



Enhanced extraction of PAHs hindered in fly ashes with supercritical water

K.-A. Hsueh^a, F.-C. Chang^a, H. Paul Wang^{a,b,c,*}, H.-C. Wang^d, Y.-J. Huang^e, H.-L. Huang^f, Y.-J. Tuan^{a,b}

^a Department of Environmental Engineering, National Cheng Kung University, Tainan 70101, Taiwan

^b Sustainable Environment Research Center, National Cheng Kung University, Tainan 70101, Taiwan

^c Center for Micro/Nano Science and Technology, National Cheng Kung University, Tainan 70101, Taiwan

^d Division of Chest Medicine, Department of Medicine, Veterans General Hospital-Kaohsiung, Kaohsiung 81362, Taiwan

^e Department of Biomedical Engineering and Environmental Science, National Tsing Hua University, Hsinchu 30100, Taiwan

^f Department of Safety, Health and Environmental Engineering, National United University, Miaoli 36000, Taiwan

ARTICLE INFO

Article history:

Received 19 March 2012

Received in revised form 31 August 2012

Accepted 7 September 2012

Keywords:

PAHs

Supercritical water extraction

Fly ashes

BaP

BghiP

ABSTRACT

Many polycyclic aromatic hydrocarbons (PAHs) which are toxic and suspected carcinogens are frequently found in incineration fly ashes. However, there is a lack of quality data on the levels of PAHs in fly ashes primarily due to the fact that the conventional Soxhlet extraction fails to yield significant recovery of any of the PAHs from fly ashes. With the supercritical water (SCW) at 673 K and 240 bar, PAHs hindered in fly ashes containing a wide range (0.1–21%) of unburned carbon can be extracted, which gives a more detailed finger-print PAH pattern. The extraction efficiencies of PA, BbF, BaP, and BghiP from the incineration fly ash with SCW are greater than those with Soxhlet extraction by 15, 25, 56, and 13 times, respectively. The relatively high extraction efficiency of PAHs from the fly ashes with SCW may be mainly associated with the solvent property (i.e., dielectric constant). In addition, as the unburned-carbon contents in fly ashes increase, more PAHs (NaP excluded) can be extracted.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Polycyclic aromatic hydrocarbons (PAHs) consisting of two or more fused rings in linear, angular or cluster arrangements, are considered to be the precursors of soot [1]. Many PAHs are toxic and suspected carcinogens [2]. Generally, PAHs are initially generated in the gas phase during combustion (or incineration), and undergo adsorption, absorption or encapsulation in particulate matters eventually [3–6]. Fly ashes are, in general, the main species accessible from the turbulent mixing of the high-temperature combustion chamber in an incineration process. Thus the possibly preserved finger-print profiles of the PAHs in fly ashes may reveal a better understanding of the chemistry and reaction process for formation of PAHs in the high-temperature reactions. However, there is a lack of quality data on the levels of PAHs in fly ashes primarily due to the fact that the conventional Soxhlet extraction fails to yield significant recovery of any of the PAHs from fly ashes [7,8].

Supercritical fluid extraction (SFE) has been extensively used for environmental samples because of its advantages of speed, variable solvent characteristics, and reduction of organic solvent usage

[9–12]. The analytical SFE has focused on the use of supercritical CO₂, mainly because it has little toxicity and is environmentally acceptable [13–15]. However, the low polarity of CO₂ makes it an inappropriate extraction solvent for many environmental contaminants of moderate or greater polarity [16].

The dielectric constant of water can be dramatically lowered in mild conditions by simply increasing the temperature under moderate pressures [17–19]. The solubility of low polarity organics can be increased by heating the water under moderate pressure. High pressure solvent extraction is a relatively new application of the theory of using variable combinations of temperature and pressure to optimize effectiveness of a solvent [20–23]. Thus, the main objective of this work was to study more detailed finger-print PAH patterns in fly ashes by supercritical water (SCW) extractions. For comparison, extraction experiments with subcritical water (S_bCW) and Soxhlet organic solvent were also carried out. Specifically, PAHs extracted from fly ashes sampled from sludge incineration, coal combustion, and steel smelter containing 0.01–21% of unburned-carbon were investigated.

