

**ENVIRONMENTAL AND ECONOMIC RESEARCH AND DEVELOPMENT PROGRAM**

# Economic and Environmental Impact of Biomass Types for Bioenergy Power Plants

Final Report  
August 2013

**PREPARED BY:**

**TROY M. RUNGE**, ASSISTANT PROFESSOR  
BIOLOGICAL SYSTEMS ENGINEERING,  
UNIVERSITY OF WISCONSIN-MADISON

**CONTRIBUTORS:**

**CHUNHUI ZHANG**, POST-DOCTORAL RESEARCH ASSOCIATE  
UNIVERSITY OF WISCONSIN-MADISON

**JEFF MUELLER**, GRADUATE RESEARCHER  
BIOLOGICAL SYSTEMS ENGINEERING,  
UNIVERSITY OF WISCONSIN-MADISON

**PAMELA WIPPERFURTH**, GRADUATE RESEARCHER  
BIOLOGICAL SYSTEMS ENGINEERING,  
UNIVERSITY OF WISCONSIN-MADISON



## Table of Contents

1. Introduction .....	1
1.2. Energy sources.....	1
1.3. Biomass combustion.....	1
1.4. Fuel characteristics affecting boiler operations .....	2
1.5. Fuel characteristics affecting air emissions .....	3
2. Biomass Properties Survey.....	3
2.1. Biomass Property Study Materials and Methods.....	3
2.2. Biomass Survey Results and Discussion.....	6
2.2.1. Moisture Content.....	6
2.2.2. Heating Value .....	7
2.2.3. Ash Content.....	9
2.2.4. Fixed carbon and volatiles.....	11
2.2.5. Nitrogen .....	12
2.2.6. Sulfur .....	13
2.2.7. Chlorine .....	14
2.2.8. Mercury.....	16
2.2.9. Fouling Index .....	18
2.3. Biomass Combustion Quality Survey Summary.....	20
3. Improving Biomass for Combustion.....	22
3.1. Review on Methods to Treat Biomass prior to Combustion .....	22
3.1.1. Biomass Densification .....	22
3.1.2. Biomass Torrefaction .....	23

3.1.3. Biomass Leaching .....	23
3.1.4. Liquid Hot Water Treatment .....	24
3.2. Extraction Study Objectives.....	24
3.3. Extraction Study Experimental .....	25
3.3.1. Biomass Samples for Extraction Studies .....	25
3.3.2. Liquid Hot Water Extraction Experiments.....	25
3.3.2. Characterization of Liquid Fraction .....	26
3.3.3. Characterization of the Solid Fuel .....	26
3.4. Results and Discussion.....	27
3.4.3. Solid Fuel Properties of the Extracted Biomass .....	30
3.5. Biomass Extraction Summary .....	36
4. Overall Conclusions.....	37
5. References .....	38

## **1. Introduction**

### **1.1 Project objectives**

This research project seeks to investigate biomass fuel characteristics that offer the best environmental and economic efficiencies for combustion. Specifically, biomass feedstocks obtained in conjunction with the planned University of Wisconsin's Charter Street Heating Plant were characterized to assess their suitability for combustion. Based on this work, it became apparent that many fuels were not of sufficient quality, due to high amounts of inorganics that lowered their quality and increased air emissions. Additional experiments were performed to investigate the possibility of a liquid hot water extraction to improve the combustion quality of high ash low density biomass.

### **1.2. Energy sources**

Fossil fuels in the US provide for more than 85% of the all the energy consumed and are responsible for 99% of the carbon dioxide emissions.<sup>1</sup> Similarly in Wisconsin 81% of our energy resources consumed are from fossil fuels with approximately 30% from coal, 28% from petroleum, and 23% from natural gas and Wisconsin produces only 5.2% of its own energy needs from renewable resources, with biomass accounting for over 55.9% of the renewable portfolio, with ethanol, biogas, hydro, and wind accounting for 22.2%, 11.7%, 6.1%, and 4.1% respectively.<sup>2</sup> Biomass has an obvious role in Wisconsin's energy future that should be cultivated, with several biomass to energy projects announced in the last 3 years.<sup>3-</sup>

5

### **1.3. Biomass combustion**

Coal, used primarily for electricity production, has the largest greenhouse gas and hazardous air pollutant emissions of all the fossil fuels. Because of this several coal burning power plants have retrofitted their boilers to either co-fire or wholly use biomass as an alternative fuel.<sup>6</sup> Although there is reluctance to further increase the use of biomass as coal is typically more profitable,<sup>7</sup> biomass combustion may provide a desirable alternative for compliance with regulatory requirements as it has been shown to reduce Hg, SO<sub>x</sub>, and NO<sub>x</sub> emissions.<sup>8-11</sup> While biomass combustion may be seen as a favorable renewable energy to pursue, there are considerations that should be taken to insure the benefits are realized.

Biomass combustion is a complex process that consists of consecutive chemical reactions which result in the production of heat as the majority of these reactions are exothermic.<sup>12</sup> In ideal combustion, the dry organic portion of the fuel is completely oxidized into the CO<sub>2</sub> and H<sub>2</sub>O.<sup>13</sup> Unfortunately real biomass contains both water and inorganic chemicals that can create issues arising in one or more of the following areas: low efficiencies, hazardous air emissions, boiler deposit and corrosion problems, and ash agglomeration.<sup>8, 10, 14, 15</sup>

There are several important logistical issues that need to be considered in order to consider biomass as a sustainable alternative to coal. Biomass materials are often harvested during a limited harvesting season; therefore, they need to be stored and the utilized at processing facilities year-round.<sup>16</sup> In their

original form, they have high moisture content, irregular shape and size, and low bulk density. Biomass materials are very difficult to handle, transport, store, and utilize for energy production.<sup>17</sup> Additionally, there is variability in the feedstock from year-to-year, and even day-to-day depending on harvesting conditions. These logistical issues can be partially addressed through drying, mixing, and densification of the biomass materials into pellets or briquettes. By drying and mixing the biomass to create a more formulated homogenous solid fuel much of the source variability can be removed. Densification can increase the bulk density of unprocessed or baled biomass material from 40 to 200 kg/m<sup>3</sup> to a final bulk density of 600 to 800 kg/m<sup>3</sup> through compaction to remove inter- and intra-particle voids<sup>18</sup>. Additionally, the densified biomass can be formed into a consistent shape that is easier to handle, store and feed into processing equipment.<sup>16, 17</sup>

#### ***1.4. Fuel characteristics affecting boiler operations***

Lignocellulosic biomass materials such as agricultural residues (left over material from crops including corn stover, sugarcane bagasse, and wheat straw), forestry wastes (chips and sawdust from lumber mills, dead trees, and tree branches), and dedicated energy crops (fast growing trees and grasses including switchgrass, miscanthus, and hybrid poplar) are a promising source of renewable energy<sup>19</sup>. Wisconsin is fortunate to have a wide variety of biomass materials with land and water resources to grow more. Unfortunately, that variety also creates feedstocks with a wide range of chemical and physical properties that affect processing and emissions.

The primary properties of biomass solid fuel that affect combustion in boiler operations are moisture, volatiles and fixed carbon, particle size, and energy density.<sup>8, 20</sup> Moisture content reduces the maximum possible combustion temperature leading to an increased residence time in the combustion chamber. The necessary increased residence time in combustion chambers leads to a need for larger combustion chambers. Increased moisture content also reduces the Lower Heating (LHV) of the fuel reducing the efficiencies.<sup>8, 21-23</sup> Volatiles in biomass form a higher content than they do in coal, and char forms a lower content in biomass than in coal. The high volatile and low fixed carbon content makes biomass a highly reactive fuel which makes biomass burnout faster than coal.

Boiler design should ensure that the volatile content undergoes complete combustion to improve efficiency and reduce incomplete combustion related emissions. The optimum airflow levels for biomass may be different to that of coal due to differing volatile and char contents and the speed at which they burn. Energy density determines the combustion chamber volume for a designed heat or power output of the fuel.<sup>8, 23</sup> Particle size can affect handling systems and residence time of fuel. Smaller particles need lower residence times because there is a larger active surface area that influences the reactivity of the fuel. Handling systems for fuel are determined on their fuel particle size.<sup>8</sup> Biomass combustion can raise operational issues such as ash agglomeration, deposit, and corrosion. Ash agglomeration can occur when ash sinters or melts to the grate due to low ash sintering and melting temperatures determined by elemental composition of ash. Deposits and corrosion can occur due to fly-ash sintering and other aerosols and emissions related to the elemental composition of the ash and unburned biomass fuel. Deposits and corrosion degrade heat transfer surfaces leading to lower

efficiencies and shorten the life of those surfaces increasing capital costs. Agglomeration on feed grates can negatively affect the fuel feeding systems.<sup>8</sup>

Chlorine corrosion can be severe in biomass boilers that reach high temperatures. Severe corrosion can occur above steam temperatures of 450 C.<sup>24, 25</sup> The alkaline metals N and Ka affect corrosion on combustion surfaces in combination with S and Cl. The alkaline metals also form alkali chlorides which deposit on heat exchanger surfaces then react with S to form alkali sulfates releasing chlorine that is corrosive on heat exchanger surfaces. The alkali chlorides can cause severe corrosion well below the melting temperature of the salts. The chlorine released plays a catalytic role in the corrosion of heat exchanger surfaces. Also, alkali sulfates are corrosive and are the typical corrosion mechanism in coal fired applications. Alkali sulfate corrosion is less severe than chlorine related corrosion.<sup>8, 24-26</sup> Gases containing HCl, Cl<sub>2</sub>, KCl, and NaCl may also cause direct corrosion. HCl and Cl<sub>2</sub> are the most common gas phase corrosion mechanisms. Gaseous NaCl is also found to have a corrosive effect on protective layers of Cr<sub>2</sub>O<sub>3</sub>.<sup>25</sup>

### ***1.5. Fuel characteristics affecting air emissions***

Biomass like other solid fuels can contain elements such as sulfur, nitrogen, chlorine, and heavy metals,<sup>8, 27</sup> which can create hazardous air pollutants (HAPs) during combustion. Combusting biomass with high levels of these elements can lead to sulfur oxides (SO<sub>x</sub>), nitrogen oxides (NO<sub>x</sub>), hydrogen chloride (HCl), dioxin and furans, and heavy metal emissions<sup>28, 29</sup>. Additionally, biomass that has high levels of ash or that is not completely combusted can lead to higher levels of particulate emissions. These emissions have been found by the EPA<sup>29</sup> to have a negative impact on human health and the environment with effects including smog, particulate formation in the atmosphere, acid rain, and carcinogenic effects. Like other solid fuels, the HAPs from combusting biomass can reduce air quality if no mitigation steps are taken. These emissions can be greatly reduced with the proper boiler operation practices and controls. Common combustion process to minimize emission include insuring adequate mixing of air and fuel, staged combustion, sufficient oxygen available, and high enough combustion temperatures and residence times to reduce combustion emissions<sup>23, 28</sup>. Additionally, air emission control equipment of filters, wet scrubbers, alkali injection, and activated carbon can be used. However beyond these practices, to achieve low HAPs emissions may require these contaminants to be minimized in the incoming solid fuel.

## **2. Biomass Properties Survey**

Wisconsin is fortunate to have a wide variety of biomass materials with land and water resources to grow more. Unfortunately, that variety also creates feedstocks with a wide range of chemical and physical properties that affect processing and emissions. Little data has been published that compiles the composition data on biomass and its suitability for combustion. This research was to provide a survey of the composition of Wisconsin's bioenergy feedstocks in regards to combustion operations and emissions.

### ***2.1. Biomass Property Study Materials and Methods***

Thirty-five biomass samples were collected from Wisconsin through collection of samples from around the state and working with potential suppliers for the planned Charter Street combined heat and power plant at the University of Wisconsin in Madison, WI. These materials represent a fuel survey as to what Wisconsin biomass fuel suppliers thought to be a quality fuel for combustion. A listing of the materials collected by category is shown in Table 1 with qualitative descriptions. The fuels were analyzed for desirability based on operations and emissions characteristics and in regard to the emissions characteristics the fuels were analyzed for a larger combustion application where emission restrictions are tighter and as a result the conclusions on permissible emissions from certain fuels may not apply to smaller combustion applications. The results are analyzed to determine best fuels for combustion and to provide information for fuel suppliers to improve the quality of their feedstocks. Although the fuel suppliers could not be disclosed due to confidential procurement practices through the Charter Street Heating Plant project, a map with locations for the fuels was produced and is shown in Figure 1. The samples were collected, air dried, and cold stored (4°C) prior to testing. Each sample was tested for Ultimate (C,H,N,O, and S) and Proximate (Fixed Carbon, Volatiles, Ash, and Moisture), Mercury, and Chlorine analyses. Mineral ash analyses (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, CaO, MgO, K<sub>2</sub>O, Na<sub>2</sub>O, SO<sub>3</sub>, P<sub>2</sub>O<sub>5</sub>, SrO, BaO, MnO<sub>2</sub>) were performed only on select samples due to resource considerations. Materials were tested either by the commercial testing facility Twin Ports Testing in Superior, WI or our biomass characterization lab in Madison, WI following the same ASTM protocols shown in Table 2.

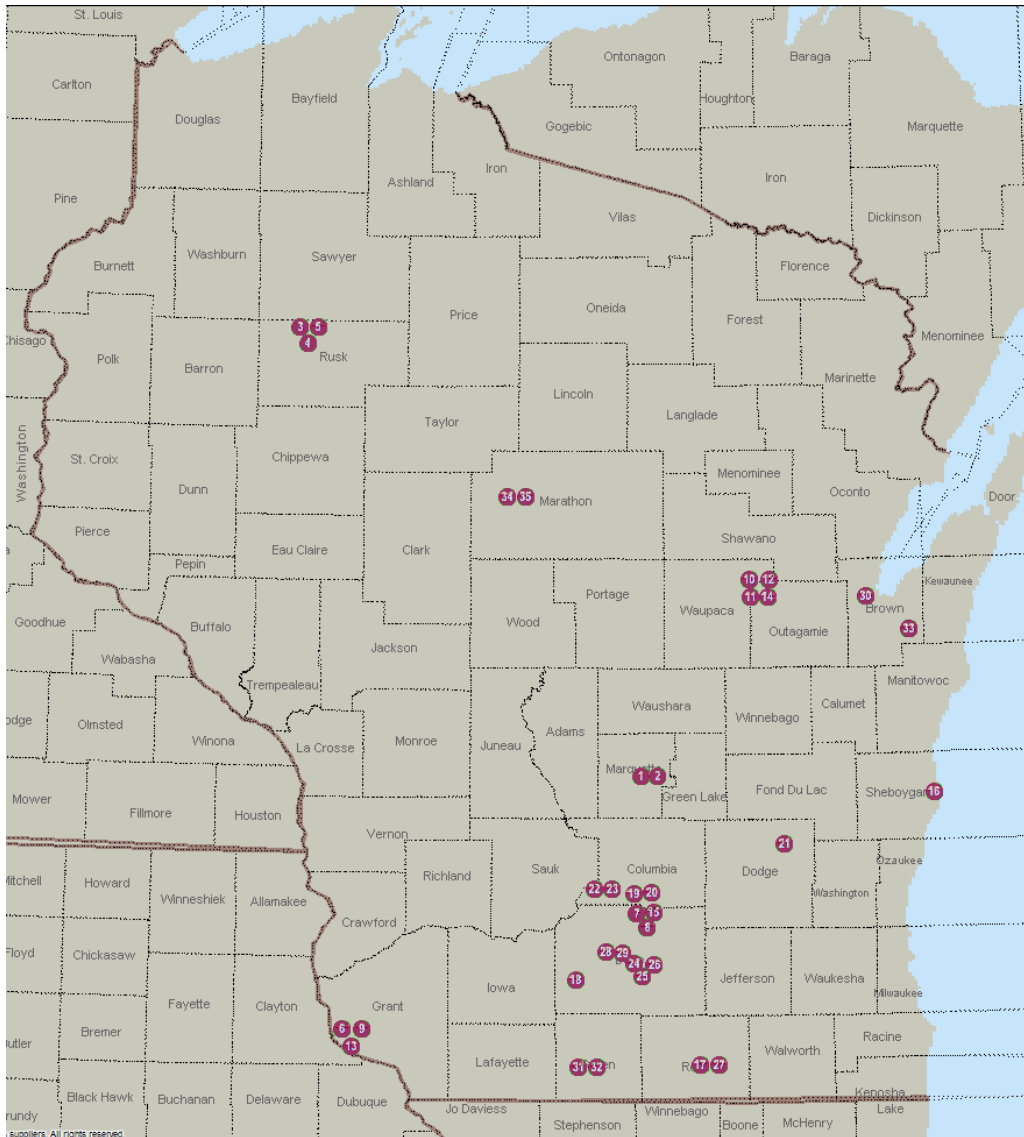
**Table 1. Biomass sample descriptions.**

