
Characterization and Partitioning of the Char Ash Collected after the Processing of Pine Wood Chips in a Pilot-Scale Gasification Unit

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Abstract

Southern yellow pine wood chips were used as the feedstock for a pilot-scale gasification unit coupled with a 25 kW generator. The pulp-grade wood chips were relatively free of bark and low in ash content. Processing this feedstock yielded a black/sooty by-product that upon combustion in a muffle furnace resulted in an ash content of about 48%. The term “char ash” was coined to account for the two main components of the material, char and ash. The char ash was further analyzed to determine its composition and options for fractionation. Since the ash component is analogous to wood ash obtained by conventional combustion, char ash has the potential to be used in similar applications such as a nutrient source and/or liming agent. Alternative applications may focus on the utilization of the char component whereby simple operations such as suspending the char ash in solvents may afford a means to produce chars with lower ash contents.

Introduction

Biomass gasification affords a combustible gas that can be sufficiently cleaned to be used in an inter-

nal combustion engine. Coupling the engine to a generator allows for the production of electricity. Small-scale gasification units are of particular interest as a means to produce electricity on demand to remote facilities or provide portable supplies of electricity following power disruptions from electrical grids. The concept of using locally available biomass resources is advantageous given the savings in fuel transportation and the possibility of utilizing biomass resources having little or no commercial value.

A by-product of biomass gasification is a mixture comprised of two main components: “char,” the carbonaceous material remaining from the incomplete consumption of the bulk of the biomass, and “ash,” derived from the inorganic constituents. Terms used to identify this gasification by-product as a whole, specifically “char” and “gasification (fly) ash,” are confusing in that they imply that the mixture is primarily carbonaceous or inorganic, respectively. Whereas the ash from biomass combustion is mostly inorganic, “gasification fly ash” from biomass can have unburned carbon contents ranging from 10 to 60% (Leiva et al. 2007). In this study, the term “char ash” is used to describe the solid by-product of biomass gasification to account for both the char and ash components.

As to be expected, char ashes can be extremely variable, dependent upon the nature of the starting biomass feedstock, the design of the gasifier, and its operation. This impacts the options for utilization, which include use as a fuel, incorporation in construction materials (e.g., concrete, plasterboard), and agricultural applications (e.g., stabilizer, liming agent). The composition of the char ash is critical. For example, as a fuel, the carbon content needs to be sufficiently high for adequate combustion (Leiva et al. 2007). High carbon contents are also advantageous for soil stabilization and carbon sequestration (Chan

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et al. 2008). Alternatively, a high level of inorganics is useful for raising soil pH and providing nutrients (Chirenje and Ma 2002, Vance 1996). The caveat being char ash can also contain significant amounts of polycyclic aromatic hydrocarbons (PAHs) (Leiva et al 2007) and toxic heavy metals (Odlare and Pell 2009). In the present study, the char ash produced from processing pine wood chips in a pilot-scale gasification unit was characterized as an initial step for assessing the various options for utilization.

Experimental Procedures

Char Ash Collection

The 25 kW pilot-scale gasification unit (BioMax 25, Community Power Corporation, Littleton, CO) is equipped with a filtration system comprised of filter bags through which the producer gas is passed before being sent to the engine. The char ash was collected in a bin under the filter bags and transferred to a separate storage container via an auger. Char ash, ash clinkers, and debris that accumulated between the gasifier and the filtration system, especially in the heat exchanger, were not included in this study. The char ash in the collection drum, fitted with a heavy plastic liner, was opened outdoors to allow any combustible and toxic vapors (e.g., CO, H₂) to dissipate. After about 30 minutes, the drum liner was sealed. All samples were subsequently kept in closed containers and stored in air-conditioned laboratories.

General Characterizations and Solubility

Values for moisture content were determined by heating samples overnight in an oven (100°C). Ash contents were determined in a muffle furnace set to 550°C. Acetone solubles were assessed by stirring char ash (2 g) in acetone (50 ml, 15 min.). The extract, collected by filtration over a glass fiber filter in a Büchner funnel, was dried *in vacuo* and weighed. Water solubles were determined by suspending char ash (2 g) in deionized water (150 ml) and boiling for 30 minutes with magnetic stirring. After filtering, the total volume of the extract was measured, and aliquots taken and dried to quantify the hot-water solubles. The water-extracted char ash was rinsed with acetone (50 ml) and the resultant light yellow extract dried *in vacuo* to quantify the residual acetone solubles. Acid solubles were determined by suspending char ash (2 g) in deionized water (150 ml) and heating to boiling (30

minutes). The pH was determined to be approximately 10 using ColorpHast (EM-Reagents) indicator strips. Concentrated HCl was then added drop wise to lower the pH to less than 3. After cooling, the suspension was filtered over a glass fiber filter, rinsed with deionized water until near neutral, and the filtrate discarded. The char ash was rinsed with acetone (50 ml) and the resultant light yellow filtrate dried *in vacuo* and weighed. The amount of acid soluble materials was calculated as the difference between the char ash before and after treatment, accounting for the acetone solubles.

