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# EFFECT OF POTASSIUM HYDROXIDE ON PAH FORMATION DURING TOLUENE INCINERATION

## Yu-Ling Wei

Department of Environmental Science, Tunghai University, Taichung City, Taiwan 407, R.O.C. Tel: (Int'l code)+886 4 359 1368. Fax: (Int'l code)+886 4 359 6858. E-mail: yulin@s867.thu.edu.tw

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## ABSTRACT

A laboratory-scale liquid-injection incinerator was used to incinerate toluene at 750  $^{\circ}$ C and PAH emission was analyzed. The results indicate that the emission of solid-phase PAHs considerably increased when potassium hydroxide was added into a fuel-lean toluene flame; more potassium hydroxide resulted in more solid-phase PAHs. But this phenomenon was not observed for the fuel-rich toluene flame. The enhanced PAH formation is proposed as by-product of the partial oxidation or incomplete burning of soot in the secondary flame zone of the fuel-lean flame. It is suggested that reducing soot formation via potassium hydroxide addition may increase PAHs. ©1998 Elsevier Science Ltd. All rights reserved

## **1 INTRODUCTION**

Approximately 30 % of non-halogen-containing solvents spent in USA was not recycled or recovered [1-2]. Upon incineration of used solvent, the trace toxic substances emitted with flue gas streams listed in the 1990 Clean Air Act Amendments as hazardous air pollutants (HAPs) have been a great public concern [1-2]. Most PAHs are carcinogenic and/or mutagenic; they are listed as HAPs [3, 4]. PAHs are generally of anthropogenic origin, and their primary source is incomplete combustion. Sixteen of them (from two to six fused benzene rings) are listed as the priority pollutant PAHs [3, 4]. For liquid-injection incineration of waste solvent, most solid-phase PAHs are adsorbed by soot if the waste solvent is relatively free of inorganic contaminants.

Because soot represents an inefficient usage of energy or an incomplete destruction of incinerated . waste which turns into an air pollution problem, a large number of studies have focused upon soot formation, characteristics, and reduction. Compounds of alkali, alkali earth, transition metals, halogens, sulfur, nitrogen, etc. have often been added into flames to study the reduction of soot formation [6-18]. Many previous studies showed that the addition of metal salts was generally effective in reducing soot formation with some minor exceptions. Although PAHs have long been considered as precursors of soot and/or side products during soot formation, most previous studies relating to the effects of metal salts have focused on soot alone. The effect of metal salts upon sixteen priority pollutant PAH formation seems to have been neglected, and to our knowledge no such data have been reported.

Therefore, the objective of this study was to investigate the formation of PAHs when potassium hydroxide solution was added into toluene incineration flames. The potassium hydroxide was used to represent the inorganic impurity in the waste toluene, or to represent the soot suppressor during combustion in many previous studies.

# **2 EXPERIMENTAL**

#### 2.1 Liquid-injection incinerator

Although liquid waste can be incinerated in various types of incinerator including fluidized-bed, fixed-hearth, rotary-kiln, and the liquid-injection types, liquid-injection incinerator has the advantage of low capital and maintenance cost. It is generally simple, consisting of refractory-lined cylinders equipped with waste burners [1-2]. The vertically aligned liquid-injection incinerator is usually a better choice when liquid waste is high in inorganic salts; the horizontally oriented one is suitable for low-salt liquid waste [1-2]. The most frequent problems for liquid-injection incinerators are associated with atomizer clogging, especially when the waste solvents are mixed with inorganic materials. Such clogging problems were relatively easier to solve, compared with various complicated problems associated with other types of incinerators; thus, a laboratory-scale liquid-injection incinerator was chosen to study the effects of equivalence ratio and sodium hydroxide solution upon PAH formation from toluene incineration.

The laboratory-scale liquid-injection incinerator was made of a stainless steel (s.s.) pipe with an inside diameter of 6.0 cm, and a height of 100 cm, of which 40 cm was electrically heated and the remaining 60 cm served as an entrance region for air preheating. Ceramic fiber was wrapped around the s.s. pipe, and Ni/Cr heating wire of 2.0 mm diameter and 0.4297  $\Omega$ /m electrical resistance coiled around the ceramics-wrapped incinerator. Four k-type thermocouples were inserted into the incinerator to measure the temperature at different heights. Temperature controllers with digital display were connected to the thermocouples. An error of  $\pm$  5 °C within the pre-set temperature was always obtainable with this incinerator. Due to the small scale of the incinerator, electrical heat (rather than auxiliary fuels) was supplied to heat the incinerator to the pre-set temperature.

