Reaction Mechanism of Arsenic Capture by a Calcium-based Sorbent during the Combustion of Arsenic-Contaminated Biomass: A pilot-scale experience

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Abstract

Large quantities of contaminated biomass due to phytoremediation were disposed through combustion in low-income rural regions of China. This process provided a solution to reduce waste volume and disposal cost. Pilot-scale combustion trials were conducted for in site disposal at phytoremediation sites. The reaction mechanism of arsenic capture during pilot-scale combustion should be determined to control the arsenic emission in flue gas. This study investigated three \textit{Pteris vittata} L. biomass with a disposal capacity of 600 kg/d and different arsenic concentrations from three sites in China. The arsenic concentration in flue gas was greater than that of the national standard in the trial with no emission control, and the arsenic concentration in biomass was 486 mg/kg. CaO addition notably reduced arsenic
emission in flue gas, and absorption was efficient when CaO was mixed with biomass at 10% of the total weight. For the trial with 10% CaO addition, arsenic recovery from ash reached 76%, which is an ~eight fold increase compared with the control. Synchrotron radiation analysis confirmed that calcium arsenate is the dominant reaction product.

**Keywords:** Arsenic contamination; Phytoremediation; Emission control; Calcium-based sorbent; Biomass disposal; pilot-scale combustion.
1. Introduction

*Pteris vittata* L. was found to be a promising plant to remediate arsenic (As)-contaminated soils, as demonstrated in various lab and pilot-scale studies (Chen et al., 2006; Kertulis-Tartar et al., 2006). A 19.5ha field pilot-scale application of planting *P. vittata* L. was conducted in China for 2 years (Wan et al., 2016).

However, a main constraining factor for the wide and profitable application of phytoremediation is the disposal of large quantities of As-hyperaccumulator plant biomass (Dhir et al., 2012; Sas-Nowosielska et al., 2004). Many previous studies have suggested thermochemical biomass conversions, such as combustion, gasification, and pyrolysis, to achieve biomass volume reduction and renewable energy production (Jiang et al., 2015). Many previous studies have shown that As, Pb, Cd, and Zn are found in gaseous emissions at low temperatures during thermochemical processes (Nzihou and Stanmore, 2013; Pudasainee et al., 2014). In particular, studies have shown that As is mostly present in the gas phase as arsenic oxide (As$_2$O$_3$) at low temperature during the thermochemical treatment of As-contaminated biomass (<500 °C) (Nzihou and Stanmore, 2013; Contreras et al., 2009). Considerable previous studies on controlling elemental contaminant emissions during coal combustion have suggested the injection of mineral sorbents to capture As and other metal elements *in situ* in a combustion system (Gullett and Raghunathan, 1994; Jadhav and Fan, 2001; Mahuli et al., 1997). Gullett and Raghunathan (Gullett and Raghunathan, 1994) used four mineral sorbents in a pilot-scale combustion study to determine the As capture efficiency. They showed that Ca(OH)$_2$ and CaO remarkably improve the recovery of As and other trace...
elements in the processed ash. Subsequently, Mahuli et al. (Mahuli et al., 1997) investigated the As capture efficiency of four mineral sorbents, namely, Ca(OH)$_2$, kaolinite, alumina, and silica. X-ray diffraction and synchrotron radiation analysis showed that calcium arsenate (Ca$_3$(AsO$_4$)$_2$) is the dominant reaction product in the ash and indicated that chemical absorption is the main As capture mechanism. Jadhav and Fan (Jadhav and Fan., 2001) conducted a laboratory-scale study about the reaction mechanism of As capture by using a calcium-based sorbent. As$_2$O$_3$ vapors were used as the source of arsenic with a concentration ranging from 7 ppm to 32 ppm in each experiment. The reaction of As$_2$O$_3$ with CaO was evaluated over a wide temperature range of 300 °C–1000 °C. The thermal stability of the generated arsenates increased in the order CaAs$_2$O$_6$ (750 °C) < Ca$_2$As$_2$O$_7$ (950 °C) < Ca$_3$As$_2$O$_8$ (1400 °C). Most of the previous experimental studies have dealt with either coal or chromated copper arsenate (CCA)-treated wood. As normally exists in coal either in organic/pyrite bound and micro-mineral forms (Liu et al., 2009) or as CrAsO$_4$ precipitate in CCA-treated wood (Helsen and Van Den Bulck, 2000). However, As is a biologically accumulated element and mostly exists as arsenite in plant biomass, such as As accumulating fronds of *P. vittata* (Huang et al., 2004). In addition, the combustion conditions are relatively different for the considerable variations of proximate analysis and element concentrations of biomass and coal. Thus, an experimental study is needed to better understand the volatilization of As and the effectiveness of calcium sorbents during the combustion of As-accumulating plant biomass. This study reported the feasibility and efficiency of adding calcium-based sorbents during the phytoremediation of biomass combustion in a pilot-scale combustion furnace with a disposal
capacity of 600 kg/d. A pilot-scale experiment is difficult to control compared with laboratory-scale work. To the best of our knowledge, this is the first reported large-scale study that investigates the injection of sorbents during the phytoremediation of biomass combustion. This study provides valuable insight into As emission control during the thermochemical treatment of As-contaminated biomass. The result serves as a guide to enhance the feasibility and environmental benefits of phytoremediation projects.

