### INNOVATIVE STRATEGIES FOR THE UTILIZATION OF BIOMASS ASH

by

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### ABSTRACT

Bioenergy production using woody biomass is a fast developing application since this fuel source is considered to be carbon neutral. The harnessing of bioenergy from these sources produces residue in the form of ash. As the demand for bioenergy production increases, ash and residue volumes will increase. Major concerns arising from the management of this byproduct include: storage availability, usage, product disposal and the implications of the presence of unburned carbon. This research studies various ash types, identifying specific fractions of technological, environmental and economic viability. Fractions of energy importance, inorganic distribution and catalytic properties of specific ash types are investigated. Ash from three systems were investigated, an industrial boiler, a fixed bed updraft gasifier and a wood pellet burner. Analyses of the boiler ash included particle fractionation, proximate and ultimate analysis, Brunauer-Emmett-Teller (BET) surface area, thermogravimetric analysis (TGA) and bulk density. Samples were separated into various fractions based on particle sizes. The fixed carbon in the as-received boiler ash samples was 30 and 50 % and the higher heating value (HHV) ranged from 5 - 25 MJ/kg of the different fractions. 68 % or more of the energy could be recovered in fractions  $\geq$ 425 µm. High carbon ash was successfully gasified in a fluidized bed reactor at low temperatures and atmospheric pressure. The pH of the as received samples for the gasifier, boiler and pellet burner were 10.36, 12.49 and 13.46, respectively. Ni with a concentration of 229 mg/kg in the pellet burner ash, exceeded the maximum limit for soil amendments (in British Columbia, Canada) within the particle size fraction  $\geq$  850 µm but < 2000. All samples were significantly enriched in both Ca (50-61 %) and K (10-26 %). Wood ash derived catalyst obtained from a gasifier and a wood pellet burner influenced

gasification reactivity. The pellet burner ash was a more effective catalyst than the gasifier ash at similar catalyst to char loadings. High carbon ash could have potential end uses as a fuel and soil additive, while ash may be used as a fertilizer, liming agent and as a catalyst, in all cases promoting the common goal of sustainable development.

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# NOMENCLATURE

(FAO)	Food and Agriculture Organization		
AI	Alkali index (AI)		
AR	As-received		
BA	Boiler ash		
BET	Brunauer-Emmett-Teller		
d.w.	Dry weight		
DTG	Differential thermogravimetric		
EA	Elemental Analyzer		
ER	Equivalence ratio		
FC	Fixed carbon		
GA	Gasifier ash		
H <sub>2</sub> /CO	Hydrogen to carbon molar ration (mol/mol)		
HHV	Higher heating value (MJ/kg or MJ/m <sup>3</sup> )		
I.D.	Internal diameter (m)		
IC	Ion Chromatography		
ICP-MS	Inductively coupled plasma mass spectrometry		
LHV	Lower heating value (MJ/kg or MJ/m <sup>3</sup> )		
PA (PBA)	Pellet burner ash		
РАН	Polycyclic aromatic compounds		

r	Char reactivity (s <sup>-1</sup> )
R <sub>b/a</sub>	Base-to-acid ratio
R <sub>s</sub>	Reactivity index (min <sup>-1</sup> )
S/B	Steam/biomass
t	Time (s)
Т	Temperature (°C)
to.5	Gasification time taken to reach a carbon conversion of 50 %.
TG	Thermogravimetric
TGA	Thermogravimetric Analyzer)
VM	Volatile matter
Wash	Mass of ash in char sample after gasification
Wo	Initial mass of char at the beginning of gasification (mg)
Wt	Mass of sample at time t (mg)
wt.%	Weight percent
х	Carbon conversion
XRD	X-ray Diffraction
ρв	Bulk density (kg/m <sup>3</sup> )

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Gurkaran Sarohia, "yuh a dih boss".

# **CO-AUTHORSHIP STATEMENT**

I conducted all experimental work, data analysis, and prepared all the drafts of manuscripts in this thesis with the exception of the italicized comments. All drafts of manuscripts and publications have been reviewed and strengthened through input given by my supervisors Dr. Steve Helle and Dr. Ronald Thring. Other persons that have been instrumental in the successful completion and editing of specific chapters are listed below:

- Chapter 1 H. Ghuman (contributed parts of pages 4-8)
- Chapter 2 Dr. P. Rutherford
- Chapter 3 Dr. P. Rutherford, G. Sarohia
- Chapter 4 Dr. P. Rutherford, Dr. J. Grace, M. Masnadi
- Chapter 5 Dr. P. Rutherford, Dr. J. Grace, M. Masnadi (M. Masnadi assisted in carrying out aspects of the TGA experiments)

### **THESIS OUTLINE**

The thesis is presented in a manuscript-based format, presenting various applications for different types of ash, identifying specific fractions of technological, environmental and economic viability. Each chapter addresses specific concerns and identifies suitable process and applications. Chapter 1 entitled "Ash Management Review - Applications of Biomass Bottom Ash", serves as an introduction as well as a comprehensive review paper, addressing issues related to the management of ash, specifically bottom ash. The second chapter, "Characterization of Biomass Bottom Ash Obtained from an Industrial Scale Fixed-bed Boiler by Fractionation", discusses how the presence of unburned carbon in some bottom ash suggests potential beneficial uses, for example as an energy source. A comparative study characterizes two bottom ash samples obtained from an industrial scale fixed-bed boiler. The physical and chemical properties of each bottom ash, as well as their respective particle fractions obtained by sieving, are analyzed and discussed. "Characterization of the Inorganic Elements in Woody Biomass Bottom Ash from a Fixed-bed Combustion System, a Downdraft Gasifier and a Wood Pellet Burner", Chapter 3, directs the reader's attention to the environmental significance of ash, particularly as a soil additive. Chapter 3 is focused on identifying suitable applications of bottom ash based predominantly on its chemical properties. Having identified and characterized ash with high unburned carbon content in Chapter 2, Chapter 4 investigates the feasibility of gasifying high carbon wood ash particles smaller than 3 mm. This chapter is entitled "Investigation of Air and Air-steam Gasification of High Carbon Wood Ash in a Fluidized Bed Reactor". Chapter 5 investigates the use of two types of combustion ash, gasifier ash and a pellet burner ash, for their catalytic effects on woody biomass CO2 gasification by varying the percent catalyst loading. This chapter "Catalytic Effect of Calcined Wood Ash During CO2 Gasification of Biomass Char" will report the pertinent findings. The thesis concludes with Chapter 6, providing a comprehensive overview of the technological, environmental and economic importance of biomass ash. Chapter 6 contextualizes the findings of this research within the geographical framework of British Columbia, Canada, but can be applied in other geographical regions. The theoretical framework serves to conceptualize the research by outlining the objectives of each chapter.

# **Theoretical Framework**

# Investigation of Air and Air-Steam Gasification of High Carbon Wood Ash in a Fluidized Bed Reactor

To determine:

- The behavior of high carbon ash during gasification
- The potential of producing a low to medium calorific value producer gas
- Optimal operating conditions during gasification

## Characterization of Biomass Bottom Ash from an Industrial Scale Fixed-bed Boiler by Fractionation.

To determine:

- The physical and chemical properties of wood ash and fractions of specific particle sizes
- The thermal behavior using thermogravimetric analysis (TGA)
- The fractions of energy importance

# Current State

- Increasing demand for bioenergy.
- Increasing ash production and ash volumes.

## Catalytic Effect of Calcined Gasifier and Pellet Burner Ash during CO<sub>2</sub> Gasification of Biomass Char

To determine:

- The effectiveness of using wood ash as a catalyst
- The rate of carbon conversions
- Gasification reactivities

# Ash Management

# Challenge

• How to manage and utilize ash sustainably and economically?

## Primary Concerns

• Storage

- Disposal
- Usage
- Unburned carbon

Characterization of Inorganic Elements in Biomass Bottom Ash from a Fixed-Bed Combustion System, Downdraft Gasifier and a Wood Pellet Burner by Fractionation.

To determine:

- The inorganic elemental distribution of specific particle size fractions
- The pH and anion distribution
- Correlations between carbon content and inorganic distribution

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## Preface

Chapter 1 of this thesis is a version of the published article:

James, A. K.; Thring, R.W.; Helle, S.; Ghuman, H. S. Ash Management Review—Applications of Biomass Bottom Ash. *Energies* 2012, 5, 3856-3873.

# CHAPTER 1: Ash Management Review — Applications of Biomass Bottom Ash

### **1.1 Introduction**

In industrialized countries, it is expected that the future generation of electricity will be from the direct combustion of residues and wastes obtained from biomass (1). Biomass boilers are one medium for efficiently combusting the biomass and obtaining its energy. According to Demirbas *et al.* (1), increased efficiencies can be attributed to large scale combustion processes, thus improving heat recovery. Many combustion technologies are available for biomass combustion such as fixed bed, fluidized bed and pulverized bed combustion (2). According to Saidur *et al.* (2), fluidized bed combustion is the best technology to burn a fuel with low quality, high ash content and low calorific value. In addition, the authors noted that the other firing systems present limitations and are techno-economically unviable to meet the challenges of biomass fuel properties. Sandberg *et al.* (3) also noted that fluidized bed systems are the most suitable for converting biomass into energy, because of their ability to handle different fuels, flexibility, low operating temperature and low emissions.

Because of the ash content that is present in biomass (see Table 1.1), boiler combustion processes are known to produce large amounts of ash. Also, as the demand for bioenergy production increases the ash and residue volumes will increase. Major challenges will arise relating to the efficient management of these products. The primary concerns are ash storage, ash disposal, ash usage and the presence of unburned carbon. The continual increase in ash volume will result in decreased ash storage facilities (in cases of limited room for landfill expansion), as well as increased handling, transporting and spreading costs.

Proximate Analysis (wt %)	Rice husk	Rice husk pellet	Larch dust	Willow	Miscanthus	Pine
Moisture	3.6	9.2	2.6	7.2	6.1	5.5
Volatile matter	60	65.1	76.7	78.1	67.9	81.2
Ash	16.3	9.3	0.8	1.0	12.9	1.2
Fixed carbon	20.1	16.4	19.9	13.7	13.1	12.1

**Table 1.1.** Properties of woody biomass samples (4)(5).

Due to the variety of biomass fuel sources with differing ash properties, finding one application that will be suitable for all of the ash is unlikely. Identifying the characteristics of the ash will provide valuable information as to the likely methods for processing. Gomez-Barea *et al.* (6) proposed three main utilization categories for fly ash derived from biomass: (1) Use in agriculture; (2) Use as fuel and (3) Use in construction.

The potential utilization of ash is influenced by contaminants such as heavy metals and the extent to which the ash is sintered (7). Clean biomass contains minerals and important trace elements and therefore can be recycled to forest grounds, however, these trace metals must be clearly quantified and their impacts studied if they are to be applied to soils. Effective environmental monitoring and protection must be carried out to ensure that ash disposal does not become an environmental hazard.

In addition, high levels of unburned carbon can be found in the ash produced from boilers. According to Demirbas (8), the fly ash from biomass-fired grate boilers contain high levels of unburnt carbon and is not suitable for recycling to the forest. Grate boilers often produce a fly ash with 50% or more of unburnt carbon. The presence of this carbon indicates inefficient fuel use and can reduce ash stabilization (chemical hardening) and significantly increases ash volume. If the carbon contents are to be reduced it would become necessary to reburn the ash. The utilization of ash has also seen its application in the construction industry. According to Gomez-Barea *et al.* (6), fly ash can be used as a cement replacement in concrete, for soil stabilization, as a road base, structural filler in asphalt and asphalt base products, light weight bricks and synthetic aggregate.

While much research has been conducted on fly ash utilization, a lot still remains to know about the effective management and utilization of bottom ash.

#### **1.2 Ash from Biomass Combustion**

The ash content of wood chips normally depends on the bark content of the mixture since the minerals are usually more concentrated in that region (9). Ash is the inorganic uncombustible part of fuel left after complete combustion, and contains the bulk of the mineral fraction of the original biomass (7). Ash is an integral part of the plant structure and consists of a wide range of elements (10). In wood, ash represents less than 2 percent, while in agricultural crop materials it can be 5 - 10 % and up to 30 - 40 % in rice husks and milfoil.

Biomass-based products produce solid residue ash, a result of thermochemical degradation. These thermochemical processes include combustion, pyrolysis, and incineration of woody biomass. Bottom ash and fly ash are usually the two types of ash produced and may vary in properties due to the different types of biomass available, operating conditions and the type of system used. High ash contents significantly reduce the energy output derived from a specific biomass source.

#### 1.2.1 Estimate of Potential Increase in Ash Production

An estimate of the potential ash production may be derived by carefully studying the amounts of woody biomass that are used or may be used for processes that produce ash. The analysis of Table 1.1 presents an example of the percentage composition of ash based on different types of woody biomass. Subsequently this composition along with the quantity of biomass produced can be used to estimate the total amount of ash produced.

Wood residue forms a significant input for energy related uses such as in gasification, pyrolysis, combustion and other systems based on harnessing the energy potential of woody biomass. Wood residues are defined by the FAO (11) as wood by-products which have not been reduced to small pieces. They consist principally of industrial residues, e.g., sawmill rejects, slabs, edgings and trimmings, veneer log cores, veneer rejects, sawdust, bark (excluding briquettes), residues from carpentry and joinery production, etc. Residues produced at industrial processing sites, like bark and sawdust in sawmills, are the largest commercially used biomass source (12).

According to the Food and Agriculture Organization (FAO) (11), approximately  $98.2 \times 10^7$  m<sup>3</sup> of wood residue was generated globally, as a yearly average from 1992 to 2010. For the sample period the top five wood residue generating countries produced  $15.3 \times 10^7$  m<sup>3</sup> from China,  $14 \times 10^7$  m<sup>3</sup> from Brazil,  $13 \times 10^7$  m<sup>3</sup> from USA,  $7.9 \times 10^7$  m<sup>3</sup> from the Russian Federation and  $7.7 \times 10^7$  m<sup>3</sup> from France. These residues have the potential for supplementing current wood fuel consumption. Comparing these statistics to coniferous wood-fuel used, USA had  $9.5 \times 10^7$  m<sup>3</sup> of wood-fuel,  $91 \times 10^7$  m<sup>3</sup> for China,  $13 \times 10^7$  m<sup>3</sup> for Brazil,  $19 \times 10^7$  m<sup>3</sup> for the Russian Federation and  $2.7 \times 10^7$  m<sup>3</sup> for France in 2010. This data can help us draw some conclusions about ash production from the current wood-fuel use, and the potential increase in ash production from the combustion of wood residues. Ash produced from wood residue or wood chips has distinct

chemical and physical properties that vary in part due to factors such as origin of biomass, type of energy harnessing process, chemical reactions occurring during high heat conditions in the furnace and storage and treatment of fuel (13). Literature reported values vary between 1% (wt %) ash content for clean wood without bark to 5 - 15 % ash content for contaminated bark (14). An estimate of the ash generated from potentially using wood residue may be obtained. Table 1.2 reports bulk densities for different kinds of residual woody biomass. We may use these values and arrive at an approximate value of bulk density for wood residue, equivalent to 0.16 and 0.21 ton/m<sup>3</sup> for wood chips and wood fuel.

Wood	Bulk density (ton/m <sup>3</sup> ) Dry ash free tonnes
Hardwood chips	0.23
Softwood chips	0.18-0.19
Sawdust	0.12
Planer Shavings	0.10

Table 1.2. Bulk densities of different types of wood (15).

Assuming that the entire wood residue produced in the world were to be incinerated, gasified or combusted to harness energy we can use the bulk density of residue and weight percentage of ash to establish an approximation of the ash produced. Table 1.3 shows the ranges of ash produced from fuel wood and the potential addition by increasing the use of residual woody biomass in combustion, incineration or pyrolysis processes.

**Table 1.3.** Estimate of potential ranges of net ash production based on complete wood residue utilization in global leaders of wood residue generation, and complete wood fuel utilization in global leaders of wood fuel production. The lower and upper limits use 5 and 10 % (wt %) ash respectively.

Country	Ash from wood residue combustion (10 <sup>5</sup> tons)	Ash from wood fuel combustion (10 <sup>5</sup> tons)
China	1.2–2.4	9.5–19.1
Brazil	1.1–2.2	1.4-2.7
USA	1.04-2.1	0.99–2.0
Russia	0.63-1.3	1.99-4.0
France	0.61–1.2	0.28-0.57

The ash is fixed at 5 - 10 % (wt %) for wood used in a commercial and large scale energy systems. The lower limit of 5 % and the upper limit of 10 % will give a good range for the quantities of ash produced. This range is relatively higher for clean wood without bark (<1 % ash), but seems to fit the values for the ash content of dominant types wood present in the wood available for use. These include: bark (3 – 4 % ash), contaminated bark (5 – 15 %), contaminated reject wood (0.5 – 19 %) and clean reject wood (0.5 – 3 %) (14). We must also consider studies that suggest the actual amount of ash generated is higher due to inefficiencies in the boilers and furnaces. This range will be used to calculate the upper and lower approximates of ash produced from fuel-wood and wood residue. These values for the upper and lower limits of ash produced are reported in the Table 1.3.

According to Obenberger *et al.* (16), while the 2005 production of ash in European Union amounted to  $5.6 \times 10^7$  tons, the future trend in biomass for energy is expected to double by 2020, and might lead to production of  $15.5 \times 10^7$  tons of ash in the EU-27. Our estimates of current ash production fall into proportion, as Europe produced  $140 \times 10^7$  m<sup>3</sup> of fuel wood for 2005. This translates to about a range of  $1.6 \times 10^7$  to  $3 \times 10^7$  tonnes of ash produced in 2005 from domestically produced fuel wood. Fuel wood imports and industrial utilization of wood residues are not considered in this estimate. They also contribute positively to the net ash production of a region. A detailed calculation of the total ash produced is difficult to determine. This is due to the lack of understanding and information about all biomass sources and their net contribution to ash production processes.

Literature reported values for current biomass use as a fuel compared to its potential use, vary from 16 % in North America, 12 % in Latin America, 22 % in Europe and 108 % in Asia (12)(17)(18). This averages to 38 % for the world (12)(17)(18). This implies that countries such as USA, Canada, and other European nations have immense potential for developing bio-energy based technologies. These figures point out clearly to a future increase in exploitation of this potential, and a subsequent increase in ash generation. Limited understanding of ash behaviour and its environmental impacts acts as a hindrance for the complete utilization of combusted wood residue. The probable alternative fate for most wood-processing residues currently used for power production is landfill disposal (19).

#### 1.3 Elements in Ash of Environmental Significance

The major inherent ash forming elements in biomass include Ca, Si, Al, Ti, Fe, Mg, Na, K, S and P (7)(9). The composition of ash affects its behaviour under high temperatures of combustion and gasification reactors (10). These problems may include clogged ash-removal caused by slagging ash, sintering, deposition, erosion, corrosion and pollutant emissions that are mainly created by the presence of alkali metals, alkaline earth metals, silicon, chlorine and sulphur in the ashes (10)(20)(21).

#### 1.3.1 Presence of Metals in Ash

The presence of volatile heavy metals contained in ash residue may also have negative environmental impacts if irrationally managed and disposed, due to the possible leaching into underground and surface waters (20). According to Khan *et al.* (7), the potential utilization of ash is influenced by contaminants such as heavy metals which are often present depending on the biomass source. According Demirbas (8), the composition of ash is dependent on the plant species, growth conditions and ash fraction. For example, Vamvuka (20) suggested that the high concentration of the Ni and Cr present in the olive kernel ash under study was most likely due to the soil parent material. According to the author the soil type is laden with Ni/Cr which is transferred to the plant through rootlets. Wood ash generally has a higher concentration of As, Cd, Pb and Hg than agricultural residue, such as the ash from wheat, straw and fruit shells.

While the Khan *et al.* (7) review pointed out that the heavy metals are typically concentrated in fly ash, these metals, though lower in concentration, are also present in bottom ash. With the large quantities of bottom ash being generated annually, their metal concentrations and the cumulative metal concentrations from deposition and landfilling must be investigated. Vamvuka (20) investigated the thermal behaviour of olive kernel ash that was produced in a fixed and fluidized bed combustor. The environmental impacts of the ash upon disposal to local soils were also analyzed. A 150 cm long with 7 cm inner diameter cylindrical stainless steel lab scale reactor tube was used. For the fluidized bed, olive kernel with 1 % moisture was fed at a rate of 480 kg/h to a bed temperature of 900 °C. A batch of 0.5 kg fuel was loaded for the fixed bed and air was supplied at 6 m<sup>3</sup>/h with an excess of 20 % to ensure complete combustion. Bottom and fly ash samples were collected and analyzed for each reactor. According to Vamvuka (20), the elements Cr, Cu, Ni and Mn were enriched in olive kernel ash derived from fixed bed experiments, while the toxic elements Se and Pb were below 9 ppm. Cr had the highest concentrations of 2000 ppm which the researcher attributed to the soil parent type of the fuel. The results also showed that trace elements were very low in cyclone ash and may have escaped in the flue gas due to the short time for re-condensation during fluidised bed combustions. The leachates analysis produced negligible quantities (ppb) of all constituents except Cr, Se and Pb levels, <3 ppb were found to be the lowest and Mn the highest at 5872 ppb.

#### 1.3.2 Applications of Ash for Soil Amendment and Agriculture

However, some mineral nutrients of the ashes may have a vitalizing effect on its application to agricultural or forests soils. Olanders *et al.* (9) in their work reported that the ash from biomass fuel contains only trace amounts of heavy metals, which makes them fairly easy to dispose of and they can be good fertilizers. A two part research was carried out by Gomez-Barea *et al.* (6) in which they looked at the optimization of the operating conditions to achieve better ash quality and then assessing the ash quality in order to explore its potential utilisation. Two types of biomass, orujillo and meat and bone meal (MBM) were gasified in a bubbling fluidized bed gasifier with bed materials ofite and limestone. The operating temperatures ranged from 700 to 850 °C with a fuel feed rate of 6–35 kg/h. The potential utilisation of ash as a soil conditioner, soil rehabilitation and plant growing medium, soil nutrient and fertilizer and as a neutralizing agent and liming agent was investigated.

High concentrations of P and Ca were found in MBM ashes while high K levels were found in orujillo ashes but low solubility levels were obtained for these elements for both fuel types (Gomez). P in MBM ashes measured a solubility level of less than 1 % in DIN leaching test. The research concluded that due to this low solubility of P and Ca, the use of these ashes in common soils were doubtful for use as a fertilizer. In relation to the heavy metals, both orujillo and MBM ash had a high Cr concentration but was thought to be as a result of the decomposition of the steel in the reactor from abrasion. Of concern in this research according to Gomez-Barea et al. (6), was the Cl content of the orujillo ash, which they highlighted as probably the main handicap of this ash. A Cl content of 0.5 - 1.5 wt % was obtained for the fuel. Both MBM and orujillo had a high PAH, around 100 mg/kg. While sustainable methods are constantly being sought for the utilisation of fly ashes Gomez-Barea et al. (6) concluded that fly ash from these two waste were not suitable for some applications because of the high carbon content, chlorine content, alkali content and in some cases heavy metal content. Physical or thermal pre-treatment of the ashes were proposed so as to make the ash more usable. A few suggestions included: washing so as to remove alkali or chlorine content, applying low temperature combustion for carbon removal and using high temperature treatments for more persistent contaminants. The fly ash from waste material gasification did not meet the requirements for fertilisers. These requirements were in accordance with the utilization standards for, Metal limit values for ash utilization in cultivation in Finland and recommended minimum and maximum values for components in ash produced in Sweden.

In similar research conducted by Nurmesniemi *et al.* (22), the physical and chemical properties of bottom ash and fly ash obtained from a 115 MW bubbling fluidized bed combustion plant were investigated. One problem cited as influencing the research was the rapid increase in large amounts of fly and bottom ash generation due to the increase use of wood-based biomass for energy production. These energy sources are considered to be carbon neutral. Other problems included the increased costs of landfill disposal in the form of waste tax or deposit fee as well as the difficulties in acquiring new landfill sites and stricter EU landfill directives. Hence, the need to find recycling options for ash. Ash from the bubbling fluidized bed boiler operated at 800 °C

was withdrawn and stored at 4 °C in a refrigerator. A strong alkaline pH value of 11.9 was recorded for the bottom ash. This was attributed to some of the dissolved metals occurring as basic metal salts, oxides and carbonates.

