

Lowering Ash Content of Biomass Using Hot-Water Extraction (HWE) and Hot-Water Extracted Lignin

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Lowering Ash Content of Biomass Using Hot-Water Extraction (HWE) and Hot-Water Extracted Lignin

Final Report: Part I

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Abstract

Lignocellulosic biomass (LCB) is a renewable resource that is an alternative to coal and petroleum. Hot water extraction (HWE) is a process that removes mostly xylan-based hemicelluloses. Lignin can be recovered from HWE and utilized in other applications. Pelletizing can improve the handling and transportation of LCBs for commercial use. However, fuel pellets pose health hazards due to the accumulation of carbon monoxide in storage.

This research examines the impact of HWE on shrub willow, miscanthus, and wheat straw as LCBs and as fuel pellets. Lignin is also recovered from the HWE process and its efficacy in biomaterial products is examined.

HWE resulted in a material with a lower ash and carbohydrate content, and a higher energy, lignin, and cellulose content. Pellets were made from nearly all LCBs and HWEed LCBs on the pilot scale. HWEed LCB pellets had lower ash and higher energy contents. HWEed LCB pellets exhibited more resistance to moisture absorption. Results regarding the impact of HWE on durability, bulk density, and pellet length were inconclusive and more work is needed. Carbon monoxide off-gassing of the HWEed LCB pellets was consistently greater than LCB pellets. These emission values were lower than commercially available pellets (softwood/hardwood blend).

Keywords

lignocellulosics, hot water extraction, miscanthus, willow, wheat straw, fuel pellets, lignin, carbon monoxide, delignification

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Acronyms and Abbreviations

ANOVA	Analysis of Variance
GC-MS	Gas Chromatography—Mass Spectroscopy
HPAEC/PAD	High pH Anion-Exchange Chromatography with Pulsed Amperometric Detection
H-NMR	Proton Nuclear Magnetic Resonance
HWE	Hot Water Extraction
HWEed	Hot Water Extracted
HWEed LCB	Hot Water Extracted Lignocellulosic Biomass
ISO	International Organization for Standardization
LCB	Lignocellulosic Biomass (willow, wheat straw, miscanthus)
M/K	Refers to the Company M/K and their Products
TAPPI	Technical Association of the Pulp and Paper Industry

Summary

Biomass is becoming an increasingly important renewable resource for modern society. It is utilized in products and for energy as an alternative to non-renewable resources. However, it can be difficult to use biomass for more advanced products and energy demands. One reason is the natural recalcitrance—or resistance to physical, biological, and chemical degradation—of lignocellulosic materials. Another reason is the difficulty to handle, process, transport, and store these materials. The utilization of treatment processes can address the recalcitrance of lignocellulosics and yield biomass that is easier to process. Treatment byproducts can also provide additional revenue streams for complete utilization of biomass. Pelletization of the biomass can address issues with handling, transporting, and storing compared to other methods of processing, such as wood chips. The storage of these pellets, however, has safety implications due to the buildup of carbon monoxide in storage rooms and tanks. This research focused on the use of hot water extraction (HWE) to treat biomass. The biomass was pelletized to observe the impact of HWE on various pellet properties, including off-gassing of carbon monoxide.

Willow, wheat straw, and miscanthus (lignocellulosic biomass [LCB]) were acquired and hot water was extracted (HWEed) from the biomass. HWE utilizes autohydrolysis to address the recalcitrance of lignocellulosics. HWE was performed on three scales (Table 7) to examine the properties of the HWEed biomass (or HWEed LCB) and determine scaling factors. These included a bench-top scale with a Parr Reactor as a small scale, a M/K Digester as a “intermediate” scale, and a Pilot Digester as a large scale (see Appendix C. Equipment Information for more clarification). The LCB and HWEed LCB were characterized to determine the effects of HWE. Lignin was recovered from the HWE process to be utilized in bioproducts and as an additive in pelletizing. LCB and HWEed LCB were then ground to different particle sizes and pelletized with a laboratory scale and pilot scale pelletizer. The pellets were characterized to determine the impact of HWE on pellet properties.

Overall, there were differences in the ash, lignin content, and carbohydrate content (including cellulose) of HWEed LCB compared to the LCB (Table 9, Table 10). There was a decrease in ash and carbohydrate content (not including cellulose) and an increase in lignin and cellulose content upon HWE. Pelletization of LCB and HWEed LCB was possible utilizing the pilot scale pelletizer, though there were production issues with the HWEed LCB in some cases. Several factors regarding pelletization are examined in this research (Table 5). First are the differences in the lignocellulosic materials prior to HWE. Willow is a

short rotation coppice, miscanthus is an energy crop, and wheat straw is an agricultural residue. Second is the HWE of these LCB. Utilization of different pelletizer dies are observed between a pilot scale flat die and laboratory scale ring die pelletizer (Figure 2, Appendix C. Equipment Information). Particle size distribution is also examined in which the LCB and HWEed LCB were ground with different hammermill screen sizes [6 millimeter (mm), 3 mm, and 1 mm pore/mesh]. The addition of lignin recovered from HWE as an additive was also observed in this project.