Sample #	Category	Description
1	Woody	Industrial Pellet - 80% Hardwood (debarked), 20% recycled ag. plastic
2	Woody	Industrial Pellet 90% Hardwood (debarked), 10% recycled ag. Plastic
3	Woody	Premium Wood Pellet Fuel
4	Woody	Premium Wood Pellet Fuel
5	Woody	Premium Wood Pellet Fuel
6	Woody	Wood chips - Mixed softwoods
7	Woody	Wood chips - Mixed hardwoods
8	Woody	Hardwood hog fuel - primarily bark waste
9	Woody	Wood chips - Mixed hardwoods
10	Woody	Wood - Locust (whole tree)
11	Woody	Wood - Pine (whole tree - high amount of needles)
12	Woody	Wood - Maple (whole tree)
13	Woody	Mixed hardwood (whole tree)
14	Woody	Mixed softwood (red & white pine)
15	Woody	Municipal Tree Trimmings
16	Woody	Woody Biomass, Whole tree
17	Herbaceous	Switchgrass Pellets
18	Herbaceous	Switchgrass Pellets
19	Herbaceous	Switchgrass
20	Herbaceous	Switchgrass
21	Herbaceous	Briquetted corn stover
22	Herbaceous	Corn stover
23	Herbaceous	Corn stover
24	Herbaceous	Ditch grass bale 1
25	Herbaceous	Ditch grass bale 2
26	Herbaceous	Ditch grass bale 3
27	Herbaceous	Big Bluestem Pellets
28	Herbaceous	Miscanthus stalks
29	Herbaceous	Miscanthus stalks
30	Residuals	Industrial pellet made from paper mill sludge, waste paper, film waste
31	Residuals	Distiller's Grains - Ethanol Plant A
32	Residuals	Distiller's Grains - Ethanol Plant B
33	Residuals	Manure briquette - Dried & densified manure, bedding, and sawdust
34	Residuals	Manure briquette - Dried & densified manure, bedding, and sawdust
35	Residuals	Manure & sawdust bedding

**Table 2. Characterization test methods.**

Test	Standard Method
Moisture	ASTM E871
Ash	ASTM D1102
Volatile matter & Fixed Carbon	ASTM E872
Heating Value	ASTM E711
Elemental analysis, C, H, N, O	ASTM D5373
Elemental analysis S	ASTM D4239
Elemental analysis Cl	ASTM D6721
Elemental analysis Hg	ASTM D6722
Mineral Ash Analysis	ASTM D3682





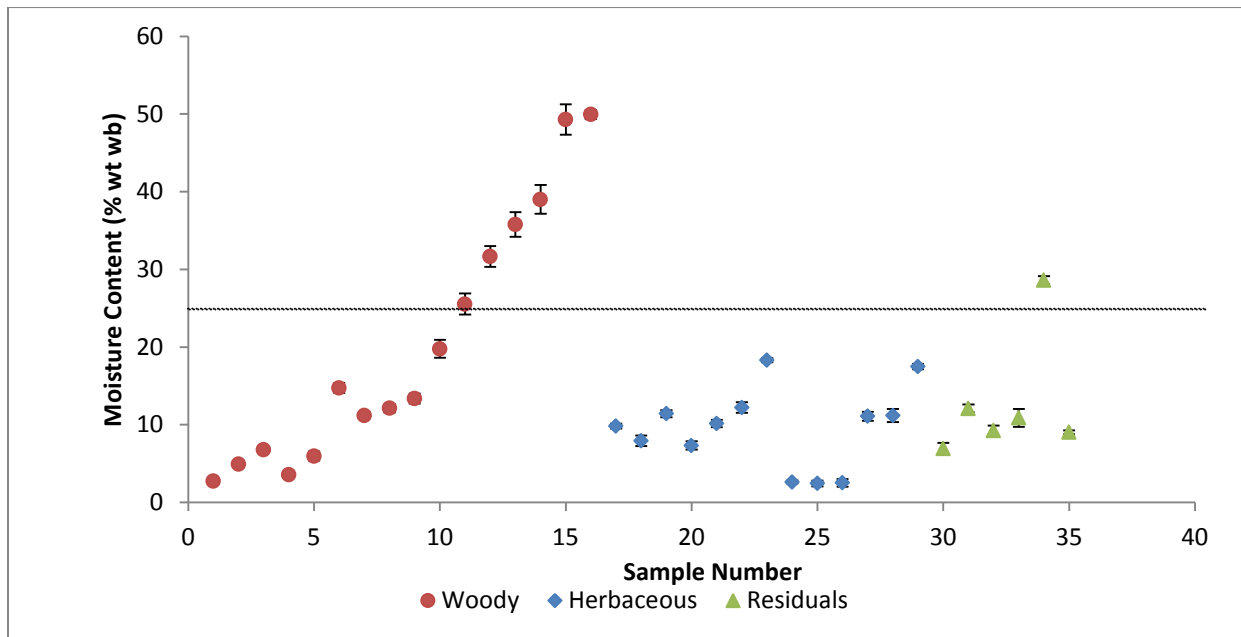
**Figure 1. Location of source of 35 biomass fuel samples**

**2.2. Biomass Survey Results and Discussion**

**2.2.1. Moisture Content**

Biomass moisture content were found to vary widely in the samples, depending mostly on the biomass and the pre-treatment method employed. Typical values are 25-60% wt (w.b.) for woody materials, agricultural residues, and energy crops. Weather conditions and harvesting season have a major impact on moisture content. Low moisture of less than 10% wt (w.b.) are found in dry wood processing residues or biofuels in pellet form.<sup>30, 31</sup> High moisture content of biomass can have adverse effects, including formation of mold during handling and storage, decomposition and loss of dry matter, formation of feeding blockades, delayed ignition, increased drying times that delay de-volatilization and char combustion stages, and a reduction in the adiabatic temperature that decreases the burnout of the volatiles and char. Moisture decreases lower heating values due to the energy consumption for

evaporation and a higher volume of flue gas is produced due to increased fuel utilization.<sup>30, 31</sup> The moisture contents for the samples were measured at a temperature of 103°C for 16 hours then measured at 1 hour increments until weight change was under specified weight change by ASTM E-871. The averages for the moisture of the samples were calculated and plotted with 95% confidence interval in Figure 1.



**Figure 1: Biomass sample moisture contents with 95% CI.**

The data in Figure 1 indicate that moisture content of most biomass considered by suppliers as fuels have either been air-dried or oven dried to maximize the fuel quality. This is necessary to insure fuel stability as microbial decay can occur rapidly above 25% moisture, especially in herbaceous biomass. The majority of samples that were above the 25% moisture were whole trees that had been chipped or ground in field. These materials are generally lower cost to produce due to simplified handling and the absence of drying but represent a low quality fuel.

### 2.2.2. Heating Value

Heating value is generally correlated to the presence of C, H and O.<sup>32</sup> Carbon and hydrogen have an effect of increasing the heating value, while a decrease is observed with higher degrees of oxidation. The typical range of heating values for biomass fuels is lower than that bituminous coal due to the increased oxygen concentration; however, biomass exhibits comparable heating value to several lignite varieties.<sup>33</sup> Heating value in biomass fuels can also be correlated to the presence of cellulose, hemicellulose, and lignin. Of those three components, lignin possesses the highest heating value while hemicellulose the lowest due to the high degree of oxidation.<sup>33</sup> Higher heating values (HHV) or gross calorific value (GCV) of combustion includes the latent heat of the water vapor products of combustion because the water vapor is allowed to condense to liquid water. The lower heating value subtracts the

heat of vaporization of the water vapor and represents a closer approximation of the useful energy content since most US combustion applications do not recover low quality heat energy from the flue gas. Lower heating value (LHV) is a function of the moisture content, and was calculated by Equation 1.<sup>28</sup> The averages for HHV and LHV were plotted in Figure 2 and Figure 3 respectively with 95% confidence intervals.

$$LHV = \left[ HHV * \left( 1 - \frac{w}{100} \right) - 2.444 * \frac{w}{100} - 2.444 * \frac{h}{100} * 8.936 * \left( 1 - \frac{w}{100} \right) \right] * C_f$$

**Equation 1. Lower heating value<sup>28</sup>**

Where:

LHV = Lower heating value in Btu / lb (w.b.) with  $C_f$  and MJ/kg fuel without  $C_f$

HHV = Higher heating value in MJ/kg fuel (d.b.)

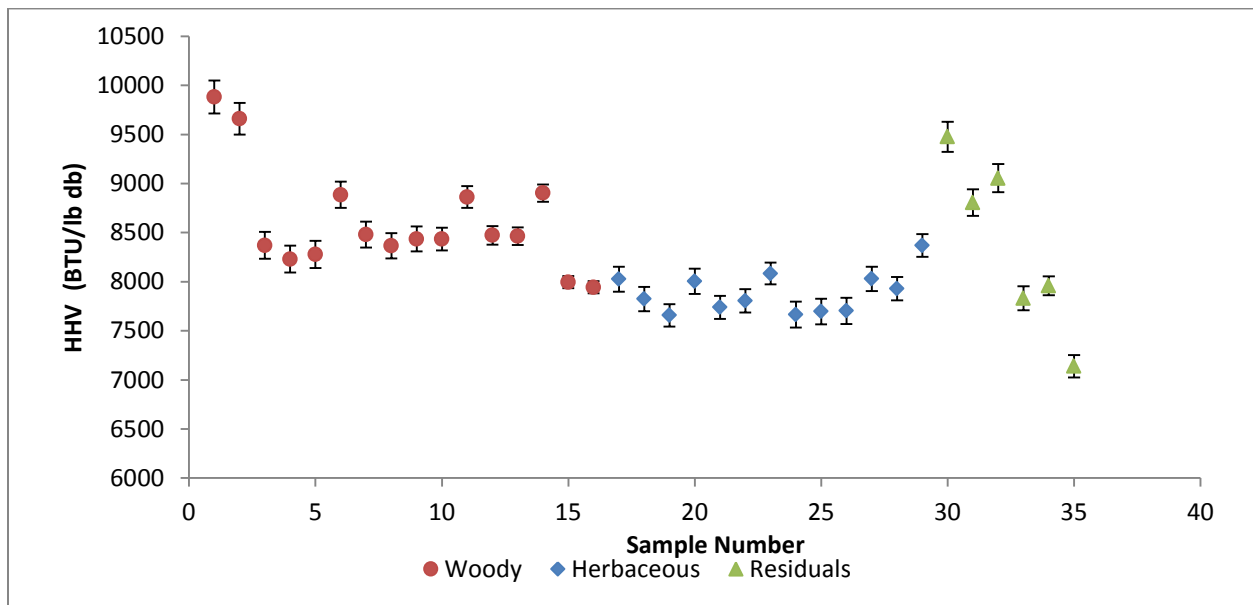
2.444 = enthalpy difference between gaseous and liquid water at 25°C

8.936 =  $M_{H_2O} / M_{H_2}$ ; molecular mass ratio between  $H_2O$  and  $H_2$

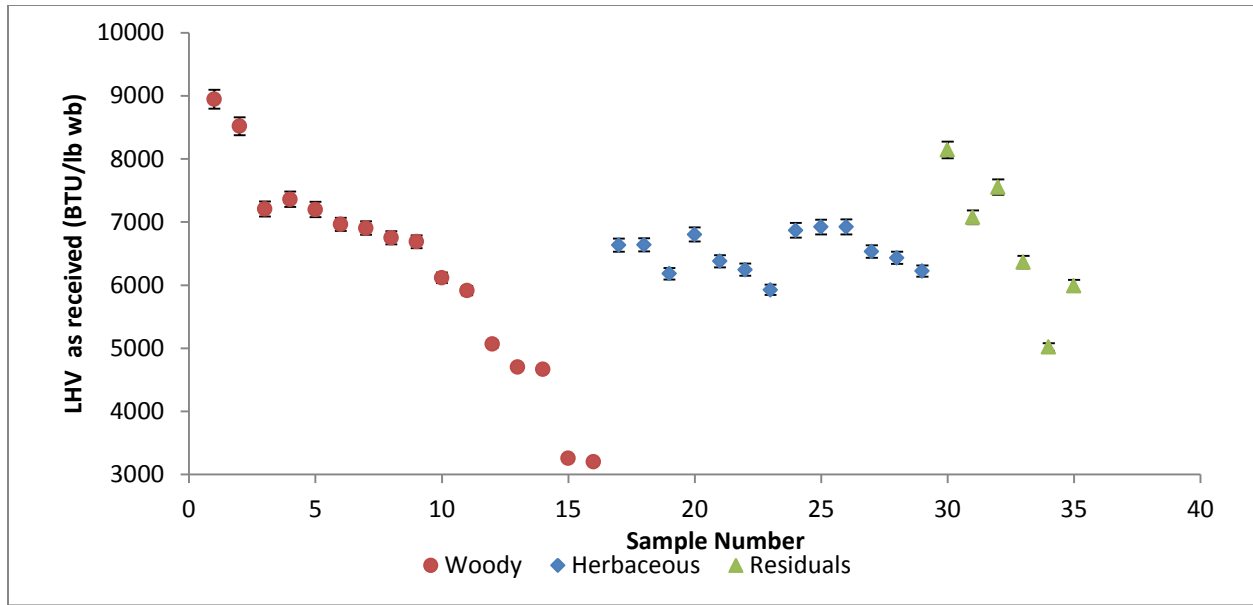
w = moisture content of fuel % wt (w.b.)

h = hydrogen content of fuel %wt (d.b.)

$C_f$  (conversion factor) = 429.9226 (MJ / kg (w.b.)) to (Btu / lb (w.b.))



**Figure 2: Biomass sample measured higher heating values (Btu/lb (d.b.)) with 95% CI.**



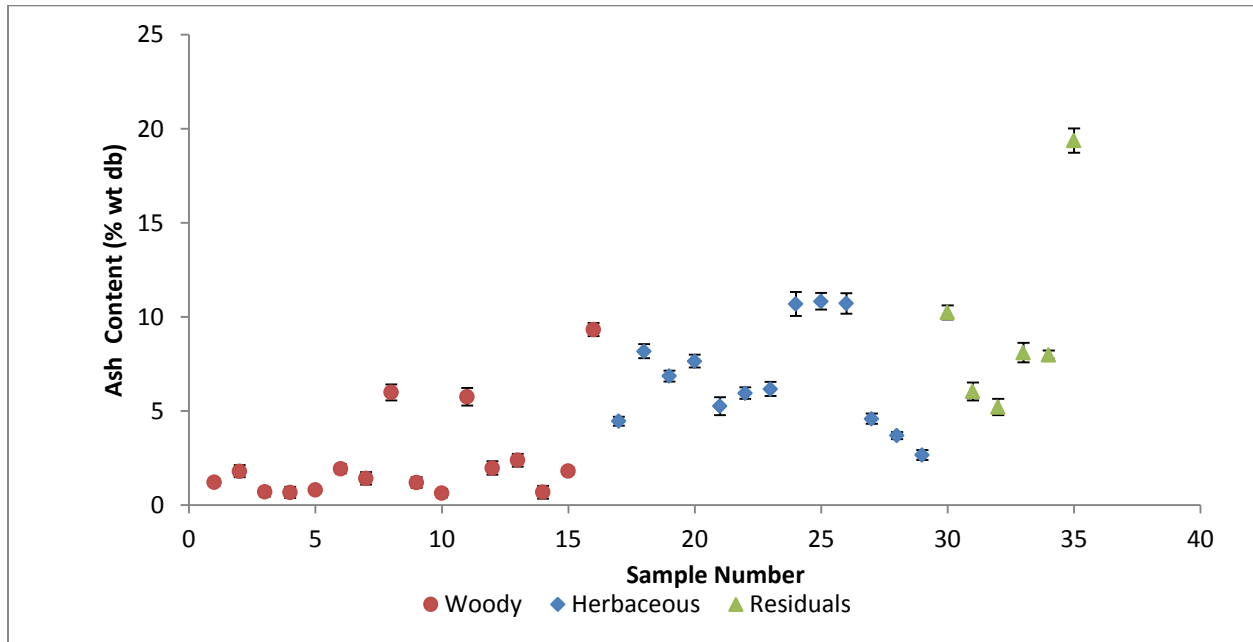
**Figure 3: Biomass sample calculated lower heating values as received (Btu/lb (w.b.)) with 95% CI.**

### 2.2.3. Ash Content

Biomass combustion can also create areas of concern with particle emissions and heavy metal emissions. Particle emissions from complete combustion result from fly ash particles exiting with the flue gas and aerosols. Particle emissions can increase with increased ash content. The heavy metal emissions can occur due to evaporation or the heavy metals or attachment to particle emissions. Particle emissions have negative effects on the human respiratory system and some heavy metal emissions can be toxic or carcinogenic.<sup>8</sup>

The ash content of different biomass fuels varies broadly with agricultural residues typically generating significantly more ash content than woody biomass, partially due to harvesting techniques and partially due to inherent differences in the biomass.<sup>28, 34</sup> It has been demonstrated that heating values are negatively related to ash content, with every 1% increase in ash concentration decreasing the heating value by 0.2 MJ/kg.<sup>35</sup> In addition the ash and its inorganic elements produced during combustion may cause a number of problems to the power plants through slagging, corrosion, and fouling. Fouling is defined as the accumulation of unwanted materials on the surfaces of processing equipment leading to a decrease in the exchanger efficiency, slagging is related to the low melting point of deposits and causes the formation of a glassy layer that must be removed, and corrosion is caused by the interaction between deposits and metal surface of the exchanger, which involves extra costs in maintenance while significantly decreasing the plant life.<sup>34</sup> The degree of fouling, slagging, and corrosion is strictly dependent on ashes and minerals release during combustion. Increased ash content can also lead to an increase in particulate emissions which is documented in a study of emission controls of small wood fired boilers where the peak value of particulate emissions was obtained from combustion of a low quality fuel having notable quantities of dirt and rock.<sup>36</sup> They also found that bark content can increase particulate matter emissions. Both bark and contaminants such as dirt and rock have higher ash content

which is likely the reason for the higher particulate matter emissions. Figure 4 shows the averages for ash content of the fuels plotted with 95% confidence intervals.



