Physical treatments for reducing biomass ash and effect of ash content on pyrolysis products

by

Ujjain Pradhan

A thesis submitted to the Graduate Faculty of
Auburn University
in partial fulfillment of the
requirements for the Degree of
Master of Science

Auburn, Alabama
August 1, 2015

Keywords: biomass, ash content, physical treatments, pyrolysis, characterization

Approved by

Sushil Adhikari, Co-chair, Associate Professor of Biosystems Engineering
Oladiran Fasina, Co-chair, Professor of Biosystems Engineering
Timothy McDonald, Associate Professor of Biosystems Engineering

Abstract

There is increasing concern of greenhouse gas effect and the depletion of fossil fuels. Different renewable energy sources such as hydro, wind, solar have been considered as a potential replacement for fossil fuel. Bio-energy, energy produced from biological component such as animal and plant products, is one of the renewable energy that is extensively being researched around the globe. Biofuels produced from woody biomass is largely affected by its properties such as moisture content, ash content, heating value and particle size. Woody biomass is pretreated and preprocessed such that the resulting properties best suit the conversion process. Soil particles, also known as detrital ash lowers, energy value of biomass and its thermochemical conversion process into products. This study aims to reduce the amount of soil contaminants in woody biomass and study the effect of ash content on pyrolysis products.

Vibratory sieve shaker, hammer mill, and mixer were selected as the physical treatment processes used to remove soil particles from surface of woodchips and thereby reducing the ash content. Vibratory sieve shaker produces vibratory force, mixer generates rotary motion as a result woodchips collide with each other which can separate the soil particles form the woodchips. Hammer mill breaks the woodchips by beating action of the hammer, and the impact force generated can separate the dirt particles from the woodchips.

The treatments were tested on (i) sweetgum, (ii) residual pinewood, (iii) whole pinewood, and (iv) dirty pinewood that were at different levels of ash and moisture contents. The ash and moisture contents of dirty pinewood was maintained at required levels by adding calculated amount of soil and water. All of the three treatment processes significantly reduced ($p<0.05$) the ash content of the whole pinewood, residual pinewood and sweetgum that had initial ash contents of about 2%. Mixer reduced the ash content of sweetgum, whole pinewood and residual pinewood from 2.14%, 2.31% and 1.69% to 1.71%, 1.73% and 1.20%, respectively. Similarly vibratory sieve shaker reduced the ash content to 1.66%, 1.90% and 1.24%. However, the hammer mill treatment was more efficient in reducing the ash content for pinewood with higher ash content (>5%) significantly compared to other two process. The ash content of pinewood with initial ash content of 6.64%, 8.34% and 10.40% was reduced to 1.88%, 3.36% and 3.15%, respectively by hammer mill treatment. The reduction in ash content resulted into increases in volatile matter and heating value of the treated biomass. Ash reduction rate was highest at 10% moisture content for samples treated with vibratory sieve shaker and with mixer. Hammer mill significantly reduced ash content at different moisture content level but no significance reduction between different moisture contents was observed.

Pyrolysis was carried on the woodchips at ash contents 0.56%, 1.16%, 2.77%, 4.40%, 6.87%, 8.35% and 15.52% to understand the effect of ash reduction from physical treatments. Increasing ash content of biomass decreased the volatile matter, carbon and hydrogen contents of biomass thereby reducing bio-oil yield reduced from 47.09 % to 26.28 %. The water content and ash content of bio-oil increased with increase in ash content of biomass. The carbon and hydrogen content of the bio-char decreased with the increase in the ash content of the biomass. Furthermore, the ash content of the bio-char increased which resulted in the decrease of heating value of the bio-char.

Acknowledgement

My deepest gratitude goes to Dr. Sushil Adhikari and Dr. Oladiran Fasina who have given me this opportunity to work with them in this research. Their constant guidance and encouragement has been extremely helpful for me to gain much insight on this research. I would also like to thank my committee member Dr. Timothy McDonald for the support he showed to me.

I am also thankful to James Johnson and Jonathan Griffith for helping me with the procurement of biomass feedstocks. I would also like to appreciate the patience of Michael E. Miller to train me on SEM system for char analysis. I would also like to thank the support of my research group members Jaskaran, Anshu, Gbenga, Tosin, Femi, Thomas, Avanti, Ravindra, Sneha, Rajdeep, Ravishankar, Liang, Zhouhong and Narendra, who have helped me with the learning of different equipment in lab and designing my experiments.

I am grateful for my parents Mr. Jagdish Pradhan and Mrs. Urmila Pradhan, and my sisters Miss Jasmine Pradhan and Miss Jenisha Pradhan, who have supported me throughout this research with words of encouragement. I would also like to thank Erena Pradhan, who have provided me with emotional support.

Lastly, I would like to acknowledge the funding provided by the United States Department of Agriculture (USDA)-National Institute of Food and Agriculture (NIFA) through Integrated Biomass Supply Systems (IBSS). I would also like to acknowledge the faculty members and fellow graduate students of Department of Biosystems Engineering.

Table of Contents

List of Tables

List of Figures

CHAPTER ONE

INTRODUCTION

1.1 Rationale

The world's economy highly depends upon fossil fuel sources such as coal, oil and natural gas. The extensive use of these fossil fuel sources to produce fuels, chemical products and electricity has depleted the fossil fuel resources and has further increased concerns over greenhouse gas emissions (Lynd and Wang, 2003; Uihlein and Schebek, 2009). The global consumption of fossil fuel was estimated to increase to 92 million barrels per day in 2014, which will further grow by 1 million barrels per day in both 2015 and 2016. The United States imports more than nine million barrels of oil per day to meet its energy requirement (EIA, 2015). The Energy Independence and Security Act (EISA, 2007) has mandated the use of 36 billion gallons of transportation renewable fuels by 2022. In addition to the environmental impact of utilizing fossil fuels, there are economic implications due to dominance by the Organization of Petroleum Exporting Countries (OPEC) for crude oil supply.

Biomass is a viable replacement for crude oil because it contains high concentration of carbon and hydrogen (Lepori and Soltes, 1985) and thus, can be a potential alternative source of liquid fuels, chemical products that are currently obtained from the crude oil. Biomass is renewable source of energy which can be used in waste-to-energy conversion facilities such as production of heat and electric power (Maglinao et al., 2008). The conversion of biomass into solid and liquid fuel can take place by thermochemical or biochemical conversion processes.

The issues with the thermochemical conversion process include presence of inorganic compounds in biomass known as ash content. Major (Al, Ca, Fe, K, Mg, Na, P, Si, Ti) and minor (As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Tl, V, Zn) ash forming elements present in the biomass are not converted into fuels and further can change the properties of the energy product. Presence of inorganic compounds leads to slagging, fouling, bed agglomeration and corrosion (Werkelin et al., 2010).

Ash is introduced into biomass in two ways: the first through uptake of mineral for growth and second through harvesting and storage during biomass handling. Study by Werkelin et al. (2005) reported dry ash content of branch bark of pine to be maximum of 3.3% but the ash content in woody biomass depends upon the handling and storage operation after the woody biomass is harvested and thus can result in higher ash content (Dukes et al., 2013; Baernthaler et al., 2006; Bakker and Elbersen, 2005). This is because of the soil and sand contamination during biomass handling and storage. Removal of soil particles will improve the quality of biomass feedstock and increase its energy potential during thermochemical conversion.

The fast pyrolysis process is considered as one of the most effective means of converting biomass to useful products due to its high liquid yield, quick conversion and the useful application of by-products such as char and syngas (Bridgwater et al., 1999; Piskorz et al., 1989). The bio-oil produced from fast pyrolysis can be directly utilized as fuel or as an additives to fossil fuels, boilers and heating furnaces (Czernik and Bridgwater, 2004). The quality and quantity of bio-oil produced is dependent on various factors such as temperature, residence time, particle size and feedstock composition (Park et al., 2008; Sensoz et al., 2000; Boateng, 2007). Studies have also documented that the bio-oil yield is largely dependent on the ash content of the biomass. Ooasmaa et al. (2010) conducted pyrolysis at 480-500^{o}C for nine different biomass such was pine saw dust, eucalyptus and rapeseed straw whose ash content varied from 0.10% to 6.10% and found that bio-oil yield decreased with increment in the ash content as shown in Figure 1.1.

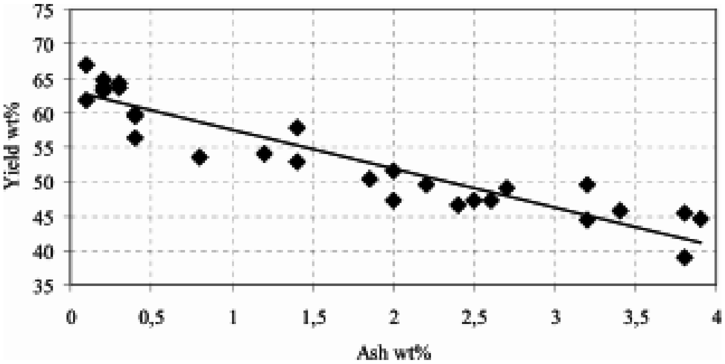


Figure 1.1 Correlation of bio-oil yield and feedstock ash in pyrolysis of biomass (Ooasmaa et al., 2010)

1.2 Goals and objectives

The overall objective of this study was to reduce soil contaminants in woody biomass thereby reducing the ash content and to establish a general understanding on the effect of ash content on the bio-oil produced from fast pyrolysis. This overall objective was accomplished by two specific objectives listed below.

1.2.1 To reduce the ash content of biomass following three physical treatment processes and to study the effect of moisture content and initial ash content on the reduction efficiency.

1.2.2 To understand the effect of ash content on characteristics and quantity of pyrolysis products.

1.3 Structure of thesis

The thesis has been divided into four chapters.

- Chapter one encompasses the brief introduction of the objectives and structure of the research.
- Chapter two focuses on the literature review carried out during this study in order to develop an understanding of the fundamentals for this study. It includes review of the different methods to remove or reduce the ash content and a brief review of fast pyrolysis process.
- Chapter three covers the experimental setup used for ash reduction in this study. It also includes the results obtained from analysis of treated biomass.
- Chapter four comprises the experimental study, methodology and results obtained from fast pyrolysis experiment carried on biomass at ash contents that vary from 0.5% to 15%.
- Chapter five consists of the conclusions obtained from this study and discusses upon the future recommendations.

1.4 References

Baernthaler, G., Zischka, M., Haraldsson, C., & Obernberger, I. (2006). Determination of major and minor ash-forming elements in solid biofuels. *Biomass and Bioenergy*, *30*(11), 983-997. Bakker, R.R., and H. W. Elbersen. 2005. Managing ash content and quality in herbaceous biomass: an analysis from plant to product. *14th European Biomass Conference*. Paris. 210-213

Bakker, R. R., & Elbersen, H. W. (2005, October). Managing ash content and quality in herbaceous biomass: an analysis from plant to product. In *14th European Biomass Conference* (pp. 210-213).

Boateng, A. A., Daugaard, D. E., Goldberg, N. M., & Hicks, K. B. (2007). Bench-scale fluidized-bed pyrolysis of switchgrass for bio-oil production. *Industrial & Engineering Chemistry Research*, *46*(7), 1891-1897.

Bridgwater, A. V., Meier, D., & Radlein, D. (1999). An overview of fast pyrolysis of biomass. *Organic Geochemistry*, *30*(12), 1479-1493.

Czernik, S., & Bridgwater, A. V. (2004). Overview of applications of biomass fast pyrolysis oil. *Energy & Fuels*, *18*(2), 590-598.

Dukes, C. C., Baker, S. A., & Greene, W. D. (2013). In-wood grinding and screening of forest residues for biomass feedstock applications. *Biomass and Bioenergy, 54,* 18-26.

EIA. (2015). United States Energy Information Administration. Available at *http://www.eia.gov/forecasts/steo/pdf/steo_full.pdf*. Accessed 17 March, 2015

EISA. (2007). Public law 110-140-Dec 19, 2007. Energy Independence and Security Act of 2007. Available at *http://www2.epa.gov/laws-regulations/summary-energy-independence-and-security-act.* Accessed 02 Feb, 2015

LePori, W. A., & Soltes, E. J. (1985). Thermochemical conversion for energy and fuel. *Biomass Energy: A Monograph*, (2), 9.

Lynd, L. R., & Wang, M. Q. (2003). A Product-Nonspecific Framework for Evaluating the Potential of Biomass-Based Products to Displace Fossil Fuels.*Journal of Industrial Ecology, 7*(3-4), 17-32.

Maglinao, A., S.C. Capareda, C. B. Parnell Jr, and D. Carney. (2008). Demonstration and simulation of a fluidized bed gasification system for power generation. *ASABE Paper No. 084935, St. Joseph, Mich: ASABE*

Oasmaa, A., Solantausta, Y., Arpiainen, V., Kuoppala, E., & Sipilä, K. (2009). Fast pyrolysis bio-oils from wood and agricultural residues. *Energy & Fuels,24*(2), 1380-1388.

Park, H. J., Park, Y. K., & Kim, J. S. (2008). Influence of reaction conditions and the char separation system on the production of bio-oil from radiata pine sawdust by fast pyrolysis. *Fuel Processing Technology, 89*(8), 797-802.

Piskorz, J., Radlein, D. S. A., Scott, D. S., & Czernik, S. (1989). Pretreatment of wood and cellulose for production of sugars by fast pyrolysis. *Journal of Analytical and Applied Pyrolysis*, *16*(2), 127-142.

Şensöz, S., Angın, D., & Yorgun, S. (2000). Influence of particle size on the pyrolysis of rapeseed (Brassica napus L.): fuel properties of bio-oil. *Biomass and Bioenergy*, *19*(4), 271-279.

Uihlein, A., & Schebek, L. (2009). Environmental impacts of a lignocellulose feedstock biorefinery system: an assessment. *Biomass and Bioenergy, 33*(5), 793-802.

Werkelin, J., Skrifvars, B. J., & Hupa, M. (2005). Ash-forming elements in four Scandinavian wood species. Part 1: Summer harvest. *Biomass and Bioenergy*, *29*(6), 451-466.

Werkelin, J., Skrifvars, B. J., Zevenhoven, M., Holmbom, B., & Hupa, M. (2010). Chemical forms of ash-forming elements in woody biomass fuels. *Fuel*, *89*(2), 481-493.

CHAPTER TWO

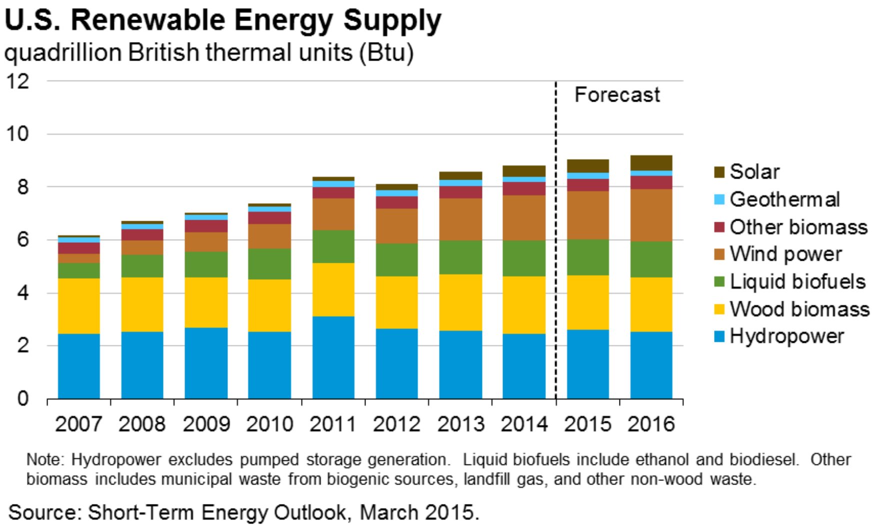
LITERATURE REVIEW

2.1 Energy scenario

The development and financial progress of a country depends upon its energy production and consumption. The major sources of energy that currently fuels the modernization of today's society are obtained from fossil fuels such as coal, oil and natural gas. However, the use of fossil fuel in the long run is not sustainable and can further cause environmental problems such as greenhouse gas emissions (Uihlein and Schebek, 2009).

The global consumption of fossil fuel was 92.2 million barrels per day for the year 2014 which is further expected to increase by 1 million barrels per day in the year 2015 and 2016. In addition, the U.S. liquid fuels consumption increased by an estimate of 0.4% in the year 2014 with motor gasoline consumption increased by 0.9%, distillate consumption increased by 4.8% and jet fuel consumption increased by 2.5% in the year 2014. It is estimated that the total liquid fuel consumption to grow by 340,000 barrels per day (1.6%) in the U.S (EIA, 2015). Close to 72% of the U.S energy demand and 87% of the world energy demand is obtained from fossils fuels. (EIA, 2014).

The continuous extraction of fossil fuel not only depletes the reservoir of fossils fuels but it also imposes adverse environmental impacts. The ongoing search for alternative source of energy can include studies on renewable energy source such as wind energy, solar energy, biomass energy and geothermal energy (IEA, 2006; Stelt et al., 2011). The energy attained from renewable sources was about 9% in the United States (EIA, 2013). It is further projected that energy from renewables in electricity and heat generation section will grow by 2.9% in 2015 and 1.9% in 2016.



Note: Hydropower excludes pumped storage generation. Liquid biofuels include ethanol and biodiesel. Other biomass includes municipal waste from biogenic sources, landfill gas, and other non-wood waste.

Source: Short-Term Energy Outlook, March 2015.

Figure 2.1 Renewable energy supply in Unites States (EIA, 2015)

Figure 2.1 shows the increase in the use of hydropower, wood biomass and liquid biofuels as an effective source of energy in the U.S. The figure also shows that woody biomass has been constantly and steadily utilized to generate energy.

Biomass are organic or living material such as agricultural crops, forest products and residues, insects and animal wastes. Primary sources of biomass includes the forest and agricultural crops (Hodge, 2010; ASABE, 2011). Biomass is mainly comprised of cellulose, hemicellulose, lignin, extractives and ash content (Zhou et al., 2015). Biomass has important advantage as a combustion feedstock due to its high volatility of fuel and the high reactivity of the fuel (Demirbas, 2004). Out of all the renewable sources of energy, biomass is the only source of sustainable carbon.

The success of use of biomass as an alternative sources depends upon biomass logistics and energy conversion process (Tembo et al., 2003). Biomass can be converted into biofuel or bioenergy through thermochemical or biochemical pathways (Demirbas, 2001). The energy value of the biomass is largely dependent on its volatile matter, fixed carbon and ash content. Biomass with high volatile matter, high carbon and low ash content is preferable for energy conversion. The properties of some biomass feedstock are summarized in Table 2.1. The ash content of woody biomass such as poplar, sawdust are typically in the low range of 2% whereas the ash content of the herbaceous biomass are higher with rice husk having ash content of 22.6%.

Table 2.1 Common properties of biomass (dry basis)

Fuel sample	**Ash content (%, d.b.)**	**Volatile matter (% d.b.)**	**Fixed carbon (%, d.b.)**	**Source**
Hazelnut shell	1.5	76.3	21.2	Demirbas, 1997
Sawdust	2.8	82.2	15.0	Abbas et al., 1994
Corn stover	5.1	84.0	10.9	Claar et al., 1981
Poplar	1.3	74.0	16.4	Ebeling and Jenkins, 1985
Sugarcane bagasse	11.3	ND	15.0	Ebeling and Jenkins, 1985
Rice husk	22.6	61.0	16.7	Hartiniati and Youvial, 1989
Alfafa stalk	6.5	76.1	17.4	Tilman, 2000
Switchgrass	8.9	76.7	14.4	Tilman, 2000

Note: ND stands for not determined.

Woody biomass is the most reliable, easily available and viable source of biomass due to the abundant forest land present in the United States. It is estimated that nearly 258 to 340 million dry tons per year of woody biomass is available now, which will be further increased to 770 million to 1.6 billion tons per year by the year 2030 (Perlack et al., 2011).

2.2 Biomass logistics

Biomass logistics includes the harvesting and collection, storage, transportation and pre-processing that are carried out on biomass before they are supplied to the conversion plant (Figure 2.2). The success of bioenergy sector to replace fossil fuel is largely dependent on the efficient flow and supply of the biomass feedstock from the point of origin to the throat of bio-refinery conversion (BRDB, 2010).

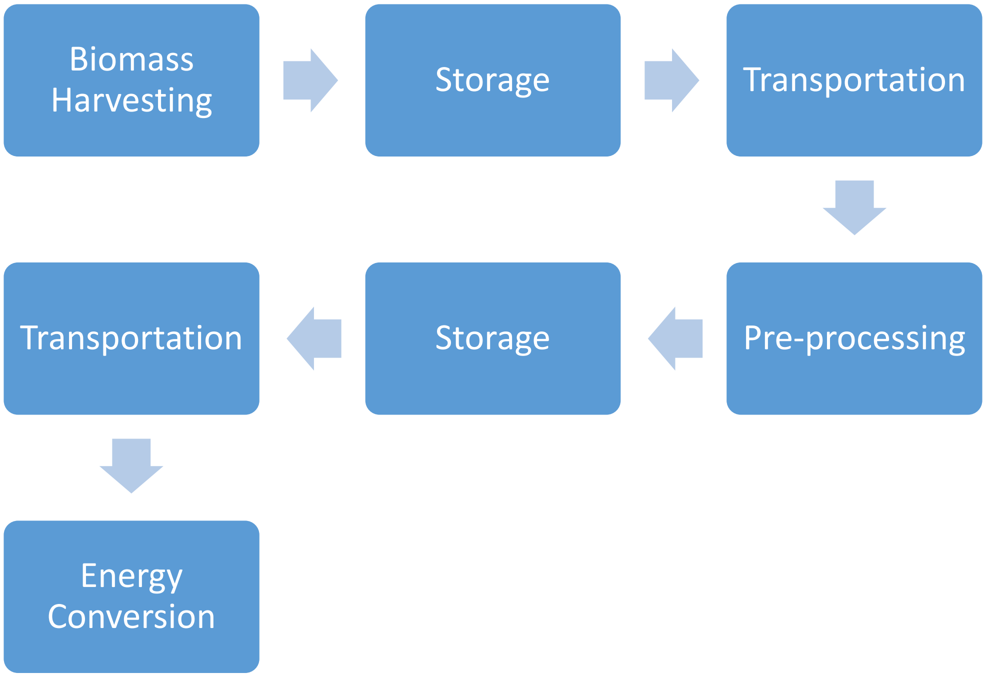


Figure 2.2 Biomass logistics

Pre-processing of woody biomass includes altering the properties of the biomass to best suit its transportation, storage and quality. Pre-processing includes decreasing the moisture content, size reduction and reducing ash content of biomass. The freshly felled tree has moisture content in the region of or greater than 50% which not only has a significant influence on the quality of fuel produced but also influences the degradation of the woody biomass during storage (Bedane et al., 2011). The reduction in moisture content further attributes to the reduction in the storage and transportation cost as the amount of moisture or water in the biomass is reduced. Also the combustion efficiency increased as less energy is required to remove water during the combustion process (Murphy et al., 2012). Drying can be obtained with air drying or oven drying at increased temperature.

Size reduction involves use of chippers to reduce the logs and stem of trees into woodchips with size ranging from 5 to 50 mm and mills (hammer mill, knife mill, needle mill, ball mills and shredders) that further reduces the size of the woodchips to less than 10 mm (Naimi et al., 2006; Zhang et al., 2010). Size reduction offers increased load density, improves handling quality (Pottie and Guimier, 1985) and furthermore is necessary as biomass with homogeneous fuel particles (size less than 1 mm) is required for the efficient energy conversion process (Manzone and Spinelli, 2013).

2.3 Ash content

Ash content is the inorganic compound in biomass which does not combust during conversion to energy and is left behind as ash. The major inorganic element for biomass ash are Al, Ca, Fe, K, Mg, Na, P, Si, Ti while minor elements are As, Ba, Cd, Co, Cr, Cu, Hg, Mn, Mo, Ni, Pb, Sb, Tl, V, and Zn. Major inorganic elements are highly responsible for ash melting, deposit slag formation, and corrosion in the conversion equipment while minor elements are responsible for particulate emission (Baernthaler et al. 2006).

Ash content in biomass can be divided into two parts, authigenic ash and detrital ash. Authigenic ash is found inside the plant which is accumulated through water and soil uptake during growth. It basically is the nutrient deposit inside the plant fibers from water uptake. Detrital ash on the other hand is the inorganic compound on the surface of the wood due to contamination from water, soil and air during growth and pre-processing operations.

2.3.1 Authigenic ash

The ash-forming inorganic elements in trees or plants are the result of biochemical and biogenic processes, water uptake and mineral transportation within the plant (Kozlowski et al., 1997; Vassilev et al., 2012). It is also generated after the plants death via evaporation and precipitation.

Of the 92 known elements on earth, 17 are known to be required by plants. They are divided as macronutrients and micronutrients. The macronutrients are C, H, O, Ca, K, N, S whereas micronutrients include Cl, B, Cu, Fe, Mn, Mo, Ni and Zn. The macronutrients in plants are present at amount greater than 1000 mg per kg whereas the micronutrients are present at amount less than 100 mg per kg (Pilon-Smits et al., 2009). Carbon, hydrogen and oxygen are derived in plants from interaction with atmosphere, soil, and water. The remaining elements are supplied either from soil minerals or organic and inorganic fertilizers (Silva and Uchida, 2000)

Phosphorus plays a major role in energy storage and transfers as adenosine di- and triphosphate and di- and tri-phosphyridine. It is also a major part of RNA and DNA and is the major components of genetic information. Potassium acts as enzyme activator and promotes metabolism. Calcium plays a major role in formation of cell wall and is also an activator of several enzyme systems in protein synthesis. Magnesium is involved in photosynthesis. Sulfur is involved in metabolism of the B vitamins biotin-thiamine and co-enzyme A. Iron is essential for synthesis and maintenance of chlorophyll in plants (Silva and Uchida, 2000; Tucker, 1999).

2.3.2 Detrital ash

The detrital ash is mostly finely dispersed mineral grains introduced into the plant by water suspensions during syngenesis and is present and fixed outside the biomass but is fixed into it. It is also a fine layer of soil and sand contaminants coated at the surface of the wood during collection, handling, transportation and other subsequent processing of biomass (Vassilev et al., 2012).

Sources: *http://www.sherbrooketreeservice.com/*

http://www.ekantipur.com/2011/05/23/national/govt-to-lift-tree-felling-ban/334417.html

Figure 2.3 Skidding and storage of biomass feedstocks at harvest site

Detrital ash is present mainly because of the handling of the biomass. During the biomass logistics, as the tree is felled using feller machine, the tree limbs falls on the ground and comes in contact with the soil. As the skidder skids the tree limbs along the soil, the soil particles are collected with the biomass. Furthermore, during the delimbing and debarking process, the separated limbs, leaves and barks (forest residues) are left on the ground. The collection of soil particles is unavoidable during the collection of the forest residues through forwarder (Hartsough et al. 2002; Mooney et al, 2000; Lanford and Stokes, 1996). The skidding of logs and temporary storage of logs in the harvest site are shown on Figure 2.3.

2.4 Factors affecting ash quantity

2.4.1 Plant type

The ash content of the herbaceous biomass is higher than the woody biomass. The ash content of standing woody biomass in dry basis is less than 1% whereas for different herbaceous biomass it is greater than 2% as shown in Table 2.2 (Bakker and Elbersen, 2005)

Table 2.2 Ash content of different plant types (dry basis)

Biomass	Ash Content (%)	Type of plant
Cotton stalk	7	C3
Wheat straw	4	C3
Poplar wood	1	C4
Switchgrass	4	C4
Douglas fir wood	1	C4
Barley straw	6	C3
Rice straw	13	C3
Bagasse	11	C3

C3 plants such as wheat, sorghum, reed canary grass etc. show higher yield potential in temperate and cold climates whereas C4 plants such as sugar cane, maize, miscanthus, switchgrass etc. show higher yield potential in warm condition. Thus, C3 plants require higher water uptake and as inorganic compound is directly related to water intake, the ash content of C3 plants is higher compared to that of C4 plants. The ash content of some of the biomass feedstock are listed in Table 2.2.

2.4.2 Growing conditions

Elbersen et al. (2002) determined total ash and nutrient content of five switchgrass grown on clay and sandy soil and found that switchgrass grown on sandy soil consistently showed lower ash content compared to clay soils. The difference in total ash content among the soil types can be largely explained by the higher soluble silica level in clay soils, which results in high ash levels in crops grown on clay soils.

2.4.3 Plant fraction

The distribution of inorganic compounds vary between different plant fractions. As the inorganic nutrients are carried through the plant body via water, the deposition of ash content differs. Werkelin et al. (2005) measured the ash contents of different plant fractions (stem-wood, branch-wood, stem-bark, branch-bark, twigs, needles, and shoots/leaves) of four woody biomass (Spruce, pine, birch and aspen) and found out that the ash content was higher at the bark and leaves as shown in the Table 2.3. The ash content was highest at the bark, branches, leaf and needles of the tree because the water escapes the plant from these section as a result the inorganic nutrients are concentrated in these sections.

Table 2.3 Ash content of fractions in a plant (wt. %, dry basis.) (Werkelin et al., 2005)

Plant fractions	Spruce	Pine	Birch	Aspen
Stem wood	0.3	0.3	0.3	0.4
Branch wood	0.5	0.4	0.4	0.6
Stem bark	2.6	2.4	2.5	4.1
Branch bark	4.1	3.3	4.2	6.1
Twigs	2.3	2.1	2.0	3.9
Needles	5.2	2.5	ND	ND
Shoots/leaves	4.0	3.0	5.2	7.5

Note: *ND stands for not determined in the study.*

2.4.4 Storage

Storage of biomass plays an effectual role on biomass in terms of its ash content. The biomass can come in contact with soil and water contaminants which contains high amount of inorganic components such as silica, potassium and calcium etc. and thus the ash content in biomass are increased. Storage largely influences the increase in detrital ash in biomass.

Afzal et al. (2009) conducted a study of white birch storage, and found out that as the storage time of the biomass increased, reduction in energy content and dry matter, and an increase in ash content and carbon content occurred. Their study reported the increase in ash content from 0.43% to 1.06% and 1.09% for covered and uncovered white birch woodchips pile respectively. Similarly, Casal et al. (2010) reported an increase of about 1.4% in ash content of pine woodchips during a storage period of 12 months.