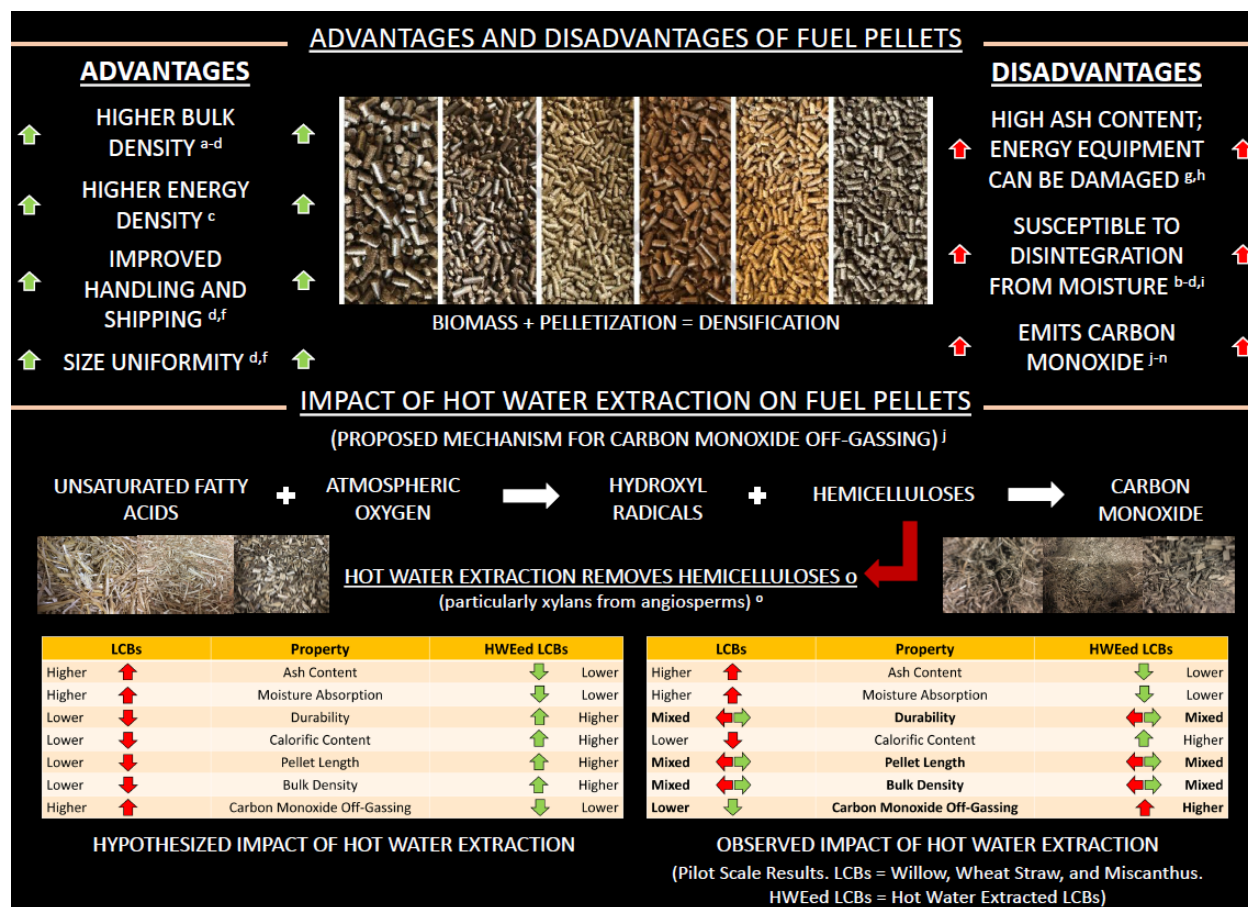
This report covers the results of the pilot scale pelletization of LCB and HWEed LCB with 6 mm and 3 mm biomass particle sizes. Future updates will include results of laboratory scale pelletization of LCB and HWEed LCB with 3 mm and 1 mm biomass particle sizes, as well as the impact of lignin addition.

The pellets made from HWEed LCB had a lower ash content, higher energy value, and less moisture absorption compared to LCB pellets, with many of these being statistically significant differences with ANOVA (Analysis of Variance) analysis (Table 21). Impacts of HWE on durability, bulk density, and pellet length were inconsistent with the current results. HWEed LCB pellets produced more carbon monoxide compared to LCB pellets on a consistent basis. LCB and HWEed LCB produced less carbon monoxide than commercially available pellets containing a hardwood/softwood blend.

A summary of the fuel pellet research, proposed mechanism for carbon monoxide off-gassing,¹ the anticipated impacts of HWE on pellet properties, and the currently observed impacts of HWE on pellet properties can be seen in Figure S-1.

This work is currently in progress and future updates will expand upon the materials in this report.