**Figure 4. Biomass sample ash content (% wt (d.b.)) with 95% CI.**

Ash levels of biomass can impact the choice of boiler design and particulate removal systems because a significant quantity of ash will be released as fly ash particles entrained in the flue gas or as aerosols<sup>28</sup>. Ash chemistry is also very important to assessing particulate matter from aerosols and the ash content indicates that magnitude of the extent (discussed in alkali fouling index). Three wood samples showed higher than typical ash values for woody fuels, ranging from 0.5-2.5% wt (d.b.)<sup>28</sup>. Also, sample 18, identified as whole tree woody biomass, had a noticeably greater ash value than other materials of 9% wt (d.b.). This is very high for wood samples and was likely contaminated with soil. Bark ash levels range from 5-8% wt (d.b.)<sup>28</sup> and could contribute to a higher ash percentage, but soil or some other inorganic contamination would have to occur to reach a 9% wt (d.b.) ash value. The high ash value would likely lead to an increase in particulate matter emissions while combusting that fuel. Except for the three ditchgrass samples, the ash content for the herbaceous fuels fell within typical ranges reported in literature for herbaceous fuels, 2-8% wt (d.b.)<sup>28</sup>. The ditch grass samples had slightly noticeably higher values of ash than other herbaceous materials which could be attributed to their proximity to where they were harvested from, highway 151 in Dane County, Wisconsin.

Of the residuals, the manure & sawdust sample had a very high ash value indicating large potential problems as a fuel. The other residuals were close to levels of the herbaceous fuels with the paper waste pellets having similar content to the ditchgrass samples. The acceptable ash level will depend on the boiler design and the control technology used. Lower ash levels are more desirable and will lead to lower dust emissions and the amount of ash handling, storage and utilization or disposal occurring during and after the combustion process. Woody biomass appeared to have the most favorable ash content, but during harvest woody biomass can become contaminated and proper quality controls need

to exist in establishing and maintaining fuel supply to prevent contamination of fuel. Herbaceous fuels and residuals had higher levels of ash compared to woody fuels and the ranges should be considered in boiler design or particulate control technology if these fuels are to be used. Although herbaceous fuels have inherently higher ash content than woody fuels, the results show they can be as low as 2.66% wt (d.b.) (sample 30) indicating with proper harvesting techniques ash content can be kept low.

#### 2.2.4. Fixed carbon and volatiles

Characterization methods have been developed for solid fuels such as coal, which consists of chemical energy stored in two forms, fixed carbon and volatiles<sup>37</sup>. Compared with coals, agricultural residues and woody biomass are characterized by higher volatile contents which is the portion driven-off as a gas including moisture by heating<sup>37</sup> typically in the range of 65-85% wt (d.b.).<sup>13,31</sup> The more volatile a fuel the more reactive a fuel source is indicating that biomass is easier to ignite and burn.<sup>31,33,38</sup> During combustion approximately 70 -80% wt (d.b.) of dry matter in biomass is converted into volatiles, which is much higher than that of hard coal where only 10-35% wt (d.b.) is converted.<sup>33,38</sup> As a result most of the weight loss exhibited during combustion occurs during the de-volatilization phase, and most of the heat contribution of the biomass combustion is due the volatile matter. Typical products of the de-volatilization phase include light hydrocarbons, carbon monoxide, carbon dioxide, moisture, hydrogen, hydrogen cyanide, ammonia, and tars.<sup>33</sup> Yields and rate of release are dependent on fuel characteristics, such as lignin content as well as on temperature and heating rate. Volatile matter was measured by placing a biomass sample in a muffle furnace at 950°C for 7 minutes. The weight loss percentage from that test minus the moisture content is the percentage of weight of volatile matter on a wet basis. The volatile matter can be re-calculated on a dry basis as well. The measured values indicate that all of these fuels are within typical ranges for volatile content. Figure 5 shows the average values of the volatile matter of the fuels plotted with 95% confidence intervals.

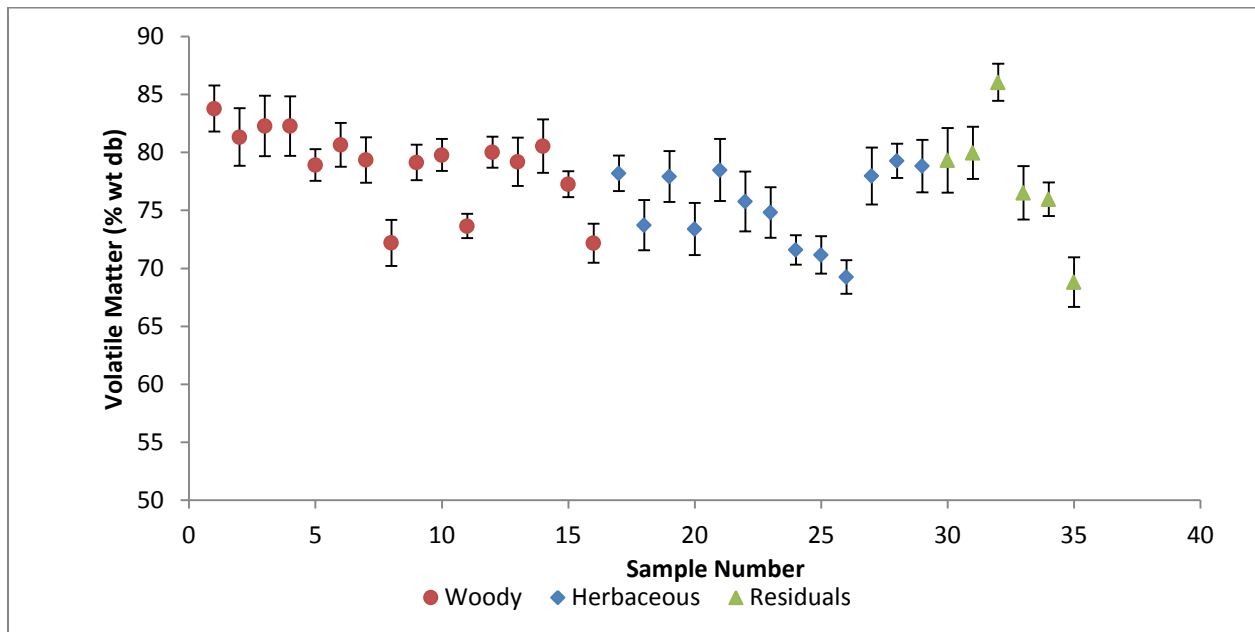


Figure 5: Biomass sample volatile matter (% wt (d.b.)) with 95% CI.

### 2.2.5. Nitrogen

Combusting biomass with high N leads to nitrogen oxide emissions, which contribute to smog formation and particulate formation in the atmosphere that have negative effects on the respiratory system. Nitrogen oxides also lead to acid rain that can damage plant and corrode infrastructure and materials. Nitrogen content is measured to assess the fuel's potential for hazardous nitrogen oxide emissions that can cause smog and particulate formation in the atmosphere having a negative impact on human health. Average nitrogen content for the fuel samples is plotted in Figure 6 with a 95% confidence interval. Nitrogen content was compared to limits from literature indicating nitrogen oxide emission potential and the measures needed to reduce them with the limits being 6000 ppm (d.b.) and 25000 ppm (d.b.). To reduce nitrogen oxides from the 6000 to 25000 ppm (d.b.) range staged combustion is needed and for nitrogen levels above 25000 ppm (d.b.) more aggressive selective catalytic reduction (SCR) or selective non-catalytic reduction processes (SNCR).

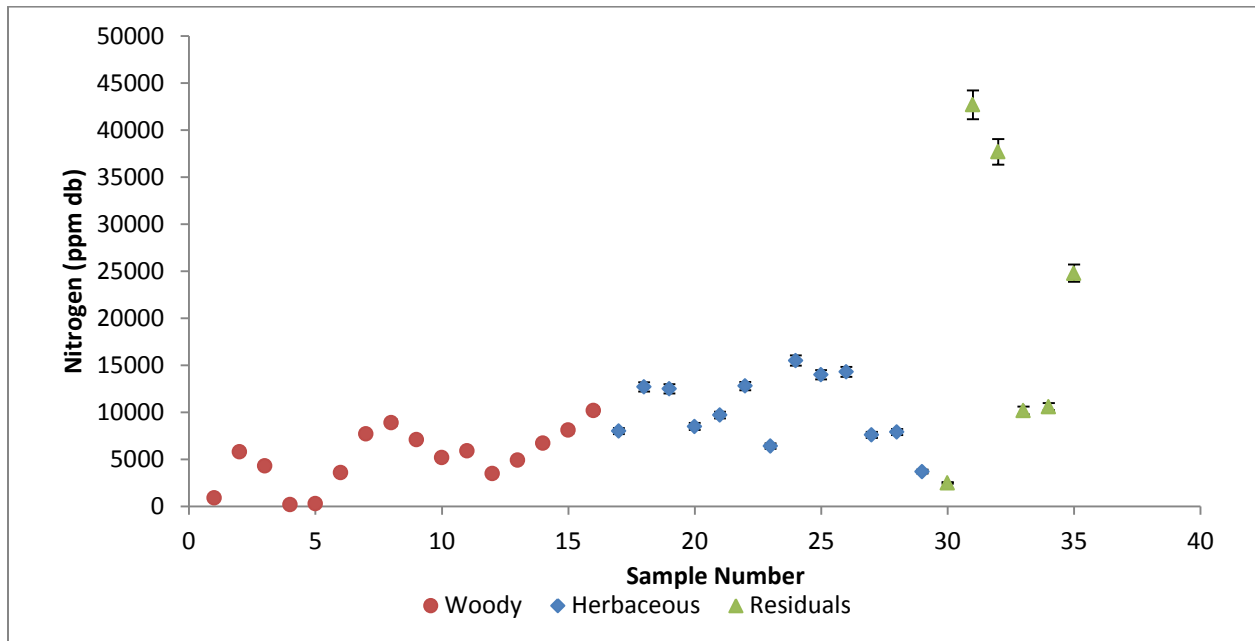


Figure 6: Biomass sample nitrogen content (ppm (d.b.)) with 95% CI.

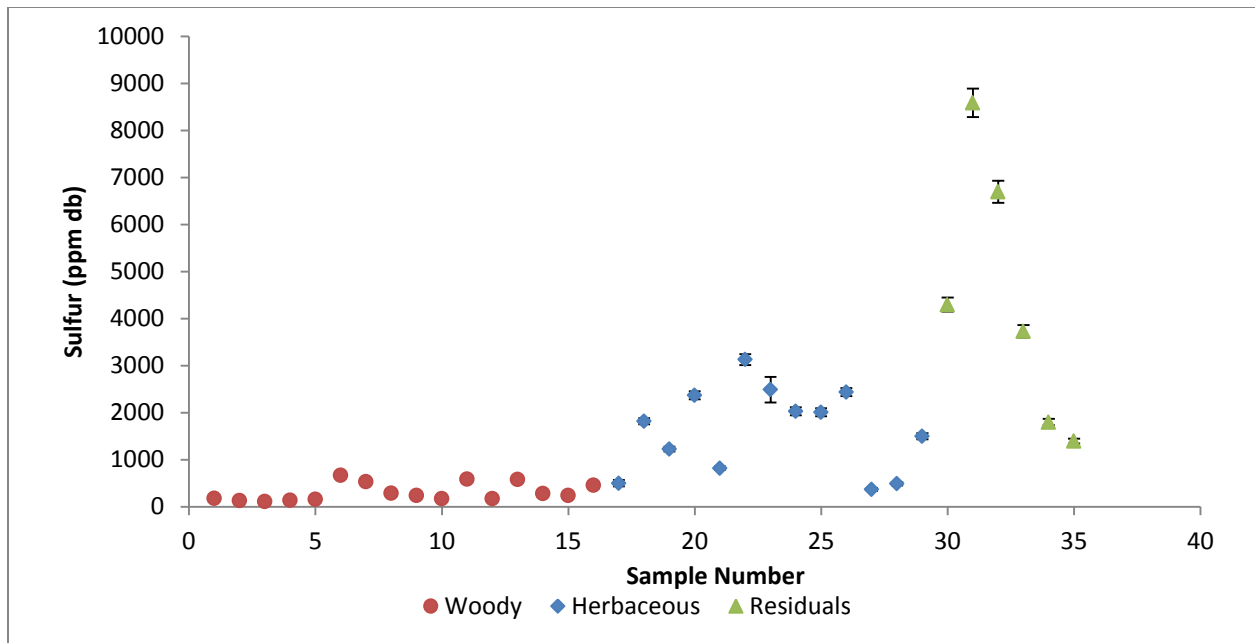
Ten of the eighteen woody biomass samples were below the first limit of 6000 ppm (d.b.) and the rest of the woody biomass samples were below the 25000 ppm (d.b.) limit, one herbaceous sample was below the first limit of 6000 ppm (d.b.) and the rest of the herbaceous samples were below the 25000 ppm (d.b.) limit, and the paper mill waste was the only residual sample below the 6000 ppm (d.b.) limit. As a result the woody, herbaceous, and paper mill waste feedstocks showed low nitrogen content and are suitable for systems with staged combustion for reduction of  $\text{NO}_x$ . The two manure briquettes and the manure and sawdust samples were below the 25000 ppm (d.b.) limit, but the manure and sawdust sample was significantly higher in nitrogen content than the briquette samples and very close to the second limit. The manure samples show that nitrogen content can reach noticeably higher levels of

nitrogen than other materials and reach levels near the limit requiring more aggressive technology. It is likely this can be controlled by mixing in larger amounts of sawdust or bedding (woody or herbaceous) or mixing with other solid fuels. Other factors such as feed or animal may have significant effects on this value. The manure samples show some potential to be fired in systems with staged combustion for reduction of  $\text{NO}_x$ . The dried distiller's grains were high in nitrogen content which is expected due to its high protein content which is naturally high in nitrogen content. The DDG's showed very high levels of nitrogen content and should not be combusted without more aggressive emission control technology (SCR or SNCR systems) and are likely more valuable as a feed than a fuel as a result. Fuel mixing is another solution to utilize the high nitrogen fuel mixed with low nitrogen fuel so emission limits are not exceeded.

#### 2.2.6. Sulfur

Combusting biomass with high Sulfur (S) content can lead to sulfur oxide emissions. Sulfur oxides have a negative effect on respiratory systems and can lead to formation of acid rain. Sulfur oxide emissions from biomass combustion typically are lower than that of coal or oil combustion. 40-90% of S content is bound in the ash during combustion depending on design and controls.<sup>8,27</sup> Sulfur content in fuel can lead to hazardous sulfur dioxide emissions that have a negative effect on human respiratory systems and can lead to acid rain. Sulfur can also have a corrosive effect when deposited on boiler surfaces. Average sulfur content for the samples is plotted on Figure 7 with a 95% confidence interval. Sulfur was compared to values from literature for corrosion and emission potential: from 1000 to 2000 ppm (d.b.) sulfur presents potential corrosion concerns via alkali sulfate corrosion, the typical coal corrosion mechanism and appropriate mitigation of this form of corrosion can be achieved by periodically cleaning heat exchanger surfaces, coating of boiler tubes, or appropriate material selection. Values above 2000 ppm (d.b.) indicate high emission potential and can be reduced with dry sorption or scrubbers.





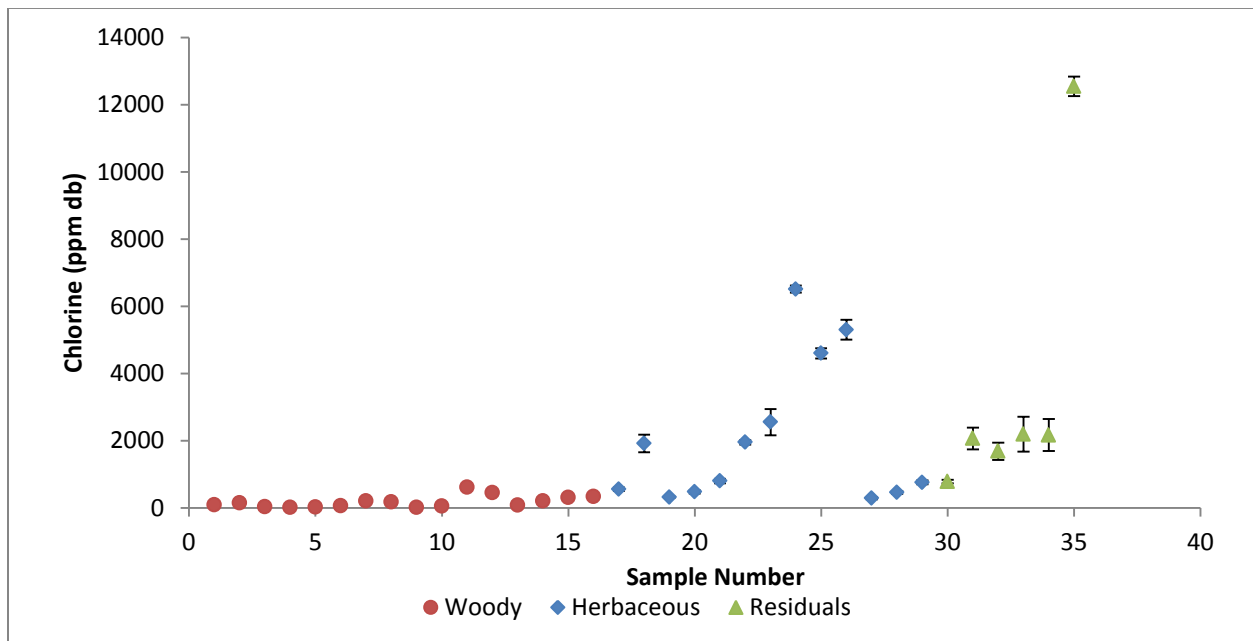
**Figure 7: Biomass sample sulfur content (ppm (d.b.)) with 95% CI.**

Wood was the feedstock with the most favorable composition and had no samples with values above 1000 ppm (d.b.) indicating low sulfur oxide emissions and low sulfur related corrosion. Herbaceous biomass had a wide range of sulfur content from very low to high levels indicating that a combustion applications using herbaceous fuels may need a sulfur emissions control technology and periodic cleaning to protect surfaces. While the manure & sawdust sample was in the medium range the manure briquettes registered one sample in the medium and one in the high range indicating manure has an ability to reach a high level of sulfur content. Either fuel supply controls or sulfur emission controls will need to be applied to properly control sulfur emissions and periodic cleaning of surfaces will be necessary with the manure and sawdust material. Paper mill waste and DDGs showed high levels of sulfur suggesting this fuel should not be combusted without proper periodic cleaning and sulfur emissions controls.