2. Experimental

Biological sludge wastes were burned on a 20 TPD (tons per day) fluidized-bed incinerator at 1023–1223 K. The sludge incineration fly ash was sampled from the bag-house filters at 423 K. The coal-fired power plant fly ash sample was obtained from electrostatic

* Corresponding author at: Department of Environmental Engineering, National Cheng Kung University, Tainan 70101, Taiwan. Tel.: +886 6 276 3608; fax: +886 6 275 2790.

E-mail address: wanghp@mail.ncku.edu.tw (H.P. Wang).

precipitators of a coal fired power plant. The steel smelter fly ash was collected from the electrostatic precipitators in a steel smelter process. Fractions of unburned carbon in the fly ashes of sludge incineration, coal combustion, and steel smelter are 0.01, 6.3, and 21%, respectively.

The SCW and S_b CW extraction experiments were carried out in a autoclave lined with Pyrex glass. The autoclave having a volume of about 20 mL was installed with pressure and temperature gauges. In addition, to better control the autoclave pressure at elevated temperatures, 10–15 mL of water was delivered into the autoclave with a liquid pump. About 0.3–1.0 g of the fly ashes was extracted with SCW (673 K and 240 bar), S_b CW₂₀₄ (573 K and 204 bar), and S_b CW₉₀ (573 K and 90 bar) for 20 min. Dissolved oxygen in water was reduced by purging with high-purity N₂ for at least 30 min to decrease possible oxidation of hydrocarbons.

The conventional Soxhlet extraction (8–12 min per cycle) of PAHs from fly ashes was carried out following the EPA standard method (3540A). The fly ashes were placed in a pre-cleaned cellulose thimble and extracted with a mixed solvent (200 mL) of n-hexane and dichloromethane (50 vol.%) for 18 ± 2 h. Soxhlet extracts were concentrated to 3 mL by purging with ultra-high purity nitrogen.

Water and other undesired species in extracts that may disturb the separation and analysis of PAHs were further cleaned up in a column containing glass wool, 15 g of 6% deactivated silica gel in n-hexane and anhydrous sodium sulfate. About 40 mL of n-hexane was added to the column packing materials (sodium sulfate, silica gel, and glass wool). The concentrated extracts were then cleaned up in the column and flushed with 180 mL of hexane solvent to elute extracts completely from the column. The eluant was collected and concentrated to about 2 mL which was then transferred into a K-D column. Acetonitrile was used to replace the hexane solvent and internal standards were added into the extract making a total volume of 1 mL. The sample was then filtered through a 0.2 μm PVDF syringe filter to remove particles. All samples were preserved at 273 K in a refrigerator for further quantitative analysis.

Identification of PAHs was accomplished using gas chromatography (hp Model 5890) with a Model 5972 mass selective detector (GC/MS). Quantitation of the spiked test compounds was measured by GC/FID. A hp Ultra 2 capillary column (50 m × 0.32 mm × 0.17 μm) separated the sample constituents.

Quantification of 16 unsubstituted PAH priority pollutants: naphthalene (Nap), acenaphthylene (AcPy), acenaphthene (Acp), fluorene (Flu), phenanthrene (PA), anthracene (Ant), fluoranthene (FL), pyrene (Pyr), benzo(a) anthracene (BaA), chrysene (CHR), benzo(b) fluoranthene (BbF), benzo(k)fluoranthene (BkF), benzo(a) pyrene (BaP), indeno(1,2,3-cd)pyrene (IP), dibenzo(a,h)anthracene (DBA), and benzo(ghi)perylene (BghiP) was carried out by external calibration against a series of standards made up from a stock solution (Supelco Company). Samples were analyzed in triplicate. Coefficients of variance between analyses were on an average between 5 and 20%. Certified reference materials were included routinely in the sample batches (one reference material was included for every ten samples). The confirmation standards were run to check the calibration. All results were corrected for recoveries and calculated from a matrix spike containing all 16 PAHs quantified. For the SCW and Soxhlet extractions, recoveries of the spike ranged from 76 to 90% for individual PAHs (see Table 1). Residual oxygen was minimized by preparing samples and water in a nitrogen box.

