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Characterization and Utilization Potential of Wood Ash from Combustion Process and Carbon Residue from Gasification Process

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The aim of this research was to study the physical and chemical properties of fly ashes from combustion process and carbon residue from gasification process whilst comparing the results between these two types of solid residues, as well as against literature values. Ashes from the combustion process and carbon residue from gasification process are formed in different conditions, and it can be assumed that they will be best suited to contrasting utilization applications. The most notable differences between these types of solid residues were that the carbon content and loss-on-ignition value was higher for gasification carbon residue, and the liming capacity was higher for combustion ashes. The calculated liming capacity for combustion ashes and the fact that these ashes were strongly alkaline, together with high nutrient concentrations, indicate that combustion ashes can provide a liming effect. As a result, these ashes could potentially be utilized as a soil conditioning agent to substitute for commercial lime. The carbon content in gasification carbon residue was high which indicates, together with high porosity, that carbon residue would be an ideal sorbent and it could also be used as a fuel.

*Keywords: Utilization; Fly ash; Carbon residue; Physical and chemical properties; Heavy metals; Biomass*

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INTRODUCTION

In recent years, energy generated from biomass-based heat and power production has become more established due to higher electricity prices and the introduction of green electricity certificates. The use of wood for energy production has many advantages since it is renewable, local, and creates jobs, especially in areas of dispersed development. Energy can be generated in different ways, for example, by wood gasification or combustion. However, energy generated from biomass produces a considerable amount of solid residue that must be utilized economically. Utilization of solid residue (*e.g.* ash from combustion process or carbon residue from gasification process) is part of sustainable power generation from biomass and contributes to a green energy image (EU 2008; Hakkila 2006; James *et al.* 2012; Knoef 2005; Kumar *et al.* 2009; Kuokkanen *et al.* 2006; Pan and Eberhardt 2011). According to Pan and Eberhardt (2011), the solid residues obtained from the thermochemical processing of biomass (gasification) are typically mixtures of char and ash, and therefore referred to as biochar. In this article, solid residue formed in the wood gasification process is called a carbon residue. The term biochar is not suitable in that case, because biochar is formed in a limited supply of

oxygen, and our samples are obtained from gasifiers where gasification is done by air (Wang *et al.* 2012).

Combustion and gasification are thermochemical conversion methods that are used to convert biomass to energy. Gasification is a process that converts carbonaceous materials such as biomass to gas. In the combustion process, oxidation is substantially complete in a one-step process, but in the gasification process the chemical energy of carbon is converted into a combustible gas in two stages. Biomass can be converted at either high temperatures to syngas, which mainly contains CO and H_2, or at low temperatures into a product gas that contains CO, H_2, CH_4, and other hydrocarbons (C_xH_y). Syngas produced via gasification can be used directly as an internal combustion engine fuel or used as a chemical feedstock to produce liquid fuels. Biosyngas and product gas after purification can also be used as a raw material in catalytic processes to synthesize products such as methanol, oils, and ammonia, as seen in Fig. 1. Biomass is a variable feedstock and the use of gasification can convert low or even negative value feedstock, for example wet materials or waste materials from public gardens, into fuels and chemicals (Knoef 2005; Kumar *et al.* 2009; McKendry 2002).
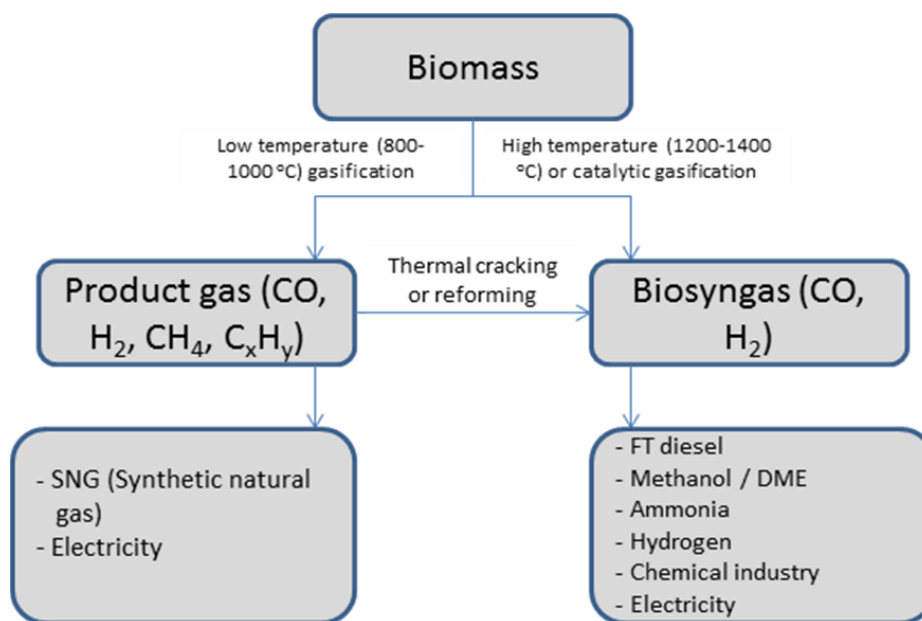
Fig. 1. Differences between syngas and product gas and their typical utilization applications (Knoef 2005)

The characteristics for carbon residues formed in the gasification process are that the calorific value is high as a result of the high carbon content, which is even 90%. Gasification carbon residues typically have properties that are different compared to combustion ashes. According to the literature, many potential utilization applications have been presented for ash from the combustion process; however, few exist for carbon residues formed in the gasification process. Ashes from the combustion process may be utilized in the concrete industry, road construction, building industry, and as a fertilizer and as a soil conditioning agent (Ahmaruzzaman 2010; Gómez-Barea *et al.* 2007;