In relation to the liming effect of the ash, Nurmesniemi *et al.* (22) investigated the acid neutralizing value (NV) by looking at the cations of Ca, Mg and K. A NV 8.7 % (Ca equivalents, d.w.) was obtained for bottom ash which they suggested that a ca. of 4.4 tonnes of this residue would correspondingly be required to replace 1 tonne of commercially ground limestone. The research concluded that fly ash would act as a better soil liming agent to neutralize soil acidity than bottom ash. While the research agrees that fly ash is a better forest fertilizer, plant nutrient agent and soil improvement agent than bottom ash, the large quantities of bottom ash generated makes it of environmental importance. For the bottom ash, elements such as Mg, Ca and K concentrations (d.w.) were 0.6, 6.0 and 2.6 % respectively while fly ash concentrations were 2.6%, 20.5% and 3.9% respectively. The researchers noted that the Cl levels were also below the Finnish maximum limit value (2.0 %; d.w.) recording <0.1 % for bottom ash and 0.5 % for fly ash.

A total P of 0.3 % (d.w.) with a negligible water soluble P content was recorded for bottom ash. The research noted that water soluble P is the amount of P that is readily available to plants. The poor water solubility of P was highlighted as a draw back in the application of wood ash to soils since only a small portion P is extractable and available for plants when used in forest fertilizers. On the other hand, the paper referenced Moilanen *et al.* (23), who suggested that waterinsoluble forms of P in forest fertilizers minimise the risk of P leaching into water bodies.

The research highlighted two heavy metals, Cr and Pb having concentrations that were 1.8 and 110 times higher in fly ash than bottom ash, respectively. The bottom ash concentrations for Cr and Pb were 39 mg/kg and <3.0 mg/kg, respectively. Nurmesniemi *et al.* (22) concluded that the

concentrations of all elements in the fly and bottom ash were lower than the Finnish limit values and therefore does not restrict the use of wood ash as a forest fertilizer.

Dahl et al. (24) conducted a series of similar studies on the heavy metal concentrations in bottom ash and fly ash fractions from a large-sized (246 MW) fluidized bed boiler with respect to their Finnish forest fertilizer limit in values. The study assessed whether the physical and chemical properties, nutrients and heavy metals concentrations in the various ash fractions supported their use as a forest fertilizer. Fifty percent of the fuel was from forest residue while the other 50 % was from commercial peat fuel. The results were in agreement with many of the other studies, obtaining high nutrient concentrations for the ashes. This would suggest the possibilities of utilizing bottom ash and fly ashes as a forest fertilizer. Dahl et al. (24) indicated that these ashes should be put to better use than to be deposited at a landfill. In addition, the authors suggested that ash utilization should be seen as an example of sustainable utilization of industrial residue since minerals would be returned to the forest environment and would reduce the need for fertilizers. In all cases, the fly ash concentrations were higher for all the heavy metals and alkali metals under study than bottom ash. However, a point of interest in the results was that the Hg content in the bottom ash was too low for detection. With Hg being one of the elements of extreme environmental scrutiny a low concentration is undoubtedly preferred in biomass ash.

Another interesting finding of this research related to the element As. A slightly elevated As concentration of 40 mg/kg (d.w.) was seen in one of the fly ashes under study (24). According to the paper, the Finnish limit for this metal was 30 mg/kg (d.w.), which makes the fly ash containing 40 mg/kg of As unsuitable for use as a forest fertilizer. On the other hand, if both fly ashes were combined the residue could be suitable for use as a fertilizer since all other fly ash at different particle sizes were all below 10 mg/kg (d.w.).

Most of these researchers mentioned above seem to consider ash as an effective fertilizer and soil amendment. While fly ash in some cases seems to contain high amounts of heavy metals, alkali metals and PAH which may exceed the allowable environmental limits, bottom ash appears to fall within the allowable limit. However, larger quantities of this bottom ash residue would be required to provide the adequate soil nutrients.

Considering the facts that ash fractions have varied concentration of metals, the application of a mixture of bottom and fly ash to soils could also be explored. The utilization of bottom ash has the advantage of lower heavy metal concentrations but the disadvantage of higher nutrient losses. Mixtures of fly ash and bottom ash may be useful to achieve optimum nutrient delivery within limits for heavy metal concentrations (16). Also, if there is significant ash recycling to soil, bottom ash and some fly ash could be combined while the additional fly ash would be directed to landfill or other uses in order to prevent build-up of heavy metals.

It is also important to consider the origin of the biomass source and the characteristics of the ash that will be produced. For example, Rejinders *et al.* (25) referenced the Minnesota Office of Environmental Services (26) who reported that the wet disposal of coal ash has been related to abnormalities in animals. The elemental concentrations may vary with ashes from biomass or coal or other combustion materials. In light of this, the ash from each fuel source must be carefully analyzed before land applications are considered. Perhaps, constant testing and monitoring of landfills could also provide valuable information as to the cumulative long-term impacts that ash storage could have. This could provide valuable information as to likely changes over time if applied to soils.

Questions relating to the authenticity of the leachate test have also arisen. Reijnders *et al.* argue in a review (25) that it is possible that an accurate analysis of the leaching test conducted in

the laboratory may not accurately reflect the leaching behaviour in the field. The review noted that reactions such as weathering, the dissolution of amorphous phases, the formation of minerals, the effect of flow conditions, ionic strength of pore solutions and kinetically determined processes can never be truly determined from the laboratory phase.

#### 1.3 Technologies in Place for Processing Unburned Carbon in Ash as a Fuel

As previously mentioned, high contents of unburned carbon in bottom ash or fly ash indicates inefficient fuel use (8). This unburned carbon concentration often varies for combustion systems and has led a number of researchers to investigate the varying reasons for this change as well as to determine the amounts of carbon that may be present in combustion ashes. According to Bahadori *et al.* (27), when coal is combusted a potential significant loss is that of unburned carbon. According to Gomez-Barea *et al.* (6), the carbon present in fly ash is generally present in large amounts, typically 10 - 60 % of the ash mass while Duan *et al.* (28) suggested a range of 10 - 30%. Their work referenced Turner *et al.* (29) supporting the idea that all coal-fired steam generators and coal-fired vessels inherently suffer an efficiency debit attributable to unburned carbon. Duan *et al.* (28) highlighted two possible reasons for the high carbon content in fly ash of Circulated Fluidized Bed (CFB) boilers as the short residence time, resulting in incomplete burnout of char and the high ash content which covers the char and prevents the free movement of gases to the core of the char. There is a need to find efficient technologies that could be used to reduce unburned carbon content in both fly ash and bottom ash. Additionally, optimizing the use of existing technologies could also improve combustion efficiency.

Demirbas (8) proposed that the fly ash could be reburned to remove additional carbon and that CFB boilers are suitable for doing so since they are fuel-flexible and produce well burnout

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ashes. The review noted that unburnt carbon has replaced 1–2 %of the fuel input to a CFB boiler, reducing fuel costs and NOx emissions by about 20 - 30 % depending on the amount of ash. However, Gomez-Barea *et al.* (6) looked at the idea of recycling fly ash in gasifiers but concluded that this processing method would be technically impossible. While the researchers considered fly ash from biomass to be a rational option as a fuel source in boilers and power plants, the heavy metals, as well as Cl and K would severely limit the mixing of these ashes with specific biomass before feeding the boiler. The paper cited corrosion-derived problems caused by K<sub>2</sub>O and HCl as major reasons for rejecting the technique. However, useful suggestions were offered as to how to effectively reduce the carbon content in the cyclone fly ash by their investigation of the impact of bed temperature on carbon content. When orujillo was gasified at different temperatures, the carbon content in the fly ash decreased when temperature was increased (6). At 700 °C the carbon content was 20.18 % while at 820 °C the carbon content reduced to 9.09 %.

Duan *et al.* (28) investigated a fly ash recirculation technique called fly ash recirculation by bottom-feeding (FARBF). The fly ash was recirculated from the bottom of the dense bed to the air plate. A FARBF system was installed on a 75 t/h boiler burning mixture of 60 % coal sludge and 40 % Chinese medium coal and was operated between the 980–1050 °C for the dense bed and 850 °C for the secondary zone. The experiments were accomplished by varying the recirculation rate, making it 0, 25, 50, 75 and 100 % of the total fuel ash fed into the furnace. Each test was carried out for 4 h until a stable condition was achieved. The boiler dense bed temperature decreased from 960 to 880 °C with a 70 % recirculation rate. This change was considered to be as a result of the fly ash absorbing heat when recirculated from the bottom of the boiler. The unburnt carbon in fly ash saw a decrease from 14.1 to 7.5% as the recirculation rate increased from 0 to 8 t/h and from 14.1 to 8.8 with a 70 % recirculation. Duan *et al.* (28) explained that these results were obtained

due to the intensive material turbulence inside the dense bed, crashing into the shell of the ash and exposing the unburnt carbon to the high temperature environment. Longer residence times were also said to influence burning out of the coal particles. The researchers concluded that FARBF can help to reduce the unburnt carbon in fly ash thus improving combustion efficiency.

Batra *et al.* (30) looked at characterizing the unburned carbon in bagasse fly ash obtained from two different sugar mill boilers in India and found more than 25 % present. They noted that the unburned carbon posed disposal problems, presented obstacles when used in cement compositions and would therefore be better if used for other applications. The research showed that, industrially, carbon separation can be carried out using industrial scale sieve shakers for removal of the coarse carbon rich fraction. Three fractions were investigated, "as-received" fraction, sieve fraction greater than 425  $\mu$ m and fractions between 150 and 425  $\mu$ m. Maximum carbon removal was obtained when a sieve fraction greater than 425  $\mu$ m was used or when a separation by fraction floatation in water was used. This conclusion was carried out by thermal gravimetric analysis for the different fractions. The study concluded that over 25 wt % of unburned carbon is present in bagasse fly ash. They proposed that the high carbon content present in boiler fly ash could be used as household fuel or gasifier feed after briquetting or pelletizing.

Carbon content in wood-ash has a direct impact on process efficiency and ash recycling in that, as more carbon is converted the higher the efficiency and the lower the volume of ash generated. While there is obvious potential for bottom ash to be recycled as fuel not much research has gone into the area. The researches mention mostly the idea of recycling ashes into a CFB. However, the need for more critical analysis of the unburned carbon present in bottom ash and effective ways of capturing this energy as a fuel need to be investigated. Most papers seem to suggest that there is only energy potential in ash if pelletized or briquetted. As mentioned previously, the carbon content in ash varies depending on the processing conditions, types of combustion equipment and fuel source. Subsequently, process efficiencies will vary, affecting the degree of unburnt carbon that may be present in ash. Therefore, a backup system or technology should be in place to deal with variations of carbon that may be present in the waste or combustion residue. This will not only improve efficiency but will reduce the volumes of ash produced as well as the additional costs incurred for disposal.

#### 1.4 Reviews and Suggestions of Proposed Ash Processing Methods

Most of the work on ash and the presence of unburned carbon have been on fly ash especially from coal. However, more research needs to be undertaken relating to bottom ash as the volumes significantly increase industrially. Effective recycling and processing measures must be identified to ensure maximum energy use so as to eliminate some of the ash related storage and disposal problems.

The presence of unburned carbon in bottom ash suggests its potential for uses other than as a waste product. In this dissertation, we present the separation of unburned carbon in wood biomass bottom ash from a fixed-bed combustion system by sieve fractionation, followed by the application of the gasification technology to particle sizes of energy importance.

Demirbas *et al.* (1) in a review pointed out that biomass gasification is the latest generation of biomass energy conversion processes and is being used to improve the efficiency and to reduce investments costs of bioelectricity generation. According to Quaak (10), gasification produces gaseous fuel that is easily handled, produces very little excess air when combusted and contains low levels of contaminants. For this reason, a gasifier may be used to harness any additional energy that the conventional boiler could not obtain by using the boilers waste as a fuel for the gasifier. Biomass gasification is one of the technologies of energetic use of biomass as heat and electricity may be produced from using such process (31)(32). It is a thermochemical process of gaseous fuel production by partial oxidation of a solid fuel (32). In this process, the chemical energy of the solid fuel is converted into the chemical and thermal energy of the product gas. The result of gasification is the producer gas, containing carbon monoxide, hydrogen, methane and some other inert gases (31).

An updraft fixed gasifier may be used to combust the unburned carbon. Fixed bed gasifiers are relatively simple, high charcoal burnout and an internal heat exchange that leads to low gasexit temperatures and high energy efficiencies (10)(32). The system also allows for variation in fuel particle sizes as it is able to process relatively small fuel particles (10). The presence of tars in the product gas is usually a concern in this system. However, it is anticipated that the boiler ash will have very little negative impacts on the gasifier as it relates to the presence of tars. This is because most of the tar would have been consumed from the boiler combustion stage. Of particular concern is the potential slagging that may result due to the high ash content of the feedstock. According to Quaak *et al.* (10) the updraft gasifier is able to accommodate fuels with a maximum moisture content of 60 %, particle size 5-100 mm, maximum ash content of 25 % and should be able to produce 5 - 6 kJ/Nm<sup>3</sup>.

The energy recovery may be measured based on the composition of the gases produced. Hence, the ash-carbon content will be reduced using gasification with energy recovery in the form of heat and syngas production. The application of gasification technology in the reduction of ashcarbon content and the ability to recover any useful energy in the combustion residue presents promising prospects.
In order to separate and characterize ash and unburned carbon based on its particle size, the "as-received" ash must be separated in its fractions by sieving. Sieve sizes ranging from 0 to 2000  $\mu$ m may be used but the upper limit is based on the size of combustion residue obtained. Each separated fraction must be characterized in terms of its physical and chemical properties in order to identify fractions in bottom ash with high organic/carbon content and those with high mineral content as well their impact on the overall volume of ash stored or disposed of. Based on their characteristics, suitable applications for each fraction can be determined.

Limited information and results were found relating to the sieving of ash for unburned carbon recovery. Alternate suggestions for effective utilization of inorganic content in ash included the pre-treatment of ash whether by washing or sieving (6). It is hoped that some metals could be washed and Cl in particular could be removed from these ash fractions using these techniques.

According to Dahl *et al.* (24) sieving methods have been applied to process ash containing heavy metals, separating them into various fractions. This separation produces ash fractions with low heavy metal concentrations, making them applicable in road construction and cement blends. Sieves were used to separate ash into particle sizes 2.0 - 0.5, 0.5 - 0.125 and <0.125 mm. The elemental concentrations of the heavy metals were noted based on the particle fraction. The bottom ash remained within the limits of elemental concentrations for all the particle sizes, however, one fly ash of particle size lower than 0.125 mm exceeded the limit value of As, while Pb exceeded its environmental limit within particle size 0.5-2.0 mm. However, it should be note that any pretreatment will incur additional processing costs.

It is anticipated that fractions containing high levels of unburnt carbon could be a useful fuel source in the gasification process. As previously mentioned, some researchers have proposed pelletizing or briquetting bottom ash for fuel use. Research results for pelletization of bottom ash

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for use as a fuel could not be found, even after an extensive literature search. However, limited papers and studies exist as it relates the pelletization of bottom ash from biomass for other uses. In must be noted that this process comes with inherent challenges. According to Lövgren *et al.* (13), a high content of unburnt organic matter interferes with the agglomeration of ash particles. To deal with this situation, pelletizing (roll pelletizing) has proven to be an efficient method. This method helps to prepare ash for recycling of basic cations, and acid neutralizing lime components back to the forest (33)(34).

Several studies have described hardening and carbonation (treatment with carbon dioxide) of ash as an effective method to handle ash. Accelerated carbonation positively affects the hardening of an ash product, which may then be easily transported and used as a fertilizer. Also, well hardened products show slow leaching patterns, which are considered good for applications in fertilizing land (35)(36)(37). However, it is difficult to harden ash with high carbon content.

In a TNO Report (14), it pointed out that if ash is to be re-used it is important to know its particle size and particle density. These will better aid in understanding the potential of ash for environmental applications and its contribution to reducing ash volumes. Obtaining the bulk densities for various particle sizes could give valuable information on dumping and storage cost. According to the TNO-report, the dumping costs in The Netherlands can be relatively high. A point of interest is that ashes produced from different wood sources may vary in bulk densities. The report suggested that the difference in bulk densities were relative to the fuel source and the combustion process and technology employed (See Table 1.4).

Type of fuel ash fraction		Particle size (µm)	Bulk density (kg/m³)	
Sawdust	Grate fire ash 10–30.000		662	
	Cyclone fly ash	2-100	283	
Shredded Wood	Grate fire ash	15-15.000	960	
	Cyclone fly ash	2-160	430	

**Table 1.4.** Showing particle size and bulk density in the combustion of sawdust and shredded wood (14).

## **1.5 Technological Implications When Processing Ash**

While there are obvious benefits to some soil properties, other ash related problems remain as some of the main obstacles to the economical and viable applications of biomass gasification (21). According to Vamvuka (20), the successful design of a combustion system using agroresidue as feedstock will partly depend on the ability to control the technical and environmental problems associated with the inorganic constituents.

During combustion some of the inorganic species formed are a result of the interactions with the organic portion of the biomass. According to Olanders *et al.* (9), the organic structures are decomposed and the ash formers are released. The alkaline earth metals leave the combustion zone as solid particles while the alkaline metals are transported in vapour form as chlorides, hydroxides and oxides. These species can react with SO<sub>2</sub> to form sulphate particles which results in the formation of hard deposits on surfaces leading to corrosion problems (9)(38). Olanders' *et al.* (9) research showed that the first steps in ash-forming process involves calcium, potassium, silicon, sulphur and chlorine forming carbonates, sulphates, chlorides and small amounts of silicates. A fixed-bed furnace with temperature 1100 - 1200 °C for wood fuels and 1000 - 1100 °C for straw was used to make such conclusions.

Obernberger *et al.* (39) in an analysis of the various inorganic elements in biomass fuels, noted that Si in combination with K can lead to the formation of low melting silicates in fly-ash particles, K is relatively volatile, forming chlorides, hydroxides and sulphates which plays an important role in corrosion. Ca also forms chlorides and sulphates but is less volatile than K and generally increases the melting point of ashes which are also true for Mg. It was also observed that at higher temperatures and longer heating times, oxides and silicates become dominant. A notable trend also was that silicon and iron are more effectively bound in bottom ash under oxidizing conditions than reducing conditions while Ca was less (9).

#### 1.6.1 Softening and Melting of Ash

If ash is to be reburned, the likely conditions under which it softens and melts must be known. Olanders *et al.* (9) used TGA/DTA determination on ash collected from the same fixedbed furnace mentioned above, to understand the various temperatures at which softening and melting would occur relative to the biomass type. The research showed that straw ash softened at a much lower temperature than wood/bark. Initial softening of straw ash was at 700 °C and melting occurred at 975 – 1025 °C. On the other hand, wood bark softened at 1000 – 1200 °C and had a melting point of 1480 °C. Ohman *et al.* (40) showed initial melting at 850 – 1025 °C. According to the research, the lowest melting temperature when stored bark was used as fuel, occurred at 866  $\pm$  7 °C. All other samples had temperatures between 980 °C and 1025 °C. The research concluded that the total ash and critical inorganic elements in some raw materials could result in ash related problems such as slagging and the forming of deposits on burners. They showed that the elemental distribution in the slag samples varied significantly between samples for different fuels. According to Vamvuka (20), fixed bed ash softens at 1221 °C and fluidises at 1258 °C for olive kernel ash. On the other hand, fluid bed fly ash softens at 1293 °C and fluidises at 1360 °C for the same ash. When combustion takes place in fixed beds, these should be operated at temperatures below 1100 °C, to avoid ash melting and accompanying problems.

A number of researchers have tried to determine the likelihood of slagging and fouling occurring. While a definite number cannot be ascertained, equations have helped in such predictions. According to Ohman *et al.* (40) slagging is considered to be the melting of ash. Two important parameters are the alkali index (AI) and the base-to-acid ratio ( $R_{b/a}$ ) of wood-ash (24).

Vamvuka (20) noted that the alkali index (AI) expresses the quantity of alkali oxides in the fuel per unit of fuel energy:

$$AI = kg(K_2O + Na_2O)/GJ$$

According to Vamvuka (20), when AI values are in the range 0.17 - 0.34 kg/GJ fouling and slagging is probable, while when these values are greater than 0.34 fouling or slagging is virtually certain to occur.

The base-to-acid ratio  $(R_{b/a})$  can also be used to help determine the likely hood of fouling of the ash. This can be written as follows (24):

$$R_{b/a} = \frac{\%(Fe_2O_3 + CaO + MgO + K_2O + Na_2O)}{\%(SiO_2 + TiO_2 + Al_2O_3)}$$

The label for each compound makes reference to its weight concentration in the ash. As  $R_{b/a}$  increases, the fouling of a fuel ash increases.

A number of researchers have also investigated the addition of other compounds to minimize or prevent softening or melting of the ash. Ninomiya *et al.* (41) showed that efficient gasification of a particular coal depends, sensitively on the melting behaviours of the ash produced from that coal and that the high melting temperature ash can be controlled by adding basic oxides which cause a decrease in ash melting temperatures and slag viscosity. The work showed that CaCO<sub>3</sub> additive is an efficient fluxing element for the control of ash melting, particularly, Al<sub>2</sub>O<sub>3</sub>-rich ash melting (20). Wilen *et al.* (42) also suggested that the addition of a powdery additive, kaolin, talc and ceramic feldspar would increase the fusion temperature. While this would increase the cost of pellets by 5% and also increase the ash content thereby lowering the heating value, it would also result in cheaper maintenance and equipment cost.

## **1.7 Conclusion**

Biomass based energy systems for heat and electricity will have an important place in the overall energy setup to meet increasing consumer demands. Woody biomass in the form of wood chips, wood residue, planer shavings, sawdust etc. forms the basis for most combustion processes that uses the energy value of this waste material. All of these combustion systems produce a significant amount of ash, which varies from 5 to 15 % (by weight) of biomass processed. A careful evaluation of data for wood residue and wood chips, the two major sources of wood biomass available for energy generation, shows us that current use levels are well below potential. These facts along with the shift towards cleaner and carbon neutral fuels are expected to contribute to an exponential increase in ash production across the world. This has significant implications for waste management and handling. The limited understanding of ash behaviour, properties and its long-term environmental impacts pose a risk in the scenario of excessive ash generation. The importance of better technologies for producing energy from biomass is also significant. Improved technologies that produce less ash volumes and increase carbon reduction should be considered to assist in ash management related issues.

Ash utilization is limited by the presence of heavy metals and other inorganic compounds, which are formed as a result of the thermochemical reactions that the biomass undergoes when combusted. The variability in heavy metal concentration in ash arises from the differences in properties of feedstock, and hence no singular inorganic composition profile for ash is true. Subsequently, no one application will be suitable for all kinds of ash. Inefficiencies in boilers and furnaces also result in high percentages of unburned organic matter in ash. This carbon content may be recycled to the boiler or furnace to improve energy output and increase the process efficiency. Suggested uses for ash includes the application of ash as agricultural fertilizers, as a fuel due to the presence of high unburned carbon content and/or as an additive in construction materials.

The presence of alkali metals, alkaline earth metals, chlorine, sulphur and silicon influences the reactivity and leaching to the inorganic phases. Ash may be utilized as a neutralizing and liming agent. Research also indicates that bottom ash has significantly lower concentrations of heavy metals than fly ash, as such, a mixture of fly ash and bottom ash may be suitable for application as a soil amendment to forest soils. This should assist in maintaining the nutrient cycling instead of landfilling these important nutrients.

Unburned carbon present in ash allows for the exploration of using ash as a fuel. This unburned organic matter has been investigated as a fuel source in some studies that suggest recirculation of ash, increasing residence times and increasing material turbulence inside the boiler. The presence of carbon in ash limits its applications as it decreases its binding properties in construction material. The high carbon content also presents challenges for pelletization and briquetting as it decreases the binding properties. The need for other ash processing methods should be investigated. We propose sieve fractionation as a suitable method for the separation of unburnt carbon present in bottom ash obtained from a fixed-bed combustion system, followed by the application of the gasification technology to particle sizes of energy importance. The use of the gasification technology in the reduction of ash-carbon content and the ability to recover any useful energy in the combustion residue presents promising prospects. Sieve fractionation may also assist in identify fractions in bottom ash with high organic/carbon content and those with high mineral content as well their impact on the overall volume of ash stored or disposed of.