2. Materials and Methods

2.1 Biomass fuel materials

The aerial parts of *P. vittata* biomass used in this study were collected from three pilot-scale As phytoremediation sites, namely, Jiyuan (JY), Hunan (HN), and Guangxi (GX). The arsenic concentration of biomass remarkably varies among the three sites. The JY site is located in Henan Province in Central China. Phytoremediation work started in 2012, and the site was contaminated with high concentrations of As and other metal contaminants released by local metal smelting industries. An area of 4,667 m² *P. vittata* planting was established on the site with a plant density of 50 cm × 50 cm.

The HN site is located in Hunan Province in South Central China. The remediation project started in 2014 on a legacy site owned by a local As smelting factory. The *P. vittata* planting area on the site is 73,337 m², and the entire site was divided into three different plots. Plant densities were expressed as follows: 4667 m² at a plant density of 40 cm × 40 cm, 54003 m² at 30 cm × 40 cm, and 12000 m² at 30 cm × 30 cm.
The GX site is located in South Central China. Similar to the two other sites, As contamination was caused by a local smelting factory, which was closed in 2005. Phytoremediation work started in 2014 on the site with an area of 4267 m$^2$ of *P. vittata* and planting density of 40 cm $\times$ 40 cm.

2.2 Biomass Feedstock Preparation and Characterization

All *P. vittata* biomass samples used in this study were air-dried until a water content of ~8% was achieved. The dried samples were shredded into ~5 mm size and pelletized into small granules with 1 cm diameter and 4.5 cm length and a density of 1.34 g/cm$^3$. The pelletized material is suitable as fuels due to its low calorific value (CV). Pelletized feedstocks have high particle and bulk densities compared with other biomass (Simone et al., 2012). Pelletization increases the combustion stability and reduces the volume of raw material by 7 to 10 times and achieves a remarkable reduction in storage space. For As chemical capture tests, CaO was blended with JY biomass as a chemical sorbent at 5%, 10%, and 15% of feedstock weight. CaO and biomass was blended by using a rotary mixer until the CaO and biomass are thoroughly mixed. The mixtures were pelletized into the same size of granules as other biomass samples. The mixing and compacting processes ensure the maximum contact between CaO additive and biomass, which promote the reactions (Neeft et al., 1997).

