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Analysis of the fly ash from the processing of wood chips in a pilot-scale downdraft gasifier: Comparison of inorganic constituents determined by PIXE and ICP-AES

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ARTICLE INFO

Article history:

Received 17 May 2011

Received in revised form

30 November 2012

Accepted 20 January 2013

Available online 13 February 2013

Keywords:

Bioenergy

Gasification

Heavy metals

Fertilizer

Waste disposal

ABSTRACT

Gasification of biomass ultimately generates at least one solid byproduct in which the inorganic constituents of the biomass are concentrated. Given the potential for utilization, or issues with disposal, facile methods are needed for determining the compositions of the fly ashes from recently-available gasifier-based bioenergy systems. Proton induced x-ray emission spectroscopy (PIXE) and inductively coupled plasma atomic emission spectroscopy (ICP-AES) were used to characterize the fly ash recovered from a pilot-scale (25 kW) modular bioenergy system operated with wood chips as the feedstock. The composition of the fly ash from the downdraft gasifier showed some similarities to compositions reported for boiler wood ashes, apart from one half of the material being unburned carbon. Although ICP-AES showed greater sensitivity for the analysis of the fly ash, especially for small amounts of heavy metal contaminants, PIXE proved to be a powerful analytical tool for screening of elements from sodium to uranium. Such broad spectrum screenings could prevent the inadvertent land application of unsuspected pollutant elements. Fly ashes from biomass gasification appear to be suitable for use as ash-based fertilizers for forest lands; however, combustion to remove unburned carbon may be advisable.

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1. Introduction

Increasing energy demands, and the anticipated depletion of fossil fuel reserves, has led to the acceleration of biomass utilization for energy. While aspects of sustainability and matters of climate change continue to develop, biomass is generally viewed as a clean and carbon-neutral fuel source [1–3]. Wood processing residues have long been burned in power boilers and cogeneration facilities that supply electricity and/or heat needed for industrial operations. Recently, small-scale gasifier-based power plants have become commercially available to produce electricity with locally-available biomass resources. In all cases, there is ultimately the generation of at

least one solid byproduct in which the inorganic constituents of the biomass are concentrated. The combustion of woody biomass either openly, or in boilers, generates mostly inorganic ashes which have at times been sold as a commodity [4,5]. With gasifier-based power plants, resultant fly ashes are comprised of both concentrated inorganic constituents and unburned carbon, the latter ranging from 10 to 60% of the fly ash by mass [6–8].

In the United States, coal-fired power plants generated 119 billion kg of ash, roughly one half of this being classified as fly ash [9]. While some coal-derived ashes can be used for the manufacture of products (cements, structural fill, road base), much of it is destined for disposal because the heavy metals

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0961-9534/\$ – see front matter Published by Elsevier Ltd.

<http://dx.doi.org/10.1016/j.biombioe.2013.01.020>

naturally occurring in coal are concentrated in the ash [9,10]. Fly ashes from biomass-based power plants can face similar problems for utilization or disposal. Facile methods are therefore needed for determining their compositions. This would be especially applicable for biomass collected from phytoremediation efforts whereby plantings are being evaluated as a means to draw out contaminants from soil. In a study on willow trees grown on a sediment disposal site, the processing of the wood in a gasifier-based power plant provided both energy and a means to concentrate the extracted soil contaminants in the ashes generated [11]. In situations where construction waste is used, the accidental inclusion of treated wood products is likely thus necessitating the close monitoring of fly ash compositions [12]. Anthropogenic activities have been reported to release heavy metals to the atmosphere that upon accumulation in forests leads to their concentration in wood and thus, wood ashes [13]. Even in the absence of anthropogenic inputs, woody biomass is reported to concentrate heavy metals present in the soil [14].

