Emissions of polycyclic aromatic hydrocarbons (PAHs) from the pyrolysis of scrap tires

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Abstract

This work investigated the PAHs generated in a waste-tire pyrolysis process and the PAHs removal by a wet scrubber (WSB) and a flare. IND, DBA, and BaP were found to dominate in the powders of scrap tires before the pyrolysis. The PAHs in the carbon blacks formed in the pyrolysis were mainly 2-, 3-, 6-, and 7-ring PAHs. Nap was the most predominant water-phase PAH in the WSB effluent. About 40% of the water-phase total-PAHs in the WSB effluent were contributed by nine carcinogenic PAHs. NaP, IND, and COR displayed higher mean gas- and particulate-phase concentrations than the other PAHs in the flare exhaust. The mean removal efficiencies of individual PAHs, total-PAHs, and high carcinogenic BaP + IND + DBA were 39.1–90.4%, 76.2%, and 84.9%, respectively for the WSB. For the flare, the mean removal efficiencies of gaseous, particulate, and combined (gaseous + particulate) total-PAHs were 59.8%, 91.2%, and 66.8%, respectively, whereas the removal efficiencies were 91.0%, 80.1%, and 89.1%, respectively for the total-BaPeq. However, the gaseous BaA displayed a negative mean removal efficiency. The total PAH emission rate and factor estimated for the scrap tire pyrolysis plant were $42.3\,\mathrm{g\,d^{-1}}$ and $4.00\,\mathrm{mg\,kg\text{-}tire^{-1}}$, respectively.
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1. Introduction

In the past few years, over 2,500,000 ton of tires were produced per year in the European Union and this figure was similar in the USA (Mastral et al., 2000). About 103,054 ton of scrap tires were recovered in Taiwan in 2005 (Taiwan EPA, 2005). The production/consumption of tires is growing recently; however, it is environmentally concerned for the disposal and recycling of waste tires.

Pyrolysis techniques can be used to treat or recycle the waste tires. Via pyrolysis, scrap/waste tires can be decomposed in the absence of oxygen in

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high temperature, leading to the production of solid carbon residues, condensable fractions and gases (Diez et al., 2004). The thermal decomposition of tires could be related to tire composition and temperature. Williams and Besler (1995) pyrolyzed the major components of rubber tires: styrene–butadiene rubber (SBR), natural rubber (NR), and polybutadiene rubber (BR). They indicated that SBR and NR decomposed mainly at high and low temperatures, respectively, whereas BR decomposed at both high and low temperatures. Moreover, the char yield from the rubber tire pyrolysis was about 32–42 wt% but that from the pure rubber component pyrolysis were all <4 wt% to suggest that the main source of char was the carbon black component in tires. Gonzalez et al. (2001) reported that the products of automobile tire waste pyrolysis in an N_2 atmosphere were approximately 37–40% char, 55% oil, and 4–11% gas. They also found that the char had a high fixed-carbon content and could be used to manufacture category-A briquettes, aliphatic and aromatic hydrocarbons and hydroxyl compounds were the major components of the oil, and the gases were identified as H_2, CO, CH_4, CO_2, C_2H_4 and C_2H_6. Dissimilarly, the product distribution ratio of gas/tar/char was about 21/44/35 at 800 °C and more gases were identified in a study performed by Leung et al. (2002) using a pyrolyzer with high heating rates. In another study, Laresgoiti et al. (2000) found that no significant influence of temperature on tire pyrolysis for the yields of solid, liquid, and gas at temperatures over 500 °C.

However, it is also possible to generate PAHs in the pyrolysis of tires. After the pyrolysis of tires, sulfur and chorine are concentrated in solid carbon residues although the chlorine in liquid and gas fractions is negligible (Diez et al., 2004). In the oil from tire pyrolysis, Williams and Bottrill (1995) identified sulfur-polycyclic aromatic hydrocarbons (PASHs, mainly dibenzothiophene, methyl/dimethyl/trimethyl dibenzothiophenes, and naphthothiophenes and their methyl derivatives). Moreover, increasing pyrolysis temperature increased the concentrations of PASHs due to a Diels–Alder-type aromatization reaction. Through the Diels–Alder aromatization reactions, the alkenes and dienes generated from alkanes pyrolysis may react together to produce mono- and polycyclic aromatic species that can subsequently form PAHs (Williams and Bottrill, 1995). Atal et al. (1997) observed significant amounts of PAHs in the effluent of the combustion of pulverized coal and tire crumbs under sufficiently

fuel-rich conditions, especially under pyrolytic conditions in N_2. They suggested that pyrosynthesis was the major contributing mechanism to the PAH emissions from the combustion of these fuels and the survivability of parent PAHs was a minor mechanism at very high equivalence ratios.

Nevertheless, little information about the characteristics of PAHs emitted from the pyrolysis of scrap tires is available. Therefore, this study investigated the PAH emission from a scrap tire pyrolysis plant equipped with two air pollution control devices (APCDs) (a WSB and a flare). The contents/concentrations of PAHs in the scrap tires, pyrolysis products, and the samples collected before/after the APCDs were determined. The removal efficiencies of these APCDs were compared and the total PAH emission rate and factor for the scrap tire pyrolysis plant were estimated.

2. Experimental

2.1. The scrap tire pyrolysis plant and its operating condition

The scrap tires used in this work were from a pyrolysis plant (in southern Taiwan) that collected used or waste tires mainly from scrap heaps or motor repair shops. The scrap tires were powdered by crumbling machines before the pyrolysis (Fig. 1). The samples were taken at five sites (A–E) in the pyrolysis process as shown in Fig. 1. These five sampling points include the feeding inlet of scrap tires (Site A), the upcast location of the carbon black storage (Site B), the location of WSB effluent (Site C), the center of pipe between the 2-stage WSB and flare (Site D), and the exit of stack flue gas (Site E). Table 1 lists the specified operating conditions for the different units in the scrap tire pyrolysis process. During operation, batch feeding of scrap tires was used and the processing time was 4 h for each batch. Therefore, the sampling time covered all the consumed time periods at the five sites.

