	100	64	37	nd	nd	I

TABLE 3 (Continued)

	pyrolysis			combustion				behavior type
	p850–100	c850–100	c850–61	c850–40	c850–30	c850–21	c850–15	
Yields of Semivolatile Organic Compounds (mg/kg Scrap Tire)								
1-heptadecanol ^{b,d}	nd	83	3	550	270	110	7	II
1 <i>H</i> -phenale-1-one ^{c,d}	180	27	nd	nd	nd	nd	nd	I
benzo[<i>def</i>]fluorene ^b	1800	370	130	100	52	nd	nd	I
phenanthrene, 9-methyl- ^{b,d}	240	41	nd	nd	nd	nd	nd	I
hexadecanoic acid ^{c,d}	nd	nd	nd	60	280	57	54	II
2-phenylnaphthalene ^{b,d}	2900	630	170	93	nd	nd	nd	I
aliphatic hydrocarbon 20–30 ^{b,d}	17	17	190	2000	2100	2800	5500	II
9,10-dimethylanthracene ^b	270	50	28	nd	nd	nd	nd	I
fluoranthene ^{b,d}	2100	450	160	150	91	20	23	I
2-methoxyphenantrene ^b	270	140	4000	1100	360	20	28	II
pyrene ^{b,d}	10600	4200	4400	1400	500	80	27	I
M-terphenyl ^b	nd	84	30	260	520	590	230	II
benzonaphthofuran ^{b,d}	nd	40	81	180	nd	nd	nd	II
decanedioic acid, dibutyl ester ^b	nd	nd	nd	78	520	120	26	II
benzo[<i>b</i>]naphtho 2,3-furan ^b	nd	nd	59	60	80	140	160	III
benzo[<i>c</i>]phenantrene ^b	230	180	140	nd	nd	nd	nd	I
acetic acid, octadecyl ester ^c	nd	nd	nd	110	81	790	36	II
11 <i>H</i> -benzo[<i>b</i>]fluorene ^{b,d}	1800	730	580	300	59	nd	nd	I
2-eicosanoxyethanol ^b	nd	nd	49	1500	760	69	6	II
9-octadecenamide ^c	nd	nd	nd	6100	1600	7700	5100	II
benzo[<i>b</i>]naphtho-2,3- <i>d</i> thiophene ^{b,d}	310	190	163	nd	nd	nd	nd	I
fluorene, 9-phenyl- ^{b,d}	150	nd	nd	nd	nd	nd	nd	I
benzo[<i>ghi</i>]fluoranthene ^b	996	460	455	321	59	nd	nd	I
chrysene ^{a,d}	3800	1900	1300	130	180	1000	nd	I
dodecanoic acid, tetradecil ester ^c	nd	nd	nd	nd	nd	430	610	III
2-methylchrysene ^b	110	nd	nd	nd	nd	nd	nd	I
1,2'-binaphthalene ^b	650	270	nd	nd	nd	nd	nd	I
anthracene, 9-phenyl- ^b	nd	48	nd	nd	nd	nd	nd	I
benzo[<i>j</i>]fluoranthene ^b	12000	2100	170	110	nd	nd	nd	I
perylene ^a	5100	640	270	210	nd	nd	nd	I
benzo[<i>j</i>]aceanthylene, 3-methyl ^b	580	63	nd	nd	nd	nd	nd	I
1,2:7,8-dibenzphenanthrene ^b	500	nd	nd	nd	nd	nd	nd	I
aliphatic hydrocarbon >=30 ^b	nd	nd	24	44	31	1800	8100	III
benzo[<i>ghi</i>]perylene ^b	3200	380	77	nd	nd	nd	nd	I
dibenzo DEF, <i>p</i> -chrysene ^c	210	nd	nd	nd	nd	nd	nd	I
total semivolatile compds	11000	33000	25000	25000	11900	23000	22000	

^a Authentic quantitative standard. ^b Forward values (forward value = $100 * \sum [(I_{lib} \cdot I_{unk})^2]^{1/2} / \sum I_{lib} \cdot \sum I_{unk}$ where I_{lib} = refers to the intensity of the method spectrum at a given mass and I_{unk} = refers to the intensity of the "unknown" sample spectrum at a given mass) larger than 90 and quantification using internal standard. ^c Forward values (see definition in footnote b) between 80 and 90 and quantification using internal standard. ^d Difference in Lee and Kovad's index lesser than 1% respect index published in refs 9 and 10). ^e Not detected: nd.

it decreases for λ above 0.45. CO was not detected for values of λ above 1. These yields of CO₂ and CO show that the assumption made in the calculation of the bulk air ratio was acceptable.