The dried biomass samples were digested by using 1 ml of concentrated HClO$_4$ solution and 5 ml of concentrated HNO$_3$ following the method from Yan (Yan et al., 2008) and Chen (Chen et al., 2002). The As concentration in the solutions was analyzed by using an atomic fluorescence spectrometer (AFS-9800, Haiguang Instrumental Co., China). Other elements (P,
K, Na, Ca, Mg, Pb, Cu, Zn, and Fe) were determined by using an ICP-MS (Optima 5300 DV, PE, USA). Standard reference materials for plants (GBW-07603 and GBW-08501) obtained from the China National Center for Standard Reference Materials were processed and analyzed by using the same method. Proximate analysis was conducted by using standard analytical methods (ASTM E871 and E872) to determine the moisture, ash, and volatile matter content. C, H, N, O, and S compositions of the sample were analyzed by using an elemental analyzer (Elementar Analysensysteme GmbH, Germany). The elemental analyzer operating at CHNS mode with oxygen content was calculated based on difference. CVs for the samples were determined in accordance with ASTM D2015. Samples were dried to constant weight and finely ground before analyzing the high heating values using a bomb calorimeter (SDC5015, Hunan Sundy Co. Ltd., China).

Thermal behavior of *P. vittata* samples were investigated by using a simultaneous thermogravimetric (TG) analyzer (SDT-Q600, TA Instruments, US). Biomass samples were ground into fine powder by using a mesh grinder fitted with an 80 mesh (0.074 mm). Biomass sample (20 mg) was placed in the crucible, where the temperature was measured by using a thermocouple attached to the container. The temperature increased from ambient temperature (30 °C) to 800 °C at a heating rate of 25 °C min⁻¹. Air was used as the carrier gas for the tests with the gas flow rate maintained at 20 ml min⁻¹.

**2.3 Combustor Assembly, Biomass Combustion, and As Chemical Capture Experiment**

Biomass combustion experiments were conducted in a chain-grate boiler type incinerator with a combustion furnace internal volume of 5 m³. The burner is connected to an emission
collection system with a cooling tower, that is, a bag-type dust collector and a water spraying tower. During operation, the combustion temperature was monitored and maintained at 850±10 °C by using a thermocouple. For each combustion trial, biomass feedstock was fed in the boiler at a constant rate of 1.25 kg min\(^{-1}\) for 1 h, and the feedstock was burned. The gas residence time in the boiler was 1.25 s. Bottom ashes were collected in ash collection unit 1 with hot flue gas cooled first before entering the dust collector and spray tower. Fly ash was captured at the cooling tower, and dust and ash were collected in ash collection units 2 and 3, respectively. Following the gas cleaning process, flue gas was discharged in the spray tower before discharge in the atmosphere via a chimney, and the spray tower was used to settle the particles in the flue gas. The flow rate was modulated by controlling the by-pass valve of the blower. A schematic of the incineration equipment is shown in Fig. 1.

Three biomass combustion test controls were conducted on pelletized HN, GX, and JY biomass samples. In addition, another three biomass combustion tests were performed on JY biomass samples with CaO addition at 5%, 10%, and 15%. The operational parameters for all combustion trials are shown in Table 1.
2.4 Ash and flue gas sampling and analysis

After each combustion test, bottom and fly ashes collected in ash collection units were weighed. Representative ash samples were digested by using US Environmental Protection Agency Method 3050B. The digested solutions were analyzed for As concentration by using an atomic fluorescence spectrometer (AFS-9800, Haiguang Instrumental Co., China).

X-ray absorption fine structure (XAFS) was performed to investigate the bottom and fly ash samples to provide key structural information of calcium–arsenic compounds. The ash samples were prepared and analyzed based on a standard method (ASTM D934). Briefly, ash samples and a reference As compound Ca$_3$(AsO$_4$)$_2$ were packed in a 3 cm × 0.7 cm sample holder. As K-edge (11867 eV) X-ray absorption spectra were operated at the extended X-ray adsorption fine structure (EXAFS) station on Beamline 1W1B of Beijing Synchrotron Radiation Facility. The X-ray absorption near edge structure (XANES) spectra were collected at room temperature in fluorescence mode. The energy range of the incident X-ray beam was 11800–12800 eV. A gold foil was placed between the second and third ionization chambers for energy calibration. The entire XAF spectra were background corrected and normalized. Data reduction was accomplished in IFFEFIT software package.