The feeding system included two injection needles driven by two syringe pumps. The sizes of the syringes were 5.0 and 20.0 ml to contain potassium hydroxide solution and toluene, respectively. The

openings of the injection needles were placed near the centerline of the s.s. pipe at the same height in opposite directions. Two s.s. guiding pipes were welded to the incinerator, and their opening ends were each equipped with a teflon septum to avoid gas leakage. Because the septum was about 17 cm away from the outer wall of the incinerator, thermal deformation of the septum and resulting leakage were avoided. The feeding rates of both the potassium hydroxide solution and toluene were measured to be within  $\pm 1\%$  error from the preset rates.

#### 2.2 Incineration and sampling

A filter cassette was placed in the first position of the sampling setup to intercept the soot in the flue gases coming out from the exit of the s.s. incinerator. A condenser followed the filter cassette to collect the condensed water which contained some condensed PAHs at this stage. After the condenser, there were four sorbent tubes: two XAD-2 tubes to adsorb PAHs, and two charcoal tubes to trap the unburned toluene. The four after pumps sampled at the same flow rate. The XAD-2 and charcoal tubes were considered broken-through if the amount of PAHs or toluene adsorbed in the rear section exceeded 20% of that in the front section. The experimental run associated with any breakthrough of the tube was discarded.

The dried combustion air (without moisture content) entering the incinerator was obtained by pumping the atmospheric air through a dryer to strip the moisture from the air. To keep the nominal gas residence time at ca. 2.5 seconds for all experimental runs (fuel-lean or fuel-rich), the flow rate of the dried combustion air was fixed at 8 liters/min, and the feeding rate of toluene was changed to provide oxygen-rich or oxygen-deficient conditions during incineration. Two equivalence ratios  $\psi$ , 0.75 (fuel-lean) and 1.25 (fuel-rich) were chosen for this study. The  $\psi$  was defined as the ratio between the stoichiometric air flow rate for a theoretical complete combustion and the air flow rate actually pumped into the incinerator. The reason for choosing 0.75 and 1.25 was as follows.

Dempsey and Oppelt made a critical review of incineration of hazardous waste, and compiled data relating to several on-site liquid-injection incinerators. Their compiled data indicated that the percent excessive oxygen in the flue gas stream was  $3.1 \sim 13.2 \%$  [2], which could be converted to an equivalence ratio of  $0.85 \sim 0.37$ , or a percent excess air of  $17.3 \sim 169 \%$ . In our study, the equivalence ratios used were 0.75 and 1.25, which were equivalent to a percent excess air of 33 and -20 % excess air. In other words, our fuel-lean toluene incineration was so chosen that the percent excess air was within the range for the on-site liquid-injection incinerators compiled by Dempsey and Oppelt. On the other hand, although no on-site liquid-injection incinerator has been operated under fuel-rich conditions, experimental runs of fuel-rich toluene incineration were still performed to gain some preliminary idea on how the equivalence ratio might affect the pollution outcome from toluene incineration. The knowledge of PAH formation under fuel-rich conditions is also useful when one tries to understand the pollution level of PAHs from the failure-mode operation of an incinerator. The incineration temperature was set at 750 °C and the gas residence time set at ca. 2.5 seconds.

The reason is given next.

As pointed out in a previous study, the collective data from the US-EPA incineration test program revealed that there was no absolute correlation between the level of incinerator performance and incineration temperature or gas residence time [2]. Gas residence times from 0.1 to 6.5 seconds and temperatures from 648 °C to 1450 °C were used as test parameters to study their relationship with the 99.99 % DRE [2]. Therefore, a residence time of ca. 2.5 seconds and a temperature of 750 °C were selected as experimental parameters in this study.

#### 2.3 Sample pretreatment

The feeding syringes and the glassware were all sequentially cleaned with detergent, distilled water, deionized distilled water, acetone, n-hexane, and DCM. The feeding syringes were further cleaned with toluene. Procedure for sampling pretreatment, sample treatment, and PAH analysis was designed based upon US OSHA (Occupational Safety and Health Association) Method 5506, Method 5515, US EPA Method TO 13, Method 610, and a previous study [5]. Before sampling, the glass fiber filter was oven-dried at 350 °C for 6 hours, then dried in a desiccator for 48 hours or until a constant weight reached. The purchased XAD-2 tubes were cut open at both ends right before the incineration experiment began. The sample treatment after five minutes of sampling is listed in Figure 1.