### 2.2.7. Chlorine

Biomass combustion with Cl-laden material can lead to hydrogen chloride (HCl) formation. The majority of the chlorine content is retained in the ash, but higher levels of chlorine content in herbaceous biomass such as switchgrass and miscanthus can lead to increased hydrogen chloride emissions. Hydrogen chloride emissions have negative effects on the human respiratory systems, acid rain formation, toxic effects and plays a role in dioxin and furan formation. 40-85% of Cl is bound in the ash during combustion depending on design and controls.<sup>8</sup> Biomass with high chlorine content can lead to hydrogen chloride formation during combustion, which can have negative effects on the human respiratory systems and can cause acid rain formation. Chlorine can also react with organic compounds under certain conditions to create small amounts of high toxic chlorinated dioxins and furans. Although much of the chlorine content is retained in the ash, 40-85% depending on boiler design and combustion

conditions, higher levels of chlorine content in feedstock will lead to hazardous emissions.<sup>13,28</sup> Average chlorine content of the biomass is plotted in Figure 8 with 95% confidence intervals. The figure indicates three general levels for corrosion and emissions considerations. Biomass with chlorine levels below 1000 ppm (d.b.) can be considered to be acceptable for most modern systems, with lower levels being desired.<sup>13,28</sup> Chlorine levels from 1000 to 3000 ppm (d.b.) create potential for corrosion and hydrogen chloride emissions and should be used sparingly in systems, with practices employed to mitigate corrosion. Hydrogen chloride emissions can be controlled by the same means of sulfur oxides emissions which is dry sorption or scrubbers. Biomass with chlorine content above 3000 ppm (d.b.) has the potential to cause high dioxin and furans emissions in addition to hydrogen chloride emissions and corrosion potential.<sup>13,28</sup> Fuels with this high of chlorine content should be avoided or more advanced emission control practices should be employed such as sorption with activated carbon.



**Figure 8: Biomass sample chlorine content (ppm (d.b.)) with 95% CI.**

Wood again is the feedstock that had the most favorable composition and had very low levels of chlorine with no samples above 1000 ppm (d.b.). When wood is the only feedstock it can be expected that no chlorine related control technology is necessary, but periodic cleaning of boiler surfaces may still be necessary even at low values due to the highly corrosive nature of chlorine.

Several herbaceous fuel samples had high levels of chlorine, potentially from fertilizer use. It is worth noting that it is possible to control the amount of chlorine in the fuel by using non-chlorine based fertilizers or rain leaching in the field.<sup>28</sup> The three herbaceous samples with values above 3000 ppm (d.b.) are ditch grass samples that were removed from the side of highway 151 in Dane County, Wisconsin in October. It appears that road salt operations in the winter for de-icing could have lead to increased levels of chlorine in the ditch grass, and that precipitation over the spring, summer, and fall did not remove enough salt to reduce chlorine content in the grass. It does present a contamination risk for agricultural residues or energy crops planted near roads that are salted in the winter for de-icing purposes although more information on whether the chlorine could migrate past a ditch to the field is

important. Herbaceous fuels may need dry sorption or scrubbing technology to reduce hydrogen chloride emissions.

Paper mill waste was the only residual fuel that had a low chlorine level, below 1000 ppm (d.b.), indicating it doesn't have a need for emission control technology. The DDGs had moderate levels of chlorine in the 1000-3000 ppm (d.b.) range and may need hydrogen chloride emissions abatement equipment and a need to periodically clean boiler surfaces. The manure briquettes also showed moderate levels of chlorine, but the manure & sawdust sample showed very high levels of chlorine indicating that either the fuel needs to be controlled in pre-processing, or more advanced emission control equipment may be necessary.

### 2.2.8. Mercury

Mercury has a negative effect on human health which can cause harm to the brain, heart, kidneys, lungs, and immune system when exposed to high levels.<sup>39</sup> According to the revised and proposed EPA Boiler MACT rules, mercury emissions will be limited to 3.1 lb/10<sup>12</sup> Btu (3.1E-06 lb/MMBtu) and 0.86 lb/10<sup>12</sup> Btu (8.6E-07 lbs/MMBtu) for existing solid fuel boilers and new solid fuel boilers respectively for major source emitters.<sup>40</sup> The maximum mercury content available per 10<sup>12</sup> Btu was calculated using Equation 2 and the values are displayed in Figure 9. This calculation assumes all of the mercury in the sample would be emitted as a worst case scenario, which is unlikely as much remains in the ash, but since the EPA allows major source boilers to control mercury by proving there is not enough available in the fuel to exceed limits.<sup>40</sup> Also, typical combustion control equipment such as fabric filters, scrubbers, and SCR's can have an effect of reducing mercury emissions.<sup>41</sup>

$$Hg_{avail} = \left( \frac{Hg_{ppm,db}}{HHV_{\frac{Btu}{lb}}} \right) * 1000,000$$

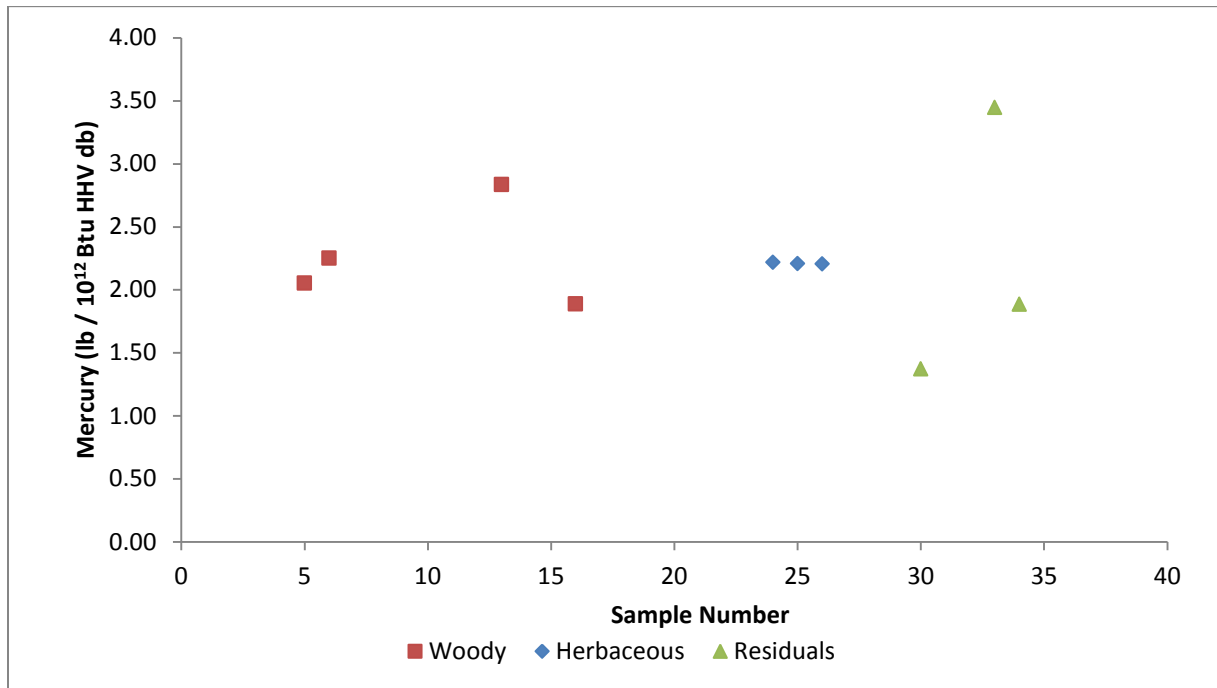
**Equation 2. Modified equation to calculate mercury available in units of lb/10<sup>12</sup> Btu, HHV (d.b.)**<sup>40</sup>

Where:

Hg<sub>ppm, (d.b.)</sub> – is mercury content in ppm (d.b.) (or mg/kg (d.b.))

HHV<sub>Btu/lb</sub> – is the HHV in Btu/lb (d.b.)

Hg<sub>avail</sub> – is the maximum available mercury that could be emitted in lb/10<sup>12</sup> Btu



**Figure 9: Biomass sample mercury content per heat available (lb/10<sup>12</sup> Btu, HHV (d.b.))**

With the exception of one sample, all fuel samples tested had potential mercury emissions below the limit for existing boilers, meaning these fuels were not capable of exceeding the proposed emission limit for existing boilers. A manure briquette had a value above the existing limit and some form of emissions equipment would be necessary if more than 90 % of the mercury from that sample exited with the flue gas after combustion.

None of the samples with detectable mercury had values below the limit for the new solid fuel boilers. Also, it is worth mentioning that the given the detection level of 0.01 ppm (d.b.) of the mercury test it could not prove the other fuels were below the 0.86 lb/10<sup>12</sup> Btu limit which indicates use of a test method with a lower detection limit may be required depending on the fraction of mercury in fuel that would be emitted after combustion with no control technology. A study from 2005 determined mercury values using EPA method 1631E and was able to determine mercury contents with a lower detection limit.<sup>42</sup> Mentz et. al. found the mercury content to average 1.42 lb / 10<sup>12</sup> Btu and 0.28 lb / 10<sup>12</sup> Btu in bark and stemwood respectively.<sup>36, 42</sup> None of the stemwood values exceeded the proposed limit for new boilers while the bark mercury content ranged from 0.57 lb / 10<sup>12</sup> Btu to 3.14 lb / 10<sup>12</sup> Btu which means woody fuel with bark or contaminants may require control technology to reduce the mercury content of the fuel depending on the fraction of mercury that is emitted from the total available. The three values of the herbaceous category that had detectable mercury values were the three ditchgrass samples and they may have been contaminated from a nearby point source of mercury emissions such as a coal fired power plant or a large number of motor vehicle.<sup>43</sup> As a result, herbaceous fuels located near a mercury contaminate source show a risk of having increased mercury levels

otherwise they are typically very low in mercury concentration. The results also appear to show that mercury can be concentrated in bioprocessing systems, with manure samples and the paper waste showing elevated values of mercury. All biomass fuels have the potential for mercury values above the EPA’s proposed major source MACT limits indicating emissions monitoring or installation of a control technology may be required if these new regulations are enacted.

### 2.2.9. Fouling Index

The mineral ash analysis can provide insight into the ash physical properties and whether it will agglomerate into structures that are difficult to remove from the ash bed of the furnace. The ash can also deposit onto boiler surfaces, referred to as fouling. Of particular interest are the heat exchanger surfaces because the fouling will reduce the effectiveness of heat transfer due to the deposits low thermal conductivity. Typical elements that influence the melting point of the ash are Ca, Mg, K, Na, and Si. Ca and Mg typically increase the ash melting temperature, and K and Na will typically decrease the ash melting temperature. Si can form low-melting silicates with K and Na that lead to fly-ash sintering and deposit and corrosion issues.<sup>8</sup>

Mineral ash analysis was completed on select biomass samples and a fouling index based on coal research was calculated using Equation 3.<sup>44</sup> Due to cost and material constraints the mineral ash analysis was not performed for all samples. A listing of the samples tested for mineral ash and their descriptions can be found in Table 3. The fouling index was then plotted in Figure 10, with three regions of interest. Values below 0.4 lb alkali/MMBtu (0.17 kg alkali/GJ) suggests little potential to foul, probable fouling at values greater than 0.4 lb alkali/MMBtu (0.17 kg alkali/GJ) and virtually certain fouling at values greater than 0.8 lb alkali/MMBtu (0.34 kg alkali/GJ).

**Table 3. List of Samples for Alkali Fouling Index**

Sample #	Category	Description
1	Woody	Industrial Pellet 90% Hardwood (debarked), 10% recycled ag. Plastic
2	Woody	Premium Wood Pellet Fuel
3	Woody	Premium Wood Pellet Fuel
4	Woody	Premium Wood Pellet Fuel
5	Woody	Wood - Pine (whole tree - high amount of needles)
6	Woody	Wood - Maple (whole tree)
7	Herbaceous	Switchgrass Pellets
8	Herbaceous	Switchgrass
9	Herbaceous	Corn stover
10	Herbaceous	Big Bluestem Pellets
11	Herbaceous	Miscanthus stalks
12	Residuals	Industrial pellet made from paper mill sludge, waste paper, film waste
13	Residuals	Manure briquette - Dried & densified manure, bedding, and sawdust
14	Residuals	Manure briquette - Dried & densified manure, bedding, and sawdust

$$Fouling\ Index = \left(\frac{1}{Q}\right) * Y_f^a * (Y_{K_2O}^a * Y_{Na_2O}^a)$$

**Equation 3: Alkali fouling index<sup>44</sup>**

Where:

$Q$  = HHV [GJ/kg (d.b.)] or [MMBtu/lb (d.b.)]

$Y_f^a$  = mass fraction of ash in the fuel ((d.b.))

$Y_{K_2O}^a$  = mass fraction of  $K_2O$  in the fuel ((d.b.))

$Y_{Na_2O}^a$  = mass fraction of  $Na_2O$  in the fuel ((d.b.))

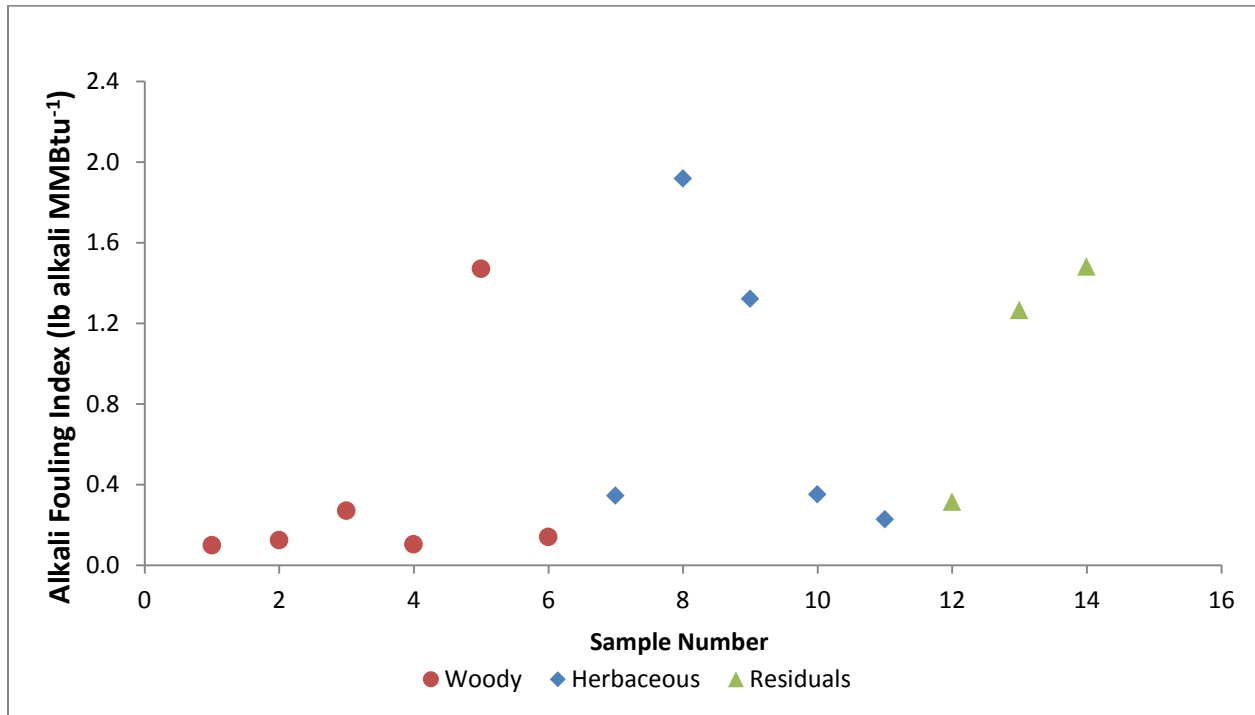


Figure 10: Biomass sample alkali fouling index (lb alkali MMBtu<sup>-1</sup>).

Six of the seven woody samples fell below the 0.4 lb alkali/MMBtu limit indicating low fouling behavior. This is expected due to woody fuels very low ash levels. The pine sample was above the 0.8 lb alkali/MMBtu limit at 1.471 lb alkali/MMBtu which indicates that fouling would be likely and the sample showed a considerably higher value than other woody fuels due to a high ash value and high  $K_2O$  value which could be elevated as a result of the amount of visible needles and bark or possible soil contamination or both. Two of the five herbaceous samples, switchgrass and corn stover, had high levels over 0.8 lb alkali/MMBtu indicating high fouling behavior which would result from high ash and potassium content. While the rest of the herbaceous samples were below the 0.4 lb alkali MMBtu<sup>-1</sup> limit the switchgrass pellets and big bluestem pellets were close to the first limit. Paper waste pellets had a low fouling potential and densified manure was found to have a high fouling potential, likely a result of high ash and potassium.