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Kuokkanen *et al.* 2006; Pels *et al.* 2005; Pöykiö *et al.* 2005). Gómez-Barea *et al.* (2007) studied fly ashes formed in the gasification process, and they have found that gasification fly ashes may be utilized as a fuel if the carbon content is high enough or, for example, used in construction as a filler in asphalt products or as a fire-resistant material. Some gasification ashes could also be used as a fertilizer in agriculture or as a soil enhancer (Gómez-Barea *et al.* 2007). Leiva *et al.* (2007) found that fly ashes from fluidized-bed gasification have a potential to be used as the main constituent in lightweight wallboards.

Because the carbon content is high, carbon residues from the gasification processes could also be used as an adsorbent, for example removing toxic metals and organic compounds from wastewater. Due to the large surface area and carbon content of carbon residues, it could be used to replace activated carbon or zeolites in environmental applications, or used in air and water pollution treatment as sorbent (Ahmaruzzaman 2010; Kilpimaa *et al.* 2012; Leechart *et al.* 2009; Sun *et al.* 2008).

In Finland, legislation that affects the utilization of waste materials states that the properties of solid waste have to be known when it is either transferred to a landfill site or utilized in other ways, because metals or other harmful contaminants could be dissolved in the environment (Kuokkanen *et al.* 2006). Finnish waste legislation is based on EU legislation, but there are, in some cases, stricter standards and limits compared to EU legislation. The most important pieces of legislation concerning waste in Finland are: 1) Government Decree 214/2007, or Assessment of Soil Contamination and Remediation Needs, 2) Government Decree 591/2006, or Utilization of Certain Waste Materials in Earth Construction, 3) Ministry of Agriculture and Forestry Decree on Fertiliser Products 12/07 (In Finnish), 4) Government Decree 202/2006, or Waste Disposal in Landfills. In the Government Decree (VNa 214/2007) the general criteria of fees and charges related to the development, analysis, and verification of documentation for registration in the land cadaster are presented.

The assessment of soil contamination and remediation needs shall be based an assessment of the hazard or harm to health or the environment represented by the harmful substances in soil, and for example concentration and overall amounts of hazardous substances shall be taken into account in the assessment. The scope of the Government Decree (VNa 591/2006) is to promote recovery of wastes that could be utilized without environmental permit, which is needed in accordance with the Environmental Protection Act (86/2000). In the Ministry of Agriculture and Forestry Decree on Fertiliser Products 12/07, the maximum concentration values of heavy metals that are allowed to exist in fertilizers for forestry and agricultural use are given. The Government Decree (VNa 202/2006) describes the principles of the assessment of an appropriate landfill class for a particular waste.

The aim of this study was to obtain information about the physical and chemical properties of wood ashes from combustion and carbon residues from gasification processes whilst comparing the results between these two types of solid residues for evaluating their potential utilization applications. Solid residues from the combustion and gasification processes are formed in different conditions, and it can be assumed that they will be best suited to contrasting utilization applications. Results obtained in this study were compared against existing literature values for two fly ashes formed in a bubbling fluidized bed boiler.

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EXPERIMENTAL

Materials

This investigation examined a total of four solid residues, two each from the biogasification and combustion processes. All solid residues (carbon residue 1, 2 and ash 1, 2) were produced in Finland, and samples were collected from different types of gasification or combustion techniques. Gasification carbon residue 1 was produced from a 1 MW gasifier at around 900 ^{o}C, which possessed an updraft and downdraft gasifier combination. 100% Finnish wood (birch tree and evergreen tree) was used as the raw material at a fuel consumption rate of 333 kg h^{-1}. Carbon residue 2 was acquired from a gasification pilot-plant which involved a 150 kW downdraft gasifier at around 1000 ^{o}C. 100% Finnish wood was again used as the raw material for the fuel at a rate of 50 kg h^{-1}. Both were classified as low temperature gasifiers as was presented in Fig. 1. Carbon residues are collected from a water container because there is no separate carbon residue collector in the gasifier and the gas produced in gasification process is washed by a water scrubber. Ashes 1 and 2 (combustion process) were both collected in the form of fly ash from a thermal power plant involving a bubbling fluidized-bed boiler. Each fly ash was sampled from an electric filter; however, the ratio of raw material used and the boiler properties employed were different. A combination of 75% Finnish wood and 25% peat was used to produce ash 1, whilst a 50/50 ratio was used for ash 2. The total power output of the boiler was 24 MW (6 MW electricity and 18 MW heat) at a pressure of 60 bar for ash 1 and 70 MW (20 MW electricity and 50 MW heat) at a pressure of 80 bar for ash 2. The temperature and fuel consumption was 510 ^{o}C and 8 kg s^{-1} for ash 1, and 482 ^{o}C and 27 kg s^{-1} for ash 2.

All of the samples were then dried in an oven at 105 ^{o}C to allow the neutralizing value, reactivity, and total element concentration to be determined. For the remaining analysis, dried sample was crushed and sieved to ensure a uniform quality and to achieve particles under 150 μm.