Figure S-1. Overall Summary of Fuel Pellet Research Project Based on Pilot Scale Pelletizing Results



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Figure notes continued on the next page.

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1 Background

Biomass—such as lignocellulosic and microbial biomass—are renewable resources that are experiencing increased use for material and energy needs. Current research on lignocellulosic biomass focuses on the creation of materials and energy that can function as an alternative to non-renewable resources, such as coal and petroleum-based products. However, the utilization of biomass as a more complex material and energy source can be difficult. Lignocellulosics consist of cellulose, hemicelluloses, lignin, and other compounds that form natural recalcitrance or resistance to biological, physical, and chemical attack.² As such, biomass requires treatment to break the material into its constituents for further processing into products. These products can include platform chemicals, biomaterials, and energy.

Hot water extraction (HWE) is one method of treatment studied at State University of New York, College of Environmental Science and Forestry (SUNY-ESF) that employs autohydrolysis to disrupt the lignocellulosic matrix in biomass.³ This process utilizes hot water and pressure to induce a mildly acidic environment from the natural response of acetylated compounds in the biomass to the water, reducing the need for additional chemicals compared to other methods of pretreatment.^{3,4} This is beneficial as resources do not need to be allocated toward the purchase, transport, storage, and disposal of chemicals on the production site compared to other methods of lignocellulosic treatment [such as dilute acid pretreatment (DAP) with sulfuric or hydrochloric acid, or alkaline treatment with sodium hydroxide (NaOH)²]. With HWE, hemicelluloses—mainly xylans—tend to be targeted and removed from the biomass along with other compounds like inorganics and some lignin.⁴ However, this lignin can be recovered with acidification of the hydrolysate. This lignin can then be utilized in a variety of applications, such as hydrogels,⁵ polymer blends,⁵ adhesives,⁶ and as an additive for other biomaterials. HWE works more efficiently on angiosperms like hardwoods compared to gymnosperms like softwoods due to differences in the hemicelluloses and the natural components of hardwoods and softwoods.

However, utilizing biomass for material and energy applications faces an additional hurdle: dealing with transportation, processing, storing, and transportation costs. Biomass, compared to other fuel types like coal, typically has a lower bulk density in chip, chopped, or baled form, which can make transportation expensive relative to current fuels.^{7,8} Additionally, biomass tends to have size and shape variation when chipped, cut, or chopped, which can make handling and processing more difficult and costly.^{9,10}

Pelletizing addresses this issue by increasing the bulk density of biomass and providing a more uniform material that is easier to ship, handle, and store compared to wood chips, which are

commonly used in modern applications.^{8,10–13} Storing a large amount of this densified biomass in storage enclosures creates safety hazards and risks due to the accumulation of carbon monoxide in poorly ventilated areas,^{14,15} presenting another challenge to utilizing biomass. This can and has resulted in both injury and death to those in contact with wood pellet storage areas.^{14,15}

It is hypothesized that the carbon monoxide off-gassing reaction mechanism involves the autoxidation of fatty acids naturally present in biomass with oxygen in the atmosphere to produce radicals.¹ These radicals then react with hemicelluloses in the biomass to create carbon monoxide.¹ In a recent study, it was shown that hemicelluloses—particularly a sample utilizing xylan-based compounds—were involved in the production of carbon monoxide compared to cellulose, which remained rather inert.¹

In this study, we first measure the characteristics of willow, wheat straw, and miscanthus (LCB). The HWE process is then applied on multiple scales (Table 7), including a Pilot Scale (Figure 1, Appendix C. Equipment Information). The hot water extracted LCB (HWEed LCB) is then characterized for ash, lignin content, carbohydrate content, cellulose content, and other properties to determine the effect of HWE (Table 9, Table 10). Lignin is also recovered from the HWE of willow, miscanthus, and wheat straw, characterized for similar properties (Table 14), and utilized in lignin-based biomaterial research^{5,6} and as an additive to pellets.

LCB and HWEed LCB are then pelletized with different hammermill screen sizes and with different pelletizers (Figure 2) to examine the effect of HWE on fuel pellet properties, including the off-gassing of carbon monoxide (CO) (Figure 3). Moisture content, ash content, energy content, moisture absorption, bulk density, durability, pellet length and density, and CO off-gassing are measured (Table 5, Table 21). These are compared to commercially available fuel pellets (hardwood/softwood blend).

Additional work in the use of recovered lignin from HWE of willow as an additive to fuel pellets is also examined. The novelty of this research includes the HWE of willow, wheat straw, and miscanthus; the utilization of HWE recovered lignin in a variety of products; the pelletization of HWEed wheat straw and miscanthus using two pelletizers of different designs and capacities; and the study of CO off-gassing properties of LCB and HWEed LCB. Several publications, posters, conferences, and dissertations/theses have been developed due to this work, with additional publications to be completed.

This work is ongoing and will be updated further in the future.