Table 3 also shows the behavior of the different compounds detected. The behavior of the volatiles or light hydrocarbons is the expected one, with yields decreasing as λ increases. A fact to note is that the benzene and the toluene are more resistant to oxygen atmosphere than the other semivolatile compounds.

Semivolatile compounds have been classified according to their behavior against λ . Three types were found (see Table 3): I. Compounds whose yields decrease as the bulk air ratio (λ) increases (see Figure 4a): monoaromatic compounds and polyaromatic hydrocarbons (PAHs). Note that all compounds of this group are formed by pyrolysis ($\lambda = 0$). II. Compounds whose yields increase as λ increases for low λ values and decrease for very high λ values (see Figure 4b). These compounds are partially oxidized: alcohols, organic acids, furans and some amides; the total amount of compounds in this group is lower than the amount in group I. The compounds of this group are not formed or one is formed with very low yields by pyrolysis, but their presence is favored at intermediate bulk air ratio; the yields decrease at high values of λ due to the oxidation or combustion reactions. III. Compounds whose yields increase as λ increases. This group

is formed (see Figure 4c) by aliphatic hydrocarbons and other amide compounds. The formation of these compounds is favored by the presence of air, and it seems that they are quite stable vs oxygen at 850.

Effect of Temperature. Table 4 shows the total approximate yields of volatile and semivolatile organic compounds detected in the runs at different temperatures with λ equal to 0.25.

Two different behaviors when varying the temperature can be found: Type A or compounds whose yields decrease with temperature. This group is formed principally by monoaromatic hydrocarbons and partially oxidized compounds. Figure 5a shows the yields of some compounds type A vs the temperature. Type B or compounds with a maximum yield. This group is formed by the light hydrocarbons with greater yields (benzene, toluene, methane, ethylene, and acetylene) and the PAHs. It can be observed (see Figure 5b) that the yields of these compounds have maximums at intermediate temperatures (750–850 °C).

Discussion

The total oxygen consumed in the combustion runs at different λ was calculated using the yields of the compounds analyzed (Table 3). Water and sulfur dioxide yields were estimated also using the ultimate scrap tire analysis. A new parameter for batch combustion can be defined: the total

TABLE 4. Yields and Behavior of Volatile and Semivolatile Compounds for the Runs at Different Temperatures^e