The flue gas of each combustion trial was sampled by using a heated isokinetic probe placed at the gas sampling port of the chimney. The temperature of isokinetic probe was maintained at 120 ± 20 °C. The gaseous elemental emissions were absorbed and retained by 5% (v/v) nitric acid (HNO$_3$)/10% hydrogen peroxide (H$_2$O$_2$) in two
ice-bath-chilled impingers. This method is in accordance with the China State Environmental Protection Administration standard method for monitoring and analysis of air and flue gas. The collected flue gas samples were analyzed for total As content by using an atomic fluorescence spectrometer (AFS-9800, Haiguang Instrumental Co., China).

2.5 Chemical Sorbent Performance Indicator

The percentage of As recovered in ash content ($E_{\text{ash}}$) during a combustion trial is calculated by using Equation 1:

$$E_{\text{ash}} = \frac{C_1 \times M_1 + C_2 \times M_2 + C_3 \times M_3 + C_4 \times V}{C_0 \times M_0 \times (1-\eta)} \times 100\%.$$  

(Equation 1)

where:

- $C_1$, $C_2$, and $C_3$ are the As concentrations (in mg kg$^{-1}$) in bottom, condensation fly, and dedusting fly ashes, respectively.
- $M_1$, $M_2$, and $M_3$ are the weights of (in kg) bottom, condensation fly, and dedusting fly ashes, respectively.
- $C_4$ is the As concentration in spray liquid (mg l$^{-1}$), $V$ is the volume of the spray liquid (l), $C_0$ is the As concentration in biomass feedstock (in mg kg$^{-1}$), $M_0$ is the input feedstock weight (kg), and $\eta$ is the moisture content of the feedstock (in %).

The As content in flue gas can be calculated by using Equation 2:

$$A_{\text{flue}} = c \cdot Q \cdot t.$$  

(Equation 2)

where $c$ is the As concentration (in L/min) in flue gas, $Q$ is the gas flow rate (in L/min), and $t$ is the combustion time (in min).

To understand the mass balance of As during combustion, total As recovery ($E_{\text{total}}$) is calculated by using Equation 3.
3. Results and Discussion

3.1 Sample analysis and characterisation

The proximate and ultimate analysis results and trace element concentrations of \( P. vittata \) biomass samples are summarized in Tables 2 and 3. The weight of biomass samples remarkably reduced based on the result of TG analysis (TGA) in Figure 2. The ash contents of \( P. vittata \) biomass from three different origins were found to be JY>GX>HN. This finding is in agreement with the TG results.

TGA on \( P. vittata \) biomass samples indicated a typical four-stage thermal devolatilization process, namely, stage1: drying, stage2: devolatilization (char forming), stage3: char combustion, and stage4: ash decomposition, as shown in Figure 2. The key thermal devolatilization characteristics of HN, GX, and JY biomass samples are summarized in Table 4.

3.2 Fate of As during Combustion Trials

As contaminants undergoes a solid-to-gaseous phase transformation during the combustion of \( P. vittata \) at low combustion temperature. An improved understanding of the As distribution in the processed ash, flue gas, and spraying liquor is key for As emission control and potential As recovery. During each combustion trial, the quantities of As in the processed ash, spray liquor, and flue gas were calculated. The results are summarized in Table 5. The flue gas testing list includes soot, blackness, CO, NOx, SO\(_2\), HCl, and HF. All concentration levels of other pollutants were below
the national standards for pollution control. The concentrations of other pollutants in flue gas are shown in Table 6. For the control combustion trials without CaO addition, the As found in the ash residual only accounted for ~10% of the total As in the biomass feedstock. Meanwhile, for the combustion trials with CaO addition, the percentages of retained As in the processed ash remarkably increased to 48%, 76%, and 69% for the three CaO addition ratios of 5%, 10%, and 15%. This condition resulted in a reduction of As concentration in the flue gas from 6.1×10^{-2} mg l^{-1} in the control trial to 1.1×10^{-2}, 0.5×10^{-2}, and 0.8×10^{-2} mg l^{-1}. The CaO mixing ratio at 10% appears to be the most efficient to achieve high As retention in ash forms (~five fold increase in bottom ashes and ~34-fold increase in fly ashes compared with the control). This condition remarkably reduced the As emissions in the flue gas, as shown in Table 5.