Elemental analyses of wood, and the resultant fly ashes obtained during gasification, have been carried out by inductively coupled plasma atomic emission spectroscopy (ICP-AES) after digesting the materials in nitric, hydrochloric and hydrofluoric acids [11]. The amount of hydrofluoric acid (HF) can be adjusted to address high silicate levels (EPA Method 3052) [15]. Nevertheless, refractory compounds including TiO_2 , alumina, and other oxides may not completely dissolve and prevent a complete elemental analysis [15]. Alternatively, proton induced x-ray emission spectroscopy (PIXE) has been used to monitor elements in coal fly ash [16] and wood boiler ash [17]. The advantages of the technique are that a wide range of elements can be quantified (sodium through uranium) and the sample need not be subjected to hazardous digestions. Despite its utility, this technique has only rarely been applied to biomass-derived fly ashes [12]; in one case, it was used to analyze the water soluble constituents from fly ash mixed with biomass [18]. Wider use has been with the direct analysis of biomass [19,20] or following the concentration of the inorganic constituents by combustion [21–23]. In the present study, PIXE was used to characterize a wood-derived fly ash recovered from a pilot-scale (25 kW) modular bioenergy system. Results are compared to those from analyses by the more traditional methods, acid digestions followed by ICP-AES. The data reported herein will prove to be invaluable given that byproduct utilization and/or disposal issues will undoubtedly impact the decision making process for future commercialization of small gasifier-based power plants targeting the generation of electricity from locally available biomass resources.

2. Materials and methods

2.1. Gasifier fly ash generation and collection

Pulp-grade southern yellow pine wood chips (mostly *Pinus taeda* L.) were obtained from a local chip mill in Winnfield, LA and 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, prepared from

recently harvested trees, was relatively free of bark and dirt. The yield of the resultant black/sooty fly ash was estimated to be less than 1% by weight of dry wood consumed over a cumulative estimate of 60 h of operation [24]. The gasifier is equipped with a filtration system comprised of filter bags through which the producer gas is passed before being sent to an internal combustion engine and/or flare. Fly ash collected by this system is transferred to a plastic-lined collection drum via an auger. After venting to dissipate toxic and combustible gases (e.g., CO, H_2), grab samples were sealed in plastic bags and stored under ambient conditions in the laboratory.

2.2. General analyses

Samples of fly ash were ground in a Wiley mill to pass an 850 μm screen to improve homogeneity and reduce the particle size for the chemical analyses. Moisture contents were determined by heating samples overnight in an oven (100 °C). Inorganic (ash) contents were determined by combusting samples using a muffle furnace ramped to a final temperature of 550 °C at which it was held for 6 h. Modifications to the method for volatile matter determination [25] included the use of a standard muffle furnace and Vicor glass crucibles (30 mL, 40 mm ID) fitted with matching lids. All percentages are reported on a dry-weight basis. FTIR spectra were collected using a Nicolet Nexus 670 spectrometer equipped with a Thermo Nicolet Smart Golden Gate MKII single reflection ATR accessory; samples were analyzed by applying a small amount of sample directly on the diamond crystal.

2.3. Elemental analyses

Elemental analyses by proton induced X-ray emission (PIXE) were performed by Elemental Analysis Inc., Lexington, KY. Carbon, hydrogen and nitrogen contents were determined using a CHN analyzer (i.e., combustion analysis). Elemental analyses were also conducted by inductive coupled plasma atomic emission spectroscopy (ICP-AES) after digestion in *aqua regia* [26,27] or nitric acid alone [28]. Aliquots of fly ash (ca. 0.500 g) were accurately weighed into glass digestion tubes. Deionized water (0.5 g) was used to wet the dusty samples. Then, 12.0 mol dm^{-3} HCl (6 mL), 15.8 mol dm^{-3} HNO_3 (2 mL) were added in a dropwise manner to each tube; with nitric acid alone, 8 mL of 15.8 mol dm^{-3} HNO_3 was used. All tubes were allowed to stand for 16 h at room temperature before refluxing for 2 h at 120 °C. The reflux condenser was then removed and the volume of liquid in each tube was reduced to between 1.5 and 2 mL. The contents of each tube were then rinsed with 0.5 mol dm^{-3} HNO_3 into a volumetric flask (50 mL). After any solids (presumably undigested silicates) had settled, the liquid was decanted and subjected to elemental analysis ICP-AES.