run no.	c650–100	c750–100	c850–100	c950–100	c1050–100	
temp (°C)	650	750	850	950	1050	
mass (g)	0.100	0.100	0.100	0.100	0.100	
	c650–100	c750–100	c850–100	c950–100	c1050–100	behavior type
Yields of Volatile Compounds (mg/100 mg Scrap Tire)						
CO ₂ ^a	125	119	149			
CO ^a	24	15	26			
methane ^a	3.7	4.7	6.6	5.5	1.3	B
ethane ^a	0.37	0.25	0.032	nd	nd	A
ethylene ^a	3.9	4.2	4.20	0.94	0.06	B
propane ^a	0.044	0.005	nd	nd	nd	A
propylene ^a	1.1	0.44	0.047	0.008	0.001	A
acetylene ^a	0.51	0.45	0.84	1.2	0.38	B
CS ₂ ^a	0.053	0.040	0.007	0.003	0.001	A
butane ^a	nd	0.006	nd	nd	nd	A
butylene ^a	0.52	0.06	0.001	nd	nd	A
1,3-butadiene ^a	0.005	0.002	nd	nd	nd	A
pentane ^a	0.30	0.370	0.022	0.015	0.004	A
propyne ^a	0.34	nd	0.061	0.009	nd	A
pentene ^a	0.029	nd	nd	nd	nd	A
butyne ^a	0.47	0.22	0.001	0.020	0.003	A
hexane ^a	0.006	0.004	0.042	0.013	0.001	A
benzene ^a	4.5	5.6	8.2	5.5	0.60	B
toluene ^a	1.0	0.90	0.40	0.026	0.005	A
total light hydrocarbons	16.7	17.2	20.5	13.2	2.3	
Yields of Semivolatile Organic Compounds (mg/kg Scrap Tire)						
ethylbenzene ^b	800	45	nd	nd	14	A
phenylethyne ^b	1600	970	250	300	77	A
styrene ^b	4900	5200	1400	320	84	A
benzene, ethylmethyl- ^b	140	nd	nd	nd	nd	A
benzaldehyde ^c	1800	150	nd	nd	nd	A
mesitylene ^b	1000	120	nd	nd	84	A
phenol ^b	4800	2400	nd	nd	nd	A
benzonitrile ^b	240	580	420	120	nd	A
benzene, ethenylmethyl- ^b	2400	1700	240	nd	25	A
benzene, 1-ethenyl-3-methyl ^b	630	510	nd	nd	34	A
1-hexanol, 2-ethyl ^b	65	53	36	65	52	--
benzene, 1-propenyl- ^b	1700	2800	1800	290	81	A
benzene, 1-ethyl-2,3-dimethyl- ^b	130	nd	nd	nd	nd	A
acetophenone ^c	360	28	0	0	0	A
phenol, 2-methyl- ^b	2400	55	nd	nd	nd	A
O-isopropenyltoluene ^b	240	170	32	72	26	A
styrene, 2,5-dimethyl- ^b	84	34	nd	nd	nd	A
benzofuran, 2-methyl- ^c	123	54	nd	nd	nd	A
benzene, 1,3-diethenyl- ^b	100	58	24	nd	nd	A
1H-indene, 1-methylene ^c	410	150	nd	nd	nd	A
benzaldehyde, ethyl ^b	26	8	37	23	139	
naphthalene ^{a,d}	600	680	3900	2200	840	B
benzo[b]thiophene ^{b,d}	140	200	500	230	70	B
decanal ^c	21	21	17	17	20	
naphthalene, 1,2-dihydro-6-methyl- ^b	44	18	nd	nd	nd	A
thieno[3,2-c]pyridine ^c	38	14	nd	nd	nd	A
isoquinoline ^{b,d}	3	16	50	0	0	B
naphthalene, 1,2-dihydro-2-methyl- ^b	5	nd	nd	nd	nd	A
benzo[b]thiophene, 6-methyl- ^{b,d}	13	40	39	nd	nd	B
naphthalene, methyl ^{b,d}	470	500	nd	nd	nd	A
naphthalene, 1-methyl ^{b,d}	340	350	400	27	5	A
1H-indene, 1-ethylidene- ^b	10	12	nd	nd	nd	A
biphenyl ^{b,d}	340	510	1300	370	38	B
acenaphthylene ^{b,d}	120	200	130	24	0	B
naphthalene, 1,7-dimethyl ^{b,d}	110	480	nd	nd	nd	B
naphthalene, ethenyl- ^{b,d}	290	38	630	34	nd	B
biphenylene ^b	409	890	2600	1300	500	B
acenaphthene ^{a,d}	140	58	160	nd	nd	A
biphenyl, 4-methyl- ^{b,d}	140	5900	nd	nd	nd	B
2-naphthalenol ^{c,d}	200	79	6	nd	nd	A
dibenzofuran ^{b,d}	310	340	310	26	nd	A
naphthalene, 1,4,5-trimethyl- ^{b,d}	190	100	59	12	nd	A
phenalene ^{b,d}	70	150	59	nd	nd	B
fluorene ^{b,d}	390	820	1000	140	23	B
aliphatic hydrocarbon <20	23	21	110	17	39	B

TABLE 4 (Continued)