In general, wood is expected to have low fouling behavior but contaminants can cause problems and with herbaceous fuels more fouling is expected. The waste paper pellet showed a reasonably low propensity for fouling even though it has considerable ash content and the densified manure has

considerable tendency towards fouling. The higher fouling fuels will require periodic cleaning more often to maintain efficiency of heat transfer surfaces or reduce corrosion.

### ***2.3. Biomass Combustion Quality Survey Summary***

Solid biofuels represent an important resource for reaching renewable energy goals, but there can be large ranges in some chemical characteristics of solid biofuels due to inherent differences between species or differences between harvesting methods that need to be properly accounted for in the design and operation of the bioenergy project.

Woody fuel represents the feedstock with the most favorable composition for a combustion application with the least amount of complications indicated from the chemical compositions. Due to the nitrogen content in wood, there is a need for staged combustion. High moisture and ash content are problems that can arise with woody fuel that can be controlled through proper harvesting and pre-processing (drying) of the material to lower moisture and minimize ash. Operational modification such as particulate matter filters and periodic cleaning of equipment can be employed to reduce high ash content related operational and emission related problems. Bark content can sporadically create issues with mercury which appear to be problematic for the proposed MACT major source new boiler standards. The contamination appears to be site specific and likely is due to contamination from nearby coal combustion or other industrial sources.

The next most desirable fuel would be between paper mill waste and herbaceous fuels and would depend on the design of the combustion plant and control technologies. Paper waste was high in sulfur, had detectable mercury levels, and had high ash content. Due to herbaceous fuels nitrogen content staged combustion would be required. They were also high in sulfur content and had potential for high ash content and fouling indices. Both fuels had levels of chlorine that indicate potential corrosion and hydrogen chloride emission problems. Since staged combustion is typical technology for medium to large scale projects herbaceous fuels low mercury content makes it more desirable than paper waste. Residuals fuels are high in variability and the results show that they should be reviewed on a case by case basis. Comparing the similar residuals of the manure briquette and manure & sawdust results there is significant variation in the elemental compositions of nitrogen, sulfur, and chlorine. The manure briquettes even showed a significant difference in chlorine content between the two samples. All residuals except the paper mill waste had significant enough levels of nitrogen to require staged combustion. The DDG's had very high levels of nitrogen that would require more aggressive SCR or SNCR emission abatement equipment and DDGs had levels of sulfur and chlorine requiring scrubbing or dry sorption equipment and would need cleaning to prevent corrosion. As a result, DDG's are likely more valuable as an animal feed rather than a fuel. Manure briquettes had a range of sulfur and chlorine values that indicate dry sorption or scrubbing equipment would be necessary to reduce sulfur oxides and hydrogen chloride emissions and that proper cleaning would be required to protect the boiler from chlorine and sulfur related corrosion. The manure and sawdust had levels of nitrogen near the limit requiring SCR or SNCR equipment and very high levels of chlorine requiring more aggressive activated carbon sorption equipment to reduce dioxin and furan and hydrogen chloride emissions.

Assuming emission reduction equipment and corrosion increase the cost of biomass heat and power production woody fuel is most favorable fuel based on composition in biomass only systems because there would be a lesser need for emissions reduction equipment. Herbaceous fuels that don't have elevated chlorine contents are the second most desirable fuel creating some sulfur and chlorine related emissions and operational concerns. Paper waste is the next most desirable fuel with need for sulfur and mercury emissions reduction equipment and corrosion prevention measures. DDGs and manure based residuals present a need for more aggressive emissions reduction equipment. Table 4 **Error! Reference source not found.** summarizes the ranges of woody, herbaceous, and residuals fuels and Table 5 summarizes the elemental emissions and corrosion considerations and technological methods for reducing those contents to guiding ranges.



**Table 4. Summary of Ranges of Woody, Herbaceous, and Residual Fuels.**

Fuel Characteristic	unit	Woody	Herbaceous	Residuals
Moisture	(% wt (w.b.))	2.74% - 49.94%	2.45% - 18.32%	6.96% - 28.62%
LHV	Btu/lb	3200 - 8946	5926 - 6923	5019 - 8145
Ash	(% wt (d.b.))	0.63% - 9.33%	2.66% - 10.83%	5.21% - 19.38%
N	ppm (d.b.)	200 - 10200	3700 - 15500	2500 - 42700
S	ppm (d.b.)	110 - 670	370 - 3130	1400 - 8590
Cl	ppm (d.b.)	19 - 617	293 - 6516	786 - 12550
Hg	ppm (d.b.)	<0.001 - 0.024	<0.001 - 0.017	<0.001 - 0.027
Fouling Index	lb alkali/MMBtu	0.099 - 1.471	0.227 - 1.919	0.314 - 1.482

**Table 5. Guiding values for nitrogen, sulfur, and chlorine content and technological methods for reducing to guiding ranges.<sup>28</sup>**

Element	Limiting Value	Limiting Issue	Technological methods for reducing to guiding ranges
N	< 6000 ppm (d.b.)	NOx emissions	Staged combustion
	< 25000 ppm (d.b.)	NOx emissions	SCR or SNCR
S	< 1000 ppm (d.b.)	Corrosion	heat exchanger cleaning coating of boiler tubes appropriate material selection
	< 3000 ppm (d.b.)	SOx emissions	dry sorption scrubbers
Cl	< 1000 ppm (d.b.)	Corrosion	heat exchanger cleaning coating of boiler tubes appropriate material selection
	< 1000 ppm (d.b.)	HCl emission	dry sorption scrubbers
	< 3000 ppm (d.b.)	Dioxans and Furans	sorption with activated carbon

### 3. Improving Biomass for Combustion

Based on these tests it is apparent that many of biomass fuels contains non-desirable chemical attributes for combustion including low heating value, high ash content, and high nitrogen and chloride content. This coupled with logistical issues of a limited harvesting season; creating the need for storage<sup>16</sup>, high moisture content, irregular shape and size, and low bulk density makes biomass materials difficult to handle, transport, store, and utilize for energy production.<sup>17</sup>

#### 3.1. Review on Methods to Treat Biomass prior to Combustion

##### 3.1.1. Biomass Densification

Logistic issues can be partially addressed through densification of the biomass materials into pellets or briquettes. Biomass densification is defined as the compression or compaction of biomass to remove inter- and intra-particle voids.<sup>18</sup> Densification can increase the bulk density of the biomass material

from 40 to 200 kg/m<sup>3</sup> (baled density 100 to 200 kg/m<sup>3</sup>) to a final bulk density of 600 to 800 kg/m<sup>3</sup>. Additionally, the densified biomass can be formed into a consistent shape that is easier to handle, store and feed into processing equipment.<sup>16, 17</sup>

### 3.1.2. Biomass Torrefaction

Logistical issues can also be improved through a thermal pretreatment of the biomass called torrefaction. Torrefaction is a thermal treatment which aims to remove moisture, low weight volatile organic components, and depolymerizes polysaccharides.<sup>45-47</sup> This produces a hydrophobic solid with an increased energy density by decomposing the hemicellulose fraction.<sup>48</sup> The process is characterized by low particle heating rates of less than 50°C per minute, which results in a long residence time (typically one hour).<sup>45, 46, 49</sup> Torrefaction is also sometimes referred to as roasting, as this process was adopted from the process of roasting coffee beans. During the torrefaction process the biomass is partly decomposed which results in the release of various types of volatiles. Gases produced by torrefaction contain 30% of the original biomass and 10% of the initial energy content. Torrefied biomass, sometimes called biochar, or biocoal contains 70% of the original biomass and 90% of the initial energy content. Due to the changes in composition, the energy density increases by a factor of 1.3 on a mass basis.

One of the main attractions of torrefied biomass over untreated, or fresh biomass, for co-firing power plants is its superior grindability.<sup>45-47</sup> Before torrefaction the raw biomass is highly fibrous with a mixture of large particles and fibers. The fibers form links between the particles causing the raw biomass to be more difficult to grind into smaller particles. After the biomass has been torrefied it becomes easier to grind, with particle size decreasing with an increase in temperature and residence time of torrefaction. Also, during torrefaction the particles become more spherical due to the reduction in the length of the particles, with very little change to the diameter.<sup>45, 46</sup> According to P.C.A Bergman,<sup>55</sup> treated willow and woodcuttings reduced power consumption for size reduction by 80-90% and increases the chipper capacity by 10 times compared to untreated willow and woodcuttings, as seen in Figure 10. Because of this, the biomass becomes more like coal and in terms of grind ability characteristics and energy density which makes it easier to use in existing coal-fired power plants.<sup>45</sup> Unfortunately torrefaction does not remove inorganics in the biomass and thus does not improve many of our low-quality biomasses that have high ash, Cl, N, or S.

### 3.1.3. Biomass Leaching

Use of low temperature chemical washes has been researched primarily as a means of extracting inorganics to improve biomass quality for combustion. Water leaching is a simple method that removes most of the water soluble ions of K, Na, Ca, Cl, S, and Mg. Leaching efficiencies depend on the biomass type, particle size, water to biomass ratio, leaching time and temperature. In removing these materials, the biomass ash content is not only lowered, but its quality for thermal conversion is improved.<sup>50-52</sup> Additionally, as the inorganic content typically contains value as nutrients or fertilizers, the extracts can be land-applied to benefit future biomass production.

In a simple leaching system, biomass is left in the field and exposed to repeated rainfalls until its ash content has been reduced.<sup>14, 53, 54</sup> This simple system has the benefits of being inexpensive and returns the nutrients back to the field.<sup>55</sup> Drawbacks include lack of control on the washing due to weather variability and a high loss of organic material due to bio-deterioration.<sup>56</sup> Water washing of straw has been shown to be equally effective as rain washing and can be accomplished through a combination of crushing, soaking and dewatering operations.<sup>50, 57, 58</sup>

Removing ash after charring the biomass has also been proposed.<sup>51, 59</sup> In this process, the biomass is first pyrolyzed at moderate temperatures at which most of the inorganic materials are retained in the char, which are then extracted by water washing.<sup>51, 60</sup> Because some inorganic elements are water-insoluble and cannot be easily removed by water, washing with dilute acid (including nitric, hydrochloric, and acetic) has also been investigated.<sup>57, 61</sup> Compared to water washing, acid leaching can remove almost all inorganic constituents' components. However, this technique leads to additional costs to cycle the nutrients from the leachate, since it cannot be easily land applied like the water washing systems due to the presence of the acids.

#### *3.1.4. Liquid Hot Water Treatment*

Liquid hot water (LHW) treatment of biomass uses water at elevated temperatures to solubilize saccharides, predominantly hemicelluloses. The treatments range from 160°C to 240°C with times up to an hour.<sup>62</sup> The reactions that occur are described as autohydrolysis which combines the hydrolytic properties of water with the actions released organic acids to catalyze hydrolysis reactions.<sup>63, 64</sup> The autohydrolysis process solubilizes the more reactive hemicellulose, disrupts the lignocellulosic matrix, and thus generates more reactive cellulose.<sup>65</sup> The solubilized biomass portion, primarily saccharides from hemicellulose and a portion of the lignin, is separated from the insoluble biomass, primarily cellulose and lignin and can be used to either create fuels and materials from the saccharides after further hydrolysis.<sup>66</sup> Inhibitory byproducts can also form within the liquid fraction of this process and include furfural, acetic acid, 5-hydroxymethylfurfural (HMF), formic acid, and other organic acids.<sup>67</sup> Variability in results was related to the biomass type with high lignin solubilization impeding recovery of hemicellulose sugars.<sup>67-69</sup>

Several researchers have investigated hemicellulose extraction as part of a manufacturing scheme that either goes on to produce pulp with the extracted biomass and ethanol or some other valued chemical from the extract.<sup>70-73</sup> A recent study by Pu et al.<sup>63</sup> has extended this concept using hot water extraction on hardwoods to create a higher energy content extracted material as the carbohydrates were partially removed, concentrating the lignin, thereby increasing the heating value. This concept described as value prior to combustion, was done primarily as means to extract low thermal energy sugars in wood species to increase the pellet heating value.

### **3.2. Extraction Study Objectives**

This research explores an alternative to torrefaction through extracting inorganics along with a portion of the hemicellulose while increasing the energy density and hydrophobicity of the solid fraction. It is hypothesized that removing the hemicellulose material via aqueous extraction will provided many of the

advantages of torrefaction while also removing inorganics. In this research hot water aqueous treatments will be explored to determine if sugars can be extracted to create both an improved solid fuel and a sugar stream that can be used for the creation of liquid fuel or chemicals. Since a washing step was to be employed after the hydrolysis for ash removal, lower severity conditions of 150-170°C were employed to minimize yield loss from saccharide solubilization, following previous work<sup>74</sup>. Beyond looking at ash removal, this study was also designed to investigate solid fuel properties of LHW treated biomasses, as it was hypothesized that LHW treatments can create an improved solid fuel considering not only the heating value but also ash reduction and ability to be densified into a high quality solid fuel pellet.

### **3.3. Extraction Study Experimental**

#### **3.3.1. Biomass Samples for Extraction Studies**

Four biomass samples were acquired and utilized for these experiments representing low cost biomass due to their high growth rates or availability as agricultural residuals. NM-6 hybrid poplar biomass, *Populus maximowiczii* x *nigra*, was harvested from northern Wisconsin after ten years of age and seasoned for three months before use. The wood was hand debarked, chipped, screened to 2 - 8 mm chips and air dried. Corn stover, *Zea mays*, was collected from Lodi, Wisconsin, aged three months before being chopped and screened to 25 mm samples. Miscanthus, *Miscanthus giganteus*, and switchgrass, *Panicum virgatum*, were harvested from the University of Wisconsin agricultural stations in Dane County after senescence, were air dried, chopped and screened to 25 mm samples.

#### **3.3.2. Liquid Hot Water Extraction Experiments**

Liquid Hot Water extraction experiments were performed using rotating pressure reactors in an oil bath. The reactors were filled with the desired biomass (hybrid poplar, corn stover, miscanthus or switchgrass) and water at varying water to biomass ratios (4/1, 5/1 or 6/1). The reaction was controlled by time (30, 45 or 60 min) and temperature (150, 160, or 170°C) after which the bombs were removed and cooled in ice water for 10 minutes. Pressure was monitored during the reactions and found to be at approximately the saturated steam pressure for the given temperature. The solids and liquor were separated using vacuum filtering. The solids were washed by mixing with de-ionized water at a 10/1 water to biomass ratio and refiltered (done twice). Mild conditions, shown in Table 6, were employed to minimize hemicellulose solubilization and solid yield loss and were centered around 160°C, 45 min, with a 5/1 water to biomass ratio.

**Table 6. Liquid Hot Water Extraction Experimental Conditions.**

Run #	Temperature (°C) / Pressure (kPa)	Time (min)	Water: Biomass	CSF
1	150 / 476	30	4	3.55
2	150 / 476	60	4	3.85
3	150 / 476	30	6	3.73
4	150 / 476	60	6	4.03
5	160 / 618	45	5	4.12
6	170 / 792	30	4	4.14
7	170 / 792	60	4	4.44
8	170 / 792	30	6	4.32
9	170 / 792	60	6	4.62

For the extraction conditions a calculated combined severity factor (CSF) was used to integrate the effects of reaction times and temperature into a single variable [40]. Additionally, since the water-to-biomass ratio also was seen to have an impact on hemicellulose extraction, a modified CSF was used in this study to incorporate this variable and is defined as:

$$CSF = \log \left\{ t * \exp \left[ \frac{T_H - T_R}{14.75} \right] * R \right\}$$

Where, t is the reaction time for the extraction in minutes,

$T_H$  is the reaction temperature in °C,

$T_R$  is the reference temperature (100°C), and

R is the water to biomass ratio.

### 3.3.2. Characterization of Liquid Fraction

The solids of the liquid fraction were determined by ASTM Test Method E 1756-08. The determination of total saccharides was accomplished by hydrolyzing a sample from the liquid fraction hydrolysis [41,42] with dilute sulfuric acid solution, neutralizing, diluting with RO water, filtered through a 0.2 µm nylon syringe filter (Whatman, GE), and analyzed on a Dionex ICS-3000 system, equipped with a BioLC CarboPac PA 20 analytical column (3 x 150 mm), and an integrated amperometric detector with disposable gold electrode. The eluent was RO water at 0.35 mL/min with 0.5 mol/L NaOH used as a post-column eluent, and the column compartment was kept at 30°C. Acids and furans, including acetic acid (AA), furfural (Fur), levulinic acid (LA), and 5-hydroxymethylfurfural (HMF), in the hydrolysate were measured by HPLC using a Supelcogel C-610H column (30 cm x 7.8 mm ID), and an UV/Vis detector set at 205 nm. The eluent was 0.1% H<sub>3</sub>PO<sub>4</sub> solution at 0.60 mL/min, and the column temperature was kept at 50°C.

### 3.3.3. Characterization of the Solid Fuel

All solid samples were air-dried and milled using an IKA Works MF10 Mill fitted with a 20 mesh screen. Next the moisture, ash, and heating value were determined according to ASTM E-871, ASTM D-1102 and ASTM D-5865, respectively. The elemental ratio (CHN/O) of the samples was analyzed using a Series II CHNS/O Analyzer from PerkinElmer. Milled samples were also made into pellets using a MTS tensile

frame and cylindrical stainless steel die, with a pellet production chamber of 6.91 mm diameter and a 6.40 mm diameter plunger. A 0.5 g sample, conditioned to 14% moisture, was placed into a pre-heated die (100° C), and then loaded into the MTS tensile frame between stainless steel compression platens. After the die was placed on the compression platens, a custom TestWorks 4.0 software procedure, compressed the biomass in the fixture at a crosshead speed of 25 mm/min to the desired load of 4500 N, which was then held for 60 seconds to produce a pellet. A set screw at that bottom of the die was utilized for pellet removal. Pellet weights were measured with a top loading scale and dimensions with a Mitutoyo Standard Electronic Caliper to calculate a density. Additionally, the compressive strength of the pellets were measured using a MTS tensile frame fitted with stainless steel compression platens at a speed of 1.27 mm/min.