2 Methods and Materials

2.1 Obtaining Biomass Feedstocks

Three types of biomasses were obtained for use in this project (Table 1); a short rotation coppice, an energy crop, and an agricultural residue.

Table 1. Lignocellulosics Utilized in Research Project

Lignocellulosic	Scientific Name	Source
Shrub Willow	<i>Salix</i> sp. ^a	<i>Dr. Tim Volk, SUNY-ESF, Tully Field Station</i> Unknown Cultivar from Family 9882 (2016) Mixed Cultivars (2021)
Miscanthus	<i>Miscanthus</i> sp. ^b	<i>Mesa Bioenergy Services, LLC</i> Batches: Miscanthus-2012 Miscanthus-2015
Wheat Straw	<i>Triticum</i> sp. ^a	<i>Mesa Bioenergy Services, LLC</i>

^{a.} Nagardeolekar A, Ovadias M, Wang K-T, Bujanovic B. Willow Lignin Recovered from Hot-Water Extraction for the Production of Hydrogels and Thermoplastic Blends. *ChemSusChem*. 2020;13(17):4702–4721. <http://doi.org/10.1002/cssc>. doi:10.1002/cssc

^{b.} Wang K-T, Jing C, Wood C, Nagardeolekar A, Kohan N, Dongre P, Amidon T, Bujanovic B. Toward complete utilization of miscanthus in a hot-water extraction-based biorefinery. *Energies*. 2018;11(1). doi:10.3390/en11010039

Willow was chipped (2 cm long pieces) without bark removal. Miscanthus and wheat straw were chopped (<1.9 cm). All biomass was stored either in the Department of Chemical Engineering at SUNY-ESF or the SUNY-ESF Tully Field Station in supersacks.

2.2 Hot Water Extraction of Lignocellulosic Feedstocks

Hot water extraction (HWE) was performed on willow, miscanthus, and wheat straw (LCB) in three scales (Table 2). The laboratory scale utilized a Parr reactor with biomass ground in a Wiley Mill at 15 mesh. Results concerning the yield of solid residue from the initial Parr Reactor experiments can be found in Table 6. The “middle” scale or intermediate scale digester was an M/K Digester that served as the bridge between the laboratory and pilot scale extractions. The Pilot Scale Digester (Figure 1) utilized biomass directly unloaded from the supersacks to perform HWE on a large scale. A comparison of the

various conditions between the scales regarding miscanthus as an example can be found in Table 7. More information about the operating conditions, yield, and extract pH of the Pilot Plant Digester experiments can be found in Table 8. More information about the HWE equipment can be found in Appendix C. Equipment Information. All equipment was located in the Department of Chemical Engineering at SUNY-ESF.

Table 2. Scales of Hot Water Extraction in Research Project

Information about equipment can be found in Appendix C. Equipment Information.

Digester	Scale	Operating Conditions
Parr Reactor	Laboratory/Benchtop	1 Hour, 160°C: Miscanthus-2015
		2 Hour, 160°C: All Except Mixed Cultivar Willow
M/K Digester	Middle/Intermediate	2 Hour, 160°C: Miscanthus
Struthers-Well Pilot Digester	Pilot/Large	1 Hour, 160°C: Wheat Straw
		2 Hour, 160°C: All LCB

The process of HWE in the Pilot Scale digester occurred over three days. Biomass was first loaded into the digester after determining the moisture content of the biomass for solid-loading and moisture-loading information. Then, water was added to the system to achieve a specific liquid-to-biomass ratio, depending on the biomass (Table 8). After loading, the HWE process occurred. The hydrolysate was discharged, and the biomass was washed with tap water and cooled prior to removal from the digester (Figure 1). Finally, the biomass was spread to dry over several days and turned periodically to minimize biological growth and improve drying.

Two Pilot Scale HWEs of miscanthus occurred in January 2016. The operating conditions, digester yield, and extract pH from the miscanthus trials can be seen in Table 7. A Pilot Scale HWE of wheat straw was performed in March 2016 and May 2016 at two operating conditions (Table 2). This was due to differences in cellulose loss with the two-hour process. However, lack of successful xylan removal at the one-hour condition resulted in a third Pilot Scale HWE of wheat straw in May 2016. A Pilot Scale HWE of willow was performed in June 2016. Additional HWE of wheat straw and willow occurred in May 2017 and June 2021, respectively.

The hydrolysate discharged after HWE was either diluted for disposal or collected for lignin recovery. Upon cooling, concentrated sulfuric acid was carefully added to the hydrolysate and stirred until a pH range of approximately 2.0–2.3 was reached. For this process, the pH should be lowered to a point below 2.5 to neutralize the lignin functional groups for precipitation. However, the pH should not drop below

2.0 to preserve the lignin structure and prevent degradation. So long as the pH is within this range, satisfactory precipitation will occur. The acidified hydrolysate was then left for several days undisturbed to allow the lignin to precipitate and settle on the bottom of the storage containers. The remaining hydrolysate was then decanted, and the lignin was recovered using a combination of scraping and acetone water (9:1) to collect the lignin. This process of loading, cooking, discharging, drying, and lignin recovery in the Pilot Plant Scale was applied similarly to wheat straw and willow biomass with minor modifications (Table 8).