	c650–100	c750–100	c850–100	c950–100	c1050–100	behavior type
Yields of Semivolatile Organic Compounds (mg/kg Scrap Tire)						
biphenyl, 4-vinyl ^{b,d}	nd	nd	60	nd	nd	B
acridine, 9,10-dihydro ^c	42	nd	nd	nd	nd	A
benzophenone ^b	nd	nd	160	nd	nd	B
9H-xanthene ^b	85	39	nd	nd	nd	A
1H-phenalene ^{b,d}	nd	11	nd	nd	nd	B
1,1'-biphenyl, 2,4'-dimethyl-	10	nd	nd	nd	nd	A
1,2-dihydrophenanthrene ^{b,d}	41	13	66	16	6	B
9H-fluorene, 1-methyl ^b	76	95	nd	nd	nd	A
fluoren-9-one ^{b,d}	140	74	nd	17	nd	A
dibenzothiophene ^{b,d}	130	160	340	140	18	B
phenanthrene ^{a,d}	560	470	2900	1900	320	B
anthracene ^{c,d}	170	370	890	nd	24	B
naphthalene, 1-phenyl ^{b,d}	270	640	440	45	8	B
1-heptadecanol ^{b,d}	13	17	83	49	nd	B
1H-phenale-1-one ^{c,d}	190	nd	27	nd	nd	A
benzo[def]fluorene ^b	49	79	370	180	nd	B
4H-cyclopenta[def]phenanthrene ^b	50	180	nd	nd	nd	B
phenanthrene, 9-methyl ^{b,d}	150	170	41	nd	nd	A
benzyl-naphthalene ^c	16	19	nd	nd	nd	A
2-phenyl-naphthalene ^{b,d}	330	290	630	190	nd	B
aliphatic hydrocarbon 20–30	78	60	17	79	29	A
9,10-dimethylantracene ^b	67	98	50	13	0	A
naphthalene, 1–8-di-1-propynyl ^c	0	17	nd	nd	nd	A
fluoranthene ^{b,d}	150	230	450	210	34	B
2-methoxyphenanthrene ^b	82	110	140	71	26	B
pyrene ^{b,d}	300	600	4200	3100	840	B
M-terphenyl ^{b,d}	50	68	84	nd	nd	B
benzonaphthofuran ^{b,d}	25	32	40	nd	nd	B
naphthalene, 2-benzyl ^c	8	5	nd	nd	nd	A
benzo[b]naphtho 2,3-furan ^b	82	14	nd	nd	nd	A
benzo[c]phenanthrene ^c	109	240	180	31	7	B
11H-benzo[b]fluorene ^{b,d}	260	700	730	130	nd	B
2-eicosanoxyethanol ^b	35	18	nd	nd	nd	A
5,6-dihydrochrysene ^b	33	43	nd	nd	nd	A
benzo[b]naphtho-2,3-d thiophene ^{b,d}	5	93	190	56	nd	B
benzo[ghi]fluoranthene ^b	94	320	460	330	120	B
chrysene ^{a,b}	100	250	1900	590	53	B
benzanphrenone ^b	56	41	nd	nd	nd	A
bis(ethylhexyl)phthalate ^b	69	63	nd	nd	nd	A
triphenylene, 1-methyl ^c	15	24	nd	nd	nd	A
dodecanoic acid, tetradecil ester ^c	nd	490	nd	nd	nd	B
2-methylchrysene ^b	85	64	nd	nd	nd	A
1,2'-binaphthalene ^b	29	130	260	46	nd	B
anthracene, 9-phenyl ^b	13	61	48	nd	nd	B
benzo[j]fluoranthene ^b	500	630	2100	740	44	B
perylene ^a	60	220	640	370	77	B
benzo[j]aceanthylene, 3-methyl ^b	17	63	63	nd	nd	B
1,2:7,8-dibenzphenanthrene ^b	nd	39	nd	nd	nd	B
benzo[ghi]perylene ^b	nd	nd	380	370	66	B
total semivolatile compounds	33000	34000	33000	14000	3800	

^a Authentic quantitative standard. ^b Forward values (forward value = $100 \cdot \sum [(I_{lib} \cdot I_{unk})^2]^{1/2} / \sum I_{lib} \cdot \sum I_{unk}$ where I_{lib} = refers to the intensity of the method spectrum at a given mass and I_{unk} = refers to the intensity of the "unknown" sample spectrum at a given mass) larger than 90 and quantification using internal standard. ^c Forward values (see definition in footnote b) between 80 and 90 and quantification using internal standard. ^d Difference in Lee and Kovad's index lesser than 1% with respect to index published in refs 9 and 10. ^e Not detected: nd.

out bulk air ratio (λ_{out}^T) that equals the ratio between the total oxygen consumed and total stoichiometric oxygen. A value of $\lambda_{out}^T = 1$ would mean that only stoichiometric oxygen was consumed in the run. Note that λ represents the instantaneous ratio between the stoichiometric and actual oxygen and that λ_{out}^T is related to the total oxygen fed.

In the batch combustion two possible ways can be considered. One way is that the combustion takes place in one step only with the volatile and nonvolatile matter burning at the same time as the sample is introduced into the furnace. Another possibility is a process with two steps: in the first step the volatile matter (volatile and semivolatile compounds) burns at the same velocity as the sample is introduced into the furnace, and in the second step the nonvolatile matter is burned. The combustion of nonvolatile matter depends

only on the total oxygen fed during the run and does not depend on the instantaneous amount of oxygen (related to λ) because the nonvolatile matter does not leave the solid if no reaction with the oxygen occurs. A theoretical λ_{out}^T was calculated from a mass balance for the two ways assuming that all oxygen available reacted with the volatile and semivolatile compounds and that the nonvolatile fuel is composed only by carbon.