Grit Removal

In an attempt to remove grit (sand, debris) in the char ash, a sample (10 g) was first transferred to an Erlenmeyer flask (500 ml) suspended in acetone (300 ml). After swirling the flask by hand, and briefly allowing some of the larger particles to settle, the still suspended fine particles were decanted into a Büchner funnel with a glass fiber filter. The material retained, fraction 1, was set aside and the filtrate transferred back to the flask. Further agitation and filtration afforded fraction 2 having somewhat larger particles. Finally, the gritty material still in the flask, fraction 3, was collected by filtration. A similar experiment was also carried out in which a deionized water:acetone (90:10) mixture was used and the decanting operation only conducted once to get a fraction of suspended particles (fraction 1) separated from the gritty material (fraction 2) that rapidly settled.

Sequential Extraction

A modified three-step BCR (Bureau Communautaire de Références, now Standards, Measurement and Testing Programme) sequential extraction procedure (Rauret et al. 1999) was used to assess the extractable trace elements for the char ash. Aliquots of oven-dried char ash (ca. 0.5 g) were accurately weighed (3 significant figures) into 50 ml polyethylene centrifuge tubes and extracted as follows:

Step 1. An aqueous acetic acid solution (0.11 M, 20 ml) was added and the centrifuge tubes shaken for 16 h at room temperature using an orbital shaker. Extracts were separated from the solid residues by centrifugation (3000 x g, 20 min.) and set aside for subsequent analysis. Distilled water (10 ml) was added to the residue, which was then shaken for 15 minutes. After centrifugation, the resultant supernatants were

discarded and the residues subjected to the second extraction step.

Step 2. A freshly prepared hydroxylamine hydrochloride solution (0.5 M, 20 ml) was added to each of the centrifuge tubes, still containing the residues from step 1, and shaken for 16 hours. Extracts and residues were processed as in step 1.

Step 3. Hydrogen peroxide (30%, 5 ml) was then added to each of the centrifuge tubes still containing the residues from step 2. The centrifuge tubes were loosely covered to prevent substantial loss of hydrogen peroxide. Digestion at room temperature was allowed to proceed for 1 h with occasional manual shaking and followed by digestion (85°C, 1 h). The centrifuge tubes were then uncovered and heating continued to reduce the volume between 1 and 1.5 ml. Hydrogen peroxide (5 ml) was again added to each centrifuge tube. After covering, the samples were further digested (85°C, 1 h). Volumes were again reduced between 1 and 1.5 ml. An aqueous solution of ammonium acetate (1.0 M, 25 ml) was then added to each centrifuge tube. After shaking for 16 h at room temperature, the collection of the supernatant, and rinsing of the residues, was repeated as in step 1.

To eliminate the matrix interferences from extraction reagents, liquid samples from sequential extraction steps 1 and 2 were digested according to a standard method (AWPA 2004) but with only 3 ml of nitric acid. Digested samples were brought to volume (50 ml) with distilled water that had been acidified with nitric acid to a pH of 1.5. Concentrations of selected elements were determined by inductive coupled plasma atomic emission spectroscopy (ICP-AES).

Results and Discussion

Yield and General Characterizations

Operation of the gasification unit for 60 hours used about 1360 kg wood chips and generated about 9.7 kg char ash (0.7% yield). The char ash was black in color with a wide particle size range from extremely fine and dusty to larger particles up to a few millimeters in length. The ash (inorganic) content of the char ash was determined to be 48% after correcting for a volatiles (e.g., light organics, water) content of 9.7%. Together, the non-volatile organic compounds and presumably amorphous carbon comprised approximately one half of the sample. This result approached the higher end of the carbon content range (10 to 60%) reported for gasifier fly ashes from biomass (Leiva et al. 2007). The ash content of the wood chips was also determined and gave a moisture-corrected value of 0.3%. Feedstocks with higher ash contents would undoubtedly impact the ash content of the char ash and/or its yield.