2.5 Impacts of ash content

Ash content has direct effect on heating value of biomass as it reduces the combustible compounds in biomass. As ash content increases, the heating value of the biomass decreases. The increase in inorganic compounds limits combustible compounds in the biomass and thus the heating potential of the biomass decreases. Trischler et al. (2014) reported that for biomass with ash increasing from 0.1% to 6.8%, the heating value of the biomass decreased from 3.32 MWH/m^3 to 0.9 MWH/m^3.

During combustion, the conversion of the biomass is affected by slagging and fouling caused by ash content in biomass. Slagging is the deposit of inorganic compounds within furnace, in areas directly exposed to flame radiation such as furnace walls and some widely spaced pendant super-heaters due to the melting of the inorganic compounds. Slagging thereby takes place in the hottest parts of the furnace. High content of some elements (e.g. Si, K, and Na) lower the ash melting temperature (Khan et al., 2009; Jenkins et al., 1998) and high content of K, Si, Mg and P thereby increases the tendency to produce more slagging (Vassilev et al., 2013). Fouling is the deposit in areas not directly exposed to flame radiation but at the more closely spaced tubes in convection sections of furnace. Fouling occurs when hot gases and suspended fly ash, which contains vaporized inorganic compound, cools down in the flue pipes. Biomass is a complex feedstock with diversity of chemical composition that results in different fuel properties. Technical challenges such as slagging, fouling, agglomeration, and corrosion in combustion facilities occur due to combustion of biomass (Khan et al., 2009; Jenkins et al., 1998; Obernberger et al., 2006; Vassilev et al., 2010). These technical challenges can cause physical damage to boilers and bioreactors and can hamper the smooth functioning of the conversion process (Bostrom et al., 2011; Werkelin et al., 2010).

Slagging and fouling, as seen in Figure 2.4, reduces the life and performance of the furnace. As the inorganic compounds adhere to the walls of the furnace, it can corrode the inner lining. Furthermore, large layer of inorganic compounds due to slagging and fouling can obstruct the actual flow of gases which will reduce the operating efficiency of the system. The prevalence of slagging and fouling increases in energy conversion system with increase in biomass ash content. Also as detrital ash increases, at high temperature, silica reacts with the bed material i.e. sand which causes it to be sticky and cause bed agglomeration problems. (Tran et al., 2005; Skrifvars et al., 1999).

Source: http://biomassproject.blogspot.com; http://www.powermag.com

Figure 2.4 Ash slagging and fouling (left and right respectively)

Detrital ash also has financial impact during the logistics. The impact is most prominent during the transportation of the biomass from the harvesting site to the conversion plant. Tahvanainen and Anttila. (2011) calculated the tentative cost of transportation of woody biomass per metric ton per km for different transportation system such as trucks and railways. For trucks, the transportation charge was \$ 0.07 per metric volume of biomass per km and for railroad, the charge was \$0.04 per metric volume of biomass per km. If the ash content of the raw biomass is high, energy and fuel is wasted on transporting higher amount of detrital ash which will add to the financial cost of transportation of fuel wood.

2.6 Ash reduction technique

The authigenic ash, inherent in the biomass, can be removed through chemical processes. Literature has shown that the particular ash component can be reduced via chemical leaching and water washing.

2.6.1 Leaching with chemicals

Jiang et al. (2013) compared the efficacy of leaching with acids at 5 wt. % solutions that are mixed at 10 ml/g ratio with the sample. The samples were stirred for 2 hours at room temperature, rinsed with deionized water until neutral pH was achieved. The results given in Table 2.4 showed that chemical leaching is effective in reducing the ash component.

Table 2.4 Demineralization of rice straw (Jiang et al., 2013)

Sample	Demineralization efficiency (%)				
	K	Na	Ca	Mg	Fe
DI-H_2O-RS	82.3	80.4	17.1	33.5	56.6
CH_3COOH-RS	99.4	81.6	21.8	91.3	54.2
HCl-RS	99.7	88.1	97.9	99.2	76.3
H_2SO_4-RS	99.8	88.5	95.7	98.6	68.5
HNO_3-RS	99.7	84.8	96.8	99.1	65.0
H_3PO_4-RS	99.7	86.2	62.3	98.7	57.9

Note: RS stands for rice straw

Harrison et al. (2013) reported that some acids are more effective than others when used as solvent during steam explosion. Steam explosion ruptures the rigid structure of biomass by defibrillating cellulose bundles and partially hydrolyzing cell wall components. Steam explosion also has been proven to reduce the ash component in Eucalyptus and Acacia fibers. Water leaching was further used to reduce ash content. The ash content was reduced from 0.57% to 0.16% for Eucalyptus and 0.76% to 0.4% for Acacia. (Supantamart et al., 2009)

Pottahil et al. (2011) performed a series of experiments to reduce the ash content of biomass by using alcohol and acid to yield a reaction mixture which was later separated to get solid and liquid fractions. Biomass was then processed to extract proteins and obtain bio-crude fraction. The bio crude fraction included biomass after protein extraction. The bio-crude fraction contained mostly carbohydrates and some protein. The biomass was treated with anhydrous hydro chloric acid (HCl) at 65°C and hydrous HCl at 65° C and 25° C for nearly 60 minutes. The results showed that the bio crude from unprocessed biomass contained about 20% ash, while the ash content of the treated biomass was 8.50% when subjected to anhydrous HCL at 65°C, 8.30% when subjected to HCL at 65 °C and 5.30% when subjected to HCl at 25 °C ash shown in Table 2.5.

Table 2.5 Ash content of the starting biocrude and treated biocrude

Sample	HCL	Methanol	Incubation	Duration	Untreated ash (%)	Treated ash (%)
Biocrude	Anhydrous HCL 1N	Ratio 3 wt/1 wt	65° C.	60 minutes	20.30	8.50
Biocrude	HCL 1N	Ratio 3 wt/1 wt	65° C.	60 minutes	20.30	8.30
Biocrude	HCL 1N	Ratio 3 wt/1 wt	25° C.	60+ minutes	20.30	5.30
Protein treated	Anhydrous 1N	Ratio 3 wt/1 wt	65° C.	60 minutes	12.40	3.92

2.6.2 Leaching with water

Miles et al., (1995) has categorized inorganics into four different types: refractories (Si, Ti, Al) with little or no solubility, alkali and alkaline earth metals (Na, K, Ca, Mg) with varying degree of solubility, nonmetallic elements (Cl, S, P) and iron.

Miles et al., (1995) performed leaching on agricultural residues, wood, grasses and straws where the biomass was soaked in hot water for 16 hours. Si, Ti and Al was not affected but potassium was reduced by 50-90%, Na by 10-90%, Ca by 5-35%, Cl by 30-100% and iron by 0-30%. Saddawi et al., (2012) soaked willow, eucalyptus, miscanthus and wheat straw at room temperature for 20 hours with constant stirring which resulted in more than 30% reduction in sodium, 45% reduction in potassium and 4% reduction in calcium. Werkelin et al., (2010) soaked four species of woody biomass in water at room temperature and reported the following reductions: 75% potassium, 65% sodium, 25% calcium, 10% aluminum, 5% iron and 5% silica.

Turn et al. (1997) removed most of the alkali compounds present in Banagrass using the combination of mechanical compression and leaching of the plant material. Rinsing was done in a barrel which consisted of 52 liters of tap water in which the pressed sample was lowered for about 3 minutes. The untreated biomass consists of K, Si, Cl, Ca and Mg and the ash content was nearly about 3.91%. Ash content decreased with increasing treatment severity, it decreased to 3.1% when undergone through pressed treatment and to about 2.7% when undergone through pressed and rinsed treatments.

Washing biomass with water at ambient temperature can reduce the ash content of the fuel but the efficiency of the removal decreases with the increment in particle size and increases with the increment in the washing temperature. But the impact of washing is minimal on high heating value and further reduces the tendency of fouling and slagging (Gudka et al., 2015).

2.6.3 Physical/Mechanical treatments

The treatment methods explained in the previous section uses water and chemical which produces chemical and water waste. In addition, this requires additional space, treatment cost and disposal cost. Furthermore, these treatments cannot be performed at the harvest site because most of these sites are in remote locations with little or no water availability and facilities for chemical feedstock handling. Hence, physical treatments are more suitable for reducing on-site detrital ash content reduction.

Debarking and delimbing of trees are utilized to obtain clean woodchips. As literature have shown that the ash content in barks, leaves, and branches are higher than the main stem of the tree body, bark and branches are removed and only the central stem are processes as clean woodchips. This is an effective way to achieve biomass with reduced ash content, generally in the region less than 0.8%. However, barks and limbs constitute more than 20% of a tree. Therefore, the loss of such high amount of biomass affects biomass sustainability and the disposal of residual crops.

Dukes et al. (2013) studied the use of trommel screen to reduce ash levels in woody biomass residues at time of production in the harvest site. A trommel screen is a cylindrical body with screener placed in the cylindrical walls. The screen is rotated by an external source in its horizontal axis. The biomass when fed in, are subjected to centrifugal force, resulting in finer particles being removed out from the screen. This approach was made to reduce the amount of fine material contaminants at the source, before the fuel is transported to an energy conversion facility in this study. The ash content level reduced from 4% to 1.4% in roundwood and 11.9% to 6% in chipped wood.

2.7 Energy conversion processes

The structural part of biomass consists of cellulose, hemicellulose, lignin, extractives and other compounds such as minerals. Cellulose is an organic compound with generic formula $(C_6H_{10}O_5)_n$. It consists of linear chain of 100-1000 glucose polymer linked by β (1→4) glycosidic bonds (Crawford, 1981). Hemicellulose is a branched polymer of D-xylose, D-mannose, D-galactose, D-glucose, and L-arabinose with degree of polymerization ranging from 70-200. Lignin is a complex cross-linked phenolic macromolecule with high molecular masses. Lignin is not soluble in water and it is optically inactive. Cellulose fiber is constituted by micro fibrils which is covered by lignin and hemicellulose (Perez et al., 2002; O'Sullivan, 1997, Boerjan et al., 2003). The general structure of cellulose, hemicellulose and lignin can be observed in the Figure 2.5.

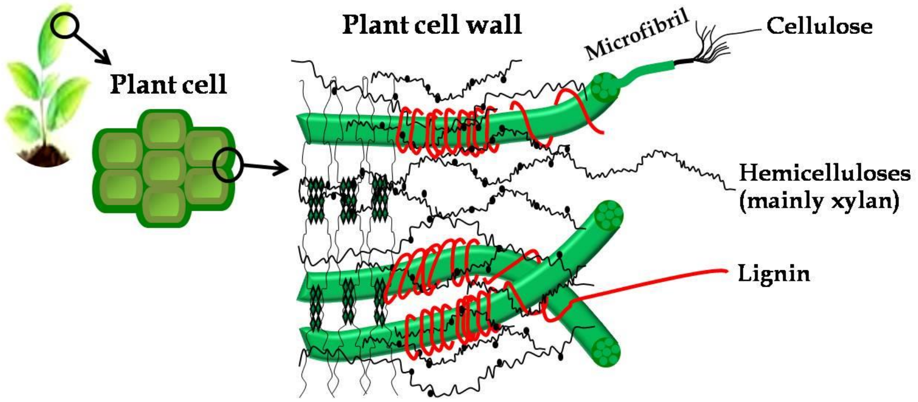


Figure 2.5 Structure of lignocellulosic plant biomass (Tomme et al., 1995)

Lignocellulosic biomass can be converted into biofuels through thermochemical conversion, biochemical conversion and combustion. Biochemical conversion includes the treatment of biomass with microorganisms or enzymes to produce bio-methanol, bioethanol or bio-butanol.

This process can take up to 2 to 5 days. Thermochemical methods require heat and inorganic catalyst for biomass conversion and takes less than an hour (Stevens, 2011).

Thermochemical conversion process, which includes gasification and pyrolysis, has been widely studied. Gasification is partial combustion of carbonaceous fuel to produce a mixture of combustible gases known as syngas which can be used in generation of heat and electricity. Gasification is carried out at temperature greater than 700 ^{o}C (Stevens and Brown, 2011; Sheth and Babu, 2009). Pyrolysis of biomass involves heating of biomass at 450-600 ^{o}C in absence of oxygen which results in the production of char, liquid yield, non-condensable gases and aerosols.

2.8 Fast pyrolysis

Fast pyrolysis is characterized by high heating rates and short vapor residence time in the reactor. The thermal degradation of biomass occurs in absence of oxygen which generally depends upon the size of the biomass, heating rate, temperature of the reactor, the reactor mechanism and presence of impurities in the biomass and reactor itself (Brownsort, 2009). Pyrolysis produce char, non-condensable gases, volatile vapors and aerosols. Volatile vapors and aerosols under rapid cooling condenses to give bio-oil. Criteria for the fast pyrolysis are: moderate temperature of 400-600^{o}C, high heating and transfer rates and short residence time of less than 2 s.

2.8.1 Pyrolysis mechanism

Pyrolysis is an endothermic reaction and heat transfer occurs via conduction and convection. The major events occurring during the pyrolysis in the reactor was studied by Mohan et al., (2006) and Gupta and Demirbas, (2010). The heat transferred from the source increases the temperature of the biomass which initiates the pyrolysis and releases volatiles and char. The heat from volatiles is transferred to heating of biomass as well. The condensation of volatile takes place which is followed by secondary reactions to produce tar. Residence time and temperature defines the rate of decomposition, reforming, water-gas shift reaction, radical combination and dehydration (Kilzer and Broido, 1965).

The main component of biomass; cellulose, hemicellulose, lignin, extractives and ash contribute to the product yield when heated at pyrolysis temperature (Brownsort, 2009) as shown in Figure 2.6. The primary products of the cellulose and hemicellulose are organic liquids, water and non-condensable gases. Lignin decomposes to give char, organic liquids and non-condensable gas. Extractives, generally smaller organic molecules of polymers, decomposes to give liquid and gas products either through simple volatilization or decomposition.

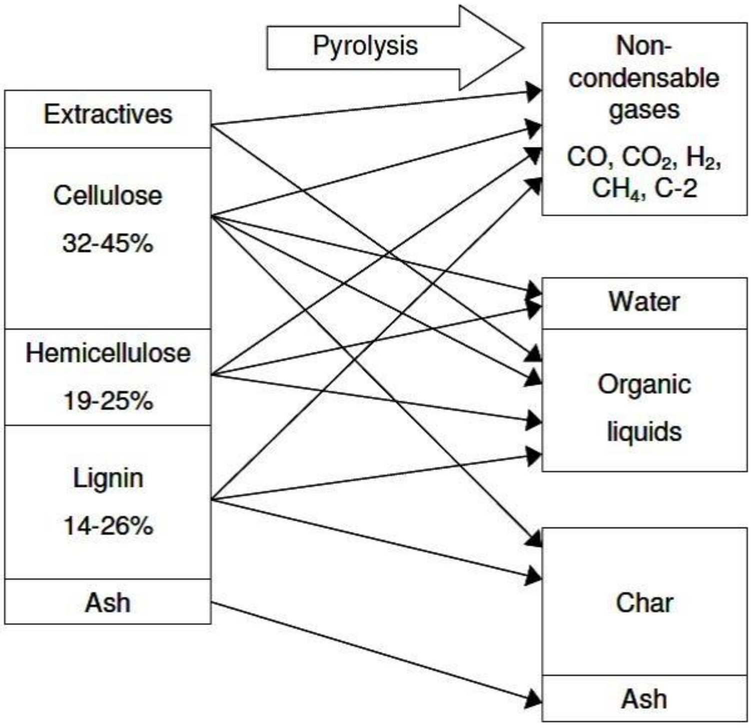


Figure 2.6 Simplified representation of biomass pyrolysis (Brownsort, 2009)

2.8.2 Pyrolysis reactors

Pyrolysis reactors that are commonly used to produce bio-oil from biomass include ablative pyrolysis reactors, bubbling and circulation fluidized bed reactor, vacuum pyrolysis and auger reactor. Reactor design plays an important role in bio-oil yield and distribution of compounds in bio-oil (Bridgwater and Peacocke, 2000; Scott et al., 1999). In ablative pyrolysis reactors, biomass is pressed against the heating surface and rapidly move and as a result thin film of bio-oil is left. In the fluidized bed and circulating fluid bed pyrolysis, heat is transferred by conduction and convection and an external carrier gas is required. The heating rate for vacuum pyrolysis are lower than the ablative and fluidized bed reactors. The vapor are removed by the vacuum pump which allows higher yield of bio-oil. Auger reactor uses auger to feed the biomass inside the heated cylinder which does not require carrier gas. Residence time of the solids can be managed by the speed of the auger.

2.9 Bio-oil characteristics

Bio-oil of woody biomass is viscous dark brown colored liquid with heavy distinct smell (Jahirul et al., 2012). The quality of bio-oil is determined from properties such as pH, TAN, water content, viscosity, density, heating value and elemental analysis.

- Density and viscosity defines the flow properties of the bio-oil. They are needed to design pump and pipe line for combustion systems that use bio-oil as fuel. The density of bio-oil in general is around 1100-1300 kg/m^3 for bio-oil with water content of approximately 25% (ASTM D, 7544). Viscosity of bio-oil varies with the amount of water in the bio-oil, oxygen content and storage condition of bio-oil. Hence, it may be in the wide range of 35-1000 cp at 40^{o}C. (Diebold and Czernik, 1997).

- The oxygen content of fast pyrolysis bio-oil is typically about 35-40%. It is found to be embodied with more than 300 compounds identified in bio-oil.
- Water content in bio-oil is present due to the moisture content of biomass and as a by-product of dehydration reactions taking place during pyrolysis. It is present either in dissolved state or exists as a micro emulsion and cannot be removed by physical separation process. The water content in biomass in general is less than 30% and ASTM recommends water content on bio-oil below 30 wt.% for the use in industrial (ASTM D, 7544)
- pH and TAN number is a measure of the acidity of the bio-oil. The acidity of bio-oil is mainly due to the presence of volatile acids, acetic acids and formic acid in bio-oil. The phenolic compound also increases the acidity of the bio-oils. The pH of bio-oils is less than 3 for woody biomass and TAN is generally in the region of 100 (Agblevor et al., 2010; Oasmaa et al., 2010)
- The higher heating value of bio-oil is greater than 17 MJ/kg which is almost half of the other conventional fossil fuel oils. The energy density (MJ/m^3) of bio-oil is greater than that of the biomass and thus is effective in storage and transportation.

2.10 References

Abbas, T., Costen, P., Kandamby, N. H., Lockwood, F. C., & Ou, J. J. (1994). The influence of burner injection mode on pulverized coal and biomass co-fired flames. *Combustion and flame, 99*(3), 617-625.

Afzal, M. T., Bedane, A. H., Sokhansanj, S., & Mahmood, W. (2009). Storage of comminuted and uncomminuted forest biomass and its effect on fuel quality.*BioResources, 5*(1), 55-69.

Agblevor, F. A., & Shao, J. (2010, November). Rapid method for the determination of total acid number (TAN) of biooils. In *Proceedings of the AIChE 2010 Annual Meeting*.

ASABE Standards. (2011). S593.1: Terminology and Definitions for Biomass Production, Harvesting and Collection, Storage, Processing, Conversion and Utilization. *ASABE*, St. Joseph, MI 49085-9659

ASTM D 7544. (2009). Standard specification for pyrolysis liquid biofuel, in petroleum standards (D02.E0). Book of standards. Volume: 05.04.2009. *ASTM International West Conshohocken*, PA, USA

Baernthaler, G., Zischka, M., Haraldsson, C., & Obernberger, I. (2006). Determination of major and minor ash-forming elements in solid biofuels.*Biomass and Bioenergy, 30*(11), 983-997.

Bakker, R. R., & Elbersen, H. W. (2005, October). Managing ash content and quality in herbaceous biomass: an analysis from plant to product. In *14th European Biomass Conference* (pp. 210-213).

Bedane, A. H., Afzal, M. T., & Sokhansanj, S. (2011). Simulation of temperature and moisture changes during storage of woody biomass owing to weather variability. *Biomass and bioenergy, 35*(7), 3147-3151.

Boerjan, W., Ralph, J., & Baucher, M. (2003). Lignin biosynthesis. *Annual review of plant biology, 54*(1), 519-546.

Boström, D., Skoglund, N., Grimm, A., Boman, C., Ohman, M., Broström, M., & Backman, R. (2011). Ash transformation chemistry during combustion of biomass. *Energy & Fuels, 26*(1), 85-93.

BRDB. (2010). Biomass Research and Development Board. Biofuel feedstock logistics: Recommendations for research and commercialization. *http://www.biomassboard.gov/pdfs/biomass_logistics_2011_web.pdf*. Accessed on 16th April 2015.

Bridgwater, A. V., & Peacocke, G. V. C. (2000). Fast pyrolysis processes for biomass. *Renewable and sustainable energy reviews, 4*(1), 1-73.

Brown, R. (2009). Bio-char Production Technology. In J. Lehmann and S. Joseph (eds.) *Bio-char for Environmental Management*. Earthscan, London

Brownsort, P.A. (2009). *Biomass pyrolysis processes: performance parameters and their influence on bio-char system benefits*. University of Edinburgh, UK

Casal, M. D., Gil, M. V., Pevida, C., Rubiera, F., & Pis, J. J. (2010). Influence of storage time on the quality and combustion behaviour of pine woodchips. *Energy*, *35*(7), 3066-3071.

Claar, P.W. II, Buchele, W.F., & Marley, S.J. (1981). Development of a concentric-vortex agricultural-residue furnace. In *ASAE Publ.; (United States)* (Vol. 4–81). United States.

Crawford, R. L. (1981). *Lignin biodegradation and transformation* (p. 154). New York: Wiley.

Demirbas, A. (2004). Combustion characteristics of different biomass fuels. *Progress in energy and combustion science*, *30*(2), 219-230.

Demirbaş, A. (1997). Calculation of higher heating values of biomass fuels. *Fuel*, *76*(5), 431-434.

Demirbas A. (2001). Biosource facilities and biomass conversion processing for fuels and chemicals. *Energy conversion and management*. 42, 1357-1378

Diebold, J. P., & Czernik, S. (1997). Additives to lower and stabilize the viscosity of pyrolysis oils during storage. *Energy & Fuels, 11*(5), 1081-1091.

Dukes, C. C., Baker, S. A., & Greene, W. D. (2013). In-wood grinding and screening of forest residues for biomass feedstock applications. *Biomass and Bioenergy, 54*, 18-26.

Ebeling, J. M., & Jenkins, B. M. (1985). Physical and chemical properties of biomass fuels. *Transactions of the ASAE (American Society of Agricultural Engineers), 28*(3), 898-902.

EIA. (2013). U.S. Energy Information Administration: *International Energy Outlook 2013*. Available at http://www.eia.gov/forecasts/ieo/pdf/0484(2013).pdf. Accessed 17 March, 2015

EIA. (2014). United States Energy Information Administration: *International Energy Outlook 2014*. Available at http://www.eia.gov/forecasts/ieo/pdf/0484(2014).pdf. Accessed 17 March, 2015

EIA. (2015). United States Energy Information Administration: *International Energy Outlook 2015*. Available at *http://www.eia.gov/forecasts/steo/pdf/steo_full.pdf*. Accessed 17 March, 2015

Elbersen H.W. et al. (2002). Switchgrass as an alternative energy crop in Europe, *Final Report FAIR 5-CT97-3701*. Available at www.switchgrass.nl

Gudka, B., J.M. Jones, A.R. Lea-Langto, A. Williams. A. Saddawi. (2015). A review of mitigation of deposition and emission problems during biomass combustion through washing pre-treatment. *Journal of Energy Institute In press.* Available online on March, 2015

Gupta, R. B., & Demirbas, A. (2010). *Gasoline, diesel and ethanol biofuels from grasses and plants*. Cambridge University Press.

Harrison, M. D., Zhang, Z., Shand, K., O’Hara, I. M., Doherty, W. O., & Dale, J. L. (2013). Effect of pretreatment on saccharification of sugarcane bagasse by complex and simple enzyme mixtures. *Bioresource technology, 148*, 105-113.

Hartiniati, S. A., & Youvial, M. (1989, May). Performance of a pilot scale fluidized bed gasifier fueled by rice husks, pyrolysis and gasification. In *Proceedings of the international conference in Luxembourg* (pp. 23-25).

Hartsough, B. R., Spinelli, R., & Pottle, S. J. (2002). Delimbing hybrid poplar prior to processing with a flail/chipper. *Forest products journal, 52*(4), 85-93.

Hodge, B. K., & Hodge, B. K. (2010). *Alternative energy systems and applications* (p. 129). Wiley.

IEA. (2006). International Energy Agency. *World energy outlook 2006.*

Jahirul, M. I., Rasul, M. G., Chowdhury, A. A., & Ashwath, N. (2012). Biofuels production through biomass pyrolysis—a technological review. *Energies, 5*(12), 4952-5001.

Jenkins, B. M., Baxter, L. L., & Miles, T. R. (1998). Combustion properties of biomass. *Fuel processing technology, 54*(1), 17-46.

Jiang, L., Hu, S., Sun, L. S., Su, S., Xu, K., He, L. M., & Xiang, J. (2013). Influence of different demineralization treatments on physicochemical structure and thermal degradation of biomass. *Bioresource technology, 146*, 254-260.

Khan, A. A., De Jong, W., Jansens, P. J., & Spliethoff, H. (2009). Biomass combustion in fluidized bed boilers: potential problems and remedies. *Fuel processing technology, 90*(1), 21-50.

Kilzer, F. J., & Broido, A. (1965). Speculations on nature of cellulose pyrolysis. *Pyrodynamic, 2*(2-3), 151.

Kozlowsky, T. T., Pallardy, S. G., & Kramer, P. J. (1997). Physiology of woody plants. *University of California, Berkeley*.

Lanford, B. L., & Stokes, B. J. (1996). Comparison of two thinning systems. Part 2. Productivity and costs. *Forest Products Journal, 46*(11/12), 47.

Manzone, M., & Spinelli, R. (2013). Wood chipping performance of a modified forager. *Biomass and Bioenergy, 55*, 101-106.

Miles, T. R., Miles Jr, T. R., Baxter, L. L., Bryers, R. W., Jenkins, B. M., & Oden, L. L. (1995). *Alkali deposits found in biomass power plants: A preliminary investigation of their extent and nature. Volume 1* (No. NREL/TP--433-8142-Vol. 1; SAND--96-8225-Vol. 1). National Renewable Energy Lab., Golden, CO (United States); Miles (Thomas R.), Portland, OR (United States); Sandia National Labs., Livermore, CA (United States); Foster Wheeler Development Corp., Livingston, NJ (United States); California Univ., Davis, CA (United States); Bureau of Mines, Albany, OR (United States). Albany Research Center.

Mohan, D., Pittman, C. U., & Steele, P. H. (2006). Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy & Fuels*, *20*(3), 848-889.

Mooney, S. T., Boston, K. D., & Greene, W. D. (2000). Production and costs of the chambers delimbinator in first thinning of pine plantations. *Forest products journal*, *50*(4), 81.

Murphy, G., Kent, T., & Kofman, P. D. (2012). Modeling air drying of Sitka spruce (Picea sitchensis) biomass in off-forest storage yards in Ireland. *Forest Products Journal*, *62*(6), 443-449.

Naimi, L. J., Sokhansanj, S., Mani, S., Hoque, M., Bi, T., Womac, A. R., & Narayan, S. (2006, July). Cost and performance of woody biomass size reduction for energy production. In *CSBE/SCGAB 2006 Annual Conference, American Society of Agricultural and Biological Engineers, Edmonton, Alberta*.

O'Sullivan, A. C. (1997). Cellulose: the structure slowly unravels. *Cellulose*, *4*(3), 173-207.

Oasmaa, A., Elliott, D. C., & Korhonen, J. (2010). Acidity of biomass fast pyrolysis bio-oils. *Energy & Fuels*, *24*(12), 6548-6554.

Obernberger, I., Brunner, T., & Bärnthaler, G. (2006). Chemical properties of solid biofuels—significance and impact. *Biomass and Bioenergy*, *30*(11), 973-982.

Pérez, J., Munoz-Dorado, J., de la Rubia, T. D. L. R., & Martinez, J. (2002). Biodegradation and biological treatments of cellulose, hemicellulose and lignin: an overview. *International Microbiology*, *5*(2), 53-63.

Perlack, R. D., Eaton, L. M., Turhollow Jr, A. F., Langholtz, M. H., Brandt, C. C., Downing, M. E., ... & Lightle, D. (2011). US billion-ton update: biomass supply for a bioenergy and bioproducts industry.

Pilon-Smits, E. A., Quinn, C. F., Tapken, W., Malagoli, M., & Schiavon, M. (2009). Physiological functions of beneficial elements. *Current opinion in plant biology*, *12*(3), 267-274.

Pottathil, R., Bowers Jr, J. S., & Havemann, G. D. (2011). *U.S. Patent Application 13/157,293*.

Pottie, M. A., & Guimier, D. Y. (1985). *Preparation of forest biomass for optimal conversion* (p. 112). Forest Engineering Research Institute of Canada.

Saddawi, A., Jones, J. M., Williams, A., & Le Coeur, C. (2012). Commodity fuels from biomass through pretreatment and torrefaction: effects of mineral content on torrefied fuel characteristics and quality. *Energy & Fuels, 26*(11), 6466-6474.

Scott, D. S., Majerski, P., Piskorz, J., & Radlein, D. (1999). A second look at fast pyrolysis of biomass—the RTI process. *Journal of Analytical and Applied Pyrolysis*, *51*(1), 23-37.

Sheth, P. N., & Babu, B. V. (2009). Experimental studies on producer gas generation from wood waste in a downdraft biomass gasifier. *Bioresource Technology*, *100*(12), 3127-3133.

Silva, J. A., & Uchida, R. S. (2000). Plant Nutrient Management in Hawaii's Soils: Approaches for Tropical and Subtropical Agriculture.

Skrifvars, B. J., Öhman, M., Nordin, A., & Hupa, M. (1999). Predicting bed agglomeration tendencies for biomass fuels fired in FBC boilers: a comparison of three different prediction methods. *Energy & Fuels*, *13*(2), 359-363.