### **3.4. Results and Discussion**

#### *3.4.1. Biomass Characterization*

Samples from the four biomass species were analyzed for saccharides, lignin, and ash to characterize the material. The sugar analysis provides insight into the amount and type of hemicelluloses present with arabinose, galactose, xylose, and mannose being found only in hemicelluloses and glucose exists primarily as cellulose. Additionally, since the acidolysis used in the sugar analysis creates organic acid and furans, the major degradation products of formic acid, acetic acid, levulinic acid, 5-hydroxy-methyl-furfural, and furfural were also characterized. The results shown in Table 7 are as expected for the four species, with higher saccharide content for the switchgrass and corn stover, primarily in the form of hemicellulose, and higher ash for the three agricultural crops. Totaling the measured components we were able to recover near 100% of the original biomass, which suggest other non-measured materials such as extractives were only present in trace amounts in the aged materials.

**Table 7. Biomass Chemical Characterization reported as Averages ( $\bar{x}$ ) of 3 tests with Standard Deviations (s).**

	Poplar Wt %		Miscanthus Wt %		Switchgrass Wt %		Corn Stover Wt %	
	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
Arabinose	0.29	0.004	2.200	0.015	3.06	0.029	3.3	0.020
Galactose	0.46	0.040	0.62	0.051	1.26	0.027	1.4	0.041
Glucose	40.74	0.362	38.19	0.093	40.54	0.143	38.62	0.346
Xylose	13.3	0.069	18.89	0.083	19.71	0.085	21.23	0.314
Mannose	3.01	0.013	0.47	0.010	0.88	0.043	0.69	0.015
<b>Total sugars</b>	<b>57.8</b>	<b>0.371</b>	<b>60.37</b>	<b>0.136</b>	<b>65.45</b>	<b>0.176</b>	<b>65.24</b>	<b>0.470</b>
Acetic acid	3.71	0.033	3.37	0.013	2.39	0.019	2.6	0.014
Levulinic acid	0.38	0.015	0.19	0.017	0.19	0.012	0.25	0.011
HMF	0.47	0.013	0.73	0.016	0.46	0.011	0.4	0.012
Furfural	1.14	0.170	1.97	0.154	1.58	0.098	1.76	0.159
<b>Total furans &amp; acids</b>	<b>5.70</b>	<b>0.174</b>	<b>6.26</b>	<b>0.156</b>	<b>4.62</b>	<b>0.101</b>	<b>5.01</b>	<b>0.160</b>
Total sugar	57.8	0.371	60.37	0.136	65.45	0.176	65.24	0.470
Total furans & acids	5.70	0.174	6.26	0.156	4.62	0.101	5.01	0.160
Acid insoluble lignin	26.3	0.876	24.02	0.896	18.95	0.677	17.28	0.459
Acid soluble lignin	3.63	0.261	2.15	0.213	2.76	0.263	3.06	0.208
Ash	0.92	0.060	5.20	0.058	5.79	0.044	6.07	0.064
<b>Total Measured</b>	<b>94.34</b>	<b>1.003</b>	<b>98.00</b>	<b>0.946</b>	<b>97.57</b>	<b>0.755</b>	<b>96.66</b>	<b>0.710</b>

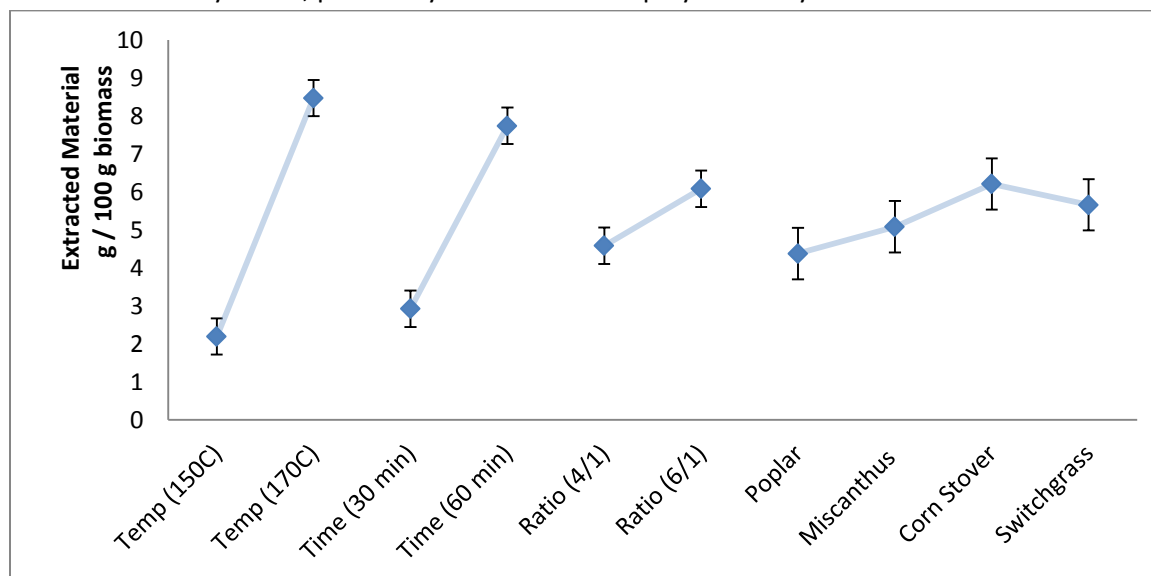
The biomass was also analyzed for higher heating value and elemental analysis, shown in Table 8. The biomass samples displayed typical heating values with the higher lignin woody material being slightly higher than the herbaceous samples. Lignin has been reported to have a HHV of approximately 26.7 kJ/g (11,480 Btu/lb) whereas cellulose and hemicellulose are lower at approximately 17.5 kJ/g (7,530 Btu/lb) [43]. The calculated carbon to oxygen (C:O) ratio trended with the HHV, being presumably higher due to higher lignin:carbohydrate ratios. Cellulose and hemicellulose have atomic C:O ratios of approximately 1 whereas lignin has a ratio of approximately 3.

**Table 8. Biomass Heating Value Characterization reported as Averages ( $\bar{x}$ ) of 3 tests with Standard Deviations (s).**

	Poplar Wt %		Miscanthus Wt %		Switchgrass Wt %		Corn Stover Wt %	
	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s	$\bar{x}$	s
HHV (cal/g)	4585	41	4408	38	4390	29	4336	40
C (wt%)	50.54	0.1746	47.37	0.2248	46.5	0.8907	46.01	0.2934
H (wt%)	6.01	0.1182	5.69	0.0289	5.15	0.0910	5.38	0.0552
N (wt%)	0.32	0.0044	0.85	0.0028	1.21	0.0019	1.25	0.0171
O (calculated wt%)	42.21		40.89		41.35		41.29	
O:C atomic ratio	0.63		0.65		0.67		0.67	
H:C atomic ratio	1.43		1.44		1.33		1.40	

### 3.4.2. Assessment of the Liquid Hot Water Treatment of Biomass

The initial assessment on the liquid hot water extractions was to determine the amount of biomass solubilized from the treatment. The variables impact on extraction were isolated by creating a Least Square Means Plot, shown in Figure 11, which demonstrated the time, temperature, and water to biomass ratio to all have a significant effect on extraction, thus prompting the use of a modified combined severity factor, previously described to simplify the analysis and discussion.

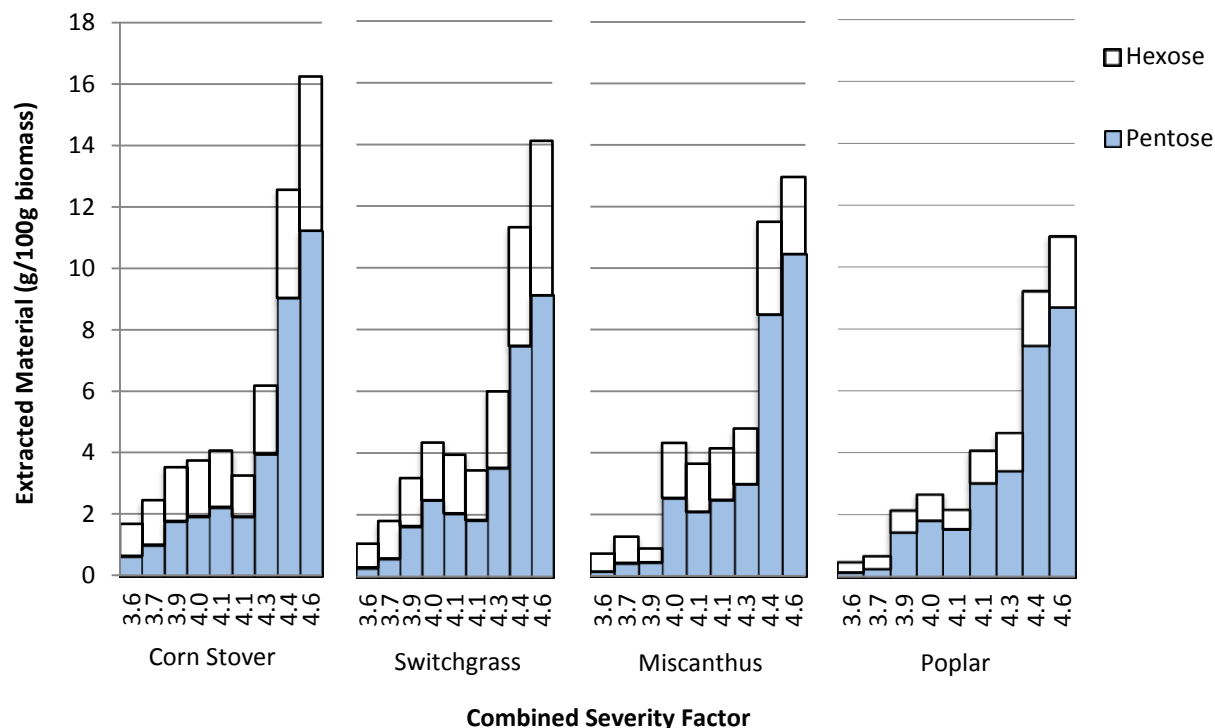


**Figure 11. Least Square Means with 95 Confidence Intervals to Demonstrate Variable Impact on Extracted Organics under Different Hydrolysis Conditions.**

The primary materials extracted from these experiments were saccharides, presumably hemicellulose. These materials were further hydrolyzed, analyzed, and plotted as either a hexose or pentose saccharide in Figure 12. The results indicate, as expected, harsher conditions resulted in the solubilization of significant more saccharides. Additionally 2-3 times more pentosan material was extracted than hexosan, confirming that hemicellulose was predominantly being hydrolyzed over cellulose. The mildest



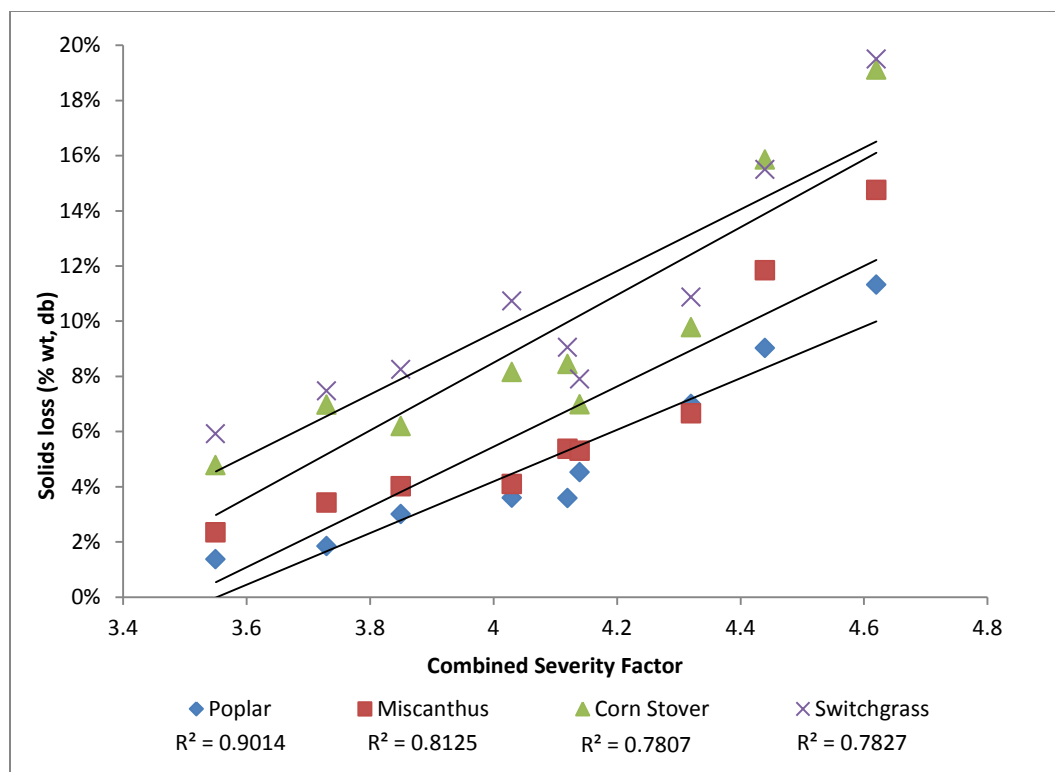
conditions, with a CSF of 3.6, were able to minimize biomass solubilization to less than 2%, whereas the harshest studied condition, CSF of 4.6, removed 11 – 16% biomass depending on the type.



**Figure 12. Composition of Extracted Organics under Different Liquid Hot Water Conditions**

### 3.4.3. Solid Fuel Properties of the Extracted Biomass

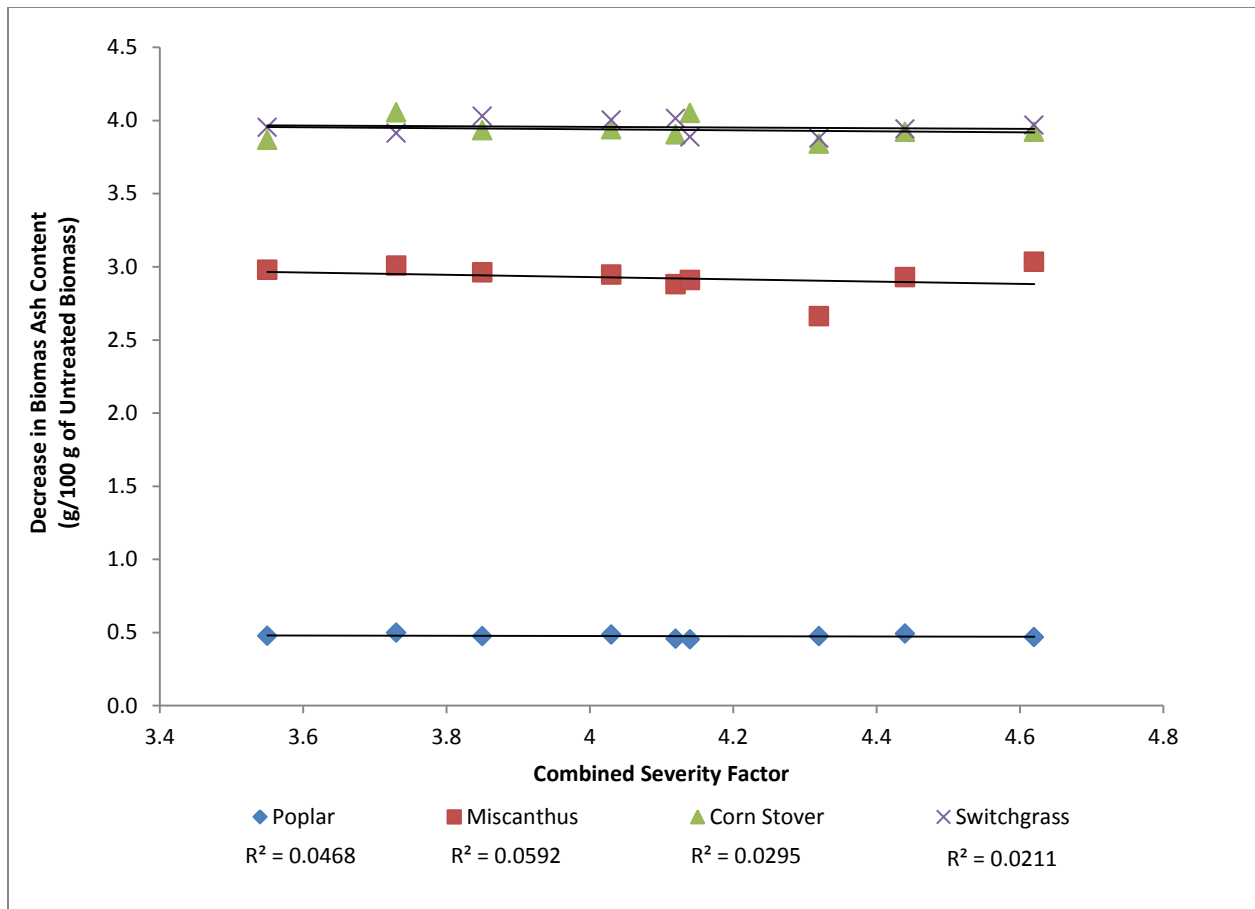
The extracted biomass samples were characterized to determine solid fuel quality changes. The first test was to determine the amount of material extracted from the biomass. Due to potential loss of material during transfer from the reactor, solids determination of the liquid and a mass balance was applied to determine the amount of material loss, shown for the 9 conditions (as a combined severity factor) and the four biomass samples in Figure 13. The results indicate, as expected, harsher conditions were able to solubilize more biomass for all four biomass types, with the harshest conditions solubilizing 10-20% of the biomass, presumably a combination of hemicellulose and ash. The corn stover, switchgrass, and Miscanthus showed the greatest amount of solubilization presumably due to the higher hemicellulose and ash content than the woody poplar sample. The more severe conditions had a compound effect of providing more time and energy to assist the kinetics, but also lowering the pH due to the liberation of acetyl and uronyl groups as acetic and uronic acid from the hemicellulose. Final pH value ranged between 3.5 and 5.5 with the lower values for the more severe conditions.



