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Effect of Addition of Sodium Hydroxide and Calcium Nitrate on Polycyclic Aromatic Hydrocarbon Emission from Benzene Incineration

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Waste organic solvents can damage human health due to their great toxicity. In Taiwan, most solvents are disposed of through incineration. However, if this is done without proper combustion control, products of incomplete combustion (PIC's) such as polycyclic aromatic hydrocarbons (PAHs) and soot will be generated. They will either be collected as part of bottom and fly ashes or emitted into the atmosphere. They may pollute the atmosphere, or contaminate soil and underground water, if proper treatment is not enforced. PAHs are defined as a group of compounds that contain at least two fused aromatic rings; some of them are characterized by mutagenicity and carcinogenicity. In general, their formation mechanisms can be divided into two categories: pyrolysis and thermal synthesis (Mastral and Callën 2000). Previous research indicated that their mutagenicity and/or carcinogenicity are closely associated with their bay-region structures (Josephson 1991; Klaassen et al. 1986). To date, there is considerable literature related to studies on PAHs emitted from incineration of plastics, diesel, household waste, etc. Hawley-Fedder et al. incinerated polystyrene (PS), polyvinyl chloride (PVC), and polyethylene (PE) and measured the emission of PAHs (Hawley-Fedder et al. 1984a; 1984b; 1984c). They concluded that PS was most apt to form PAHs during incineration at 850—900℃, while PE incineration produced only little PAHs. PVC incineration also formed considerable PAHs at 950℃. Another article reported that the suppression of soot formation during PS incineration was achievable by the addition of alkali and alkali earth metal compounds. The effectiveness of suppression was in the following decreasing order: K > Na > Li for alkali, and Ba > Sr > Ca > Mg for alkali earth (Chung and Lai 1992). However, an excessive dose of these metal compounds did not necessarily suppress more soot formation (Chung and Lai 1992). Similar results were obtained with the addition of these metal compounds into an ethylene flame (Bonczky 1987; Bonczky 1988); they found that alkali earth was always more effective than alkali in suppressing soot formation. Addition of manganese compound into diesel oil (400 mg Mn/kg diesel) could reduce PAH emission by 37.2% (Yang et al. 1998); they also reported that PAHs of greater molecular weight were more reduced, i.e., by 64.5% (Yang et al. 1998). These studies showed that the formation of soot and PAHs was influenced by factors such as fuel/waste type, incineration temperature, percent excess oxygen, etc.

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Phenomena and mechanisms of soot suppression by salt addition into flames have been extensively studied (Howard and Kausch 1980; Richter and Howard 2000; Böhm and Jander 1999; Bonczky 1997; Bonczky 1988; Ndubizu and Zinn 1982). PAHs were considered as soot precursors (Howard and Kausch 1980; Richter and Howard 2000; Böhm and Jander 1999). However, although salt addition could suppress soot formation, its effect on PAH formation has not been clear so far. The objective of this research was to study the effect of addition of NaOH and $Ca(NO_3)_2$ into a liquid-injection incinerator that burnt benzene on the formation of 16 priority PAHs. Both solid-phase and gas-phase PAHs were collected under various incineration conditions, analyzed, and discussed.

MATERIALS AND METHODS

The liquid-injection incinerator was made from cylindrical 304 stainless steel. It had a height of 40 cm and an inner diameter of 6 cm. The incinerator was electrically heated by applying 220V electricity to a few Ni/Cr heating coils wrapped around it. Thermocouples were used to detect the temperature inside the incinerator and the temperatures were fed back to on-off electricity controllers. The on-off controllers turned the electrical current on or off based on a comparison between the read temperature and the pre-set temperature. Quartz wool was used for insulation to prevent heat loss. This cylindrical incinerator was operated perpendicular to the ground. Air needed for incineration flowed into it through the bottom end, and the flue gas flowed out from the top end. Benzene was fed into the incinerator through a syringe that was perpendicular to the air flow direction. A solution of NaOH or $Ca(NO_3)_2$ was fed through another syringe, that faced the benzene syringe in the opposite position and also perpendicular to the air flow direction. Figure 1 shows the incinerator and the sampling system. The flue gas from the top end of the incinerator first flowed through a glass wool and a filter to collect soots for the analysis of solid-phase PAHs, then was cooled using a heat-exchange condenser, and finally flowed through four XAD-2 adsorbents to collect gas-phase PAHs before it was pumped to the atmosphere.