Stelt, M. J. C., Gerhauser, H., Kiel, J. H. A., & Ptasinski, K. J. (2011). Biomass upgrading by torrefaction for the production of biofuels: a review. *Biomass and bioenergy, 35*(9), 3748-3762.

Stevens, C. (2011). *Thermochemical processing of biomass: conversion into fuels, chemicals and power*. R. C. Brown (Ed.). John Wiley & Sons.

Supantamart, N., Laemsak, N., Sirisansaneeyakul, S., Vanichsriratana, W., & Parakulsuksatid, P. (2009). Effect of steam explosion on chemical compositions of biomass from Eucalyptus and Acacia. In *3rd international conference on fermentation technology for value added agricultural production, Thailand*.

Tahvanainen, T., & Anttila, P. (2011). Supply chain cost analysis of long-distance transportation of energy wood in Finland. *Biomass and Bioenergy, 35*(8), 3360-3375.

Tembo, G., Epplin, F. M., & Huhnke, R. L. (2003). Integrative investment appraisal of a lignocellulosic biomass-to-ethanol industry. *Journal of Agricultural and Resource Economics,* 611-633.

Tillman, D. A. (2000). Biomass cofiring: the technology, the experience, the combustion consequences. *Biomass and Bioenergy, 19*(6), 365-384.

Tomme, P., Warren, R. A. J., & Gilkes, N. R. (1995). Cellulose hydrolysis by bacteria and fungi. *Advances in microbial physiology, 37*(1), 1-81.

Tran, K. Q., Iisa, K., Steenari, B. M., & Lindqvist, O. (2005). A kinetic study of gaseous alkali capture by kaolin in the fixed bed reactor equipped with an alkali detector. *Fuel*, *84*(2), 169-175.

Trischler, J., Sandberg, D., & Thörnqvist, T. (2014). Evaluating the Competition of Lignocellulose Raw Materials for their Use in Particleboard Production, Thermal Energy Recovery, and Pulp-and Papermaking. *BioResources*, *9*(4), 6591-6613.

Tucker, M. R. (1999). *Essential plant nutrients: their presence in North Carolina soils and role in plant nutrition*. Department of Agriculture and Consumer Services, Agronomic Division.

Turn, S. Q., Kinoshita, C. M., & Ishimura, D. M. (1997). Removal of inorganic constituents of biomass feedstocks by mechanical dewatering and leaching. *Biomass and Bioenergy*, *12*(4), 241-252.

Uihlein, A., & Schebek, L. (2009). Environmental impacts of a lignocellulose feedstock biorefinery system: an assessment. *Biomass and Bioenergy*, *33*(5), 793-802.

Vassilev, S. V., Baxter, D., Andersen, L. K., & Vassileva, C. G. (2010). An overview of the chemical composition of biomass. *Fuel*, *89*(5), 913-933.

Vassilev, S. V., Baxter, D., Andersen, L. K., Vassileva, C. G., & Morgan, T. J. (2012). An overview of the organic and inorganic phase composition of biomass. *Fuel*, *94*, 1-33.

Vassilev, S. V., Baxter, D., & Vassileva, C. G. (2013). An overview of the behaviour of biomass during combustion: Part I. Phase-mineral transformations of organic and inorganic matter. *Fuel*, *112*, 391-449.

Werkelin, J., Skrifvars, B. J., & Hupa, M. (2005). Ash-forming elements in four Scandinavian wood species. Part 1: Summer harvest. *Biomass and Bioenergy*, *29*(6), 451-466.

Werkelin, J., Skrifvars, B. J., Zevenhoven, M., Holmbom, B., & Hupa, M. (2010). Chemical forms of ash-forming elements in woody biomass fuels. *Fuel*, *89*(2), 481-493.

Zhang, M., Song, X., Pei, Z. J., & Wang, D. H. (2010, January). Effects of mechanical comminution on enzymatic conversion of cellulosic biomass in biofuel manufacturing: a review. In *ASME 2010 International Manufacturing Science and Engineering Conference* (pp. 497-504). American Society of Mechanical Engineers.

Zhou, C., Jiang, W., Via, B. K., Fasina, O., & Han, G. (2015). Prediction of mixed hardwood lignin and carbohydrate content using ATR-FTIR and FT-NIR. *Carbohydrate polymers*, *121*, 336-341.

CHAPTER 3

REDUCTION OF ASH CONTENT OF BIOMASS

3.1 Abstract

Woody biomass is a potential bioenergy feedstock but the collection of soil particles during harvesting and preprocessing and lowers its energy value. Moreover, the presence of ash affects thermochemical conversion process such as pyrolysis and lowers the production yield and heating value of the bio-oil produced. This study aims to reduce the amount of soil contaminants in woody biomass by physical treatments with vibratory sieve shaker, hammer mill and concrete. The three treatment processes were tested on the residual pine wood, whole pine wood, sweetgum, and pine wood maintained at three ash content levels (5%, 8% and 10%) and at three moisture content levels (10%, 20% and 30%). Ash and moisture content of dirty pinewood were adjusted to desired levels by adding calculated amount of soil and water. All of the three treatment processes significantly ($p<0.05$) reduced the ash content of the whole pinewood, residual pinewood and sweetgum that were at initial ash content level of about 2%. Mixer reduced the ash content of sweetgum, whole pinewood and residual pinewood from 2.14%, 2.31% and 1.69% to 1.71%, 1.73% and 1.20%, respectively. Similarly, vibratory sieve shaker reduced the ash content of sweetgum, whole pinewood and residual pinewood to 1.66%, 1.90% and 1.24%, respectively. However, the hammer mill treatment was more efficient in reducing the ash content for pinewood with coated ash content (>5%) compared to the other two processes. Hammer mill reduced the ash content of dirty

pinewood from 6.64%, 8.34% and 10.40% to 1.88%, 3.36% and 3.15%, respectively. The reduction in ash content resulted in increases in volatile matter and heating value of the biomass. The effect of moisture content (10%, 20% and 30%) on ash content reduction was also quantified. Ash reduction rate was highest for samples at 10% moisture content that were treated with vibratory sieve shaker and with mixer. Hammer mill significantly reduced ($p<0.05$) ash content at different moisture content levels but no significant effect of moisture content was observed. The ash content of samples treated with vibratory sieve shaker reduced by 48% at 10% of moisture content compared to 13.29% at 30% of moisture content. Similarly for mixer, the reduction rate was 40.41% at 10% of moisture content for biomass at 10% of ash content compared to reduction rate of 8.59% at 30% of moisture content. The ash reduction rate of samples treated with hammer mill was greater than 50% at all the moisture levels.

3.2 Introduction

In the Southeastern United States, biomass is the most promising renewable energy resource. Stable climate and soil favors abundant biomass production, and more than half of the southeastern United States is covered in forests (Walsh et al., 2000). In fact about 60% of U.S. timber product is produced from over 80 million ha of southeastern timberland. Furthermore, the forest industry is highly developed in this region and already operates efficient pine production on a commercial scale (Kline and Coleman, 2010). Hardwoods are of special interest as potential feedstock for a biofuel industry because of their high rates of production, physical characteristics favorable for some energy-conversion processes, and recent progress with genetic mapping (Tuskan et al., 2006). Softwoods such as pine has received less attention as a feedstock for conversion to liquid transportation fuels (e.g., ethanol) because relatively high levels of secondary chemicals in pine create impediments for biochemical conversion.

Round year availability of biomass is essential for the smooth operation of bio-refineries. Biomass logistics involves the unit operations that are used to prepare biomass for energy conversion such as harvesting, storage, preprocessing, transportation and handling. Hence, biomass logistics plays an important role (BRDB, 2010) and the method used to handle biomass can alter its properties. For example, biomass moisture content and ash content can vary significantly during logistics.

Ash content is present in biomass because of natural process, and of handling process. Soil and water uptakes during growth leads to absorption of different inorganic elements such as iron, calcium, phosphorus and manganese which are required for growth. The ash content accumulated inside the biomass is known as authigenic ash content. Woody biomass are also contaminated with soil/sand particles during felling and skidding that results in higher ash content. The ash content accumulated on the surface of the biomass as a result of this contamination is known as detrital ash. Literature have shown that the biomass with lower ash content have higher volatile matter, and energy content that ultimately results in higher yield of bio-oil (Mani et al., 2004; Dhiman, 2014). Hence, preprocessing operations that remove or reduce the ash content in biomass is advantageous.

Water and acids such as hydrochloric acid, nitric acid and sulphuric acids have been used to reduce the ash content of biomass by leaching. Jiang et al. (2013) showed that demineralization efficiency for potassium, calcium, sodium, magnesium and iron present in rice straw was more than 60% when hydrochloric acid, nitric acid and sulphuric acids were used. Similarly, Supantamart (2009) showed that ash content was reduced to 0.16% from 0.57% for Eucalyptus by water leaching. However, leaching requires use of water and chemicals that increases handling and disposal issues of the water and chemicals after the treatment. Physical treatments at site presents a much more direct approach to reduce the ash content as studied by Dukes et al. (2013). It can further reduce the transportation cost of biomass as the biomass will have less impurities in terms of soil contamination.

The objective of this study was to utilize physical treatment processes to reduce the ash content of the biomass. The effectiveness of the physical treatment was tested by applying the treatment processes to biomass at different ash content levels. Since moisture content in the biomass increases the adhesion force between woodchips and ash content, the effect of moisture content on the reduction of ash content was also tested.

3.3 Experimental Setup

Residual pinewood, whole pinewood and sweetgum were obtained from local forest of Tuskegee, Alabama for this study. Residual pinewood contained stem, bark and leaves whereas whole pinewood contained only stem and bark of freshly felled tree. Sweetgum contained stem and bark. The samples were obtained at high moisture content (greater than 50%) and were air dried for seven days as shown in Figure 3.1. The moisture content of the air dried samples were 8.65 ± 0.17 % for residual pinewood, 8.14 ± 0.15% for whole pinewood and 8.73 ± 0.24% for sweetgum on dry basis. Moisture content determination was carried out according to ASABE Standard S358.3 (ASABE Standards, 2012) by oven drying about 10 g samples at 105°C for 24 hours.

The objective for this study required woodchips with varying ash content as high as 10% and at varying moisture content of 10, 20 and 30%. The ash content of residual pinewood, whole pinewood and sweetgum gum was less than 3% which was measured according to National Renwable Energy laboratory (NREL, 2005) analytical process. The woodchips with required ash content level were not available for procurement hence dried clean pinewood was used for adjusting moisture and ash content. Pinewood was obtained at initial moisture content of 10.52%

from Auburn University. Rewetting was carried out and soil was added to the clean pinewood to obtain the necessary ash content and moisture content.

Figure 3.1 Air drying of residual pinewood, whole pinewood and sweetgum

3.3.1 Sample Preparation

Residual pinewood, whole pinewood and sweetgum were used to study the effect of initial ash content of biomass. Furthermore, clean pinewood, obtained from Auburn University, was rewetted with water and soil coating was done to attain the biomass at different initial ash content level of 5%, 8% and 10% (d.b.) and moisture content level of 10%, 20% and 30% (d.b.), respectively.

The clean pine woodchips were fractionated to the size of 7mm-45mm using TMI chips classifier (model 36852 – 07, Testing Machines, Inc., New Castle, Del.) prior to rewetting and soil coating to ensure the homogenous coating of soil particles on the woodchips The moisture content of the clean pine wood was 10.52% and ash content was 0.56% (d.b.). Soil, collected from the University ground, with ash content of 85.11% was used to increase the ash content. Tap water was used to increase the moisture content. Calculated amount of water and soil was added to adjust the moisture content and ash content of the woodchips (Pradhan et al., 2008; Sacilik et al., 2003). 20% excess of soil was added because from the preliminary experiments, it was observed that the calculated amount of soil always gave less ash content as compared to the calculation. It was because the soil particles adhered to the walls of mixer where the mixing was done.

Calculated mass of water was added to maintain the moisture content at 40%. The samples were then oven dried at 35^{o}C for 6 hours, 24 hours and two days respectively to attain the moisture content level of 30%, 20% and 10% respectively.

Fine mixture of water and soil was prepared which was added to 5 kg of pine woodchips. The sample was then mixed using concrete mixer for 15 minutes to obtain the homogenous mixture of the soil water and woodchips as shown in Figure 3.2. The samples were then stored in black polythene bag in room temperature for 10 days.

Figure 3.2 Soil and water mixture (left); Coating in mixer (right)

3.3.2 Instruments setup and working parameters

Three methods were used for physical reduction of ash in the biomass samples prepared in Section 3.3.1. The methods are based on the use of: vibratory sieve shaker (Kason Corp., model K30-2-8S, NJ, USA), concrete mixer, and hammer mill (C.S. Bell Co., model 10HBLPK, Tiffin, OH, USA).

Figure 3.3 Vibratory sieve shaker used for separating soil particles (fine)

Vibratory sieve shaker (Kason Corp., model K30-2-8S, NJ, USA) (Figure 3.3) works on the principle of sieve shaking separation. The dirty woodchips with high ash content was fed in from the top of the sieve shaker and processed for three minutes. The sieve shaker separated the dirty woodchips into treated clean woodchips and fine residues. Fine residues passed through the screen and were collected as waste product. From the preliminary study, three minute was sufficient for the separation of some of the dirt particles from 2 kg of biomass as the flow of fine particles stopped at around 3 minutes. A screen size of 500 micron was used for separation since the average particle size was less than 0.5 mm for soil components, 0.003-0.06 mm for silt and 0.004mm for clay (UCL, 2015). Furthermore, the size of dust has been defined as material capable of passing through U.S. No. 35 standard sieve (500 microns) by NFPA, (2013). Therefore, the 500 microns screener enabled the removal of both the soil particles and the dust particles to eliminate the dust explosion hazard.

Concrete mixer (Figure 3.4) was used to treat the dirty woodchips by inducing rotatory force that separates the dirt particles (soil particles) from the surface of the woodchips. The mixer rotates at the speed of 20-25 rpm. Due to this rotation, the woodchips inside the mixer collide with each other. The collision between the woodchips can scrape the soil particle from the surface of the woodchips. The mixer was run for three minutes to keep in line with the running time of the vibratory sieve shaker. The treated samples from mixer was then fed into vibratory sieve shaker for separation of the small detached particles (< 500 microns) from the chips.

Figure 3.4 Concrete mixer used for separation of soil particles from woodchips

The third process includes hammer mill (C.S. Bell Co., model 10HBLPK, Tiffin, OH, USA) (Figure 3.5), which beats the woodchips with hammers reducing the size of the woodchips. The force generated by the hammer to reduce the size of the woodchips was sufficient to separate the soil particles from the surface of the woodchips from the impact force. The screen size used in the hammer mill was 25 mm in diameter. As the woodchips were roughly in 7-45mm in size, the 25 mm screener was used to hold the chips inside the hammer mill for the separation of soil particles. The woodchips were fed into the hammer mill at rate of 2 kg per minute. The samples were then fed into the vibratory sieve shaker to separate the fine residues from the woodchips.

Figure 3.5 Hammer mill used for separation of soil particles from woodchips

The schematic flow of the experiment is given in the Figure 3.6. The dirty woodchips with high ash content is treated with three treatment methods: vibratory sieve shaker, mixer and hammer mill. The treatment equipment remove the soil particles from the surface of the woodchip. The treated samples are collected and again fed to the vibratory sieve shaker, which separates the fine soil particles which are collected as waste product or residue. The woodchips collected after the sieve shaker are clean woodchip with reduced ash content and are prepared for different physiochemical analysis.

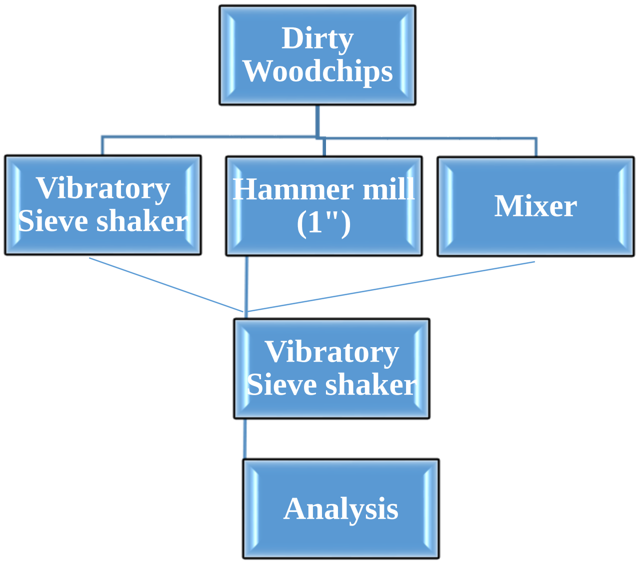


Figure 3.6 Experiment design of physical treatment process

3.3.3 Data collection

The mass of the woodchips before and after the treatment and mass of fine residue after each treatment were recorded to calculate the mass balance and to understand the loss of mass as fome residues during the treatment. Residue is the fine particles separated out from the vibratory sieve shaker, which mostly comprised of soil particles (ash). Mass difference was calculated as difference between the initial mass of the sample and treated sample.

Proximate and ultimate analyses were carried out on the dirty and treated woodchips. Since some of the woodchips were treated at higher moisture content of 20% and 30%, they were first oven dried at 35^{o}C to reduce the moisture content to less than 10%. The samples were then ground through 3.175 mm screener in hammer mill and 1 mm screener in Wiley mill. Proximate analysis (ash content, volatile matter and energy content), particle density and particle size were then measured and calculated for the dirty and treated samples. Moisture content was measured on the samples on the day of the experiment.

3.3.3.1 Moisture content

Moisture content of the woodchips and ground material of the samples from each treatment was measured following ASABE Standard S358.3 (ASABE Standards, 2012). The experiment was performed in triplicates and equation 3.1 was used to estimate the moisture content of the samples in wet basis.

$$\text{Moisture content (M.C)} = \frac{\text{wi}-\text{wf}}{\text{wi}} \text{ x } 100\% \qquad (3.1)$$

where,

wi = initial mass of sample (g)
wf = final mass of sample after drying (g)
MC = moisture content of the sample (%)

3.3.3.2 Particle density

Particle density was measured by gas pycnometer (Model AccuPyc II 1330, Micrometrics Instrument Corp., and Norcross, GA) (Figure 3.7). Particle density was calculated for both dirty woodchips ground through 1 mm Wiley mill and treated woodchips ground through 1 mm Wiley mill. The AccuPyc works by measuring the amount of displaced gas [helium]. The pressures observed upon filling the sample chamber and then discharging it into a second empty chamber allow computation of the sample solid phase volume. Gas molecules rapidly fill the tiniest pores of the sample; only the truly solid phase of the sample displaces the gas.

Nearly 2/3rd to 3/4th of the container was filled with sample and was weighed with a digital balance (New Classic ML Analytical Balance, Model MS303SE) accurate to 0.0001g. The sample was then used in the pycnometer which gave average volume of the compound along with standard deviation. The ratio of the sample to the volume was used to compute the particle density.

Figure 3.7 AccuPyc II 1330 Pycnometer to measure the volume of biomass

3.3.3.3 Particle size determination

The particle size distribution of the dirty and treated woodchips ground through 1mm Wiley mill was determined using a camsizer (Retsch Technology, Haan, Germany) (Figure 3.8). The camsizer uses the principle of digital image processing. The particles drop between an extended light source and two digital cameras. The projected particle shadows are recorded at a rate of more than 60 images per second and analyzed. In this way every single particle in the bulk material flow is recorded and evaluated. The particle size distribution on volume basis of the sample was recorded and analyzed by the software provided by the equipment manufacturer.

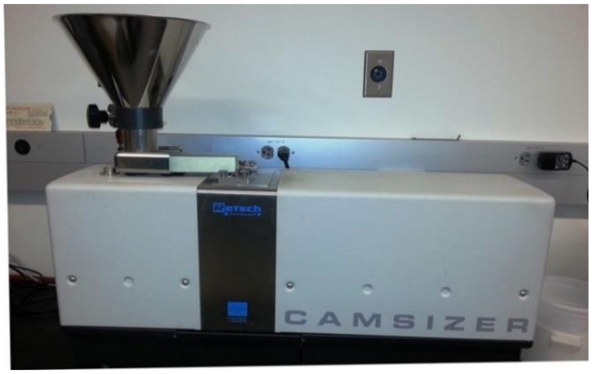


Figure 3.8 Camsizer to determine the particle size distribution of biomass

3.3.3.4 Energy content

The heating value of the raw and treated woodchips ground through 1 mm Wiley mill was obtained with a bomb calorimeter, IKA C200 calorimeter (IKA Works, Wilmington, N.C.) (Figure 3.9). A press (IKA Works Inc, model C21, Wilmington, NC, USA) was used to make pellets out of 0.5-1 g of sample. The energy content was measured by the heat created by the pellet when burned under an oxygen atmosphere in a closed vessel, which is surrounded by water, under controlled conditions. The pellet was placed inside a stainless steel container, “Decomposition vessel”, pressurized with 34 bar of oxygen. Then the sample was ignited through a cotton thread connected to an ignition wire inside the decomposition vessel and burned (combusted). The heat released was calculated from the heat received by the water surrounding the decomposition vessel. The experiment was carried out in triplicates.

Figure 3.9 Bomb Calorimeter; Oxygen Compressor; Mechanical compressor

3.3.3.5 Ash content

The ash contents of raw and treated sample were measured according to National Renewable Energy laboratory (NREL, 2005) analytical procedure. The porcelain crucibles were heated in the furnace (Thermoscientific, model F6020C, Dubue Iowa, USA) (Figure 3.10) at a temperature of around 575 ^{o}C for three hours. Afterwards, the crucibles were kept in desiccator to cool down to room temperature. Then the empty crucibles were weighed in analytical balance and nearly 1 g of each sample was added to the crucibles and again the crucible with sample was heated in the furnace at 105 ^{o}C for 12 minutes. Furnace was then ramped to 250 ^{o}C at 10 ^{o}C/min and held for 30 minutes. Furnace was finally ramped to 575 ^{o}C at 20 ^{o}C/min and heated for three hours. The samples were allowed to cool down to 105 ^{o}C and cooled down to room temperature in desiccators and the final mass of the samples were measured. Ash content was calculated according to the equation 3.2.

$$\text{Ash content} = \left(\frac{\text{mf}-\text{m}}{\text{mi}-\text{m}}\right)\text{x}\left(\frac{100}{100-\text{MC}}\right) 100\% \qquad (3.2)$$

where,

m = mass of empty crucible (g)

mi = mass of empty crucible + mass of sample taken (g)

mf = mass of empty crucible + mass of sample after heating (g)

MC = moisture content of the biomass

Figure 3.10 Thermo scientific muffler furnace to calculate ash content

3.3.3.6 Volatile matter

The volatile matter of ground raw and treated samples were determined following the ISO 562 standards (ISO 562, 2002) using volatile matter furnace (VMF Carbolite, model 10/6/3216P, England) (Figure 3.11). Crucibles with their lids were heated at 900^{o}C and cooled down to room temperature. Nearly 1 g of each sample was placed into crucible heated at a temperature of 900 ^{0}C for 7 minutes and placed in a desiccator to cool down. The mass difference was used to calculate the volatile matter of samples in dry basis using the equation 3.3.

$$\text{Volatile matter} = \left(\frac{\text{mi}-\text{mf}}{\text{mi}-\text{m}}\,\text{x}\,100\%\right)\text{x}\left(\frac{100}{100-\text{MC}}\right) \qquad (3.3)$$

where,

m = mass of empty crucible (g)
mi = mass of empty crucible + mass of dry sample taken (g)

mf = mass of empty crucible + mass of sample after heating (g)

MC = moisture content

Figure 3.11 Carbolite muffle furnace to calculate volatile matter

3.3.3.7 Ultimate analysis

Ultimate analysis was performed on both dirty and treated woodchips ground through 1 mm Wiley mill using an elemental analyzer (Perkin Elmer Model 2400 CHNS/O, Waltham, MA). The analyzer uses the combustion method to convert the sample elements to simple gases such as CO_2, H_2O and N_2. The halogens present in the gases are removed by scrubbing reagents in the combustion zone of the instrument and the resulting gases are homogenized and controlled to exact conditions of pressure, temperature and volume. The homogenized gases are allowed to de-pressure through a column where they are separated in a stepwise steady-state manner and detected as a function of their thermal conductivities. (Perkin Elmer Model 2400 CHNS/O manual)

The oxygen content is easily obtained by subtracting the sum of percentage of carbon, hydrogen, nitrogen, sulphur and ash content. Nearly 1.5mg to 2.5mg of sample was weighed in a tin capsules and sealed properly. The sample was fed into the elemental analyzer that gives the carbon, hydrogen, nitrogen and sulfur content in dry basis.

3.3.3.8 Elemental analysis of ash content

Elemental analysis of the ash was done to quantify the composition of the elements present in the ash. Ash was prepared by heating the sample at 575 ^{o}C following the method given in the Section 3.3.3. The ash was sent to Hazen Research Inc. Golden, CO for elemental analysis.

3.3.4 Experimental design and statistical analysis

Dirty biomass used in this experiment were the predictors along with their initial ash content while the results from the characterization of biomass were the response variables. All the three physical treatments were performed in duplicates and the proximate and ultimate analysis on ground woodchips obtained for each duplicates were performed in triplicates. Statistical significance test was performed using SAS JMP program for six data points for each response variable. Tukey test was also used to compare the means of different proximate and ultimate analysis of the dirty wood chips, treated wood chips and residues.

3.4 Result and discussion

3.4.1 Proximate analysis of untreated feedstock

Proximate analysis was performed on the samples and its summary is presented on the Table 3.1. Sweetgum, which only consisted of main stem and bark, had ash content of 2.14% d.b. Whole pine tree, consisting of stem, bark and leaves showed higher ash content of 2.31% compared to ash content of residual pine tree 1.69% , consisting of stem and bark only. Werkelin, et al., (2010) reported the ash content of pine bark to be 2.40% which is greater than the residual pinewood, whole pinewood and sweetgum as they contained barks and stem body. The higher ash content of whole pine tree can be explained by the fact that as the woodchips were obtained on separate days and thus may not be from the same standing tree. Furthermore, it goes to explain that soil contamination during the harvesting can increase the ash content. The moisture content of the chips were in the range of 8.14% to 8.73% which was attained by air drying for 5 days.

The results of rewetting and soil contaminants addition is also shown in Table 3.1. The measured ash content and moisture content were close to the targeted. For the targeted level of 5% of ash content, ash contents obtained were in the range of 5.32 – 6.65%. Similarly, 7.97-8.67 % range of ash content was obtained for targeted range of 8% and range of 9.17-10.41% range of ash was obtained for targeted range of 10%. The moisture contents shown in the Table 3.1 is for the woodchips with moisture content targets of 10%, 20% and 30% was obtained.

Table 3.1 Proximate analysis of dirty feedstock (%)

Sample	Ash content (%, d.b.)	Moisture content (%, w.b.)	Volatile matter (%, d.b.)
Sweetgum	2.14 ± 0.13	8.73 ± 0.24	81.28 ± 0.81
Whole pine tree	2.31 ± 0.25	8.14 ± 0.15	79.35 ± 1.13
Residual pine tree	1.69 ± 0.18	8.65 ± 0.17	81.84 ± 0.71
P_5_10	6.64 ± 0.62	10.32 ± 0.03	79.21 ± 0.36
P_5_20	5.32 ± 0.62	21.54 ± 1.70	79.92 ± 0.95
P_5_30	6.27 ± 0.22	31.45 ± 2.41	79.20 ± 0.36
P_8_10	8.35 ± 0.32	11.23 ± 0.06	75.17 ± 0.34
P_8_20	7.97 ± 0.32	22.37 ± 1.44	76.98 ± 1.06
P_8_30	8.67 ± 0.34	32.01 ± 2.40	76.98 ± 1.04
P_10_10	10.41 ± 0.72	11.88 ± 0.44	72.16 ± 0.76
P_10_20	10.22 ± 0.30	18.78 ± 0.89	74.90 ± 0.97
P_10_30	9.14 ± 0.22	31.52 ± 1.01	75.08 ± 0.27

Note: *The values after the ± sign denote the standard deviation. For the samples with P_num_num denotation, the first number shows the target ash content and the second number shows the target moisture content. d.b. stands for dry basis and w.b. stands for wet basis.*

Literature have shown that ash content of pinewood to be less than 1% for the clean processed woodchips. Dirty woodchips are known to have high ash content, 4% for roundwood and 11.9% for residual chipped wood, as reported by Dukes et al., (2013). The increase in the ash content of the biomass from 5.32% to 10.22% had a negative impact on volatile matter as it decreased from 79.92% to 74.90%. Volatile matter in biomass are present due to the thermal decomposition of organic compounds present in biomass (Jenkins et al., 1998). The increase in inorganic compounds limits the amount of organic compound and thus the volatile matter is reduced. Similar results were obtained in the study of Dhiman, (2014). The values of volatile matter for the samples in Table 3.1 are similar to the values reported by Shrestha, (2014) for pine chips (81.19%) and for pine bark (72.76%).

3.4.2 Mass balance from experiments

The mass balance during the experiments from vibratory sieve shaker, mixer and hammer mill for all the samples are shown in Table 3.2. The unaccounted mass loss are the mass of samples which were uncollectable during the experiments. Fine layer of biomass on the base of vibratory sieve shaker and walls of mixer were not collectable. Mass difference is the difference between dirty woodchips and treated woodchips and is the total of residue and unaccounted mass loss.

The mass difference from the vibratory sieve shaker and mixer was low as compared to the mass difference in the hammer mill. The mass difference for vibratory sieve shaker and hammer mill for all the samples was less than 4%. The unaccounted mass loss in these two experiment setup can be from the residue particles adhered in the base of the vibratory sieve shaker and walls of the mixer which could not be retrieved for data analysis. The mass loss on the hammer mill was the highest because the ground particles escaped from the collection bucket during grinding from air leaks. Furthermore, the residue (fine particles) obtained was greater in hammer mill as compared to the mixer and vibratory sieve shaker. It is because of the grinding effect of hammer mill during treatment which led to the size reduction of the biomass and thus greater amount of biomass was fractionated and separated out as residue from the vibratory sieve shaker.

The calculated mass difference of biomass is lower than the reported biomass loss occurring during the debarking and delimbing process (greater than 20%). Hence, the three treatments prevents the huge biomass loss experienced in the debarking and delimbing process.