Figure 1. Pilot Scale Hot Water Extraction Process

Pictured left (A and B) is the Pilot Scale Reactor loaded with wheat straw in the May 2017 HWE. The hydrolysate (C) was collected and acidified to precipitate lignin. This lignin is recovered (D), washed, and dried (E) prior to utilizing in lignin materials and applications. The HWEed LCB is air dried and collected for further use (F). The HWEed LCB are in the containers to the right. From top to bottom, the LCB and HWEed LCB are wheat straw, miscanthus, and willow.



2.3 Chemical Characterization of Lignocellulosic Feedstocks and Lignin

Chemical characteristics of the LCB and HWEed LCB were examined (Table 3). The methods used for characterization are referenced and described in previous work⁴ but are summarized below.

Table 3. Biomass Properties and Methods Utilized for Characterization

H-NMR = Proton Nuclear Magnetic Resonance. HPAEC/PAD = High pH Anion-Exchange Chromatography with Pulsed Amperometric Detection. TAPPI = Technical Association of the Pulp and Paper Industry.

Biomass Property	Method of Characterization
Extractives Content	TAPPI Standard T-204 ^a
Cellulose Content	Seifert's Method ^b
Lignin Content	Klason Lignin Method ^c Acetyl Bromide Method ^d
Carbohydrate Analysis	Acid Hydrolysis and ¹ H-NMR ^e HPAEC/PAD ^f
Ash Content	TAPPI Standard T-413 ^g
Phenolic Hydroxyl Group Content	Periodate Oxidation Method with ¹ H-NMR ^e

- a. Technical Association of the Pulp and Paper Industry. T 204 Solvent extractives of wood and pulp. TAPPI Standard Methods. 2007;cm(-07):1-4.
- b. Wright P, Wallis A. Rapid determination of cellulose in plantation eucalypt woods to predict kraft pulp yields. TAPPI Journal. 1998;81(2):124-128.
- c. Corbett D, Mante O, Bujanovic B. Toward valorization of lignin: Characterization and fast pyrolysis of lignin recovered from hot-water extracts of electron-beam irradiated sugar maple. Tappi Journal. 2017;16:213-226. doi:10.32964/TJ16.4.213
- d. Fukushima R, Hatfield R. Comparison of the Acetyl Bromide Spectrophotometric Method with Other Analytical Lignin Methods for Determining Lignin Concentration in Forage Samples. Journal of Agricultural and Food Chemistry. 2004;52(12):3713-3720. <https://doi.org/10.1021/jf035497l>. doi:10.1021/jf035497l
- e. Wang K-T, Jing C, Wood C, Nagardeolekar A, Kohan N, Dongre P, Amidon T, Bujanovic B. Toward complete utilization of miscanthus in a hot-water extraction-based biorefinery. Energies. 2018;11(1). doi:10.3390/en11010039
- f. Davis M. A rapid modified method for compositional carbohydrate analysis of lignocellulosics by high pH anion-exchange chromatography with pulsed amperometric detection (HPAEC/PAD). Journal of Wood Chemistry and Technology. 1998;18(2):235-252. doi:10.1080/02773819809349579
- g. Technical Association of the Pulp and Paper Industry. T 413 Ash in wood, pulp, paper and paperboard: combustion at 900°C. TAPPI Standard Methods. 2017;om (-17):1-5.

2.3.1 Extractives Content

Extractives content was determined in accordance to Technical Association of the Pulp and Paper Industry (TAPPI) Standard T-204.¹⁶ All biomass samples were extracted via the Soxhlet method using either ethanol:toluene (1:2 ratio) or dichloromethane (DCM). This organic-solvent pre-extracted biomass (or extractive-free biomass) was used for lignin and cellulose measurements.

2.3.2 Seifert Cellulose

The cellulose content in the biomass was determined on extractive-free samples by Seifert's method.¹⁷ The amount of residual lignin in Seifert cellulose was determined by the acetyl bromide method.¹⁹ The reported results are an average of two experiments.

2.3.3 Lignin Content

Klason lignin (or acid-insoluble lignin) and acid-soluble lignin for the biomass and the recovered lignin samples were measured using a modified Klason lignin method.¹⁸ In this method, samples were sonicated for one hour in 72% sulfuric acid at room temperature in contrast to the standard method which includes occasional stirring of the mixtures at room temperature without sonication. The reported results are an average of three experiments.

2.3.4 Carbohydrate Analysis

Carbohydrates in biomass were examined with the use of ¹H-NMR with glucosamine used as an internal standard. Prior to analysis, biomass was exposed to acid hydrolysis by placing extractive-free biomass in a sonicator (Appendix C) with 72% sulfuric acid. Sonication occurred for one hour at room temperature. Afterwards, DI water was added to dilute the acid to 4%. The mixture was then placed in a hot water bath for one hour at 80 °C. Intermittent mixing whilst in the hot water bath occurred as well. The mixture was filtered, and the filtrates were analyzed for carbohydrate content. The reported results are an average of two experiments.

