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Short communication

Elemental analyses of chars isolated from a biomass gasifier fly ash

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ABSTRACT

Processing of pine wood chips in a pilot-scale downdraft gasifier generated a carbon-rich fly ash as a byproduct. Studies on biomass-derived fly ashes have generally focused on their direct characterisation, as generated, to develop options for utilisation or disposal. Analogous to studies on coal-derived fly ashes, strategies were applied here to assess the feasibility of isolating chars for value-added applications and to determine their elemental compositions relative to that for the feedstock. The inorganic ash content of the biomass-derived fly ash was 48.4%. Sieving followed by washing with deionized water afforded large char particles (>10 mesh) with an ash content of only 3.59%. A subsequent acid treatment reduced the ash content to 1.55%; further demineralization treatments to obtain lower ash contents were deemed impractical. Elemental analyses showed calcium was the most abundant inorganic element in the feedstock, fly ash, and water-washed char. The apparent removal of calcium carbonate by the acid treatment afforded a char in which potassium was the most abundant element. Results suggested that the chars surviving gasification may function as adsorbents *in situ* for elements that are volatile under the conditions of gasification.

1. Introduction

Gasifier-based power plants are receiving increased interest as an option for producing electricity with locally-available biomass resources. Given numerous system design options, there may be several points at which solid byproducts inadvertently accumulate or are specifically collected. For example, applying a series of cleaning steps to the producer gas from a downdraft gasifier system can afford several solid byproducts such as bed, bottom, cyclone, and filter fly ashes [1]; using a different configuration, one can obtain different byproducts, such as separator and scrubber ashes [2]. The carbon contents of fly ashes from the processing of biomass by gasification typically range from 10% to 60% [3,4]. The ratio of char (carbon) to inorganic constituents is important since it can have a significant impact on the options for utilisation. For example, to recycle fly ash as a fuel, high carbon contents are beneficial [4,5]. Conversely, low carbon contents are preferable when fly ash is used in concrete products [6].

Studies related to the utilisation of biomass-derived ashes have generally focused on determinations of their total chemical compositions. For the mostly inorganic combustion ashes, analyses tend to focus on determining the levels of beneficial elements (e.g., macronutrients, micronutrients) or presence of heavy metal contaminants [7–9]. Analyses of fly ashes must also take into account the presence of significant amounts of unburned carbon. Studies on the carbon-rich fly ashes from coal, but not biomass, have focused on processing steps to activate the carbon *in situ* [10,11] or separate it from the fly ash in anticipation of developing value added products [6,12,13]. Operations including sieving, water washing, and acid treatment have been used for product development [12], and characterisation [14,15]. In the present study, we applied similar strategies to a fly ash from the gasification of pine wood chips to assess the feasibility of isolating chars and to determine their elemental compositions relative to that for the feedstock.

2. Materials and methods

2.1. Sample generation

Pulp-grade pine wood chips (mostly *Pinus taeda* L.) were used as the feedstock for a pilot-scale downdraft gasifier coupled with a 25 kW generator (BioMax 25, Community Power Company, Littleton, CO, USA). The feedstock was relatively free of bark and low in ash content (0.32%). The fly ash yield was less than 1% of the dry weight of wood consumed [16] using standard operating conditions [17]. Briefly, the fly ash was separated from the producer gas by a filtration system that ultimately transferred the byproduct to a collection drum. A grab sample taken from the drum was used in the present study.

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Table 1
Fraction weights and ash contents for different particle size classes recovered from fly ash.

Size class	Fraction weight (%)	Ash content	
		Average (%)	SD (%)
>10 mesh	11.4	11.8	1.2
10–20 mesh	12.6	14.6	1.4
<20 mesh	76.0	62.4	0.7

2.2. Fly ash partitioning

Fly ash was separated into three particle size classes (>10, 10–20, and <20 mesh) using a set of stainless steel sieves (W.S. Tyler), covered with a lid, that were gently shaken by hand in a fume hood. The escape of fine particles was minimal. Only the sample of >10 mesh char particles (200 g) received further processing. After transferring to a glass beaker, the char particles were suspended in deionized water (3 L) with a small amount of acetone (10 mL) added to facilitate particle wetting. The buoyant char particles were scooped from the beaker and vacuum filtered. The debris that settled on the bottom of the beaker included small stones, rust flakes, and sinters; excluding these contaminates resulted in some losses of char. The water-washed char particles were dried (100 °C) and weighed (65% yield). A sample of this char (100 g) and deionized water (2 L) were combined in a glass beaker with a magnetic stir bar. The pH of the stirred suspension was *ca.* 8. Concentrated hydrochloric acid was added dropwise until a pH of *ca.* 2 was maintained. The acid-washed char particles were vacuum filtered and rinsed with deionized water (10 L). After soaking in deionized water (2 L) overnight, and further rinsing (5 L), the acid-washed char was vacuum filtered, dried, and weighed (95% yield).