Determination of the Physical and Chemical Properties

The pH and electrical conductivity values of the sample were determined with a Hach Lange HQ40d pH electrode and a conductivity electrode, respectively. Electrical conductivity value is an index of the total dissolved electrolyte concentration. This was achieved by dissolving sample into distilled water so that a liquid to solid ratio (L/S) of 10 (w/w) was obtained. Analysis of the dry matter content of sample was performed in accordance to European standard SFS-EN 12880 (SFS-EN 2000a), where the sample was dried overnight to a constant mass in an oven at 105 ^{o}C. The organic matter content, measured by observing the loss-on-ignition value (LOI), was determined according to the European standard SFS-EN 12879 (SFS-EN 2000b), where the previous sample dried at 105 ^{o}C is heated in a muffle furnace overnight at 550 ^{o}C.

Determination of the dissolved organic carbon (DOC) concentration was carried out in accordance to the European standard SFS-EN 1484 (SFS-EN 1997) using a Sievers 900 Portable TOC analyzer that implements the oxidation method. Organic compounds are oxidized to carbon dioxide using UV radiation and ammonium persulfate, which is used as a chemical oxidizing agent. Carbon dioxide is measured using a sensitive, selective membrane-based conductometric detection technique (Sievers 900 Portable Total Organic Carbon Analyser 2006).

The total carbon content (TC) was calculated by elementary analysis using a Perkin Elmer CHNS analyzer, the method for which is based on combustion, where the sample elements are converted to simple gases (CO_2, H_2O, N_2, and SO_2) in a pure oxygen atmosphere. Gases are homogenized and detected by controlling the exact conditions of pressure, temperature, and volume. The homogenized gases are de-pressurized through a column where they are separated and thus identified as a function of their thermal conductivities (Perkin-Elmer 1991).

Both the neutralizing value and reactivity are important quantities when considering the liming effect, and are measured according to the European standards SFS-EN 12945 (SFS-EN 2002) and SFS-EN 13971 (SFS-EN 2003), respectively. The principle behind measuring the neutralizing value is to dissolve the dried sample in a specific quantity of hydrochloric acid. The excess acid is then titrated with a standard sodium hydroxide solution. The neutralizing value is one of the most important indicators when evaluating the utilization potential of ash or carbon residue as a liming agent in acidic soil. The capacity of the liming agent to neutralize soil acidity depends on its content of soluble and hydrolysable bases (oxides, hydroxides, carbonates, and silicates). Reactivity is the determination of the speed and effectiveness of the neutralizing potential of sample, the reaction of which is generated by a potentiometric titration with hydrochloric acid. The analysis of the reactivity value is based on the following reaction,

$$MeCO_3 + 2\,H^+ \rightarrow Me^{2+} + H_2O + CO_2 \qquad (1)$$
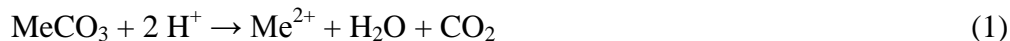
where metal carbonates decompose with acid. The consumption of hydrochloric acid in the titration is a direct measure of the reaction rate of the sample being tested.

With the aid of an IKA Calorimeter system C200 system the authors were able to measure combustion heat of a sample in a calorimeter under specific conditions. This was achieved by placing a solid fuel sample into a decomposition vessel and then measuring the increase in temperature through combustion. In addition, the decomposition vessel is filled with pure oxygen to a pressure of 30 bar to ensure the optimization of the combustion process.

The buffer solution is able to retain an almost constant pH when a small amount of acid or base is added to a solution. In normal circumstances, the pH of a solution will decrease when an acidic substance is added due to the presence of hydrogen ions in the acid. However, the pH levels will not decrease as much if the solution also possesses ions that have the ability to neutralize the added hydrogen ions. These ions may include hydrogen carbonates, carbonates, and hydroxides. In this study, buffer capacity was determined by shaking ash or carbon residue sample and distilled water for 1 hour in a liquid to solid ratio of 10 (w/w). Titration was then performed in a solution of hydrochloric acid.

Particle size determination was carried out using a Beckman Coulter LS 13 320 laser diffraction particle size analyzer involving a measurement range of 0.4 to 2000 μm. This type of analyzer utilizes a laser diffraction technique that is based on the principle that a laser beam will scatter light at an angle that is directly related to the particle size. The scattering angle increases logarithmically when the particle size decreases. Small particles scatter light at wider angles with low intensity whilst large particles scatter light at narrow angles with high intensity (Allen 1997). The specific surface area of samples was determined from nitrogen adsorption-desorption isotherms at the same temperature of liquid nitrogen ($-196\,^{\circ}C$) by using a Micromeritics ASAP 2020 instrument. The same

equipment was also used for the determination of average pore size and total pore volume. Microscopic analysis was performed using a field emission scanning electron microscope (FESEM, Zeiss Ultra Plus Gemini), whilst sample density was calculated by measuring the mass of a sample under compression using a 7.7 g cm^{-3} weight on top of the sample layer for 3 min.

Determination of the Nutrient Concentration

The determination of easily soluble nutrients in samples was performed according to the procedure employed by MTT Agrifood Research Finland (Yli-Halla and Palko 1987). In this procedure, nutrients are extracted into a mixture of 0.5 M acetic acid and 0.5 M ammonium acetate (pH = 5.0). The liquid to solid ratio between the sample and the extraction solution was set to 10 (w/w), whilst the extraction time was 1 h. Cu and Zn were calculated using the same procedure, but in this situation the extraction solution was 0.5 M acetic acid, 0.5 M ammonium acetate, and 0.02 M ethylenediaminetetra-acetic acid disodium salt (Na_2EDTA) (pH = 4.7). Before the analysis, the extract was separated from the solid residue by filtration using a 0.45 µm membrane filter. The concentration of the elements in the extract was determined by ICP-MS (Thermo Elemental).