Table 3.2 Mass balance of different samples from three treatment process

Sample	Treatment	Mass difference %	Unaccounted mass loss %		Sample	Treatment	Mass difference %	Unaccounted mass loss %
Sweetgum	**VI**	0.56	0.28		**P_8_10**	**VI**	2.45	1.00
	HVI	13.18	11.87			**HVI**	9.43	4.73
	MVI	1.71	1.58			**MVI**	3.56	1.96
Whole pinewood	**VI**	0.66	0.35		**P_8_20**	**VI**	1.29	0.65
	HVI	12.28	11.16			**HVI**	7.48	4.22
	MVI	1.16	0.69			**MVI**	1.09	0.57
Residual pinewood	**VI**	3.17	3.09		**P_8_30**	**VI**	1.34	0.58
	HVI	5.46	4.34			**HVI**	7.28	4.75
	MVI	0.71	0.55			**MVI**	2.48	1.98
P_5_10	**VI**	2.85	1.12		**P_10_10**	**VI**	5.00	1.79
	HVI	9.62	4.07			**HVI**	8.96	2.93
	MVI	3.72	0.52			**MVI**	4.30	1.37
P_5_20	**VI**	1.97	1.46		**P_10_20**	**VI**	3.50	1.11
	HVI	6.14	3.45			**HVI**	8.50	3.97
	MVI	1.99	1.48			**MVI**	1.82	0.49
P_5_30	**VI**	2.63	1.94		**P_10_30**	**VI**	1.35	0.69
	HVI	4.63	2.75			**HVI**	6.78	3.49
	MVI	2.16	1.29			**MVI**	0.91	0.33

Note: *For the samples with P_num_num denotation, the first number shows the target ash content and the second number shows the target moisture content. The treatment VI indicates vibratory sieve shaker, HVI indicates hammer mill followed by vibratory sieve shaker and MVI indicates mixer and vibratory sieve shaker.*

3.4.3 Properties of treated and untreated feedstock

3.4.3.1 Particle size and particle density

Particle density of dirty and treated biomass are shown in Table 3.3. The particle density of biomass with higher ash content was higher. The particle size density of sweetgum (2.14% of ash) was 1435.6 kg/m^3 where as that of pinewood at 10% of ash was 1538 kg/m^3 i.e. the density of the biomass with higher ash content is greater as mentioned in the literature. Similarly if we look at the particle density of the treated biomass, the particle density of the biomass treated with hammer mill was significantly ($p<0.05$) lowest. Particle density of soil represents the density of all the minerals composing the soil which is reported to be near 2650 kg/m3 (Thien and Graveel, 1997). The presence of higher amount of ash content increases the particle density of biomass as the amount of inorganic elements with higher ash content increases. Figure 3.12 shows the relation between the ash content and particle density. As the ash content in the biomass increases, the particle density increased too. Since, hammer mill had the highest reduction of ash content and produced treated biomass with lowest ash content, particle density of the biomass treated with hammer mill had the lowest particle density.

Table 3.3 Particle density of treated and dirty biomass (kg/m^3)

	Raw	**Treated**		
		Vibratory Sieve shaker	**Hammer mill**	**Mixer**
Sweetgum	1435.60 ± 8.65 ^{a}	1435.85 ± 11.98 ^{a}	1435.55 ± 14.18 ^{a}	1428.50 ± 20.21 ^{a}
Whole	1433.62 ± 9.79 ^{a}	1436.28 ± 14.43 ^{a}	1436.08 ± 15.88 ^{a}	1422.37 ± 13.49 ^{a}
Residual	1409.03 ± 4.77 ^{a}	1429.54 ± 1.07 ^{a}	1415.66 ± 2.70 ^{a}	1418.20 ± 0.94 ^{a}
Pine_10_10	1538.57 ± 20.20 ^{a}	1510.60 ± 18.14 ^{a,b}	1493.38 ± 14.69 ^{b}	1513.70 ± 20.54 ^{a,b}
Pine_8_10	1500.74 ± 7.10^{a,b}	1497.55 ± 7.86 ^{a,b}	1481.28 ± 4.33 ^{b}	1507.04 ± 16.36 ^{a}
Pine_05_10	1497.71 ± 7.00 ^{a}	1472.70± 15.37 ^{a,b}	1460.30 ± 19.78 ^{b}	1474.53 ± 11.24 ^{a,b}

***Note:** For the samples with P_num_num denotation, the first number shows the target ash content and the second number shows the target moisture content. The values after the ± sign denote the standard deviation. The values with the same letter are not significantly different ($p<0.05$) for each row.*

Particle size distribution for different treated and untreated samples are shown in Figure 3.13. All the samples showed left skewness in particle size distribution which is typically obtained for log-normal distribution (Fasina, 2008). Biomass with higher ash content had their peaks on lower particle size as compared to biomass with lower ash content. As the particle size of soil and sand is lower (< 0.5mm), the biomass with higher ash content had their peaks more skewed towards the left.

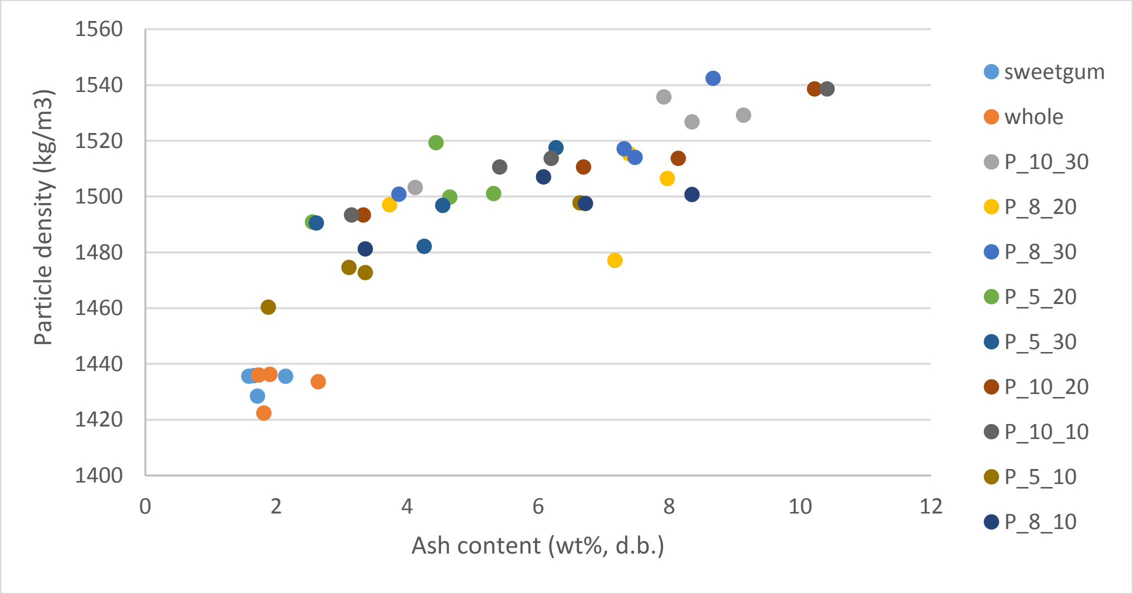


Figure 3.12 Particle density of dirty and treated biomass at lower moisture content (<10%)

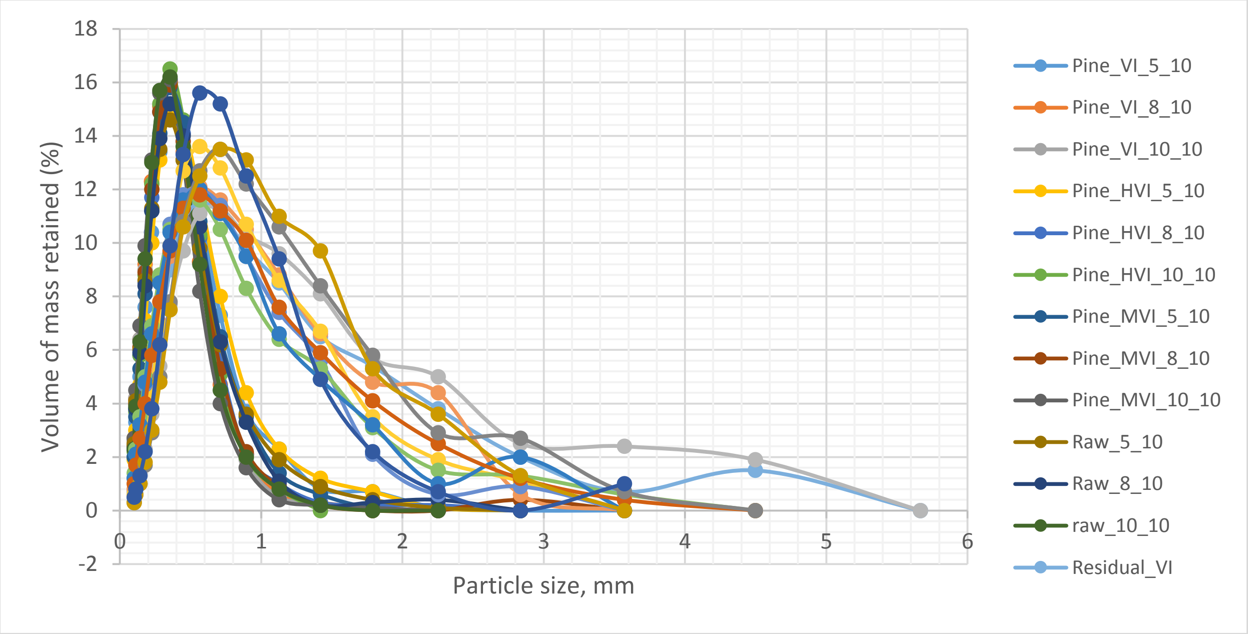


Figure 3.13 Particle size distribution of treated and untreated biomass at lower moisture content (<10%)

3.4.3.2 Ash reduction and proximate analysis

The treatments reduced the ash content by more than 20% for all the biomass feedstocks when they were at lower moisture contents of less than 10% as seen in the Figure 3.14. When the uncoated feedstocks were initially at lower ash contents of less than 2.5%, there was no significant effect ($P<0.05$) of treatment type on ash content reduction. For the uncoated biomass, the soil particles must be already lower in amount, and which was reduced and separated by all the three treatments. The biomass in this study contained bark and branches and Werkelin et al., (2010) reported the ash content of the bark to be around 2.4% which is greater than the reduced ash content of biomass in this study.

The reduction rate increased with the increase in initial ash content of dirty woodchips. Hammer mill treatment reduced the ash content by greater than 70% for samples with ash content higher than 5%. The reduction of ash content was higher for hammer mill as compared to the mixer and vibratory sieve shaker. For all the ash content levels, vibratory sieve shaker and mixer treatment were equally effective in ash reduction. The impact force from the hammer mill was high enough to separate most of the soil particles that adhered to the surface of the woodchips. However, the collision force generated by the vibratory sieve shaker and mixer was not high enough and therefore only some of the soil particles that adhered to the woodchips was detached and separated and hence there was low reduction rate.

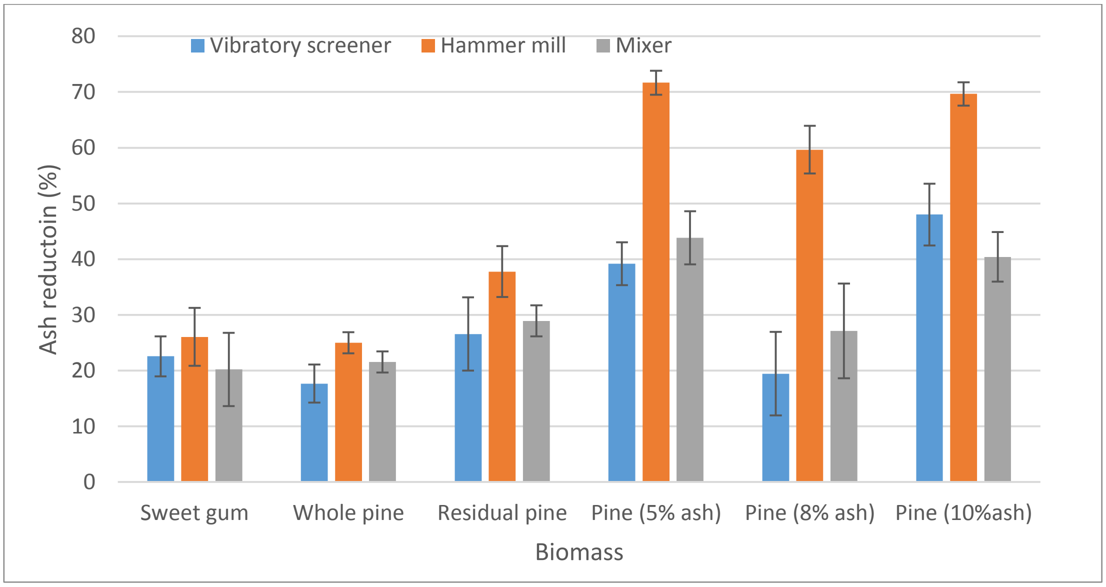


Figure 3.14 Ash reduction of biomass treated at 10% moisture content

Table 3.4 through Table 3.6 shows ash content, volatile matter and energy content of dirty and treated sweetgum, whole pine tree and residual pine respectively. The decrease in ash content of treated biomass had no effect on the volatile matter and energy content of the biomass. This can be attributed by the fact that although there was reduction in inorganic compound, the reduction was however not large enough to affect the organic compound. As a result no significant change ($p<0.05$) in volatile matter and energy content was observed. The energy content of biomass with reduced ash content for pine in the range of 1.05 % to 1.9 % was found to be 19.67 MJ/kg to 20.28 MJ/kg, respectively. The results obtained in this study are similar to the heating value reported by McKendry, (2002) for pine at 21.2 MJ/kg and Cuiping et al., (2004) for pine at 19.38 MJ/kg

Table 3.4 Proximate analysis of Sweetgum, dry basis

Sample	Ash content (%)	Volatile matter (%)	Energy content (MJ/kg)
Sweetgum dirty	2.14 ± 0.14 ^{a}	81.28 ± 0.81 ^{a}	20.35 ± 0.23 ^{a}
VI	1.66 ± 0.07 ^{b}	81.57 ± 0.83 ^{a}	20.58 ± 0.20 ^{a}
HVI	1.58 ± 0.11 ^{b}	81.55 ± 1.09 ^{a}	20.42 ± 0.15 ^{a}
MVI	1.71 ± 0.14 ^{b}	81.75 ± 0.86 ^{a}	20.53 ± 0.10 ^{a}

Table 3.5 Proximate analysis of Whole pine tree, dry basis

Sample	Ash content (%)	Volatile matter (%)	Energy content (MJ/kg)
WHOLE dirty	2.31 ± 0.25 ^{a}	79.35 ± 1.13 ^{a}	18.98 ± 0.40 ^{a}
VI	1.90 ± 0.07 ^{b}	78.58 ± 0.71 ^{a}	19.67 ± 0.13 ^{a}
HVI	1.73 ± 0.04 ^{b}	78.87 ± 0.51 ^{a}	19.67 ± 0.03 ^{a}
MVI	1.81 ± 0.04 ^{b}	78.63 ± 0.23 ^{a}	19.68 ± 0.11 ^{a}

Table 3.6 Proximate analysis of residual pine tree, d.b.

Sample	Ash content (%)	Volatile matter (%)	Energy content (MJ/kg)
Residual dirty	1.69 ± 0.18 ^{a}	81.84 ± 0.71 ^{a}	20.26 ± 0.24 ^{a}
VI	1.24 ± 0.11 ^{b}	81.59 ± 0.93 ^{a}	20.25 ± 0.15 ^{a}
HVI	1.05 ± 0.07 ^{b}	81.33 ± 0.47 ^{a}	20.16 ± 0.14 ^{a}
MVI	1.20 ± 0.04 ^{b}	80.84 ± 0.60 ^{a}	20.28 ± 0.10 ^{a}

Note: *The treatment VI indicates vibratory sieve shaker, HVI indicates hammer mill followed by vibratory sieve shaker and MVI indicates mixer and vibratory sieve shaker. The values after the ± sign denote the standard deviation. The values with the same letter are not significantly different ($p<0.05$) for each column.*

Table 3.7 through Table 3.9 show the treatment results for pine with higher ash content. All three treatment process significantly ($p<0.05$) reduced the ash content. Hammer mill was more effective in reducing ash content as compared to the vibratory sieve shaker and mixer. Ash from 6.64% was reduced to 1.88%, 8.34% to 3.36% and 10.40% to 3.15%, respectively through hammer mill. Vibratory sieve shaker and mixer also produced the significant reduction and was not significantly different from each other. The volatile matter increased significantly ($p<0.05$) in all the cases as observed in Table 3.7 - Table 3.9.

Table 3.7 Proximate analysis of Pine at 5% ash, d.b.

Sample	Ash content (%)	Volatile matter (%)	Energy content (MJ/kg)
Dirty P_05_10	6.64 ± 0.65 ^{a}	79.20 ± 0.36 ^{c}	18.02 ± 0.08 ^{b}
VI	3.36 ± 1.66 ^{b}	81.58 ± 0.47 ^{b}	18.49 ± 0.18 ^{b}
HVI	1.88 ± 0.14 ^{c}	83.57 ± 0.60 ^{a}	20.16 ± 0.11 ^{a}
MVI	3.11 ± 1.55 ^{b}	82.11 ± 0.44 ^{b}	18.56 ± 0.23 ^{b}

Table 3.8 Proximate analysis of pine at 8% ash, d.b.

Sample	Ash content (%)	Volatile matter (%)	Energy content (MJ/kg)
Dirty P_08_10	8.34 ± 0.31 ^{a}	75.16 ± 0.34 ^{c}	17.63 ± 0.00 ^{c}
VI	6.72 ± 0.62 ^{b}	80.05 ± 0.75 ^{b}	18.22 ± 0.10 ^{b}
HVI	3.36 ± 0.35 ^{c}	83.44 ± 1.01 ^{a}	19.37 ± 0.15 ^{a}
MVI	6.08 ± 0.70 ^{b}	80.30 ± 0.28 ^{b}	18.32 ± 0.20 ^{b}

Table 3.9 Proximate analysis of pine at 10% ash, d.b.

Sample	Ash content (%)	Volatile matter (%)	Energy content (MJ/kg)
Dirty P_10_10	10.40 ± 0.71 ^{a}	72.15 ± 0.76 ^{c}	17.63 ± 0.19 ^{c}
VI	5.41 ± 0.57 ^{c}	78.44 ± 0.58 $_{b}$	18.82 ± 0.26 ^{a,b}
HVI	3.15 ± 0.21 ^{d}	82.50 ± 0.60 ^{a}	19.10 ± 0.10 ^{a}
MVI	6.20 ± 0.46 ^{b}	79.73 ± 0.50 ^{b}	18.27 ± 0.19 ^{b,c}

***Note:** For the samples with P_num_num denotation, the first number shows the target ash content and the second number shows the target moisture content. The treatment VI indicates vibratory sieve shaker, HVI indicates hammer mill followed by vibratory sieve shaker and MVI indicates mixer and vibratory sieve shaker. The values after the ± sign denote the standard deviation. The values with the same letter are not significantly different (p<0.05) for each column*

Similarly, the reduction in ash content also increased the energy content significantly (p<.0.05) with the highest energy content being produced from hammer mill treatment. The volatile matter improved to 83.57% from 79.2% for pine with 5% of ash from hammer mill treatment. The energy content improved to 20.16 MJ/kg from 18.02 MJ/kg.

Figure 3.15 shows the relation between the ash content and volatile matter of the coated biomass. It clearly shows that volatile matter decreased with the increase in the ash content. As the ash content is increased, the inorganic compound in the biomass increases thus limiting the volatile and organic compound in the biomass.

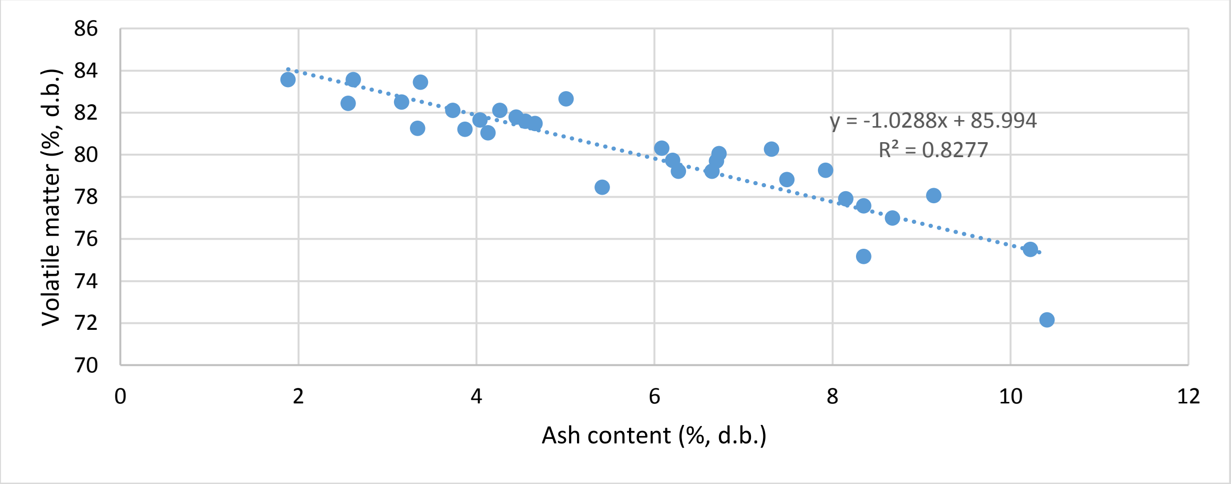


Figure 3.15 Volatile matter of biomass at different ash content

Similarly, Figure 3.16 showed the negative relation between ash content and energy content. As the ash content is increased, the heating value is decreased which is also reported by the study of Mani et al., (2004).

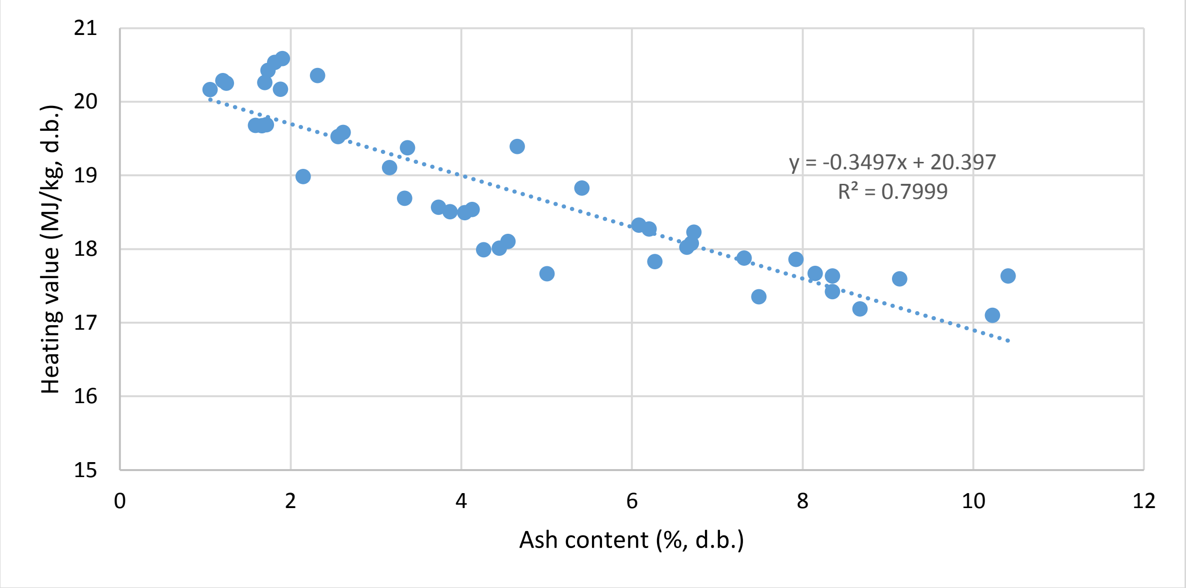


Figure 3.16 Energy content of biomass at different ash content

3.4.3.3 Ash content of residue

Table 3.10 shows the ash content of the residue particles that were separated from the vibratory sieve shaker. The residue is the fine waste products that passed through 500 micron sieve shaker. From the results, it was observed that the ash contents of the residues from the hammer mill treatment are lower than the ash content of residues from vibratory sieve shaker and mixer treatments. This is because that during grinding in hammer mill, some of the woodchips is reduced in size such that they passed through 500 microns sieve shaker. This diluted the soil particles that are separated from the woodchips. This is also evident from the high mass of residue that separated out during hammer mill treatment as shown in Table 3.2. The ash content of residues from hammer mill was in the range of 6-8% for sweetgum and residual pinewood whereas it was in the range of 14-21% for vibratory sieve shaker and mixer.

Table 3.10 Ash content of residue

Sample	**Ash content**		**Sample**	**Ash content**
SVI	14.13 ± 0.41		**PVI_5_10**	86.15 ± 0.64
SHVI	6.64 ± 1.09		**PHVI_5_10**	63.12 ± 4.46
SMVI	21.79 ± 6.75		**PMVI_5_10**	72.42 ± 7.67
WVI	77.63 ± 1.57		**PVI_8_10**	83.02 ± 3.40
WHVI	38.72 ± 2.31		**PHVI_8_10**	72.74 ± 2.70
WMVI	76.87 ± 1.25		**PMVI_8_10**	81.55 ± 0.83
RVI	19.80 ± 2.42		**PVI_10_10**	93.59 ± 0.27
RHVI	8.08 ± 1.10		**PHVI_10_10**	81.87 ± 6.25
RMVI	20.66 ± 0.31		**PMVI_10_10**	93.11 ± 0.96

Note: *For the samples with P_num_num denotation, the first number shows the target ash content and the second number shows the target moisture content. The treatment PVI indicates vibratory sieve shaker, PHVI indicates hammer mill followed by vibratory sieve shaker and PMVI indicates mixer and vibratory sieve shaker*.

Furthermore, the ash content of the residues was also directly affected by the initial ash content of the feedstocks. The ash content of the residues for pine with initial ash of 10% was 93.59% for vibratory sieve shaker, 81.87% for hammer mill and 93.11% for mixer and similarly ash content of the residues for pine with initial ash of 5% was 86.15% for vibratory sieve shaker, 63.12% for hammer mill and 72.42% for mixer. The ash content of the residues was greater for biomass with higher initial ash content. This is because more detrital ash was removed from the woodchips with higher ash content as compared to woodchips with lower ash content.

Dukes et al, (2013) reported the ash content of fine residues at 14.70% obtained by treating biomass with ash content of 4% with trommel screener with biomass at ash content of 4%. Furthermore, the high ash content in residue of biomass with higher ash content of 5%, 8% and 10% suggests that the treatment processes are more effective for reduction of soil contaminants from the biomass.

3.4.3.4 Effect of Moisture content

The effect of moisture content on ash reduction was tested for vibratory sieve shaker, hammer mill and mixer. The biomass samples were maintained at moisture content level of 10%, 20% and 30% respectively. Figure 3.17 shows the reduction rate of ash content of biomass treated with vibratory sieve shaker, hammer mill and mixer respectively.

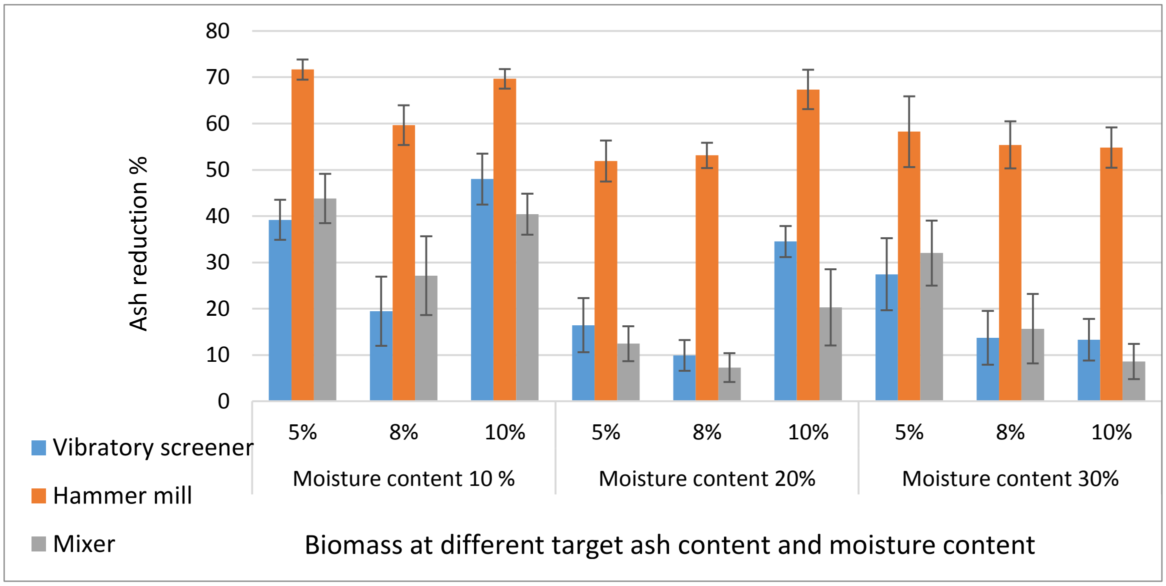


Figure 3.17 Ash content reduction of biomass at 5%, 8% and 10% of ash content level and 10%, 20% and 30% of moisture content level

The reduction rate was highest for the hammer mill for all the cases as observed in Figure 3.17. Hammer mill reduced the ash content by 71% for biomass at 5% of ash content and 10% of moisture content. Both vibratory sieve shaker and mixer had the lowest reduction at 30% of moisture content as compared to 10% of moisture content. As the moisture is increased, the presence of water induces adhesive force between the soil particles and surface of the woodchips (Pidwirny, 2006.). As a result greater force is required to free the soil from the surface of the woodchips. Hammer mill had sufficient impact force during size reduction as a result, the moisture content had no effect on ash reduction. However for mixer and vibratory sieve shaker, the vibration force and rotary force created is not able to separate the soil particles at higher moisture content rate as compared to the hammer mill.