2.2. The sampling system of PAHs

For solid material sampling (at Sites A and B), ~30 g of scrap tire powders and a similar amount of carbon black powders were collected using aluminum foils. The samples (~200 ml each) of WSB effluent (Sites C) were collected using glass bottles (pretreated with 10% nitric acid, rinsed with
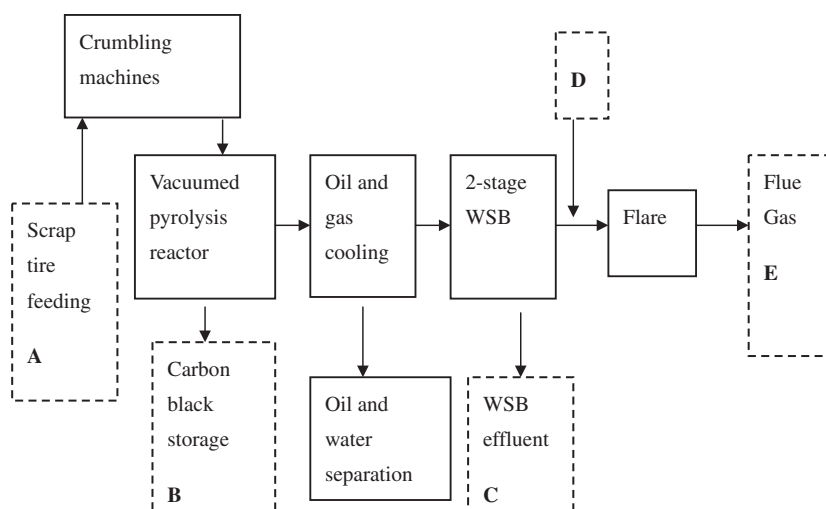
Fig. 1. PAH sampling sites (A–E) in the scrap tire pyrolysis process.

Table 1
Specified operational conditions for the scrap tires pyrolysis process

Unit	Feeding rate of scrap tires (ton h^{-1})	Production rate of carbon blacks (ton h^{-1})	Flowrate of wastewater effluent (ton h^{-1})	Flowrate of stack flue gas (m^3 h^{-1})	Combustion temperature (°C)
Thermal pyrolysis reactor	0.44	0.90	NA	NA	500
Wet scrubber (WSB)	NA	NA	0.17	NA	NA
Flare	NA	NA	NA	8200	800

NA: not available.

distilled water, and then wrapped with aluminum foils). For stack flue gas sampling (Sites D and E), the modification of USEPA's sampling method 5 (MM5) (40CFR60) by Graseby was adopted for the sampling of stack flue gases. The flue gases were isokinetically sampled from the stack by a PAH sampling system that has been adopted for sampling PAHs in various industrial stacks (Yang et al., 1998; Chen et al., 2001; Mi et al., 2001a; Tsai et al., 2001; Lee et al., 2002).

The PAH sampling system was equipped with a sampling probe, a cooling device, a glass cartridge, a pump, a flow meter, and a control computer. Tube-type glass fiber filters (cleaned by heating up to 450 °C) were used to collect particle-phase PAHs. A glass cartridge packed with XAD-2 resins and supported by a polyurethane foam (PUF) plug was used to collect the gas-phase PAHs in each sampling. After each sampling cycle, the sampling train was rinsed with *n*-hexane. Breakthrough tests

were investigated using a three-stage XAD-2/PUF cartridge. Each stage sample of the cartridge was analyzed individually and compared to examine the PAH mass collected. Breakthrough test results showed that no significant PAH mass was collected in the third stage of cartridge. To ensure the good reproducibility, all the experiments were repeated at least three times. All samples were stored at 0 °C in an ice chest until they were received at our analytical laboratory, after which they were refrigerated at 4 °C.

2.3. The extraction and analysis of PAHs

The PAH species determined included a 2-ring (Naphthalene [Nap]), five 3-ring (Acenaphthylene [AcPy], Acenaphthene [Acp], Fluorene [Flu], Phenanthrene [PA], Anthracene [Ant]), four 4-ring compounds (Fluoranthene [FL], Pyrene [Pyr], Benzo(a)anthracene [BaA], Chrysene [CHR]), six

5-ring (Cyclopenta(c,d)pyrene [CYC], Benzo(b)fluoranthene [BbF], Benzo(k)fluoranthene [BkF], Benzo(e)pyrene [BeP], Benzo(a)pyrene [BaP], Perylene [PER]), four 6-ring (Indeno(1,2,3,-cd)pyrene [IND], Dibenzo(a,h)anthrance [DBA], Benzo(b)chrycene [BbC], Benzo(ghi)perylene [BghiP]), and a 7-ring (Coronene [COR]) PAH compounds.

For PAHs extraction and analysis, all samples (including stack flue gas, bottom ash, and WSB effluent samples) were extracted in a Soxhlet extraction apparatus for 24 h with 1:1 (v/v) *n*-hexane/dichloromethane. The extracts were then concentrated, cleaned via a silica column, and reconcentrated by purging with ultra-pure nitrogen to 1.0 or 0.5 ml prior to analysis. The identification and quantification of PAHs was performed via gas chromatograph/mass spectrometer (GC/MS) measurements using a GC (Hewlett-Packard 5890A) with a Hewlett-Packard capillary column (HP Ultra 2-50 m × 0.32 mm i.d., 0.17 μm film thickness), a mass selective detector (MSD) (Hewlett-Packard 5972). Controlled by a computer workstation and equipped with a HP-7673A automatic sampler, the GC/MS instrument operated with the following conditions: injection volume = 1 μl, splitless injection = 300 °C, ion source temperature = 310 °C; oven heating from 50 to 100 °C at 20 °C min^{-1}, 100 to 290 °C at 3 °C min^{-1}, and then 290 °C-held for 40 min. A scan mode was employed to determine the masses of molecular and fragment ions of pure PAH standards in GC/MS analysis. The quantification of PAHs was performed using a selectivity ion-monitoring (SIM) mode. The system was calibrated with a diluted standard solution containing sixteen PAH compounds (PAH Mixture 610-M from Supelco) plus five individual PAH compounds (from Merk). The response factors of the PAH standard solution were used to calculate the masses of sampled PAHs at the same GC/MS relative retention time (RRT).