Determination of the Total Element Concentrations

Acid decomposition was performed in order to determine the total element concentration in sample. A dried sample was decomposed with a mixture of HCl (3 mL) and HNO_3 (9 mL) in a microwave oven with Teflon vessels using the US EPA method 3052. After decomposing, the cooled solutions were transferred into 100 mL volumetric flasks and diluted with ultrapure water. The water was generated with a Elgastat Prisma reverse osmosis and an Elgastat Maxima ion exchange water purification system. Except for Hg, the total element concentrations in the solutions were measured with a Thermo Elemental IRIS Intrepid II XDL Duo inductively coupled plasma optical emission spectrometer (USEPA 3051A (revision 1) 2007). Finally, the concentration of Hg was determined by Perkin-Elmer Analyst cold-vapour atomic absorption spectrometry (Norwalk, USA).

RESULTS AND DISCUSSION

Physical and Chemical Properties

Table 1 summarizes the physical and chemical properties of the investigated samples. The results indicate that all of the studied ashes and carbon residues were clearly alkaline, with ashes from the combustion process possessing a notably higher pH than carbon residues formed from gasification. A similar trend was observed for the values obtained for an electrical conductivity value, an index of the total dissolved electrolyte concentration, whose value was quite high for ash produced by the combustion process. A high electrical conductivity value indicates that parts of the dissolved metals may occur as dissolved basic metal salts, *e.g.* oxides and hydroxides (Nurmesniemi *et al.* 2005). Dry matter content was found to be very low in carbon residues from the gasification process, which indicates that moisture was present because there is no separate carbon residue collector in the gasifier. The gas produced in the gasifier was washed with a water scrubber, and the carbon residue formed in the process was collected from the water container.

Table 1. The Physical and Chemical Properties in the Four Investigated Ashes

| Parameter	Unit	Carbon residue 1	Carbon residue 2	Ash 1	Ash 2
pH (1:10)		10.7	9.0	12.4	12.4
Electrical conductivity (1:10)	mS cm^{-1}	1.0	0.46	7.9	10.1
Dry matter content	%	18.7	16.4	99.8	99.9
Loss on ignition	%	94.8	68.4	8.7	1.5
DOC	mg kg^{-1}	649	565	0.84	0.46
TC	%	89.4	60.9	6.5	1.3
Neutralizing value	% Ca	3.8	8.0	13.3	11.3
Reactivity value	% Ca	1.6	6.6	10.0	5.1
Liming capacity	t t^{-1}	10	4.8	2.9	3.4
Combustion heat	MJ kg^{-1}	29.7	20.0	1.44	0.035
Specific surface area	m^2 g^{-1}	100	15	29.8	5.9
Pore size (average)	nm	3.9	15.9	3.2	4.8
Pore volume (total)	cm^3 g^{-1}	0.098	0.056	0.024	0.007
Density	g cm^{-3}	0.178	0.274	0.544	0.674

Further evidence of this is provided by the lack of dust problems during handling compared to ashes 1 and 2, which exhibited high dry matter content and a significant increase in the amount of dust during handling. Loss-on-ignition values (LOI) were high for carbon residues 1 and 2, which indicates that they contain organic matter. This is further supported by high DOC values; however, it should be noted that the determination of LOI values is not an accurate measuring method for the amount of residual carbon in sample that was not burned (Brown and Dykstra 1995; Kuokkanen *et al.* 2006). Carbon residue could, therefore, be used as a fuel if its carbon content is greater than 35%, or if the gross heat value is more than 15 MJ/kg (Pels *et al.* 2005). In this study, the results show that both carbon residues have the potential to be used as a fuel due to their high carbon content. Ashes 1and 2 from the combustion process have a low carbon content, which indicates that the burning of organic matter in the boiler has been completed (Kuokkanen *et al.* 2006).

In terms of using the investigated ashes and carbon residues as a potential source for a soil conditioning agent, the results were mixed. The liming effect of commercial limestone produced by SMA Saxo Mineral Ltd. was known to be 38% (Ca equivalents; d.w.); however, the neutralizing values for the investigated samples were much lower than those for commercial limestone. Low neutralizing values indicate that the ash or carbon residue must be used in large quantities to replace the commercial limestone. Out of the four investigated samples, ash 1 had the greatest liming capacity; it required 2.9 tonnes to replace 1 tonne of commercial limestone produced by SMA Saxo Mineral Ltd. (Nurmesniemi *et al.* 2005). Combustion ashes contain a great amount of calcium carbonate, but gasification carbon residues do not, which could explain this difference in liming effects.

Specific surface area, pore size, pore volume, and particle size distribution are important physical properties that determine the quality and utilization potential of ashes or carbon residues, *e.g.* as a sorbent. Differences in the surface area and porosity of particles within a material can affect its performance characteristics. Both gasification carbon residues had high carbon contents, and the specific surface area of carbon residue

1 was also quite high. To put this into context, graphite and carbon black powder, depending on its preparation, have typical specific surface areas of 10 to 300 $m^2\ g^{-1}$ and 100 to 2500 $m^2\ g^{-1}$, respectively (Stüber *et al.* 2005). For the other three samples, their specific surface areas are quite low; however some pre-treatment methods, for example physical or chemical activation, could be tested to obtain a higher surface area (Ahmadpour and Do 1996). The adsorption properties of ashes or carbon residues would be better suited if the specific surface area was larger, since pore size affects the type of molecules that can be adsorbed by the surface. Total pore volumes were higher for carbon residues 1 and 2 compared with ashes 1 and 2. The average pore size is notably high for carbon residue 2 which can cause the quite high total pore volume; even the specific surface area is not very large. The densities for combustion ashes were higher than carbon residues formed through gasification, which indicates that combustion ashes were heavier.