Table 3.11 Proximate analysis of samples at 5%, 8% and 10% of ash content treated at 20% of moisture content

Sample	Ash content (% d.b.)	Volatile matter (%, d.b.)	Heating value (MJ/kg, d.b.)
RawP_10_20	10.22 ± 0.29 ^{a}	74.90 ± 0.90 ^{d}	17.09 ±0.97 ^{c}
VI	6.69 ± 0.34 ^{c}	79.69 ± 1.30 ^{b}	18.07 ± 1.28 ^{b}
HVI	3.33 ± 0.43 ^{d}	81.26 ± 0.96 ^{a}	18.68 ± 0.65 ^{a}
MVI	8.14 ± 0.84 ^{b}	77.91 ± 0.59 ^{c}	17.66 ± 0.62 ^{b,c}

Sample	Ash content (% d.b.)	Volatile matter (%, d.b.)	Heating value (MJ/kg, d.b.)
RawP_8_20	7.97 ± 0.35 ^{a}	76.98 ± 1.06 ^{c}	17.83 ± 0.06 ^{c}
VI	7.17 ± 0.26 ^{b}	78.82 ± 0.66 ^{b}	18.05 ± 0.06 ^{b}
HVI	3.73 ± 0.21 ^{c}	83.44 ± 1.02 ^{a}	19.10 ± 0.04 ^{a}
MVI	7.39 ± 0.24 ^{b}	78.26 ± 0.49 ^{b}	18.01 ± 0.05 ^{b}

Sample	Ash content (% d.b.)	Volatile matter (%, d.b.)	Heating value (MJ/kg, d.b.)
RawP_5_20	5.31 ± 0.62 ^{b}	79.92 ± 0.95 ^{b}	17.68 ± 0.43 ^{b}
VI	4.44 ± 0.31 ^{a}	81.78 ± 0.71 ^{a}	18.01 ± 0.70 ^{b}
HVI	2.55 ± 0.23 ^{c}	82.44 ± 0.88 ^{a}	19.52 ± 0.88 ^{a}
MVI	4.65 ± 0.20 ^{b}	81.48 ± 0.51 ^{a}	19.39 ± 0.50 ^{a}

Note: *For the samples with P_num_num denotation, the first number shows the ash content and the second number shows the moisture content. The treatment VI indicates vibratory sieve shaker, HVI indicates hammer mill followed by vibratory sieve shaker and MVI indicates mixer and* *vibratory sieve shaker. The values with the same letter are not significantly different ($p<0.05$) for each column*

Table 3.7-3.9, Table 3.11 and Table 3.12 shows the ash content, volatile matter and energy content of the biomass for the treated and raw biomass treated at 10%, 20% and 30% of moisture content. Hammer mill treatment produced the woodchips with the least ash content as compared to vibratory sieve shaker and mixer treatment. As mentioned in previous sections, reduction in ash content levels reflected in increased volatile matter and energy content of biomass.

Table 3.12 Proximate analysis of samples at 5%, 8% and 10% of ash content treated at 30% of moisture content

Table 3.13 **Sample**	**Ash content (% d.b.)**	**Volatile matter (%, d.b.)**	**Heating value (MJ/kg, d.b.)**
RawP_10_30	9.13 ± 0.21 ^{a}	75.08 ± 0.27 ^{c}	17.59 ± 0.26 ^{b}
VI	7.92 ± 0.40 ^{b}	79.25 ± 0.85 ^{b}	17.85 ± 0.86 ^{b}
HVI	4.12 ± 0.39 ^{c}	81.04 ± 0.94 ^{a}	18.53 ± 0.93 ^{a}
MVI	8.35 ± 0.34 ^{b}	77.56 ± 1.06 ^{b,c}	17.41 ± 1.28 ^{b}

Sample	**Ash content (% d.b.)**	**Volatile matter (%, d.b.)**	**Heating value (MJ/kg, d.b.)**
RawP_8_30	8.67 ± 0.34 ^{a}	76.98 ± 1.06 ^{c}	17.18 ± 1.05 ^{c}
VI	7.48 ± 0.50 ^{b}	78.82 ± 0.66 ^{b}	17.35 ± 0.65 ^{c}
HVI	3.87 ± 0.44 ^{c}	81.21 ± 0.57 ^{a}	18.5 ± 0.57 ^{a}
MVI	7.31 ± 0.65 ^{b}	80.26 ± 0.49 ^{a,b}	17.87 ± 0.49 ^{b}

Sample	**Ash content (% d.b.)**	**Volatile matter (%, d.b.)**	**Heating value (MJ/kg, d.b.)**
RawP_5_30	6.26 ± 0.21 ^{a}	79.20 ± 0.36 ^{c}	17.82 ± 0.36 ^{b}
VI	4.54 ± 0.48 ^{b}	81.58 ± 0.47 ^{b}	18.10 ± 0.47 ^{b}
HVI	2.61 ± 0.47 ^{c}	83.57 ± 0.57 ^{a}	19.58 ± 0.60 ^{a}
MVI	4.26 ± 0.44 ^{b}	82.11 ± 0.45 ^{b}	17.99 ± 0.44 ^{b}

Note: *For the samples with P_num_num denotation, the first number shows the ash content and the second number shows the moisture content. The treatment VI indicates vibratory sieve shaker, HVI indicates hammer mill followed by vibratory sieve shaker and MVI indicates mixer and* *vibratory sieve shaker. The values with the same letter are not significantly different ($p<0.05$) for each column*

3.4.4 Elemental analysis

Elemental analysis of the elements in the biomass ash was carried out to quantify the composition of the elements present in the ash. The results obtained are given in Table 3.13. Ash of dirty and treated biomass subjected to hammer mill treatment was used for the elemental analysis since hammer mill produced the larger reduction in the ash content.

From the elemental analysis of dirty biomass, it is clear that the major inorganic compound present in the biomass is silica followed by aluminum, iron and calcium. The presence of high amount of silica and aluminum suggests the presence of soil or sand in the biomass. The treatment process was able to reduce the amount of silica, aluminum and titanium.

The treatment of pine with 10% of ash shows that all the element of the biomass was reduced thus confirming the presence of high amount of soil particles in the biomass and removal of these soil particles by hammer mill treatment. However, for the whole pine wood, which had lower initial ash content showed increase in Ca, Fe, Mg and K. The similar increment was also seen in the study of Turn et al., (1997). Dukes et al. (2013) also showed the increment in K and P in their study even though there was overall reduction in the ash content.

The increase in the concentration of Ca, Fe, Mg and K can be explained by the reduction of detrital ash in the biomass which constitutes Si and Al, which means that there was no actual addition of the Ca, Fe, Mg and K. The amount of silica and aluminum was largely reduced which caused the concentration of Ca, Fe, Mg and K to increase because of the compositional percentile changes of other detrital ash compounds.

Table 3.13 Major inorganic composition in dirty and treated biomass from hammer mill (g/kg)

		Dirty whole pine	Treated whole Pine		Dirty P_10_10	Treated P_10_10	Soil
Element (g/kg)	**SiO_2**	19.20 ± 0.19	6.60 ± 1.16		80.60± 3.64	15.04 ± 1.66	667.48 ± 5.38
	Al_2O_3	1.26 ± 0.38	1.04 ± 0.16		11.79 ± 2.66	7.45 ± 0.60	114.47 ± 0.72
	TiO_2	0.10 ± 0.02	0.06 ± 0.00		0.56 ± 0.02	0.34 ± 0.02	5.72 ± 0.08
	Fe_2O_3	0.35 ± 0.08	0.72 ± 0.62		3.07 ± 0.31	2.10 ± 0.38	31.12 ± 0.55
	CaO	1.38 ± 0.13	2.73 ± 0.10		2.03 ± 0.43	1.10 ± 0.13	12.81 ± 0.34
	MgO	0.31 ± 0.01	0.63 ± 0.07		0.75 ± 0.15	0.47 ± 0.02	3.62 ± 0.12
	Na_2O	0.01 ± 0.00	0.01 ± 0.00		0.18 ± 0.05	0.05 ± 0.00	1.06 ± 0.04
	K_2O	0.54 ± 0.05	1.04 ± 0.15		1.34 ± 0.02	0.81 ± 0.04	8.66 ± 0.29
	P_2O_5	0.19 ± 0.05	0.33 ± 0.00		0.27 ± 0.05	0.17 ± 0.05	0.25 ± 0.08

Note: The values after the ± sign denote the standard deviation. Control biomass is the dirty biomass and treated biomass is treated with hammer mill. P_num_num denotation: the first number shows the ash content and the second number shows the moisture content. PVIH is the treatment of pine with hammer mill.

3.4.5 Ash balance

Ash balance was carried out by computing the difference in ash present in the raw biomass to that of treated and residue. The ash loss percentage shows the amount of unaccounted ash loss during the treatment. From the Table 3.14, it is clear that the ash loss was higher in hammer mill as compared to the treatments from the vibratory sieve shaker and hammer mill.

Table 3.14 Ash loss (%) of all the treatments

Treatment	Sweetgum	Whole pine	Residual pine
VI	2.53	7.71	6.51
HVI	15.31	15.34	9.10
MVI	2.48	8.21	6.38

Biomass	Treatment	Moisture content (%)		
		10	**20**	**30**
Pine with 10% Ash	**VI**	14.69	9.06	5.11
	HVI	18.40	21.56	21.81
	MVI	9.48	5.71	1.75
Pine with 8% Ash	**VI**	5.43	2.57	3.21
	HVI	17.31	19.71	23.95
	MVI	12.33	1.08	9.90
Pine with 5% Ash	**VI**	7.28	7.25	14.05
	HVI	17.04	10.11	27.60
	MVI	14.30	2.76	14.29

Note: *The treatment VI indicates vibratory sieve shaker, HVI indicates hammer mill followed by vibratory sieve shaker and MVI indicates mixer and vibratory sieve shaker. The ash loss % is the average of duplicates.*

The ash loss can be explained by the mass loss during the experiments as explained in section 3.4.2. The fine particles were not collected from the walls of vibratory sieve shaker and mixer, and higher unaccounted mass loss occurred in the hammer mill treatment. Since, the ash content of the residue was higher, the ash content of the unaccounted mass could be high too as shown in Table 3.11. The high ash content of the unaccounted mass loss could have attributed to the ash loss for the experiments. The loss in hammer mill was higher because of the high mass loss observed in hammer mill because of air leaks during the treatment.

3.5 Summary

- All the three treatment processes reduced the ash content of residual pine, whole pine and sweetgum (biomass at lower ash content 2%) significantly ($p<0.05$) but there was no significant differences ($p<0.05$) between the treatment types. However, the reduction in ash did not affect the volatile matter and energy content.
- For biomass with higher ash content (ash coated pinewood with ash content higher than 5%), all the three processes significantly reduced ($p<0.05$) the ash content. But the hammer mill treatment had the highest reduction rate. The increment in the volatile matter and energy content was significant ($p<0.05$).
- Hammer mill was more effective in reducing ash content for ash coated biomass with higher ash content (>5%) at all moisture content (10%, 20% and 30%) compared to vibratory sieve shaker and mixer.
- Elemental analysis showed that the major inorganic constituent of the biomass was silica which was reduced by the hammer mill treatment. The physical treatments are successful in removing the detrital ash only.

3.6 References

ASABE Standards. (2012). S358.3: Moisture Measurement — Forages. St. Joseph, Mich.: *ASABE*.

BRDB. (2010). Biofuel feedstock logistics: recommendations for research and commercialization. *Biomass Research and Development Board*, 1-52. Available at http://www.biomassboard.gov/pdfs/feedstocks_literature_review.pdf

Cuiping, L., Chuangzhi, W., & Haitao, H. (2004). Chemical elemental characteristics of biomass fuels in China. *Biomass and bioenergy*, *27*(2), 119-130.

Dhiman, J. (2014). *Prediction of Heating and Ignition Properties of Biomass Dusts Using Near Infrared Spectroscopy* (Doctoral dissertation, Auburn University).

Dukes, C. C., Baker, S. A., & Greene, W. D. (2013). In-wood grinding and screening of forest residues for biomass feedstock applications. *Biomass and Bioenergy*, *54*, 18-26.

Fasina, O. O. (2008). Physical properties of peanut hull pellets. *Bioresource technology*, *99*(5), 1259-1266.

ISO 562. 2010. Hard coal and coke. *Determination of volatile matter. International Organization for Standardization*. Geneva, Switzerland

Jenkins, B.M, L.L. Baxter, T.R, Miles Jr., and T.R. Miles, 1998. Combustion properties of biomass. Fuel Proc. Tech. 54(1-3):17-46

Jiang, L., Hu, S., Sun, L. S., Su, S., Xu, K., He, L. M., & Xiang, J. (2013). Influence of different demineralization treatments on physicochemical structure and thermal degradation of biomass. Bioresource technology, 146, 254-260.

Kline, K. L., & Coleman, M. D. (2010). Woody energy crops in the southeastern United States: two centuries of practitioner experience. *Biomass and bioenergy*, *34*(12), 1655-1666.

Mani, S., Tabil, L. G., & Sokhansanj, S. (2004). Grinding performance and physical properties of wheat and barley straws, corn stover and switchgrass. *Biomass and Bioenergy*, *27*(4), 339-352.

McKendry, P. (2002). Energy production from biomass (part 1): overview of biomass. *Bioresource technology*, *83*(1), 37-46.

NFPA. (2013). Recommended practice for the classification of combustible dusts and of hazardous locations for electrical installations in chemical process areas online. *NFPA 499*. Quincy, Mass: National Fire Protection Association

NREL. (2005). Determination of Ash in Biomass by Laboratory Analytical Procedure. *National Renewable Energy Laboratory*. NREL/TP-510-42622

Pidwirny, M. (2006). "Physical Properties of Water". *Fundamentals of Physical Geography, 2nd Edition*. Date Viewed. http://www.physicalgeography.net/fundamentals/8a.html Accessed 10 Nov. 2013

Pradhan, R. C., Naik, S. N., Bhatnagar, N., & Swain, S. K. (2008). Moisture-dependent physical properties of Karanja (Pongamia pinnata) kernel. *Industrial Crops and Products*, *28*(2), 155-161.

Sacilik, K., Öztürk, R., & Keskin, R. (2003). Some physical properties of hemp seed. *Biosystems Engineering*, *86*(2), 191-198.

Shrestha, R. (2014). Experimental Analysis and Modeling of Biomass Gasification using a Downdraft Gasifier. (Doctoral dissertation, Auburn University).

Supantamart, N., Laemsak, N., Sirisansaneeyakul, S., Vanichsriratana, W., & Parakulsuksatid, P. (2009). Effect of steam explosion on chemical compositions of biomass from Eucalyptus and Acacia. In *3rd international conference on fermentation technology for value added agricultural production, Thailand*.

Thien, S. J., & Graveel, J. G. (1997). *Laboratory Manual for Soil Science: Agricultural & Environmental Principles*. WCB/McGraw-Hill.

Turn, S. Q., Kinoshita, C. M., & Ishimura, D. M. (1997). Removal of inorganic constituents of biomass feedstocks by mechanical dewatering and leaching. *Biomass and Bioenergy*, *12*(4), 241-252

Tuskan, G. A., Difazio, S., Jansson, S., Bohlmann, J., Grigoriev, I., Hellsten, U. ... & Henrissat, B. (2006). The genome of black cottonwood, Populus trichocarpa (Torr. & Gray). *Science*, *313*(5793), 1596-1604.

UCL. (2015). Particle Size Analysis (for soils/sediments). *University College London*. Available at http://www.geog.ucl.ac.uk/about-the-department/support-services/laboratory/laboratory-methods/particle-size-analysis/particle-size-analysis-for-soils-sediments. Accessed 1 Jan, 2015.

Walsh, M. E., Perlack, R. L., Turhollow, A., de la Torre Ugarte, D., Becker, D. A., Graham, R. L., ... & Ray, D. E. (2000). Biomass feedstock availability in the United States: 1999 state level analysis. *Bioenergy Information Network, Bioenergy Feedstock Development Program, Oak Ridge National Laboratory*.

Werkelin, J., Skrifvars, B. J., Zevenhoven, M., Holmbom, B., & Hupa, M. (2010). Chemical forms of ash-forming elements in woody biomass fuels. *Fuel*, *89*(2), 481-493.

CHAPTER FOUR

STUDY OF EFFECT OF BIOMASS ASH ON PYROLYSIS PRODUCTS

4.1 Abstract

The product yield, and physical and chemical properties of the pyrolysis products from woody biomass are dependent upon the properties of biomass used. In this study, pinewood at different level of ash content was used as feedstock in fast pyrolysis. The ash content of pinewood was increased by mixing soil with clean pinewood and later treated by three physical treatments to understand the effect of treatment. The ash content of pinewood were at 0.56%, 1.16%, 2.77%, 4.40%, 6.87%, 8.35% and 15.52%. The increase in the ash content of biomass from 0.56% to 15.52% decreased the bio-oil yield from 47.09% to 26.28%, respectively showing the presence of high concentration of ash has direct effect on pyrolysis. As the ash content was increased, the carbon and hydrogen content of the biomass decreased which decreased the heating value of the feedstock. The water content and ash content of the bio-oil increased with the increment in the ash content of the biomass. The water content was in the region of 20.72%-24.99% and ash content was in the region of 0.09% - 0.55% with the increase in the ash content of the biomass from 0.56% to 15.52%. Furthermore, pH value of bio-oil decreased significantly ($p<0.0001$) and TAN increased significantly ($p=0.026$) until 2.77% of ash in biomass. At higher ash content level of biomass, with silica as major element, the acidity of the bio-oil increased. Since silica is the deoxidizing agent, the O/C molar ratio of the bio-oil was reduced from 0.74 to 0.32 for biomass with increasing ash content from 0.56% to 15.52% suggesting dehydration of bio-oil. The carbon

and hydrogen content of the bio-char decreased with the increase in the ash content of the biomass and furthermore, the ash content of the bio-char increased too, which resulted in the decrease of heating value of the bio-char. SEM EDS analysis showed the formation of longitudinal cells in the transversal section shows the fragility and lightness of the char particles and the mineral particles were more abundantly dispersed in the case of bio-char with higher ash content.

4.2 Introduction

Biomass is an important renewable and alternative source of energy. Woody biomass has low content of sulfur, nitrogen and ash contents and contributes to the reduction of atmospheric CO_2 emissions (McKendry, 2002). Furthermore, it is the only renewable source of carbon, which can be converted to liquid, solid and gaseous fuels (Huang et al., 2015; Amutio et al., 2012).

There are several methods such as physical, thermal, chemical and biological that are used to convert biomass into biofuels and chemicals. Of all the different processes, pyrolysis and gasification are the main thermal methods used (Gao et al., 2013). Fast pyrolysis is preferred over slow pyrolysis because of the higher liquid yield and the ease of storing and transporting of the resulting liquid (bio-oil) product. When the biomass is heated rapidly in the absence of oxygen, biomass is decomposed to char, aerosols and gas. The aerosols are condensed to obtain bio-oil which is a complex mixture of more than 300 compounds (Bridgwater, 1999; Gupta and Demirbas., 2010; Diebold, 2000).

Various studies has been performed regarding the operating conditions for the pyrolysis process. The effects of pyrolysis temperature, heating rate and vapor residence time on the quantity and quality of bio-oil produced has been well studied and documented (Bridgwater, 2012; Thangalazhy-Gopakumar et al., 2010; Mourant et al., 2013). The physical and chemical properties of the biomass also affect the product yield of pyrolysis process. Various studies have been performed to understand the effect of ash content of biomass on pyrolysis. Chen et al. (2008) studied the catalytic effect of eight inorganic additives (NaOH, Na_2CO_3, Na_2SiO_3, NaCl, TiO_2, HZSM-5, H_3PO_4, $Fe_2\ (SO_4)_3$) and found out that all the additives increased the liquid yield except Na_2SiO_3 and HZSM-5. Oasmaa et al. (2010) studied the product yield of 12 different biomass samples with varying ash content and concluded that bio-oil yield decreases with increase in the ash content. Yildiz et al. (2015) studied the effect of biomass ash in catalytic and non-catalytic fast pyrolysis. Biomass ash was prepared by heating pine at 600^oC. The major constituents of the biomass ash was calcium. The metal compound present in the biomass decreased the bio-oil yield along with the increase in the char product from pyrolysis process (Aho et al., 2013).

The studies carried out were mainly focused on the authigenic ash present in the biomass which are bound to the biomass at carboxylic and/or phenolic groups (Kozlowsky et al., 1997). Furthermore, the studies are more based on the ash removal by chemical treatments or leaching methods which affects the properties of the biomass (Aho et al., 2013; Miles et al., 1995; Turn et al., 1997).

No major studies have been carried out to evaluate efficacy of physical treatment processes to reduce detrital ash in the biomass and to quantify the effect of physical treatment processes on the characteristics of biomass subjected to pyrolysis. For this study, pinewood at different level of ash content was chosen ranging from 0.56% to 15%. Pinewood was chosen as it is widely available biomass in the US. The ash content was maintained at required level by adding detrital ash as studied in the previous chapter.

4.3 Methodology

4.3.1 Biomass preparation

Biomass at seven ash content levels, obtained from different treatments, were taken for pyrolysis. The ash contents were 0.56%, 1.16%, 2.77%, 4.40%, 6.87%, 8.35%, and 15.52% at moisture content less than 10%. Biomass with 0.56% ash content was the clean pinewood and biomass with 15.52% of ash content was prepared from rewetting and ash coating as explained in Section 3.3.1. Biomass with ash contents 1.16%, 2.77%, 4.40%, 6.87% and 8.35% were obtained from different treatments from previous chapter as shown in Table 4.1.

Table 4.1 Sources of feedstock and their ash content

S.N	**Biomass source**			**Pyrolysis feedstock**
	Biomass type	**Treatment**	**Ash content (%, dry basis.)**	
1	Residual pinewood	Hammer mill	1.05 ± 0.07	**Pine_1.16**
2	Dirty pine at 5% ash	Hammer mill	1.88 ± 0.14	**Pine_2.77**
3	Dirty pine at 8% ash	Hammer mill	3.36 ± 0.35	**Pine_4.40**
4	Dirty pine at 8% ash	Vibratory sieve shaker	6.72 ± 0.62	**Pine_6.87**
5	Dirty pine at 10% ash	Mixer	6.20 ± 0.46	**Pine_8.35**

The samples were ground using hammer mill through 1.58mm screen and fractionated to obtain samples that passed through 40 micron screen and retained on 35 micron screen. The fractionated biomass prepared for pyrolysis had higher ash content because the inorganics are more grindable and are easily separated into finer fractions which increases the ash content of the fine samples.

4.3.2 Experimental setup

Bench scale fluidized bed reactor was used for carrying out fast pyrolysis experiments. It consists of a screw feeder, reactor, cyclone, collectors, electrostatic precipitator, activated carbon and moisture absorber. Figure 4.1 shows the schematic setup of the reactor.

The screw feeder system was run by speed controlled DC motor which carried biomass fed from hopper and to the base of the reactor. The reactor was made of stainless steel with 25.4 mm diameter and 482.6 mm in height. The carrier gas was fed from the bottom of the reactor and a distribution plate (Ace glass, porosity B) was placed at the bottom of the reactor. The cyclone was used for char separation and collection, which was heated externally at 300^{o}C. Three condensers in ice bath and one electrostatic precipitator (ESP) were used as the liquid collectors. The non-condensable gas passed through water separator and then through activated carbon absorber and moisture absorber. The water separator was used to collect any tar produced. Activated carbon absorber was used to collect any carbon in the gas and moisture absorber collected the water in the gases. Quartz sand with particle size (150-300 microns) was used as the bed material for fluidization.

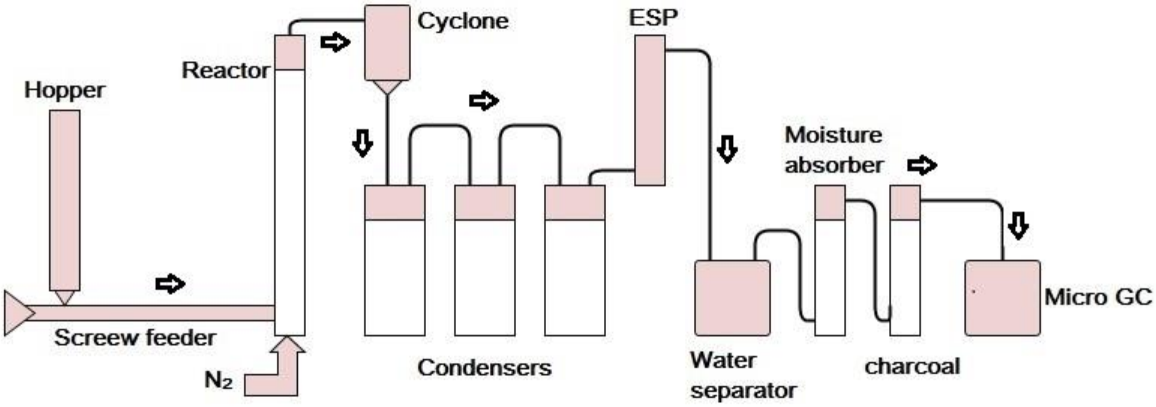


Figure 4.1 Schematic representation of pyrolysis experiment setup

The feed hopper was initially loaded with 60 g of biomass sample and the reactor was loaded with 20 g of bed material (sand). The reactor was preheated to the temperature of 500^{o}C. The average feed rate of the biomass sample was 20 g/h. The fluidization gas flow rate of nitrogen was set at 5 L/min. The biomass was not fed in until the constant temperature was attained in the reactor.

4.3.3 Data collection

The dry mass of reactor, cyclone, pipings, condensers and ESP was taken before and after the experiment. The difference in the mass of reactor and sand added was used to estimate the mass of the char in the reactor. The difference in mass of the cyclone was the mass of the char collected in the cyclone. The difference in mass of pipings, ESP and condensers was the mass of the bio-oil produced.

The amount of bio-oil and char was calculated by the mass difference of the experimental set up components. The amount of non-condensable gas produced was calculated from the mass difference of initial biomass added and bio-oil and char produced (Equation 4.1).

$$\text{Amount of non-condensable gas (\%)} = 100\% - \text{bio-oil (\%)} - \text{char (\%)} \qquad (4.1)$$

4.3.4 Characterization of bio-oil, char and gas

4.3.4.1 Bio-oil analysis

The bio-oil was analyzed for pH, TAN, water content, ash content, volatile matter and heating value. The chemical component of bio-oil was measured by gas chromatograph/mass spectrometer (GC/MS). pH shows the strength of acidity of the bio-oil and was measured with a digital pH meter (Oakton, Model PC 510). Total acid number (TAN) was determined using Mettler Toledo T50 by performing potentiometric titration. The water content of the bio-oil was determined using volumetric Karl Fischer titrator (Mettler Toledo, model V20). Chemical composition of bio-oil was analyzed using Agilent 7890 GC/5975 MS equipped with DB-1701 column. Approximately 150 mg of bio-oil was dissolved in 3 mL of methanol and was diluted to 10 mL with dichloromethane. The diluted sample was injected into the column and analysis was carried out in duplicates. The initial temperature of the column was maintained at 40^oC for 2 min and increased to 250^oC at 5 ^oC/min. The final temperature was held at 8 min. Helium was used as the carrier gas at flow rate of 1.25 mL/min. Bio-oil compounds were identified by comparing the mass spectra with the NIST (National Institute of Standards and Technology) mass spectral library.

The calculation and measurement of heating value, ash content and volatile matter content are already explained in Section 3.3.3.

4.3.4.2 Char analysis

The char was analyzed for ash content, heating value and volatile matter. Ash content, volatile matter and heating values were measured as explained in the Section 3.3.3.

Scanning electron microscope (SEM) (Zeiss EVO 50VP) was used to observe the magnified structure of char. The char was coated with gold in sputter coating (EMS 550X). The magnified images were observed to understand the structure of the char produced. EDS (Energy Dispersive X-ray Spectroscopy) was used to perform the quantitative elemental analysis.

4.3.4.3 Gas analysis

Micro gas chromatograph (Agilent technologies) was used to analyze the chemical component of non-condensable gas. Micro GC was equipped with two columns (M5A BF and PPU) using high-purity helium and argon gas as carrier gases. Both the columns were 10 m in length. Helium was fed to carrier 1 with a column temperature of 80 ^oC and pressure of 150 kPa whereas Argon was fed to carrier 2 with column temperature of 100 ^oC and pressure of 100 kPa.

4.4 Results and discussion

4.4.1 Analyses of feedstock

Seven ground pine samples at different ash content levels were used for the pyrolysis experiment. The biomass with ash content from 1.17% to 8.35 % were obtained from different treatment from first objective of this study as shown in Table 4.1. The ash content of the pyrolysis feedstock (1.16 - 8.35 %) as shown in Table 4.2 are higher as compared to that of the source samples (1.05 - 6.20 %) as shown in Table 4.1. Fractionated pyrolysis feedstock had higher ash content than ground feedstock because the inorganic content is more grindable and are easily separated into finer fractions from lignocellulosic structure of biomass during grinding (Hehar, 2013). Liu and Bi (2011) also obtained similar results with switchgrass sample milled to obtain size less than 1 mm. Ash content of switchgrass sample increased from 4.31% to 10.53% as the sieve size of the fraction decreased from >0.95 mm to <0.15 mm (Dhiman, 2014). A summary of the proximate analysis is presented in Table 4.2. The ash content of the biomass were chosen from 0.56% to 15.52% to correlate with the biomass found from harvesting and bio-refineries. The moisture content of the biomass were oven dried at 35°C to less than 10%.

Table 4.2 Proximate analysis of biomass feedstock for pyrolysis

Biomass	Ash content (wt %, d.b.)	Volatile matter (wt %, d.b.)	Moisture content (%, w.b.)	HHV (MJ/kg, d.b.)
Pine_0.56	0.56 ± 0.05 ^{f}	81.29 ± 0.59 ^{c}	7.16 ± 0.79 ^{a,b}	20.12 ± 0.55 ^{a,b}
Pine_1.16	1.16 ± 0.11 ^{f}	81.59 ± 0.93 ^{b,c}	8.49 ± 0.14 ^{a}	20.25 ± 0.15 ^{a,b}
Pine_2.77	2.77 ± 0.47 ^{e}	83.57 ± 0.60 ^{a}	6.29 ± 0.90 ^{b}	20.16 ± 0.11 ^{a}
Pine_4.40	4.40 ± 0.35 ^{d}	83.44 ± 1.01 ^{a,b}	8.57 ± 1.01 ^{a,b}	19.37 ± 0.15 ^{b}
Pine_6.87	6.87 ± 0.50 ^{c}	78.82 ± 0.66 ^{d}	5.99 ± 0.02 ^{a,b}	17.35 ± 0.65 ^{c}
Pine_8.35	8.35 ± 0.34 ^{b}	77.56 ± 1.06 ^{d}	7.24 ± 0.09 ^{a,b}	17.41 ± 1.28 ^{c}
Pine_15.52	15.52 ± 0.91 ^{a}	72.15 ± 0.76 ^{e}	7.88 ± 0.04 ^{a,b}	17.63 ± 0.19 ^{c}

Note: The values after the ± sign denote the standard deviation. d.b. and w.b. stands for dry basis and wet basis respectively. The values with the same letter are not significantly different ($p<0.05$) for each column. d.b. stands for dry basis.