If ash is to be reburnt, the likely conditions under which it softens and melts must be known since this may cause severe negative impacts on the combustion equipment leading to corrosion. It is expected that the production of bottom ash will increase greatly; therefore, continued research is needed to find suitable applications and processing technologies for ash.

## References

- 1. Demirbas, F.; Balat, M.; Balat, H. Potential contribution of biomass to sustainable energy development. *Energy Convers. Manag.* 2009, *50*, 1746–1760.
- 2. Saidur, A.; Abdelaziz, E.; Demirbas, A.; Hossain, M.; Mekhilef, S. A review on biomass as a fuel for boilers. *Renew. Sustain. Energy Rev.* 2010, 15, 2262–2289.
- 3. Sandberg, J.; Karlsson, C.; Fdhila, R. A 7 year long measurement period investigating the correlation of corrosion, deposit and fuel in a biomass fired circulated fluidized bed boiler. *Appl. Energy* 2011, *88*, 99–110.
- 4. Yoon, S.; Son, Y.; Kim, Y.; Lee, J. Gasification and power generation characteristics of rice husk and rice husk pellet using a downdraft fixed-bed gasifier. *Renew. Energy* 2011, 42, 1–5.
- 5. Ryu, C.; Yang, Y.; Khor, A.; Yates, N.; Sharifi, V.; Swithenbank, J. Effect of fuel properties on biomass combustion: Part 1. Experiments-fuel type, equivalence ratio and particle size. *Fuel* 2006, *85*, 1039–1046.
- 6. Gomez-Barea, A.; Vilches, L.; Campoy, M.; Fernandez-Pereira, C. Plant optimization and ash recycling in fluidised waste gasification. *Chem. Eng. J.* 2009, *146*, 227–236.
- 7. Khan, A.; Jong, W.; Jansens, P.; Spliethoff, H. Biomass combustion in fluidized bed boilers: Potential problems and remidies. *Fuel Process. Technol.* 2009, *90*, 21–50.
- 8. Demirbas, A. Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues. *Prog. Energy Combust. Sci.* 2005, *31*, 171–192.
- 9. Olanders, B.; Steenari, B. Characterization of ashes from wood and straw. *Biomass Bioenergy* 1994, *8*, 105–115.
- 10. Quaak, P.; Knoef, H.; Stassen, H. Energy from Biomass, A Review of Combustion and Gasification Technologies; World Bank: Washington, DC, USA, 1999.
- 11. FAO STAT. Available online: <u>http://faostat3.fao.org/</u> (accessed on 15 June 2012).

- Thrän, D.; Kaltschmitt, M. Biomass for sustainable energy provision systems—State of technology, potentials and environmental aspects. In World Renewable Energy Congress VII; Sayigh, A.M., Ed.; Pergamon: Oxford, UK, 2002.
- Lövgren, L. Roll pelletizing of ash—Cost efficient handling and improved product with accelerated carbonatization. In Proceedings of Conference on Ash Utilization 2012: Ashes in a Sustainable Society, Stockholm, Sweden, 25–27 January 2012.
- Van Alkemade, I.; Loo, S.; Sulilatu, W. Exploratory Investigations into the Possibilities of Processing Ash Produced in the Combustion of Reject Wood; Netherland Organization for Applied Scientific Research (TNO): Apeldoorn, The Netherlands, 1999.
- 15. McKendry, P. Energy production from biomass (part 1): Overview of biomass. *Bioresour*. *Technol.* 2002, *83*, 37–46.
- Obernberger, I.; Supancic, K. Possiblities of ash utilization from biomass combustion plants. In Proceedings of the 17th European Biomass Conference and Exhibition, Hamburg, Germany, 29 June-3 July 2009.
- 17. Parikka, M. Global Biomass fuel resources. Biomass Bioenergy 2004, 27, 613-620.
- 18. Kaltschmitt, M.; Neubart, J. Biomass for Energy: An Option for Covering the Energy Demand and Contributing to the Reduction of GHG Emissions. In *Integrating Biomass Energy with Agriculture, Forestry and Climate Change Policies in Europe*, London, UK, December 2000.
- 19. National Renewable Energy Laboratory (U.S.); United States. Department of Energy; United States. Department of Energy. Office of Scientific and Technical Information; Morris, G. *The Value of the Benefits of U.S. Biomass Power*. The Office of Scientific and Technical Information, U.S. Department of Energy: Washington, DC, USA, 2000.
- 20. Vamvuka, D. Comparative fixed/fluidized bed experiments for the thermal behavious and environmental impact of oliive kernel ash. *Renew. Energy* 2009, *34*, 158–164.
- Wang, L.; Weller, C.; Jones, D.; Hanna, M. Contemporary issues in thermal gasification of biomass and its application to electricity and fuel production. *Biomass Bioenergy* 2008, 32, 573-581.

- 22. Nurmesniemi, H.; Manskinen, K.; Poykio, R.; Dahl, O. Forest fertilizer properties of the bottom ash and fly ash from a large-sized (115 MW) industrial power plant incinerating wood-based biomass residues. J. Univ. Chem. Technol. Met. 2012, 47, 43-52.
- Moilanen, M.; Pietilainen, P.; Issakainen, J. Longterm effects of apatite and biotite ont the nutrient status and stand growth of scots pine (*Pinus sylvestris* L.) on drained peatlands. Suo (Helsinki) 2005, 56, 115-128.
- 24. Dahl, O.; Nurmesniemi, H.; Poykio, R.; Watkins, G. Heavy metal concentrations in bottom ash and fly ash fractions from a large-sized (246 MW) fluidized bed boiler with respect to their Finnish forest fertilizer limit values. *Fuel Process. Technol.* 2010, *91*, 1634–1639.
- 25. Reijinders, L. Disposal, uses and treatments of combustion ashes: A review. *Resor. Conserv. Recycl.* 2005, 43, 313–336.
- 26. Minnesota Office of Environmental Services. Issue document: Managing Mn/DOT environmental liability resulting from use of regulates solid wastes in Mn/DOT administered transportation systems. Part 1 Coal ash. Available online: <u>http://www.dot.state.mn.us/environment/research</u> (accessed on 1 June 2012).
- 27. Bahadori, A.; Vuthaluru, H. Estimation of potential saving from reducing unburned combustible losses in coal-fired sysytems. *Appl. Energy* 2010, *87*, 3792–3799.
- 28. Duan, L.; Liu, D.; Chen, X.; Zhao, C. Fly ash recirculation by bottom feeding on aa circulating fluidized bed boiler co-burning coal sludge and coal. *Appl. Energy* 2012, *95*, 295–299.
- 29. Turner, W.; Doty, S. *Energy Management Handbook*, 6th ed.; Fairmont Press: Lilburn, GA, USA, 2007.
- 30. Batra, V.; Urbonaite, S.; Svensson, G. Characterization of unburned carbon in bagasse fy ash. *Fuel* 2008, *87*, 2972–2976.
- 31. Overview of Gasification Technology. Available online: <u>http://cturare.tripod.com/ove.htm</u> (accessed on 13 March 2010).
- 32. Rade, K.; Karamarkovic, V. Energy and exergy analysis of biomass gasification at different temperatures. *Energy* 2010, *35*, 537–549.
- 33. Lövgren, L.; Lundmark, J.; Jansson, C. Adaptation for Recycling of Bio Asashes: Evaluation of New Technologies for Pelleting of Bio Ash with Respect to the Operational Characteristics,

and Environmental Impacts in the Forest; Project P11647-1; Swedish National Energy Administration: Eskilstuna, Sweden, 2000.

- 34. Svantesson, T.; Petersson, T.; Jedfelt, D. Evaluation of Trial Roll Pelleting Method; Technical Report for Automated Manufacture of Fertilizing Agglomerates from Burnt Wood Ash; University of Kalmar: Nybro, Sweden, 2004.
- 35. Sarenbo, S.; Melbo, P.; Stalnacke, O.; Claesson, T. Reactivity and Leaching of wood ash pellets dehydrated by hot air and flue gas. *Open Waste Manag. J.* 2009, *2*, 47–54.
- Jianguo, J.; Maozhe, C.; Yan, Z.; Xin, X. Pb stabilization in fresh fly ash from municipal solid waste incinerator using accelerated carbonation technology. J. Hazard. Mater. 2009, 161, 1046–1051.
- 37. Zhang, H.; Hem, P.; Shao, L.; Lee, D. Temporary stabilization of air pollution control residues using carbonation. *Waste Manag.* 2008, *28*, 509–517.
- Liao, C.; Wu, C.; Yan, Y. The characreristics of inorganic elements in ashes from a 1 MW CFB biomass gasification power generation pplant. *Fuel Process. Technol.* 2007, 88, 149– 156.
- 39. Obernberger, I.; Biedermann, F.; Widmann, W.; Riedl, R. Concentrations of inorganic elements in biomass fuels and recovery in the different ash fractions. *Biomass Bioenergy* 1997, *12*, 211–224.
- 40. Ohman, M.; Boman, C.; Nordin, A.; Bostrom, D. Slagging tendencies of wood pellet ash during combustion in resendtial pellet burners. *Biomass Bioenergy* 2004, 27, 585-596.
- 41. Ninomiya, Y.; Sato, A. Ash melting behaviour under coal gasification conditions. *Energy* Convers. Manag. 1997, 38, 1405–1412.
- 42. Wilen, C.; Stahlberg, P.; Sipila, K.; Ahokas, J. Pelletization and combustion of straw. *Energy Biomass Waste* 1987, *10*, 469–484.

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## Preface

Chapter 2 of this thesis is a version of the article accepted for publication:

James, A. K.; Thring, R.W.; Rutherford, P. M.; Helle, S. Characterization of Biomass Bottom Ash from an Industrial Scale Fixed-bed Boiler by Fractionation. *Energy and Environment Research* 2013.

# CHAPTER 2: Characterization of Biomass Bottom Ash from an Industrial Scale Fixed-bed Boiler by Fractionation

## 2.1 Introduction

Increased use of bioenergy has significantly increased ash generation in many countries. Large-scale utilisation of wood and wood residues for district heating plants, process heating plants and combined heat and power plants has resulted in large volumes of ash production. It is projected that by 2020, the thermal application of biomass in European countries will result in an annual ash production of approximately 15.5 million tons per year (1).

Ash formed during biomass combustion can be divided into bottom ash and fly ash (2). Bottom ash is the fraction produced on the grate in the primary combustion chamber. While many studies have investigated fly ash, bottom ash usually accounts for 60 to 90 % of the total ash generated (1).

A number of barriers to the utilization of wood ash have been identified, including heavy metal concentrations and the presence of organic pollutants (1). High amounts of organic carbon in the ash indicate incomplete combustion of biomass, which suggests inefficient fuel use (2)(3). The presence of carbon in ash limits its application in forest soils since carbon dilutes the liming and fertilization effects and also restricts the hardening of the ash (3)(4). Ash hardening is used to improve handling, reduce dust and to decrease the ash dissolution rate. Unburned matter, as indicated by high carbon content, increases ash volumes and results in higher handling, transportation, disposal and spreading costs (3)(5). For many environmental applications, it has been shown that the carbon content should be below 5 wt % (dry basis) (6). In addition, the high

combustibility of char, restricts the application of high carbon ash to some lands due to increased forest fire risk (7).

According to Emilsson, a high content of uncombusted material in ash leads to difficulty in the ash hardening for ash use in construction materials and also suggests that high charcoal content in the ash can be recombusted (8). High content of uncombusted material also poses problems when used in cement compositions.

The relationship between bulk density and the presence of unburnt carbon in ash is important when considering ash transport and storage. High bulk densities may reduce ash volumes, thus decreasing the need for additional storage space and reducing transportation costs. Bulk density decreases with the fineness of the ash fraction (6). The authors reported that ash from straw and cereal combustion showed low density due to its specific chemical matrix, containing more salts and less minerals when compared to wood ash. The bulk density of bottom ash from bark combustion and woodchip combustion, both from a moving grate underfeed stoker, had densities of 950 kg/m<sup>3</sup> (9). On the other hand, the bulk density of bottom ash from sawdust combustion (from an underfeed stroker) was 650 kg/m<sup>3</sup>. Thus, fuel type may influence the bulk density of the produced ash.

While improving combustion system efficiency is integral to reducing the carbon content of bottom ash, identifying effective recycling methods are also essential in dealing with high carbon ash. The unburned carbon content in bottom ash varies amongst combustion systems. Short residence time (10) and high ash content are considered as major factors for the incomplete burnout of char. High ash content may result in an ash layer covering the char and preventing the free movement of gases to the core of the char during combustion. State-of-the-art fluidized bed combustion systems have combustion efficiencies of over 95 % irrespective of ash content (11).

In these systems, the only ash fraction that may contain a high carbon content is the coarse fly ash fraction (as precipitated in cyclones) which is reintroduced into the combustion chamber.

A possible use of ash, depending on the carbon content, is as a fuel (5). Preliminary research on this idea has been carried out predominantly on fly ash (10). Gasification of high-carbon fly ash has been investigated and the resulting ash shows positive results in the production of C-fix blocks, a concrete-like material that uses a heavy petroleum residue as a binder (9). The high carbon content in some forms of ash could also make it useful as a fuel after briquetting or if pelletized (12)(13). Combustion of the high carbon ash presents a number of operational problems. Related problems include corrosion (14) and scouring. Based on the design of the boilers, the ash may be carried with the flue gas through the boiler tubes (11). The variability in particle sizes as the feedstock becomes more burnt-out also causes inherent problems in fixed bed systems. Fixed bed systems usually require a feedstock that is as uniform as possible so as to avoid channeling (15) (16).

This study investigates the high carbon bottom ash from fixed bed boilers generated by a large pulp and paper producer in Canada. Large volumes of high carbon ash are produced and are typically sent to landfill due to the low potential economic and environmental benefit for other applications. The costs associated with changing the system to a more recent boiler design are considerably high. If the high carbon fraction can be separated from the low carbon fraction of the ash other applications may become viable. Separation methods for isolating carbon from ash include floatation in a continuous mode and fractionation by sieving (5). Industrially, carbon separation can be carried out using industrial scale sieve shakers for removal of the coarse carbon rich fraction or by scaling up floatation methods.

The objective of this research is to characterize bottom ash from an industrial scale fixed bed boiler and to identify the ash fractions with potential energy importance. This work examines the physical and chemical properties of the ash and ash fractions. Fractions with high carbon contents are identified and an analysis of the combustion behavior is carried out. The data obtained enhances knowledge about the utilization and storage of woody biomass bottom ash.

#### 2.2. Experimental Section

Wood ash from a Canfor Pulp Limited Partnership pulp mill fixed-bed boiler in Northern British Columbia was used in the study. Boiler feed is hog fuel, a mixture of bark and sawdust primarily derived from pine wood with variable particle sizes. Based on an ultimate analysis, the hog fuel is 49 % C and 6 % H on a dry basis. Hog fuel moisture content varies depending on sawmill feedstock, ranging from 25 to 50 %; ash content is approximately 2.5 %. Typically fixed bed boilers operate within 850 to 1400 °C (17). This fixed bed boiler produces approximately 27 MW of power and has a lower grate temperature of 255 °C with an outlet flue gas temperature of 170 °C. Ash samples, denoted B1 and B2 were collected from the system on November 17, 2010 –B1 and on April 27, 2012 – B2. The boiler has a dry ash removal system, and the ash was sampled from the ash bins shortly after removal from the boiler. The samples were separated into different particle fractions as described in section 2.1.

#### 2.2.1 Particle size distribution

Approximately 100 g of "as-received" (original sample obtained from boiler) ash was separated into different size fractions using a stack of five sieves (2000  $\mu$ m, 850  $\mu$ m, 425  $\mu$ m, 250  $\mu$ m, 150  $\mu$ m) arranged in decreasing diameter openings (18). The ash was poured on the top sieve

(largest opening), which was then covered; the sieve stack was placed on an automatic shaker for 15 minutes after which the stack was removed. Each sieve with the retained material was gently tapped on the sides before being removed from the stack and weighed. Retained ash was removed and stored, while the sieve trays were thoroughly cleaned and reweighed to obtain the mass of ash retained on each tray. The analyses were repeated twice and an average value calculated and reported.

The following retained fractions were used for subsequent analyses:

AR = as-received wood-ash,

 $\geq$  2000  $\mu$ m,

 $\geq 850~\mu m$  and  $< 2000~\mu m,$ 

 $\geq$  425 µm and <850 µm,

 $\geq$  250 µm and < 425 µm,

 $\geq$  150 µm and less than 250 µm

<150 µm.

For convenience, the above fractions will simply be denoted as 2000  $\mu$ m, 850  $\mu$ m, 425  $\mu$ m, 250  $\mu$ m, 150  $\mu$ m and <150  $\mu$ m.

Each of the retained fractions were weighed and then stored for further analysis.

### 2.2.2 Proximate and ultimate analysis of wood ash

The proximate analysis of each sample fraction was carried out according to American Society for Testing and Materials (ASTM) method D1762-84. The fixed carbon (FC), volatile matter (VM) and ash content were determined on a dry basis. Samples were dried for 3 h at 105

°C to remove all moisture. VM analyses was carried out at 950 °C for 7 min in capped crucibles and then ash content was determined at 550 °C for 6 h in open crucibles. The FC was determined by difference as shown in Equation (2.1). The ash content is defined as the remaining inorganic contents after the complete removal of fixed carbon, volatile matter and moisture. All analyses were performed on three replicates and the averages presented.

$$FC = 100 - VM - Ash \tag{2.1}$$

where FC, VM and Ash content are wt.% expressed on a dry basis.

Ultimate analysis of carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) was conducted using a Costech<sup>TM</sup> Elemental Analyzer, ECS 4010 Elemental Combustion System. Reactor conditions were: 1000 °C, helium carrier gas at 105 mL/min, Gas Chromatography (GC) Column #051080, SS 5 mm x 2 m, at 100 °C, 450 L x 18 mm reaction tube, and HayeSep Q 60/80GC column packing. A Thermal Conductivity Detector was used. Results are presented in wt.% and on a dry basis.

## 2.2.3 Thermal analysis

Thermal characteristics were determined using a TA Instrument TGA-50/50H Shimadzu thermogravimetric analyzer. The analyses were conducted using air at a flow rate of 50 mL/min, under atmospheric conditions. For each test, approximately 10 mg of the sample was heated from room temperature to 800 °C at a heating rate of 10 °C/min. A thermocouple was located on the inside of the analyser above the sample. The TGA analysis was done only on B1 sample for the AR portion,  $\geq$  425 µm fraction and < 425 µm fraction. The thermogravimetric (TG) plots describe the weight loss of the sample with increasing temperatures while the differential thermogravimetric (DTG) plot illustrates the derivative of sample mass with time at a specific

temperature. The analysis were repeated three times to ensure that the thermal distributions, trendlines, weight losses and peaks were similar for the repeats. Also, when the flow rate of air was varied (data not shown) no difference was seen in the thermal distribution of the char.

#### 2.2.4 Surface Area

Brunauer–Emmett–Teller (BET) surface area measurements were carried out with N<sub>2</sub> at -196 °C using a single–point Micromeritics FlowSorb 11 2300 surface area analyzer. The surface area was determined only on char particles that were  $\geq 2000 \ \mu m$  for both B1 and B2 samples. Particles in this fraction were more homogeneous due to the absence of finer ash particles and more char-like particles.

#### 2.2.5 Heating Value

The gross calorific value was determined for each fraction using a Parr Oxygen Bomb with approximately 1 g of boiler ash. Results were determined in accordance with ASTM D-5865/E711 and were calculated relative to sample weight on an oven dried basis.

#### 2.2.6 Bulk Density

The bulk density for each fraction was determined as follows. Approximately 50 ml of sample was placed into a 100 ml graduated measuring cylinder (1 ml divisions). The cylinder was then tapped 6 times on a rubber surface from a height of approximately 1.5 in. The mass and volume of the sample were then obtained and used to calculate bulk density. This procedure was repeated three times and an average value obtained for each sample. All bulk density determinations were expressed on a dry basis.

## 2.3. Results and Discussion



## 2.3.1. Particle size distribution of ash

Figure 2.1 Percent retained weight against particle size (µm) for boiler ash samples on a dry basis.

Distribution of the particles in the boiler samples are shown in Figure 2.1. Fractions  $\geq 250$  µm showed a similar distribution for both ash samples. The B2 sample was approximately 10 % higher in mass than B1 for the fractions 250 µm, 425 µm and 850 µm. As the particle sizes became smaller, that is for fractions 150 and < 150 µm, the mass of B1 was higher than B2. For B1, fraction < 150 µm accounted for the highest weight with 25 % of the total mass passing through the 150 µm sieve. The same fraction for B2 was approximately 20 % lower than B1. The difference in the particle size distributions of the samples is likely associated with the variation in the char contents of the AR samples. As char becomes more combusted, the sample particle sizes will decrease due to an increase in ash formation. Therefore, B2 is expected to have greater carbon content in the AR sample.

### 2.3.2. Results of proximate analysis and ultimate analysis

The results of the proximate analysis and ultimate analysis of the wood ash samples are shown in Table 2.1. Percent volatile matter ranged from 0 to 20 % for all samples. The volatile matter for the samples appeared to slightly increase as particle size decreased. This may be due to an increase in inorganic content such as carbonates and oxides that are usually present in wood ash (19). Ash content increased with decreasing particle size. Fractions 425  $\mu$ m and higher for B1 and B2 ranged from ~ 17 to 34 % ash content, while fractions 250  $\mu$ m and below ranged from ~ 60 to 70 %. The ash content in the 425  $\mu$ m fractions of B1 and B2, respectively, were 32 % and 23 % lower when compared to their 250  $\mu$ m fractions. In general, the FC content increased with increasing particle size. B2 showed a gradual increase from 10 to 70 % in FC as particle size increased. For both B1 and B2, fractions 425  $\mu$ m and larger contained 50 % or more FC while

fractions 250  $\mu$ m and smaller had ~ 26 % or less FC. The high FC seen in the larger fractions are a result of incomplete combustion of the sample and the presence of char-like particles.

	B1			B2		
Particle size (µm)	FC (wt.%)	Vm (wt.%)	<b>Ash</b> (wt.%)	FC (wt.%)	Vm (wt.%)	Ash (wt.%)
<150	13.8	19.1	67.1	10.0	19.6	70.4
150	9.5	17.5	73.0	10.6	17.1	72.3
250	16.0	17.4	66.6	25.3	17.4	57.4
425	51.1	14.9	34.0	51.9	13.8	34.3
850	63.6	16.7	19.7	67.8	13.5	18.7
2000	59.0	14.8	26.2	67.4	14.9	17.7
AR	29.3	15.9	54.8	54.0	15.8	30.2

Table 2.1. Proximate analysis for fixed bed boiler bottom ash samples (B1 & B2).

All results are on a dry weight basis

AR = as received (i.e. not separated into particle size fractions)

Table 2.2 displays the results of the ultimate analysis, and shows the total C, H, and N for each particle fraction. In general, the total % C increased with increasing particle size fraction. The weight percent distribution of C for most samples was greater than those from the proximate analysis (i.e. C greater than FC). This is anticipated since the total carbon includes the organic and inorganic C such as carbonates. All samples had H concentrations of 1 % or less, and N concentrations of less than 0.3 %. S was below detection limits. These low concentrations of H are expected since the H present in the wood is converted to  $H_2O$  during the combustion process. Also, sulphur is usually not present or is only present in small amounts in woody biomass samples unless the soil is very high in sulphur content.

Particle		B1			B2	
size	C	Н	N	С	Н	Ν
μm	wt.%	wt.%	wt.%	wt.%	wt.%	wt.%
<150	22.70	0.41	0.06	17.17	0.65	0.04
150	15.99	0.27	0.04	13.85	0.56	0.03
250	13.13	0.21	0.01	21.56	0.59	0.01
425	55.32	0.81	0.70	52.76	0.79	0.06
850	63.92	0.98	0.06	66.41	0.71	0.18
2000	68.15	0.76	0.12	70.73	0.53	0.25
AR	38.17	0.42	0.11	51.79	0.68	0.08

 Table 2.2 Ultimate analysis of fixed-bed boiler bottom ash samples (B1&B2).