The total-PAHs concentration was regarded as the sum of the concentrations of 21 PAH species for each collected sample. To assess the PAH homolog distribution of each sample, the concentrations of PAH species with low molecular weight (LMW-PAHs, 2-/3-ring PAHs), middle molecular weight (MMW-PAHs, 4-ring PAHs), and high molecular weight (HMW-PAHs, 5-/6-/7-ring PAHs) were determined. The sums of the concentrations of BaP, IND, and DBA were also determined to evaluate the carcinogenic potencies of PAH for different cases discussed.

2.4. Quality control and assurance

Procedural blanks were analyzed concurrently with the samples. No detectable PAHs were present in the procedural blanks. Field blanks were treated exactly as samples except that no air was drawn through the filter/adsorbent cartridge assemblies. No significant contamination (GC/MS integrated area < detection area) was found for the field blanks including the aluminum foils, bottles, glass fiber filters, and PUF/XAD-2 cartridges. Quantification of PAHs was according to the retention times and peak areas of the calibration standards. At least five standard concentrations covering the concentrations of interest were used in PAH analysis calibration. Correlation coefficients of the calibration curves were ⩾ 0.999. In each week, the GC/MS was routinely calibrated with a diluted standard solution containing 16 PAH compounds (PAH Mixture-610 M from Supleco) plus five additional individual PAHs obtained from Merck. Ten consecutive injections of a PAH 610-M standard yielded an average relative standard deviation (RSD) of GC/MS integration area of 3.0% with a range of 0.8–5.1%. The recovery efficiencies of 21 individual PAHs were determined by processing a solution with known PAH concentrations through the same experimental procedures used for the samples. The total recovery efficiencies of PAHs ranged from 74.8% to 110.3% and averaged 86.1%. Mean RSDs of the recovery efficiencies were about 17% and the potential errors for PAHs analysis were around 16%.

Analyses of serial dilutions of PAH standards showed the detection limit of GC/MS between 0.023 and 0.524 μg for the 21 PAH compounds. The limit of quantification (LOQ) was defined as the limit of detection divided by the sampling volume. The LOQ values of the 21 PAH compounds for scrap tire powder, carbon black, and WSB effluent samples were between 0.076 and 0.175 μg N m^{-3}, 0.008 and 0.016 μg g^{-1}, and 0.102 and 2.47 μg L^{-1}, respectively.

3. Results and discussion

3.1. PAHs in the feeding scrap tire powders (Site A)

The PAH contents in scrap tire powders collected at the A sampling site may provide the inherent PAHs information in the feeding materials. The mean content of total-PAHs was 77 μg g^{-1} in the
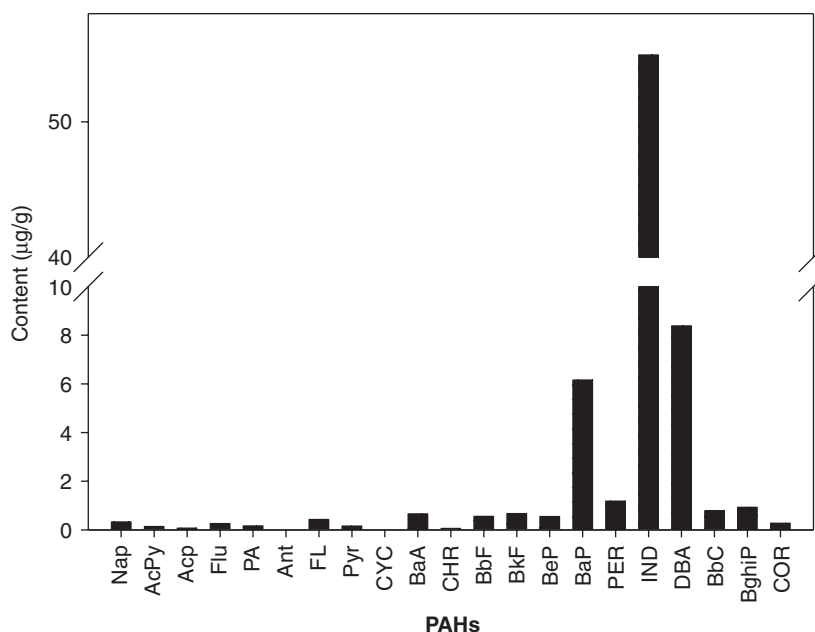
Fig. 2. Contents of 21-PAHs in the scrap tires.

powders of scrap tires (Fig. 2). The mean content of total-PAHs was dominated by HMW-PAHs; additionally, IND, DBA, and BaP accounted for 71.3% ($54.9 \mu g\,g^{-1}$), 10.9% ($8.38 \mu g\,g^{-1}$), and 8.0% ($6.16 \mu g\,g^{-1}$) of the mean content of total-PAHs in the feeding powders of scrap tires, respectively. The contents of other PAHs were less than $2 \mu g\,g^{-1}$.