**Figure 13. Biomass Solids Loss under Different Hydrolysis Conditions**

Ash content of the LHW treated biomass samples were measured and compared to the initial biomass ash content to determine the relative decrease. The results indicate that significant amounts of ash (50-70%) could be removed from all 4 biomass samples from the LHW treatments, with the initial calculations showing a surprisingly negative trend of higher ash contents for biomass samples with harsher treatments. However, when correcting the numbers to determine the absolute ash removed (see Figure 14) it was determined that the ash removed was not actually impacted by the severity of the treatment, but rather was constant relative to the initial biomass weight. It was found that the increase in ash content initially observed with treatment severity was due to the loss of solubilized biomass. In short, the measured ash decrease was due to enrichment in the sample due to loss of organic content.

One of the initial study objectives was to determine if there would be any impact from harsher LHW conditions that would remove more ash with the hemicellulose. It was hypothesized that disruption of the lignocellulosic matrix and a decrease in pH from autohydrolysis conditions would facilitate ash removal. Unfortunately the data does not support this hypothesis. Although the majority of ash can be removed from the washing conditions employed during a LHW treatment, the hydrolysis and removal of hemicellulose does not appear to assist the leaching of ash.



**Figure 14. Ash Removed from Initial Biomass under Different Hydrolysis Conditions**

The reduction of ash and solubilization of the hemicellulose and corresponding enrichment in lignin was expected to increase the higher heating value (HHV) of the biomass, which was measured for the 4 samples at the 9 conditions and plotted in Figure 15. The figure indicates a similar trend as the solids loss shown in Figure 13 with heating values increasing about 5% for the wood poplar samples and approximately 10% for the three herbaceous samples. Accounting for the solids loss and the specific heating value gain, the biomass' gross energy change could be calculated. Although it was expected to decrease with loss of material, it was shown that for every 2% of biomass solubilized during hot water treatments only approximately 1% of energy was lost (Figure 16). This is due to both the ash loss which does not contribute energy value, and the loss of predominantly saccharides which have lower specific energy content than lignin.

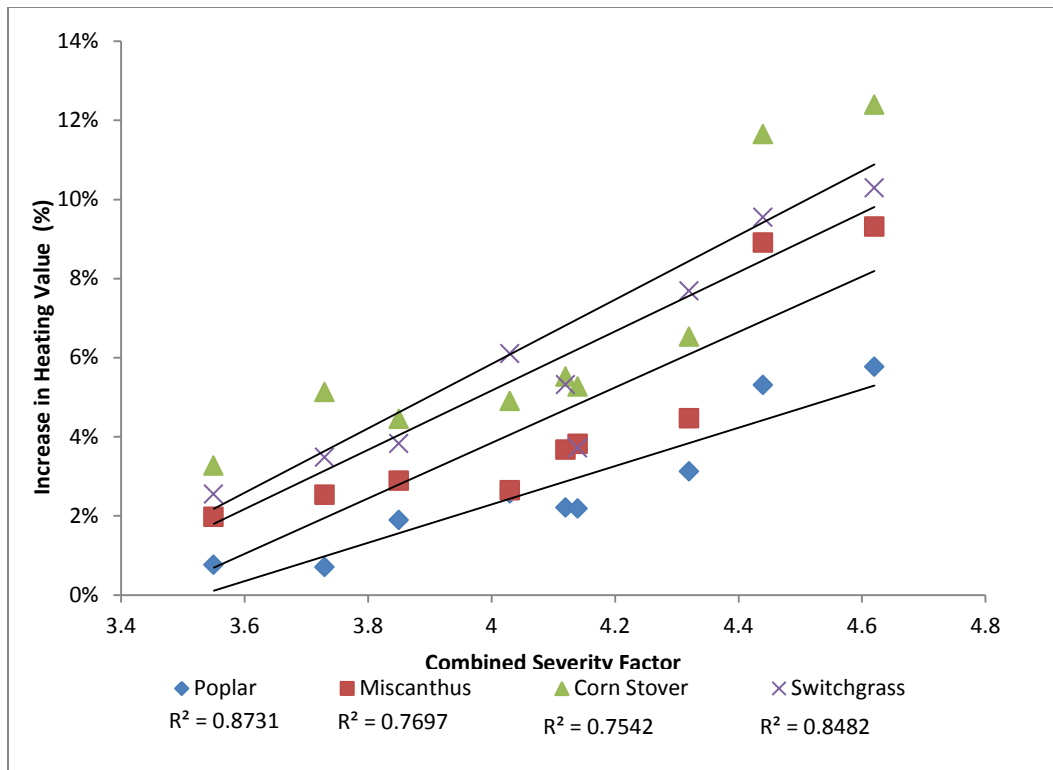


Figure 15. Heating Value Increase from Initial Biomass under Different Hydrolysis Conditions.

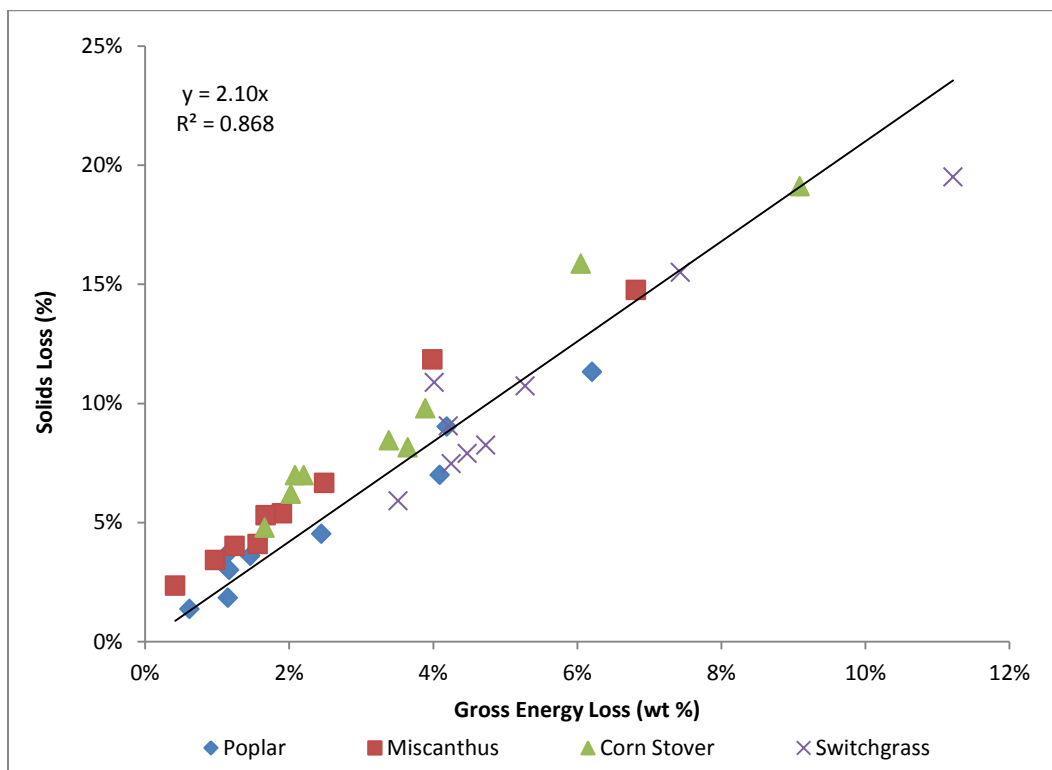
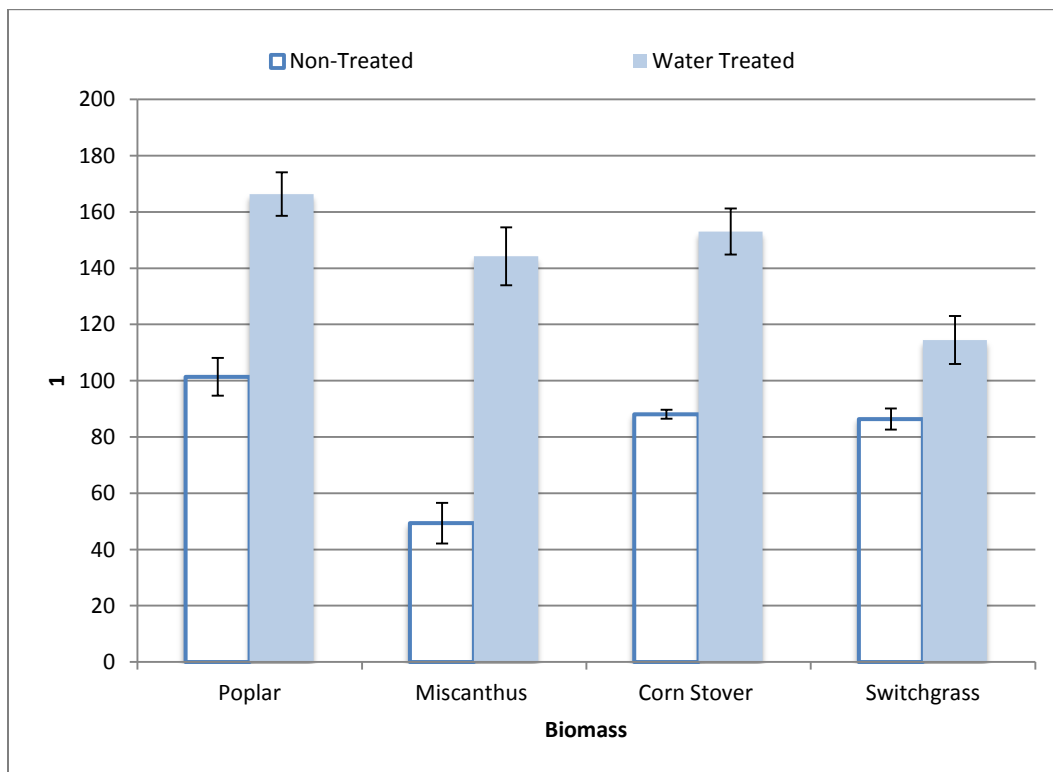


Figure 16. Comparison of Solids to Gross Energy Loss under Different Hydrolysis Conditions.

### 3.4.3. Pellet Durability

Pellet durability was also investigated to understand the biomass quality changes due to the LHW treatment. Pellets were produced individually through an electromechanical compression testing device that allowed control of stress and strain. Only the 4.62 CSF condition, which showed the highest HHV, was employed for this portion of the study. The produced pellets were conditioned for several weeks before testing for compressive strength to provide an assessment of their durability, shown in Figure 17. Conventional ASABE pellet durability testing was not done as significant quantities of pellet samples are required, beyond the capability of our controlled pellet production method.

The figure demonstrates that water treated biomass pellets had a significantly higher compressive resistance than the untreated control samples, although the magnitude of increase was quite variable between the biomass types due presumably to the variability in pellet production at this small scale. To hypothesize why this might occur, one must envision the pelleting process where biomass particles are heated and densified allowing the natural binders, primarily lignin, in the feedstock to flow as the glass transition temperature is surpassed.[44]. The water treated biomass pellets, with their increase in lignin-to-carbohydrate content, would have more natural binders per gram and thus should be able to have more bonds within the pellet, creating a stronger pellet.



**Figure 17. Compressive Resistance of Pellets made from Non-treated and Liquid Hot Water treated Biomass (Combined Severity Factor of 4.62). Error bars represent 95% Confidence Intervals.**

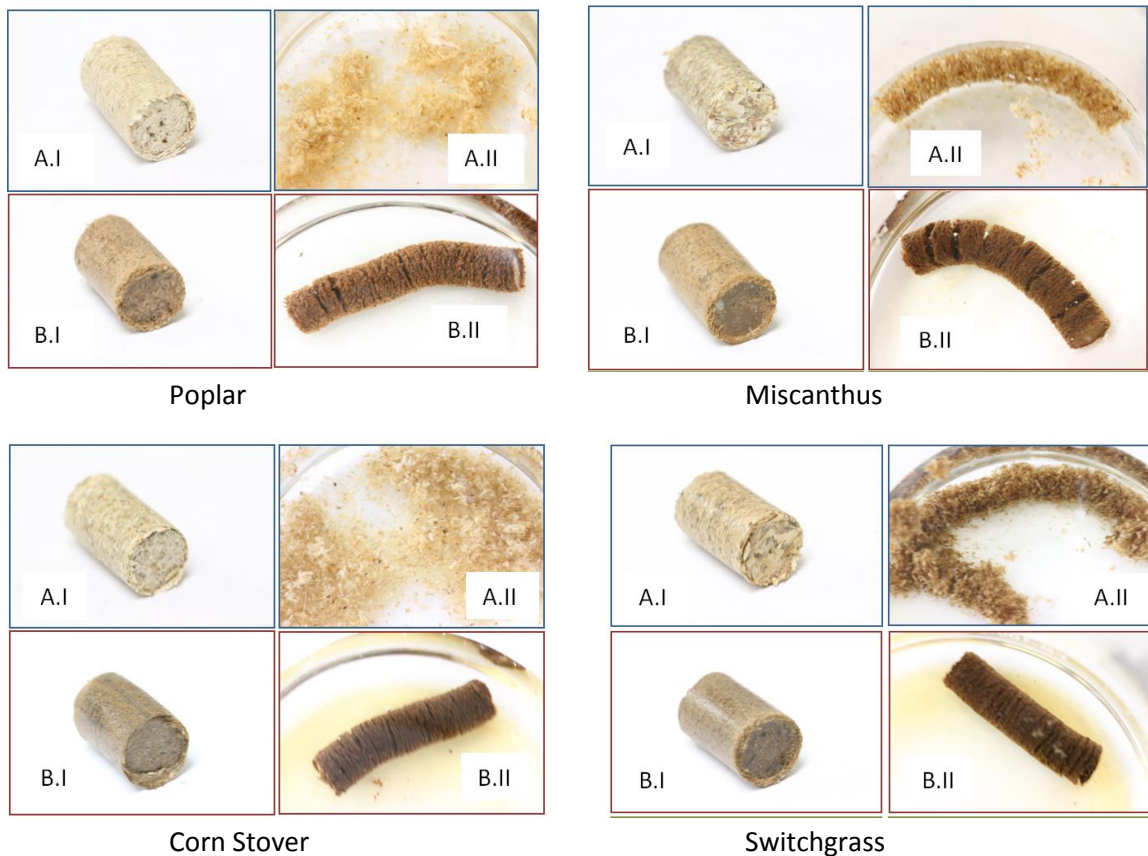
The LHW-treated biomass pellets were also found to have a higher density compared to the original non-treated pellets (Table 9). This may be explained by that these pellets had higher relative amounts

of natural binder through enrichment of lignin. The densities measured were individual pellet density, not the more common bulk density. However, as the pellets size was maintained it was expected to have a similar effect. Both the change in HHV and density were calculated from the treatment (Table 9) and ranged from 5- 12%. Additionally these two increases can be coupled into and an energy density term. This term represents the amount of energy per volume of pelleted biomass, which is of importance for harvest, storage and transportation of the solid fuel. Inspecting the changes to the solid fuel quantity through this lens, it is apparent that an increase of 16 to 25% is possible through the LHW treatment.

**Table 9. Energy and Physical Density Averages and Standard Errors on Pellets made from Non-treated and Liquid Hot Water treated Biomass (Combined Severity Factor of 4.62).**

	HHV (J/g)	Density (g/cm <sup>3</sup> )	Energy Density (J/cm <sup>3</sup> )	Δ HHV (%)	Δ Density (%)	Δ Energy Density (%)
<b>Poplar</b>	1094±15	1.04±0.024	1137±31			
<b>Poplar - LHW treated</b>	1157±10	1.17±0.021	1348±27	5.8%	12.1%	18.5%
<b>Switchgrass</b>	1048±9	1.13±0.018	1182±21			
<b>Switchgrass - LHW treated</b>	1145±10	1.20±0.019	1372±25	9.3%	6.2%	16.1%
<b>Miscanthus</b>	1052±15	1.05±0.012	1105±20			
<b>Miscanthus - LHW treated</b>	1182±15	1.17±0.011	1382±22	12.4%	11.3%	25.1%
<b>Corn Stover</b>	1035±15	1.11±0.019	1152±26			
<b>Corn Stover - LHW treated</b>	1142±19	1.22±0.014	1388±28	10.3%	9.3%	20.5%

Wet durabilities of the biomass were qualitatively assessed by placing pellets in 50 mL of de-ionized water for 4 hours. All four of the untreated biomass pellets swelled within seconds and completely disintegrated, as shown with photos in Figure 18. The liquid hot water treated biomass at the harshest condition did show more wet integrity, swelling slowly over the 4 hours, but remaining intact in beaker. Unfortunately the material became too fragile to allow additional mechanical testing. The results suggest that LHW treatment can improve the wet durability of the pellet by increasing the density and hydrophobicity through extraction of hemicellulose material, but not to a great enough extent to allow the material to have wet strength sufficient to allow uncovered storage.