Figure 6 shows the relation λ_{out}^T vs λ . It can be seen that the experimental values present an intermediate situation between the two ways: at low values of λ , the values λ_{out}^T approach the first way because the high production of volatile compounds does not allow the oxygen to reach the nonvolatile matter. When λ is close to 1, oxygen is available for nonvolatile fuel combustion and the second mechanism is

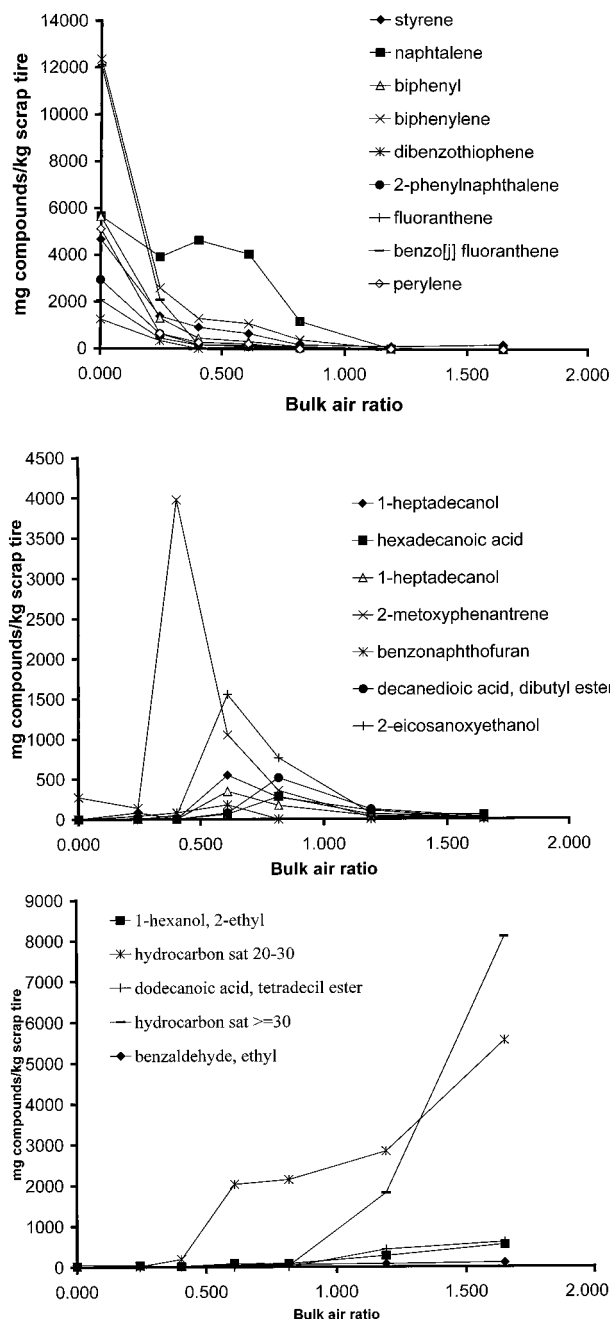


FIGURE 4. (a) Some type I compounds, (b) some type II compounds, and (c) some type III compounds.

more important. For λ over 1 the total oxygen consumed is equal to the stoichiometric oxygen; therefore $\lambda_{out}^T = 1$. Values of λ_{out}^T greater than unity are only due to experimental errors.

Figure 4a shows the yield vs bulk air ratio λ for some type I compounds. A strong decreasing behavior was also observed for monoaromatic and polyaromatic compounds for 0.5 bulk air ratio, and the yields decrease more than five times in these types of compounds. The strong decreasing behavior indicates that this group is very reactive with the oxygen. Only the most resistant compounds (naphthalene, phenanthrene, ..., etc.) maintain their yields, due probably in part to the fact that the oxygen is limited and reacts with the less stable compounds. All volatile compounds (or light hydrocarbons) have this behavior similar to the type I semivolatile compounds. Note that these compounds, formed by pyrolysis and cracking of tars, logically compress from light hydrocarbons and to structures of high molecular weight as a consequence of cracking, addition, and cyclation reactions.