3.2. PAHs in the carbon blacks (Site B)

Fig. 3 shows that the contents of 21 PAHs in the carbon blacks formed in the pyrolysis at Site B were mainly 2–3 rings PAHs (i.e. NaP, AcPy, Acp, and Flu) and 6–7 rings PAHs (i.e., IND, BghiP, and COR). In the carbon blacks, the content of BaP + IND + DBA was $\sim 210 \mu g\,g^{-1}$ and the contents of LMW-, MMW-, and HMW-PAHs were 48, 12, and $240 \mu g\,g^{-1}$, respectively; the IND displayed the highest content ($207 \mu g\,g^{-1}$) among the PAHs. Carbon blacks are very fine-powdered elemental carbon and can be obtained from the process of partial combustion or thermal decomposition of hydrocarbons. The pyrolysis of scrap tires can produce commercial carbon blacks (Sahouli et al., 1996). The formation of carbon blacks involves the combustion of vapor-phase hydrocarbons such as semi-volatile organic compounds (e.g., PAHs). The PAHs are expected to be formed due to the free radical reactions resulted from the cracking of the

feedstocks. Styrene–butadiene and NRs are the major components in scrap tires; the combustion of these rubbers may generate low-carbon hydrocarbons (e.g., butadiene) and other compounds (i.e., CO, CO_2, H_2) (Diez et al., 2004). The butadiene may precede a series of reactions to form PAHs with different rings (Catallo, 1998). Cryres and Bettens (1989) also indicated that both Nap and PA might be formed from the reactions of gas products generated in the pyrolysis of scrap tires.

3.3. PAHs in WSB effluent/exhaust and PAH removal by the WSB

3.3.1. PAHs in WSB effluent (Site C)/exhaust (Site D)

The water-phase PAH concentrations in effluent of the wet scrubber were higher for the 2- (i.e., Nap) and 6-ring (i.e., IND and DBA) PAHs than for the others. The water-phase concentrations of Nap, IND, and DBA in the WSB effluent were 8.82–63.5 (mean = 46), 5.22–46.3 (mean = 16.7), and 0.76–23.8 (mean = 7.45) $\mu g\,L^{-1}$, respectively (Fig. 4). LMW-PAHs were the predominant water-phase PAHs in the wet-scrubber effluent because the water solubilities were commonly higher for LMW-PAHs than for HMW-PAHs (Lee et al., 1998). The concentration sum of nine carcinogenic PAHs (BaA + CHR + BbF + BkF +
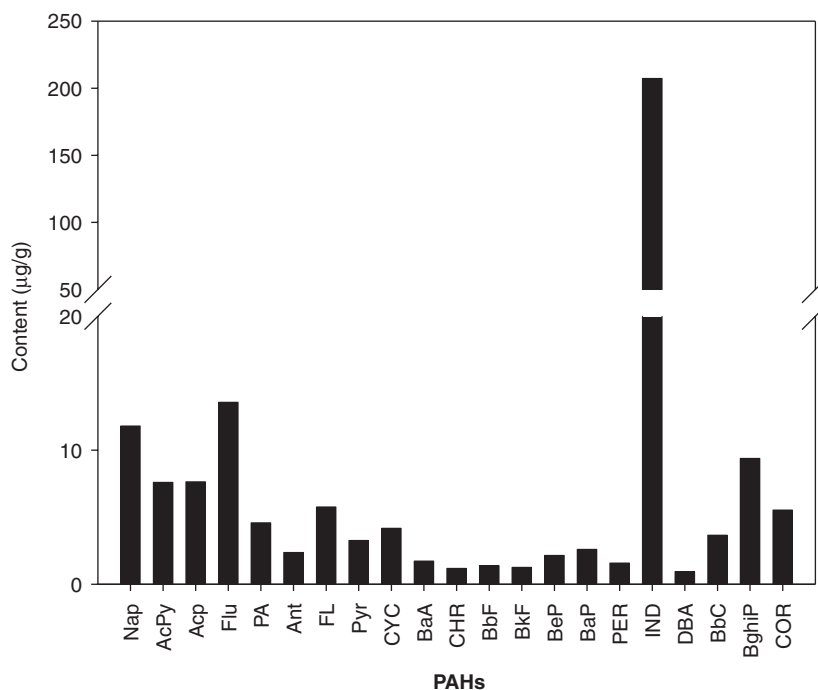
Fig. 3. Contents of 21-PAHs in the carbon blacks (Site B).
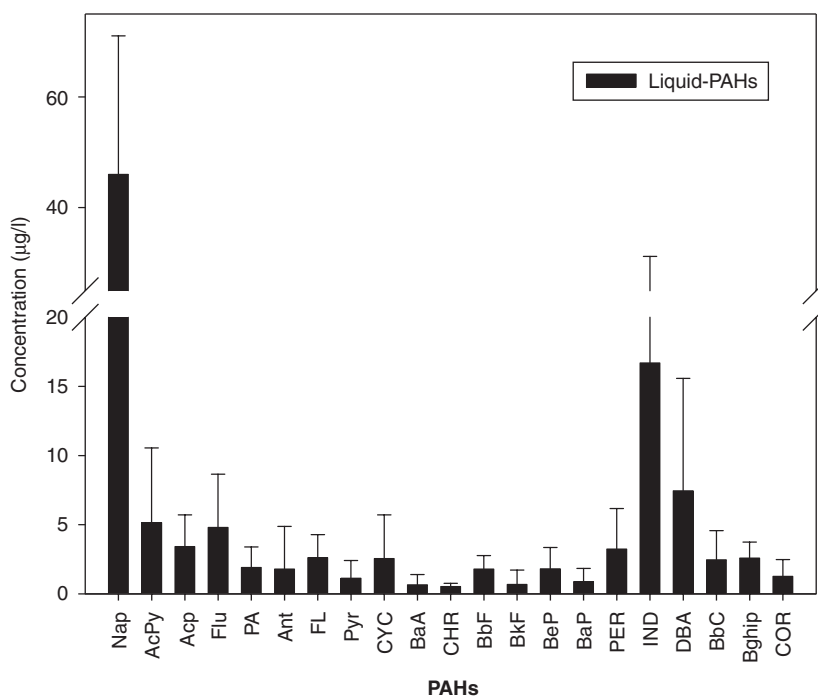

Fig. 4. Concentrations of individual liquid-phase PAHs in the WSB effluent (Site C).