3. Results and discussion

3.1. General analyses

Processing of the pine wood chip feedstock in the downdraft gasifier afforded a fly ash comprised of black char particles

(up to 5 mm length) dispersed in a seemingly equivalent volume of fine black dust. Consistent with this observation, classification of the fly ash through Tyler sieves gave a particle size distribution as follows: greater than 2 mm, 11.4%; 850 μm to 2 mm, 12.6%; 180 μm –850 μm , 28.4%; less than 180 μm , 47.6%. The low ash content (0.32%) of the wood pine chip feedstock validated the observation that it was relatively free of dirt. Samples of fly ash were also combusted in a muffle furnace and gave inorganic (ash) contents near 50% after correcting for moisture (2%), the latter likely including some light organic compounds. The volatile matter analysis is analogous to an ash content determination, except that the sample is placed in a tightly-covered crucible and a higher temperature (950 °C vs. 550 °C) is used for a shorter period of time (7 min vs. 6 h). As a control, a sample of the pine wood was subjected to the analysis and gave a value of 77.1% which was close to the 80.6% reported for pine sawdust [29]. Similar values were also obtained for various hardwoods and waste wood samples [30,31]. Thus, our modifications to the method (crucible specifications, furnace type) did not appear to have a significant impact on the results. For a sample of fly ash, the volatile matter content was 14.3% which was similar to a value of 19.7% for a low volatiles coal [29].

3.2. Elemental analyses

The analyses of the fly ash then focused on the inorganic constituents to be determined by PIXE and ICP-AES. In total, data was obtained for 23 different elements by at least one of these two methods. Five elements (S, Cl, Ti, Rb, Sr), for which data was obtained by PIXE, were not analyzed by ICP-AES. One element (B), an important micronutrient, cannot be determined by PIXE. Results for the most abundant elements, including the macronutrients necessary for plant growth, are found in Table 1. Less abundant elements, including micronutrients and undesirable heavy metals, are found in Table 2. Note that the units between these two tables are different (g kg^{-1} vs. mg kg^{-1}), reflecting the significantly different concentrations.

Among the most abundant elements (Table 1), the results between the PIXE and ICP-AES analyses were in fairly good agreement for Mg, Al, P, Mn, and Fe; the results for these

elements were also in fairly good agreement between the two different reagents (nitric acid vs. *aqua regia*) used in the digestions prior to the ICP-AES analyses. The typically most abundant elements in wood ash, Ca and K [32,33], were also among the most abundant elements in the fly ash. Although this was anticipated, it should be noted that some metals are more volatile during gasification than others thus explaining why the fly ash in one study had a significantly different composition than the bed ash at the bottom of a downdraft gasifier, the latter resembling more the ash composition of the feedstock [34]. Typically, in wood ash obtained by simple combustion, Ca and K are found in the forms of carbonates and phosphates [32]. Analysis of the fly ash by FTIR spectroscopy gave a very simple spectrum with signals at 1392 and 870 cm^{-1} which are consistent with the presence of carbonates (Fig. 1a); after treatment of the fly ash with hydrochloric acid [35], these signals were no longer present in the spectrum of the washed and dried residue (Fig. 1b). As for the concentrations determined for Ca and K, the PIXE results were consistently lower than those obtained by ICP-AES. Interference effects can have a significant impact on ICP-AES data [36]. Likewise matrix effects, such as particle size were shown to significantly depress the PIXE signal in aerosols and ashes [37]; the cause(s) for the observed differences remain to be resolved.