All results are on a dry weight basis



**Figure 2.2.a** Distribution of fixed carbon (g) and ash (g) in 100 g (dry basis) of B1 sample based on particle size fraction distribution.



**Figure 2.2.b** Distribution of fixed carbon (g) and ash (g) in 100 g (dry basis) of B2 sample based on particle size fraction distribution.

Figure 2.2a and 2.2b shows the distribution of fixed carbon (FC) in 100 grams of boiler ash samples B1 and B2. The 850 µm fraction for both B1 and B2 were the highest in FC content, 12 g and 20 g respectively. Fraction 425 µm had the second highest FC contents of 7 and 10 g respectively. The two boiler ash samples showed a variation in FC distribution. This could be due to a number of factors such as variations in retention time in the reactor, incomplete combustion, temperature variations and fluctuations, moisture content of fuel etc. Also, the moisture content and composition of the biomass feedstock may vary depending on when and where it was sourced. Higher moisture content will reduce the rate of combustion of the fuel. Also, because of the variability in energy demand of the plant, ash may be removed from the grate before complete combustion. This is in addition to the other ash related challenges that occur in the boiler as previously mentioned in the introduction. The 250 µm fractions for B1 and B2 had the highest ash contents of approximately 14 and 26 g. As previously seen in the proximate analysis, fractions 425 µm and higher in both boiler samples contain more than 50 % FC. Combined, fractions 425, 850 and 2000  $\mu$ m contained ~ 72 % of the total FC in sample B1. These same fractions accounted for only ~ 36 % of the total sample mass. For B2, the 425  $\mu$ m and higher fractions contained ~ 82 % of the total FC and accounted for 59 % of the total mass. The high FC present in boiler ash provides an opportunity for re-burning or reusing its energy.

## 2.3.3. Thermogravimetric analysis



Figure 2.3. TGA graph of weight change as a function of temperature for B1 boiler ash sample from a fixed bed boiler. Lines displayed represents AR sample, fractions  $\geq$  425 µm and < 425 µm.



Figure 2.4. DTGA graph displaying rate of mass loss as a function of temperature for B1 boiler ash sample from a fixed bed boiler. Lines displayed represents AR sample, fractions  $\geq$  425  $\mu$ m and < 425  $\mu$ m.

Figure 2.3 shows the thermal behaviour of the as-received, combined fractions  $\geq 425 \ \mu m$ and combined fractions  $< 425 \mu m$  for boiler ash B1 when heated under air at atmospheric conditions. The results are only shown for B1, however, the results for B2 as received show similar thermal distributions (not shown). The TGA analyses showed that the mass of the boiler sample decreased as temperature increased. The weight loss occurred in phases which is linked to the removal of specific components of the sample such as water, carbonates, aluminates, silicates, oxides, organic carbon and other components (20). All three samples displayed a similar pattern in thermal distribution. The first weight loss was seen between  $\sim 25 - 110$  °C and accounted for the removal of moisture from the sample. A further mass loss was seen up to ~ 350 °C. This change is generally attributed to the removal of moisture, carbon monoxide, and volatiles such as tars and other organic carbons that may have condensed on the sample (14). The most noticeable change in mass of the AR,  $\geq$  425 µm and < 425 µm fractions was seen between the temperatures 350 to 440 °C and accounted for ~ 32, 43 and 14 % mass loss, respectively. This is assumed to be organic carbon (char). Further mass losses occurred between 440 to 610 °C and between 610 to 670 °C. The decomposition of mineral components such as carbonates  $(CaCO_3)$  and some of the other metal carbonates and oxides present in the sample may occur during this phase. For the range of temperatures studied, the AR,  $\geq$  425 and < 425 µm fractions lost ~ 44, 56 and 26 % of initial mass by 800 °C, respectively. Therefore, fractions  $\geq$  425 µm had the highest combustible content. The sample burnout time corresponding to the burnout temperatures, that is, the temperature that shows no further mass loss on the TGA (21)(22) are shown in Table 2.3. The fraction  $\geq$  425 µm had a slighter shorter burnout time but was not significantly different from the other two samples under study.

The DTGA analysis in Figure 2.4 shows two distinct peaks. These peaks are associated with the thermal oxidation of different components in the particles such as carbonized material, heavy organic molecules, condensed tars and inorganic compounds (23). As seen in Table 2.3, the AR sample, fractions  $\geq$  425 and < 425 µm had the highest rate of mass losses at ~ 1.2082 mg/min at 383 °C, 1.3843 mg/min at 362 °C, and 0.6642 mg/min at 405 °C, respectively. Lignocellulosic samples heated in air typically have well resolved peaks at ~ 400 °C (24)(25). The fractions containing higher carbon contents were observed to have lower peak temperatures. Peak temperature determines how easily a fuel is ignited and is defined as the maximum rate of weight loss due to volatilization accompanied by the formation of carbonaceous residue, on the DTGA curve (21). Low peak temperatures mean that the fuel is easier to ignite. Since the  $\geq 425 \ \mu m$ fraction was found to have the highest rate of mass loss at a lower temperature, faster reaction times and lower ignition temperatures could be observed if re-burned, when compared to the other two samples. The samples showed clearly defined thermal phases when heated and oxidized and contained substantial amounts of combustible material, particularly char for the AR sample and particle fractions  $\geq$  425  $\mu$ m.

Sample	Temperature range (°C)	Weight Loss (wt. %)	Peak Temperature Tp (°C)	DTGmax (mg/min)	Sample burning time (min)
AR	110-350	4.28			35.33
	350-440	31.98	383	1.2082	
	440-610	3.54			
	610-670	3.79	649	0.2023	
	670-800	0.36			
$\geq$ 425 $\mu m$	110-350	6.49			34.23
	350-440	43.59	362	1.3843	
	440-610	3.71			
	610-670	2.25	648	0.1357	
	670-800	0.4			
< 425 μm	110-350	2.94			34.47
	350-440	14.44	405	0.6642	
	440-610	4.81			
	610-670	3.83	646	0.1815	
	670-800	0.15			······

Table 2.3. Combustion characteristic of fixed bed boiler bottom ash (B1) samples

Results are on a dry basis.

### 2.3.4. Surface Area

The N<sub>2</sub>-BET surface area absorption B1 and B2 ( $\geq 2000 \ \mu m$  fraction) were 850 and 770 m<sup>2</sup>/g, respectively. The high surface areas obtained are expected for wood ash chars (26)(27)(3). This may influence the reactivity rate during combustion or gasification processes. A larger available surface area provides more sites for oxygen to bond with carbon (28) increasing

oxidation. It has also been reported that wood chars that are produced at higher temperatures have a higher surface area (29). Lower pressures also increase the surface area of charge (27).

#### 2.3.5. Higher heating Value (HHV)

Table 2.4 displays the higher heating values for the various size fractions of the B1 and B2 ash samples. Heating values within each size class were relatively similar between the two ash samples. A range of approximately 5 - 25 MJ/kg was obtained for both samples. As the particle size fraction increased, the heating value of the fraction also increased. A slight decrease in the heating value was observed when moving from 850 to 2000  $\mu$ m for both B1 and B2. The obtained HHVs suggest that the waste being disposed of has good energy potential and is comparable to some forms of biomass used in energy production processes (30).

Particle size (µm)	B1 MJ/kg	B2 MJ/kg
<150	7.02	8.89
150	5.58	6.86
250	7.40	10.40
425	15.77	19.33
850	22.96	24.56
2000	20.83	23.54
AR	10.77	14.42

Table 2.4. Higher Heating value of boiler bottom ash samples separated within particle fractions

All results are on a dry weight basis.

#### 2.3.4. Bulk Density

The bulk density was calculated for each fraction and is represented as a function of particle size in Figure 2.5. B2 has lower bulk densities in all fractions. The as-received samples of B1 and B2 were 244 and 172 kg/m<sup>3</sup> respectively. For both B1 and B2, fractions 425  $\mu$ m and higher had significantly lower bulk densities than fractions 250  $\mu$ m and below. B1 fractions 425  $\mu$ m and higher had a bulk density range of ~ 100 - 150 kg/m<sup>3</sup>. Bulk density was ~ 50 % less for fractions 250  $\mu$ m and lower. For B2, bulk density was also 50% less for fractions 250  $\mu$ m and lower compared to fractions 425  $\mu$ m and higher.

The bulk densities were lower with samples of higher FC contents. Figure 2.6 shows the correlation of bulk density with percent FC within the various particle fractions. A linear relationship is established and shown in Equation 2.2. While the value of  $R^2$  is 0.8692, the graph shows a significant reduction in bulk densities of fractions with higher FC contents. If the carbon is reduced or eliminated in ash, the bulk density increases. This may be important in the transportation and storage of ash. With increasing bulk densities, greater amounts of ash could be transported from combustion plants to landfills.

 $\rho_{B} = -4.9579 \text{ FC} + 406.73 \text{ R}^{2} 0.8692 \tag{2.2}$ 

 $\rho_B$ - Bulk density



Figure 2.5. Bulk density as a function of particle size  $(\mu m)$  for boiler ash.



Figure 2.6. Bulk density versus percent fixed carbon for boiler ash.
## 2.4. Summary of Results

Parameter	B1 AR	B1 ≥425 μm	B1 <425 μm	B2 AR	B2 ≥425 μm	B2<425 μm
Mass (kg)	100.0	37.2	62.8	100.0	60.0	40.0
Energy density (MJ/kg)	10.8	20.0	6.7	14.4	22.4	9.7
Energy content (GJ)	1.08	0.74	0.42	1.44	1.34	0.39
FC (%)	29.3	58.3	13.2	54.0	61.6	21.5
Ash (kg)	54.8	9.7	42.8	30.2	14.8	24.4
Bulk density (kg/m <sup>3</sup> )	244.0	106.6	448.3	172.0	81.5	385.3
Volume (m <sup>3</sup> )	0.41	0.35	0.14	0.58	0.74	0.10

Table 2.5. Properties of boiler bottom ash of major ash fractions, based on 100 kg sample.

Bulk density calculated from Equation 2.2

Table 2.5 summarizes some of the main results by reporting data obtained for the as-received fractions, combined fractions  $\geq 425 \ \mu m$  and combined fractions  $< 425 \ \mu m$  for B1 and B2. When samples are collected from fractions  $\geq 425 \ \mu m$ , the energy density can be increased by approximately 50 % and 64 % for B1 and B2 respectively when compared to the AR for both samples. In addition, the majority of the energy content is in the larger fraction ( $\geq 425$ ), 64 % for B1 and 78% for B2. On a mass basis, less than half of the ash is in the larger fractions ( $\geq 425$ ). The bulk density analysis shows that the low carbon fractions of ash have four times the bulk density, compared to the high carbon fractions. This suggests a good opportunity for volume reduction. By reburning the larger size fraction, ash volumes can be decreased by over a half, while recovering more than two-thirds of the energy present in the as-received sample.

## 2.5. Conclusions

The boiler ash studied shows variability in carbon contents that may be a result of variations in retention time in the reactor, incomplete combustion, temperature variations and fluctuations and variations in moisture content. However, unique to both ash samples is a high carbon content in the larger size fractions, specifically for the fractions  $\geq$  425  $\mu$ m. Separating and re-using particle sizes 425 µm and higher would recover over 50 % of the unburnt carbon that is present in this bottom ash. Sieve fractionation may allow for easy accessing of the carbon and may present itself as a cost effective pre-treatment method for reburning high carbon ash, in order to obtain the highest energy components. The reintroduction of ash in the combustion system may present challenges due to problems related to corrosion, scouring and fouling as experienced with the fixed bed boiler that produces this high carbon ash. Thermogravimetric analysis shows that this high carbon ash may be combusted and displays thermal phases similar to the combustion of lignocellulosic biomass. The highest rate of mass loss was 1.3843 mg/min for fractions  $\geq$  425  $\mu$ m. This occurs at a lower peak temperature when compared to the other samples, resulting in lower ignition temperatures. There was no significant difference in the burn-out time for all 3 samples. The high surface area of the char particles could increase combustion or gasification reactivity rates, since a large surface area is available for oxidation. A linear correlation was identified between the FC and bulk density, where samples with higher concentrations of fixed carbon have lower bulk densities.

In an effort to ensure environmental sustainability and sustainable use of our biomass resources, efficient use must be realized. The use of woody biomass in bioenergy process must be such that all possible energy is extracted. It is preferred that bioenergy processes are able to so. However, should that be not possible due to system limitations or fuel type etc, other options must be employed in conjunction with existing technologies to ensure maximum use of the resource. Finally, the need for an in-depth analysis of the inorganic distribution within fractions of bottom ash should also be investigated for possible environmental and technical utilization. For example, there are likely to be similarities in the properties of ash and biochar. Biochar may have beneficial soil applications, for example biochar has been suggested to enhance seedling growth (31)(32). Perhaps high carbon ash could also have similar results for soil applications.

## References

- Obernberger, I.; Supancic, K. Possibilities of ash utilisation from biomass combustion plants. Proceedings of the 17th European Biomass Conference & Exhibition. Hamburg : *ETA Renewable Energies*, June/July 2009.
- 2. Picco, D. Technical assistance for the development and improvement of technologies, methodologies and tools for enhanced use of agricultural biomass residues. Gorizia : s.n., February 2010.
- 3. Demirbas, A. Potential applications of renewable energy sources, biomass combustion problems in boiler power systems and combustion related environmental issues. *Progress in Energy Combustion Science*. 2005, Vols. 31171-192.
- 4. Sarenbo, S. Wood ash dilemma-reduced quality due to poor combustrion performance. *Biomass and Bioenergy*. 2009, Vol. 33, 1212-1220.
- Gomez-Barea, A.; Vilches, L.; Campoy, M.; Fernandez-Pereira, C. Plant optimization and ash recycling in fluidised waste gasification. *Chemical Engineering Journal*. 2009, Vol. 146, 227-236.
- 6. Van Loo, S.; Kopejan, J. The handbook of biomass combustion and co-firing. s.l. : *Earthscan Publications*, 2008. ISBN:9781844072491.
- 7. Dimitrakopoulous, A. Thermogravimetric analysis of Mediterranean plant species. *Journal of Analytical and Applied Science*. 2001, Vol. 60, 123-130.
- 8. Emilsson, S. International handbook. From extraction of forest fuels to ash recycling. Jonkoping : *Swedish Foresty Agency*, 2006. ISBN 91-975555-1-7.
- Pels, J.; de Nie, D.; Kiel, J. Improvement of the economics of biomass/waste gasification by higher carbon conversion and advanced ash management. [Online] n.d. [Cited: October 20, 2012.] http://www.ecn.nl/docs/library/report/2006/c06038.pdf.
- 10. Duan, L.; Liu, D.; Chen, X.; Zhao, C. Fly ash recirculation by bottom feeding on a circulating fluidized bed boiler co-burning coal sludge and coal. *Applied Energy*. 2012, Vol. 95, 295-299.
- 11. Saidur, R.; Abdelaziz, E.; Demirbas, A.; Hossain, M.; Mekhilef, S. A review on biomass as a fuel for boilers. *Renewable and Sustainable Energy Reviews*. 2011, Vol. 15, 2262-2289.
- 12. Batra, V.; Urbonaite, S.; Svensson, G. Characterization of unburned carbon in bagasse fly ash. *Fuel.* 2008, Vol. 87, 2972-2976.

- 13. Cetin, E.; Moghtaderi, B.; Gupta, R.; Well, T. Influence of pyrolysis conditions on the structure and gasification reactivity of biomass chars. *Fuel.* 2004, Vol. 2004, 2139-2150.
- 14. Khan, A.; Jong, W.; Jansens, P.; & Spliethoff, H. Biomass combustion in fluidized bed boilers: potential problems and remidies. *Fuel Processing Technology*. 2009, Vol. 90, 21-50.
- Ryu, C.; Yang, Y.; Khor, A.; Yates, N.; Sharifi, V.; Swithenbank, J. Effect of fuel properties on biomass combbustion: Part 1. Experiments - fuel type, equivalence ration and particle size. *Fuel.* 2006, Vol. 85, 1039-1046.
- 16. Warnecke, R. Gasification of biomass: comparison of fixed bed and fluidized bed gasifier. *Biomass and Bioenergy*. 2000, Vol. 18, 489-497.
- Quaak, P.; Knoef, H.; Stassen, H. Energy from biomass. A review of combustion and gasification technologies. Washington, D.C. : World Bank Technical Paper; 422. Energy series, 1999. 0-8213-4335-1.
- 18. Herrman, T.; Baker, S. Evaluating particle size. Kansas : Kansas State University Agricultural Experiment Station and Cooperative Extension Service, 2002.
- Liao, C.; Wu, C.; Yan, Y. The characteristics of inorganic elements in ashes from a 1 MW CFB bimass gasification power generation plant. *Fuel Processing Technology*. 2007, Vol. 88, 149-156.
- Zhang, H.; Zhao, Y.; Jingyu, Q. Termal characterization of fly ash from municipal solid waste incinerator (MSWI) in Shanghai. *Process Safety and Environmental Protection*. 2010, Vol. 88, 269-275.
- Idris, S.; Rahman, N.; Ismail, K. Combustion characteristics of Malaysian oil palm biomass, sub-bituminous coal and their respective blends via thermogravimetric analysis (TGA). *Bioresource Technology.* 2012, Vol. 123, 581-591.
- 22. Miranda, T.; Esteban, A.; Rojas, S.; Montero, I.; Ruiz, A. Combustion analysis of different olive residues. *International Journal of Molecular Science*. 2008, Vol. 9, 512-525.
- Miguel, G.; Dominguez, M.; Hemandez, M.; Sanz-Perez, F. Characterization and potential applications of solid particles produced at a biomass gasification plant. *Biomass and Bioenergy*. 2012, Vol. 47, 134-144.
- 24. Elder, T.; Kush, J.; Hermann, S. Thermogravimetric analysis of forest understory grasses. *Thermochimica Acta*. 2011, Vol. 512, 170-1771.
- 25. Di Blasi, C. Combustion and gasification rates of lignocellulosic chars. *Energy Combustion Science*. 2009, Vol. 35, 121-140.

- Link, S.; Arvelakis, S.; Hupa, M.; Yrjas, P.; Kulaots, I.; Paist, A. Reactivities of the biomass chars originating from reed, douglas fir and pine. *Energy and Fuels*. 2010, Vol. 24, 6533-6539.
- Hanaoka, T.; Sakanishi, K.; Okumura, Y. The effect of N2/CO2/O2 content and pressure on charcateristics and CO2 gasification behaviour of biomass-derived char. *Fuel Processing Technology*. 2012, Vol. 104, 287-294.
- 28. Moulijn, J.; Kapteijn, F. Towards a unified theory of reactions of carbon with oxygencontaining molecules. *Carbon.* 1995, Vol. 8, 1155-1165.
- 29. James, G.; Sabatini, D.; Chiou, C.; Rutherford, D.; Scott, A.; Karapanagioti, H. Evaluating phenanthrene sorption on various wood chars. *Water Research*. 2005, Vol. 39, 4, 549-558.
- 30. Liao, C.; Chuangzhi, W.; Yanyongjie, Haitao, H. Chemical elemental characteristics of biomass fuels in China. *Biomass and Bioenergy*. 2004, Vol. 27, 119-130.
- Robertson, S.; Rutherford, M.; Lopez-Gutierrez, J.; Massicote, H. Biochar enhances seedling growth and alters root symbioses and properties of sub-boreal forest soils. *Canadian Journal* of Soil Science. 2012, Vol. 92, 329-340.
- 32. Knapp, B.; Insam, H. Recycling of biomass ashes: current technologies and future research needs. [book auth.] Insam H Knapp B. *Recycling of Biomass Ashes*. Heidelberg : Springer, 2011.

## Preface

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# CHAPTER 3: Characterization of Inorganic Elements in Woody Biomass Bottom Ash from a Fixed-bed Combustion System, a Downdraft Gasifier and a Wood Pellet Burner by Fractionation

#### 3.1. Introduction

The employment of wood combustion technologies have resulted in a rapid increase in the use of woody-biomass residues for energy production. Boilers, gasifiers and pellet burners are but some of the systems available for wood energy production. A disadvantage of using biomass for energy production is that large amounts of residual ash are generated (1). Ash from these combustion processes vary in quality depending on the fuel type, operating conditions of the system and the type of combustion system (2). Ideally, biomass ash should be recycled whenever possible, but large amounts of wood ash are typically landfilled (3). Countries such as Sweden and the United States of America (USA) use landfills to dispose the majority of their ash (4)(5)(6). The quality of the ash in part determines recycling options; some options such as land spreading require low trace element concentrations to prevent environmental pollution (7). The application of wood ash to soils may counteract soil acidification and correct for nutrient deficiencies; this is widely used in regions that carry out extensive forest harvesting, such as Northern Europe and parts of North America (6)(8)(9). In Canada, biomass ash is mainly landfilled but land applications are more common in some provinces than others. In British Columbia the use of ash for soil applications is relatively limited due to current provincial regulations. Until adequate research is carried out the majority of ash generated in B.C. may be limited to landfilling or other uses outside of soil applications.

Limiting factors for the use of wood ash in soils include trace element concentrations and potential organic pollutants (10)(11). Elevated concentrations of trace elements in ashes may limit

utilization of ash in soils and therefore also the recycling of nutrient elements (e.g. Ca, Mg, K, P), too. The handling and application of ash is improved by hardening or aggregation; but, ash with a high organic C content does not harden properly (12).

The physical and chemical characteristics of wood ash may vary with particle size fraction (1)(13)(14). Particle size fractions high in undesirable trace element concentrations could be separated from some ashes, thereby improving the overall quality of the residual ash material (and therefore improving recycling options). Previous research shows that arsenic concentrations in fly ash exceeded the Finnish environmental limits for the particle size fraction less than 0.125 mm (1). Particle separation may be carried out by sieve fractionation and may influence variables such as trace element concentrations, pH, organic carbon concentration, bulk density and other chemical-physical properties.

Should the properties vary significantly in particle size fractions, greater applications of ash as a soil amendment or as a raw material for products requiring specific properties could be employed. Ash-producing industries may find this particularly useful when considering disposal or utilization methods for ash.

The objective of this research was to characterize ash from the three systems. A comparative study of the chemical properties of each bottom ash, as well as their respective fractions, obtained by sieving, was carried out. This paper will identify the inorganic elemental distribution of specific particle size fractions, pH and anion distribution of boiler, gasifier and wood pellet burner bottom ash. It is hoped that these results will assist in finding specific applications for bottom ash.

#### 3.2. Experimental

Wood ash from from three types of combustion systems, a fixed-bed boiler (Canfor Pulp Mill), a downdraft gasifier (University of Northern British Columbia - UNBC) and a wood pellet burner (UNBC) were used in the study. The downdraft fixed bed gasifier is capable of producing a thermal output of 5 MW and operates at  $\sim 1250$  °C. The wood pellet burner 0.4 MW and an industrial scale fixed bed boiler, 27 MW. The fuel for the gasifier and boiler is hog fuel comprised predominantly of softwood sawmill waste and is primarily derived from pine wood. The pellet burner utilizes wood pellets made locally from soft-wood saw dust. Two ash samples were collected from each system. The boiler bottom ash sample was collected on April 27, 2012 – BA. The gasifier bottom ash sample was collected July 18, 2012 – GA. Pellet burner sample was collected March 5, 2010 – PA. Henceforth, the boiler sample is denoted as BA, gasifier sample GA and pellet burner sample, PA. The ash samples were separated into different particle fractions as follows.

#### 3.2.1 Particle size distribution

Approximately 100 g of air-dried "as-received" ash original sample obtained from boiler, gasifier, or pellet burner was separated into different size fractions using a stack of 5 sieves (2000  $\mu$ m, 850  $\mu$ m, 425  $\mu$ m, 250  $\mu$ m, 150 $\mu$ m, arranged in decreasing diameter openings (15). Ash was poured on the top sieve (largest opening), which was then covered; the sieve stack was then placed on an automatic shaker for 15 minutes after which the stack was removed. Each sieve with the retained material was gently tapped on the sides before being removed from the stack and weighed. Retained ash was removed and stored, while the sieve trays were thoroughly cleaned and reweighed to obtain the mass of ash retained on tray. The analyses were repeated twice and an

average of the results taken. The following retained fractions were used for subsequent analyses: as-received wood-ash,  $\ge 2000 \ \mu\text{m}$ ,  $\ge 850 \ \mu\text{m}$  but  $< 2000 \ \mu\text{m}$ ,  $\ge 425 \ \mu\text{m}$  but  $< 850 \ \mu\text{m}$ ,  $\ge 250 \ \mu\text{m}$ but  $< 425 \ \mu\text{m}$ ,  $\ge 150 \ \mu\text{m}$  but less than 250  $\ \mu\text{m}$  and  $< 150 \ \mu\text{m}$ .