The results from the ultimate analysis are shown in Table 4.3. Carbon content ranged from 44% to 49%, hydrogen from 5.7% to 6.74% for all the feedstock. Biomass with lowest ash content had the highest carbon as compared to the biomass with the lower ash content. The nitrogen value for biomass with modified ash and moisture content was not detected by the CHNS analysis.

Table 4.3 Elemental analysis of biomass (d.b.,%)

Biomass	C	H	N	O
Pine_0.56	49.81 ± 0.38 ^{a,b}	6.64 ± 0.05 ^{a}	0	42.98 ± 0.43 ^{a,b}
Pine_1.16	51.21 ± 0.39 ^{a}	6.74 ± 0.20 ^{a}	0.08 ± 0.11	40.81 ± 0.08 ^{a,b}
Pine_2.77	49.74 ± 0.03 ^{a,b}	6.62 ± 0.07 ^{a}	0	39.23 ± 0.04 ^{b}
Pine_4.40	47.59 ± 0.22 ^{a,b,c}	6.42 ± 0.23 ^{a}	0	43.22 ± 0.44 ^{a,b}
Pine_6.87	46.17 ± 1.60 ^{b,c,d}	6.15 ± 0.11 ^{b}	0	39.36 ± 1.72 ^{b}
Pine_8.35	43.16 ± 1.01 ^{d}	5.72 ± 0.09 ^{c}	0	44.25 ± 0.92 ^{a}
Pine_15.52	44.33 ± 1.88 ^{c,d}	5.91 ± 0.03 ^{b}	0	34.23 ± 1.90 ^{c}

Note: The values after the ± sign denote the standard deviation. d.b. stands for dry basis. The values with the same letter are not significantly different ($p<0.05$) for each column. d.b. stands for dry basis.

4.4.2 Product yield

The bio-oil produced were collected from three condenser bottles and ESP. Bio-char was collected from the cyclone. The amount of bio-oil in first condenser was greater than second and third condensers in the flow line. The bio-oil from all the three condensers were stored in a container and mixed thoroughly.

Figure 4.2 shows the product yield distribution of feedstock at different ash content level. The scatter in the product yield was less than 5% indicating sufficient reproducibility. The highest bio-oil yield was obtained at lowest ash content level of biomass. The bio-oil yield decreased from 47.09% to 26.28% with ash content of biomass increasing from 0.56% to 15.52%. The significant ($p<0.05$) reduction of the bio-oil yield can be attributed to the fact that at higher ash content level, the combustible part of the biomass is less and thus the bio-oil obtained decreased. Furthermore, the catalytic effect of ash itself on the primary pyrolysis vapors results in the decreased production of bio-oil (Yildiz et al., 2015)

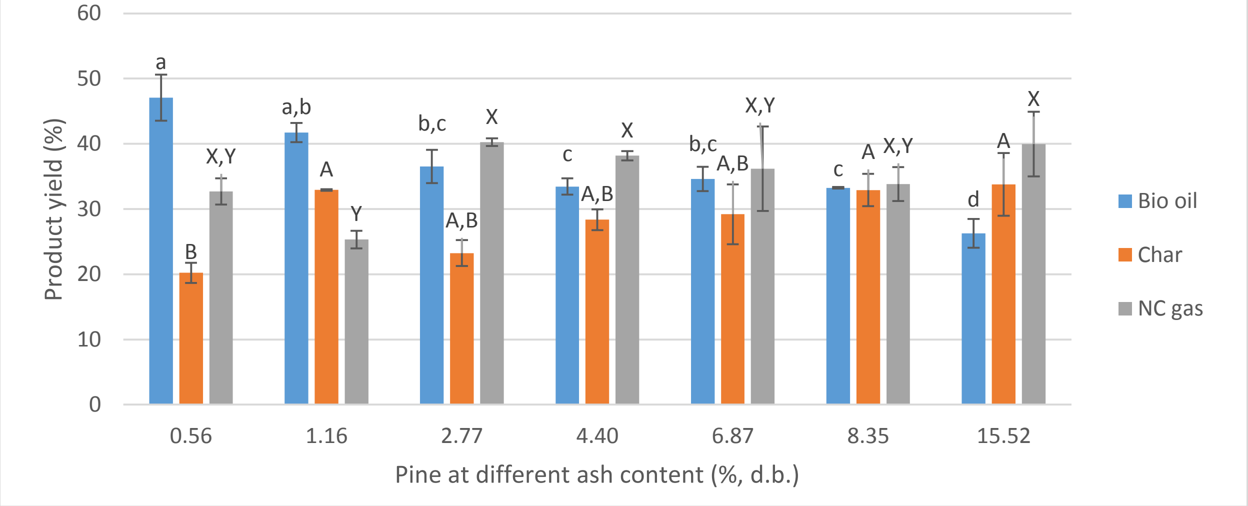


Figure 4.2 Product Yield of pyrolysis of biomass at different ash content (same letter for each group (Bio-oil, char and gas) indicates that it is not statistically different ($p<0.05$))

4.4.3 Bio-oil analysis

The C, H and O content of the bio-oils are given in Figure 4.3 and the corresponding O/C and H/C molar ratios are given the Figure 4.4. From Figure 4.3, it can be seen that with the increase in the ash content of the biomass, hydrogen and oxygen contents decreased suggesting dehydration reaction is taking place from the effect of ash content in the biomass.

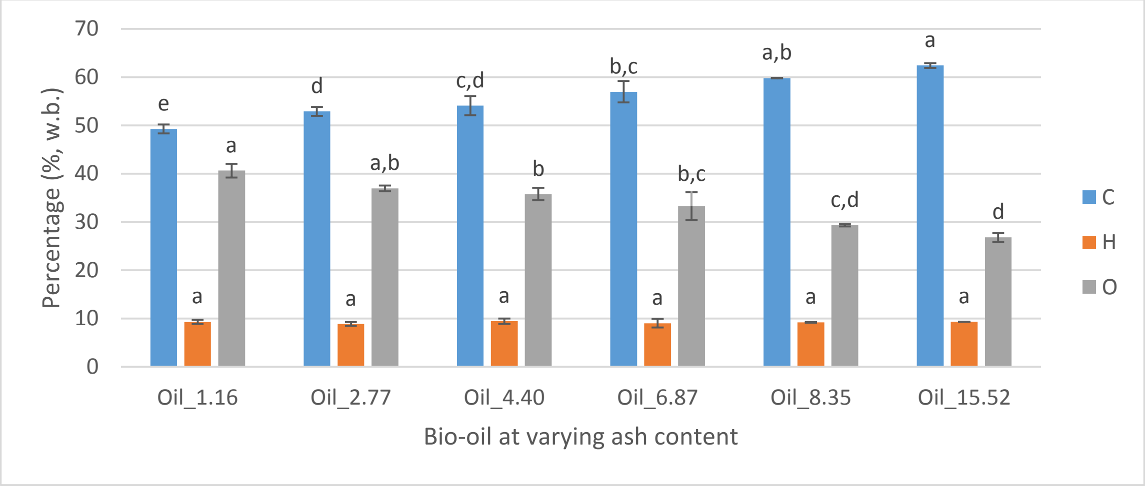


Figure 4.3 Elemental analysis of bio-oil

Note: For the samples with Oil_num denotation, the num is the ash content of the biomass from which the bio oil is produced. Same letter for each group (Bio-oil, char and gas) indicates that it is not statistically different (p<0.05).

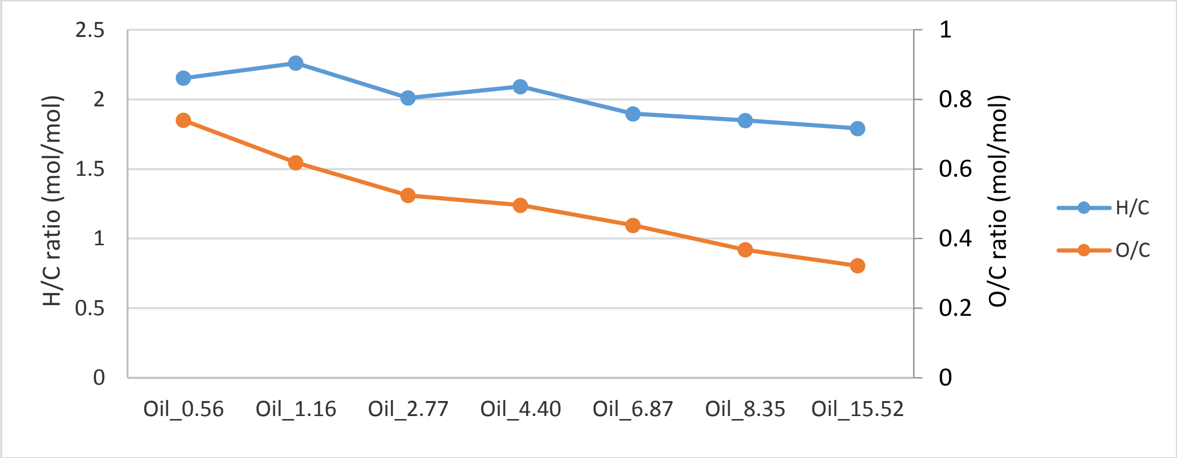


Figure 4.4 H/C and O/C molar ratio of bio-oils produced from biomass with increasing ash content

Note: Oil_num denotation, the num is the ash content of the biomass.

The decreasing trend of O/C ratio in Figure 4.4 shows that the presence of ash in the biomass can cause deoxygenation in bio-oil. There was a drop in O/C ratio of 0.74 to 0.32 with the increment in the ash content of the biomass from 0.56% to 15.52%. As from the elemental analysis, the major component of the ash was silica and aluminum. Hence, the presence of high amount of ash content of biomass, with silica and aluminum as major element, can have the catalytic effect which causes dehydration of the bio-oil. The presence of ash, also decreased the hydrogen in the bio-oil as seen from the drop in H/C ratio, where H/C dropped from 2.26 to 1.79.

Bio-oil consists of more than 300 chemical compounds which constitutes anhydrosugars, phenols, acids and hydrocarbons. The main groups of chemical compounds identified are represented in Figure 4.5. Depolymerization reaction takes place in pyrolysis which decomposes cellulose and hemi-cellulose to form different anhydrosugars and furans which is shown in the figure. The conversion of anhydrosugars to furans increased with the increase in the ash content indicating the ability of dehydration reactions (Mahadevan et al., 2015). The phenolic compound was reduced with the increase in the ash content of the biomass and since the biomass ash in this study was rich in silica and aluminum, which are both deoxygenating agents and are acidic in nature, could have produced the catalytic effect of deoxygenation as the cracking of the heavier phenolic compounds to produce lighter phenolics. Mahadevan et al. (2015) reported the similar reduction in phenolic compounds when zeolite was used as catalyst. The total acidic compounds in the bio-oil increased with the increase in the ash content and similar trend was observed in aldehydes and ketones. Acidic compounds in the bio-oil induces corrosiveness whereas aldehydes and ketones relates to instability of bio-oil during storage and transportation (Iliopoulou et al., 2013).

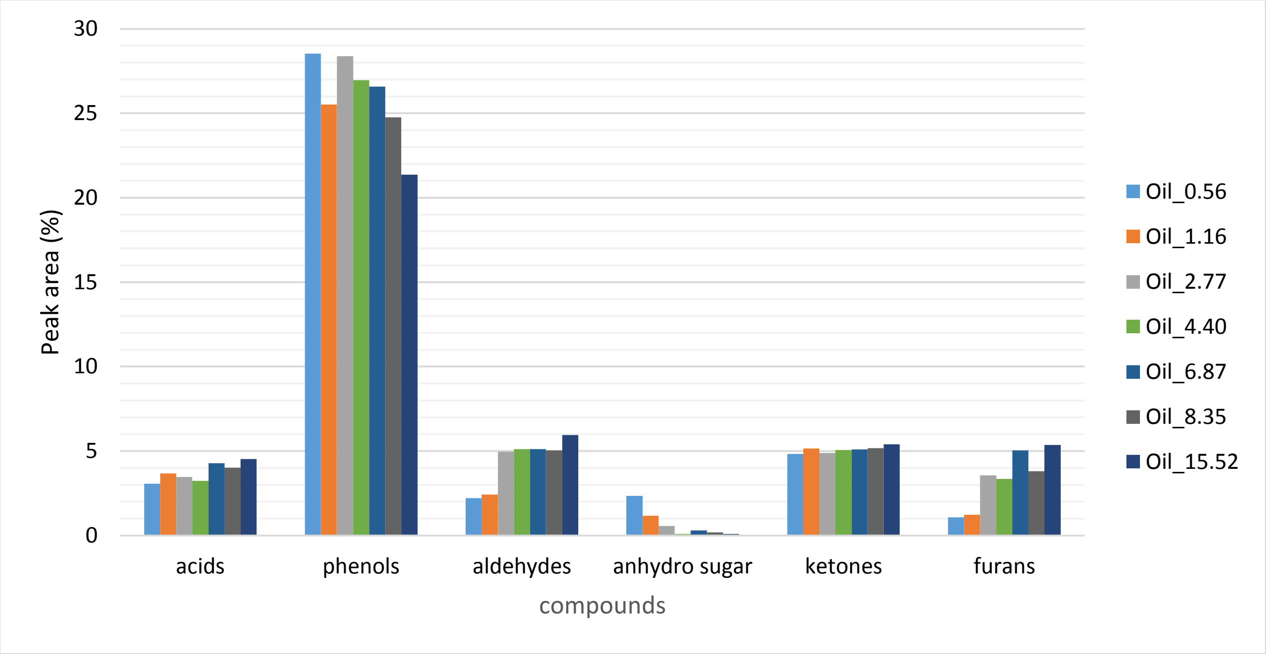


Figure 4.5 Chemical composition of bio-produced from biomass at different ash content

Note: For the samples with Oil_num denotation, the num is the ash content of the biomass from which the bio oil is produced.

Table 4.4 shows the properties of the bio-oil produced from biomass at different ash content level from pyrolysis. The water content increased for the bio-oils produced from biomass with greater ash content. The water content of bio-oil produced from biomass at 0.56% of ash was 20.72%. Although there was increasing trend in the water content, there was no significant difference ($p<0.05$) in the water content for bio-oils produced from biomass of ash content 0.56% to 8.35%. As deoxidation and dehydration was apparent from decreasing H/C and O/C ratio, dehydration reaction was enhanced with the increase in the ash content suggesting the catalytic effect from the ash content during pyrolysis process.

Table 4.4 Properties of bio-oils produced from pine wood at different ash content

Bio-Oil	Water content (%)	Ash content (wt%, d.b.)	pH	TAN(High)	Energy content MJ/kg (wt%, d.b.)
Oil_0.56	20.72 ± 1.20 ^{b,c}	0.14 ± 0.01 ^{b,c}	2.71 ± 0.06 ^{a}	106.00 ± 1.41 ^{b}	22.51 ± 0.17 ^{c}
Oil_1.16	19.74 ± 0.21 ^{c}	0.09 ± 0.06 ^{c}	2.54 ± 0.10 ^{b}	108.93 ± 2.55 ^{a,b}	22.17 ± 0.42 ^{c}
Oil_2.77	19.31 ± 0.37 ^{c}	0.13 ± 0.01 ^{c}	2.28 ± 0.04 ^{c}	110.43 ± 8.30 ^{a,b}	22.58 ± 0.00 ^{c}
Oil_4.40	19.72 ± 0.13 ^{c}	0.13 ± 0.01 ^{b,c}	2.25 ± 0.05 ^{c}	106.29 ± 1.76 ^{a,b}	22.94 ± 0.84 ^{b,c}
Oil_6.87	20.42 ± 0.01 ^{b,c}	0.13 ± 0.00 ^{c}	2.28 ± 0.06 ^{c}	109.00 ± 1.91 ^{a,b}	22.90 ± 0.10 ^{b,c}
Oil_8.35	22.30 ± 0.05 ^{b}	0.37 ± 0.07 ^{a,b}	2.22 ± 0.03 ^{c}	115.92 ± 0.28 ^{a,b}	24.44 ± 0.22 ^{a,b}
Oil_15.52	24.99 ± 0.86 ^{a}	0.55 ± 0.11 ^{a}	2.22 ± 0.09 ^{c}	116.75 ± 2.10 ^{a}	24.85 ± 0.33 ^{a}

Note: *For the samples with Oil_num denotation, the number shows the ash content of the biomass from which the bio-oil was produced. The values after the ± sign denote the standard deviation. The values with the same letter are not significantly different ($p<0.05$) for each column. d.b. stands for dry basis.*

The ash content of the bio-oil increased with the increase in the ash content of the feedstock. There was a decreasing trend in the pH and increasing trend in the TAN (high) value of the bio-oil produced from biomass with increasing ash content suggesting the acidic nature of the bio-oil produced with the increase in the ash content. The heating value of the bio-oil increased with the increase in the ash content of biomass. The heating value was significantly ($p<0.05$) different for bio-oils produced from biomass with ash content 0.56% to 2.77% and 4.40% to 8.35%. The heating value increased significantly for bio-oil produced from biomass with ash content of 15.52%. The increase in the heating value is due to the increment in the carbon content of the bio-oil at higher ash content of biomass. The value of pH, TAN and heating value was in coherent with bio-oil produced from pinewood from the study of Mahadevan et al. (2015).

4.4.4 Bio-char analysis

Table 4.5 shows the ash content and heating value of the bio-chars produced. The ash content of the char produced from biomass with 0.56% of ash content was 9.67%. But as the ash content of the biomass was increased, the ash content of the bio-chars increased significantly ($p<0.05$). The ash content of the bio-char produced from biomass with 15.53% of ash was highest at 29.12%. Kim et al., (2012) produced bio-char at 500^{o}C using fluidized bed reactor from pitch pine and reported ash content as 7.7% for the bio-char produced.

The high ash content can be explained as the metal component of the biomass deposited in the char during the pyrolysis. The heating value of the bio-char produced is higher as compared to the biomass and bio-oil because of the high carbon content present in the bio-char. The heating value of the bio-char decreased from 27.85 MJ/kg to 19.55 MJ/kg when ash content of the biomass was increased from 0.56% to 15.52%. The decrease in the heating value may be due to the increasing ash content in the bio-char and reducing carbon content as seen in Table 4.6.

Table 4.5 Energy content and ash content of char produced from biomass at different ash content

	Energy content (MJ/kg, d.b.)	**Ash content (wt%, d.b.)**
Char_0.56	27.85 ± 0.11 ^{a}	9.67 ± 0.21 ^{d}
Char_1.16	26.24 ± 0.64 ^{a,b}	10.50 ± 0.76 ^{d}
Char_2.77	24.48 ± 0.94 ^{b,c}	14.39 ± 1.03 ^{c}
Char_4.40	23.75 ± 0.34 ^{b,c,d}	17.16 ± 2.46 ^{b,c}
Char_6.87	21.09 ± 1.20 ^{c,d,e}	18.40 ± 0.87 ^{b,c}
Char_8.35	21.48 ± 2.93 ^{d,e}	28.30 ± 1.59 ^{a}
Char_15.52	19.55 ± 1.01 ^{e}	29.12 ± 2.31 ^{a}

Note: *For the samples with Char_num denotation, the number shows the ash content of the biomass. The values after the ± sign denote the standard deviation. The values with the same letter are not significantly different ($p<0.05$) for each column. d.b. stands for dry basis.*

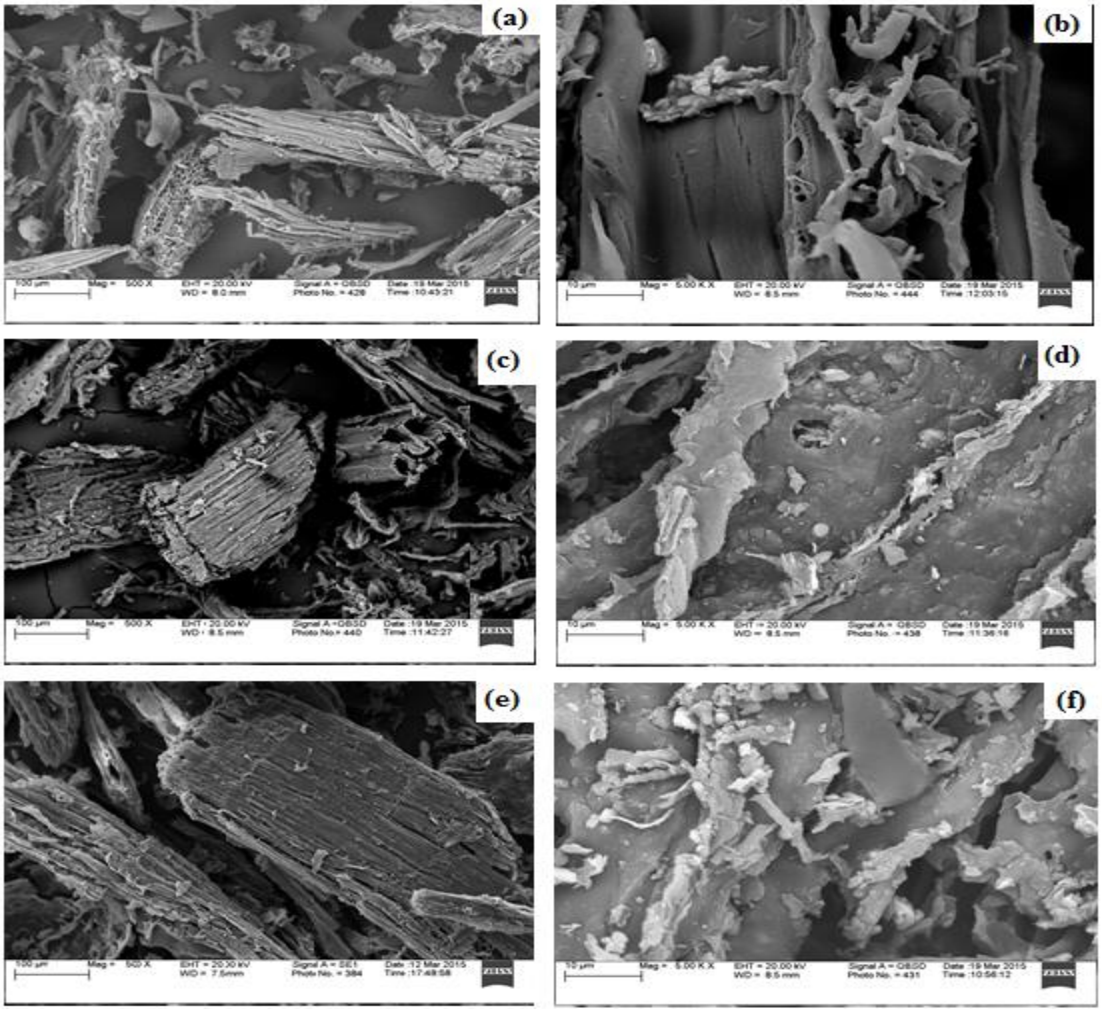
Table 4.6 Elemental analysis of bio-char (wt%, d.b.)

Char Sample	C	H	N	O	Ash content (wt%, d.b.)
Char_1.16	66.38 ± 1.25 ^{a}	3.58 ± 0.08 ^{a,b}	0.06 ± 0.02 ^{b}	19.49 ± 1.25 ^{a}	10.50 ± 0.76 ^{d}
Char_2.77	64.15 ± 1.22 ^{a,b}	3.27 ± 0.18 ^{b,c}	0.07 ± 0.03 ^{b}	18.12 ± 1.29 ^{a}	14.39 ± 1.03 ^{c}
Char_4.40	61.84 ± 0.86 ^{b,c}	3.23 ± 0.04 ^{b,c}	0.09 ± 0.00 ^{b}	17.69 ± 0.90 ^{a,b}	17.16 ± 2.46 ^{b,c}
Char_6.87	59.45 ± 0.83 ^{c,d}	3.52 ± 0.32 ^{a,b,c}	0.11 ± 0.05 ^{b}	18.52 ± 0.80 ^{a}	18.40 ± 0.87 ^{b,c}
Char_8.35	56.34 ± 2.51 ^{d,e}	3.99 ± 0.21 ^{a}	0.09 ± 0.05 ^{b}	11.28 ± 2.35 ^{c}	28.30 ± 1.59 ^{a}
Char_15.52	54.66 ± 1.50 ^{e}	2.98 ± 0.09 ^{c}	0.25 ± 0.02 ^{a}	13.00 ± 1.57 ^{b,c}	29.12 ± 2.31 ^{a}

Note: *For the samples with Char_num denotation, the number shows the ash content of the biomass. The values after the ± sign denote the standard deviation. The values with the same letter are not significantly different ($p<0.05$) for each column. d.b. stands for dry basis.*

Table 4.6 shows the elemental analysis of the bio-char produced from biomass at different ash content level. As the ash content of the biomass increased, the carbon content decreased from 66.38% to 54.66%. This can be correlated with the increasing amount of ash content of the char itself (Table 4.4). Kang et al. (2006) studied the effect cyclone as char separator and found that the carbon content of char was 73.5%, hydrogen was 3.1% which is similar to our results.

Char surface morphology with different ash content of biomass from pyrolysis can be observed by comparing the SEM images of the char particles. SEM-EDS analysis was performed for the char produced from three different ash content: 1.16%, 6.87% and 15.52%. The SEM images are given in Figure 4.6. Figure 4.6 (a) and (b) shows the bio-char structure produced from biomass at 1.17%, Figure 4.6 (b) and (c) shows bio-char produced from biomass at 6.67% and Figure 4.6 (d) and (e) shows bio-chars produced from biomass at 15.52%. The formation of longitudinal cells in the transversal section shows the fragility and lightness of the char particles as observed in Figure 4.6 (a), (c) and (e). Furthermore we can see the rough appearance of the char which can be explained by the escaping of the volatile species with open pores appearing in the char surface.



Note: Figure (a), (c) and (e) shows the char at 500x magnification and figure (b), (d) and (f) shows the char at 5000x magnification.

Figure 4.6 SEM pictures of the chars obtained at different ash content: (a) and (b) 1.16%; (c) and (d) 6.87%; (e) and (f) 15.52%

The mineral matter appears to be dispersed through the surface of the char. The dispersion is higher in case of biomass with higher ash content as compared to the biomass with lower ash content. It is clear in Figure 4.5 (b), (d) and (f). Similar roughness in the bio-char surfaces and dispersion of mineral compounds were observed in the study performed by Fu et al., (2012).

SEM-EDS was used to estimate the mineral compound present in the char. The results of the analysis is shown in the Table 4.7. The amount of silica was highest compared to the other elements present in the bio-chars. As the ash content increased, the minerals composition of the char increased. The increment in the elemental disposition in the bio-chars with the increase in the ash content is also supported by the increment in the bio-char yield in the fast pyrolysis experiment.

Table 4.7 Elements compositions (wt %) of bio-char at different ash content level from SEM-EDS

Elements	Char_1.16	Char_6.87	Char_15.52
Mg	0.10 ± 0.03	0.21 ± 0.07	0.11 ± 0.02
Al	0.18 ± 0.08	1.54 ± 0.53	1.42 ± 0.25
Si	2.14 ± 0.37	1.75 ± 0.64	2.91 ± 0.56
K	0.34 ± 0.10	0.40 ± 0.10	0.29 ± 0.05
Ca	0.47 ± 0.14	0.52 ± 0.14	0.51 ± 0.08
Ti	ND	0.08 ± 0.03	0.08 ± 0.02
Fe	0.12 ± 0.04	0.66 ± 0.19	0.74 ± 0.16

Note: *For the samples with Char_num denotation, the number shows the ash content of the biomass. The values after the ± sign denote the standard deviation. ND stands for not detected.*

4.4.5 Gas analysis

The non-condensable gases produced from pyrolysis consists of hydrogen, methane, carbon monoxide and carbon dioxide as shown in Figure 4.7. The production of carbon monoxide was high as compared to the other gases. Yildiz et al. (2015) also reported the similar finding of CO as the major component in the non-condensable gases.

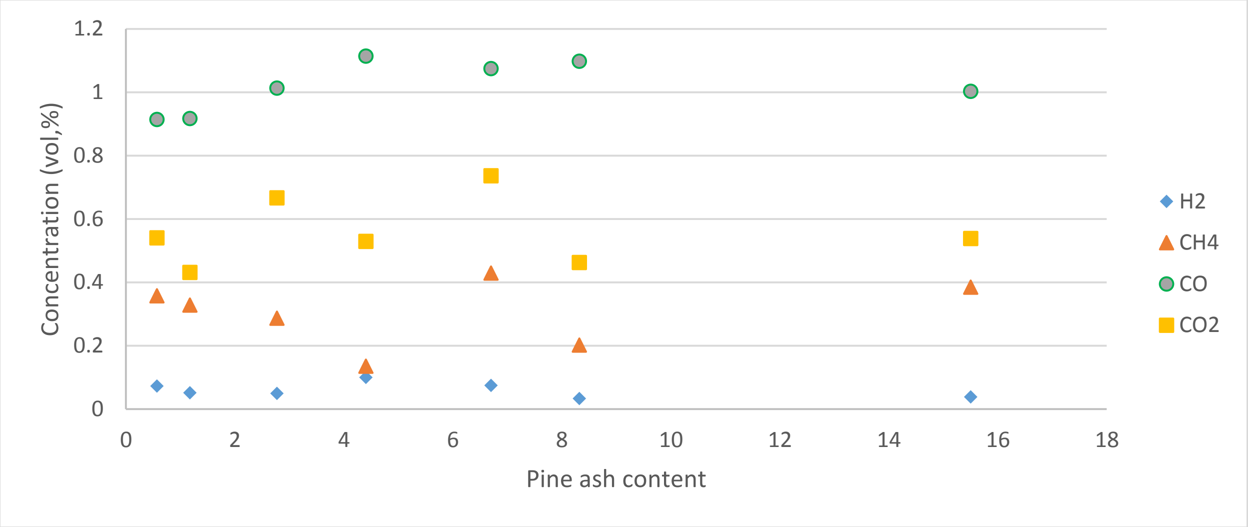


Figure 4.7 Micro GC analysis of non-condensable gases

4.5 Summary

- Presence of high concentration of ash has direct effect on the properties of biomass. As the ash content was increased, the carbon and hydrogen content of the biomass decreased which resulted in the decreased of the heating value of the feedstock.
- Bio-oil yield decreased with the increase in the ash content of the biomass. The water content and ash content of the bio-oil increased with the increase in the ash content of the biomass. Furthermore, pH value of bio-oil decreased significantly and TAN increased

significantly ($p<0.05$) until 2.77% of ash in biomass. At higher ash content level of biomass, with silica as major element, the acidity of the bio-oil increases.