BeP + BaP + IND + DBA + BghiP) with toxicity equivalence factors (TEFs) $\geqslant 0.01$ (Nisbet and LaGoy, 1992) was $41.5\,\mu g\,L^{-1}$ accounting for 40%

of the water-phase total-PAHs in the WSB effluent. The water-phase mean concentration of IND was approximately 2 folds higher than that of DBA and
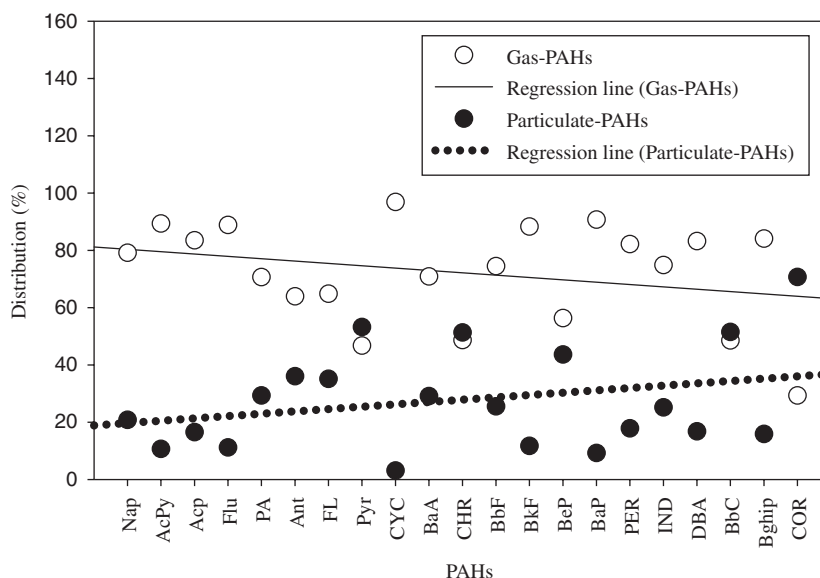
Fig. 5. Individual PAH distribution (%) between gaseous and particulate phases in the exit stack flue gas of WSB.

the two were responsible for 15.2% and 6.8% of the water-phase total-PAHs, respectively, in the effluent (Fig. 5).

In the WSB exhaust, most PAH compounds (except Pyr, CHR, BbC, and COR) displayed more fractions in gaseous phase than in particulate phase (Fig. 4). About 90% of CYC and BaP were retained in the gaseous phase; furthermore, 80% distribution in gaseous phase was observed for AcPy, Acp, Flu, BkF, PER, DBA, and BghiP. With a concentration summation of $94.8\,\mu g\,m^{-3}$, the nine carcinogenic PAHs also distributed mainly in gaseous phase; among the nine compounds, the IND displayed the highest concentration of $51.5\,\mu g\,m^{-3}$ whereas the concentration of BaP (the most toxic) was $3.40\,\mu g\,m^{-3}$.

3.3.2. PAH removal by the WSB

The concentrations of individual PAHs in WSB effluent (Site C) ranged 0.03–$51.5\,\mu g\,L^{-1}$ and the mean content of total-PAHs was $104\,\mu g\,L^{-1}$ (Table 2). For the WSB effluent, the mean effluent rates of individual PAHs and that of total-PAHs were 0.04–3.73 and $8.87\,mg\,min^{-1}$, respectively. Nap exhibited the highest effluent rate among the PAHs. For the WSB, the mean removal efficiency of LMW-PAHs (74.8%) was similar to that of HMW-PAHs (75.8%) but lower than that of MMW-PAHs (81.1%). The mean removal efficiencies of individual PAHs and total-PAHs were 39.1–90.4%, and 76.2%, respectively, correspond-

ing to the mean emission factors of 0.001–0.164 and $0.378\,mg\,kg\text{-waste}^{-1}$, respectively. The mean removal efficiency of high carcinogenic BaP + IND + DBA was 84.9%. The high PAH removal by the WSB is possibly associated with the efficient grasp of the PAHs by scrubbing water.

3.4. Concentrations of PAHs in the exhaust of flare (Site E)

According to Table 3, the mean gaseous phase PAH concentrations in the flare exhaust were 0.05–150 and $182\,\mu g\,N\,m^{-3}$ for individual PAHs and total-PAHs, respectively. Among the PAH species, the NaP, IND, and COR displayed higher mean gaseous phase concentrations (150, 7.47, and $5.47\,\mu g\,N\,m^{-3}$, respectively) than the others. That the Nap dominated in the flare exhaust is similar to the observations reported by Yang et al. (1998) for various industrial stack gases. On the other hand, the mean particulate phase PAHs concentrations in the flare exhaust were not detected (ND)—1.17 and $11.4\,\mu g\,N\,m^{-3}$ for the individual PAHs and total-PAHs, respectively. Again, the NaP, IND, and COR displayed higher mean particulate phase concentrations (1.17, 6.08, and $0.46\,\mu g\,N\,m^{-3}$, respectively) than the others. For the residual PAHs in sampling tubes, the mean concentrations of Nap, PA, and IND (5.39, 3.80, and $3.18\,\mu g\,N\,m^{-3}$, respectively) were apparently higher than those of the others; additionally, the mean residual

Table 2
PAH removal rates/efficiencies for the WSB (Sites C and D) ($N = 7$)