For reporting data purposes, the fractions will be denoted as  $2000\mu m$ ,  $850\mu m$ ,  $425\mu m$ ,  $250\mu m$ ,  $150\mu m$  and  $<150\mu m$ . Each of the retained fractions were weighed and then stored for further analysis.

#### 3.2.2. pH analysis

The pH of ash fractions were determined following methods described in Kalra and Maynard (16). The pH was measured potentiometrically using the pH of saturated paste method. A 400 ml beaker was half-filled with ash, then sufficient deionized water was added to saturate sample. The sample was left to sit for 1 hour after which pH readings were taken. Analysis of all fractions were repeated twice and an average of the results taken.

#### 3.2.3 Concentration and distribution of trace elements and major ash-forming elements

Selected elements within each fraction were determined by ICP-MS at UNBC. Samples were prepared by microwave digestion, using a Milestone MLS 1200 Mega digestion system, with concentrated HNO<sub>3</sub>. Metal characterization was done by an inductively coupled plasma (ICP-MS) on an Agilent 7500 ICPMS machine. This was used to determine the alkali, alkali earth and trace elements.

## 3.2.4 Anion analysis

Anion concentrations were determined using the Dionnex IC-5000 system. Ten (10) ml of deionized water was added to  $\sim 400$  mg of samples and shaken for 12 hrs. The samples were then removed from shaker and centrifuged for 15 min, after which  $\sim 2$  ml of sample was obtained for analysis using Ion chromatography. All results shown are considered to be only water soluble amounts. Duplicate analyses were conducted and an average concentration reported.

## 3.3. Results and Discussion

## 3.3.1. Particle size distribution of ash



Figure 3.1. Retained Weight as a function of particle size distribution for boiler, gasifier and pellet burner ash samples (Data referenced) (14).

	*Carbon			pН	
BA	GA	PA	BA	GA	PA
wt.%	wt.%	wt.%			
70.73	3.07		10.41	9.69	
66.41	3.71	5.94	10.49	10.05	11.16
52.76	5.76	6.62	10.74	10.28	12.13
21.56	3.24	19.16	12.12	10.36	13.2
13.85	6.11	36.08	12.56	10.41	13.36
17.17	3.67	5.75	12.22	10.43	13.53
51.79	5.13	5.64	12.49	10.36	13.46
	BA wt.% 70.73 66.41 52.76 21.56 13.85 17.17 51.79	*Carbon BA GA wt.% wt.% 70.73 3.07 66.41 3.71 52.76 5.76 21.56 3.24 13.85 6.11 17.17 3.67 51.79 5.13	*Carbon           BA         GA         PA           wt.%         wt.%         wt.%           70.73         3.07           66.41         3.71         5.94           52.76         5.76         6.62           21.56         3.24         19.16           13.85         6.11         36.08           17.17         3.67         5.75           51.79         5.13         5.64	*Carbon         BA         GA         PA         BA           wt.%         wt.%         wt.%         wt.%         wt.%           70.73         3.07         10.41         66.41         3.71         5.94         10.49           52.76         5.76         6.62         10.74         21.56         3.24         19.16         12.12           13.85         6.11         36.08         12.56         12.56         17.17         3.67         5.75         12.22           51.79         5.13         5.64         12.49	*Carbon         pH           BA         GA         PA         BA         GA           wt.%         wt.%         wt.%         wt.%            70.73         3.07         10.41         9.69           66.41         3.71         5.94         10.49         10.05           52.76         5.76         6.62         10.74         10.28           21.56         3.24         19.16         12.12         10.36           13.85         6.11         36.08         12.56         10.41           17.17         3.67         5.75         12.22         10.43           51.79         5.13         5.64         12.49         10.36

Table 3.1. Mean total carbon contents and pH of bottom ash samples of boiler, gasifier and pellet burner.

\*Data referenced from (15) and on a dry basis

#### 3.3.2. pH analysis

Table 3.1 shows the distribution of the pH for the PA, GA and BA samples. Ash from all three systems was high in pH but recorded different pH readings. Ash from the gasifier was the least alkali, followed by the boiler then the pellet burner. The as-received (AR) samples for the gasifier, boiler and pellet burner were 10.36, 12.49 and 13.46 respectively. It was observed that the pH increased for all ash samples as the particle size fraction decreased, with the exception of the particle size fractions < 150  $\mu$ m for the for BA. The increase in pH may have been due to the increase in concentrations of the alkali earth metals (described later) as the particle size fractions decreased potentially leading to higher concentrations base-forming metal salts.

Particle Size									_
(µ)m	Cr	Cu	Ni	Pb	V	Co	Mo	As	Cd
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
PA									
850	49.58	61.23	229.59	7.22	14.70	6.74	3.13	0.49	0.50
425	47.32	108.91	175.40	3.55	15.03	6.90	3.55	0.80	1.91
250	79.91	135.53	109.48	4.17	14.30	7.67	4.01	0.85	3.69
150	52.09	153.60	69.70	2.07	12.85	7.54	4.52	0.84	4.45
<150	52.38	170.72	40.65	2.74	10.18	7.93	5.24	0.98	9.46
AR	54.13	132.47	54.50	0.44	10.55	7.20	4.82	0.92	7.71
Gasifier ash									
2000	23.40	16.66	20.00	0.63	29.37	5.29	0.48	1.39	0.03
850	12.81	37.75	19.09	7.36	21.95	4.17	1.15	1.76	0.04
425	18.54	31.30	27.23	1.72	20.71	4.63	0.74	1.40	0.07
250	35.33	60.97	68.13	5.12	29.65	7.35	4.30	6.31	0.30
150	44.54	66.37	67.74	4.10	28.57	7.04	3.33	4.85	0.31
<150	47.57	207.57	78.81	4.20	33.41	7.86	5.33	7.49	0.44
AR	33.51	43.38	60.74	1.64	28.53	6.78	4.13	5.42	0.27
Boiler ash									
2000	5.84	34.01	6.89	3.34	3.50	1.56	1.51	0.52	2.21
850	4.64	81.52	6.31	9.59	4.14	1.86	1.40	0.69	2.85
425	10.36	50.42	11.06	7.09	12.16	3.23	1.61	1.14	4.11
250	19.87	77.59	19.05	9.99	18.54	5.17	2.29	1.82	6.18
150	30.00	107.49	25.07	9.00	24.49	6.70	2.71	2.07	6.18
<150	28.97	419.58	25.36	13.86	24.66	6.99	2.79	2.37	7.52
AR	11.82	32.85	13.39	4.89	12.44	3.79	1.88	1.45	4.76
*Environmental									
Limits	1060	2200	180	500		150	20	75	20
*Environme	ntal limi	ts for ash	intended	for land	applicat	tion in B	.C., Can	ada (17)	

 Table 3.2. Concentration and distribution of trace elements for samples of boiler, gasifier and pellet burner bottom ash (dry basis).

(Expressed on an AR basis)

### 3.3.3 The concentration and distribution of elements in ashes and anion distribution

## Trace elements

The concentrations of elements for the as-received ash and within specific particle size fractions of Cr, Cu, Ni, Pb, V, Co, Mo, As and Cd are shown in Table 3.2. Of the as-received ash samples analysed, Cu from the Pellet burner system was highest in trace element concentration; 132 mg/kg for Cu (Table 3.2). Cu was enriched in pellet burner ash by  $\sim$  3 and  $\sim$  4 times that of the gasifier and the boiler samples, respectively. This could have been from the contamination of metals used in manufacturing the pellet burner. The elements Ni and Cr followed next in concentrations, ranging from 33 - 55 mg/kg for the pellet burner and gasifier as-received ash. The boiler samples were  $\sim$  5 times lower than the pellet burner ash in both Ni and Cr contents. In most results, the boiler samples were slightly lower in trace metal concentrations. All elements in the as-received fractions of the 3 ash samples were well within the British Columbia soil amendment limits (17).

Table 3.2 also shows the distribution of trace elements within particle size fractions for the respective ash. For most elements, a slight increase in concentration was observed as the particle size fraction decreased in all ash types. All fractions for each element were within the environmental limits for soil amendments in British Columbia, except the 850  $\mu$ m fraction of Ni, obtained from the pellet burner ash; concentration of 229 mg/kg. While not exceeding the limit, the 425  $\mu$ m fraction also had a high concentration of 176 mg/kg Ni. It is evident that some elements are more concentrated in specific fractions of ash. The results suggest that fraction separation can be a useful method to isolate fractions containing higher amounts of some metals.

This method may be a useful technique for isolating elements exceeding environmental exposure limits and at the same time rendering the residual ash useful.

Elements	BA	GA	PA
	wt.%	wt.%	wt.%
Ca	60	61	55
K	15	10	21
Mg	6	6	11
Al	4	7	2
Mn	4	3	6
Fe	3	6	1
Р	3	3	2
Na	2	2	1
Remaining elements	2	2	1

Table 3.3. Percent total metal distribution in boiler, gasifier and pellet burner ash.

(Expressed on an AR basis)

Table 3.3 displays the percent of total ash forming elements in each ash sample. These percentages were obtained by taking the sum of all the total metal content found in 1 kg (d.b) of ash. All samples were significantly enriched in both Ca (50-61 wt.%) and K (10-26 wt.%). The high weight percent metal content found in these ash are expected for woody biomass ash. The elements Mg, Al, Mn, Fe, P and Na each contributed 10 % or less to the total elemental portion of the ash. The other inorganic elements present in ash, though not mentioned in the table cumulatively contributed 2 % or less to the total metal content of the ash under study and are not discussed in this paper. All analysis were based on the top eight most concentrated elements Ca, K, Mg, Al, Mn, Fe, P and Na.

The elements Al, P, Mg, Mn, Na, Fe, K, and Ca are shown in Table 3.4. The table shows that the concentration of P, Mn, Mg, K and Ca were found to be higher in pellet burner ash when compared to the other two ash types. The elements Al, Fe, and Na were present in higher quantities in the gasifier ash when compared to the other two ash types. Additionally, the pellet burner ash contained  $\sim 4$  times higher concentrations of K, Mg and Mn, than the other ash types.

Ca was only ~2 times higher in pellet ash. Some degree of variation in concentrations is expected due to the likely variation of fuel types, temperatures and other factors. Research has shown that calcium concentrations increase at temperatures below 900 °C which is primarily due to the decomposition of calcium carbonates (18). Above 900 °C, the Ca concentration also increases due to the dissociation and volatilization of potassium oxide formed after dissociation. The variation in oxide and/or carbonate concentrations bound to the ash will affect the concentration of the elements in samples when concentration is calculated on a weight basis.

Particle Size								
(µ)m	Ca	Al	Mg	Na	K	Р	Mn	Fe
	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
PA								
850	136000	9270	25100	1610	61800	3880	11200	9970
425	196000	10500	35200	2760	99300	6610	16900	9060
250	240000	9760	46100	3460	113000	8110	22600	8880
150	253000	9190	51400	3410	106000	8260	25200	7990
<150	263000	7560	56500	2850	95700	8550	28100	6170
AR	246000	7690	50900	2850	95200	8080	25800	6660
GA								
2000	20900	11900	4970	4970	5000	932	854	12700
850	19800	9900	4210	4210	9120	1080	1020	10700
425	27400	11900	5360	5360	12900	1380	1510	11900
250	141000	16100	14000	14000	20800	6960	7270	12700
150	113000	16300	12200	12200	20700	5570	6070	12900
<150	167000	15900	15700	15700	18400	8180	8460	12800
AR	125000	14900	12300	12300	20100	6030	6520	12300
BA								
2000	46400	2420	4520	2460	26000	2090	2690	1560
850	51600	2730	4950	2550	25300	2420	2970	1800
425	62700	6210	6450	2470	22500	3060	3620	4730
250	122000	10000	12200	2620	22400	6480	7230	7610
150	153000	12100	14900	2790	20800	8260	9080	10100
<150	167000	12100	16300	2790	21500	9140	10100	9760
AR	92600	6760	8970	2510	23400	4850	5390	5190

Table 3.4. The concentration of major ash forming elements within particle size fractions for boiler, gasifier and pellet burner on a dry basis.

#### Major elements general trends (AR)

## Major elements general trends (within fraction)

Within fractions, it was observed that P, Mg, Mn, Na, and Ca either increased with decreasing particle size or remained relatively constant. Ca was highest in concentration within each fraction and for all ash types (Table 3.4). The highest values reported for Ca were seen in Pellet burner ash, from ~136,000 to ~262,000 mg/kg moving from fractions 2000  $\mu$ m to <150  $\mu$ m. Additionally, K was found to be highest in the pellet burner ash, containing concentrations ranging from ~62,000 to ~112000 mg/kg when moving from 2000  $\mu$ m to 250  $\mu$ m fractions. While most of the elements were present in higher quantities in pellet burner ash as compared to other ash types, Al, Na and Fe were present in higher concentrations in gasifier ash.

The concentration of each element not only varies across different systems but within fractions as well. This variation in concentrations poses a difficulty in the general application of bottom ash to soils due to the lack of standardization in ash quality. According to (19), ash recycling to agricultural lands can help reduce the use of artificial fertilizers and close the natural mineral cycle. This is largely due to the presence of N, P and K in biomass ash. However, (7) suggests that the use of biomass ash as a soil fertilizer is limited due to a number of deficiencies in ash. The author noted that biomass ash can only be a source of K because ash from thermal sources is low in N and the P present has a very low solubility at soil conditions. In previous research on the same ash, the ultimate analysis showed N content all less than 1 wt.% on a dry basis for all ash samples (14). Wood naturally has low N contents. Furthermore, due to the conversion of most of the wood N to NH<sub>3</sub>, NOx and/or N<sub>2</sub> during the combustion of the wood, it is expected that the nitrogen content be low (18)(20)(11).

sieve	BA	GA	PA	
size/ µm	mg/kg_	mg/kg	mg/kg	
2000	2.29	0.74		
850	2.57	0.15	0.29	
425	0.35	0.32	3.64	
250	-	0.22	1.67	
150	-	0.1	1.87	
<150	~	0.23	0.66	
AR		0.08	0.83	

Table 3.5. The concentration (dry ash basis) of water soluble phosphates relative to particle size distribution for boiler gasifier and pellet burner ash.

While the percent mass of phosphorus in the metal contents of the samples ranged from 1-3%, the amount that is available for plant uptake or that is water soluble must be considered, this was measured in the form of phosphates (PO<sup>-3</sup><sub>4</sub>). Phosphorous, may exist in both organic and inorganic forms (17). The total and plant available phosphorous may vary. Water soluble phosphorus is the amount of phosphorus that is readily available to plants (21) (22). Research conducted on wood based biomass in an incinerator reported that the water soluble phosphorus content in bottom ash sample is negligible (22). The research concluded that the poor water solubility of phosphorus was a drawback in the application of wood ash to soils since only a small portion P is extractable and available for plants when used in forest fertilizers. Our research showed some amounts of water soluble phosphorus present in the form of phosphates, though low in concentrations (Table 3.5). The as-received ash for the pellet burner and gasifier were 0.83 mg/kg and 0.08 mg/kg, respectively, while the boiler ash was below the detection limit. Concentrations varied within particle size fractions. The pellet ash ranged from 0.66 - 3.6 mg/kg; lowest observed in particle size fraction < 150 µm and the highest in 425 µm fraction. The gasifier ash ranged from 0.1 - 0.74 mg/kg for the different fractions. The water soluble phosphate were only detected within the three largest particle size fractions for the boiler ash and ranged between 0.35 - 2.57 mg/kg. While the three samples fractions of the boiler samples had higher concentrations of phosphorus, water soluble phosphorus were not detected for these fractions. It does suggest that the phosphorus present in these fractions may be insoluble in water.

The presence of relatively high Ca and Mg, typically in the form of oxides, hydroxides and carbonates, suggests use of these ashes as potential liming agents. This could help in controlling soil pH. As the particle size fraction decreased, the concentrations of Ca and Mg increased and so did the pH. Therefore, specific fractions could be used to achieve appropriate liming requirements. *Inorganic relationship to total carbon content* 

The results were also analysed to identify the possibilities of any relationship that may exist between the elemental distribution of major inorganic components and the total carbon content (14). Figures 3.3a and 3.3b shows a graphical display of the elements Ca, and P versus total carbon. These two elements showed a linear correlation for boiler sample; most of the carbon (over 60 %) in this sample was organic carbon. A strong correlation was obtained with  $R^2$  value of 0.9272 and 0.9218 for Ca and P, respectively. The equations are displayed in equations 3.1 and 3.2. As a general trend, as the total carbon content increases the elemental concentrations for Ca and P decrease. These equations may help in determining the approximate amount of certain nutrients that may be present in ash. It would be worth removing as much carbon as possible to increase the concentration of nutrients.

$$y = -1969C + 182159 \qquad R^2 = 0.9272 \tag{3.1}$$

$$y = -113.92C + 9973.5$$
  $R^2 = 0.9218$  (3.2)

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No major trend or correlation was observed when samples from the gasifier and pellet burner were analysed. This may have been due to the very low carbon distribution within the particle size fractions for each sample.

The presence of organic carbon in ash, if recycled to forest soils presents a challenge. Unburned carbon creates a dilution effect which reduces the concentration of inorganic nutrients available in the ash (10). This is evident from the two correlations above where the metal content increases with the decreasing carbon contents. If a high concentration of carbon is present in ash, greater amounts of ash will be required to fulfill the nutrients demand by the soil. It should be noted that high carbon ash has also been associated with elevated concentrations of environmentally harmful products of incomplete combustion, such polycyclic aromatic compounds (PAH) (10)(23); other work with these ashes has shown very low concentrations of PAHs, dioxins and furans (data not shown). The presence of carbon also reduces the ability of the ash to harden, which is integral to improving the handling of ashes and reducing its solubility (10). This property limits its application to soil. Perhaps, if suitable methods for recirculating and reburning high carbon ash are determined, higher nutrient concentrations could be obtained while at the same time tackling some of existing ash related issues.



(b)

Figure 3.2a and 3.2b Correlation of calcium (Ca) and phosphorus (P) concentrations, respectively, as a function of total carbon found in boiler ash.

On the other hand, should high carbon ash possess similar properties as biochar then it could be used to obtain positive results in soil applications. Research has shown that biochar addition to soil may enhance properties, increasing plant growth nutrient availability, cation exchange capacity, water retention and with a reduction in the release of some greenhouse gases (24)(25)(26). Further studies are needed to determine if high carbon ash could also have these positive effects.

#### **3.4 Conclusion**

The inorganic element contents, pH and phosphate distribution of wood ash samples obtained from a fixed-bed boiler, fixed-bed gasifier and pellet burner were characterised. The samples showed variations in pH values both within particle size fractions and across the three systems. The as-received (AR) samples for the gasifier, boiler and pellet burner ash had a pH of 10.36, 12.49 and 13.46, respectively. The pH increased with decreasing particle size fractions. This increase in pH may have been due to the increase in concentrations of the alkali earth metals as the particle size fractions decrease, forming higher concentrations of base-forming metal salts.

The trace element contents for the AR samples of the three ash types were all within the environmental limits for soil amendments in British Columbia, Canada. However, when analyzed within particle fractions, Ni with a concentration of 229 mg/kg from the pellet burner ash, exceeded the limit within the particle size fraction  $\geq$  850 µm but < 2000. The AR samples were significantly enriched in both Ca (50-61 wt.%) and K (10-26 wt.%) on a total metal composition. The highest values reported for Ca were seen in Pellet burner ash, from ~136,000 to ~262,000 mg/kg. Very low concentrations of water soluble phosphates were obtained for all ash types in some case below

the detection limit. A strong inverse correlation was developed between the total carbon present and the metal contents for Ca and P.

These results suggest that fraction separation can be a useful method to isolate fractions containing higher amounts of some metals. This method may be a useful technique for elements exceeding environmental exposure limits.

However, the variation in concentrations poses a difficulty in the general application of bottom ash to soils due to the lack of standardization in ash quality. As shown from the research, the inorganic content of the ash samples varied across systems and within fractions. In addition to known factors such as fuel type and temperature, the research showed that other factors such the carbon content and particle size could play a role in determining the concentrations of the available inorganics. It is therefore difficult to determine standard compositions of ash.

### References

- Dahl, O.; Nurmesniemi, H.; Poykio, R.; Watkins, G. Heavy metal concentrations in bottom ash and fly ash fractions from a large sized (246MW) fluidized bed boiler with repect to their Finnish forest fertilizer limit values. *Fuel Processing Technology*. 2010, Vol. 91, 1634-1639.
- Obernberger, I.; Biedermann, F.; Widmann, W.; Riedl, R. Concentrations of inorganic elements in biomass fuels and recovery in different ash fractions. *Biomass and Bioenergy*. 1997, Vol. 12, 211-224.
- Picco, D. Technical assistance for the development and improvement of technologies methodologies and tools for enhanced use of agricultural biomass residues. Goriza, IT : C.E.T.A- Centro di Ecologia Teorica ed Applicata, February 2010.
- 4. Clarholm, M. Granulated wood ash and a N-free fertilizer to a forest soil-effects on P availability. *Forest Ecology and Management*. 1994, Vol. 66, 127-136.
- 5. Vance, E. Land application of wood-fired and combustion boiler ashes: an overview. *Journal* of Environmental Quality. 1996, Vol. 25, 937-944.
- Demeyer, A.; Voundi-Nkana, J.; Velow, M. Characteristics of wood ash and influence on soil properties and nutrient uptake: An overview. *Bioresource Technology*. 2001, Vol. 77, 287-295.
- Pels, J.; de Nie, D.; Kiel, J. Utilization of ashes from biomass combustion and gasification. Paris, France : Published at 14th European Biomass Conference & Exhibition, October 2005.
- Stupak, I.; Asikainen, A.; Röser, D.; Pasanen, K. Review of recommnedation for forest energy harvesting and wood ash recycling. In: Roser, D.; Asaikainen, A.; Raulund-Rasmussen, K.; Stupak, I (eds). Sustainable use of forest biomass for energy. Heidelberg : Springer, 2008. pp 155-196.
- 9. Aronsson, K.; Ekelund, N. Biological effects of wood ash application to forest and aquatic ecosytems. *Journal of Environmental Quality*. 2004, Vol. 33, 1595-1605.
- 10. Sarenbo, S. Wood ash dilemma reduced quality due to poor combustion performance. *Biomass and Bioenergy*. 2009, Vol. 33, 1212-1220.