2.3. Chemical and physical analyses

Ash contents were determined using a muffle furnace set to 550 °C. Elemental analyses by proton induced X-ray emission (PIXE) were performed by Elemental Analysis Inc., Lexington, KY. Carbon and hydrogen contents were determined by combustion analysis. Elemental analysis of the feedstock was conducted by inductive coupled plasma atomic emission spectroscopy (ICP-AES) after digestion of a sample of wood chip ash in *aqua regia* [18]. Surface area and pore volume were determined by standard N_2 adsorption at 77 K using an Autosorb-1c analyzer (Quantachrome Instruments).

3. Results and discussion

3.1. Fly ash sieving

Combustion of the fly ash in a muffle furnace gave an inorganic ash content of 48.4%, thereby indicating that approximately one half of this black and dusty byproduct was char, undoubtedly with some soot and tar. Gentle sieving by hand yielded approximately 25% of the fly ash as a char fraction with particle size of at least 20 mesh (Table 1). Combustion of the larger char particles (>10 mesh) gave an ash content of only 11.8%. Consistent with this observation was the higher ash content (62.4%) for the fine fly ash particles (<20 mesh). Accordingly, simple sieving alone afforded a char fraction with an ash content approaching that found in coal.

3.2. Char particle processing

Washing of the largest char particles (>10 mesh) with deionized water proved to be an effective means of removing adhering fine particles and high-density debris (small stones, sinters, rust flakes) that contributed significantly to the ash content of the fly ash. Such debris are unavoidable in the fly ash given that the feedstock classifier installed in front of the gasifier removed most, but not all debris accompanying the feedstock. The ash content of the water-washed char was 3.59% (Table 2). This lower ash content can be partially attributed to the dissolution of water soluble salts. However, the contribution to the reduction in ash content by dissolution is likely to be minimal given the low water solubility (5.6%) of the original (unprocessed) fly ash [16]. Coinciding with the reduction in ash content was a significant increase in carbon content to 90.0%. The hydrogen content about the same suggesting that the hydrocarbons (e.g., polycyclic aromatic hydrocarbons) in the fly ash remained associated with the char component.

Treatment of the water-washed char with hydrochloric acid lowered the ash content to 1.55% and raised the carbon content to 93.7%. Hydrofluoric acid has also been used for the demineralization of carbon particles [14]; however, that was not attempted here because such a processing step would be impractical for the bulk preparation of biomass chars for utilisation. Given that the carbon and ash contents of clean pine wood are approximately 50% and 0.3%, respectively, and assuming no losses of carbon or ash, the carbonisation of clean pine wood should afford a char with an ash content of approximately 0.6%. The acid-washed char, with its ash content of 1.55%, would appear to be of similar utility as such simple wood chars.

3.3. Char analyses

The high temperatures experienced during gasification can result in the volatilisation of some elements. For example, K can form gaseous hydroxides between 800 and 850 °C, whereas Mg and P are stable up to 1500 °C in the forms of MgO and $Ca_3(PO_4)_2$, respectively [19]. Accordingly, the elements present in the chars are not necessarily present in the same proportions as in the feedstock. The fly ash, the chars separated from it, and feedstock were therefore all subjected to elemental analysis. Since ash agglomeration/sintering can be problematic during the gasification of biomass feedstocks [20–22], PIXE was used for the fly ash and char analyses to avoid losses from undigested particles (agglomerates, silicates) experienced with ICP-AES (unpublished results).

Analysis of the fly ash and feedstock showed that Ca comprised approximately one half of all inorganic elements detected (Table 3). Calcium is usually the most abundant inorganic element in pine wood, although in some cases, the amount of K is present in essentially equivalent amounts [23]. The high relative amount of Si in

Table 2
Ash, carbon and hydrogen contents for fly ash and chars.

Sample	Ash		Carbon		Hydrogen	
	Average (%)	SD (%)	Average (%)	SD (%)	Average (%)	SD (%)
Fly Ash	48.4	0.59	47.0	0.6	0.84	0.04
Water-washed char (>10 mesh)	3.59	0.33	90.0	0.2	1.08	0.02
Acid-washed char (>10 mesh)	1.56	0.37	93.7	0.1	0.91	0.05

Table 3
Elemental analyses of fly ash, chars, and wood chips (na = not analysed, nd = not detected).