In previous studies, researchers conducted several combustion experiments of *P. vittata* with 0.2000 g in each trial, and other researchers focused on the combustion of zinc and cadmium hyperaccumulator and CCA combustion with disposal capacities of 1.5 L and 10 L, respectively (Yan et al., 2008; Zhong et al., 2015; Helsen and Van Den Bulck, 2000). The disposal scale in this research is the largest in site. The combustion trials with CaO addition showed an improved As capture when the CaO was increased from 5% to 10%. This condition is due to the additional chemical sorbent that is available to react with As. However, the As capture reduced markedly compared with 10% CaO addition when CaO was added at 15% of the total feedstock weight. This condition is due to the agglomeration and scorification of feedstock particles during
combustion, which reduce the contact areas of biomass feedstock with CaO. Consequently, this condition reduces the catalytic efficiency of CaO in the thermal process and reaction rate between CaO and As oxides (Struis et al., 2002), which leads to a reduced kinetic reaction of As sorption.

The ash recovery is the ratio of the ash product content to the ash content in biomass, which increases from 52.5%, 45.8%, and 44.6% to 86.5%, 80.1%, and 81.1%, respectively, with CaO addition. This finding indicates the approximately half of the ashes are left in the combustor in the trials without CaO and approximately 80% of the ashes are left in the combustor in the trials with CaO. The As recovery is poor to a certain extent in the trials because the length of vertical stack is short to stabilize the flow to conduct credible sampling of particulates. In the inclined section leading to the vertical discharge pipe, the particles tend to settle and are lost to sampling. $E_{\text{ash-a}}$ is the As recovery by adding those As contents in the lost ash. The recovery reaches 94.85 with the addition of 10% CaO. $E_{\text{ash-a}}$ of the GX and JY trials is lower than that of the HN trial. This condition may be related to the ratio of As content to the total content of Ca and Mg in the biomass.

3.3 Reaction Mechanism of As Capture by Ash

As a medium volatile element, As is absorbed in fly ash through different means with the decrease of temperature. As is easily enriched in fly ash with microparticles (Zhang et al., 1999). As emission should be controlled during the emission of microparticles. Meanwhile, volatile gases, such as $\text{As}_2\text{O}_3$, can be dissolved in silicate melt (Guo et al., 2004), and only a fraction of As is absorbed in silicate melt during
As clearly demonstrated in the CaO addition experiment, CaO has a remarkable effect on retaining the As in solid residuals. This condition consequently reduces the gaseous As in the flue gas. Previous studies have shown that As capture by CaO involves a simple physical adsorption and results in an irreversible chemical reaction that leads to solid forms of Ca–As–O products, such as Ca$_3$(AsO$_4$)$_2$ and Ca$_2$As$_2$O$_7$ (Jadhav and Fan, 2001; Li et al., 2007; Hirsch et al., 2000; Sterling and Helble, 2003). In a previous study, AsO$_2$ and AsO were supposed to be the most possible species at temperatures higher than 800 °C with the co-combustion of coal and oil waste. As$_2$O$_5$ was the main specie when the temperature was less than 300 °C. In this condition, the interaction of As with fly ash components (Na, K, Ca, Mg, Fe, Al, and Si) was not considered. Ca(AsO$_2$)$_2$ and Ca$_3$(AsO$_4$)$_2$ exited at 650–750 °C and over 700 °C, respectively, when the interaction was considered (Contreras et al., 2009). Thus, few studies have reported the exact speciation of Ca–As–O compounds due to As capture using CaO, especially in the context of biomass combustion. In this study, detailed information on the chemical structure was obtained from fly ash and bottom ash samples through state-of-the-art XRAS instrumentation. This study provides considerable insights into the reaction mechanism of As–CaO interaction under combustion conditions.