#### 2.4 Qualitative and quantitative analyses of PAHs

The calibration curve for each PAH species was constructed using five different concentrations; triplicate injections into the HPLC were performed for each concentration. The  $r^2$  values for the calibration curves were all greater than or equal to 0.995. For the PAH identification, retention time and library match analysis (LMA) were used. The average value and the standard deviation of the retention time were calculated for each PAH. The window of the retention time was defined as (average retention time)  $\pm 3 \times$  (standard deviation) for the purpose of primary qualitative identification. The LMA method was used for the final PAH identification. To construct the "spectral analysis library", the standard solutions of the sixteen priority pollutants PAHs were injected into the HPLC, and their spectral chromatograms of ultra violet (UV) absorbency-vs.-UV frequency were stored in a microcomputer as their identification fingerprints. The UV detector had a scanning wavelength from 190 nm to 310 nm. The scan threshold was set at 5.0 m AU. A match algorithm for correlation (PC 1000 software V2.5) of the fingerprints was supplied by the HPLC maker. The quantitative calculation of each PAH was carried out based upon the calibration equation.

To obtain the weight of the collected soot, the dried glass fiber filter was weighed to  $\pm 0.1$  mg before use, and the used filter was again dried to a constant weight in a desiccator for at least 48 hours before its weight was measured. The difference between these two weights was defined as the weight of the dried soot collected from each incineration run.

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Extracting the used XAD-2 and filter with DCM for 18 hrs T Concentrating the extract to ca. 10~20 ml .L Applying the extract to an eluting column (packed with silica gel + aluminum oxide powder) T Eluting with 100ml DCM / n-hexane (30/70 by volume) T Re-concentrating the eluent to ca. 2 ml T Adding 20 ml CH<sub>3</sub>CN to the concentrate T Re-concentrating the solution to ca. 2 ml T Blowing the solution to less than 1.0 ml by N<sub>2</sub> T Adding internal standards into the concentrate 1 Quantifying the concentrate to 1.00 ml with CH<sub>3</sub>CN Injecting 20 µ 1 of the final concentrate into HPLC

## Figure 1. Flowchart for sample treatment.

## 2.5 Equipment and materials

The equipment used in this study was as follows. (1) HPLC/UV/FL: TSP P4000 quat gradient pump; software: PC1000 software V2.5; detector: Spectra Focus<sup>R</sup> UV/VIS forward optical scanning detector and FL 2000 fluorescence detector; column: Phenomenex envirosep-pp, 12.5 cm  $\times$  4.6 mm i.d.; injection volume: 20 µl. (2) GC/PID: HNU 321; detector: photo ionization detector (PID); packing column: Sulpelco 1-1734, 5 % SP-1200/1.75 % Bontone 34 on 100/120 Supelcoport, 2 m length  $\times$  0.125" i.d.; temperatures: injector 90 °C, detector 90 °C, column 70 °C; carrier gas: 18 ml N<sub>2</sub>/min; injection volume: 0.40 µl; integrator: Spectra Physics SP4600 integrator. (3) Rotary evaporator: Heidolph VV2000/W13 2000/Yamata WP-15.

(4) Syringe pump: Razel, Model A-99. (5) Sampling pump: SKC, 224-PCXR7.

The chemicals used were as follows. PAH standard powder: Supelco, PAHs kit 610-N (USA); PAH standard: Supelco, Mix 610-M (USA); de-ionized water: electrical resistance > 18 Mega  $\Omega$ /cm; DCM: Mallinckrodt Chrom Ar HPLC 99.9% (USA); acetone: Mallinckrodt Chrom AR HPLC 99.0% (USA); silica gel: Riedel-de Haen, high purity (Germany); aluminum oxide: Riedel-de Haen, high purity (Germany); acetonitrile: B.D.H. HiPerSolv TM for HPLC, 99.7% (England); charcoal sorbent tube: SKC, 6 mm o.d.  $\times$  70 mm l. (USA); XAD-2 sorbent tube: SKC, 8 mm o.d.  $\times$  110 mm l. (USA); thimble filter: Toyo, 35 mm  $\times$  120 mm (Japan); methyl alcohol: Mallinckrodt Chrom Ar HPLC,99.6% (USA); benzene: Supelco, neat compound, 5.0 mg, (USA); toluene: Supelco, neat compound, 5.0

## **3 RESULTS AND DISCUSSION**

## 3.1 Calibration and detection limit

The detection limits (DL) were obtained by seven-replicate injections of the PAH standard solution of the lowest concentration of the calibration curves. Three times the standard deviation of the peak area of the seven replicate injections was divided by the slope of the calibration equation; this value was the DL for each PAH species. They were in the 0.1~8.4 ng range.