A different process was utilized for examining carbohydrates in lignin recovered from HWE. Acid-hydrolysate resulting from the Klason lignin determination process were collected for carbohydrate analysis. Samples analyzed through the USDA-FPL (United States Department of Agriculture–Forest Products Lab).²⁰

2.3.5 Ash Content

The ash content of the biomass and recovered lignin samples was determined in accordance with TAPPI Standard T-413,²¹ which requires combustion of samples at 900 °C. The reported results are an average of three experiments.

2.3.6 Phenolic Hydroxyl Group Content Analysis

The phenolic hydroxyl group content (PhOH group) was measured for the biomass and recovered lignin samples using a periodate oxidation method. For biomass, 400 mg of sample was used, whereas only 50 mg of sample was used when examining isolated lignin. The quantification of the resulting methanol from the procedure was performed with ¹H-NMR run under the same conditions as the carbohydrate analysis.⁴ Duplicates (two experiments) were performed for this analysis.

2.3.7 Fatty Acid Characterization of Biomass

Stored extractives samples were analyzed for fatty acid content via Gas Chromatography–Mass Spectrometry (GC-MS) at the Analytical & Technical Services (ATS) at SUNY-ESF. Information about the GC-MS and settings used can be found in Appendix C. The fatty acids examined were stearic acid, oleic acid, linoleic acid, and linolenic acid (Figure 4). Palmitic acid (hexadecanoic acid or C16:0) and stearic acid (octadecanoic acid of C18:0) were representative saturated fatty acids, and oleic acid (9-octadecanoic acid or C18:1, cis-9) and linoleic acid (9,12-octadecanoic acid or C18:2 cis-9,12) were representative unsaturated fatty acids. These fatty acids were chosen based upon research by Rahman and Hopke¹ in which high concentrations of C18:0, C18:1 cis, C18:2 cis, and C16:0 fatty acids were found in lignocellulosic biomass that was analyzed for CO off-gassing.

Prior to GC-MS analysis, extractives were air dried to evaporate their respective extraction solvent (hexane, ethanol:toluene (1:2) [ET], or ethanol). Then, the residues were further dried in a vacuum oven (40°C ± 5°C). After drying and cooling, an average of 11 mg of each residue were collected for analysis. Residues were placed into amber glass GC-MS vials and 1.5 milliliter (mL) of their respective extraction solvent was added to the vials.

Alongside extractive residue samples, standards containing saturated fatty acids (stearic and palmitic acid), unsaturated fatty acids (oleic and linoleic acid), and the internal standard (0.5 mg of tetracosane) were prepared to establish elution times and peaks in the GC-MS. Standards were created with 2 mg of each fatty acid (0.5 mg of each for the combined standard (#6) and 0.5 mg of tetracosane. Residues contained 0.05 mg of tetracosane. Tetracosane was used as an internal standard based upon previous studies examining fatty acid content of lignocellulosic biomass.^{22,23}

2.3.8 Elemental Composition of Biomass

The elemental composition (carbon, nitrogen, hydrogen, oxygen, and sulfur) of LCB and HWEed LCB was analyzed. Lignocellulosic biomass samples were prepared by grinding the LCB in an Arthur Thomas Co. Wiley Mill (Philadelphia, PA) with a 30-mesh screen (0.595 mm). The LCB samples were dried in a vacuum oven at 40°C and stored in sealed scintillation vials. Samples were submitted to Midwest MicroLab (Indianapolis, IN) for elemental analysis. Information about the testing methods provided by the company can be found in Appendix D. Midwest MicroLab Testing Procedures.

2.3.9 Characterization of Lignin

The chemical composition of the lignin recovered from the HWE of willow (RecL), wheat straw, and miscanthus was examined in this work. RecL was added to hammermilled willow as a binding agent prior to pelletizing. Commercially available softwood lignin (LignoBoost, obtained from Domtar, North Carolina, courtesy of Zhiyong Cai of the USDA-FPL) was also provided for addition to hammermilled willow for laboratory scale pelletizing. Characteristics of similar lignin from the same company and location are referenced based upon work done by Hu et. Al.,²⁴ with additional literature values for other lignin properties (Table 14).

The moisture content, ash content, and energy content of RecL and ComL were also measured. Prior to characterization, RecL was ground in a coffee grinder to a fine powder instead of milling the lignin to a specific mesh. ComL was already in powder form and was used as received. Moisture content was measured using a modified version of TAPPI Standard T-412²⁵ (see Appendix A. Modifications to Testing Methods). Ash was measured in accordance with TAPPI Standard T-413.²¹

Energy content was measured with the modified version of the International Organization for Standardization (ISO) 18125²⁶ method utilized to test the energy content of fuel pellets (see Appendix A. Modifications to Testing Methods). Two additional modifications were made to this method compared to that followed for the fuel pellets, which are also described in Appendix A. Modifications to Testing Methods.