The most glaring discrepancy between the two methods was the very high content of Si detected by PIXE. Values for Si were also not in agreement between the two acid digestion methods with the amount of Si being 10-fold greater with *aqua regia*. It should be noted that difficulties were encountered during the digestions with the tendency of the char to float and some grit (undoubtedly silicates) to remain undigested at the bottom of the digestion tubes. Combusting a sample of the fly ash in a muffle furnace (550 °C) before digestion, to alleviate the former problem, did not have a significant impact on the concentration of each element (data not shown), save for nearly doubling said concentrations given the removal of unburned carbon. The exception was Si (data not shown) whereby the values with and without prior combustion were essentially the same. Accordingly, without complete digestions with extremely harsh reagents (i.e., with HF as in EPA Method 3052), Si data is highly variable and most likely

Table 1 – Comparison of PIXE and ICP-AES determinations of primary inorganic constituents identified in gasifier fly ash (na = not analyzed).

Element	PIXE			ICP-AES			
	Detection limit (mg kg^{-1})	Conc. Mass (g kg^{-1})	Error (g kg^{-1})	Nitric acid digestion		Aqua Regia digestion	
				Conc. Mass (g kg^{-1})	SD (g kg^{-1})	Conc. Mass (g kg^{-1})	SD (g kg^{-1})
Mg	217	7.07	0.17	8.02	0.06	7.91	0.02
Al	124	5.20	0.10	6.91	0.10	7.21	0.05
Si	56.5	16.8	0.17	0.15	<0.01	1.69	0.19
P	63.2	1.76	0.05	2.20	0.05	2.44	0.02
S	41.9	1.76	0.04	na	na	na	na
K	56.3	10.1	0.10	23.0	0.10	20.3	0.11
Ca	105	50.8	0.51	74.7	0.78	75.6	0.41
Mn	8.12	4.16	0.04	4.19	0.02	4.20	0.26
Fe	35.8	9.92	0.10	7.42	0.86	11.2	0.24

Table 2 – Comparison of PIXE and ICP-AES determinations of minor inorganic constituents detected in gasifier fly ash (na = not analyzed, nd = not detected).

Element	PIXE			ICP-AES			
	Detection limit (mg kg ⁻¹)	Conc. Mass (mg kg ⁻¹)	Error (mg kg ⁻¹)	Nitric acid digestion		Aqua Regia digestion	
				Conc. Mass (mg kg ⁻¹)	SD (mg kg ⁻¹)	Conc. Mass (mg kg ⁻¹)	SD (mg kg ⁻¹)
B	na	na	na	79.3	1.09	138	2.93
Na	337	nd	nd	897	12.4	834	19.8
Cl	25.2	993	25.2	na	na	na	na
Ti	13.5	377	19.8	na	na	na	na
Cr	8.93	147	6.73	37.5	3.73	38.5	11.5
Ni	2.99	60.4	2.22	47.5	1.69	47.3	3.27
Cu	2.61	33.0	1.78	37.8	1.40	37.2	3.64
Zn	2.27	364	2.02	357	3.96	345	5.05
As	2.17	7.39	2.07	5.60	0.94	10.1	10.9
Rb	8.12	47.8	6.87	na	na	na	na
Sr	9.16	367	7.86	na	na	na	na
Cd	3.13	nd	nd	4.54	0.02	4.39	0.09
Ba	94.7	nd	nd	719	5.15	703	2.02
Pb	8.36	nd	nd	12.9	0.41	11.8	0.17

underreported by ICP-AES. Results shown here demonstrate that PIXE is a more powerful screening method for fly ash analysis, especially in cases where the feedstock may be rich in silicates because of soil contamination of the feedstock.