#### 3.2 Blank test and recovery test

All blank tests were performed in four replicates. The blank tests were carried out for all solvents, filter, XAD-2 tube, and field sampling. These blank tests gave results less than the DL.

The recovery test for the solid-phase PAHs was performed on soot particulates collected from an aluminum-smelting factory. About 20 grams of the soot particulates were placed in a thimble filter in a Soxhlet extractor, and were extracted with 250 ml DCM for 24 hours; at least three repetitive extractions in Soxhlet by DCM were required to have all the 16 priority PAHs less than DL. The extracted soot was considered blank soot. Then a micro syringe was used to inject (spike) a certain amount of 16 standard priority PAHs (5~100  $\mu$ g PAH/ml) into the blank soot. The PAH-spiked soots were treated the same as the real samples. The recovery yield for the 16 PAHs was (80  $\pm$  12)~(98.5  $\pm$  9.0)% with more than 90% recovery of 12 of the 16 PAHs.

To test the recovery yield of the gas-phase PAHs, a certain amount of the 16 standard PAHs was injected into XAD-2 tube, and then both ends were capped. The PAH-spiked XAD-2 tubes were stored overnight under 4 °C for adsorption equilibrium before being extracted to checked the recovery yield. Most of the 16 priority PAHs were recovered more than 90%, except that the recovery yield for phenanthrene,

anthracene, and indeno(1,2,3-cd)pyrene were (86.4  $\pm$  3.0)%, (73.4  $\pm$  2.6)%, and (88.8  $\pm$  3.1)%, respectively.

## **3.4 PAH formation**

The effect of potassium on PAH formation was coupled with the effect of de-ionized water because potassium hydroxide added was dissolved in de-ionized water. To de-couple these two effects, the effect of de-ionized water was studied by adding pure de-ionized water into the toluene flame and PAH formation was measured. This PAH formation was used as a reference level, with which the PAH formation when potassium hydroxide solution was added to the toluene flame was compared.

Table 1a & 1b is the results of the 16 solid-phase PAH formation from toluene incineration at 750 °C. It indicated that the potassium additive was much more influential upon the solid-phase PAH formation under fuel-lean conditions ( $\psi = 0.75$ ) than under fuel-rich conditions. Under fuel-rich conditions, only a very slight change in PAH mass was observed with the potassium hydroxide added. Further, fuel-lean or fuel-rich with the addition of KOH solution, 14 of the 16 priority pollutant PAHs were detected in solid phase in the flue gas of the toluene flame. For the effect of potassium hydroxide additive upon gas-phase PAHs (see Table 2a & 2b), only a slight increase of the total gas-phase PAHs was observed under either fuel-lean or fuel-rich condition.

The formation of all-phase PAH which is defined as the summation of solid- and gas-phase PAHs was mostly produced in small ring number (see Table 3a & 3b.). The sum of 2-and 3-ring all-phase PAHs accounted for ca.  $78\sim95\%$  of the sum of the 16 all-phase PAHs under fuel-lean conditions; while it was  $69\sim74\%$  under fuel-rich conditions. The reason for this was that the excess air (or oxygen) under fuel-lean conditions accelerated the incineration of toluene and hydrocarbon fragments; thus there was less opportunity for the PAHs of higher ring number ( $4\sim6$  rings) to be pyro-synthesized.

Under fuel-lean conditions (see Table 3a), the total mass of all-phase PAHs increased with the addition of potassium into the toluene flame, and more potassium additive resulted in more emission of the all-phase PAHs. However, under fuel-rich conditions (see Table 3b), there was only a minor change in the total mass of the all-phase PAHs when potassium hydroxide was added to the toluene flame. In addition, the effect of amount of potassium hydroxide addition upon the total mass of all-phase PAHs was negligible under fuel-rich conditions.