- Knapp, B.; Insam, H. Recycling of biomass ashes: current technologies and future research needs. [book auth.] Insam H. Knapp B. *Recycling of Biomss Ashes*. New York : Springer, 2011.
- Narodoslawsky, M.; Obernberger, I. From waste to raw material the way of cadmium and other heavy metals from biomass to wood ash. *Journal of Hazardous Mateials*. 1996, Vols. 50 (2-3), 157-168.
- Liao, C.; Wu, C.; Yan, Y. The characteristics of inorgani elements in ashes from a 1MW CFB biomass gasification power plant. *Fuel Processing Technology*. 2007, Vol. 88, 149-156.
- 14. James, A.K.; Thring, R.W.; Helle, S.; Rutherford, P.M. Characterization of biomass bottom ash from an industrial-scale fixed bed boiler. Toronto, 3rd International Conference on Environmental Pollution and Remediation 2013.
- 15. Hermann, T.; Baker, S. Evaluating particle size. Kansas : Kansas State University Agricultural Experiment Station and Cooperative Extension Service, 2002.
- 16. Kalra, Y.; Maynard, D. Methods manual for forest soil and plant analysis. Alberta : Forestry Canada, 1991. Report No. NOR-X-319.
- BC Ministry of Environment. Land application guidelines for the organic matter recycling regulation and the soil amendment code of practice. New Westminister, BC : SYLVIS Environmental, 2008. Report No. 758-08.
- 18. Misra, M.; Ragland, K.; Baker, A. Wood ash composition as a funtion of furnace temoperature. *Biomass and Bioenergy*. 1993, Vols. 4, No2, pp. 103-116.
- 19. Obernberger, I.; Supancic, K. Possibillities of ash utilisation from biomass combustion plants. Proceedings of the 17th European Biomass Conference & Exhibition. Hamburg: ETA Renewable Energies, June/July 2009.
- Steenari, B.; Karlsson, L.; Lindqvist, O. Evaluation of the leaching characteristics of wood ash and the influence of ash agglomeration. *Biomass and Bioenergy*. 1999, Vol. 16, 119-136.
- Fuhrman, J. K.; Zhang, H.; Schroder, J. L.; Davis, R. L. Water-soluble phosphorus as affected by soil to extract ratios, extraction times and electrolyte. *Communication in Soil Science and Plant Analysis.* 2005, Vol. 36, 925-935.
- 22. Nurmesniemi, H.; Manskinen, K.; Pöykiö, R.; Dahl, O. Forest fertilizer properties of the bottom ash and fly ash from llarge-sized (115 MW) industrial powerplant incinerating wood-based biomass residues. *Journal of the University of Chemical Technology and Metallurgy.* 47, 2012, Vol. 1, 43-52.

- Bundt, M.; Krauss, M.; Blaser, B.; Wilcke, W. Forest fertilization with wood ash: effect on the distribution and storage of polycyclic aromatic hydrocarbons (PAHs) and poly choloronated biphenyls (PCBs). *Journal of Environmental Quality*. 2001, Vol. 30, 1296-1304.
- 24. Robertson, S.; Rutherford, M.; Lopez-Gutierrez, J.; Massicotte, H. Biochar enhances seedling growth and alterss root symbioses and properties of sub-boreal forest soils. *Canadian Journal of Soil Science*. 2012, Vol. 92, 329-340.
- 25. Laird, D. The charcoal vision: a win-win-win scenario for simultaneously producing bioenergy, permanent sequestering carbon, while improving soil and water quality. *Agron. Journal*. 2007, Vol. 100, 178-180.
- 26. Lehmann, J. A handful of carbon. Nature. 2007, Vol. 447, 143-144.

## Preface

Chapter 4 of this thesis has been prepared as a manuscript draft and will be submitted for possible publication shortly.

# CHAPTER 4: Investigation of Air and Air-Steam Gasification of High Carbon Wood Ash in a Fluidized Bed Reactor

#### 4.1. Introduction

The pulp and paper industry produces large volumes of high carbon ash obtained from boilers. While the carbon content is relatively high in this residue, the energy content of all of the ash produced is approximately 1 % of the energy content of the wood. Combustion of the high carbon ash presents a number of operational problems such as corrosion and scouring, and due to boiler design the ash may be carried by the flue gas through the boiler tubes. The variability of particles also causes inherent problems in a fixed bed system. Fixed bed systems usually require a feedstock that is as uniform as possible to avoid channeling (1) (2). The costs associated with changing the system to a more recent design is high.

High carbon ash is considered to have very little potential economic and environmental benefit at this stage and is typically sent to landfills. The application of bottom ash as a soil additive is restricted in British Columbia. Other options for utilizing high carbon ash must be explored, including use as a low cost feedstock for gasification to recover as much energy as possible, while reducing ash volume.

Biomass gasification is one technology which applies biomass to produce heat and electricity (3)(4). Biomass gasification is a thermo-chemical process of gaseous fuel production by partial oxidation of a solid fuel (3). Gasification results in producer gas containing CO, H<sub>2</sub>, CnHx and some other gases (4). The main objective is to generate a combustible gas rich in CO, H<sub>2</sub> and CH<sub>4</sub> with medium to high lower heating value (LHV) (5)(6). Operating conditions such as temperature, equivalence ratio (ER) and steam/biomass (S/B) ratio play important roles in biomass gasification.

Bed temperature is one of the most important operating parameters in gasification. Affecting both the heating value and the producer gas composition (5). The heat needed for air gasification is provided by the heat of combustion of the biomass. Therefore high temperatures improve biomass combustion and consequently increase  $CO_2$  production, lowering the heating value of the produced gas. A high bed temperature improves carbon conversion and steam cracking and reforming of tars, resulting in less char, reduced tar formation and higher gas yields (5)(7)(8).

The equivalence ration (ER) strongly influences the type of gasification. More combustion occurs at high ER, increasing CO<sub>2</sub> production (5)(9). A higher air flow rate results in higher gas velocities, improving the combustion of solid char due to improved oxygen diffusion (9)(10). An air ratio of 0.2 - 0.3 is most favourable for producing CO-rich gas (11). When steam is the gasifying agent, H<sub>2</sub> and CO<sub>2</sub> increase, while CO decreases due to the water gas shift reaction (12).

Fluidized bed reactors have been widely applied for gasification, pyrolysis and combustion of a wide range of particulate materials including biomass (13). Distinct advantages include high heat transfer, uniform and controllable temperatures, favourable gas-solid contact and the ability to handle a wide range of particulate properties such as particle diameter. Fluidized bed reactors also accommodate wide variations in fuel quality.

Air-blown biomass gasification produces low calorific value gases, with higher heating values of  $4-7 \text{ MJ/Nm}^3$ , whereas oxygen and steam-blown processes result in a HHV of 10-18 MJ/Nm<sup>3</sup> (11). Circulating fluidized bed gasifier (CFB) test using various feedstocks such as, spruce-pine-fir sawdust mixture, 1:1 ratio of pine bark and spruce whitewood mix, cypress, hemlock and cedar-hemlock mixtures have produced gases with HHV from 2.43 - 6.13 MJ/kg, with either air or air-steam as the gasifying agent. For example, in a fluidized bed experiment at atmospheric

temperature, the gasification of pine saw dust produced a LHV of  $6.74 - 9.14 \text{ MJ/Nm}^3$  in an airsteam medium at ER = 0.22 (14).

The research carried out in this study was intended to determine the feasibility of gasifying high carbon wood ash particles smaller than 3 mm to identify whether they behave similarly to unburned wood when gasified. Test were carried out to,

- 1. Determine the range of equivalence ratios for stable operation.
- 2. Determine the calorific value of the producer gas with air and air-steam agents to ascertain the potential of producing a low to medium calorific value syngas.
- 3. Measure the carbon conversion efficiency.
- 4. Calculate the product gas yield.

## 4.2. Experimental

#### 4.2.1 Feed materials

Wood ash particles from an industrial scale fixed-bed boiler (Canfor Pulp Mill, Prince George, BC) were the feedstock in the study. Hog fuel is used in this boiler comprised predominantly of softwood sawmill waste derived from pine wood. Silica sand was the inert bed material. The proximate and ultimate analyses of the ash are provided in Table 4.1.

Higher heating value (MJ/kg)	11.60	
Proximate analysis (wt.% dry basis)		
Volatile Matter	21.5	
Fixed	28.8	
Ash	49.7	
Ultimate analysis (wt. % dry basis)		
С	48.5	
Н	0.9	
0	33.4	
Ν	0.2	
S	0	
Other ash forming elements	17.0	

Table 4.1. Proximate and ultimate analyses of boiler ash

O – Calculated by difference

#### 4.2.2 Gasification setup

Air gasification and air-steam gasification were carried out in a lab-scale bubbling fluidized bed reactor. Constructed from 310 stainless steel 3-inch diameter (nominal) pipe (I.D. = 77.9 mm) of height of approximately 800 mm. Two electric heaters supplied heat to the reactor. The reactor was charged with 1.4 kg of sand as bed material. A pressure tap located in the biomass feeder was used to control and facilitate the discharge of feedstock. The bed was fluidized by air and nitrogen introduced below the distributor. Water was pumped to the reactor then vapourized, with its flow rate measured by a steam flow meter. The biomass feedstock was fed from the side of the reactor through an atomizer nozzle, covered by a cooling jacket to keep the feedstock temperature below 80°C, to avoid plugging by thermal decomposition. The produced gas flow exited the reactor at the top and passed through a cyclone to prevent tar condensation. Excess steam in the product gas was separated by a condenser, while fine ash and char particles were captured by an internal cyclone, supplemented by a filter after the condenser and a waste bin. The product gas flow rate was measured by a rotameter combined with a thermocouple and a pressure transducer.

### 4.2.3 Experimental procedure

The feedstock was added to the hopper prior to the experimental run. The gasifier and furnace heaters for air preheating were turned on, and controllers were set at the selected operating temperatures. With sand as the bed material, the reactor was charged with ~ 7 L/min of nitrogen to assist with fluidization and aid heat transfer. The feedstock was then fed at 176 g/h, with an air supply of 0.282 Nm<sup>3</sup>/h from the bottom of the reactor to provide an ER of 0.12. When the system reached steady state, gas samples were taken at 4 min intervals. Experiments were conducted at various bed temperatures within the range of 650 – 770°C. The reactor was then operated at a fixed temperature of 775°C while varying the ER.

For air-steam gasification, water was introduced to the reactor at varying steam/biomass (S/B) ratios and a fixed temperature of 715°C and a fixed ER of 0.12, with gas sampling as for air only.



Figure 4.1. Schematic diagram of biomass air and air-steam gasification in a bubbling fluidized bed. T – Thermocouple P- Pressure sensor R- Rotameter

#### 4.2.4 Gas analysis

The concentrations of H<sub>2</sub>, N<sub>2</sub>, CO, CO<sub>2</sub> and  $C_nH_x$  were measured by a micro-gas chromatograph CP-4900 (Varian Inc.) equipped with a CO<sub>x</sub> column and a thermal conductivity detector.

#### 4.2.5 Analyses of experimental results

To assess the gasification process, variables such as Equivalence Ratio (ER), carbon conversion efficiency and higher heating values (HHV) were determined as follows.

$$ER = \frac{\text{weight of air /weight dry biomass}}{\text{stoichiometric air/biomass ratio}}$$
(4.1)

$$S/B = \frac{\text{steam feed rate+ moisture introduced with fuel (g/h)}}{\text{Total fuel feed rate (g/h)}}$$
(4.2)

Carbon conversion efficiency = 
$$\frac{\text{gas velocity x1000[C0\%+C02\%+3(C3H8\%)]}\frac{12}{24.79}}{\text{biomass feed flow rate x C\%}}$$
(4.3)

where produced gases are in volume %, gas flow rate is  $(Nm^3/h)$ , feed flow rate (g/h) and C %, is the biomass percent carbon based on the ultimate analysis. The higher heating value is estimated from equation 4.4.

$$HHV = (12.75 H_2 + 12.63 CO + 39.82 CH_4 + 63.43C_2H_4 + 99C_3H_8...) / 100$$
(4.4)

where the species contents are in mol % and their heats of combustion in MJ/Nm<sup>3</sup> (11) (15).
## 4.3. Results and Discussion

#### 4.3.1 Air Gasification

### Effect of reactor temperature.

Analysis of the gas produced was carried out for reactor temperatures (electronically displayed) ranging from ~ 650 to ~ 770°C in increments of approximately 30°C. From Figure 4.2, it can be seen that the CO concentration increased with temperature. All other gas concentrations remained nearly constant, except for  $CO_2$  whose concentration decreased with increasing temperature. The gases produced were predominantly influenced by the reactions:

С	$+\frac{1}{2}O_2 \to CO$	partial oxidation	(4.5)
С	$+ O_2 \rightarrow CO_2$	complete combustion	(4.6)
С	$+H_2O \rightarrow CO + H_2$	water-gas shift	(4.7)

Hence the C present in the fuel as char reacted directly with the O supplied by the air to produce CO, an exothermic reaction. CO production favoured higher temperatures, resulting in loss CO<sub>2</sub> generation with increasing temperatures. The reactions were being carried out at ER = 0.12, below the ideal ER range of 0.2 - 0.3 (Li X, 2004). The limited O<sub>2</sub> fed resulted in a high CO : CO<sub>2</sub> ratio. This would result in greater concentrations of CO instead of CO<sub>2</sub>. The H concentration remained low and relatively constant, in part because there was very little H in the fuel. CH<sub>4</sub> could not be detected but propane was found at very low concentrations. Table 4.2 summarizes the results when temperature was varied during air gasification. The carbon



Figure 4.2. Effect of temperature on gas composition. Biomass feed rate: 176 g/h; ER: 0.12.

conversion efficiency increased from 31.2 to 52.9 %, with increasing temperature, limited by the low H content and the lack of O to the reactor. The higher heating values increased with increasing temperature from 0.77 to 1.64 MJ/Nm<sup>3</sup>. The percentage increase in HHV, increased by  $\sim 40\%$  between 657 and 675°C, thereafter approximately 10% for each temperature rise studied. The monotonic increase resulted from the improved carbon conversion, at higher temperatures. The gas yield ranged from 2.26 to 2.53 Nm<sup>3</sup>/kg and increased for the first two temperature rises then slightly decreased at 771°C.

Table 4.2. The effect of temperature on various parameters during air gasification. Biomass feed rate: 176 g/h; ER: 0.12.

Lowed Bed temperature (°C)	657	675	698	740	771
HHV (MJ/Nm <sup>3</sup> )	0.77	1.01	1.39	1.54	1.64
Carbon conversion efficiency (%)	<sup>′</sup> 31.2	45.6	48.3	49.9	52.9
Gas yield (Nm <sup>3</sup> /kg)	2.26	2.49	2.53	2.53	2.48



Figure 4.3 Effect of ER on gas composition. Biomass feed rate: 176 g/h; Temperature: 775 °C

## Effect of ER.

The effects of ER on a number of factors were studied, with ER ranging from 0.12 to 0.25 and the reactor temperature 775°C. No significant variation was seen between ER of 0.12 to 0.25. While CO concentrations remained relatively constant, the concentration of H decreased, while that of CO<sub>2</sub> increased, with increasing ER (Figure 4.3). The CO concentration was higher than that of the other gases for all ER studied. The most significant variation in the gases under study was in CO<sub>2</sub>. The other gases showed very little change in concentration. The carbon conversion efficiency increased from 52.9 to 89.9 % when ER increased from 0.12 to 0.25 (Table 4.3). This increase in carbon conversion efficiency resulted from increased CO<sub>2</sub> (14). The calculated HHV, including N ranged from 1.64 to 2.38 MJ/Nm<sup>3</sup> as shown in Table 4.3. The HHVs recorded when ER was varied were higher than when the effect of temperature was investigated, where HHV increased with increasing temperature. The gas production yield ranged from 2.48 to 2.73 m<sup>3</sup>/kg. The gas production was highest for ER = 0.25. Based on carbon conversion efficiency, the optimum point for gasification was at an ER of 0.25.

ĒR	0.12	0.16	0.19	0.23	0.25
HHV (MJ/Nm <sup>3</sup> )	1.64	1.90	1.96	2.22	2.38
Carbon conversion e (%)	efficiency 52.9	63.8	68.2	79.7	89.9
Gas Yield (Nm <sup>3</sup> /kg)	2.48	2.51	2.44	2.64	2.73

Table 4.3. Effect of ER on higher heating value, carbon conversion efficiency and gas yield during air gasification Biomass feed rate: 176 g/h; Temperature: 775°C.

## 4.3.2 Air-Steam Gasification

Effect of steam-biomass ratio.

Analysis of the gas produced was carried out at S/B ratios from 0.4 to 2.2 and temperature of  $715 \pm 5^{\circ}$ C with ER of 0.12. It was difficult to maintain a fixed reactor temperature as some heat from the reactor converted the water into steam. Likewise steam gasification is an endothermic process. Due to the water gas shift reaction, the concentrations of CO<sub>2</sub> and H<sub>2</sub> increased with increasing S/B ratio, while the CO concentrations decreased, as seen in Figure 4.4.

As the S/B ratio increased the water gas shift reaction became more integral in the process, resulting in higher concentrations of  $H_2$  and  $CO_2$ .

The carbon conversion efficiencies increased when the S/B ratio increased from 0.4 to 1.3 and decreased thereafter (Table 4.4). The highest carbon conversion efficiency of 69.7 % was at a S/B ratio of 1.3, a steam flow rate of 0.216 kg/h, while the lowest value, 51.3 % was at S/B = 0.4. HHV ranged from 1.95 to 2.50 MJ/Nm<sup>3</sup>. The heating value (including N) reached a maximum at S/B = 1.3 due to increased production of CO<sub>2</sub> and H, reducing the calorific value of the producer gas (Gabra M, 2001). The volume of gas produced ranged from 2.45 to 3.19 m<sup>3</sup>/kg.

during an-steam gasification for biomass feed rate. 170 g/n, ER: 0.12, Temperature. 775 C.						_
SB	0.4	0.8	1.3	1.7	2.2	
HHV (MJ/Nm <sup>3</sup> )	1.95	2.29	2.26	2.50	2.11	
Carbon conversion efficiency (%)	51.3	63.2	69.7	66.7	54.2	
Gas Yield (Nm <sup>3</sup> /kg)	2.45	2.93	3.06	3.19	2.90	

Table 4.4. Effect of S/B ratio on higher heating value, carbon conversion efficiency and gas yield during air-steam gasification for biomass feed rate: 176 g/h; ER: 0.12; Temperature: 775°C.



Figure 4.4. Effect of S/B ratio on produced gas concentrations. Biomass feed rate: 176 g/h; Temperature: 715 °C, ER: 0.12.



Figure 4.5. H<sub>2</sub>/CO molar ratio as a function of temperature for air gasification. Biomass feed rate: 176 g/h; ER: 0.12



Figure 4.6 H<sub>2</sub>/CO molar ratio as a function of ER for air gasification. Biomass feed rate: 176 g/h; Temperature: 775°C



## Effect of temperature, ER and steam-biomass ratio on H2/CO

The H<sub>2</sub>/CO molar ratio was analysed based on the impact of temperature, ER and S/B ratio. As shown in Figure 4.5, molar ratio of H<sub>2</sub>/CO was less than 0.3 for the temperature range investigated and decreased with increasing temperature during air blown gasification. At 775°C, all H<sub>2</sub>/CO molar ratios were below 0.17 and decreased with increasing ER. For the air-steam blown process, as S/B ratio increased the H<sub>2</sub>/CO molar ratio also increased. The ratios were higher when compared to the air-blown processes and ranged from 0.4 to 1.75 (Figure 4.7). The injection of steam as a gasifying agent increased the H<sub>2</sub>/CO molar ratio because moisture promotes both steam gasification and the water gas shift reaction (11) (16).

While all three runs were at different operating conditions, the HHV can be compared at similar conditions. At ER = 0.12 and 698°C for the air blown process and at 714°C for the steamair gasification (S/B ratio of 0.4), the HHVs (including N) were 1.39 MJ/m<sup>3</sup> and 1.95 MJ/m<sup>3</sup> respectively. The heating value for the steam fed process was approximately 29 % higher than without steam.

As previously discussed, the HHV increased with increasing ER and the optimum carbon conversion efficiency was found at ER = 0.25. The increase in HHV from ER of 0.12 to 0.25 was approximately 31 % for the air blown process. Since the air-steam gasification was carried out at an ER 0.12, it is likely that the HHV would increase if the ER was increased to 0.25, producing gas with a higher calorific value. An increase in the highest calorific value of 2.50 MJ/Nm<sup>3</sup> might be seen. Research on sugar cane residue (bagasse) showed that a gas generated at 3.5 - 4.5 MJ/Nm<sup>3</sup> did not present any problems when burned (16). However, in order to get good burning of the gas to fuel a turbine, combustion should be close to the stoichiometric conditions. The potential of an even higher heating value suggests that the producer gas could be useful.

A high superficial gas velocity may cause entrainment of fine ash and carbon particles in the producer gas while too low a value may encourage defluidization in the reactor. While oversized particle sizes may not be fluidized and cause agglomerate (17), the feedstock under study had a low density relative to sand. No noticeable fusing of ash or ash-sand particles were observed on visually inspecting the particles after opening the reactor after each run. Hence, the possibility of reducing the fluidizing gas velocity could be considered. Gasification with N as a fluidizing gas dilutes the produced gas (18). Therefore, the calorific values were calculated on a N-free basis to give an idea of what range of heating values could be achieved. The minimum fluidizing flow used for the experiments was approximately 15.0 L/min. This was achieved by adding N to give the desired operating fluidization conditions. Further investigation should be carried to reduce the fluidizing flow in an effort to produce a higher calorific value producer gas.

## 4.4 Conclusion

- High carbon ash gasification in a bubbling fluidized bed reactor was successfully gasified at low temperatures and atmospheric pressure. Ash and woody biomass showed some similar trends for gasification and product gas formation.
- 2) The higher heating value of the producer gas at equivalence ratios from 0.12 to 0.25 were in the range of  $0.77 2.50 \text{ MJ/Nm}^3$  with gas yields from  $2.26 3.27 \text{ Nm}^3/\text{kg}$ .
- 3) The carbon conversion efficiency increased with increasing temperature and reached a maximum at an ER of 0.25.
- 4) The HHV increased with increasing temperature,  $650 770^{\circ}$ C.
- 5) The heating value for the steam fed process was approximately 30 % higher than without steam at otherwise similar operating conditions.
- 6) There may be some potential in producing a gas of higher calorific value from the air-steam process, since the air-steam run was carried out at a low ER. This would encourage additional uses of high-carbon ash. Also, if possible to lower the fluidizing velocity a gas of better HHV could be achieved.
- 7) The H<sub>2</sub>/CO molar ratio increased with the addition of air-steam over the range of S/B ratios studied, compared to air blown processes where the ratio decreased with increasing ER and also with increasing temperature.
- No noticeable fusing of ash or ash-sand particles was observed on visual inspection after run completion.

## References

- 1. Warnecke, R. Gasification of biomass: comparison of fixed bed and fluidized bed gasifier. *Biomass and Bioenergy*. 2000, Vol. 18, 489-497.
- Ryu, C.; Yang, Y.; Khor, A.; Yates, N.; Sharifi, V.; Swithenbank, J. Effect of fuel properties on biomass combbustion: Part 1. Experiments - fuel type, equivalence ration and particle size. *Fuel.* 2006, Vol. 85, 1039-1046.
- 3. Rade, K.; Karamarkovic, V. Energy and exergy analysis of biomass gasification at different temperatures. *Energy*. 2010, Vol. 35, 537-549.
- 4. Biomass gasification technology and utilisation. [Online] [Cited: March 28, 2013.] http://cturare.tripod.com/ove.htm.
- 5. Alauddin Z.; Lahijani, P.; Mohammadi, M.; Mohamed, A. Gasification of lignocellulosic biomass in fluidized beds for renewable energy development: A review. *Renewable and Sustainable Energy Reviews.* 2010, Vol. 14, 2852-2862.
- 6. Skoulou, V.; Koufodimos, G.; Samaras, Z.; Zabanioutou, A. Low temperature gasification of olive kernels in a 5-kW fluidized bed reactor for H2-rich producer gas. *International Journal of Hydrogen Energy*. 2008, Vol. 33, 6515-6524.
- 7. Pinto, F.; Franco, C.; Andre, R.; Tavares, C.; Dias, M.; Gulyurtlu, I.; Effect of experimental conditions on gasification of coal, biomass and plastics wastes with air/steam in a fluidized bed system. *Fuel*. 2003, Vol. 82, 1967-1976.
- 8. Chairprast, P.; Vitidsant, T. Promotion of coconut shell gasification by steam reforming on nickel-dolomite. *American Journal of Applied Science*. 2009, Vol. 6, 332-336.
- 9. Mandl, C.; Obernberger, I.; Biedermann, F. Modelling of an updraft fixed-bed gasifier operated with softwood pellets. *Fuel*. 2010, Vol. 89, 3795-3806.
- 10. Natarajan, E.; Nordin, A.; Rao, A.; Overview of combustion and gasification of rice husk in fluidized bed reactors. *Biomass and Bioenergy*. 1998, Vol. 14, 5/6, 533-546.
- 11. Li, X.; Grace, J.; Lim, C.; Watkinson, A.; Chen, H.; Kim, J. Biomass gasification in a circulating fluidized bed. *Biomass and Bioenergy*. 2004, Vol. 26, 171-193.
- 12. Devi, L.; Ptasinski, K.; Janssen, F. A review of primary measures for tar elimination in biomass gasification processes. *Biomass and Bioenergy*. 2003, Vol. 24, 125-140.