PAHs	Effluent of WSB Site C		Exhaust flue gas of WSB Site D		PAHs mean removal efficiency (%)
	PAHs[a] mean concentration ($\mu g\,L^{-1}$)	PAHs mean effluent rate ($mg\,min^{-1}$)	PAHs mean emission rate ($mg\,min^{-1}$)	PAHs mean Emission Factor ($mg\,kg\text{-waste}^{-1}$)	
Nap	51.5	3.73	1.20	0.164	75.7
AcPy	2.22	0.42	0.12	0.016	78.4
Acp	3.91	0.28	0.07	0.010	79.7
Flu	7.91	0.39	0.12	0.016	76.9
PA	2.22	0.16	0.14	0.019	53.3
Ant	1.01	0.15	0.03	0.004	84.8
FL	2.70	0.21	0.04	0.005	83.4
Pyr	0.79	0.09	0.03	0.004	77.1
CYC	1.16	0.21	0.32	0.044	39.1
BaA	0.56	0.05	0.01	0.001	85.7
CHR	0.29	0.04	0.01	0.001	78.1
BbF	0.57	0.15	0.02	0.003	90.4
BkF	0.03	0.06	0.01	0.001	84.7
BeP	0.61	0.15	0.05	0.007	75.4
BaP	0.81	0.07	0.02	0.003	81.7
PER	0.31	0.26	0.06	0.008	80.6
IND	21.3	1.35	0.24	0.033	84.7
DBA	1.85	0.60	0.08	0.011	88.4
BbC	2.13	0.20	0.09	0.012	68.6
Bghip	1.94	0.21	0.03	0.004	86.7
COR	0.39	0.10	0.09	0.012	53.1
LMW-PAHs	0.08	5.13	1.68	0.229	74.8
MMW-PAHs	0.06	0.39	0.09	0.012	81.1
HMW-PAHs	4.87	3.36	1.01	0.138	75.8
BaP + IND + DBA	24.0	2.02	0.34	0.047	84.9
Total PAHs	104	8.87	2.77	0.378	76.2
Total BaP$_{eq}$ ($\mu g\text{-BaP}_{eq}/m^3$)	NA	171	26.4	NA	86.6

[a]Including solid- and water-phase PAHs; NA: not available.

BaP + IND + DBA and total-PAHs in the sampling tubes were 5.16 and $21.7\,\mu g\,N\,m^{-3}$, respectively. As a result, the residual LMW- and HMW-PAHs were apparently more abundant than the MMW-PAHs in the tubes. For the gaseous PAHs, The concentration of LMW-PAHs was significantly higher than those of MMW- and HMW-PAHs whereas the concentration was higher for HMW-PAHs than for LMW- and MMW-PAHs in the particulate PAHs. All the three molecular PAH groups distributed more in the gaseous phase than in the particulate phase.

Table 4 shows the removal efficiencies of PAHs for the flare. The mean removal efficiencies of individual gaseous PAH species and total-PAHs were 24.6–98.9 (except the BaA and COR) and 59.8%, respectively, whereas the mean removal efficiencies of individual particulate PAHs and

total-PAHs were 47.2–100% and 91.2%, respectively. The mean removal efficiency of gaseous COR was only 2.70%. Note that the mean concentration of gaseous BaA increased after the flare treatment to display a negative mean removal efficiency (−38.8%), possibly associated with the aromatization reactions via Diels–Alder mechanisms (Williams and Bottrill, 1995; Catallo, 1998). This phenomenon was not found for the particulate BaA, with a removal efficiency of 97.0%. As a result, the BaA displayed a negligible mean gaseous + particulate removal efficiency (0.53%). Therefore, the combined (gaseous and particulate phases) mean removal efficiencies of individual PAHs and total-PAHs were 39.9–98.8 (except the BaA) and 63.1% for the flare. The mean removal efficiency of particulate PAHs was higher for the LMW- and MMW-PAHs than for the HMW-PAHs

Table 3
Mean concentrations of gaseous phase and particulate phase PAHs in the exhaust of flare (Site E) ($N = 7$)

PAHs	Gaseous phase PAHs ($\mu g \, N \, m^{-3}$)		Particulate phase PAHs ($\mu g \, N \, m^{-3}$)		Residual PAHs[a] ($\mu g \, N \, m^{-3}$)	
	Mean	Range	Mean	Range	Mean	Range
Nap	150	0.11–543	1.17	0.57–2.19	5.39	0.25–11.6
AcPy	2.68	0.29–6.77	0.15	0.07–0.32	0.68	0.05–1.44
Acp	2.40	0.09–9.25	0.11	0.03–0.28	0.33	0.13–0.71
Flu	1.91	0.11–6.94	0.30	0.01–1.39	0.46	0.02–0.88
PA	1.72	0.17–4.54	0.17	0.01–0.90	3.80	0.22–20.7
Ant	0.28	0.01–0.65	0.35	0.01–0.80	0.94	ND–3.49
FL	0.47	0.08–2.15	0.15	0.03–0.54	0.72	0.11–3.63
Pyr	0.25	0.04–0.73	0.05	0.001–0.20	0.57	0.01–3.43
CYC	0.75	ND–4.53	0.06	ND–0.16	0.56	ND–2.11
BaA	1.86	ND–13.0	0.02	ND–0.05	0.09	ND–0.22
CHR	0.13	0.01–0.74	0.01	ND–0.02	0.07	0.01–0.26
BbF	0.95	ND–4.97	0.44	0.02–1.77	0.20	0.03–0.61
BkF	0.05	ND–0.19	ND	ND	0.15	ND–0.52
BeP	1.12	0.19–4.57	0.60	0.02–1.54	0.55	0.24–1.15
BaP	0.15	ND–0.86	0.12	ND–0.49	0.46	ND–1.64
PER	1.49	0.05–7.49	0.67	ND–3.79	0.84	0.23–3.03
IND	7.47	0.02–29.6	6.08	0.08–22.8	3.18	0.06–17.3
DBA	0.60	ND–1.36	0.15	ND–0.36	1.52	0.03–9.96
BbC	1.55	ND–9.92	0.09	ND–0.39	0.30	ND–0.78
Bghip	0.58	ND–3.43	0.23	0.01–1.15	0.04	ND–0.20
COR	5.47	0.23–18.4	0.46	0.06–0.46	0.83	0.19–2.34
LMW-PAHs	159	7.00–533	2.25	0.82–5.57	11.6	4.79–26.3
MMW-PAHs	2.71	0.16–16.6	0.23	0.03–0.76	1.45	0.25–7.54
HMW-PAHs	20.2	1.09–61.6	8.90	1.71–25.7	8.63	1.56–20.7
BaP + IND + DBA	8.22	0.02–31.8	6.35	0.08–23.6	5.16	0.09–28.9
Total-PAHs	182	8.00–569	11.4	3.10–27.8	21.7	8.05–53.5
Total-BaP$_{eq}$	1.95	125–5251	0.93	114–2685	2.36	232–11,821