With the aid of FESEM images of the four investigated samples, the authors were able to closely observe the surface features of each sample as presented in Fig. 2. A FESEM image allows the surface morphology of the sample to be viewed in detail, enabling pores and crystals that may be present to be seen. In this study, FESEM images were able to show clearly that the morphology of our samples is variable and complex.
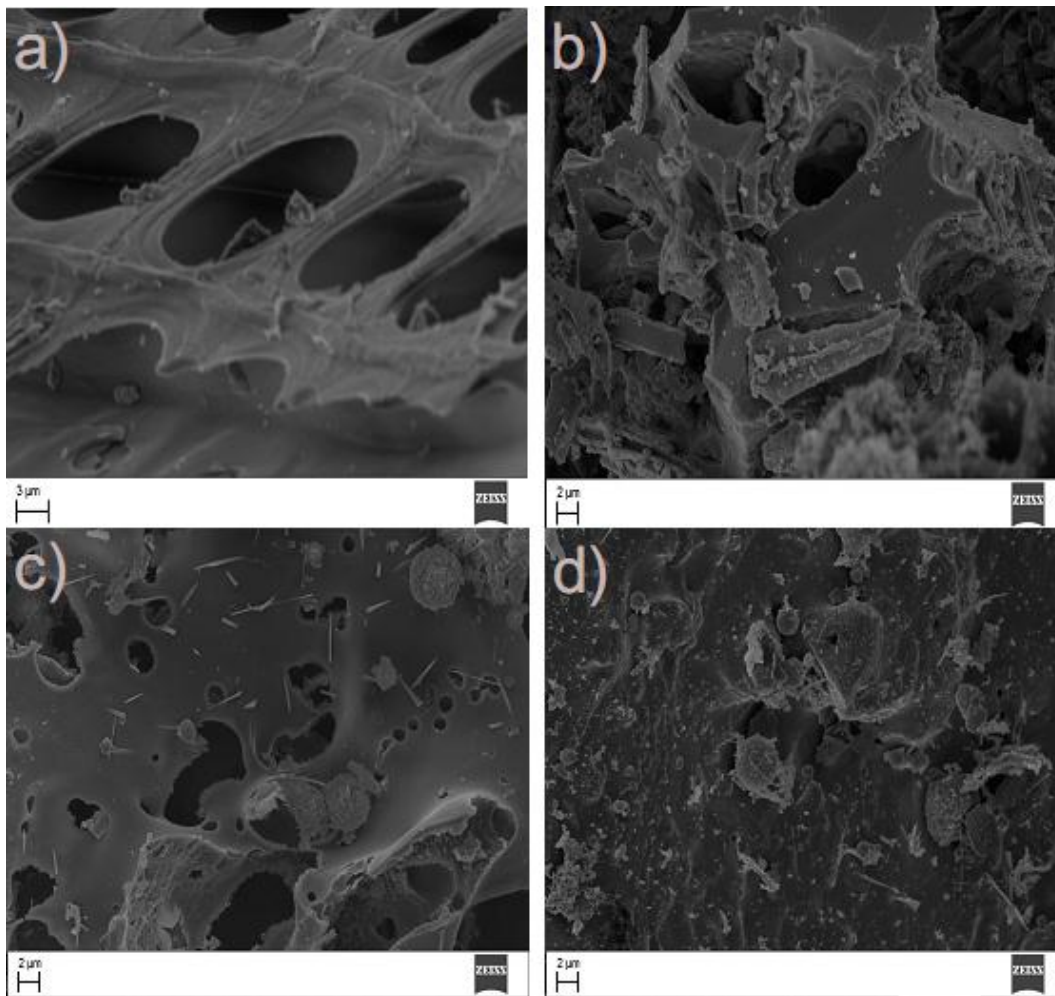

Fig. 2. FESEM images for carbon residue 1 (a) and carbon residue 2 (b) formed in the biogasification process and ash 1 (c) and ash 2 (d) from the combustion process

Carbon residue 1 was the most porous compared to the other investigated samples, whilst ash 2 was rather smooth. These observations are supported by the values obtained for specific surface areas.