Element	Fly ash		Water-washed char		Acid-washed char		Wood chips	
	Conc. mass (mg kg^{-1})	Error (mg kg^{-1})	Conc. mass (mg kg^{-1})	Error (mg kg^{-1})	Conc. mass (mg kg^{-1})	Error (mg kg^{-1})	Conc. mass (mg kg^{-1})	SD (mg kg^{-1})
Mg	7070	170	1570	30.0	188	18.1	25.7	0.0649
Al	5200	100	263	12.7	154	9.99	23.4	0.162
Si	16,820	170	388	8.82	482	7.29	5.49	0.617
P	1760	50.0	285	7.10	56.4	4.51	7.94	0.0649
S	1760	40.0	507	6.90	415	5.31	na	na
Cl	993	31.9	66.8	4.09	488	5.71	na	na
K	10,070	100	2720	30.0	1830	20.0	65.9	0.357
Ca	50,760	510	5350	50.0	758	11.1	246	1.33
Ti	377	17.0	23.4	2.17	17.6	1.47	na	na
Cr	147	6.71	5.69	0.871	12.1	0.716	0.123	0.0373
Mn	4160	40.0	871	8.71	60.8	1.12	13.6	0.844
Fe	9920	100	187	3.80	136	1.646	36.4	0.779
Ni	60.4	2.91	7.00	0.442	6.99	0.396	0.154	0.0106
Cu	32.9	2.47	7.48	0.505	9.58	0.478	0.121	0.0182
Zn	364	6.74	30.9	0.898	8.66	0.484	1.12	0.0170
As	7.39	2.05	nd	nd	nd	nd	0.0240	0.0067

the fly ash is attributed to soil contaminants in the feedstock which are unavoidable in high-volume operations. For the feedstock, the proportion of Si was not nearly as high as that in the resultant fly ash; a standard analysis method (ICP-AES) was applied to the feedstock and it is likely that some silicates went undigested. A significant drop in Si (16,820 mg kg^{-1} down to 388 mg kg^{-1})for the water-washed char reflects the removal of dense debris and grit, both undoubtedly rich in silicates.

Similar to the fly ash and the feedstock, the most abundant elements in the water-washed char were Ca and K. After treating the water-washed char with acid, the concentration for many elements were essentially unchanged, with values being only slightly higher or lower. Exceptions were significant decreases in Mg, P, K, Ca, and Mn. A small amount of As was detected in the fly ash but not the water- or acid-washed chars; any amounts of Cd and Pb were below the detection limits of 10.93 mg kg^{-1} and 1.65 mg kg^{-1}, respectively. Given that FTIR spectroscopy before and after acid treatment removed signals consistent with carbonates (unpublished results), undoubtedly, the water-washed char contained high amount of $CaCO_3$. The increase in Cl suggested that the water washes following the acid treatment were not exhaustive. Particularly intriguing is that the level of K (1830 mg/kg^{-1}) is more than double the amount of Ca (758 mg kg^{-1}) in the acid-washed char. Under the temperatures experienced during gasification, K can form gaseous hydroxides, whereas Ca may be less mobile in non-volatile forms (e.g., $Ca_3(PO_4)_2$). It remains to be determined if the chars that survive gasification function as adsorbents such that the gaseous forms of K are accumulated. Since all salts of the alkali metals are soluble in water, the retention of K suggests that this element is possibly adsorbed on the char. Regarding the adsorption properties of the fly ash, the BET surface area was 206 m^2 g^{-1} and the pore volume was 0.25 cm^3 g^{-1}. These values were significantly increased for the acid-washed char (surface area = 447 m^2 g^{-1}, pore volume = 0.39 cm^3 g^{-1}). This demonstrated that fly ash partitioning treatments, such as those applied here, can afford a char with improved adsorption properties.

4. Conclusions

These results demonstrate that the elements present in the biomass-derived fly ash, and especially those in the char(s), cannot be determined by simply extrapolating from an elemental analysis of the feedstock. Although partitioning treatments generated chars from the fly ash having relatively low ash contents, further demineralization treatments would appear to be impractical. The predominance of K in the acid-washed char raises the possibility that those chars surviving gasification may function as adsorbents *in situ* for elements that are volatile under the conditions of gasification.

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