The average gas residence time in the incinerator was set to be 2.5 seconds for all runs by fixing the air flow rate at 8 L/min. Benzene feeding was adjusted to 36.5 mL/min to obtain a fuel-lean incineration condition; and to 60.85 mL/min to give a fuel-rich incineration condition. The temperature of the incinerator was pre-set (controlled) at 740℃. This temperature was chosen for our study because it has been well accepted that benzene can be successfully destroy to a low enough emission level at ~680℃ to meet regulatory requirements (Chang 1991). The feeding rate of NaOH or $Ca(NO_3)_2$ was set at 1.00×10^{-4} mole metal/g benzene incinerated.

The operating procedure for the incineration experiment included these steps: (i) cleaning all parts involving sampling with dichloromethane (DCM), (ii) preheating the incinerator while the air was flowing through it to clean the incinerator at a high temperature, (iii) feeding in the benzene and solution of NaOH or $Ca(NO_3)_2$, (iv) waiting for the temperature to reach the pre-set temperature, (v) attaching the

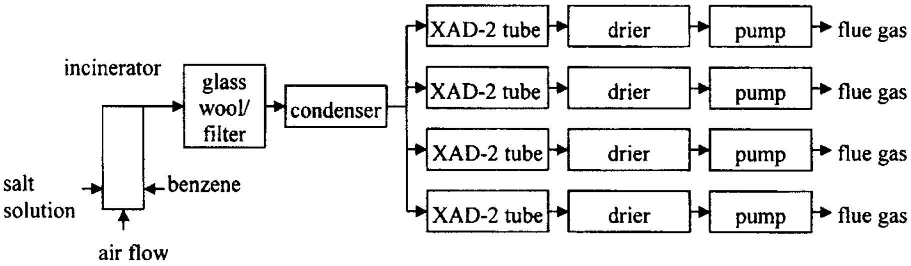


Figure 1. Sampling system

sampling system to the incinerator to guide the flue gas through the sampling system once the incinerator temperature reached the pre-set temperature, and (vi) sampling for three minutes.

The weight of the soot collected in the heat-exchange condenser, glass wool, filter, and all connecting tubing was obtained by subtracting the weight of these soot-collecting parts prior to sampling from that after sampling. Soot collected by these parts was then flushed into 250 mL DCM solvent, and then extracted with a Soxhlet extractor for 18 hr. The extract was then concentrated to 10—20 mL using a rotary evaporator, followed by flowing it through a silica gel/alumina and a LH-20 packed column (i.e. using n-hexane as eluting solvent) to separate most other organic compounds from PAHs. The last cleaned extract was finally dissolved in acetonitrile, re-concentrated to a volume less than 1.00 mL, added to an internal standard, diluted to 1.00 mL exactly with acetonitrile, and was then ready for analysis with high performance liquid chromatography (HPLC). The gas-phase PAHs sorbed in the XAD-2 tube were also extracted according to the same procedure as experienced by the solid-phase PAHs sorbed in soot.

The HPLC used for PAH analysis was equipped with a forward scanning UV detector. This UV detector can scan over a wide range of wavelengths (i.e., from 200 to 308 nm) at a step interval of 6 nm. With this procedure each PAH species was satisfactorily identified without difficulty through a comparison between the UV spectra of various PAH standards and that of the unknown sample. The forward scanning UV detector offers a much more reliable result than the conventional UV detector that in general only measures the absorbency at three different wavelengths. In addition, the average retention time for each PAH standard was used as a primary identification for that specific PAH in the unknown samples.