**Figure 18. Biomass Pellets made from Untreated (A) and LHW Treatment (B) before being immersed in Water (I) and after Immersion for 4 Hours (II).**

### **3.5. Biomass Extraction Summary**

Low cost, available biomass such as agricultural residues are not well suited to thermal conversions such as combustion or gasifying, as their low energy density and high ash can cause operational issues. We used liquid hot water (LHW) treatments to improve the fuel through both an increase in the fuels' energy density and a reduction of ash. Although ash removal is not further enhanced by using harsher treatments to enhance hemicellulose removal, using a liquid hot water treatment did increase the energy density up to 25% of several biomass types and can remove up to 70% of the incoming ash, making a higher quality solid fuel for combustion. The energy density increase was due equally to improvements in heating values as well as the ability to produce higher density pellets due to an enrichment of the natural binders in the material, presumably lignin. The higher binding of the pellet not only created higher density pellets but also more durable pellets with significant gains in dry compressive strength of the pellet as well as qualitative wet integrity. The gains in durability, especially wet durability, would need to be improved to allow uncovered storage.

#### **4. Overall Conclusions**

Thirty-five biomass samples from around Wisconsin were collected and assessed as solid fuel. Based on the testing most of the wood samples were found to have acceptable quality, but most of the herbaceous samples had issues with high ash, chlorine, and sulfur, leading to regulatory and operational issues. Additionally these samples were difficult to pelletize leading to low bulk density creating additional costs for storage and handling. Liquid hot water (LHW) extraction on several samples was shown to be able to remove a significant amount of ash and hemicellulose material. This procedure was able to both improve quality through the inorganic material removal as well as create a material that was easily size reduced and pelleted. This LHW treatment shows promise as the means to improve low quality biomass for solid fuel, although additional research is needed to derive value from the extracted hemicellulose to improve the economics of treatment.



## 5. References

1. Administration, E. I. Official Energy Statistics from the U.S. Government. <http://www.eia.doe.gov>
2. 2010 Wisconsin Energy Statistics. In Wisconsin Office of Energy Independence: Madison, WI, 2010.
3. Seely, R., Charter Street coal plant embarks on its transition to cleaner fuels. *Wisconsin State Journal* 2010.
4. Content, T., Domtar, We Energies to build biomass power plant. *Milwaukee Wisconsin Journal Sentinel* 2011.
5. Release, D. E. P., DTE Stoneman Station Biomass Power Plant Online. In <http://dteenergy.mediaroom.com/index.php?s=26817&item=72236>, 2010.
6. Nussbaumer, T., Combustion and Co-combustion of Biomass: Fundamentals, Technologies, and Primary Measures for Emission Reduction. *Energy & Fuels* **2003**, 17, (3).
7. Energy, U. S. D. o. Energy Efficiency and Renewable Energy. <http://www1.eere.energy.gov/biomass/about.html>
8. van Loo, S.; Koppejan, J., *The Handbook of Biomass Combustion and Co-firing*. Earthscan: Sterling, VA, 2008; p xix, 442 p.
9. Permchart, W.; Kouprianov, V. I., Emission performance and combustion efficiency of a conical fluidized-bed combustor firing various biomass fuels. *Bioresource Technology* **2004**, 92, (1), 83-91.
10. Obernberger, I.; Thek, G., Physical characterisation and chemical composition of densified biomass fuels with regard to their combustion behaviour. *Biomass and Bioenergy* **2004**, 27, (6), 653-669.
11. Munir, S.; Nimmo, W.; Gibbs, B. M., Co-combustion of Agricultural Residues with Coal: Turning Waste into Energy. *Energy & Fuels* **2010**, 24, (3), 2146-2153.
12. Nussbaumer, T., Combustion and Co-combustion of Biomass: Fundamentals, Technologies, and Primary Measures for Emission Reduction†. *Energy & Fuels* **2003**, 17, (6), 1510-1521.
13. Obernberger, I.; Brunner, T.; Bärnthaler, G., Chemical properties of solid biofuels--significance and impact. *Biomass and Bioenergy* **2006**, 30, (11), 973-982.
14. Jenkins, B. M.; Baxter, L. L.; Miles, T. R., Combustion properties of biomass. *Fuel Processing Technology* **1998**, 54, (1-3), 17-46.
15. Ryu, C.; Yang, Y. B.; Khor, A.; Yates, N. E.; Sharifi, V. N.; Swithenbank, J., Effect of fuel properties on biomass combustion: Part I. Experiments--fuel type, equivalence ratio and particle size. *Fuel* **2006**, 85, (7-8), 1039-1046.
16. Kaliyan, N.; R., M., Densification characteristics of corn stover and switchgrass. *ASABE* **2006**, 52, (3), 23.
17. Kaliyan, N.; Morey, R., Roll Press Briquetting and Pelleting of Corn Stover and Switch grass. *ASABE* **2008**, 52, (3), 12.
18. Balatinecz, J. J., The potential role of densification of biomass utilization. *Biomass Utilization* **1983**, 67, 9.
19. Perez, J.; Munoz-Dorado, J.; de la Ruidia, T.; Martiane, J., Biodegradation and biological treatments of cellulose, hemicellulose and lignin: an overview. *Int Microbiol* **2002**, 5, 10.
20. Rhén, C.; Öhman, M.; Gref, R.; Wästerlund, I., Effect of raw material composition in woody biomass pellets on combustion characteristics. *Biomass and Bioenergy* **2007**, 31, (1), 66-72.
21. Demirbas, A., Effects of Moisture and Hydrogen Content on the Heating Value of Fuels. *Energy Sources Part A: Recovery, Utilization & Environmental Effects* **2007**, 29, (7), 649-655.
22. Porteiro, J.; Patiño, D.; Collazo, J.; Granada, E.; Moran, J.; Miguez, J. L., Experimental analysis of the ignition front propagation of several biomass fuels in a fixed-bed combustor. *Fuel* **2010**, 89, (1), 26-35.
23. Boyle, G., *Renewable Energy: Power for a Sustainable Future*. 2nd ed.; Oxford University Press: New York, 2004; p 452.

24. Michelsen, H. P.; Frandsen, F.; Dam-Johansen, K.; Larsen, O. H., Deposition and high temperature corrosion in a 10 MW straw fired boiler. *Fuel Processing Technology* **1998**, 54, 95-108.
25. Nielsen, H. P.; Frandsen, F. J.; Dam-Johansen, K.; Baxter, L. L., The implications of chlorine-associated corrosion on the operation of biomass-fired boilers. *Progress in Energy and Combustion Science* **2000**, 26, 283-298.
26. Riedl, R.; Dahl, J.; Obernberger, I.; Narodoslowsky, M., Corrosion in fire tube boilers of biomass combustion plants. In *Proceedings of the China International Corrosion Control Conference*, Beijing, China, 1999.
27. Agency, U. S. E. P. Pollutants. <http://www.epa.gov/oms/invntory/overview/pollutants/index.htm> (July 5, 2010),
28. van Loo, S.; Koppejan, J., *The Handbook of Biomass Combustion and Co-firing*. Earthscan: Sterling, VA, 2008; p 442.
29. EPA Pollutants. <http://www.epa.gov/oms/invntory/overview/pollutants/index.htm> (July 5, 2010),
30. Demirbas, A., Combustion characteristics of different biomass fuels. *Progress in Energy and Combustion Science* **2004**, 30, (2), 219-230.
31. Werther, J.; Saenger, M.; Hartge, E. U.; Ogada, T.; Siagi, Z., Combustion of agricultural residues. *Progress in Energy and Combustion Science* **2000**, 26, (1), 1-27.
32. Demirbas, A., Calculation of higher heating values of biomass fuels. *Fuel* **1997**, 76, (5), 431-434.
33. Grammelis, P., *Solid Biofuels for Energy: A Lower Greenhouse Gas Alternative*. Springer: New York, 2011; p 241.
34. Monti, A.; Di Virgilio, N.; Venturi, G., Mineral composition and ash content of six major energy crops. *Biomass and Bioenergy* **2008**, 32, (3), 216-223.
35. Livingston, W. R. *Biomass ash characteristics and behaviour in combustion, gasification and pyrolysis systems*; Doosan Babcock Energy: 2005; p 69.
36. Hinckley, J.; Doshi, K. Emission Controls for Small Wood-Fired Boilers. [http://www.wflccenter.org/news\\_pdf/361\\_pdf.pdf](http://www.wflccenter.org/news_pdf/361_pdf.pdf) (12/10/2010),
37. McKendry, P., Energy production from biomass (part 1): overview of biomass. *Bioresource Technology* **2002**, 83, (1), 37-46.
38. Lewandowski, I.; Kicherer, A., Combustion quality of biomass: practical relevance and experiments to modify the biomass quality of *Miscanthus x giganteus*. *European Journal of Agronomy* **1997**, 6, (3-4), 163-177.
39. EPA Mercury: Basic Information. <http://www.epa.gov/hg/about.htm>
40. EPA National Emission Standards for Hazardous Air Pollutants for Major Sources: Industrial, Commercial, and Institutional Boilers and Process Heaters. <http://www.epa.gov/airquality/combustion/docs/20111202msboilerproposal.pdf> (12/9/2011),
41. EPA Controlling Power Plant Emissions: Overview. [http://www.epa.gov/hg/control\\_emissions/index.htm](http://www.epa.gov/hg/control_emissions/index.htm) (12/5/2011),
42. Mentz, K.; Pinkerton, J.; Louch, J., Potential mercury and hydrochloric acid emissions from wood fuels. *Forest Products Journal* **2005**, 55, (2), 46-50.
43. Hoyer, M.; Baldauf, R. W.; Scarbro, C.; Barres, J.; Keeler, G. J. Mercury Emissions from Motor Vehicles. (12/5/2011),
44. Jenkins, B. M.; Baxter, L. L.; Miles Jr, T. R.; Miles, T. R., Combustion properties of biomass. *Fuel Processing Technology* **1998**, 54, (1-3), 17-46.
45. P.C.A, B., et al, *Torrefaction for biomass co-firing in existing coal-fired power stations "BIOCOAL"*. Energy research Centre of the Netherlands (ECN): **2005**.
46. Arias, B., et al, *Influence of torrefaction on the grindability and reactivity of woody biomass*. *Fuel Processing Technology* **2008**, 89, (2).

47. Bridgeman, T. G.; Jones, J. M.; Shield, I.; Williams, P. T., Torrefaction of reed canary grass, wheat straw and willow to enhance solid fuel qualities and combustion properties. *Fuel* **2008**, *87*, (6), 844-856.
48. Prins, M. J.; Ptasinski, K. J.; Janssen, F. J. J. G., Torrefaction of wood: Part 1. Weight loss kinetics. *Journal of Analytical and Applied Pyrolysis* **2006**, *77*, (1), 28-34.
49. Prins, M. J.; Ptasinski, K. J.; Janssen, F. J. J. G., Torrefaction of wood: Part 2. Analysis of products. *Journal of Analytical and Applied Pyrolysis* **2006**, *77*, (1), 35-40.
50. Turn, S. Q.; Kinoshita, C. M.; Ishimura, D. M., Removal of inorganic constituents of biomass feedstocks by mechanical dewatering and leaching. *Biomass & Bioenergy* **1997**, *12*, (4), 241-252.
51. Dayton, D. C.; Jenkins, B. M.; Turn, S. Q.; Bakker, R. R.; Williams, R. B.; Belle-Oudry, D.; Hill, L. M., Release of inorganic constituents from leached biomass during thermal conversion. *Energy & Fuels* **1999**, *13*, (4), 860-870.
52. Raveendran, K.; Ganesh, A.; Khilar, K. C., Pyrolysis characteristics of biomass and biomass components. *Fuel* **1996**, *75*, (8), 987-998.
53. Jorgensen, U.; Sander, B., Biomass requirements for power production: How to optimise the quality by agricultural management. *Biomass & Bioenergy* **1997**, *12*, (3), 145-147.
54. Jenkins, B. M.; Bakker, R. R.; Wei, J. B., On the properties of washed straw. *Biomass & Bioenergy* **1996**, *10*, (4), 177-200.
55. Jenkins, B. M.; Mannapperuma, J. D.; Bakker, R. R., Biomass leachate treatment by reverse osmosis. *Fuel Processing Technology* **2003**, *81*, (3), 223-246.
56. Liu, X. L.; Bi, X. T. T., Removal of inorganic constituents from pine barks and switchgrass. *Fuel Processing Technology* **2011**, *92*, (7), 1273-1279.
57. Davidsson, K. O.; Korsgren, J. G.; Pettersson, J. B. C.; Jaglid, U., The effects of fuel washing techniques on alkali release from biomass. *Fuel* **2002**, *81*, (2), 137-142.
58. Fahmi, R.; Bridgwater, A.; Donnison, I.; Yates, N.; Jones, J. M., The effect of lignin and inorganic species in biomass on pyrolysis oil yields, quality and stability. *Fuel* **2008**, *87*, (7), 1230-1240.
59. Jensen, P. A.; Sander, B.; Dam-Johansen, K., Removal of K and Cl by leaching of straw char. *Biomass & Bioenergy* **2001**, *20*, (6), 447-457.
60. Jensen, A.; Dam-Johansen, K.; Wojtowicz, M. A.; Serio, M. A., TG-FTIR study of the influence of potassium chloride on wheat straw pyrolysis. *Energy & Fuels* **1998**, *12*, (5), 929-938.
61. Suzuki, T.; Deguchi, K.; Kimura, Y.; Funaki, M.; Yamada, T., Hydrogasification of wood for high heating-value gas production X: Effect of pretreatment of Japanese oak bark by HNO<sub>3</sub> oxidation on subsequent iron-catalyzed hydrogasification. *Journal of Wood Science* **1999**, *45*, (1), 76-83.
62. Yu, Y.; Wu, H. W., Understanding the Primary Liquid Products of Cellulose Hydrolysis in Hot-Compressed Water at Various Reaction Temperatures. *Energy & Fuels* **2010**, *24*, 1963-1971.
63. Pu, Y.; Treasure, T.; Gonzalez, R.; Venditti, R.; Jameel, H., AUTOHYDROLYSIS PRETREATMENT OF MIXED HARDWOODS TO EXTRACT VALUE PRIOR TO COMBUSTION. *Bioresources* **2011**, *6*, (4), 4856-4870.
64. Ingram, T.; Rogalinski, T.; Bockemuhl, V.; Antranikian, G.; Brunner, G., Semi-continuous liquid hot water pretreatment of rye straw. *Journal of Supercritical Fluids* **2009**, *48*, (3), 238-246.
65. Yu, Q.; Zhuang, X. S.; Yuan, Z. H.; Wang, Q.; Qi, W.; Wang, W.; Zhang, Y.; Xu, J. L.; Xu, H. J., Two-step liquid hot water pretreatment of Eucalyptus grandis to enhance sugar recovery and enzymatic digestibility of cellulose. *Bioresource Technology* **2010**, *101*, (13), 4895-4899.
66. Perez, J. A.; Ballesteros, I.; Ballesteros, M.; Saez, F.; Negro, M. J.; Manzanares, P., Optimizing Liquid Hot Water pretreatment conditions to enhance sugar recovery from wheat straw for fuel-ethanol production. *Fuel* **2008**, *87*, (17-18), 3640-3647.
67. Zhang, C.; Runge, T., Fractionating Pentosans and Hexosans in Hybrid Poplar. *Industrial & Engineering Chemistry Research* **2011**, *51*, (1), 133-139.

68. Mok, W. S. L.; Antal, M. J., UNCATALYZED SOLVOLYSIS OF WHOLE BIOMASS HEMICELLULOSE BY HOT COMPRESSED LIQUID WATER. *Industrial & Engineering Chemistry Research* **1992**, 31, (4), 1157-1161.
69. Yu, G.; Yano, S.; Inoue, H.; Inoue, S.; Endo, T.; Sawayama, S., Pretreatment of Rice Straw by a Hot-Compressed Water Process for Enzymatic Hydrolysis. *Applied Biochemistry and Biotechnology* **2010**, 160, (2), 539-551.
70. Amidon, T. E.; Liu, S., Water-based woody biorefinery. *Biotechnology Advances* **2009**, 27, (5), 542-550.
71. Liu, S. J.; Mishra, G.; Amidon, T. E.; Gratien, K., Effect of Hot-Water Extraction of Woodchips on the Kraft Pulping of Eucalyptus Woodchips. *Journal of Biobased Materials and Bioenergy* **2009**, 3, (4), 363-372.
72. Duarte, G. V.; Ramarao, B. V.; Amidon, T. E.; Ferreira, P. T., Effect of Hot Water Extraction on Hardwood Kraft Pulp fibers (Acer saccharum, Sugar Maple). *Industrial & Engineering Chemistry Research* **2011**, 50, (17), 9949-9959.
73. Lu, H. F.; Hu, R. F.; Ward, A.; Amidon, T. E.; Liang, B.; Liu, S. J., Hot-water extraction and its effect on soda pulping of aspen woodchips. *Biomass & Bioenergy* **2012**, 39, 5-13.
74. Zhang, C.; Runge, T., Fractionating pentosans and hexosans in hybrid poplar. *Industrial and Engineering Chemistry Research* **2012**, 51, (1), 133-139.