For practical application, most flames are operated under fuel-lean condition ( $\phi < 1$ ), and potassium salt additive has been extensively tested to suppress soot formation in previous studies [6]. Although previous studies confirmed the capability of soot suppression via potassium salt additive into flames, the emission of PAHs might be enhanced as observed in this study. From the environmental aspects, one might want to be careful when using potassium salt to suppress soot formation during combustion or incineration.

| PAH       | H <sub>2</sub> O | <u>K5</u>       | <u>K1</u>       |
|-----------|------------------|-----------------|-----------------|
| NaP       | 137.8 ± 9.5      | $337 \pm 31$    | $392.5 \pm 2.3$ |
| Асру      | $177.9 \pm 9.9$  | $181.2 \pm 6.7$ | $241.8 \pm 1.0$ |
| Аср       | -                | -               | -               |
| Flu       | $269 \pm 14$     | $196.3 \pm 7.4$ | $237.8 \pm 0.9$ |
| PhA       | $615.3 \pm 2.7$  | $719 \pm 24$    | $732.6 \pm 7.6$ |
| Ant       | $150.8 \pm 0.9$  | $253.3 \pm 8.2$ | $231 \pm 10$    |
| FluA      | $381.6 \pm 1.5$  | $3091 \pm 10$   | $1026 \pm 31$   |
| Pyr       | 148.6 ± 9.9      | $724 \pm 22$    | $392.2 \pm 4.0$ |
| B(a)A     | $40.7 \pm 2.5$   | $338.1 \pm 3.0$ | $185.4 \pm 1.8$ |
| Chr       | $51.5 \pm 2.3$   | $410 \pm 12$    | $262.3 \pm 2.4$ |
| B(b)F     | $28.8 \pm 0.7$   | $309.5 \pm 4.0$ | $184.7\pm0.7$   |
| B(k)F     | -                | $141.6 \pm 4.4$ | $74.3 \pm 0.8$  |
| B(a)P     | -                | $263.4\pm0.8$   | $94.3 \pm 6.6$  |
| DbA       | -                | -               | -               |
| B(g,h,i)P | -                | $174.4 \pm 3.3$ | $61.4 \pm 1.5$  |
| InP       | $34.8 \pm 5.8$   | $277.1 \pm 5.7$ | $156.3 \pm 2.0$ |
| Total     | $2037 \pm 23$    | 7416 ± 50       | $4273 \pm 35$   |

 $\phi = 0.75$  (ng PAH/g toluene).

-: non-detectable. K5:  $5 \times 10^{-4}$  mole KOH/g toluene. K1:  $1 \times 10^{-4}$  mole KOH/g toluene.

Table 1b. Solid-phase PAH formation from toluene incineration at 750 C and fuel-rich conditions,

| PAH       | H <sub>2</sub> O | K5              | K1              |
|-----------|------------------|-----------------|-----------------|
| NaP       | $145.1 \pm 4.1$  | $121 \pm 10$    | $165.0 \pm 3.9$ |
| Асру      | $388 \pm 18$     | $400 \pm 15$    | $369 \pm 12$    |
| Аср       | -                | -               | -               |
| Flu       | $571 \pm 37$     | $701 \pm 32$    | $680 \pm 40$    |
| PhA       | $1247.5 \pm 6.4$ | $1125 \pm 52$   | $1127\pm5$      |
| Ant       | $359.1 \pm 6.7$  | $299 \pm 14$    | $310.3 \pm 1.0$ |
| FluA      | $2122 \pm 145$   | $2607 \pm 179$  | $2546 \pm 62$   |
| Pyr       | $1107 \pm 52$    | $994 \pm 61$    | $830\pm36$      |
| B(a)A     | $610 \pm 17$     | $488\pm25$      | $422.1 \pm 4.8$ |
| Chr       | $724 \pm 32$     | $518 \pm 37$    | $422.4 \pm 5.8$ |
| B(b)F     | $542 \pm 16$     | $495 \pm 13$    | $412\pm20$      |
| B(k)F     | $239 \pm 23$     | $220 \pm 15$    | $165 \pm 10$    |
| B(a)P     | $374 \pm 28$     | $270.3 \pm 0.9$ | $227 \pm 15$    |
| DbA       | -                | -               | -               |
| B(g,h,i)P | $1542.2 \pm 4.1$ | $224.6\pm0.7$   | $200.8 \pm 1.1$ |
| InP       | $415.1 \pm 4.4$  | $278 \pm 24$    | $330 \pm 28$    |
| Total     | 8998 ± 170       | $8741 \pm 210$  | $8207 \pm 92$   |

 $\phi = 1.25$  (ng PAH/g toluene).