As presented in Fig. 3, ashes 1 and 2 formed in the combustion process exhibited a much greater buffering capacity when comparing them to carbon residues formed in the gasification process. As a result, hydrochloric acid, used to model acidic rainwater, could be added in greater amounts to the combustion ashes rather than to the gasification carbon residues before the pH level dropped. This is due to the fact that combustion ashes possess more ions that act like carbonates and silicates, giving the ability to neutralize any added hydrogen ions.
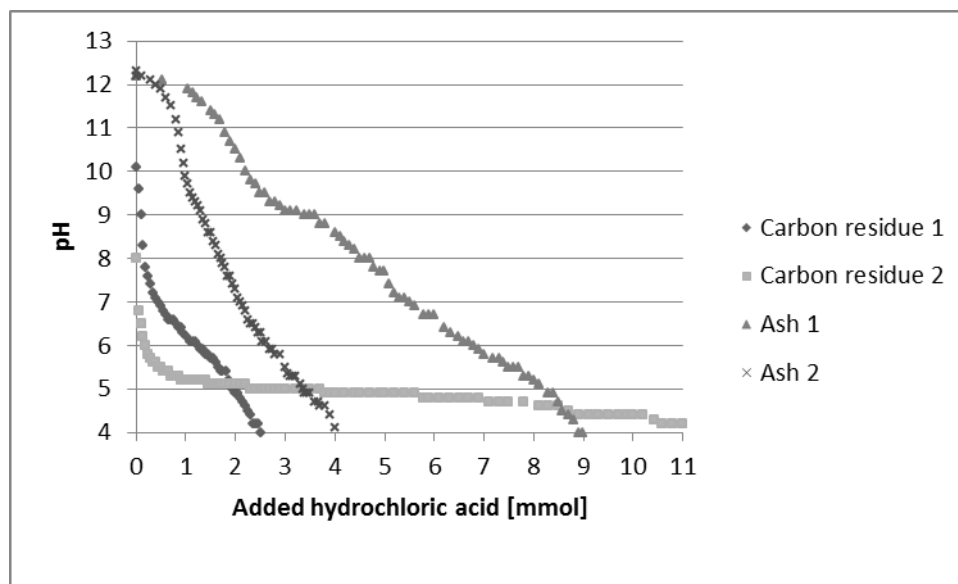
Fig. 3. Buffer capacities of the investigated ashes formed in the biogasification and combustion processes (ashes 1-4)

Particle size determination is an important quantity to consider when evaluating potential utilization applications for solid residuals from combustion and gasification processes. Therefore, particle size distribution of a material is important in understanding its physical and chemical properties, such as reactivity, which is higher for smaller particles. For the investigated samples, their particle size distributions are presented in Fig. 4, in which the x-axis is the particle diameter on the micrometer and the y-axis is the volume weighed percentage. The y-axis describes the percentage proportion of a specific particle size and was found to be quite similar for each type of samples investigated.

To allow a comparison to be made of the 4 investigated samples against existing results from combustion ashes, Table 2 presents literature values of some physical and chemical properties for two fly ashes. Fly ash 1 is from a 32 MW bubbling fluidized bed boiler, and at the time of the study the used raw material was a mixture of approximately 50% clean forest residue and *ca.* 50% peat. Fly ash 2 was also from the bubbling fluidized bed boiler (246 MW) at the pulp and paper mill complex of Stora Enso Oyj Oulu Mill. The used raw material was *ca.* 43% wood-waste (*i.e.* bark, woodchips, saw-dust) and 57% peat. According to Dahl *et al.* (2009), the boiler´s temperature in the combustion sand bed is between 810 and 830 ^{o}C, whilst in the upper zone the temperature is between 1100 and 1200 ^{o}C. Nurmesniemi *et al.* (2008) mentioned that the combustion temperature varied between 900 and 1100 ^{o}C in the combustion chamber.
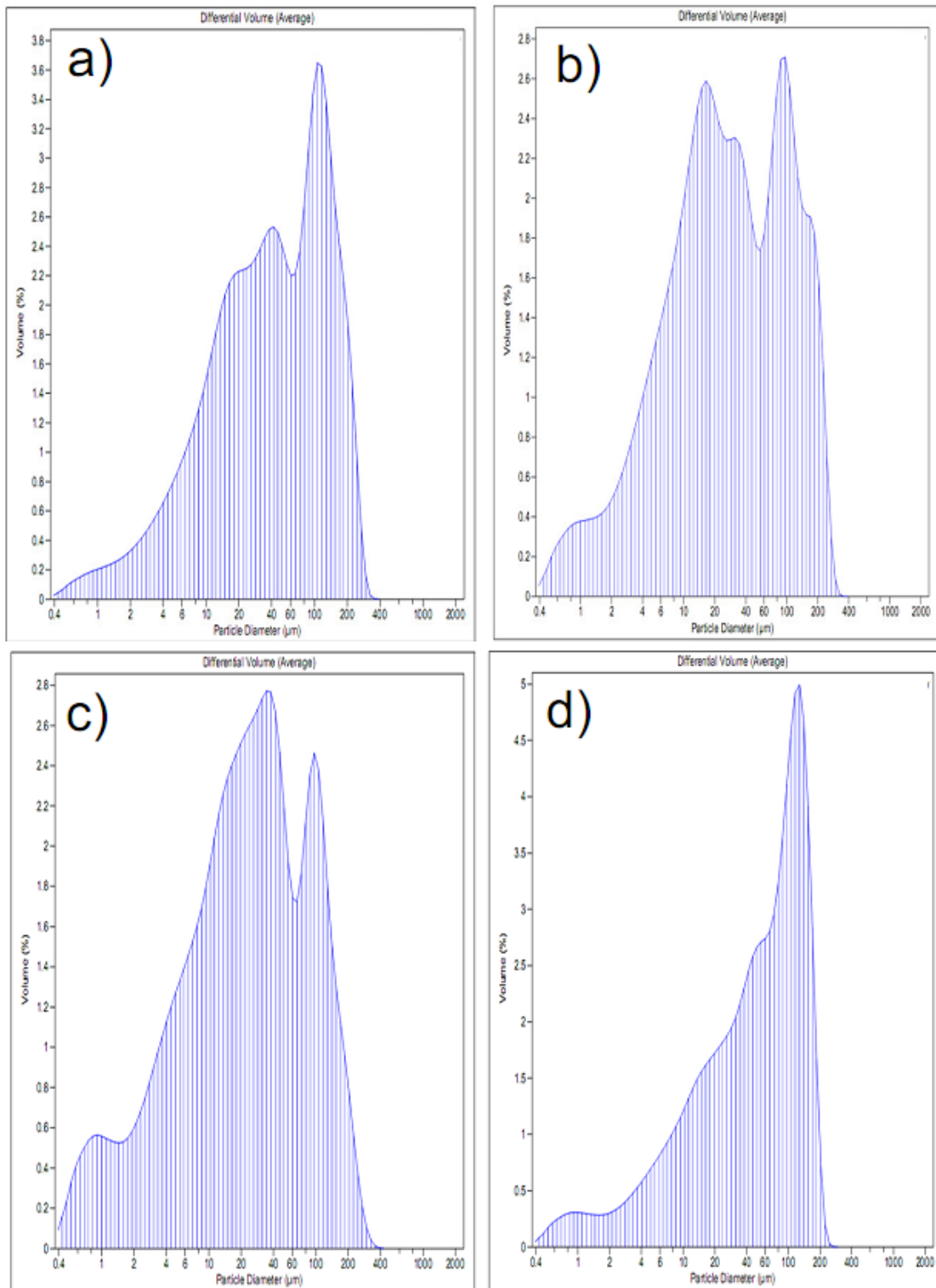
Fig. 4. Particle size distributions of a) carbon residue 1 and b) carbon residue 2 from the biogasification process as well as c) ash 1 and d) ash 2 from the combustion process whose mean value are 64.5 μm, 52.4 μm, 43.4 μm, and 66.4 μm respectively