- 13. Cui, H.; Grace, R. J. Fluidization of biomass particles: A review of experimental multiphase flow aspects. *Chemical Engineering Science*. 2007, Vol. 62, 45-55.
- Lv, M.P.; Xiong, H.Z.; Chang, J.; Wu, Z.C.; Chen, Y.; Zhu, X.J. An experimental study on biomass air-steam gasification in a fluidized bed. *Bioresource Technology*. 2004, Vol. 95, 95-101.
- 15. Zhang, Y.; Li, B.; Li, H.; Liu, H. Thermodynamic evaluation of biomass gasification with air in autotherm gasifiers. *Thermochimica Acta*. 2011, Vol. 519, 65-71.
- Gabra, M.; Pettersson, E.; Backman, R.; Kjellstrom, B.; Evaluation of cyclone gasifier performance for gasification of sugar canre resifue - Part 1: gasification of bagasse. *Biomass* and Bioenergy. 2001, Vol. 21, 351-369.
- 17. Suarez, A. J.; Beaton, A. P.; Physical properties of Cuban coffee husk for use as an energy source. *Energy Sources*. 2003, Vol. 25, 953-959.
- Gil, J.; Corella, J.; Aznar, M.; Caballero, M. Biomass gasification in atmospheric and bubbling fluidized bed: Effect of the type of gasifying agent on the product distribution. *Biomass and Bioenergy.* 1999, Vol. 17, 389-403.

## Preface

Chapter 5 of this thesis has been prepared as a manuscript draft and will be submitted for possible publication shortly.

# CHAPTER 5: Catalytic Effect of Calcined Wood Ash during CO<sub>2</sub> Gasification of Biomass Char

## **5.1 Introduction**

With increasing use of bioenergy technologies comes increasing effort to improve process efficiencies. With a range of outputs, interest in biomass gasification is growing. A primary aspect of the gasification process is the variation in the reaction rate during char conversion (1). This variation may be due to a change in the reaction area as well as the change and distribution of the catalyst during gasification.

Research on catalyst for use in gasification process is often carried out specifically in relation to gasifier design and biomass feed type (2). The use of inexpensive, strong and easily regenerated catalysts can help produce a tar-free product gas, suitable syngas composition and higher gasification reactivity. Wood ash has been investigated for its catalytic effect where the presence of alkali and alkali earth metals have been reported to promote gasification (2)(3). However, research carried out on wood ash as a catalyst is not as extensive as research on catalysts made from salts or metals such as potassium. Potassium is considered to be a good catalyst, but needs to be recycled for cost efficiency (4). The porosity of ash combined with high metal and mineral content makes ash a suitable catalyst (5). Some of the minerals present in wood ash include CaO, MgO and K<sub>2</sub>O.

A mechanism suggested for catalytic gasification consists of an oxidation-reduction cycle in which oxygen is transferred to the carbon matrix through the catalytically active alkali species followed by the rate determining decomposition of the oxidised carbon site producing CO in the process (6)(7)(8). An oxygen containing alkali species active for oxygen transfer to a free carbon site results in a surface oxygen intermediate.

Research has shown that the use of wood ash as a catalyst during gasification of bituminous coal increased the reactivity by a factor of 9 and of wood by 32 at 700 °C, when compared to the uncatalyzed reaction (2)(9). Recent work has also shown that impregnating 9.5 wt% KOH in pine wood resulted in complete char conversion within 12 min under steam gasification conditions carried out at 700 °C (10). The use of the impregnated catalyst resulted in an increase in gasification rate by a factor of 30 compared to char that was not impregnated. The research also ranked the catalytic activities of a number of salts which are stated in decreasing order,  $KNO_3 >$  $KHCO_3 \approx K_2CO_3 \approx KOH > NaOH > CaO > K_2HPO_4 > KBr > KCl.$  In another work, the presence of alkali carbonates on biomass steam gasification at 650 °C and higher, resulted in a decrease in carbon conversion to gas, during volatilization but the rate and total amount of gas produced during gasification stage increased (2) (11). CO<sub>2</sub> co-gasification of switch grass with coal and fluid coke at 750 °C and 950 °C also showed that the biomass addition enhanced the rate of gasification (3). It was also believed that the formation of potassium aluminosilicate (KAlSi<sub>3</sub>O<sub>8</sub>) may deactivate the catalyst. The catalytic effect of hardwood ash containing 12 wt% K and 47 wt% Ca was investigated during steam-char (coal) TGA experiments at 700 °C and higher (12). The findings suggested that dry mixed wood ash increased the reactivity of the process but was slightly less than an equivalent amount of  $K_2CO_3$ . The application of a dry aqueous extract of the ash containing 39 wt% K provided an equivalent increase in reactivity to K<sub>2</sub>CO<sub>3</sub>.

The percentage distribution by weight of these ash forming compounds will vary depending on the type of feedstock and the combustion process that may have been employed. Agricultural and woody biomass often vary in metal concentrations and some metals are volatilized as the temperature increases during combustion. It is for this reason that a minimum standard for the type of ash and their concentrations should be determined if wood ash is to be considered a suitable catalyst.

The need to continuously find cheap, readily available and reusable catalysts is an important factor when considering catalyst application in energy production processes. This work investigates the use of two types of combustion ash, gasifier ash and a pellet burner ash, for their catalytic effects on woody biomass  $CO_2$  gasification by varying the percent catalyst loading. The research seeks to identify the effectiveness of using ash as a catalyst by determining rate of carbon conversions, gasification reactivities and the reactivity indices as well as identifying which of the ash could be a more effective catalyst.

## 5.2 Experimental

## Wood ash samples

Wood ash from a downdraft gasifier and a wood pellet burner (both located at the University of Northern British Columbia - UNBC) and char-ash from an industrial scale fixed bed boiler were used in this study. The fuel for both the gasifier and the industrial boiler is hog fuel, comprised predominantly of softwood sawmill waste derived from pine wood. The pellet burner utilizes wood pellets made locally from soft-wood saw dust.

## 5.2.1. Char and Catalyst Preparation

Approximately 100 g of char-ash (containing significant amounts of unburned carbon) obtained from the industrial fixed –bed boiler was sieved using a 2000  $\mu$ m sieve. The particles  $\geq$  2000  $\mu$ m (char) were retained and the rest discarded. The retained fraction (henceforth referred to as char) was crushed to particle sizes ranging from 63 – 150  $\mu$ m.

Approximately 100 g of gasifier ash was separated using a 150  $\mu$ m sieve and the particle fraction < 150  $\mu$ m was retained for additional preparation while the rest was discarded. The sample was calcined by placing it in a muffle furnace at 105 °C for 3 h, after which the furnace was ramped up to 500 °C and set at a heating rate of 10 °C/min up to 800 °C, and then held at 800 °C for 4 h. After calcination was completed, the calcined ash was placed in 20 ml vials and stored in a desiccator for use as a catalyst. The procedure was repeated for the pellet burner ash. The prepared catalysts were denoted as GA catalyst for gasifier ash catalyst and PBA catalyst for pellet burner ash catalyst and these abbreviations will be used hereafter in the paper.

#### 5.2.2. Characterization Methods

The char sample was analyzed by proximate and ultimate analysis. The calcined wood ash (GA and PBA) catalysts were characterized by ultimate analysis, X-ray Diffraction (XRD), surface area and metal analyses. The proximate analysis of char was carried out according to ASTM method D1762-84. Ultimate analysis of C, H, N, S was conducted using a Costech<sup>TM</sup> Elemental Analyzer, ECS 4010 Elemental Combustion System. Reactor conditions were: 1000 <sup>o</sup>C, helium carrier gas, 105 mL/min, GC Column #051080, SS 5 mm x 2 m, at 100<sup>o</sup>C, reaction tube: 450 L x 18 mm, GC column packing: HayeSep Q 60/80. A Thermal Conductivity Detector was used. Properties, such as volatile matter (VM), ash content, fixed carbon (FC) and C, H, N, S, are

expressed on a dry weight basis. To determine alkali metals, alkali earth metals and trace elements in the catalysts, samples were prepared by microwave digestion using a Milestone MLS 1200 Mega digestion system with concentrated HNO<sub>3</sub>. Metal characterization was done by an inductively coupled plasma (ICP-MS) on an Agilent 7500 ICPMS machine.

X-ray diffraction (XRD) powder patterns of the catalyst were obtained on a Bruker D8 Advance Series II using Cu-Ka<sup>1</sup> radiation at a wavelength of 1.5406 Å with 2 $\Theta$  being varied from 10° to 90°.

BET surface area measurements were carried out with  $N_2$  at 77 K using a single –point Micromeritics FlowSorb 11 2300 surface area analyzer.

## 5.2.3. Gasification

A thermo-gravimetric analyzer (TGA, Cahn Thermax 500) was used to measure weight loss of the char during CO<sub>2</sub> gasification. The gasification experiments were performed isothermally at 800 °C and at atmospheric pressure. Approximately 20 mg of char was weighed into a crucible (half sphere with 12 mm diameter) and then heated at 15 °C/min to 800 °C under the flow of N<sub>2</sub> (400 mL/min). The gas was switched from N<sub>2</sub> to CO<sub>2</sub> (400mL/min) after reaching 800 °C and a stabilized mass. Gasification was carried out until complete conversion of the char. The experiment was repeated by adding varying percentages of the catalyst (36, 18 and 10 wt.%, dry basis) while keeping the mass of char as constant as possible.

## Analyses of experimental results

Evaluation of reactivity:

Carbon conversion in CO<sub>2</sub>-char gasification, X, is defined as,

$$X = \frac{Wo - Wt}{Wo - Wash}$$
(5.1)

where  $W_o$  is the initial mass of char,  $W_{ash}$  is the mass of ash in char sample after gasification and  $W_t$  is the mass of sample at time t.

The gasification rate per unit mass of residual fixed carbon varies with carbon conversion and can be represented as,

$$r(X) = \frac{1}{1-X} \frac{\mathrm{d}X}{\mathrm{d}t}$$
(5.2)

where r is the char reactivity.

The reactivity index,  $R_s$  (14) (15) is defined as,

$$\mathrm{Rs} = \frac{0.5}{t_{0.5}}$$

(5.3)

Where  $t_{0.5}$  is the gasification time taken to reach a carbon conversion of 50 %.

## **5.3 Results and Discussion**

Proximate analysis (wt.% dry basis)	
Volatile Matter	14.8
Fixed Carbon	59.1
Ash	26.1
Ultimate analysis (wt. % dry basis)	
С	68.15
Н	0.76
O (calculated by difference)	22.57
Ν	0.12
Ash	8.40

Table 5.1. Proximate and ultimate analysis of char

<u></u>	GA-	PBA-
Element	Catalyst	Catalyst
	mg/kg	mg/kg
Са	167000	263000
Κ	18400	95700
Mg	15700	56500
Mn	8460	28100
Р	8180	8550
Al	15900	7560
Fe	12800	6170
Other	9120	8720

 Table 5.2. Inorganic elemental distribution of GA catalyst and PBA catalyst

#### **Characterization of catalyst**

Woody biomass is known for its high concentrations of alkaline earth metals, particularly Ca. Table 5.2 shows the metal concentrations for the major elements in the PBA-catalyst and the GA-catalyst. The PBA-catalyst is significantly more concentrated in Ca, K, Mg and Mn than the GA-catalyst. These elements are known to contribute to the catalytic effects of some processes. Ca, K, Mg and Mn are respectively, approximately 1.6, 5.2, 3.6 and 3.3 times more concentrated in the PBA-catalyst than in the GA-catalyst.

Analysis of the XRD results shown in Figure 5.1(a) highlights a number of dominant peaks. The XRD pattern of PBA-catalyst shows sharp peaks at  $2^{6} = 32.4$ , 37.5, 54.0 and 64.5. These peaks were linked to CaO (Lime). The peaks at 43.3 and 62.5 were linked to MgO (Periclase). Other minerals identified included Ca(SiO<sub>4</sub>) (Calcium Silicate), Fe<sub>3</sub>Mn<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> (Iron Manganese Silicate) and Fe<sub>2</sub>O<sub>3</sub> (Hematite). Analysis of the patterns indicates that CaO has the highest mineral content in the ash. The XRD pattern of the GA-catalyst seen in Figure 5.1(b) shows CaO (Lime) and MgO (Periclase) at similar angles to those detected in the PBA-catalyst. Gehlenite Magnesian Ca<sub>2</sub>(Mg<sub>0.25</sub>Al<sub>0.75</sub>)(Si<sub>1.25</sub>Al<sub>0.75</sub>O<sub>7</sub>) was identified at 32.5 and also at some smaller peaks. Potassium aluminium silicate (KAlSi<sub>2</sub>O<sub>6</sub>) was also found to be present in the GA-catalyst. The BET surface area of the PBA-catalyst and GA-catalyst were 3.1 m<sup>2</sup>/g and 6.7 m<sup>2</sup>/g, respectively.

GA - Catalyst		PBA -Catalyst			
Formula	%	Formula	%		
CaSiO <sub>3</sub>	7.9	Ca <sub>2</sub> (SiO <sub>4</sub> )	15.2		
CaO	70.9	CaO	44.4		
MgO	1.9	MgO	24.6		
KAlSi2O6	5.0	Fe <sub>3</sub> Mn <sub>2</sub> Si <sub>3</sub> O <sub>12</sub>	8.9		
Ca2(Mg0.25Al0.75)(Si1.25Al0.75O7	3.4	Fe <sub>2</sub> O <sub>3</sub>	6.8		
SiO <sub>2</sub>	3.4				
Ca <sub>5</sub> (PO <sub>4</sub> ) <sub>3</sub> F	7.4				

Table 5.3. Semi-quantitative data of mineral distribution in GA catalyst and PBA catalyst as determined by XRD



Figure 5.1a. X-ray diffraction patterns of pellet burner ash catalyst



Figure 5.1b. X-ray diffraction patterns of gasifier ash catalyst



Figure 5.2. Observed char conversion during  $CO_2$  gasification with and without the addition of PBA-catalyst and GA-catalyst between 0-36 wt% catalyst loadings.



Figure 5.3. Gasification reactivity as a function of char conversion during CO<sub>2</sub> gasification at 800 °C using varying percent catalyst loadings for GA-catalyst and PBA-catalyst.

#### The effect of catalyst on char conversion and reactivity.

Catalyst loading was varied by changing the mass of catalyst addition from 0 to 36 wt. %. Figure 5.2 shows the gasification of char with catalyst was faster than without catalyst. Carbon conversion was different between the two catalysts, with the PBA-catalyst having a much greater effect. With the addition of PBA-catalyst or GA-catalyst, 50% char conversion took ~ 5 min and ~ 19 min respectively. For the same degree of conversion the non-catalysed char reaction took ~21 min. 90 % char conversion with 36 % PBA-catalyst loading, 36 % GA-catalyst loading, or with no catalyst loading took ~ 10 min, ~ 32 min and ~ 34 min respectively. While most of the carbon (> 90 %) was converted rapidly in the PBA-catalyst reaction, the reaction became significantly slower thereafter. This resulted in the PBA-catalyst taking the same time as the other two reactions for full carbon conversion.

Due to the low impact of the GA-catalyst on char conversion, no further investigation of this catalyst was carried out. Figure 5.2 also shows the char conversion with PBA-catalyst of loadings 18 % and 10 %. The char conversion decreased when the percent catalyst loads decreased. For 50 % carbon conversion, the conversion times with 18 % and 10 % loading were  $\sim$  8 min and  $\sim$  12 min, respectively. For 90 % conversion, the conversion times were  $\sim$  14 min and  $\sim$  23 min for the 18 % and 10 % catalyst loadings, respectively.

Figure 5.3 illustrates the gasification reaction as a function of char conversion. In all cases, the addition of a catalyst increased the gasification reactivity of the char. The highest char gasification reactivity was  $4.81 \times 10^{-4}$  /sec. The samples showed significant differences in reactivity with the PBA-catalyst loading of 36 % being the highest at  $1.82 \times 10^{-3}$ /sec. The reactivity remained relatively constant until most of the char was converted. The high gasification reactivity seen for the PBA-catalyst gasification explains the rapid carbon conversion for that sample. The

gasification reactivity decreased with decreasing catalyst loading for the PBA-catalysts of loadings 18 % and 10 %. At 18 % loading, the highest reactivity was  $1.27 \times 10^{-3}$ /sec and decreased gradually throughout the reaction while at 10 % loading the highest reactivity was significantly lower, 7.23 x  $10^{-4}$ /sec. The reactivity of the GA-catalyst at 36 % loading was the lowest for all the catalysts studied, though slightly higher than char reactivity without catalysts. The highest gasification reactivity of this catalyst was 4.82 x

 $10^{-4}$ /sec.

Table 5.4. Reactivity index of char and char-catalyzed CO<sub>2</sub> gasification reactions at 50 % char conversion.

Sample	Rs (min <sup>-1</sup> )		
Char	0.023		
Char-GA 36 %	0.026		
Char-PBA 36 %	0.100		
Char-PBA 18 %	0.062		
Char-PBA 10 %	0.042		

The reactivity index at 50 % char conversion is shown in Table 5.4. The char with PBAcatalyst loading of 36 % had the highest reactivity index of 0.100 min<sup>-1</sup>. The GA-catalyst was only slighter higher in reactivity compared to the non-catalysed char. Although the reactivity indices are small, the activity ranking can be identified in terms of percent ash loading, PBA 36 % > PBA 18 % > PBA 10 %. When comparing ash types: PBA 36 % >>> GA 36 %. This suggests that the higher concentrations of specific elements in the PBA-catalyst, as seen from the ICP analysis, results in increased gasification reactivity. Elements of importance may be Ca, K, Mg and Mn Both Ca and K are significantly higher in concentration in the PBA-catalyst. The XRD results seen in Table 5.3 identified no minerals of K but instead identified CaO as the major mineral (44.4 %) followed by MgO (24.6 %) and Ca(SiO4) 15.2 %. With these observations, it is likely that CaO and MgO play a major part in the catalytic effect on gasification reactivity. Further work on the catalytic effects of CaO, MgO and Ca could be done to investigate the validity of these assumptions. Wood ash is usually rich in metal-oxide content and may provide the necessary oxygen radicals to bond with C.

When comparing the PBA-catalyst and the GA-catalyst at the same catalyst loading, the concentration of Ca in the PBA-catalyst was 1.6 times higher (obtained from Table 5.2). This could have an impact on the gasification reactivity since analysis of the work showed that higher concentrations of the PBA-catalyst increased reactivity. The other elements of importance such as K and Mg in the GA catalyst were approximately 5.2 and 3.6 times lower in concentrations than in the PBA-catalyst. The lower concentrations of these alkali and alkali earth metals may also account for the low gasification reactivity of the GA-catalyst. The XRD results seen in Table 5.3 identified CaO as the major mineral (70.9 %) in the GA-catalyst. KAlSi<sub>2</sub>O<sub>6</sub> was also identified in the mineral content (5 %). It is possible that the presence of this mineral could inhibit the activity of the catalyst (deactivating the catalyst) as presented in similar research (3). The elements Al and Fe in the GA-catalyst were two times higher in concentration than in the PBA-catalyst. This could possibly explain the likelihood of KAlSi<sub>2</sub>O<sub>6</sub> being present as a mineral.

The K/Al concentration ratio was significantly higher in the PBA-catalyst compared to the GA-catalyst, ~12.7 and ~1.2 respectively. The lower ratio of the GA-catalyst suggests that Al is likely to have a stronger influence on the effectiveness of the GA-catalyst. The catalytic effect of K may have been limited due to Al bonding with K as seen in the formation of KAlSi<sub>2</sub>O<sub>6</sub>. On the other hand, this mineral was not identified in the PBA-catalyst.

## **5.4 Conclusion**

CO<sub>2</sub> gasification of biomass char at 800 °C, using wood ash derived catalyst obtained from an updraft fixed gasifier and a wood pellet burner influences gasification reactivity. Both catalysts were enriched in Ca, K, Mg and Mn but were significantly higher in the PBA-catalyst. The XRD results identified CaO as the major mineral in both catalyst and also MgO in the PBA-catalyst. The order of reactivity for the catalysts studied, reported as percent catalyst added to char were, PBA 36 % > PBA 18 % > PBA 10 % > GA 36 % and PBA 36 % >>> GA 36 % . Therefore, the highest gasification reactivity was achieved when 36 % pellet burner ash catalyst was added to char. It was concluded that larger catalyst loadings for the PBA-catalyst, hence higher concentrations of the alkali and alkali earth metals, increases the gasification reactivity. The GAcatalyst showed significantly lower reactivities which may have been due to the lower concentrations of elements of catalytic importance as well as the presence of potassium aluminum silicates, which are considered to inhibit catalytic activity. The K/Al ratio in both catalyst showed that the PBA-catalyst was significantly higher ~12.7 than the GA-catalyst, ~1.2. The catalytic effect of K may have been limited due to Al bonding with K as seen in the formation of KAlSi<sub>2</sub>O<sub>6</sub>.

## References

- 1. Hamilton, R.; Sams, D.; Shadman, F. Variation of rate during potassium-catalysed CO<sub>2</sub> gasification of coal char. *Fuel*. 1984, Vol. 63, 1008-1012.
- 2. Sutton, D.; Kelleher, B.; Ross.; J. Review of literature on catalyst for biomass gasification. *Fuel Processing Technology*. 2001, Vol. 73, 155-173.
- Habibi, R.; Kopyscincki, J.; Masnadi, M.; Lam, J.; Grace, J.; Mims, C.; Hill, J. Co-gasification of biomass and non-biomass feedstocks: synergistic and inhibition effects of switchgrass mixed with sub-bituminous coal and fluid coke during CO<sub>2</sub> gasification. *Energy and Fuels*. 2013, Vol. 27, 494-500.
- 4. Hauserman, W. Relalting catalytic coal or biomass gasification mechanisms to plant capital cost components. *Internation Journal of Hydrogen Energy*. 1997, Vol. 22, 4, 409-414.
- 5. Klinghoffer, N.; Castaldi, M.; Nzihou, A. Beneficial use of ash and char from biomass gasification. Proceedings of the 19th Annual North America Waste-to-Energy Conference. Lancaster, Pennsylvania : ASME, 2011. 1-5.
- 6. Meijer, R.; Weeda, M.; Kapteijn, F.; Moulijn, J. Catalyst loss and retention during alkalicatalysed carbon gasification in CO<sub>2</sub>. *Carbon*. 1991, Vol. 29, 7, 929-941.
- 7. Kapteijn, F.; Moulijn, J. Kinetics of potassium carbonate-catalysed CO<sub>2</sub> gasification of activated carbon. *Fuel.* 1983, Vol. 62, 2, 221-225.
- 8. Kapteijn, F.; Peer, O.; Moulijn, J. Kinetics of alkali carbonate catalysed gasification of carbon:1.CO2 gasification . *Fuel* . 1986, Vol. 65, 10, 1371-1376.
- 9. Hauserman, W. High-yield hydrogen production by cataltic gasififcation of coal or biomass. International Journal of Hydrogen Energy. 1994, Vol. 19, 5, (413-419).
- Nanou, P.; Murillo, G.; van Swaaij, W.; Rossum, G.; Kersten, S. Intinsic reactivity of biomassderived char under steam gasification conditions-potential of wood ash as catalyst. *Chemical Engineering Journal.* 2013, Vol. 217, 289-299.
- 11. Hallen, R.; Sealock, L.; Cuello, R.; Bridgewater, A. Research in thermochemical biomass conversion. London : Elsevier Applied Science, 1988. 157.
- 12. Hauserman, W.; Kulas, R.; Timpe, R. Catalytic effect on the gasification of a bituminous argonne premium coal sample using wood ash or taconite as additive. [Online] [Cited: April 11, 2013.]

http://web.anl.gov/PCS/acsfuel/preprint%20archive/Files/36\_3\_NEW%20YORK\_08-91\_0892.pdf.