- The carbon and hydrogen content of the bio-char decreased with the increase in the ash content of the biomass and furthermore, the ash content of the bio-char increased too, which resulted in the decrease of energy content of the bio-char.
- SEM EDS analysis showed the formation of longitudinal cells in the transversal section shows the fragility and lightness of the char particles. Furthermore, we can see the rough appearance of the char which can be explained by the escaping of the volatile species with open pores appearing in the char surface. The mineral particles were more abundantly dispersed in the case of bio-char with higher ash content.

4.6 References

Aho, A., DeMartini, N., Pranovich, A., Krogell, J., Kumar, N., Eränen, K. & Murzin, D. Y. (2013). Pyrolysis of pine and gasification of pine chars–Influence of organically bound metals. *Bioresource technology*, *128*, 22-29.

Amutio, M., Lopez, G., Artetxe, M., Elordi, G., Olazar, M., & Bilbao, J. (2012). Influence of temperature on biomass pyrolysis in a conical spouted bed reactor. *Resources, Conservation and Recycling*, *59*, 23-31.

Bridgwater, A. V. (1999). Principles and practice of biomass fast pyrolysis processes for liquids. *Journal of analytical and applied pyrolysis*, *51*(1), 3-22.

Bridgwater, A. V. (2012). Review of fast pyrolysis of biomass and product upgrading. *Biomass and bioenergy*, *38*, 68-94.

Chen, M. Q., Wang, J., Zhang, M. X., Chen, M. G., Zhu, X. F., Min, F. F., & Tan, Z. C. (2008). Catalytic effects of eight inorganic additives on pyrolysis of pine wood sawdust by microwave heating. *Journal of Analytical and Applied Pyrolysis*, *82*(1), 145-150.

Dhiman, J. (2014). *Prediction of Heating and Ignition Properties of Biomass Dusts Using Near Infrared Spectroscopy* (Doctoral dissertation, Auburn University).

Diebold, J. P. (2000). *A review of the chemical and physical mechanisms of the storage stability of fast pyrolysis bio-oils* (pp. 1-3). Golden, CO: National Renewable Energy Laboratory.

Fu, P., Hu, S., Xiang, J., Sun, L., Su, S., & Wang, J. (2012). Evaluation of the porous structure development of chars from pyrolysis of rice straw: effects of pyrolysis temperature and heating rate. *Journal of Analytical and Applied Pyrolysis*, *98*, 177-183.

Gao, N., Li, A., Quan, C., Du, L., & Duan, Y. (2013). TG–FTIR and Py–GC/MS analysis on pyrolysis and combustion of pine sawdust. *Journal of Analytical and Applied Pyrolysis*, *100*, 26-32.

Gupta, R. B., & Demirbas, A. (2010). *Gasoline, diesel and ethanol biofuels from grasses and plants*. Cambridge University Press.

Hehar, G. S. (2013). *Physicochemical and Ignition Properties of Dust from Loblolly Pine Wood* (Doctoral dissertation, Auburn University).

Huang, Y., Wei, L., Crandall, Z., Julson, J., & Gu, Z. (2015). Combining Mo–Cu/HZSM-5 with a two-stage catalytic pyrolysis system for pine sawdust thermal conversion. *Fuel*, *150*, 656-663.

Iliopoulou, E. F., Stefanidis, S., Kalogiannis, K., Psarras, A. C., Delimitis, A., Triantafyllidis, K. S., & Lappas, A. A. (2014). Pilot-scale validation of Co-ZSM-5 catalyst performance in the catalytic upgrading of biomass pyrolysis vapors. *Green Chemistry*, *16*(2), 662-674.

Kang, B. S., Lee, K. H., Park, H. J., Park, Y. K., & Kim, J. S. (2006). Fast pyrolysis of radiata pine in a bench scale plant with a fluidized bed: Influence of a char separation system and reaction conditions on the production of bio-oil. *Journal of analytical and applied pyrolysis*, *76*(1), 32-37.

Kim, K. H., Kim, J. Y., Cho, T. S., & Choi, J. W. (2012). Influence of pyrolysis temperature on physicochemical properties of biochar obtained from the fast pyrolysis of pitch pine (Pinus rigida). *Bioresource technology*, *118*, 158-162.

Kozlowsky, T. T., Pallardy, S. G., & Kramer, P. J. (1997). Physiology of woody plants. *University of California, Berkeley*.

Liu, X., & Bi, X. T. (2011). Removal of inorganic constituents from pine barks and switchgrass. *Fuel Processing Technology*, *92*(7), 1273-1279.

Mahadevan, R., Shakya, R., Neupane, S., & Adhikari, S. (2015). Physical and Chemical Properties and Accelerated Aging Test of Bio-oil Produced from in Situ Catalytic Pyrolysis in a Bench-Scale Fluidized-Bed Reactor. *Energy & Fuels*, *29*(2), 841-848.

McKendry, P. (2002). Energy production from biomass (part 1): overview of biomass. *Bioresource technology*, *83*(1), 37-46.

Miles, T. R., Miles Jr, T. R., Baxter, L. L., Bryers, R. W., Jenkins, B. M., & Oden, L. L. (1995). *Alkali deposits found in biomass power plants: A preliminary investigation of their extent and nature. Volume 1* (No. NREL/TP--433-8142-Vol. 1; SAND--96-8225-Vol. 1). National Renewable Energy Lab., Golden, CO (United States); Miles (Thomas R.), Portland, OR (United States); Sandia National Labs., Livermore, CA (United States); Foster Wheeler Development Corp., Livingston, NJ (United States); California Univ., Davis, CA (United States); Bureau of Mines, Albany, OR (United States). Albany Research Center.

Mourant, D., Lievens, C., Gunawan, R., Wang, Y., Hu, X., Wu, L., & Li, C. Z. (2013). Effects of temperature on the yields and properties of bio-oil from the fast pyrolysis of mallee bark. *Fuel*, *108*, 400-408.

Oasmaa, A., Elliott, D. C., & Korhonen, J. (2010). Acidity of biomass fast pyrolysis bio-oils. *Energy & Fuels*, *24*(12), 6548-6554.

Turn, S. Q., Kinoshita, C. M., & Ishimura, D. M. (1997). Removal of inorganic constituents of biomass feedstocks by mechanical dewatering and leaching. *Biomass and Bioenergy*, *12*(4), 241-252.

Thangalazhy-Gopakumar, S., Adhikari, S., Ravindran, H., Gupta, R. B., Fasina, O., Tu, M., & Fernando, S. D. (2010). Physiochemical properties of bio-oil produced at various temperatures from pine wood using an auger reactor. *Bioresource technology*, *101*(21), 8389-8395.

Yildiz, G., Ronsse, F., Venderbosch, R., van Duren, R., Kersten, S. R., & Prins, W. (2015). Effect of biomass ash in catalytic fast pyrolysis of pine wood. *Applied Catalysis B: Environmental*, *168*, 203-211.

CHAPTER FIVE

SUMMARY AND FUTURE WORK

5.1 Concluding remarks

This thesis was able to establish the ash reduction of woody biomass by vibratory sieve shaker, hammer mill and concrete mixer. All of the three treatment processes significantly reduced ($p<0.05$) the ash content of the whole pinewood, residual pinewood and sweetgum with initial ash level of around 2%. Hammer mill was found to be more effective in reducing the ash content of the dirty pine chips as compared to that of mixer and vibratory sieve shaker for biomass with higher ash level of greater than 5%. Hammer mill was significantly effective ($p<0.05$) in reducing ash content at moisture content levels of 10%, 20% and 30% as compared to mixer and vibratory sieve shaker, which were effective in reducing ash content at 10% of moisture content. The force generated by the breaking action of hammer to the wood chips removed the dirt particles adhered at the surface of the dirty chips and thus the ash content was reduced. The reduction in ash content was in line with the increase in volatile matter and heating value of the biomass.

Fast pyrolysis was performed at 500^{o}C on the treated samples at different ash content level to understand the effect of ash reduction by physical treatments. The bio-oil yield decreased and char production increased with the increase in the ash of the biomass as suggested from the literatures. The water content increased with the increase in the ash content because of dehydration reaction taking place as a result of catalytic effect of silica and aluminum in the ash. The same is suggested from the deoxygenation and dehydration phenomenon which was observed as decrement in O/C and H/C molar ratio. Furthermore, pH value of bio-oil decreased significantly and TAN increased significantly ($p<0.05$) until 2.77% of ash in biomass. At higher ash content level of biomass, with silica as major element, the acidity of the bio-oil increased. The carbon and hydrogen content of the bio-char decreased with the increase in the ash content of the biomass and furthermore, the ash content of the bio-char increased too which resulted in the decrease of heating value of the bio-char. SEM EDS analysis showed the mineral particles abundantly dispersed in the case of bio-char with higher ash content.

As the hammer mill treatment was able to reduce the ash content of biomass from 10 and 8% to around 3%, it not only can improve the transportation and storage cost, as the amount of inorganic element in biomass is decreased but it also improved the bio-oil yield from the fast pyrolysis. Furthermore, with the reduction of ash content, the water content of the bio-oil reduced with reduction in oxygen content and the acidity of the bio-oil reduced too. The char produced had less ash content with improved heating value as the ash was reduced from the physical treatment.

5.2 Limitations and recommendations for future work

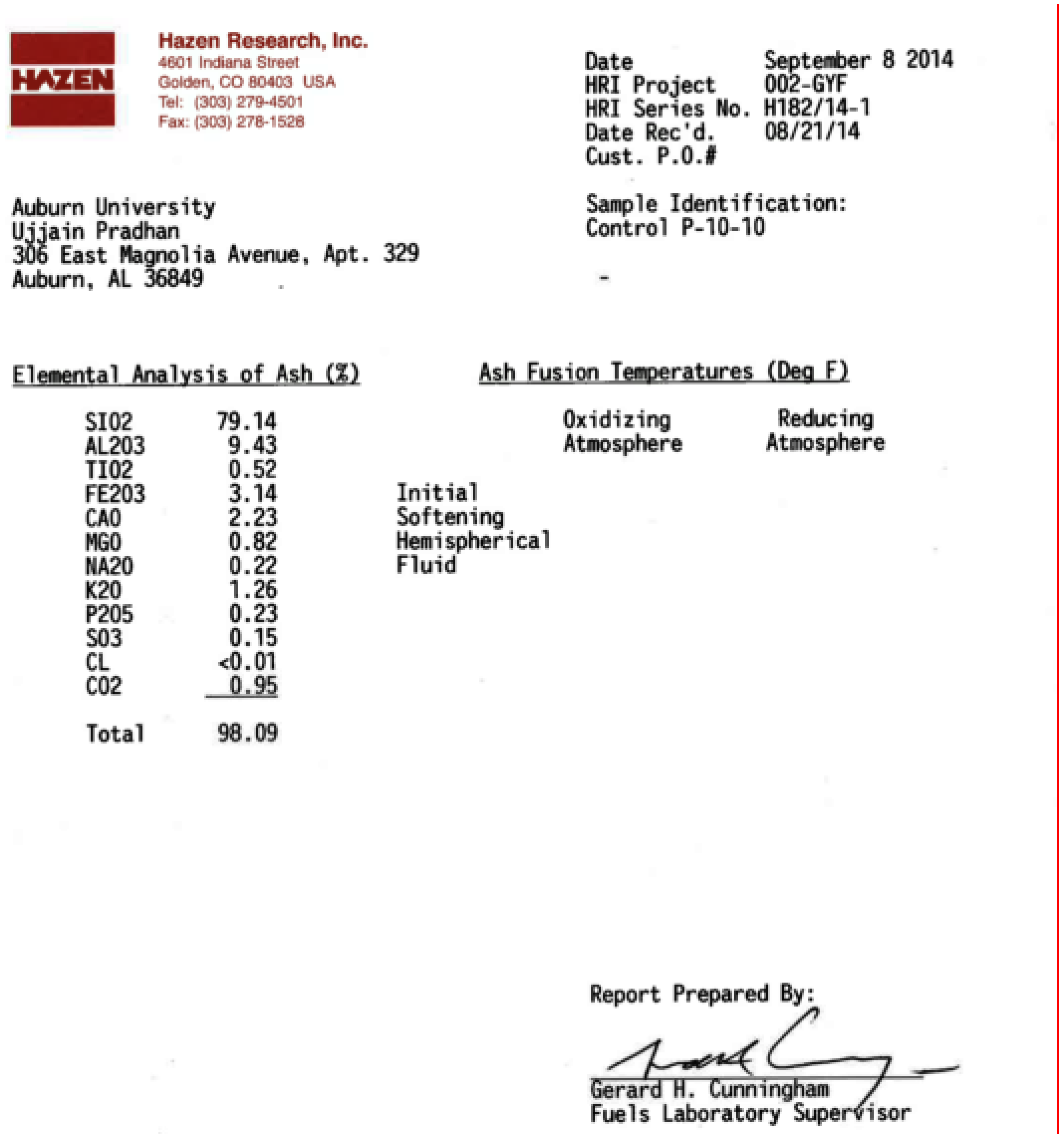
Hammer mill was found to be effective in reducing the ash content of the biomass as the breaking force generated by the hammer inside the hammer mill was great. The same concept can be used during chipping method, in which the wood logs are reduced in size to woodchips of sizes 2 to 3 inches through wood chippers. Wood chippers will create the same breaking force as that of hammer mill and thus the detrital ash can be removed when passed through vibratory sieve shaker to reduce the ash content. Furthermore, physical treatment is recommended at the harvesting site to reduce the detrital ash content of biomass which will aid the transportation of the woodchips.

There was high amount of loss of fine particles from the hammer mill through air leaks during the treatment. This also accounted for the high ash and mass loss of the feedstock. Hence, hammer mill should be performed with proper air seals.

Hammer mill was effective in reducing the ash content at higher moisture content level. Hence, leaching of dirty biomass with water followed by treatment with hammer mill can be done to reduce the authigenic ash.

The detrital ash present on the biomass is largely dependent on the logistics and handling sites. Since, in this study, due to unavailability of naturally occurring dirty woodchips of high ash content, ash coating was done with soil taken from the University ground. This affected the properties of biomass with silica as the major inorganic element and thus results of fast pyrolysis were affected too. Hence, naturally occurring dirty chips, which may have different inorganic elements as major constituent should be used to produce bio-oil to better understand the effect of ash content in fast pyrolysis. Non-catalytic fast pyrolysis was performed in this study but catalytic fast pyrolysis aids in upgrading of bio-oil and hence it should also be performed for biomass at different ash content to understand the effect of ash as catalysts.

APPENDIX A: ELEMENTAL ANALYSIS OF BIOMASS ASH AND SOIL



Hazen Research, Inc.
4601 Indiana Street
Golden, CO 80403 USA
Tel: (303) 279-4501
Fax: (303) 278-1528

Date	September 8 2014
HRI Project	002-GYF
HRI Series No.	H182/14-1
Date Rec'd.	08/21/14
Cust. P.O.#	

Auburn University
Ujjain Pradhan
306 East Magnolia Avenue, Apt. 329
Auburn, AL 36849

Sample Identification:
Control P-10-10

Elemental Analysis of Ash (%)

SI02	79.14
AL203	9.43
TI02	0.52
FE203	3.14
CAO	2.23
MGO	0.82
NA20	0.22
K20	1.26
P205	0.23
S03	0.15
CL	<0.01
C02	0.95
Total	98.09

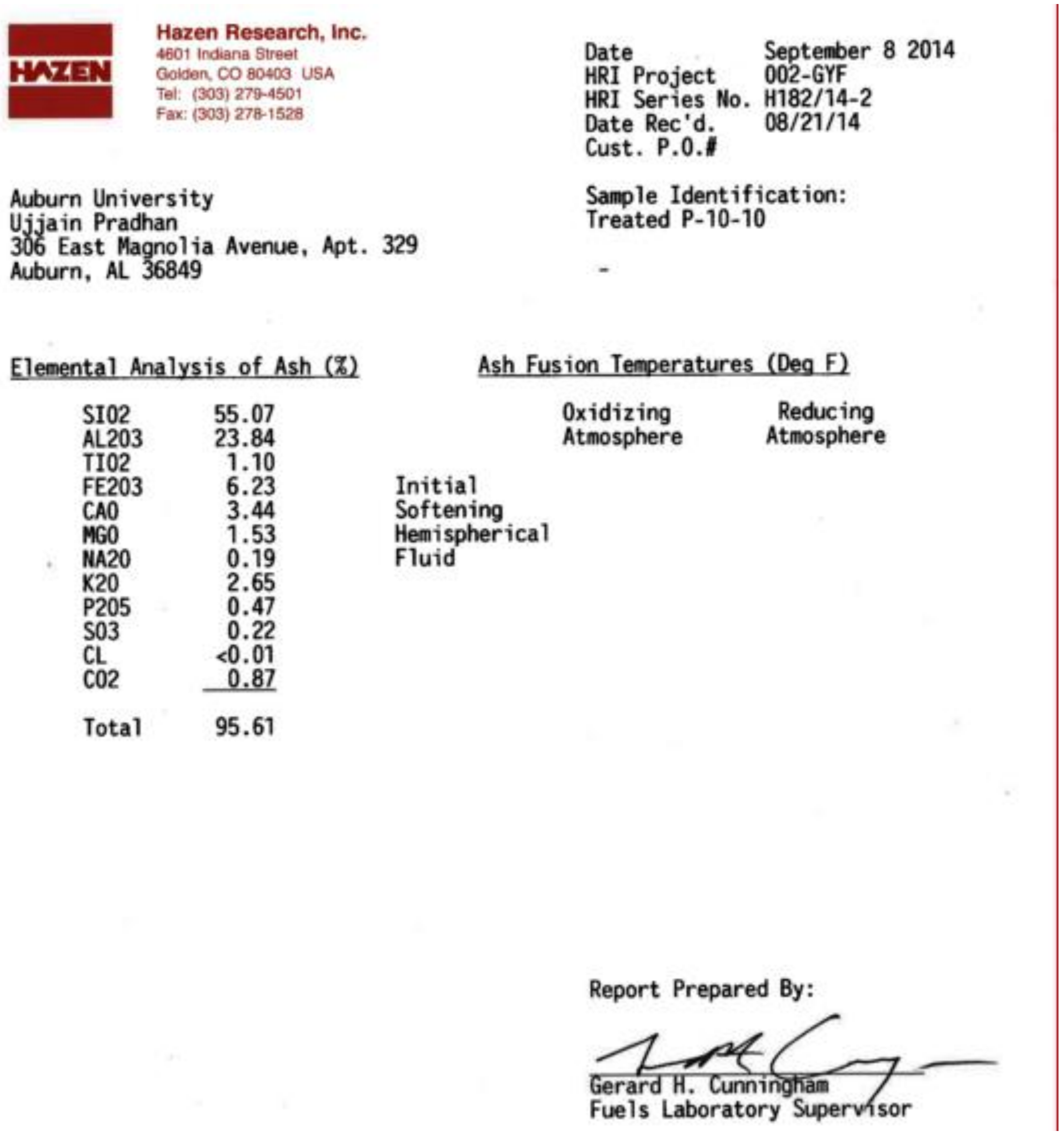
Ash Fusion Temperatures (Deg F)

	Oxidizing Atmosphere	Reducing Atmosphere
Initial		
Softening		
Hemispherical		
Fluid		

Report Prepared By:

Gerard H. Cunningham
Fuels Laboratory Supervisor

Figure A.1 Descriptive result of ash analysis of dirty biomass at 10% of ash and moisture content



Hazen Research, Inc.
4601 Indiana Street
Golden, CO 80403 USA
Tel: (303) 279-4501
Fax: (303) 278-1528

Date September 8 2014
HRI Project 002-GYF
HRI Series No. H182/14-2
Date Rec'd. 08/21/14
Cust. P.O.#

Auburn University
Ujjain Pradhan
306 East Magnolia Avenue, Apt. 329
Auburn, AL 36849

Sample Identification:
Treated P-10-10

-

Elemental Analysis of Ash (%)

SI02	55.07
AL203	23.84
TI02	1.10
FE203	6.23
CAO	3.44
MGO	1.53
NA20	0.19
K20	2.65
P205	0.47
S03	0.22
CL	<0.01
C02	0.87
Total	95.61

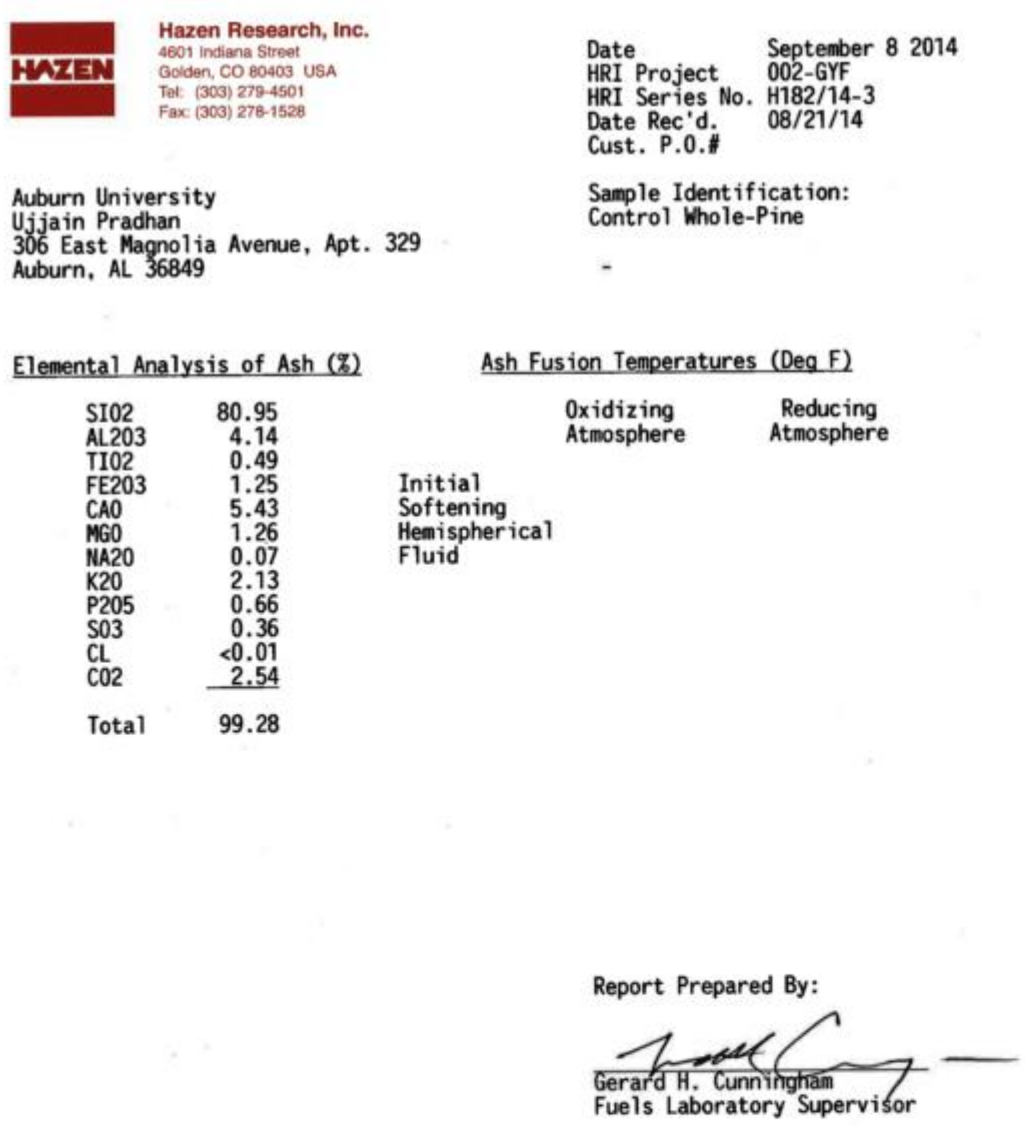
Ash Fusion Temperatures (Deg F)

	Oxidizing Atmosphere	Reducing Atmosphere
Initial		
Softening		
Hemispherical		
Fluid		

Report Prepared By:

Gerard H. Cunningham
Fuels Laboratory Supervisor

Figure A.2 Descriptive result of ash analysis of treated biomass at 10% of ash and moisture content



Hazen Research, Inc.
4601 Indiana Street
Golden, CO 80403 USA
Tel: (303) 279-4501
Fax: (303) 278-1528

Date	September 8 2014
HRI Project	002-GYF
HRI Series No.	H182/14-3
Date Rec'd.	08/21/14
Cust. P.O.#	

Auburn University
Ujjain Pradhan
306 East Magnolia Avenue, Apt. 329
Auburn, AL 36849

Sample Identification:
Control Whole-Pine

-

Elemental Analysis of Ash (%)

SI02	80.95
AL203	4.14
TI02	0.49
FE203	1.25
CAO	5.43
MGO	1.26
NA20	0.07
K20	2.13
P205	0.66
S03	0.36
CL	<0.01
C02	2.54
Total	99.28

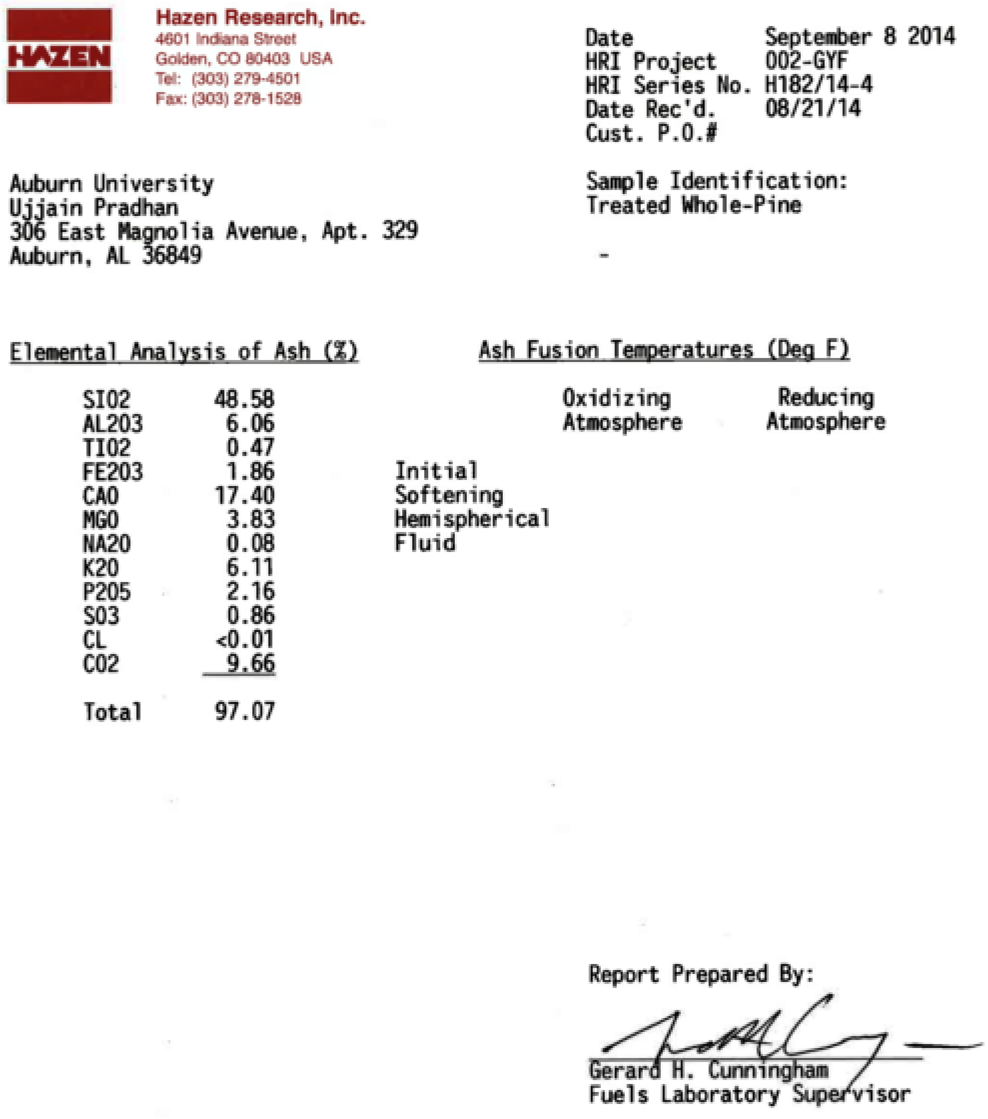
Ash Fusion Temperatures (Deg F)

	Oxidizing Atmosphere	Reducing Atmosphere
Initial		
Softening		
Hemispherical		
Fluid		

Report Prepared By:

Gerard H. Cunningham
Fuels Laboratory Supervisor

Figure A.3 Descriptive result of ash analysis of dirty whole pinewood



Hazen Research, Inc.
4601 Indiana Street
Golden, CO 80403 USA
Tel: (303) 279-4501
Fax: (303) 278-1528

Date	September 8 2014
HRI Project	002-GYF
HRI Series No.	H182/14-4
Date Rec'd.	08/21/14
Cust. P.O.#	

Auburn University
Ujjain Pradhan
306 East Magnolia Avenue, Apt. 329
Auburn, AL 36849