The LOI values are low for the fly ashes when they are compared against the LOI values measured for gasification carbon residues values presented in Table 1. Together with TOC values, it is apparent that almost complete combustion of organic matter occurred in the boiler. The TOC values are typically higher for fly ash than for bottom ash due to the fact that fly ash particles spend less time in the combustion chamber zone. This is because fly ash particles rise easily with the flue gas into the electrostatic precipitators. In addition, the neutralizing value presented in literature is notably higher for fly ash1 when comparing it to other fly ash or carbon residue samples. This means that there is an elevated concentration of calcium, which makes fly ash 1 a suitable soil conditioner agent (Dahl *et al.* 2009; Nurmesniemi *et al.* 2008).

Table 2. Literature Values for the Physical and Chemical Properties of Fly Ashes (Dahl *et al.* 2009; Nurmesniemi *et al.* 2008)

Parameter/Element	Unit	Fly ash 1 (Dahl *et al.* 2009)	Fly ash 2 (Nurmesniemi *et al.* 2008)
pH		12.5[a]	11.7[b]
Electrical conductivity	mS cm^{-1}	13.9	3.5[b]
Loss on ignition	% (d.w.)	< 0.5	5.5
TOC	g kg^{-1} (d.w.)	4	3
Dry matter content (105 ^{o}C)	%	99.9	85.6
Neutralizing value	% (Ca; d.w.)	28.5	13.0
Reactivity value	% (Ca; d.w.)	18.2	11.6

[a]1:5 ; [b]1:2.5 (v/v)

Nutrient Concentrations in Ashes

The concentrations of soluble nutrients measured in the four investigated samples are presented in Table 3. As a reference point, the typical values of K, Mg, and Ca in arable land in Central Finland are 100, 200, and 1600 mg kg^{-1}, respectively. Therefore, the relatively high soluble concentration of K measured in all four investigated samples may contribute to improving soil fertility. Furthermore, elevated Ca concentrations in ashes 1 and 2 and in carbon residue 2 indicate that these samples may also have the potential to become soil conditioning agents (Kuokkanen *et al.* 2006; Pöykiö *et al.* 2005). Tulonen *et al.* (2002) recommended that these types of ashes formed in the combustion process are ideal for nitrogen-rich peat lands that are suffering from a shortage of trace elements.

Table 3. Concentrations of Soluble Nutrients Measured in the Four Investigated Ashes and Carbon Residues

Nutrient	Unit[a]	Carbon residue 1	Carbon residue 2	Ash 1	Ash 2
K	g kg^{-1} (d.w.)	3.1	2.3	11.4	2.9
Mg	g kg^{-1} (d.w.)	1.6	3.2	4.1	2.1
Ca	g kg^{-1} (d.w.)	8.5	42.3	46.5	26.7
Na	mg kg^{-1} (d.w.)	< 101	71	1484	891
Cu	mg kg^{-1} (d.w.)	< 10.1	< 10.1	11.8	14.8
Zn	mg kg^{-1} (d.w.)	15.2	66.1	52.3	86.8

[a]Concentrations are expressed on dry weight (d.w.) basis

Table 4 presents literature values of easily soluble nutrient concentrations in two types of fly ashes, as determined by ammonium acetate extract, which is generally considered as an indication of nutrient availability (Dahl *et al.* 2009; Nurmesniemi *et al.* 2008). The authors observed that the majority of the results obtained from literature were in the same order of magnitude apart from a high Ca and Zn concentrations for fly ash 1. High levels of calcium compounds occur typically in wood and according to Kuokkanen *et al.* (2006), zinc will concentrate in fly ash due to the temperature at which ash flows are precipitated.