Among the minor elements shown in Table 2, a general observation was that while the PIXE analysis provided data for a wide spectrum of elements, it did not provide the same level of sensitivity achieved by ICP-AES. For example, Na is known to occur in wood ash [4], and was readily detected by ICP-AES. The detection limit for Na was high (337 mg kg⁻¹) by PIXE, and with the results by ICP-AES (>800 mg kg⁻¹) exceeding this value, it is somewhat surprising that Na was not detected by PIXE. Other elements that went undetected by PIXE, but detected by ICP-AES, were Cd, Ba, Pb. Here again, the detection limits by PIXE were below the amounts detected by ICP-AES. Although PIXE may sometimes be lacking in sensitivity, it does provide data for a broad array of elements thus the detection of small amounts of Cl, Ti, Rb and Sr, which were not attempted by ICP-AES. Indeed, this point is understated

since as mentioned above, within certain limits of detection, PIXE provides elemental analysis data from sodium through uranium.

3.3. Utilization and disposal constraints

The use of wood ash for forestry applications has been reviewed with recommendations being suggested [38]. The focus in that report was on boiler ashes, in particular the bottom ashes; the light fly ashes from boilers were suggested to concentrate potentially toxic heavy metals and therefore were not recommended for use as a forest fertilizer [38]. Clear guidelines for the application of biomass-based fly ashes from gasification, let alone simple combustion, are not clearly established in the United States. Pollutant limits for the land application of wastes, such as sewage sludge, are set by the United States Environmental Protection Agency (EPA) [39], and are used here as a crude guideline given the lack of guidelines specific to the aforementioned biomass-based fly ashes. Composition recommendations for the application of ashes to forest lands in Sweden were revealed during our literature search [40]. In the EPA code, ceiling concentrations are set for 9 elements (As, Cd, Cu, Pb, Hg, Mo, Ni, Se, Zn) and range between 57 and 7500 mg kg⁻¹. Six of these elements (As, Cd, Cu, Pb, Ni, Zn) were detected by either of the two analytical methods used here and were at least one order of magnitude less than the ceiling concentration. For those three elements that were not detected, the limits of detection by PIXE were roughly one order of magnitude less than the EPA ceiling concentrations and thus the lack of detection would suggest that the fly ash generated in the present study would be acceptable for land application. As for the recommendations for applying ashes to forest lands put forth by the Nation Board of Forestry in Sweden, there are also minimum concentrations of macro- and micronutrients in addition to maximum levels permissible for heavy metals. The minimum requirements for the macronutrients Ca, Mg, K and P are 125, 20, 30, and 10 g kg⁻¹, respectively [40]. If similar guidelines were imposed in the

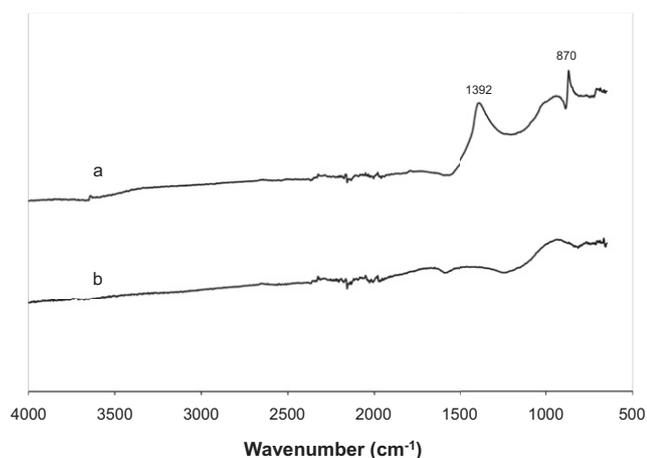


Fig. 1 – FTIR spectra of gasifier fly ash before (a) and after (b) acidification to remove carbonates and other acid-soluble materials.

Table 3 – Average percentages of primary elements in three randomly-collected grab samples of gasifier fly ash.