Results of XANES analysis (Fig. 3) showed the presence of Ca$_3$(AsO$_4$)$_2$, calcium carbonate, and unreacted CaO. No As oxides were found, which indicates that physical adsorption is not the dominant As fixation mechanism in the fly ash. The results of ash
samples indicate the oxidation of As(III) to As(V).

According to many studies (Hirsch et al., 2000; Chesworth et al., 1994; Frandsen et al., 1994; Ratafia-Brown, 1994; Bool and Helble, 1995), As mainly exists in the gaseous form of $\text{As}_2\text{O}_3$ in the combustion environment, when the temperature is greater than 500 °C. At the temperature range of 227 °C–327 °C, most of the As in the flue gas condense into a solid phase as $\text{As}_2\text{O}_5$. EXAF results show that only $\text{Ca}_3(\text{AsO}_4)_2$ is found in the flue gas, and solid residual samples are collected from the As capture experiments. No other Ca–As–O compounds were identified. This finding is consistent with a number of previous studies on $\text{As}_2\text{O}_3$–CaO reaction in the range 600 °C–1000 °C (Li et al., 2007; Sterling and Helble, 2003). Equations (4–8) were proposed based on the analytical result and previous literature records for the reaction between As and CaO, as follows:

\[
\text{CaO} + \text{CO}_2 \leftrightarrow \text{CaCO}_3 \quad \text{(Equation 4)}
\]

\[
6\text{CaO} + \text{As}_4\text{O}_{10}(g) \rightarrow 2\text{Ca}_3(\text{AsO}_4)_2, \quad \text{(Equation 5)}
\]

\[
6\text{CaCO}_3 + \text{As}_4\text{O}_{10}(g) \rightarrow 2\text{Ca}_3(\text{AsO}_4)_2 + 6\text{CO}_2, \quad \text{(Equation 6)}
\]

\[
6\text{CaCO}_3 + \text{As}_4(g) + 6\text{H}_2\text{O} \rightarrow 2\text{Ca}_3(\text{AsO}_4)_2 + 6\text{H}_2(g) + 2\text{CO}_2(g), \quad \text{(Equation 7)}
\]

\[
3\text{CaO}(s) + \text{As}_2\text{O}_3(g) + \text{O}_2(g) \rightarrow \text{Ca}_3(\text{AsO}_4)_2(s). \quad \text{(Equation 8)}
\]

4. Conclusions

As a waste management strategy, combustion was used to dispose $P$. vittata biomass derived from large-scale As phytoremediation sites in rural areas of China. This research focused on the in site pilot-scale combustion. Considerable amounts of As are emitted in the flue gas due to high As contamination in the biomass and the volatility
of As during combustion. Blending biomass with chemical sorbent CaO as emission control strategy remarkably improved the retention of As in the processed ash residual from 12.0% to 76.3% when CaO was blended with the biomass at 10% of the total fuel weight. Thus, the As emission in the flue gas remarkably decreased. XAFS analysis confirmed that $\text{Ca}_3(\text{AsO}_4)_2$ is the dominant reaction product in a post-sorption sample. The results of this study provide valuable information on the disposal of harvested As-hyperaccumulators and their biomass, which contains high As concentrations. Results also indicate economic effectiveness of this approach in low income areas with friendly environment.