General Solubility Assessments

Various treatments were applied to aliquots of char ash to assess its solubilities. After suspending char ash in acetone, 0.7% of the material was collected as a yellow tar (Table 1). Tars can be problematic in gasification units such as that used in the present study; deposits can form in both the gasifier and internal combustion engine on the generator. Preliminary data (not presented here) showed the presence of polycyclic aromatic hydrocarbons (PAHs) in the char ash. The amounts of PAHs condensing on analogous fly

Table 1. General solubility assessment of char ash: percent of total mass recovered in each fraction and ash (inorganic) contents of insoluble residues

Fraction collected	Treatments		
	Acetone (%)	Water followed by acetone (%)	Acidification followed by acetone (%)
Water soluble	Na	5.6	na
Acid soluble	Na	na	29.2
Acetone soluble (tar)	0.7	0.3	0.7
Insoluble residue	99.3	94.1	70.1
Total	100	100	100
Ash (inorganic) content of insoluble residue	44.3	46.6	29.7

Table 2. Partitioning of char ash: percent of mass recovered and ash (inorganic) content of each fraction.

Treatment	Fraction number	Material recovered (%)^a	Ash (inorganic) content (%)
Suspension in acetone	1	49	52.8
	2	10	37.8
	3	32	59.5
Suspension in water: acetone (90:10)	1	71	37.6
	2	25	72.0

a: Percent based on starting mass of char ash.

ashes were shown to be dependent upon the temperature during filtration (Padban and Odenbrand 1999). Given the toxicity of these compounds, minimizing their levels in the char ash would appear to be prudent in terms of utilization.

Treatment of the char ash with boiling water removed 5.6% of the mass in the form of a colorless solution (Table 1). It should be noted that during the filtration process, an oily film was observed in both the flask and on the surface of the wet char ash collected in the Büchner funnel. Treatment of the wet char ash with acetone afforded a yellow extract that dried down to a tar which was 0.3% the initial weight of char ash. Although the tars appear to remain associated with the char ash, they could float away from the char ash under very wet conditions. Further investigation is warranted to determine if the direct use of the char ash as a soil amendment presents an environmental hazard.

The likely presence of carbonate in the char ash was shown by the dissolution of a significant amount (29.2%) of the char ash by adjusting the pH (11 down to 2) with the addition of concentrated HCl (Table 1). Subsequent rinsing of the char ash with acetone did not have any significant impact on the recovery of tar (0.7%). High ash content of the acid-treated char ash (29.7%) suggested a high content of silicates, the primary source being dirt in the feedstock.

Grit Removal

Char ash suspensions were evaluated as a means to remove grit by decanting. With acetone alone, three fractions were obtained (Table 2). The inorganic content of the easily suspended material was similar to that for the char ash as a whole. The much lower ash content of the second fraction suggested a higher proportion of char. With a higher proportion of ash in the third fraction, these results suggest that even simple flotation may provide a means to separate the char and ash components. This was more pronounced when a water:acetone (90:10) mixture was used to separate the char ash into two fractions providing significantly different ash contents of 37.6% (fraction 1) and 72.0% (fraction 2).

Sequential Extraction

The extractabilities of selected elements in the char ash were determined by a modified BCR three-step extraction sequence typically applied to the study of soils and sediments (Table 3). The concentration of each element for each extraction step is reported in Table 4 on the basis of the mass of a given element removed relative to the starting dry mass of char ash. These values were added across each row and down each column to give the totals as shown. Among the three extraction steps used, the highest total concen-

Table 3. Outline of modified BCR three-step extraction sequence (adapted from Tokalioglu et al. 2003).

Step	Fraction	Target materials	Procedure
1	Water and acid soluble, exchangeable	Soluble species, cationic sites, carbonates	0.11 M acetic acid
2	Reducible	Iron and manganese oxyhydroxides	0.5 M hydroxylamine hydrochloride
3	Oxidizable	Organic matter and sulfides	Hydrogen peroxide followed by 1.0 M ammonium acetate