Element	Conc. Mass (%)	SD (%)
H	0.74	0.15
C	53.34	5.34
N	0.23	0.13
Mg	0.60	0.11
Al	0.45	0.06
Si	1.44	0.24
P	0.14	0.03
S	0.15	0.02
K	0.86	0.15
Ca	4.33	0.75
Mn	0.34	0.08
Fe	0.75	0.22

United States, the fly ash we generated would be unacceptable for land application as a fertilizer in its present form. To meet the minimum requirement would necessitate combusting the fly ashes to remove unburned carbon. Obviously this would concentrate the above-mentioned pollutant elements and the resultant values would be approximately double those shown in Table 2. Given that the concentrations are an order of magnitude less than the EPA ceiling concentrations, results presented here suggest that after combusting the fly ash generated in the present study, it may be suitable for use as a fertilizer for forest lands.

3.4. Fly ash variability

Finally, the results presented thus far provide a comparison of the analytical data for the same sample, thereby allowing two methods, PIXE and ICP-AES, to be compared. To provide a preliminary assessment of the variability of the fly ash generated, the average percentages for the primary elements determined by PIXE are shown for 3 grab samples (Table 3) randomly collected over several months of gasifier operation. Also provided are the results for hydrogen, carbon and nitrogen determined by combustion analysis (i.e., CHN analyzer). Undoubtedly, the variability in the feedstock and operating conditions within the gasifier could afford differences in fly ash composition. Results presented here suggest that the fly ash is sufficiently consistent, that with the same feedstock and operating parameters, the fly ash generated could remain within the above-mentioned guidelines, and could be used as a fertilizer for forest lands, albeit after combustion.

4. Conclusions

Processing a relatively clean wood chip feedstock in a commercial pilot-scale gasifier-based power plant can afford a fly ash with similar composition as conventional wood ashes, save for unburned carbon contents of approximately one half of the material. Although ICP-AES showed greater sensitivity for the analyses of the fly ash, especially for small amounts of heavy metal contaminants, PIXE proved to be a powerful analytical tool providing straightforward screening of elements from sodium to uranium. Such broad spectrum screenings

could prevent the inadvertent land application of unsuspected pollutant elements in fly ash, especially under circumstances where anthropogenic activities may have resulted in the accumulation of pollutant elements in the biomass feedstocks. Fly ashes from biomass gasification, such as that analyzed in the present study, appear to be sufficiently consistent for use as fertilizers for forest lands after combustion to remove unburned carbon.

Acknowledgments

Karen Reed (USDA Forest Service) assisted with the ash and volatile matter determinations. Brandi Downs (Louisiana State University AgCenter) carried out the digestions for ICP-AES. Assistance with combustion analyses was provided by Janet Dewey (Forestry Department, Mississippi State University). ICP-AES was conducted by Dr. Robert P. Gambrell (Louisiana State University Wetland Biogeochemistry Analytical Services). Carl Peterson and Larry Brown (Community Power Corp.) along with Drs. Les Groom, Tom Elder and Chi-Leung So (USDA Forest Service) are acknowledged for operation of the pilot-scale gasifier-based power plant during the period of sample collection.