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Highlights:

- Pilot-scale combustion is required to treat arsenic-enriched biomass in China
- CaO addition to arsenic-enriched biomass reduces arsenic emission
- CaO captures arsenic via chemical adsorption to form $\text{Ca}_3(\text{AsO}_4)_2$
Table 1
Operational parameters for *P. vittata* combustion

| Sample ID | CaO added in feedstock (%) | Atmospheric pressure (kPa) | O₂ content in flue gas (%) | Flue gas temp (°C) | Flue gas flow rate (m³ min⁻¹) |
|-----------|-----------------------------|----------------------------|------------------------------|--------------------|-----------------------------|
| HN        | 0                           | 99.4                       | 14.4                         | 46.6               | 16.9                        |
| GX        | 0                           | 99.2                       | 15.7                         | 48.0               | 19.7                        |
| JY        | 0                           | 99.4                       | 18.2                         | 47.7               | 23.5                        |
| JY        | 5%                          | 98.5                       | 17.0                         | 47.7               | 32.1                        |
| JY        | 10%                         | 98.5                       | 17.0                         | 47.0               | 32.9                        |
| JY        | 15%                         | 98.7                       | 18.6                         | 46.3               | 38.2                        |
| Sample ID | HN  | GX  | JY  |
|-----------|-----|-----|-----|
| Moisture content (%) | 9.54 | 10.01 | 9.34 |
| Ash content (%) | 9.4  | 9.9  | 12.44 |
| Volatile matter (%) | 66.87 | 65.86 | 65.48 |
| Fixed carbon (%) | 14.19 | 14.23 | 12.74 |
| CV (MJ kg\(^{-1}\)) | 18.26 | 17.67 | 17.26 |

**Elemental analysis (%) on DW basis**

| C   | 47.13 | 46.54 | 44.5 |
|-----|-------|-------|------|
| H   | 5.21  | 4.93  | 4.85 |
| O   | 36.63 | 37.61 | 36.77 |
| N   | 1.44  | 0.84  | 1.21 |
| S   | 0.19  | 0.18  | 0.23 |
Table 3
Element concentrations (mg kg$^{-1}$ on DW basis) of three *P. vittata* biomass samples

| Element | HN     | GX      | JY      |
|---------|--------|---------|---------|
| As      | 22.1±9.2 | 98.4±21.4 | 486.0±41.0 |
| P       | 1600±207 | 1100±834 | 1900±501 |
| K       | 19900±2800 | 15500±2900 | 20200±6100 |
| Na      | 62.4±12.4 | 55.5±20.6 | 99.9±28.0 |
| Ca      | 2900±372 | 3500±970 | 4460±530 |
| Mg      | 1560±660 | 10500±340 | 1870±130 |
| Cu      | 11.2±0.2 | 8.8±0.5 | 17.0±2.0 |
| Zn      | 23.9±2.4 | 25.2±12.3 | 45.0±8.7 |
| Fe      | 101±6   | 50.4±7.6 | 274±70.4 |

**Note:** All data are presented as the mean of three replicates (n = 3) ± standard deviation.
## Table 4

Key thermal characteristics of HN, GX, and JY biomass samples

| Biomass | Degradation stage | Temp (℃) | Total weight (%) | Maximum weight loss (%) | Temp @ maximum weight loss rate (℃) |
|---------|------------------|----------|------------------|-------------------------|-------------------------------------|
|         |                  | 30–150   | 7.26             | 0.0008                  | 102                                 |
| JY      | 2                | 150–350  | 55.85            | 0.0103                  | 279                                 |
|         | 3                | 350–510  | 30.89            | 0.0030                  | 371                                 |
|         | 4                | 510–800  | 0.3              | -                       | -                                   |
| HN      | 1                | 30–120   | 6.54             | 0.0008                  | 102                                 |
|         | 2                | 120–300  | 50.50            | 0.0138                  | 274                                 |
|         | 3                | 300–510  | 36.96            | 0.0020                  | 428                                 |
|         | 4                | 510–800  | 0.3              | -                       | -                                   |
| GX      | 1                | 30–150   | 5.06             | 0.0009                  | 99                                  |
|         | 2                | 150–350  | 52.65            | 0.0103                  | 283                                 |
|         | 3                | >350–510 | 33.49            | 0.0025                  | 396                                 |
|         | 4                | >510–800 | 5.9              | -                       | -                                   |
### Table 5
As distribution in solid/gaseous residuals and total As recovery