PAH calibration curves were constructed to quantify the PAH amount in the unknown samples. PAH standards at five different concentrations were triplicately injected into the HPLC to generate the calibration curves for all 16 priority PAHs; the correlation coefficient (r^2) was required to be greater than 0.995 before the curve was acceptable for calibration purposes. The instrumental detection limit (IDL) was obtained by injecting, in seven replicates, an aliquot of standard solution that contained the 16 PAHs and an internal standard (i.e., the PAH concentration in this aliquot was the same as that in the aliquot which was of the lowest PAH concentration among those injected for preparing the calibration curve). The area ratio, of 7 replicates, between the UV peaks of each PAH and the internal standard was then used to obtain the standard deviation (s). Three times the standard deviation (3s) was considered as the IDL for that specific PAH. The numerical value "3s" was then mathematically divided by the slope of the calibration curve to give the IDL (in unit of "ng") for the PAH. Table 1 lists all IDL for the 16 priority PAHs; the IDL range was 0.2—6.4 ng. Along with the correlation coefficient (r^2) for the calibration curves, the average retention time for each PAH and the internal standard are also shown in Table 1.

Blank tests for the solvent, filter, and XAD-2 sorbent were performed. To carry out the solvent blank test, 300 mL DCM or 105 mL n-hexane was each concentrated to 2—5 mL using a rotary evaporator. The concentrate was then mixed with 20 mL acetonitrile, and finally re-concentrated to 1.00 mL. A 20 µL aliquot of the final mixed solvent was then analyzed with the HPLC for blank PAHs. For the filter and XAD-2 blank tests, each of them underwent exactly the same extracting/ concentrating/cleaning procedure as that undergone by the unknown sample. The results of all blank tests indicated that all 16 priority PAHs were less than their respective IDLs.

Table 1. The HPLC retention time and the instrument detection limit (IDL) of the 16 priority PAHs along with the correlation coefficient (r^2) for the calibration curves

PAH species	average retention time[a] (min)	r^2	IDL[b] (ng)
I.S.	2.257±0.025		
NaP	6.468±0.071	0.999	6.4
AcPy	8.114±0.106	0.999	6.2
AcP	11.097±0.159	0.999	3.8
Flu	12.311±0.238	1.00	0.4
PhA	15.459±0.203	1.00	0.4
AnT	18.613±0.092	0.999	1.0
FluA	19.994±0.191	0.999	2.0
Pyr	20.963±0.215	0.999	0.8
B(a)A	25.041±0.345	0.999	1.2
Chr	25.998±0.398	0.999	1.2
B(b)F	29.099±0.349	0.999	2.8
B(k)F	30.367±0.071	0.998	1.4
B(a)P	31.490±0.398	0.999	2.8
DbA	33.263±0.441	0.999	3.2
B(g,h,i)P	34.414±0.079	0.999	3.4
InP	35.377±0.098	0.999	0.2

a : 3 replicates b : 7 replicates

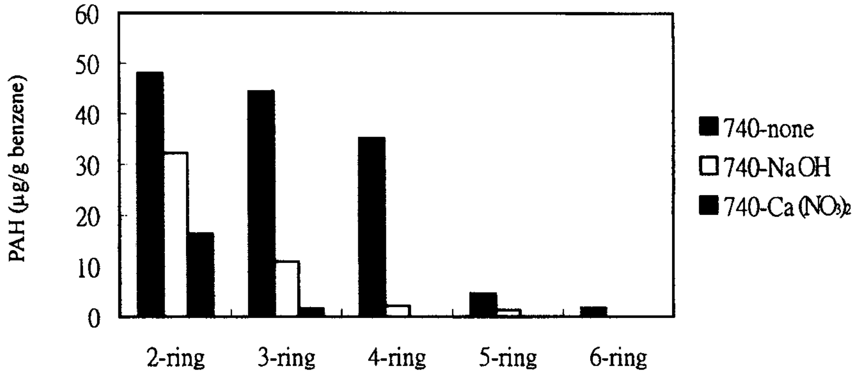
To check the PAH recovery yield, soot taken from a high-temperature process was first Soxhlet-extracted for 2—3 times to assure that their sorbed PAHs had already been stripped off to a level less than the IDLs; then this "cleaned" soot was doped with known amounts of the 16 priority PAHs. The PAH-doped soot was then treated in a way similar to the unknown samples and the 16 PAHs recovered were measured. These measured values were respectively divided (mathematically) by the added amount to give the percent recovery yield. The results indicated that the recovery percent for all 16 priority PAHs was (68 ± 0.7)% — (93 ± 4.7)%. Eleven of the 16 PAHs were recovered more than 80%.