REFERENCES

- [1] Chang MCY. Harnessing energy from plant biomass. *Curr Opin Chem Biol* 2007;11(6):677–84.
- [2] Jonsson A, Hillring B. Planning for increased bioenergy use—evaluating the impact on local air quality. *Biomass Bioenerg* 2006;30(6):543–54.
- [3] Ragauskas AJ, Williams CK, Davison BH, Britovsek G, Cairney J, Eckert CA, et al. The path forward for biofuels and biomaterials. *Science* 2006;311(5760):484–9.
- [4] Chirenje T, Ma LQ. Impact of high-volume wood-fired boiler ash amendment on soil properties and nutrients. *Commun Soil Sci Plan* 2002;33(1–2):1–17.
- [5] Vance ED. Land application of wood-fired and combination boiler ashes: an overview. *J Environ Qual* 1996;25:937–44.
- [6] Fernández-Pereira C, de la Casa JA, Gómez-Barea A, Arroyo F, Leiva C, Luna Y. Application of biomass gasification fly ash for brick manufacturing. *Fuel* 2011;90(1):220–32.
- [7] Gómez-Barea A, Vilches LF, Leiva C, Campoy M, Fernández-Pereira C. Plant optimisation and ash recycling in fluidised bed waste gasification. *Chem Eng J* 2009;146(2):227–36.
- [8] Leiva C, Gómez-Barea A, Vilches LF, Ollero P, Vale J, Fernández-Pereira C. Use of biomass gasification fly ash in lightweight plasterboard. *Energ Fuel* 2007;21(1):361–7.
- [9] Johnson J. The foul side of clean coal. *Chem Eng News* 2009; 87(8):44–7.
- [10] Pedersen KH, Jensen AD, Skjøth-Rasmussen MS, Dam-Johansen K. A review of the interference of carbon containing fly ash with air entrainment in concrete. *Prog Energ Combust* 2008;34(2):135–54.
- [11] Vervaeke P, Tack FMG, Navez F, Martin J, Verloo MG, Lust N. Fate of heavy metals during fixed bed downdraft gasification of willow wood harvested from contaminated sites. *Biomass Bioenerg* 2006;30(1):58–65.
- [12] Yamauchi S, Saitoh K, Sera K, Wada Y, Kuwahara M. Multielement analysis using PIXE for beneficial use of ashes from a biomass power plant. *J Wood Sci* 2008;54(2):162–8.