| Sample ID | Total As in biomass feedstock (g) | As in Bottom ash (g) | As in condensate fly ash (g) | As in dedusting fly ash (g) | Spray liquid (g) | Total ash recovery (%) | Total As recovered in solid residue (g) | $E_{ash}$ (As recovery in ash) | $E_{total}$ (Total As recovery) |
|-----------|----------------------------------|----------------------|-------------------------------|-----------------------------|------------------|------------------------|------------------------------------------|--------------------------------|----------------------------------|
| HN        | 1.66±0.69                        | 0.39±0.032           | 0.18±0.020                    | 0.023±0.01                  | 0.0022±0.00004   | 52.5%                  | 0.595                                    | 35.9%                          | 68.38%                           | 65.3%                          |
| GX        | 7.38±1.60                        | 1.33±0.075           | 0.22±0.092                    | 0.0014±0.0007               | 0.0019±0.00006   | 45.8%                  | 1.553                                    | 21.0%                          | 45.85%                           | 27.8%                          |
| JY control| 36.45±3.08                       | 3.30±1.09            | 0.21±0.026                    | 0.0015±0.00003              | 0.0021±0.0001    | 44.6%                  | 3.514                                    | 9.6%                           | 21.52%                           | 12.0%                          |
| JY + 5% CaO | 34.63±2.92                      | 10.62±0.81           | 5.91±1.18                     | 0.0062±0.0030               | 0.0011±0.0001    | 86.5%                  | 16.537                                   | 47.8%                          | 55.25%                           | 48.4%                          |
| JY + 10% CaO | 32.81±2.77                      | 15.83±0.61           | 9.09±3.52                     | 0.0025±0.0008               | 0.0014±0.0002    | 80.13%                 | 24.924                                   | 76.0%                          | 94.85%                           | 76.3%                          |
| JY +15% CaO | 30.98±2.61                      | 14.64±1.68           | 6.67±0.33                     | 0.0071±0.0048               | 0.0012±0.0002    | 81.07%                 | 21.318                                   | 68.8%                          | 84.86%                           | 69.4%                          |
Table 6

Concentration of other common pollutants in flue gas

| Index        | Concentration | Pollution control standard for hazardous waste |
|--------------|---------------|-----------------------------------------------|
|              | mg/m\(^3\)   | incineration (GB18484-2001) mg/m\(^3\)        |
| Soot         | 9.86          | 100                                           |
| Blackness    | Level-I       | Greenman Level-I                               |
| NO\(_x\)     | 60.5–117      | 500                                           |
| SO\(_2\)     | n.d\(^a\)     | 400                                           |
| HCl          | 12.6–20       | 100                                           |
| HF           | 0.58–0.75     | 9                                             |

\(^a\) not detected, detection limit: 2.5 mg/m\(^3\)
Fig. 1. Schematic of the incineration equipment
Fig. 2. Thermogravimetric results of *P. vittata* samples: a) TG curves of the three biomass samples, b) DTG curves of the three biomass samples.
a.) Normalized As K-edge profiles for bottom ash samples and reference As compounds.

b.) Normalized As K-edge profiles for fly ash samples and reference As compounds

Fig. 3. XANES normalized As K-edge profiles in ash samples: a) Normalized As K-edge profiles for bottom ash samples and reference As compounds. b) Normalized As K-edge profiles for fly ash samples and reference As compounds. Note: Bottom and fly ashes A, B, and C are ash samples collected from combustion trials using JY biomass blended with 15%, 10%, and 5% CaO, respectively.