[a] Residual PAHs in sampling tubes; ND: not detected.

but a reverse trend was found for their gaseous phase removal efficiencies. This phenomenon cannot be evaluated only using the very limited information from the flare combustion operation (Table 1) because PAHs' decomposition and formation are very complicated in the thermal treatment. The gaseous and particulate BaP + IND + DBA were 85.2 and 60.3% removed by the flare, respectively. The mean removal efficiencies of gaseous, particulate, and combined (gaseous + particulate) total-PAHs were 59.8%, 91.2%, and 66.8%, respectively. However, more PAHs were removed by the WSB than by the flare, when comparing the performance of these APCDs.

3.5. Emission rate and factor

According to Tables 1–4, the emission rates of gaseous, particulate, and residual (in sampling tubes) PAHs calculated were 24.9, 1.56, and 3.00 mg min^{-1}, respectively, to obtain corresponding emission factors of 3.39, 0.21, and 0.40 mg kg-tire^{-1}, respectively for the pyrolysis plant. As a result, the total PAH emission rate and factor estimated for the scrap tire pyrolysis plant were 42.3 g d^{-1} and 4.00 mg kg-tire^{-1}, respectively (Table 5). This emission rate was apparently greater but the emission factor was significantly smaller when compared with those reported by Lee et al. (2002) for two medical waste incinerators (MG-MWI and FG-MWI) although the PAH emission concentration was smaller in this study (Table 5). This observation discrepancy is attributed to the different feeding materials, APCDs, and processes used in the two different studies mentioned. Nevertheless, the emission factor observed in this study for the scrap tire pyrolysis plant, even after applying APCDs for the PAH emission reduction, was close to that for a heavy-oil-fired boiler but higher than those for a power plant (Yang et al., 1998), steel/iron plants (Yang et al., 2002), and a coal-fired boiler (Chen et al., 2004) in Taiwan. The above results warrant

Table 4
Removal efficiencies of PAHs for the flare ($N = 7$)

PAHs	PAHs mean concentrations in the entrance of flare ($\mu g \, N \, m^{-3}$)		PAHs mean concentrations in the exit from the flare ($\mu g \, N \, m^{-3}$)		PAHs mean removal efficiencies (%)		
	G_{IN}	P_{IN}	G_{OUT}	P_{OUT}	G_R	P_R	$(G+P)_R$
Nap	199	52.4	150	1.17	24.6	97.8	39.9
AcPy	21.7	2.59	2.68	0.15	87.6	94.0	88.3
Acp	12.5	2.47	2.40	0.11	80.8	95.4	83.2
Flu	21.9	2.75	1.91	0.30	91.3	89.1	91.0
PA	20.2	8.40	1.72	0.17	91.5	98.0	93.4
Ant	3.51	1.98	0.28	0.35	92.0	82.4	88.5
FL	5.78	3.13	0.47	0.15	91.9	95.2	93.0
Pyr	2.69	3.06	0.25	0.05	90.7	98.2	94.8
CYC	65.7	2.12	0.75	0.06	98.9	97.3	98.8
BaA	1.34	0.55	1.86	0.02	−38.8	97.0	0.53
CHR	1.24	1.30	0.13	0.01	89.5	99.5	94.5
BbF	2.43	0.83	0.95	0.44	60.9	47.2	57.4
BkF	1.87	0.25	0.05	ND	97.3	100	97.6
BeP	5.69	4.40	1.12	0.60	80.3	86.4	83.0
BaP	3.09	0.32	0.15	0.12	95.1	62.4	92.1
PER	10.9	2.38	1.49	0.67	86.3	71.9	83.7
IND	38.5	12.9	7.47	6.08	80.6	53.0	73.6
DBA	13.8	2.79	0.60	0.15	95.7	94.7	95.5
BbC	9.36	9.93	1.55	0.09	83.4	99.1	91.5
Bghip	5.68	1.08	0.58	0.23	89.8	78.5	88.0
COR	5.62	13.6	5.47	0.46	2.70	96.6	69.1
LMW-PAHs	279	70.6	159	2.25	43.0	96.8	53.9
MMW-PAHs	11.1	8.04	2.71	0.23	75.6	97.1	84.6
HMW-PAHs	163	50.6	20.2	8.90	87.6	82.4	86.4
BaP + IND + DBA	55.4	16.0	8.22	6.35	85.2	60.3	79.6
Total PAHs	453	129	182	11.4	59.8	91.2	66.8
Total BaP$_{eq}$ (μg-BaP$_{eq}$/Nm^3)	21.7	4.7	1.95	0.93	91.0	80.1	89.1

ND: not detected; G: gaseous phase; P: particulate phase.
PAHs mean removal efficiencies (%): $G_R = [(G_{IN} - G_{OUT})/G_{IN}] \times 100\%$, $P_R = [(P_{IN} - P_{OUT})/P_{IN}] \times 100\%$, and $(G+P)_R = \{[(G_{IN} + P_{IN}) - (G_{OUT} + P_{OUT})]/(G_{IN} + P_{IN})\} \times 100\%$.