Table 4. Literature Values of Easily Soluble Nutrient Concentrations of Fly Ashes from a 32 MW Bubbling Fluidized Bed Boiler (fly ash 1) and from 246 MW Bubbling Fluidized Bed Boiler (Dahl *et al.* 2009; Nurmesniemi *et al.* 2008)

Nutrient	Unit	Fly ash 1 (Dahl *et al.* 2009)	Fly ash 2 (Nurmesniemi *et al.* 2008)
K	g kg^{-1} (d.w.)	9.7	4.2
Mg	g kg^{-1} (d.w.)	17	1.9
Ca	g kg^{-1} (d.w.)	140	68.5
Na	g kg^{-1} (d.w.)	1.4	2.3
Cu	mg kg^{-1} (d.w.)	22.0	15
Zn	mg kg^{-1} (d.w.)	370	67

Determination of the Total Element Concentrations

Table 5 presents the concentrations of total heavy metals, expressed as dry weight (d.w), in the two investigated carbon residues and two ashes. According to Table 5, the total heavy metal concentrations in samples 1 through 4 were lower than the current Finnish maximum limit allowed in forest fertilizer. As a result, these ashes and carbon residues can be utilized in their own right as a forest fertilizer in terms of heavy metals. With respect to agriculture, the results in Table 5 show that the concentrations of cadmium in ashes 1-2 and carbon residue 2 was higher than the current maximum limit for agricultural use. The concentration of nickel in carbon residue 2 was also calculated to be higher than the current acceptable limit, whilst a similar scenario was observed for arsenic in ash 2. However, this was not the case for carbon residue 1, which could, therefore, be utilized entirely as a potential source for a forest fertilizer or for agricultural use in terms of heavy metals. For example Cd, Zn, and Pb will concentrate to fly ash because the combustion process is like a thermodynamic separation process for the different inorganic materials in the fuel.

The most notable effect was temperature; because bottom ash leaves the combustion chamber in high temperatures, bottom ash is free of volatile heavy metals. Instead, metals with low volatility, such as nickel and chromium, will concentrate in the bottom ash. Hg concentration was measured to be very low in all of the investigated samples, which is typical for wood-based solid residuals. This is a consequence of the fact that mercury is volatilized, which causes it to escape during the thermal treatment due to its high vapor pressure (Kuokkanen *et al.* 2006; Narodoslawsky and Obernberger 1996; Pöykiö *et al.* 2009). Past studies have also shown that pH has a strong effect on the mobility of heavy metals. As such, when the alkalinity of the ash decreases, the metals will become more mobile (Kuokkanen *et al.* 2006; Steenari and Lindqvist 1997).

Table 5. Total Heavy Metal Concentrations (mg kg^{-1}; d.w.) *

Element	Unit	Limit value (forest fertilizer)	Limit value (agricultural use)	Carbon residue 1	Carbon residue 2	Ash 1	Ash 2
Cd	mg kg^{-1} (d.w.)	15	1.5	< 0.3	6.3	5.0	3.0
Cu	mg kg^{-1} (d.w.)	700	600	15	130	83	81
Pb	mg kg^{-1} (d.w.)	150	100	< 3	25	27	72
Cr	mg kg^{-1} (d.w.)	300	300	7	210	82	60
Zn	mg kg^{-1} (d.w.)	4500	1500	85	134	380	530
As	mg kg^{-1} (d.w.)	30	25	< 3	< 3	19	28
Ni	mg kg^{-1} (d.w.)	150	100	3	110	36	37
Hg	mg kg^{-1} (d.w.)	1.0	1.0	< 0.040	0.040	0.56	0.47

* As measured from the four investigated samples together with the current Finnish maximum limit for biomass-derived ashes used as a forest fertilizer or in agricultural use (Ministry of Agriculture and Forestry Decree on Fertilizer Products Dec 07)

For comparison, Table 6 presents the literature values of total element concentrations for two fly ashes formed in a bubbling fluidized bed boiler. Nickel and chromium concentrations were very high in carbon residue 2 when compared with other samples. Other metal concentrations were in the same order of magnitude. Chemical composition and other properties of solid residues depends on many factors, for example the type of fuel used, tree species, growing site and climate, age of the tree, storage conditions, and the gasification or combustion technique (*e.g.* temperature, type of boiler, or gasifier) employed (Dahl *et al.* 2009; Holmberg *et al.* 2000).

Table 6. Literature Values for Total Heavy Metal Concentrations in two Wood-based Ashes. Fly ash 1 was decomposed in microwave with HNO$_3$ and HCl (Dahl *et al.* 2009) and fly ash 2 with HF and HNO$_3$ (Nurmesniemi *et al.* 2008)

Element	Unit	Fly ash 1 (Dahl *et al.* 2009)	Fly ash 1 (Nurmesniemi *et al.* 2008)
Cd	mg kg^{-1} (d.w.)	3	4.6
Cu	mg kg^{-1} (d.w.)	60	110
Pb	mg kg^{-1} (d.w.)	49	43.0
Cr	mg kg^{-1} (d.w.)	24	90.1
Zn	mg kg^{-1} (d.w.)	480	560
Ni	mg kg^{-1} (d.w.)	67	53.7

CONCLUSIONS

1. The most notable differences between combustion ashes and gasification carbon residues were that carbon content and loss-on-ignition values were much higher for carbon residues.

2. The results indicate that combustion ashes have the potential to be used as a forest fertilizer and as a soil conditioning agent, since they possess elevated concentrations of important nutrients and the liming effect was higher for combustion ashes comparing with gasification carbon residues. This is attributable to the fact that combustion ashes include for example calcium carbonates and oxides.

3. From the utilization point of view, it is notable that the total heavy metal concentrations in those solid residues studied were lower than the Finnish maximum limit allowed in forest fertilizer.

4. Gasification carbon residues are suitable for use as a fuel or they could be utilized as a sorbent due to their high carbon content and large specific surface area

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