Element	Step 1 (g kg ⁻¹)	Step 2 (g kg ⁻¹)	Step 3 (g kg ⁻¹)	Total (g kg ⁻¹)
Na	2.67 ± 0.32	1.21 ± 0.04	0.41 ± 0.04	4.30
Mg	15.75 ± 0.18	1.42 ± 0.08	0.11 ± 0.01	17.28
Al	1.01 ± 0.20	4.37 ± 0.33	0.93 ± 0.10	6.31
Si	0.80 ± 0.30	0.65 ± 0.10	0.18 ± 0.04	1.63
P	0.13 ± 0.01	2.33 ± 0.10	0.06 ± 0.01	2.52
S	1.17 ± 0.04	0.12 ± 0.00	0.30 ± 0.01	1.59
K	20.83 ± 0.48	6.75 ± 0.43	1.17 ± 0.12	28.75
Ca	136.32 ± 0.92	16.82 ± 2.35	0.62 ± 0.06	153.76
Cr	0.00 ± 0.00	0.01 ± 0.00	0.00 ± 0.00	0.01
Mn	6.69 ± 0.10	1.17 ± 0.11	0.07 ± 0.01	7.94
Fe	0.21 ± 0.09	2.52 ± 0.19	0.72 ± 0.05	3.45
Ni	0.03 ± 0.01	0.04 ± 0.01	0.01 ± 0.00	0.08
Cu	0.01 ± 0.00	0.01 ± 0.00	0.01 ± 0.04	0.03
Zn	6.29 ± 2.82	1.68 ± 1.29	2.36 ± 0.90	10.32
As	0.01 ± 0.00	0.01 ± 0.00	0.00 ± 0.00	0.02
Cd	0.00 ± 0.00	0.00 ± 0.00	0.00 ± 0.00	0.01
Pb	0.00 ± 0.00	0.01 ± 0.00	0.00 ± 0.00	0.01
Total	191.92	39.10	6.95	237.98

Table 4. Analysis of char ash by modified BCR three-step extraction sequence.

tration (191 g kg⁻¹) was obtained for step 1, which would appear to include elements bound to cation exchange sites as well as those in water and acid soluble forms (e.g., carbonates). The next highest total concentration (39.1 g kg⁻¹) was obtained for step 2 targeting reducible oxides, in particular, those of iron and manganese (Tessier et al. 1979; Tokalioglu et al. 2003). Since almost 75% of the iron was released by step 2, it would appear that this element is present in the char ash as a reducible oxide. The relatively low total concentration (6.95 g kg⁻¹) for step 3 is not surprising and merely reflects that the biomass has been converted to a relatively inert char.

Among all of the elements that were determined (Table 4), calcium had the highest total concentration (153.76 g kg⁻¹) followed by lesser total concentrations of potassium (28.75 g kg⁻¹), magnesium (17.28 g kg⁻¹), zinc (10.32 g kg⁻¹), and manganese (7.94 g kg⁻¹). Similar concentrations were reported for calcium (180 g kg⁻¹), potassium (27.9 g kg⁻¹), magnesium (9.7 g kg⁻¹), and manganese (2.43 g kg⁻¹) for the direct analysis of wood-fired boiler ash (Vance 1999). The amount of zinc in this particular sample of char ash

appeared high given the much lower amount reported for the wood ash (0.3 g kg⁻¹). The high proportion of calcium and potassium obtained from extraction step 1 is consistent with the likelihood of the elements being present as carbonates. Thus, similar to wood ash, which is rich in calcium carbonate, the ash component of the char ash may be useful as a liming agent.

Among the hazardous heavy metals analyzed (As, Cd, Cr, Pb), the concentrations were relatively low (< 0.02 g kg⁻¹) and below the ceiling concentrations allowable for bulk sludge (As, 0.075 g kg⁻¹; Cd, 0.085 g kg⁻¹; Pb, 0.84 g kg⁻¹) applied to agricultural and forest lands (EPA 2011). [Note: the ceiling concentrations are only provided here as a guideline and are not to be construed as a specific regulatory limit for char ash.] There is the possibility that the char ash could contain high levels of hazardous heavy metals; however, they would appear to be in highly stable forms. Thus, the char ash from gasification of southern pine wood chips would appear to provide a source of macro- and micronutrients with minimal concern for releasing toxic heavy metals to the environment.

Conclusions

The solid by-product from the gasification of pine chips is comprised of almost equal parts of two components, char and ash; hence, the term “char ash” was coined. Since the ash component is analogous to wood ash obtained by conventional combustion, char ash has the potential to be used in similar applications as a nutrient source and/or liming agent. Concentrations of extractable hazardous heavy metals (As, Cd, Cr, Pb) were well below the ceiling concentrations allowable for bulk sludge thus alleviating that particular concern for land applications. However, one concern remaining to be resolved is the impact, if any, of the PAHs accompanying the chars. With respect to the utilization of the char component, simple operations, such as suspending the char ash in solvents, can be used to remove gritty materials, thereby providing chars with lower ash contents.

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