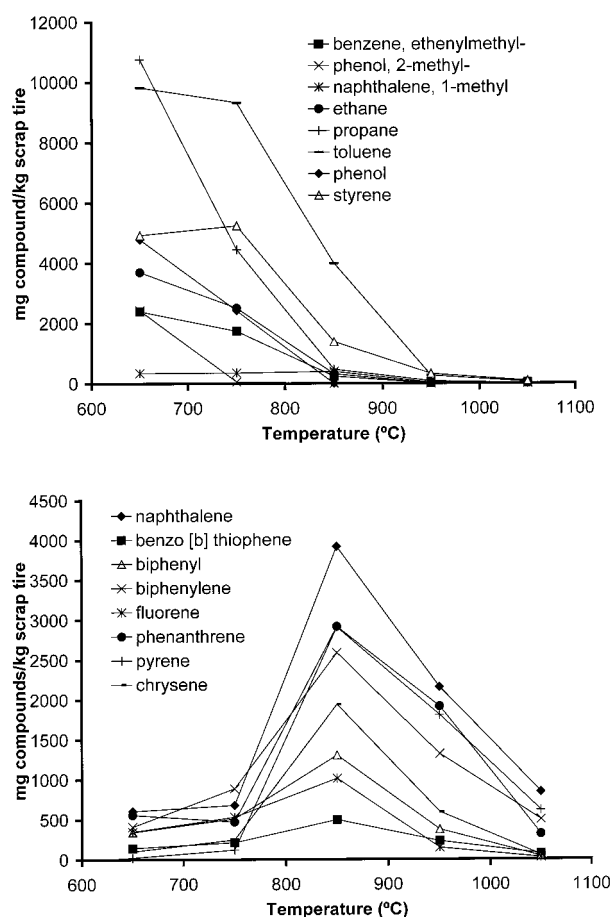


FIGURE 5. (a) Some type A compounds and (b) some type B compounds.

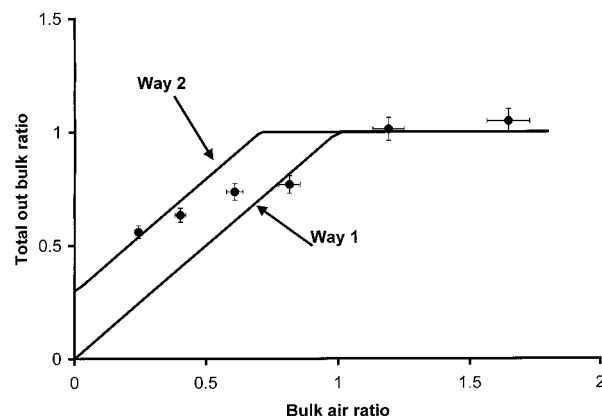


FIGURE 6. Relation between oxygen fed and oxygen consumption.

Levendis et al. (12) analyzed the effects on ϕ in PAH yields from tire waste. They found that PAH production showed an asymptotic behavior as ϕ approached zero (i.e. $\lambda = \infty$). They suggested an exponential relationship between ϕ and the level of PAH detected. This result is in accordance with the behavior of type I compounds described here.

With respect to the type II compounds (Figure 4b), we have not found any paper describing this behavior. Only a few compounds (dibenzofuran, naphthol) were identified in some papers but without describing the behavior (3, 11–13). The relative high yield of type II compounds found in this work could be due to slow cooling in the furnace (see Figure 2) that can promote the formation of the oxygenated compounds. The presence of dibenzofuran in this group must be noted, although in low yields, around 280 mg/kg.

Group III (see Figure 4c) has the most stable compounds vs the oxygen ratio. The compounds forming this group are low toxicity ones. The behavior at very high bulk air ratio cannot be deduced. It is emphasized that these compounds were detected when operating at 850 °C, and it is possible that at other temperatures their behavior could be different.

Both pyrolysis behaviors (A and B) when considering the runs with λ constant and different temperatures are a result of the competitive process between pyrosynthesis and cracking. If cracking is greater than pyrosynthesis at all temperatures, the compound would have a type A behavior. In type B, pyrosynthesis is more important than cracking at low temperatures but not at high temperatures. Figure 5a presents some compounds with type A behavior, and the compounds with type B behavior are represented in Figure 5b.