-: non-detectable. K5:  $5 \times 10^4$  mole KOH/g toluene. K1:  $1 \times 10^4$  mole KOH/g toluene.

| $\phi = 0.75$ (ng PAH/g toluene) |                  |                 |                  |  |
|----------------------------------|------------------|-----------------|------------------|--|
| PAH                              | H <sub>2</sub> O | K1              | K5               |  |
| NaP                              | 855.8 ± 8.7      | 1845 ± 73       | <b>2082</b> ± 15 |  |
| Асру                             | $1083 \pm 11$    | 593.0 ± 6.5     | $980 \pm 32$     |  |
| Аср                              | -                | -               | -                |  |
| Flu                              | 933 ± 22         | 447.7 ± 6.3     | 596 ± 41         |  |
| PhA                              | $927.7 \pm 4.3$  | $745 \pm 21$    | $619 \pm 31$     |  |
| Ant                              | $152.3 \pm 3.9$  | $241.1 \pm 3.8$ | $135.9 \pm 0.0$  |  |
| FluA                             | $72.3 \pm 2.6$   | 497 ± 15        | $71.3 \pm 3.9$   |  |
| Pyr                              | $38.5 \pm 1.7$   | 184 ± 19        | $30.6\pm2.8$     |  |
| B(a)A                            | -                | $97.5 \pm 2.2$  | -                |  |
| Chr                              | -                | $117.1 \pm 3.4$ | -                |  |
| B(b)F                            | -                | $70.7 \pm 3.2$  | -                |  |
| B(k)F                            | -                | $22.5\pm0.8$    | -                |  |
| B(a)P                            | -                | $42.7 \pm 0.1$  | -                |  |
| DbA                              | -                | -               | -                |  |
| B(g,h,i)P                        | -                | -               | -                |  |
| InP                              |                  | -               | -                |  |
| Total                            | $4063 \pm 27$    | 4903 ± 81       | $4515 \pm 63$    |  |

Table 2a. Gas-phase PAH formation from toluene incineration at 750  $\mathcal C$  and fuel-lean conditions,

-: non-detectable. K5:  $5 \times 10^{-4}$  mole KOH/g toluene. K1:  $1 \times 10^{-4}$  mole KOH/g toluene.

| Table 2b. | Gas-phase | PAH | formation <sub>.</sub> | from  | toluene  | incineratio | n al | 750 | $\mathcal{C}$ | and j | f <b>uel-r</b> ich | cond | litions, |
|-----------|-----------|-----|------------------------|-------|----------|-------------|------|-----|---------------|-------|--------------------|------|----------|
|           |           |     | d                      | 5-1.2 | 5 (ne P/ | 1H/e toluer | e).  |     |               |       |                    |      |          |

| $\varphi^{-1.23}$ (ng FAIDg totuene). |                  |                |                |  |  |  |
|---------------------------------------|------------------|----------------|----------------|--|--|--|
| PAH                                   | H <sub>2</sub> O | K1             | K5             |  |  |  |
| NaP                                   | $2070 \pm 10$    | 1884 ± 49      | $2685 \pm 55$  |  |  |  |
| Асру                                  | $385.8 \pm 4.1$  | $882 \pm 46$   | $552 \pm 17$   |  |  |  |
| Аср                                   | -                | -              | -              |  |  |  |
| Flu                                   | $182.5 \pm 4.1$  | 469 ± 28       | $232 \pm 11$   |  |  |  |
| PhA                                   | $122.9 \pm 0.8$  | $323 \pm 20$   | $163 \pm 13$   |  |  |  |
| Ant                                   | $15.0 \pm 1.2$   | $38.0 \pm 3.3$ | $13.0 \pm 0.4$ |  |  |  |
| FluA                                  | $42.0 \pm 3.1$   | $36.7 \pm 1.2$ | $35.8 \pm 1.1$ |  |  |  |
| Pyr                                   | -                | $15.4 \pm 0.7$ | -              |  |  |  |
| B(a)A                                 | -                | -              | -              |  |  |  |
| Chr                                   | -                | -              | -              |  |  |  |
| B(b)F                                 | -                | -              | -              |  |  |  |
| B(k)F                                 | -                | -              | -              |  |  |  |
| B(a)P                                 | -                | -              | -              |  |  |  |
| DbA                                   | -                | -              | -              |  |  |  |
| B(g,h,i)P                             | -                | -              | -              |  |  |  |
| InP                                   | -                | -              |                |  |  |  |
| Total                                 | $2818 \pm 12$    | $3648 \pm 76$  | $3681 \pm 60$  |  |  |  |