Additional analysis of the lignin for elemental composition (carbon, nitrogen, hydrogen, oxygen, and sulfur) was also performed. Information about the testing methods provided by the company can be found in Appendix D. Midwest Microlab Testing Procedures. Three samples of lignin were prepared for elemental analysis. The ComL was collected as received, dried in a vacuum oven at $40^{\circ}\text{C}\pm 5^{\circ}\text{C}$, and stored in a scintillation vial until sent to the testing laboratory. RecL was ground in a coffee grinder, dried, and stored in similar fashion as the ComL.

A sample of the ground RecL was also washed with cold deionized (DI) water prior to drying and storing. A modified version of the United States Department of Agriculture—Forest Products Laboratory (USDA-FPL) lignin washing method was utilized. Twenty grams (g) of lignin were added to 400 mL of DI water in a glass beaker with a stir bar. The mixture was stirred in cycles of 24 hours each. After each cycle, the stirring was stopped, and the pH of the supernatant was measured. Then, the supernatant was decanted and filtered after allowing the lignin to settle. This cycle of washing and decanting continued until the

pH of the supernatant was within the range of 4–5 (4.11). Once this pH was reached, the supernatant was decanted, and the lignin was air-dried in the hood. The lignin was then ground in the coffee grinder, dried in the vacuum oven ($40^{\circ}\text{C} \pm 5^{\circ}\text{C}$), and stored in a scintillation vial for further processing. Samples were submitted to Midwest Microlab (Indianapolis, IN) for elemental analysis.

2.4 Pelletization of Biomass Feedstocks

Pilot scale pelletizing occurred with all lignocellulosics in this project: willow, wheat straw, and miscanthus (LCB), and hot water extracted LCB (HWEed LCB). Laboratory scale pelletizing occurred with willow. Prior to pelletizing, biomass was ground to various sizes (Table 4) using a hammermill and stored onsite in supersacks or covered barrels. Two hammermills and two pelletizers were utilized in this project (Figure 2).

Figure 2. Hammermills and Pelletizers Utilized in the Research Project

The Hammermills are on the left and the Pelletizers are on the right. First: Laboratory Scale Hammermill. Second: Pilot Scale Hammermill. Third: Laboratory Scale Ring Die Pelletizer. Last: Pilot Scale Flat Die Pelletizer.



The laboratory scale hammermill (Figure 2, Appendix C. Equipment Information) was utilized for grinding biomass for both laboratory scale and pilot scale operations. The hammermill included two screens from the manufacturer with screen holes that were 6 millimeter and 3 millimeter in diameter. A custom screen was built for the hammermill with screen holes of approximately one millimeter in diameter. The pilot scale hammermill (Figure 2, Appendix C. Equipment Information) was equipped with a screen containing 6-millimeter screen holes for grinding. All 1-millimeter screen biomass was first ground using the 3-millimeter screen to reduce the particle size for the 1-millimeter screen.

Table 4. Factors Explored in Pellet Research

Hot Water Extraction	No Hot Water Extraction				Hot Water Extraction	
Pelletizer Scale*	Laboratory			Pilot		Pilot
Hammermill Screen Size	3 mm	1 mm		6 mm	3 mm	6 mm 3 mm
Lignin Addition	None	None	Recl	ComL	None	

Two types of pelletizers were utilized in this research (Figure 2). The first was a laboratory scale ring die pelletizer with options for three different compression ratios (Appendix C. Equipment Information). Vegetable oil was fed to the pelletizer via a gravity-fed chamber during startup and shutdown. A peristaltic pump for moisture control was used during pelletizing instead of the gravity-fed chamber for better water control. The feed auger was the only means of manual flow control in the laboratory scale pelletizer. Pellets were collected and stored in a cold room (set at approximately 4°C) until characterized.

The second is a pilot scale flat die pelletizer (Appendix C. Equipment Information) with multiple automated components compared to the laboratory scale pelletizer. It employed a mixing hopper, which turned the biomass, and an auger that lifted the biomass upwards to feed into the main pelletizer auger. Water was added to the biomass in the main auger with a manually controlled pump. After exiting the flat die, the pellets passed through a rotating tube to remove and recirculate dust back to the feed hopper. The pellets were then collected into buckets, cooled, and stored in a cold room (set at approximately 4°C) until characterized.

The laboratory scale equipment was located in the Department of Chemical Engineering at SUNY-ESF and the pilot scale equipment was located at the SUNY-ESF Field Station in Tully, NY.

The particle size distribution of the 6-mm and 3-mm hammermilled LCB (LCB-6, LCB-3) and HWEed LCB (HWEed LCB-6, HWEed LCB-3) was examined with the ISO 17827 method (Solid Biofuels: Determination of Particle Size Distribution of Uncompressed Fuels). The 1-mm hammermilled LCB (LCB-1) was not selected due to the limitation of screen meshes available for particle size bins in the distribution. This method was modified to incorporate procedures from ISO 17827-1:2016²⁷ and ISO 17827-2:2016.²⁸ Modifications to this method can be found in Appendix A. Modifications to Testing Methods.