- 13. Quaak, P.; Knoef, H.; Stassen, H. Energy from biomass. A review of combustion and gasification technologies. Washington, D.C. : World Bank Technical Paper; 422. Energy series, 1999. 0-8213-4335-1.
- 14. Ye, D.; Agnew, J.; Zhang, D. Gasification of Souh Australian low-rank coal with carbon dioxide and steam: kinetics and reactivity studies. *Fuel*. 77, 1998, Vol. 11, 1209-1219.
- 15. Wang, J.; Yao, Y.; Cao, J.; Jiang, M. Enhanced catalysis of K<sub>2</sub>CO<sub>3</sub> for steam gasificationn of coal char by using Ca(OH)<sub>2</sub> in char preparation. *Fuel*. 2010, Vol. 89, 310-317

## **CHAPTER 6: Conclusion and Recommendations**

Forest biomass in British Columbia (BC) is considered to be the most abundant biomass resource and could theoretically replace almost half of the Provinces yearly fossil energy consumption (1). A number of biomass feedstocks exist in the Province. Harvest residue accounts for 37 % of the total biomass energy potential and is the single largest biomass resource. Saw mill residues are readily available. Pine beetle killed wood, construction and demolition waste are also other sources of wood residue. Other sources of biomass in BC include agricultural wastes (e.g.; crop residues, liquid and solid animal wastes that can be used for energy purposes), municipal bio-waste and landfill gas, food waste, energy crops, oils and animal fat.

Securing a long-term supply of biomass feedstock is a major consideration when selecting biomass as an energy system. At this point, the pine beetle infestation has left large amounts of wood available for use. The B.C. Ministry of Forests, Lands and Natural Resource Operations estimates that the mountain pine beetle has affected a cumulative total of 18.1 million hectares of cubic meters of timber since the current infestation began (2). To put this in context, the Ministry noted that 18.1 million hectares is more than five times the size of Vancouver Island. Much of this, however is too remote to harvest economically. A major challenge as we increase bioenergy production within the Province will be the long-term availability of these woods due to: rapid decay and utilization rates, access rights to residues from existing tenures, harvesting costs including road construction, replanting and transportation (1).

The sustainable use of biomass as a resource during harvesting and utilization must also be considered, for example when biomass is used in energy production processes. The use of woody biomass in bioenergy processes must be such that all possible energy is completely extracted. However, this is likely not possible due to specific problems such as: fuel types, variations in retention time in the reactor, incomplete combustion, temperature variations and fluctuations, moisture content of fuel and other factors. For these reasons, other viable energy processing options must be identified. Ideally, these options will be explored in conjunction with existing energy technologies so as to ensure maximum use of the resource.

A major residue that is produced during bioenergy production is ash. The management of this resource often poses problems as it relates to its utilization and storage. Bottom ash usually accounts for the largest portion of ash; that is, approximately 60 to 90 % of the total ash being generated (3). In some industries the presence of large amounts of carbon has rapidly increased ash volumes, creating concerns relating to short term storage, transportation and landfill management. It is for these reasons that alternative methods for the utilization of ash of varying physical and chemical characteristics must be identified. Identifying specific fractions of technological, environmental and economic importance could assist in dealing with this "waste". However, the quality of ash obtained from combustion systems varies in unburned carbon content and in inorganic distribution.

A potential method to obtaining and characterizing the unburned carbon in ash is sieve fractionation; a technique employed in this research. Sieve fractionation allowed for easy accessing of the carbon and may present itself as a cost effective pre-treatment method for reburning high carbon ash in order to obtain the highest energy components. If large amounts of unburned carbon are present in ash, it could be used as a fuel source which would have positive impacts on reducing ash volumes, increasing bioenergy processing efficiencies and also ensuring the sustainable use of biomass. This research showed that in some ash types the unused energy potential was 10.77 and 14.42 MJ/kg. When separated into particle fractions by sieving, the energy content within the largest particle size fraction was as high as 25 MJ/kg resulting from the
carbon-carbon bonds in char. The obtained calorific values suggest that the waste being disposed of has good energy potential and is comparable to some forms of biomass used in energy production processes (4). According to Liao et al. (4), the calorific value of biomass is in the range of 16–20 MJ/kg, while bituminous coal achieves 34 MJ/kg. Data obtained from Natural Resource Canada showed that, in 2010, the average energy intensity for residential space heating in BC was 0.29 GJ/m<sup>2</sup> (5). Assuming an average house is approximately 150 m<sup>2</sup>, the energy required to satisfy this demand would be 43.5 GJ/yr. Since the high carbon ash has ~14 MJ/kg or 14 GJ/tonne, it would require ~ 3.1 tonnes/yr of high carbon ash to meet the energy demands of heating an average residential household. Using high carbon ash for space heating should be considered if there is an adequate supply due to energy content, cost saving effects and potential for environmental sustainability.

This research also showed that using a lab-scale fluidized bed gasifier was effective in reducing the high carbon content in ash. Air-steam gasification of this fuel showed that there is tremendous potential in producing a gas of a low to medium calorific value. A gas heating value of 2.5 MJ/Nm<sup>3</sup> was obtained with the potential to be even higher by increasing the equivalence ratio and reducing the volume of fluidizing gas (nitrogen). For comparison, natural gas energy density is 36 MJ/Nm<sup>3</sup>. Research carried out on sugar cane residue (bagasse) showed that a gas generated at 3.5 - 4.5 MJ/Nm<sup>3</sup> did not present any problems when it was fired and burned (6). However, in order to acquire efficient combustion of the gas so as to fuel a turbine, combustion should be done close to the stoichiometric conditions. The possibilities to obtain a producer gas higher than 2.5 MJ/m<sup>3</sup> using gasification technology suggests the fuel potential of high carbon ash. This research suggest that there are many opportunities for continued research, such as

identifying other suitable methods and technologies for processing this fuel as well as the need for continued optimization of a product gas.

Returning high carbon ash to energy conversion systems could also be beneficial in increasing process efficiencies. The need for a detailed life cycle analysis is essential in determining the cost and benefits of reusing this fuel. Wood ash could be an effective catalyst in woody biomass gasification processes by increasing the gasification reactivities. The reactivities measured in this research, varied based on the ash type, elemental concentrations and mineral content of the ash. Ash obtained from a pellet burner, when used as a catalyst increased gasification reactivities with increasing catalyst loadings. This was attributed to the high concentrations of the alkali and alkali earth metals. The high reactivity of biomass char allowed fast and efficient investigation into the effectiveness of wood ash as a catalyst during biomass gasification. Due to the lower gasification reactivity of some forms of coal when compared to wood char, wood char catalyzed reaction may assist in understanding ash catalyst reactions which may could be extended to some coal gasification research. The findings from this research could be beneficial in coal gasification processes.

It must be noted that, should high carbon ash be gasified, issues related to ash carry-over in the producer gas could be a challenge due to the fine nature and low density of some ash particles. This could result in the constant need to remove and replace gas filters, thus increasing overhead costs. The possibilities of returning high-carbon ash to existing gasifiers through co-combustion with unburned woody biomass could also be an effective way of processing the unburned carbon. Other options could be using a different type of gasifier or making pellet or briquettes.

The limited understanding of the behaviour of ash, its properties and long-term environmental impacts also pose a problem. Ash utilization is limited by the presence of heavy metals and other inorganic compounds (7) (8), which are formed as a result of the thermochemical reactions that the biomass undergoes when combusted. The variation in inorganic concentrations pose a difficulty in the general application of bottom ash to soils due to the lack of a standardized ash quality. Sieve fractionation could be helpful in obtaining and/or eliminating fractions of environmental importance. When ash from a downdraft fixed-bed gasifier, wood pellet burner and an industrial-scale fixed-bed boiler were investigated, the trace element contents for the samples were all within the environmental limits for soil amendments in British Columbia, Canada (9). On the other hand, when analyzed within particle fractions, Ni with a concentration of 229 mg/kg from the wood pellet burner ash, exceeded the limit within the particle size fraction  $\geq 850$  but < 2000  $\mu$ m.

The increase in ash volumes from increase bioenergy use, could result in its use as a fertilizer and or as a soil conditioner, should adequate concentrations of specific elements be identified. According to Obernberger et al. (10), ash recycling to agricultural lands can help reduce the use of artificial fertilizers and close the natural mineral cycle owing to the presence of N, P and K in biomass ash. This could have positive impacts on forests and farm economies assuming adequate nutrients are provided to improve tree growth. While nitrogen was absent or extremely low in all samples, high concentrations of K and P were present. Yet, the research agreed with other authors who have suggested that very little of the P may be water-soluble (11), limiting adequate P plant uptake. The need for further greenhouse trials to investigate the impact of varying concentrations of wood ash and high carbon wood ash on biomass growth with different soil types in British Columbia would be an asset in understanding the benefits of ash.

High pH's were found in the ash types studied, which may have been due to high concentrations of alkali and alkali earth metals being present. The pH increased as the particle size fractions decreased which may have been due to the higher concentrations of base-forming metal salts in smaller particle fractions. A major benefit of ash could be as a liming agent in soils. A strong linear relationship of Ca and P to C content was identified. This agrees with previous work which suggested that unburned carbon creates a dilution effect and reduces the concentration of inorganic nutrients available in the ash (7). Should ongoing studies continue to demonstrate the positive effects of ash and/or high carbon ash on soils and soil properties, farmers and foresters could possibly consider the use of ash as a cheaper fertilizing and soil amendment alternative in BC.

In addition, establishing smaller biomass plants where energy demand is lower could be considered for reburning high carbon ash. For example, wood pellet burners burn efficiently and produce very little to no unburned carbon in the ash with very little overhead costs. Therefore, if a combustion system that could reburn high-carbon ash was to be developed, this could possibly harness the left over energy in the 'waste' while dealing with the storage, transportation and handling cost related to high-carbon ash. An economic feasibility study would need to be carried out on this idea. As with most development, small biomass plants will present a relatively higher transition costs when compared to large scale biomass plants because of the increased time, effort and money to secure projects (12). Nevertheless, continued biomass supply and security must be considered and may require a diverse biomass energy portfolio.

Some communities may benefit significantly from small biomass energy technologies as these communities could become involved in operating and managing their bioenergy facilities, once they are trained. Perhaps, small scale bioenergy plants could assist in offsetting the high demand for diesel by providing some amount of heat energy. These bioenergy facilities could be a source of employment for both skilled and unskilled workers, creating much needed employment for rural areas. The plants could be used for heat generation. Based on the widespread availability of biomass, the technology would lend itself across BC. Bioenergy developments would need to consider issues such as technical experience, education, community profile, climate change mitigation, employment, health and emissions and landscape and biodiversity (12). High carbon ash generated by some industries located close to these communities could be supplied with this feedstock to be used as heating fuel. For example, the City of Prince George, British Coumbia could benefit from the large volumes of high carbon ash produced by Canfor Pulp Limited Partnership.

High carbon ash and ash with no organic carbon presents positive environmental, social and economic implications. The research has uniquely characterized ash of varying physical and chemical compositions and has shown viable applications for many of these ash types. High carbon ash can be a viable energy source, while acting as a diluent for specific metals present in ash. The fuel possesses the ability to be gasified providing additional energy in the form of producer gases. Ash is also an effective catalyst in biomass gasification processes. Fractionation is a scientifically sound method and could also be cost effective in obtaining specific chemical and physical properties of ash, possessing useful environmental benefits.

While this research has provided valuable options for forest biomass "waste", there is still room for additional research on specific findings emerging from the study. Very little research has been done on the possibilities of returning high carbon ash to energy production systems, therefore, additional work should be done on optimizing the processes in cases where a high carbon ash is being produced. Through optimization and improved gasification process efficiencies a gas of higher calorific value could be realized. The benefits of applying varying ash types to different soils is still an area requiring further knowledge. If British Columbia is to produce firm and sustainable energy, as well as ensuring environment sustainability, technologies should be efficient in extracting as much energy from our bioenergy processes as possible. Viable alternatives for obtaining the additional left over energy should also be developed for those processes that are inefficient. In addition, finding all possible ways to reuse waste in an environmentally safe manner must be the focus of development. While it may be unrealistic to expect forest biomass to replace half of the Province's current annual consumption of fossil fuels, there is potential for products of this resource to be utilized sustainably. High carbon ash could have potential end uses as a fuel and soil diluent, while ash may be used as a fertilizer, liming agent and as a catalyst, in all cases promoting the common goal of sustainable development.

## References

- Envint Consulting. An information guide on pursuing biomass energy opportunities and technology in British Columbia. [Online] March 2011. [Cited: June 3, 2013.] <u>http://www.bcbioenergy.com/wp-content/uploads/2011/05/Bioenergy-Guide-2010-final-updated-May-2011.pdf</u>.
- British Columbia Ministry of Forests, Lands and Natural Resource Operations. Facts about B.C.'s mountain pine beetle. [Online] May 2012. [Cited: June 3, 2013.] http://www.for.gov.bc.ca/hfp/mountain\_pine\_beetle/Updated-Beetle-Facts\_May2012.pdf.
- 3. Obernberger, I.; Supancic, K. Possibillities of ash utilisation from biomass combustion plants. Proceedings of the 17th European Biomass conference & Exhibition. Hamburg : ETA Renewable Energies, June/July 2009.
- 4. Liao, C.; Chuangzhi, W.; Yanyongjie, Haitao, H. Chemical elemental characteristics of biomass fuels in China. *Biomass and Bioenergy*. 2004, Vol. 27, 119-130.
- 5. Natural Resoucre Canada. Comprehensive energy use database table. [Online] [Cited: June 3, 2013.] <u>http://oee.rncan.gc.ca/corporate/statistics/neud/dpa/showTable.cfm?type=CP&sector=res&juris=bc&rn=5&page=4&CFID=30408844&CFTOKEN=efe64231a5887a09-0BA67FDB-9A22-A467-EC86BFFEAE4E40D7.</u>
- 6. Gabra, M.; Pettersson, E.; Backman, R.; Kjellstrom, B. Evaluation of cyclone gasifier performance for gasification of sugar canre resifue Part 1: gasification of bagasse. *Biomass and Bioenergy.* 2001, Vol. 21, 351-369.
- 7. Sarenbo, S. Wood ash dilemma reduced quality due to poor combustion performance. *Biomass and Bioenergy*. 2009, Vol. 33, 1212-1220.
- Knapp, B.; Insam, H. Recycling of biomass ashes: current technologies and future research needs. [book auth.] Insam H. Knapp B. *Recycling of Biomss Ashes*. New York : Springer, 2011.
- 9. BC Ministry of Environment. Land application guidelines for the organic matter recycling regulation and the soil amendment code of practice. New Westminister, BC : SYLVIS Environmental, 2008. Report No. 758-08.
- Obernberger, I.; Supancic, K. Possibillities of ash utilisation from biomass combustion plants. Proceedings of the 17th European Biomass conference & Exhibition. Hamburg : ETA Renewable Energies, June/July 2009.

- 11 Nurmesniemi, H.; Manskinen, K.; Pöykiö, R.; Dahl, O. Forest fertilizer properties of the bottom ash and fly ash from llarge-sized (115MW) industrial powerplant incinerating woodbased biomass residues. *Journal of the University of Chemical Technology and Metallurgy*. 47, 2012, Vol. 1, 43-52.
- 12. OECD/IEA. Bioenergy project development and biomass supply. [Online] [Cited: August 11, 2011.] <u>http://www.iea.org/textbase/nppdf/free/2007/biomass.pdf</u>.

# APPENDICES

# Moisture Analysis of Boiler Ash Chapter 2 & 3

ovember 17	, 2010 - B1  and  A	<u> April 27, 2012 – B</u>
	B1	B2
Sieve	Average	Average
Tray/	Moisture	Moisture
μm	Content	Content
	%	%
2000	8.8	33.3
850	10.0	32.3
425	8.4	27.9
250	4.7	35.2
150	3.8	26.0
<150	4.9	23.9
AR	6.9	8.8

Table A1. Mo	oisture content of	f boiler ash obtained
November 17	, 2010 – B1 and	April 27, 2012 – B2
	B1	B2
Sieve	Average	Average
Tray/	Moisture	Moisture
μm	Content	Content



Figure B1. Higher heating value as a function of particle size  $(\mu m)$  for boiler ash.



Figure C1. Schematic diagram of biomass air and air-steam gasification in a bubbling fluidized bed. T – Thermocouple P- Pressure sensor R- Rotameter

## APPENDIX D Experimental Procedure for Gasification (Chapter 4)

#### Before heating up

- Set up micro-GC and connect the gas line.
- Turn on the micro-GC computer and open the controlling software (Galaxy)
- Set up the micro-GC acquisition sequence
- Open N<sub>2</sub> valves of pressure regulator on gas cylinder
- Open air valve on the wall and set pressure to 100 psi
- Open cooling water valve to reading of 30
- Open 3 way valve after condenser to flow meter
- Turn on computer for recording
  - Open recording valve software (PDAVIEW) and start recording
- Open N<sub>2</sub> valves

#### Water Pump

• Set water pump to desired stroke (steam gasification)

## **After Burner**

- Turn on after burner and set final temperature to 650°C
- Open air valve for after burner

#### Heating up reactor

• Set final temperatures of top and bottom furnaces to gasification temperatures.

## **Feeding Fuel**

• Start micro-GC acquisition sequence

- Turn on water pump (steam gasification)
- Open  $N_2$  and air valve for the reactor and hopper to the required flow.
- Turn on screw feeder
- Record feed rates of N<sub>2</sub>, air and fuel
- Adjust flow meter pressure around 3 psi-g by adjusting the valve before the afterburner to make steady flow to the micro-GC

## After Gasification

- Stop screw feeder and water pump
- Open air valve to burn left over carbon

## Shutdown

- Turn off micro-GC
- Keep cooling water on
- Stop all gas flow and cooling water when all monitoring temperatures reach ambient temperature
- Turn off computer

# **APPENDIX E** Sample Spreadsheet of Gasification Parameters (Chapter 4)

Property	Symbol	Unit	Value	Equation
Fuel Flow Rate	Gfuel	g/min	2.93	
		kg/s	4.88E-05	
		g/hr	176	
		Screw		
		Feeder	150	SF = (Gfuel+0.418)/0.0223
DESIGN CRITERIA				
Ambient Temperature	Tamb	°C	20	
Furnace Temperature	Tfur	°C	700	
		K	973	
Furnace Pressure	Pfur	kPa	20	
		kPa	121.33	
Biomass N2 Purge Flow	Qpurge	mL/min m^3/s	1000 3.24E-05	
	Gpurge	kg/s	2.32E-05	
		Sec. 1	1	
FLUIDIZING GAS	DD	A/	120/	
Equivalence Katio	ER	<b>%</b> 0	12%	
Steam to Biomass Ratio	RH <sub>2</sub> O	kg/kgfuel	2.20	
N2 Fraction	KN2	kg/kgfuel	2.40	
				11.53*C+34.34(H-
Stoichiometric Dry Air Actual Dry Air To	Mda	kg/kgfuel	5.204	O/8)+4.34S
Gasifier	Tda	kg/kgfuel	0.625	Mda*EAC
Stoichiometric Wet Air Actual Wet Air To	Mwa	kg/kgfuel	0.633	Mda*(1+Ma)
Gasifier	Twa	kg/kgfuel	0.08	Mwa*EAC
				Gfuel *RH2O - Gfuel
Steam	Gsteam	kg/s	1.04E-04	*[H2O]
		g/min	6.24	
	Qsteam	m^3/s	3.85E-04	
	Qwater	mL/min strokes/min	6.3 <b>12.8</b>	Gsteam /pwater SR = (F - 0.7676)/0.4291

Table E1. Sample spreadsheet of gasification parameters for gasifying boiler ash.

Fluidizing Air	Gair	kg/s	3.09E-05	
	Qair	m^3/s	7.83E-05	2.82E-01
		L/min	1.291	
		Rotometer	22.7	R = (F+0.0757)/0.0602
Fluidizing N2	GN2	kg/s	1.17E-04	Gfuel *RN2
-	QN2	m^3/s	2.79E-04	
		L/min	5.043	
		Rotometer	7.9	R = (F-1.6736)/0.4251

Total Fluidizing Gas	GFG	kg/s	2.75E-04	
-	QFG	m^3/s	7.75E-04	
	-			
Syn Gas Flow	Qsyn gas	m^3/s	1.39E-05	
Total Gas Flow	Qtotal gas	m^3/s	7.89E-04	
Calculated Gas Velocity	UFG	m/s	0.173	
Design Gas Velocity	Ug	m/s	0.188	
Excess Velocity		m/s	-0.015	UFG - Ug
Syn Gas Flow Total Gas Flow Calculated Gas Velocity Design Gas Velocity Excess Velocity	Qsyn gas Qtotal gas UFG Ug	m^3/s m^3/s m/s m/s m/s	1.39E-05 7.89E-04 0.173 0.188 - <b>0.015</b>	UFG - Ug

BIOMASS				
Density	dp	μm	400	
Particle Diameter	-	m	0.0004	
	pbio	kg/m^3	1100	
Carbon	[C]	%	48.50%	
Hydrogen	[H]	%	0.90%	
Oxygen	[0]	%	33.40%	
Nitrogen	[N]	%	0.20%	
Sulphur	[S]	%	0.00%	
Ash	[ASH]	%	17.00%	
Moisture	[H2O]	%	5.00%	
			100.0%	
Higher Heating Value	HHV	kJ/kg	11600	



Figure F1. Calibration of screw feeder for high carbon ash.



y = 0.4291x + 0.7676

Figure F2. Calibration of water pump at 50 % stroke (IWAKI metering pump, adjustable stroke)



Figure F3. Calibration of the flow controller for air introduced at the bottom of the reactor.

## APPENDIX G

Tempera	ature	ER	Input	¥						Gas
			gas	Avg		Avg	Avg	Avg	Avg	flow
			flow	$CO_2$	Avg H <sub>2</sub>	$O_2$	$N_2$	CO	$C_3H_8$	out
<u>°C</u>			L/min	%	%	%	%	%	%	L/min
Α	657	0.12	8.418	1.97	0.89	0.13	89.57	3.44	0.22	15.69
	675	0.12	8.418	2.14	1.06	0.13	88.35	6.05	0.11	15.69
	698	0.12	8.418	1.09	1.33	0.12	89.07	6.76	0.37	15.69
	740	0.12	8.418	0.34	1.41	0.12	89.01	7.78	0.38	15.69
	771	0.12	8.418	0.11	1.39	0.12	88.53	8.67	0.38	15.69
В										
	775	0.12	8.418	0.11	1.39	0.12	88.53	8.67	0.38	15.69
	775	0.16	8.366	0.16	1.41	0.12	86.60	10.59	0.39	15.73
	775	0.19	8.643	0.39	1.35	0.12	85.88	11.13	0.39	15.81
	775	0.23	8.172	0.59	1.51	0.12	83.85	12.96	0.39	15.91
D:	775	0.25	7.936	1.24	1.55	0.11	81.87	14.13	0.40	15.95

Table G1. Gas analysis and operating conditions for air gasification of high carbon wood ash

Biomass feed rate: 176 g/h;

	Input gas			<u></u>			Gas flow
S/B	flow	Avg CO <sub>2</sub>	Avg H <sub>2</sub>	Avg N <sub>2</sub>	Avg CO	Avg C <sub>3</sub> H <sub>8</sub>	out
 	L/min	%	%	%	%	%	L/min
 0.4	7.152	0.67	3.93	85.45	8.80	0.34	14.337
0.8	7.153	1.99	7.22	80.58	9.19	0.21	15.755
1.3	7.154	2.08	8.49	78.69	9.30	0.44	16.133
1.7	7.155	2.49	8.22	79.99	8.09	0.43	16.506
 2.2	7.157	4.08	8.50	81.14	4.84	0.42	15.657

Table G2. Gas analysis for air-steam gasification of high carbon wood ash

Biomass Feed Rate - 176 g/h; ER - 0.13; Temperature - 775°C, Steam/Biomass Ratio (S/B)

Li	<b>Be</b>	Na	<b>Mg</b>	AI	Si	K	Ca	<b>Mn</b>	Fe
mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
273.9	0.1	3339.5	62648.5	8455.8	301.4	102347.0	269367.2	31016.7	7102.6
Ni	Cu	<b>Zn</b>	<b>As</b>	<b>Se</b>	<b>Mo</b>	Cd	Ba	<b>Hg</b>	Pb
mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg	mg/kg
44.2	158.7	451.6	1.0	0.5	6.1	8.7	1558.2	0.1	4.0

H1 Motel analysis for beiler ach collected Ionyany 10, 2012 Tabl