-: non-detectable. K5:  $5 \times 10^4$  mole KOH/g toluene. K1:  $1 \times 10^4$  mole KOH/g toluene.

|           | and fuel-lean conditions, | $\phi = 0.75$ (ng PAH/g toluene). |                 |  |  |
|-----------|---------------------------|-----------------------------------|-----------------|--|--|
| РАН       | H <sub>2</sub> O          | K5                                | K1              |  |  |
| NaP       | 994 ± 13                  | $2419 \pm 34$                     | $2238 \pm 73$   |  |  |
| Асру      | $1261 \pm 15$             | $1161 \pm 33$                     | $834.8 \pm 6.5$ |  |  |
| Аср       | -                         | -                                 | -               |  |  |
| Flu       | $1202 \pm 26$             | $792 \pm 42$                      | $685.5 \pm 6.5$ |  |  |
| PhA       | $1543 \pm 5$              | $1338 \pm 39$                     | $1478 \pm 22$   |  |  |
| Ant       | $303.1 \pm 4.0$           | 389.2 ± 8.2                       | $472 \pm 11$    |  |  |
| FluA      | $453.9 \pm 3.0$           | $3162 \pm 11$                     | $1523 \pm 34$   |  |  |
| Pyr       | $187 \pm 10$              | $755 \pm 22$                      | $576 \pm 19$    |  |  |
| B(a)A     | $40.7 \pm 2.5$            | $338.1 \pm 3.0$                   | $283 \pm 2.9$   |  |  |
| Chr       | $51.5 \pm 2.3$            | $410 \pm 12$                      | $379.4 \pm 4.2$ |  |  |
| B(b)F     | $28.8 \pm 0.7$            | $309.5 \pm 4.0$                   | $255.4 \pm 3.3$ |  |  |
| B(k)F     | -                         | $141.6 \pm 4.4$                   | $96.8 \pm 1.1$  |  |  |
| B(a)P     | -                         | $263.4 \pm 0.8$                   | $137.0\pm6.6$   |  |  |
| DbA       | -                         | -                                 | -               |  |  |
| B(g,h,i)P | -                         | $174.4 \pm 3.3$                   | $61.4 \pm 1.5$  |  |  |
| InP       | -                         | $277.1 \pm 5.7$                   | $156.3 \pm 2.0$ |  |  |
| Total     | 6066 ± 35                 | 11931 ± 80                        | 9176 ± 88       |  |  |
|           |                           |                                   |                 |  |  |

Table 3a. All-phase PAH (solid phase+gas phase) formation from toluene incineration at 750 % and fuel-lean conditions  $\phi = 0.75$  (ng PAH/s toluene)

-: non-detectable. K5:  $5 \times 10^{-4}$  mole KOH/g toluene. K1:  $1 \times 10^{-4}$  mole KOH/g toluene.

Table 3b. All-phase PAH (solid phase+gas phase) formation from toluene incineration at 750 % and fuel-rich conditions,  $\phi = 1.25$  (ng PAH/g toluene).

|           |                  | // /0 0         | · · · · · · · · · · · · · · · · · · · |
|-----------|------------------|-----------------|---------------------------------------|
| PAH       | H <sub>2</sub> O | K5              | <u>K1</u>                             |
| NaP       | $2215 \pm 11$    | $2806 \pm 56$   | $2049 \pm 49$                         |
| Асру      | $774 \pm 18$     | $952 \pm 23$    | $1251 \pm 48$                         |
| Аср       | -                | -               | -                                     |
| Flu       | $754 \pm 37$     | $933 \pm 34$    | $1149 \pm 49$                         |
| PhA       | $1370 \pm 37$    | $1288 \pm 54$   | $1450 \pm 21$                         |
| Ant       | $359.1 \pm 6.7$  | $312 \pm 14$    | $348 \pm 3.4$                         |
| FluA      | $2122 \pm 145$   | $2643 \pm 179$  | $2583 \pm 62$                         |
| Pyr       | $1107 \pm 52$    | $994 \pm 61$    | $845 \pm 36$                          |
| B(a)A     | $610\pm17$       | $488\pm25$      | $422.1 \pm 4.8$                       |
| Chr       | $724 \pm 32$     | $518 \pm 37$    | $422.4 \pm 5.8$                       |
| B(b)F     | $542 \pm 16$     | $495 \pm 13$    | $412\pm20$                            |
| B(k)F     | $239 \pm 23$     | $220 \pm 15$    | $165 \pm 10$                          |
| B(a)P     | $374 \pm 28$     | $270.3 \pm 0.9$ | $227 \pm 15$                          |
| DbA       | -                | -               | -                                     |
| B(g,h,i)P | $154.2 \pm 4.1$  | $224.6 \pm 0.7$ | $200.8 \pm 1.1$                       |
| InP       | $415.1 \pm 4.4$  | $278 \pm 24$    | $330\pm28$                            |
| Total     | $11816 \pm 170$  | $12422 \pm 220$ | $11855 \pm 120$                       |