RESULTS AND DISCUSSION

The top section of Figure 2 presents the amount of PAHs formed during the benzene incineration at 740 ℃ under the fuel-lean condition with and without the addition of NaOH or $Ca(NO_3)_2$ solution into the flame. It should be noted that the fuel-lean condition under which benzene was incinerated corresponded to an excess air of 33%, compared with the stoichiometric air flow rate. The 16 priority PAHs were categorized into six groups according to the number of the fused aromatic rings. In general, PAH containing more fused rings is usually considered as more toxic, although this is not always true. In addition PAHs of greater molecular weight (more fused rings) are less volatile and thus tend to exist in solid-phase form.

As shown in the top section of Figure 2, without addition of metal compound into the flame, the amounts of 2-, 3-, and 4-ring PAHs were almost equal (i.e., 35—50 μg PAH/g benzene); while the 5- and 6-ring PAHs only constituted a small percent of the total amount of the 16 priority PAHs. With the addition of NaOH or $Ca(NO_3)_2$, the amount of PAH was reduced. The extent of reduction was considerable for the 3-, 4-, 5-, and 6-ring PAHs, although there was only $\leq$ 60% reduction for the 2-ring PAHs. The considerable PAH reduction of the 3- through 6-ring PAHs via salt addition was of great environmental significance in the aspects of properly incinerating waste benzene solvent, because PAHs of greater ring number are usually of greater toxicity. The top section of Figure 2 also shows that $Ca(NO_3)_2$ additive was much more effective than NaOH in suppressing PAH formation during benzene incineration. This result can benefit the application of metal additive to suppress PAH formation given that $Ca(NO_3)_2$ is less corrosive than NaOH.

The bottom section of Figure 2 presents the results of PAH formation from benzene incineration at 740℃ under fuel-rich condition with and without the salt addition. It should be noted that the fuel-rich condition was equivalent to –20% excess air (or 20% starved air). The 3- and 4-ring PAHs represented the major portion of the 16 priority PAHs. It is also interesting to note that the amount of PAH is about two orders of magnitude greater than that under fuel-lean conditions. The addition of NaOH or $Ca(NO_3)_2$ into the benzene flame was not effective in reducing 2-, 3-, and 4-ring PAHs.



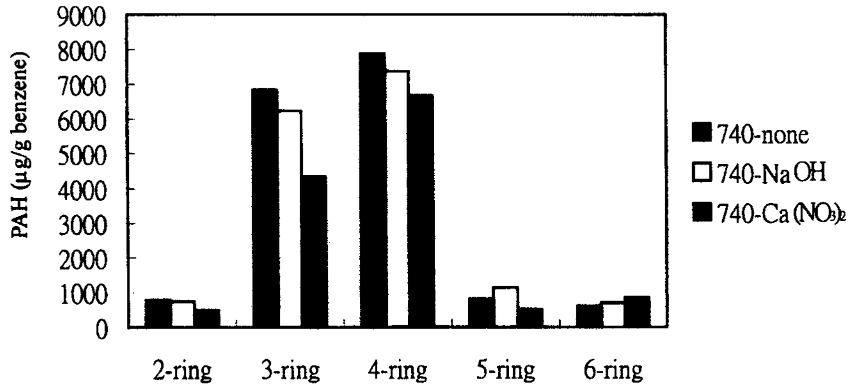


Figure 2. PAH formation from benzene incineration under fuel-lean (top section) and fuel-rich (bottom section) conditions with/without addition of metal solution

The results in the bottom compartment of Figure 2 suggest that during the failure-mode operation of benzene incineration, additional air is critically needed to provide enough oxygen to prevent a sudden increase of PAH formation. In addition, the commercial incinerators, having practical problems such as poor mixing that would lead to a locally fuel-rich condition inside the incinerator chamber, might produce considerable amounts of PAH.

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