- [13] Odlare M, Pell M. Effect of wood fly ash compost on nitrification and denitrification in agricultural soil. *Appl Energy* 2009;86(1):74–80.
- [14] Reimann C, Ottesen RT, Andersson M, Arnoldussen A, Koller F, Englmaier P. Element levels in birch and spruce wood ashes—green energy? *Sci Total Environ* 2008;393(2–3):191–7.
- [15] EPA. Method 3052 microwave assisted acid digestion of siliceous and organically based matrices [Test methods for evaluating solid waste, physical/chemical methods data base on the internet]. Washington: Environmental Protection Agency [cited 2012 Nov 19] EPA Home, Wastes, Hazardous Wastes, Test Methods, SW-846 On-Line; Available from: http://www.epa.gov/wastes/hazard/testmethods/sw846/online/3_series.htm; 2012 [Files updated annually].
- [16] Hower JC, Rathbone RF, Robertson JD, Peterson G, Trimble AS. Petrology, mineralogy and chemistry of magnetically-separated sized fly ash. *Fuel* 1999;78(2):197–203.
- [17] Lillieblad L, Szpila A, Strand M, Pagels J, Rupar-Gadd K, Gudmundsson A, et al. Boiler operation influence on the emissions of submicrometer-sized particles and polycyclic aromatic hydrocarbons from biomass-fired grate boilers. *Energy Fuel* 2004;18(2):410–7.
- [18] Baasansuren J, Bolormaa O, Tokunaga R, Kawasaki K, Watanabe M. Effect of incubation on mobility of elements in fly ash and plant residue mixture analyzed by PIXE. *Nucl Instrum Meth B* 2006;251(1):209–12.
- [19] Merela M, Pelicon P, Vavpetić P, Regvar M, Vogel-Mikuš K, Serša I, et al. Application of micro-PIXE, MRI and light microscopy for research in wood science and dendroecology. *Nucl Instrum Meth B* 2009;267(12–13):2157–62.
- [20] Saarela K-E, Harju L, Lill J-O, Rajander J, Lindroos A, Heselius S-J. Thick target PIXE analysis of chromium, copper, and arsenic impregnated lumber. *Nucl Instrum Meth B* 1999;150(1–4):234–9.
- [21] Harju L, Lill J-O, Saarela K-E, Heselius S-J, Hernberg FJ, Lindroos A. Analysis of trace elements in trunk wood by thick-target PIXE using dry ashing for preconcentration. *Fresen J Anal Chem* 1997;358(4):523–8.
- [22] Lill J-O, Harju L, Saarela K-E, Lindroos A, Heselius S-J. Increased sensitivity in thick-target particle induced X-ray emission analyses using dry ashing for preconcentration. *Anal Chim Acta* 1999;378(1–3):273–8.
- [23] Saarela K-E, Harju L, Rajander J, Lill J-O, Heselius S-J, Lindroos A, et al. Elemental analyses of pine bark and wood in an environmental study. *Sci Total Environ* 2005;343(1–3):231–41.
- [24] Pan H, Eberhardt TL. Characterization of fly ash from the gasification of wood and assessment for its application as a soil amendment. *BioResources* 2011;6(4):3987–4004.
- [25] Anonymous E. 872 – Standard test method for volatile matter in the analysis of particulate wood fuels. West Conshohocken, PA: American Society for Testing and Materials; 2006.
- [26] Rauret G, López-Sánchez JF, Sahuquillo A, Rubio R, Davidson C, Ure A, et al. Improvement of the BCR three step sequential extraction procedure prior to the certification of new sediment and soil reference materials. *J Environ Monit* 1999;1(1):57–61.
- [27] Mossop KF, Davidson CM. Comparison of original and modified BCR sequential extraction procedures for the fractionation of copper, iron, lead, manganese and zinc in soils and sediments. *Anal Chim Acta* 2003;478(1):111–8.
- [28] Wang J, Nakazato T, Sakanishi K, Yamada O, Tao H, Saito I. Single-step microwave digestion with HNO₃ alone for determination of trace elements in coal by ICP spectrometry. *Talanta* 2006;68(5):1584–90.
- [29] Biagini E, Lippi F, Petarca L, Tognotti L. Devolatilization rate of biomasses and coal-biomass blends: an experimental investigation. *Fuel* 2002;81(8):1041–50.
- [30] Fuwape JA, Akindele SO. Biomass yield and energy value of some fast-growing multipurpose trees in Nigeria. *Biomass Bioenergy* 1997;12(2):101–6.
- [31] Senneca O, Chirone R, Salatino P. A thermogravimetric study of nonfossil solid fuels. 2. Oxidative pyrolysis and char combustion. *Energy Fuel* 2002;16(3):661–8.
- [32] Misra MK, Ragland KW, Baker AJ. Wood ash composition as a function of furnace temperature. *Biomass Bioenergy* 1993;4(2):103–16.
- [33] Park BB, Yanai RD, Sahm JM, Ballard BD, Abrahamson LP. Wood ash effects on soil solution and nutrient budgets in a willow bioenergy plantation. *Water Air Soil Poll* 2004;159(1–4):209–24.
- [34] De Bari I, Barisano D, Cardinale M, Matera D, Nanna F, Viggiano D. Air gasification of biomass in a downdraft fixed bed: a comparative study of the inorganic and organic products distribution. *Energy Fuel* 2000;14(4):889–98.
- [35] Eberhardt TL, Pan H. Elemental analyses of chars isolated from a biomass gasifier fly ash. *Fuel* 2012;96(1):600–3.
- [36] Zaranyika MF, Chirenje AT, Mahamadi C. Interference effects from easily ionizable elements in flame AES and ICP-OES: a proposed simplified rate model based on collisional charge transfer between analyte and interferent species. *Spectrosc Lett* 2007;40(6):835–50.
- [37] Havránek V, Kučera J, Horáková J, Voseček V, Smolik J, Schwarz J, et al. Matrix effects in PIXE analysis of aerosols and ashes. *Biol Trace Elem Res* 1999;71-72:431–42.
- [38] Pitman RM. Wood ash use in forestry—a review of the environmental impacts. *Forestry* 2006;79(5):563–88.
- [39] Standards for the use or disposal of sewage sludge: land application – Pollutant limits 40 CFR 503.13.
- [40] Anonymous. Recommendations for the extraction for forest fuel and compensation fertilising. Sweden: National Board of Forestry, Skogsstyrelsen; 2002. Printed by JV, Jönköping.