Sample Identification:
Treated Whole-Pine

Elemental Analysis of Ash (%)

SI02	48.58
AL203	6.06
TI02	0.47
FE203	1.86
CA0	17.40
MG0	3.83
NA20	0.08
K20	6.11
P205	2.16
S03	0.86
CL	<0.01
C02	9.66
Total	97.07

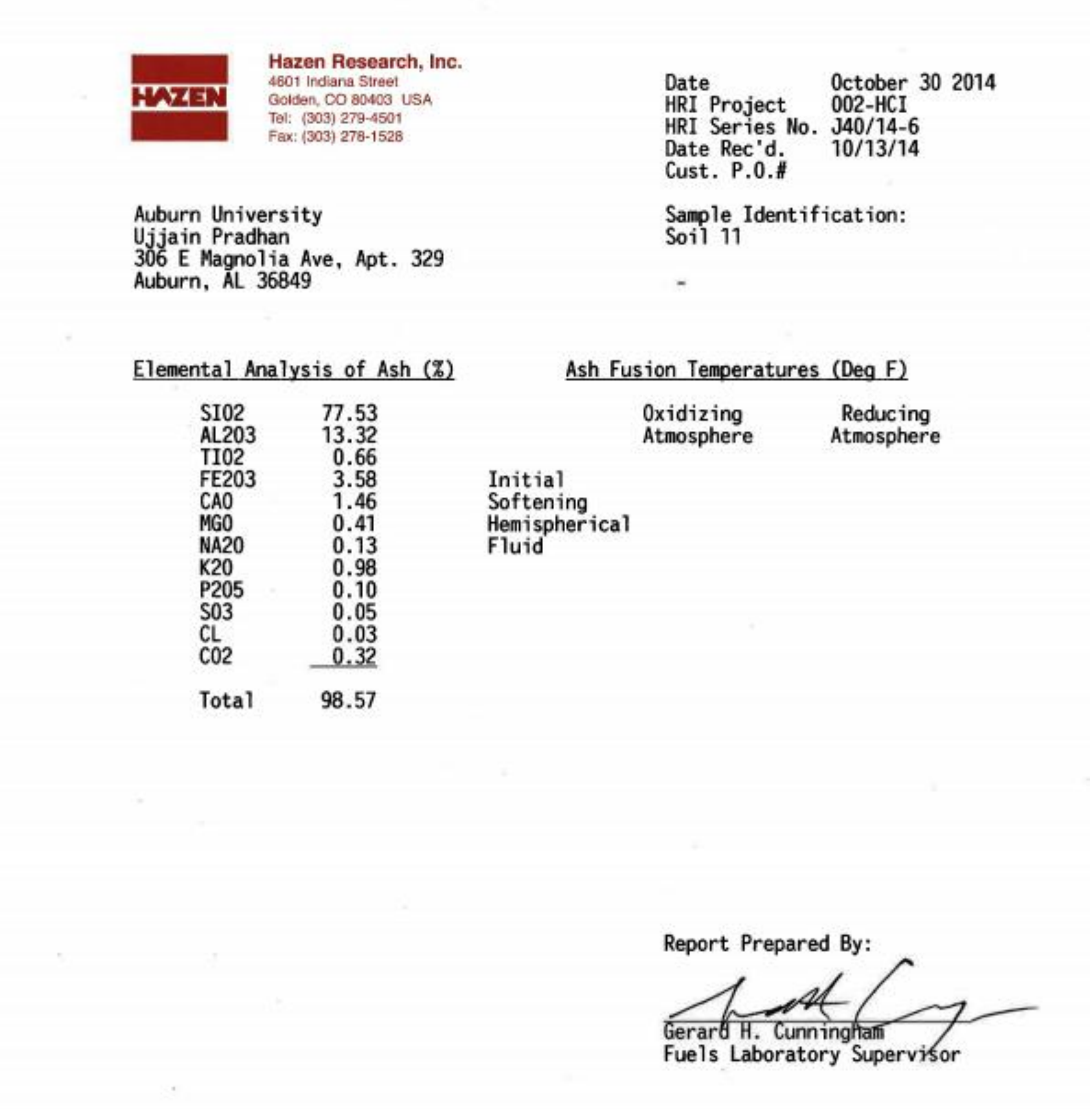
Ash Fusion Temperatures (Deg F)

	Oxidizing Atmosphere	Reducing Atmosphere
Initial		
Softening		
Hemispherical		
Fluid		

Report Prepared By:

Gerard H. Cunningham
Fuels Laboratory Supervisor

Figure A.4 Descriptive result of ash analysis of treated whole pinewood



HAZEN

Hazen Research, Inc.
4601 Indiana Street
Golden, CO 80403 USA
Tel: (303) 279-4501
Fax: (303) 278-1528

Date	October 30 2014
HRI Project	002-HCI
HRI Series No.	J40/14-6
Date Rec'd.	10/13/14
Cust. P.O.#	

Auburn University
Ujjain Pradhan
306 E Magnolia Ave, Apt. 329
Auburn, AL 36849

Sample Identification:
Soil 11

-

Elemental Analysis of Ash (%)

SI02	77.53
AL203	13.32
TI02	0.66
FE203	3.58
CA0	1.46
MG0	0.41
NA20	0.13
K20	0.98
P205	0.10
S03	0.05
CL	0.03
C02	0.32
Total	98.57

Ash Fusion Temperatures (Deg F)

	Oxidizing Atmosphere	Reducing Atmosphere
Initial		
Softening		
Hemispherical		
Fluid		

Report Prepared By:

Gerard H. Cunningham
Fuels Laboratory Supervisor

Figure A.5 Descriptive result of ash analysis of treated whole pinewood

APPENDIX B: SEM AND EDS DATA

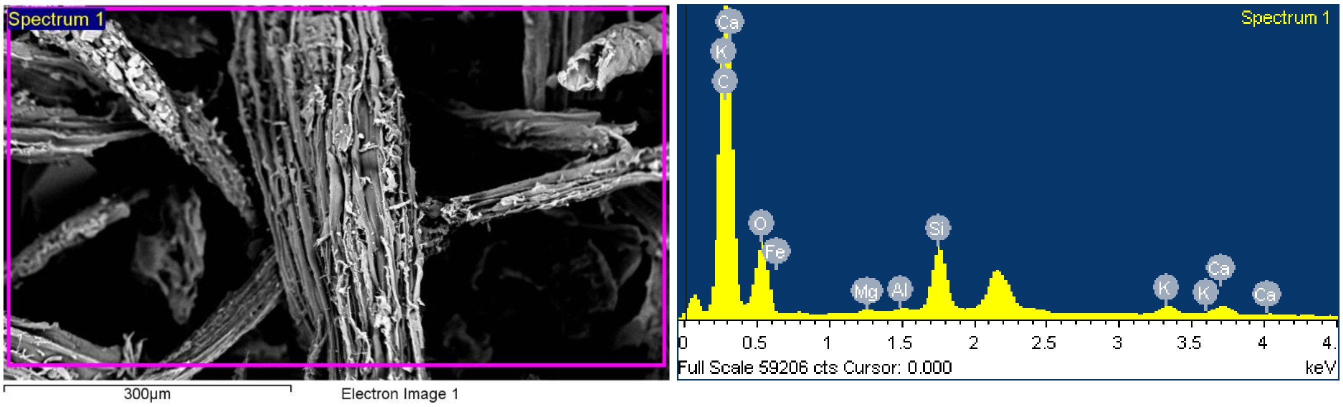


Figure B.1 SEM (left) and corresponding elemental analysis (right) at 500X of bio char produced from biomass with 1.16% ash

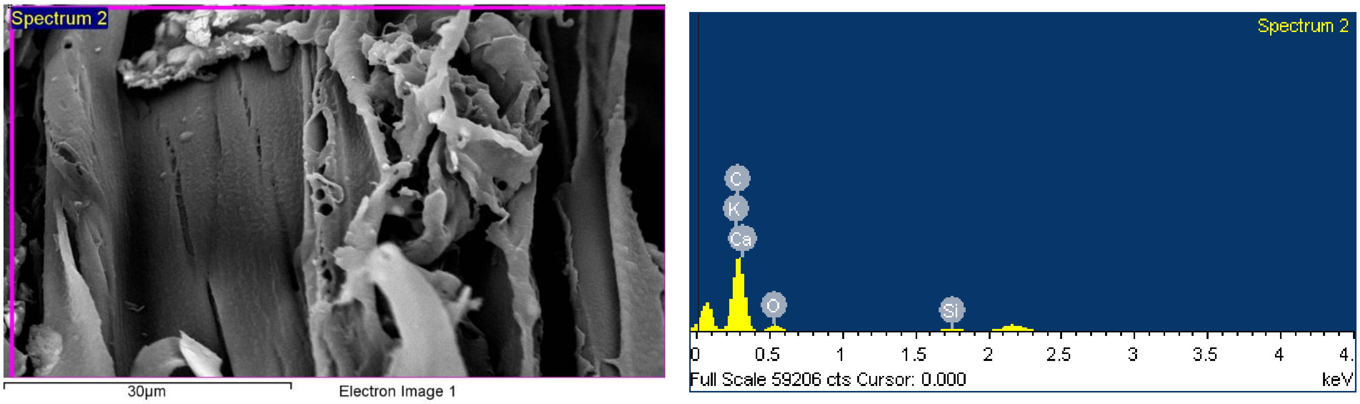


Figure B.2 SEM (left) and corresponding elemental analysis (right) at 5000X of bio char produced from biomass with 1.16% ash

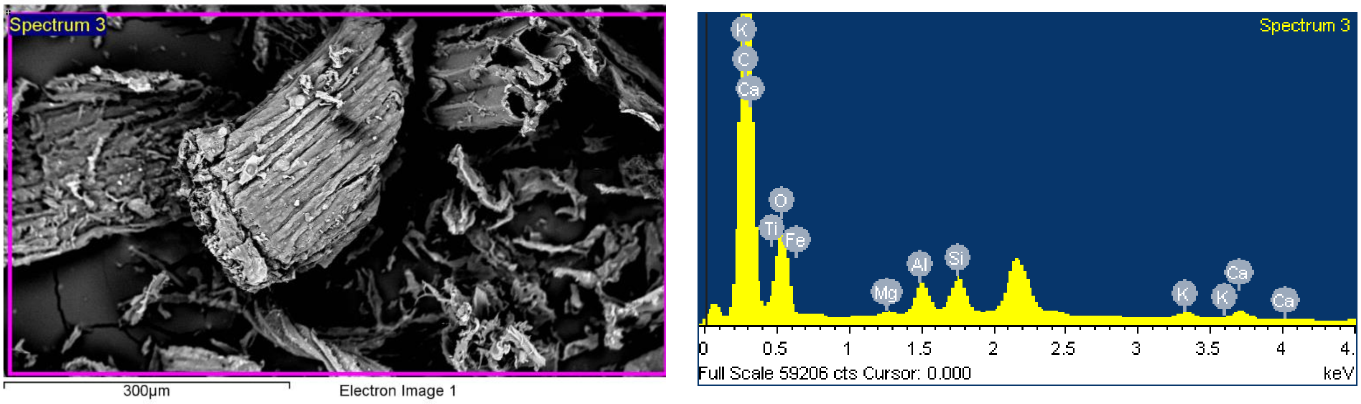


Figure B.3 SEM (left) and corresponding elemental analysis (right) at 500X of bio char produced from biomass with 6.87% ash

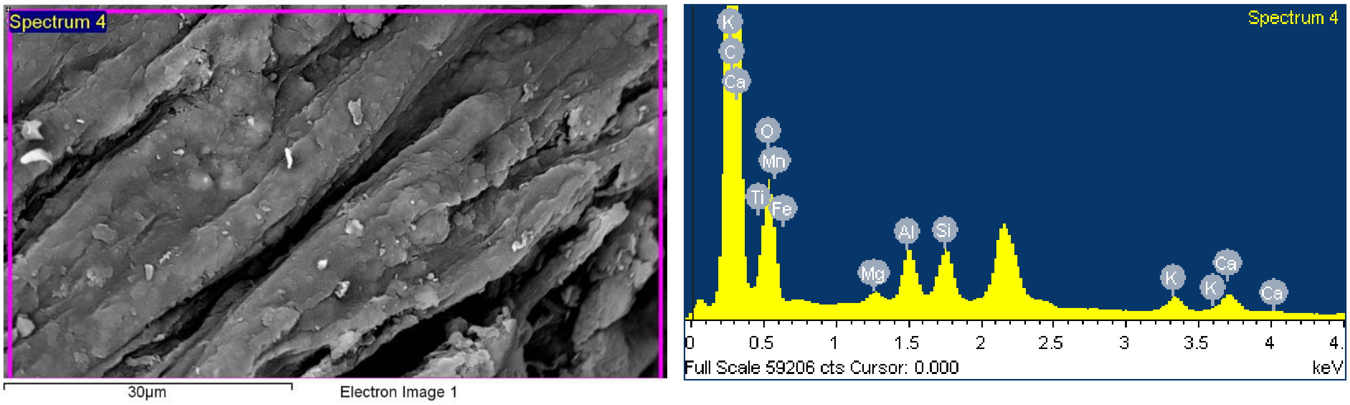


Figure B.4 SEM (left) and corresponding elemental analysis (right) at 5000X of bio char produced from biomass with 6.87% ash

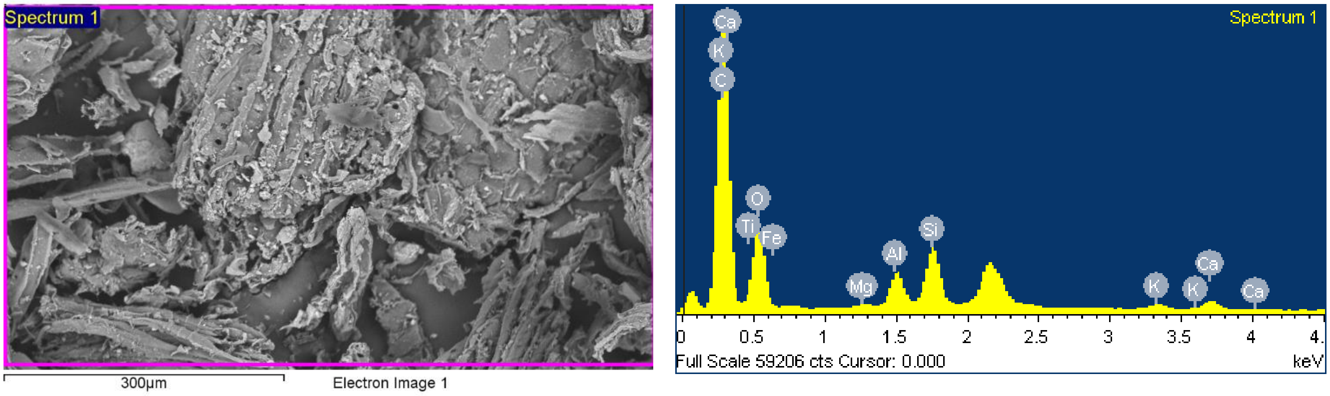


Figure B.5 SEM (left) and corresponding elemental analysis (right) at 500X of bio char produced from biomass with 15.52% ash

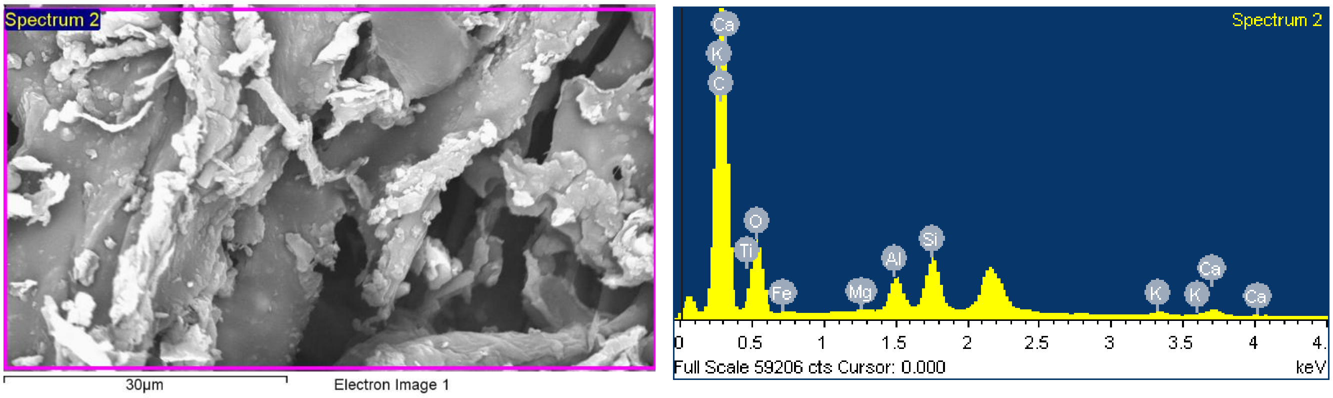


Figure B.6 SEM (left) and corresponding elemental analysis (right) at 5000X of bio char produced from biomass with 15.52% ash

	Char_1.16				**Char_15.52**				**Char_6.87**		
Magnification	**500X**		**5000X**		**500X**		**5000X**		**500X**		**5000X**
C	68.37	71.66	78.76	74.08	60.13	62.58	65.29	66.73	67.97	66.61	68.05
O	27.42	24.95	19.98	22.61	33.45	31.66	27.65	28.25	25.01	29.53	27.19
Mg	0.14	0.09	ND	0.08	0.14	0.10	0.12	0.09	0.16	0.16	0.31
Al	0.12	0.24	0.08	0.26	1.07	1.45	1.78	1.38	2.29	1.07	1.27
Si	2.69	2.07	1.66	2.15	3.76	2.55	3.08	2.26	2.66	1.26	1.33
K	0.51	0.27	0.27	0.29	0.28	0.28	0.36	0.22	0.37	0.29	0.54
Ca	0.58	0.62	0.26	0.43	0.44	0.56	0.61	0.42	0.42	0.42	0.72
Ti	ND	ND	ND	ND	0.06	0.08	0.12	0.07	0.12	0.07	0.04
Mn	ND	ND	ND	ND	ND	ND	ND	ND	0.08	ND	0.08
Fe	0.17	0.08	ND	0.10	0.66	0.74	0.99	0.57	0.93	0.59	0.47

Note: For sample with Char_num denotation, the num shows the ash content of the biomass from which the char was produced. ND stands for not detected

Table B.1 Elemental concentration (wt. %) of bio-chars using SEM-EDS

APPENDIX C: CHNS AND MICRO GC ANALYSIS DATA

Table C.1: Ultimate analysis of pine wood (a.r.)

Biomass	**C**	**H**	**N**	**S**
P_6.87	41.78	5.63	0.00	-0.43
P_6.87	43.88	5.78	00.00	-0.28
P_1.16	47.11	6.04	00.00	-0.92
P_1.16	46.61	6.30	0.14	-0.27
P_4.40	44.89	6.19	00.00	-0.29
P_4.40	44.60	5.89	00.00	-0.36
P_8.35	41.24	5.32	00.00	-0.34
P_8.35	39.90	5.44	00.00	-0.30
P_2.77	45.46	6.10	00.00	-0.46
P_2.77	45.50	6.01	00.00	-0.30
P_15.52	42.06	5.46	00.00	-0.50
P_15.52	39.61	5.42	0.02	0.040
P_0.56	45.79	6.11	00.00	-0.57
P_0.56	45.30	6.04	00.00	-0.58

Note: a.r. stands for as received. P_num: P stands for pinewood and number is the ash content

Table C.2 Ultimate analysis of bio-char (a.r.)

Char	**C**	**H**	**N**	**S**
Char_15.53	55.72	3.04	0.23	-0.60
Char_15.53	53.60	2.91	0.26	-0.53
Char_6.87	60.36	3.53	0.10	-0.55
Char_6.87	59.24	3.20	0.07	-0.84
Char_6.87	58.74	3.84	0.16	-0.64
Char_4.40	62.45	3.25	0.09	-0.85
Char_4.40	61.23	3.20	0.09	-0.74
Char_2.77	63.55	3.32	0.09	-0.49
Char_2.77	63.97	3.000	0.03	-0.74
Char_2.77	65.91	3.40	0.10	-0.73
Char_2.77	63.17	3.36	0.06	-0.59
Char_8.35	53.58	4.23	0.03	-0.73
Char_8.35	58.48	3.84	0.11	-0.50
Char_8.35	56.97	3.91	0.12	-0.85
Char_1.16	67.54	3.67	0.08	-0.56
Char_1.16	67.37	3.47	0.03	-0.65
Char_1.16	65.31	3.58	0.05	-0.49
Char_1.16	65.29	3.59	0.06	-0.59

Note: a.r. stands for as received. P_num: P stands for pinewood and number is the ash content

Table C.3 Ultimate analysis of bio-oil (a.r.)

Oil	**C**	**H**	**N**	**S**
Oil_0.56	37.01	7.38	0.10	-0.24
Oil_0.56	36.01	5.72	0.08	-0.32
Oil_8.35	46.45	7.19	0.87	-0.11
Oil_8.35	46.43	7.12	1.22	-0.21
Oil_2.77	42.09	7.47	1.21	-0.20
Oil_2.77	41.77	7.43	0.79	-0.01
Oil_2.77	43.43	6.90	0.87	-0.12
Oil_2.77	43.41	6.80	0.94	-0.21
Oil_6.87	44.08	6.39	0.05	0.20
Oil_6.87	44.57	7.76	1.06	-0.26
Oil_6.87	47.34	7.35	0.36	-0.22
Oil_1.16	39.20	7.83	1.25	-0.34
Oil_1.16	38.60	7.54	0.11	-0.05
Oil_1.16	39.79	6.88	0.05	-0.24
Oil_1.16	40.6	7.56	0.92	-0.22
Oil_15.52	46.56	7.00	0.11	-0.08
Oil_15.52	46.53	6.96	1.00	-0.97
Oil_15.52	47.33	7.00	1.06	-0.18
Oil_4.40	45.50	7.13	0.27	-0.49
Oil_4.40	43.68	7.25	0.16	-0.42
Oil_4.40	42.03	7.99	0.81	0.08
Oil_4.40	41.33	7.69	0.78	0.05

Note: a.r. stands for as received. P_num: P stands for pinewood and number is the ash content

Table C.4 Volumetric gas concentration of non-condensable gases from pine with 6.67% ash (as received)

Sample	H_2	N	CH_4	CO	CO_2
Pine_6.87	0.006	93.472	0.007	0.001	0.027
	0.008	93.494	0.035	0.045	0.061
	0.025	92.551	0.15	0.134	0.34
	0.009	86.593	0.04	0.016	0.105
	0.008	93.914	0.065	0.07	0.074
	0.009	93.959	0.093	0.223	0.083
	0.006	93.571	0.051	0.144	0.048
	0.005	93.836	0.039	0.029	0.041
	0.027	88.934	0.132	0.477	0.228
	0.019	89.79	0.051	0.217	0.196
	0.019	89.647	0.068	0.219	0.151
	0.0287	89.28	0.197	0.686	0.397
	0.015	93.26	0.062	0.061	0.141
	0.015	91.568	0.105	0.06	0.11
	0.011	90.87	0.101	0.336	0.096
	0.013	89.785	0.071	0.202	0.103
	0.006	91.369	0.071	0.165	0.074
	0.013	87.101	0.071	0.226	0.133
	0.021	95.971	0.146	0.474	0.338

Table C.5 Volumetric gas concentration of non-condensable gases from pine with 4.40% ash (as received)

Sample	H_2	N	CH_4	CO	CO_2
Pine_4.40	0.005	91.968	0.022	0.173	0.094
	0.017	91.924	0.01	0.325	0.127
	0.046	91.095	0.012	0.251	0.077
	0.013	91.004	0.028	0.212	0.033
	0.006	91.757	0.081	0.174	0.096
	0.005	90.575	0.024	0.149	0.12
	0.006	94.086	0.01	0.06	
	0.011	94.625	0.021	0.173	0.033
	0.032	90.588	0.043	0.325	0.096
	0.041	90.424	0.005	0.251	0.175
	0.012	88.42	0.025	0.212	0.094
	0.009	93.55	0.018	0.174	0.127
	0.032	76.195	0.02	0.14	0.077

Table C.6 Volumetric gas concentration of non-condensable gases from pine with 2.77% ash (as received)

Sample	H_2	N	CH_4	CO	CO_2
Pine_2.77	0.014	90.64	0.034	0.148	0.104
	0.008	90.559	0.047	0.187	0.102
	0.007	85.655	0.035	0.134	0.1
	0.007	84.727	0.038	0.158	0.087
	0.015	82.856	0.068	0.215	0.078
	0.006	84.161	0.051	0.178	0.117
	0.008	86.129	0.036	0.13	0.107
	0.014	86.05	0.102	0.278	0.193
	0.012	84.853	0.056	0.193	0.195
	0.008	85.135	0.051	0.202	0.191
	0.003	86.416	0.028	0.151	0.129
	0.006	86.90517	0.038	0.182	0.096
	0.007	86.05167	0.013	0.158	0.137
	0.007	86.90517	0.075	0.198	0.071
	0.008	88.55	0.06	0.24	0.27
	0.007	91.174	0.054	0.157	0.046
	0.01	91.025	0.055	0.157	0.046
	0.008	89.97	0.058	0.11	0.021

Table C.7 Volumetric gas concentration of non-condensable gases from pine with 8.35% ash (as received)

Sample	H_2	N	CH_4	CO	CO_2
Pine_8.35	0.011	94.64	0.0422	0.18	0.178
	0.01	94.559	0.0525	0.4	0.187
	0.006	95.655	0.0353	0.21	0.066
	0.004	94.727	0.0508	0.16	0.039
	0.003	92.856	0.0339	0.26	0.023
	0.004	92.25	0.013	0.03	0.029

Table C.8 Volumetric gas concentration of non-condensable gases from pine with 0.56% ash (as received)

Sample	**H_2**	**N**	**CH_4**	**CO**	**CO_2**
Pine_0.56	0.005	87.986	0.022	0.048	0.018
	0.011	92.505	0.052	0.127	0.047
	0.011	93.556	0.039	0.137	0.114
	0.006	94.614	0.053	0.096	0.034
	0.006	93.223	0.077	0.144	0.041
	0.011	89.372	0.051	0.143	0.035
	0.025	68.158	0.066	0.196	0.214
	0.017	87.372	0.073	0.213	0.15
	0.023	87.188	0.135	0.347	0.205

Table C.9 Volumetric gas concentration of non-condensable gases from pine with 1.16% ash (as received)

Sample	**H_2**	**N**	**CH_4**	**CO**	**CO_2**
Pine_1.16	0.016	90.919	0.025	0.104	0.018
	0.005	88.934	0.044	0.124	0.038
	0.004	86.049	0.021	0.064	0.042
	0.004	94.823	0.021	0.041	0.04
	0.006	94.669	0.059	0.11	0.058
	0.006	93.464	0.079	0.22	0.056
	0.004	91.782	0.081	0.229	0.042
	0.017	93.934	0.053	0.165	0.018
	0.011	93.86	0.032	0.028	0.015
	0.015	93.725	0.052	0.112	0.014
	0.009	89.666	0.051	0.184	0.087
	0.004	93.113	0.049	0.15	0.085
	0.011	88.776	0.093	0.35	0.082
	0.012	90.071	0.051	0.083	0.079
	0.012	88.969	0.068	0.171	0.122
	0.007	90.078	0.09	0.207	0.107
	0.019	90.506	0.115	0.397	0.398
	0.008	88.44	0.092	0.27	0.114

Table C.10 Volumetric gas concentration of non-condensable gases from pine with 15.52% ash (as received)

Sample	H_2	N	CH_4	CO	CO_2
Pine_15.52	0.007	86.549	0.0665	0.205	0.065
	0.009	86.192	0.072	0.209	0.106
	0.007	87.053	0.057	0.199	0.107
	0.007	86.948	0.033	0.136	0.095
	0.007	87.076	0.04	0.158	0.096
	0.005	86.795	0.047	0.201	0.098
	0.006	85.757	0.07	0.212	0.062
	0.008	87.331	0.0656	0.202	0.072
	0.012	87.572	0.07	0.227	0.085
	0.004	90.786	0.031	0.133	0.084
	0.003	88.991	0.002	0.087	0.108
	0.009	88.629	0.062	0.147	0.083
	0.008	88.809	0.065	0.176	0.148
	0.008	91.405	0.096	0.185	0.122
	0.007	92.651	0.084	0.205	0.142
	0.007	92.251	0.082	0.1	0.143
	0.007	92.34	0.099	0.196	0.116
	0.004	92.863	0.112	0.16	0.086
	0.006	92.843	0.123	0.078	0.046

APPENDIX D: LIST OF COMPOUNDS (GC-MS ANALYSIS)

Table D.1 List of compounds in each group-chemical composition

Anhydrosugar	**Acids**	**Phenols**	**Furans**	**Aldehydes**	**Ketones**	**Hydrocarbons**
1,6-Anhydro-.beta.-D-glucopyranose (levoglucosan)	Butanoic acid	Phenol	2-Furancarboxaldehyde, 5-(hydroxymethyl)	4-Hydroxy-2-methoxycinnamaldehyde	1,2-Cyclopentanedione	Benzene
	Methylenecyclopropanecarboxylic acid	Phenol, 2-methyl-	Furfural	Vanillin	Ethanone, 1-(4-hydroxy-3-methoxyphenyl)-	Hexane, 2,4-dimethyl-
	Nonanoic acid	Phenol, 4-methyl-	3-Furanmethanol	2-Furancarboxaldehyde, 5-methyl-	2-Cyclopenten-1-one, 2-hydroxy-3-methyl-	Decane, 2,4-dimethyl-
	Benzeneacetic acid, 4-hydroxy-3-methoxy-	Phenol, 2-methoxy-	2(5H)-Furanone	Benzaldehyde, 4-hydroxy-3,5-dimethoxy-	2(5H)-Furanone	
	Benzoic acid, 4-hydroxy-3-methoxy-, methyl ester	Phenol, 2-methoxy-4-methyl-	Furan, tetrahydro-2,5-dimethoxy-			
		1,2-Benzenediol				
		Phenol, 4-ethyl-2-methoxy-				
		1,2-Benzenediol, 4-methyl-				
		Phenol, 4-(2-propenyl)-				
		Eugenol				
		Phenol, 2-methoxy-4-propyl-				