3. Results and discussion

In Fig. 1(a), it is clear that the Soxhlet extraction, operated at 313–333 K, has a relatively low capability to extract PAHs from

Table 1

Recoveries (%) of spiked PAHs on pure silica gel with the SCW, S_b CW and Soxhlet extractions.

Extraction Solvent	SCW	S_b CW	Soxhlet
Dielectric constant	2.2	20	5.0
Temperature (K)	673	573	298
Nap	79.8	68.4	77.9
AcPy	80.4	48.9	75.5
Acp	81.0	56.1	78.7
Flu	82.3	65.1	79.6
Ant	85.0	70.3	82.2
PA	83.2	52.3	81.6
FluA	87.3	71.6	82.8
Pyr	87.0	68.2	85.3
BaA	87.8	62.3	89.6
Chr	88.1	71.6	88.9
BbF	83.0	70.7	80.2
BkF	88.2	69.7	88.9
BaP	86.6	53.0	87.6
DBA	86.0	73.2	86.9
IP	90.2	72.2	89.0
BghiP	88.4	71.6	87.3

the low unburned-carbon fly ash. The hindered PAHs with two or more fused benzene rings in the fly ashes are primarily caused by the incomplete combustion carbonaceous materials [24,25]. Supercritical water has a lower dielectric constant ($\epsilon = 2.2$) than Soxhlet mixture solvent (hexane and dichloromethane) ($\epsilon = 5.0$) [26,27], and therefore is an extremely effective solvent for moderate- and low-polarity PAHs. By the SCW extraction, relatively much more PAHs can be extracted, providing an informative PAH pattern in the fly ashes. The SCW can extract more PA, BaP, and BghiP from the sludge-incineration fly ash than the Soxhlet method by 13–56 times. Note that the incineration or combustion efficiency related PAHs such as PA, BaP, and BghiP are better observed.

The SCW extraction characteristics can be abruptly changed by decreasing its temperature or pressure. At 573 K, 10 K less than the critical temperature of SCW, relatively less PAHs can be extracted with the subcritical water (S_b CW), in some cases, even less than the Soxhlet extraction. It is worth noting that a relatively high selectivity for the S_b CW extraction of low-to-medium molecular weight PAHs (i.e., Nap, Acp, Flu, and PA) is found.

Table 1 shows the extraction efficiencies of PAHs using SCW, S_b CW and Soxhlet, which possess noticeably different dielectric contents (ϵ). The S_b CW, which exhibits the highest dielectric constant ($\epsilon = 20$) (at $T = 673$ K), appears to display a significantly lower extraction efficiency compared to that with SCW ($\epsilon = 2.2$) (at $T = 573$ K) and Soxhlet ($\epsilon = 5.0$). The fact that the extraction efficiencies of PAHs from the incineration fly ash with SCW are at least five times greater than those with Soxhlet extraction under the comparable recovery may be mainly associated with the solvent property, such as the dielectric constant.

Virtually most of the PAHs hindered in the fly ashes containing a wide range of unburned-carbon (0.01–21%) can be quantitatively extracted from the fly ashes with SCW if compared with the data obtained from the Soxhlet and S_b CW methods (see Fig. 1). A high selectivity for low-to-medium molecular weight PAHs (i.e., Nap, Acp, Flu, and PA) is also observed for the SCW extraction of the fly ashes. The 5–6 ring PAHs are relatively low extractable from the fly ashes with the Soxhlet extraction.

The fly ashes which were sampled from different feeds and incineration/combustion systems have a wide range of unburned-carbon contents. The low-to-medium molecular weight PAHs extracted from the three fly ashes can give detailed finger-print patterns. Note that extremely high BaP which is extracted from the high unburned-carbon in the steel-smelter fly ash may be

Download English Version:

<https://daneshyari.com/en/article/230664>

Download Persian Version:

<https://daneshyari.com/article/230664>

[Daneshyari.com](https://daneshyari.com)