Using batch pyrolysis of tires, Cunliffe and Williams (1) found that the concentration of PAHs increases from 1.5 to 4.4 wt % in pyrolytic oils when the temperature increases from 450 to 600 °C. These values are in accordance with type II behavior for low temperatures found in this paper.

Durlank et al. (14) analyzed the PAH production from polystyrene incineration in a vertical tubular flow furnace. They showed that the PAH yield in the gas and particulate phases as well as the number of PAH species and total mass yields increased when the temperature was increased from 800 to 1200 °C. These values are in accordance with type II behavior for high temperatures.

Mastral et al. (15, 16) analyzed the temperature influence on PAH emissions in the fluidized bed combustion of coal. They found that the total PAH had a maximum yield at 800 °C according to values in group II detected in the present work.

Bofanti et al. (17) found a behavior for the PAH yields with the temperature in the pyrolysis of coal apparently different to results found in this work. They showed a PAH increase with the temperature in a pyroprobe between 250 and 1000 °C. This behavior could be due to the very slow residence time in the pyroprobe reactor, and consequently cracking did not occur significantly. Cracking is responsible for the maximum yield PAHs in the runs of the present work. Atal (11) demonstrated, adding deuterate PAH to scrap tires, that the PAH yields are a consequence of pyrosynthesing and cracking and/or burning in the reactor.

The toxic products identified in this paper, considering bulk air ratios less than unity, are probably present in

industrial combustors, where "puffs" can be formed and do not mix perfectly with excess air. The presence of some groups of compounds identified in this work, in industrial combustors, can be useful for characterizing the combustion (temperature, residence time of volatiles, and mixing with air).

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Literature Cited

- (1) Cunliffe, A. M.; Williams P. T. J. *Anal. Appl. Pyrol.* **1998**, *44*, 131.
- (2) EPA (Environmental Protection Agency). 530-SW-90-074B; October 1991.
- (3) Lemieux, P.; Ryan, J. *Air Waste Manage. Assoc.* **1993**, *43*, 1106.
- (4) DeMarinin, D.; Lemieux, P.; Ryan, J.; Brooks, L.; Williams, R. *Environ. Sci. Technol.* **1994**, *28*, 136.
- (5) Teng, H.; Serio, M. A.; Wójtowicz, M. A.; Basilakis, R.; Solomon, P. R. *Ind. Eng. Chem. Res.* **1995**, *34*, 3102.
- (6) Conesa, J. A.; Marcilla, A. *J. Anal. Appl. Pyrol.* **1996**, *37*, 95.
- (7) Conesa, J. A.; Font, R.; Marcilla, A. *Energy Fuel* **1996**, *10*(1), 134.
- (8) Snonagel, P. Tires. In *Ullman's Encyclopedia of Industrial Chemistry*; VCS Verlagsgesellschaft: 1996.
- (9) Lee, M.; Vassilaros, D.; White, C.; Novotny, M. *Anal. Chem.* **1976**, *51* (6), 768.
- (10) Pereira, V.; Kovad, A.; Lee, M. J. *High Resolut. Chromatogr.* **1986**, *9*, 328.
- (11) Atal, A.; Levendis, Y. A.; Carlson, J.; Dunayevskiy, Y.; Vourros, P. *Comb. Flame* **1997**, *110*, 462.
- (12) Levendis, Y. A.; Atal, A.; Carlson, J.; Dunayevskiy, Y.; Vourros, P. *Environ. Sci. Technol.* **1996**, *30*, 2742.
- (13) Levendis, Y. A.; Atal, A.; Courtemanche, B.; Carlson, J. B. *Combust. Sci. Technol.* **1998**, *131*, 147.
- (14) Durkland, S. K.; Biswas, P.; Shi, J.; Bernhard, M. J. *Environ. Sci. Technol.* **1998**, *32*, 2301.
- (15) Mastral, A. M.; Callén, M.; Murillo M. *Fuel* **1996**, *75*, 1533.
- (16) Mastral, A. M.; Callén, M.; Murillo, M.; García, T. *Fuel* **1998**, *77*, 1513.
- (17) Bonfanti, L.; Comellas, L.; Lliberia, J. L.; Vallhonrat-Matalonga, R.; Pich-Santacana, M.; López-Piñol, D. *J. Anal. Appl. Pyrol* **1997**, *44*, 89.
- (18) Conesa, J. A.; Font, R.; Fullana, A.; Caballero, J. A. *Fuel* **1998**, *77*(13), 1469.

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