Table 5
Comparison of PAH emission rates and factors for different sources in Taiwan

Sources	Concentrations ($\mu g \, N \, m^{-3}$)	Emission rates ($g \, d^{-1}$)	Emission factors ($mg \, kg$-waste^{-1})	References
Scrap tires pyrolysis plant	215[a]	42.3	4.00	This study
MG-MWI	1094[a], 1290[b]	26.2	24.9	Lee et al. (2002)
FG-MWI	497[a], 587[b]	12.3	85.6	Lee et al. (2002)
Coal-fired boiler	NA	NA	0.12	Chen et al. (2004)
Heavy oil boiler	NA	NA	3.97	Yang et al. (1998)
Power plant	NA	NA	0.60	Yang et al. (1998)
Steel/iron plant	844[a,c], 1360[b,c]	NA	2.06[a]	Yang et al. (2002)

MG: mechanical grate; FG: fixed grate; MWI: medical waste incinerator; NA: not available.
[a] The mean concentration of total-PAHs with APCD treatments.
[b] The mean concentration of total-PAHs without APCD treatments.
[c] The mean value of twelve steel/iron plants.

the need for seeking better technologies to remove the PAH compounds from the scrap tires pyrolysis process investigated.

3.6. Evaluation of BaP-equivalent carcinogenicity

The TEFs estimated by Nisbet and LaGoy (1992) were adopted in this study to obtain the toxic potency (relative to that of BaP) of each PAH species. These TEFs are termed by BaP equivalent (BaP_{eq}) (the carcinogenic potency of the individual PAH divided with the carcinogenicity of BaP). ($BaP_{eq} = TEF \times PAH$ concentration (Mi et al., 2001b)) It is found that the total-BaP_{eq} content in carbon black was about $24.9\,\mu g\,g^{-1}$. The total-BaP_{eq} mean effluent rate reached $171\,mg\,min^{-1}$ for the effluent wastewater of WSB at Site C and the mean emission rate of total-BaP_{eq} was $26.4\,mg\,min^{-1}$ for the exhaust flue gas of WSB at Site D; furthermore, the WSB exhibited a removal efficiency of 86.6% in total-BaP_{eq} (Table 2). At Site E, the total-BaP_{eq} of sampling-tube residual PAHs in flare exhaust was $2.36\,\mu g\,N\,m^{-3}$ (Table 3); additionally, the total-BaP_{eq} concentrations in the entrance of flare were 21.7 and $4.7\,\mu g\,N\,m^{-3}$ for gaseous and particulate phases PAHs, respectively, whereas the concentrations were lowered to 1.95 and $0.93\,\mu g\,N\,m^{-3}$, respectively in the exit of flare (Table 4). The total-BaP_{eq} mean removal efficiencies for the gaseous and particulate PAHs were 91.0% and 80.1%, respectively, and the combined (gaseous and particulate phases) total-BaP_{eq} mean removal efficiency was 89.1% for the flare.

4. Conclusions

PAHs emission from a waste-tire pyrolysis process was investigated in this work. For the powders of scrap tires, the mean content of total-PAHs was $77\,\mu g\,g^{-1}$ dominated by HMW-PAHs (IND, DBA, and BaP). The PAHs in the carbon black formed in the pyrolysis were mainly 2-/3-ring PAHs (NaP, AcPy, Acp and Flu), and 6-/7-ring PAHs (IND [$207\,\mu g\,g^{-1}$, the highest content], BghiP and COR). LMW-PAHs (Nap) were the predominant water-phase PAHs in the wet-scrubber effluent. Distributing mainly in gaseous phase, the nine carcinogenic PAHs (BaA, CHR, BbF, BkF, BeP, BaP, IND, DBA, and BghiP) accounted for 40% of the water-phase total-PAHs in the WSB effluent. In the flare exhaust, NaP, IND, and COR displayed higher mean gas (150, 7.47, and $5.47\,\mu g\,N\,m^{-3}$,

respectively) and particulate-phase concentrations (1.17, 6.08, and $0.46\,\mu g\,N\,m^{-3}$, respectively) than the other PAHs; Nap and IND were also dominant in sampling-tube.

The mean removal efficiencies of individual PAHs, total-PAHs, and high carcinogenic BaP + IND + DBA were 39.1–90.4%, 76.2%, and 84.9%, respectively for the WSB. For the flare, the mean removal efficiencies of gaseous individual (except the BaA and COR) and total-PAHs were 24.6–98.9% and 59.8%, respectively, whereas these efficiencies were 47.2–100% and 91.2% % for particulate individual- and total-PAHs, respectively; however, the BaA displayed a negative mean removal efficiency in gaseous phase and the mean removal efficiency of gaseous COR was small. Furthermore, the mean removal efficiencies of gaseous, particulate, and combined (gaseous + particulate) total-PAHs were 59.8%, 91.2%, and 66.8%, respectively, for the flare. Therefore, more PAHs were removed by the WSB than by the flare. The flare displayed 91.0%, 80.1%, and 89.1% removal efficiencies in total-BaP_{eq} for the gaseous, particulate, and combined (gaseous + particulate) PAHs, respectively. The total emission rate and factor estimated for the scrap tire pyrolysis plant were $42.3\,g\,d^{-1}$ and $4.00\,mg\,kg\text{-}tire^{-1}$, respectively.

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