-: non-detectable. K5:  $5 \times 10^4$  mole KOH/g toluene. K1:  $1 \times 10^4$  mole KOH/g toluene.

#### 3.4 Mechanism for PAH enhancement with potassium addition

The following discussion on the mechanism of PAH enhancement via potassium addition is based upon the mechanism of soot suppression via alkali salt addition, which has been well documented [6].

Many previous studies have reported that compounds of alkali metals in Group I of the Periodic Table are effective in suppressing soot formation via an ionic mechanism due to their low ionization potential in general. Because of the great degree of ionization in flames, potassium reduced the rates of nucleation, agglomeration and surface growth, and coagulation of soot and its precursors via the mechanism of ion repulsive force [6], whereby soot formation was suppressed in flames [6].

Bulewicz et al. observed that alkali addition reduced the number of soot particles; whereas Havnes et al. observed an opposite phenomenon [6]. The contradictory observation was explained by Howard et al. The observation of low number density and low total mass of soots by Bulewicz was perhaps due to a further burnout of small soot particles by the excessive oxygen in the flame; however, such further burnout did not occur in the secondary flame zone in the fuel-rich flame used by Haynes et al. [6]. Therefore, the considerably enhanced PAH formation via potassium addition under fuel-lean conditions in this study might be considered as the byproduct of the incomplete burnout or partial oxidation of the soot particles which were repulsive to each other due to the positive-charged characteristics, and which were relatively small in diameter. This incomplete burnout or partial oxidation of soot particles did not occur in the secondary flame zone in the fuel-rich toluene flame because there was negligible oxygen in this region. Such an inference might be further supported by our observation (see Table 1a) that the considerably enhanced PAH formation was largely associated with the solid phase (i.e., the collected soot on the glass fiber filter). Under fuel-lean conditions, the percentage increase of total solid-phase PAH under fuel-lean condition was ca. 51~94% via the KOH addition; whereas the corresponding percentage increase of total gas-phase PAHs was only ca. 11~23%. This indicated that the considerably enhanced solid-phase PAHs were trapped or adsorbed onto/inside the soot particles. Most of them did not have enough time to desorb and become gas-phase PAHs because, as inferred from a previous study [6], the incomplete burnout or partial dissociation might be present in the secondary flame zone, which is quite close to the exit port of the incinerator.

#### **4 CONCLUSION**

The amount of solid-phase PAHs was much more affected by the potassium hydroxide addition under fuellean conditions than under fuel-rich conditions. More potassium hydroxide additive resulted in more formation of solid-phase PAHs. Nevertheless, the formation of gas-phase PAH was only slightly influenced by the potassium hydroxide additive for both fuel-lean and fuel-rich conditions.

Although potassium hydroxide addition could effectively suppress soot formation during incineration or combustion in many previous studies, our results indicated that formation of the 16 priority pollutant PAHs, many of which are carcinogenic and/or mutagenic, was promoted in the toluene flame under fuel-lean conditions. But the potassium hydroxide addition only had a negligible influence upon PAH formation under fuel-rich conditions. The explanation of such different observations might be that not all further burning of soot in the secondary flame zone under fuel-lean conditions was complete to  $CO_2$  and  $H_2O$ ; rather, the incomplete burning of soot resulted in considerable formation of PAHs. In contrast, because there might be virtually no further burning of soot in the secondary flame zone under fuel-rich conditions due to the very limited availability, the PAH formation was only negligibly affected by the potassium hydroxide addition.

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