Particle size distribution was measured with sieves of various mesh sizes (Table 29). Screens were arranged in descending order with the highest mesh size on top and a collection tray at the bottom under the final sieve. For each replicate, 30g of sample was spread evenly over the mesh of the top sieve. After oscillating was complete, each sieve was weighed with the biomass fraction it contained. A particle size distribution for LCB-6, HWEed LCB-6, LCB-3, and HWEed LCB-3 samples by mass percent was developed.

The particle size distribution was also used to calculate the average particle size of the LCB and HWEed LCB based upon the method described by Baker and Herrman.²⁹ This method uses the geometric mean of the diameter openings of the sieves used for particle size distribution determination and the weight basis of each sieve fraction to calculate the average particle size and standard deviation of this average. For the determination of the pan screen size, Baker and Herrman²⁹ utilized the particle size two orders below the lowest mesh sieve in the stack. For this work, a screen size of 0.15 mm (No. 100) was used to represent the pan in the calculations. This was determined from the Product Selection Guide³⁰ from W.S. Tyler (Mentor, OH), the company that sold the sieves and shaker for the particle-size distribution measurement.

2.5 Addition of Lignin to Willow for Laboratory Scale Pelletizing

Willow hammermilled with a 3-mm and 1-mm screen was utilized for laboratory scale experiments. The lignin addition occurred on the laboratory scale with two types of lignin (RecL and ComL, as described previously). This lignin was added to willow that was hammermilled with the 1-mm screen. Lignin was added in a dry powder form at 5% of the mass of the willow. Lignin was added in small amounts to buckets that were half-filled with willow. Buckets were sealed with lids and rotated several times to mix the dry lignin with the willow before more lignin was added.

2.6 Determination of Pellet Properties

Several pellet properties were examined to observe the impact of hot water extraction (HWE) on pellet characteristics (Table 5). Most properties were measured using ISO (International Organization for Standardization) Certified methods and ISO Certified equipment where available. Each method is briefly described below. More detailed information about any modifications made to the methods can be found in Appendix A. Modifications to Testing Methods. A commercially available fuel pellet made from a hardwood/softwood blend was utilized as a “comparative standard” to the biomass treatments examined

in this study. As such, the commercial pellets were exposed to the same conditioning and property testing as the willow, wheat straw, and miscanthus (LCB) pellets. Commercially available apple pellets and commercially available paper waste pellets were also used in different auxiliary studies in this research. However, most of the characterization results will include only the hardwood/softwood energy pellets.

Table 5. Pellet Properties and Methods Utilized for Characterization

Pellet Property	Method of Characterization
Moisture Content	ISO 18134-2
Ash Content	ISO 18122
Energy Content	ISO 18125
Moisture Absorption/Resistance	Non-ISO Method
Bulk Density	ISO 17828
Durability	ISO 17831
Pellet Length	ISO 17829
Carbon Monoxide Off-Gassing	Non-ISO Method

2.6.1 Moisture Content

Aluminum dishes were dried in a 105°C oven, cooled, and weighed prior to moisture content measurement. The dishes were loaded with 10–20 grams of wet or as-received pellets, weighed, and placed into the 105°C oven. Dishes were heated in hour-long increments, removed, cooled, weighed, and returned to the oven until constant mass was achieved. Constant mass is described as the change between the mass in sample checks/measurements to be within the $\pm 0.2\%$ range. The reported results are an average of three experiments.

2.6.2 Ash Content

Porcelain crucibles with lids were dried in a 105°C oven, cooled, and weighed. The porcelain crucibles and lids were then fired in a furnace at 550°C, cooled, and weighed. Fuel pellets that were already dried in the moisture content procedure were sampled for ash content. A minimum of one gram of sample was used per replicate. Moisture-free pellets were placed in pre-fired crucibles and placed in the 105°C oven. They were weighed until constant moisture-free mass is obtained. Crucibles with samples were then placed in a cold furnace and heated until combustion occurred at 550°C. The temperature schedule raised

the furnace to 250°C, held it for one hour, then raised the temperature to 550°C and held it for two hours. More information about the schedule can be found in Section 7.3 of the ISO 18122 method. The samples were then cooled initially on a block and then in a desiccator. Samples were weighed, refired, cooled, and weighed until constant mass was achieved. Constant mass was deemed to be a change in mass no lower than 0.5 mg (0.0005 grams), or 0.001 grams given equipment measurement restrictions. The reported results are an average of three experiments.

2.6.3 Energy Content

A Parr oxygen bomb calorimeter (Appendix C. Equipment Information) was used to determine the gross energy content at constant volume as per ISO 18125. Settings for the calorimeter can be found in Appendix A.: Modifications to Testing Methods. Enough fuel pellets to sample for energy content and perform a moisture content were placed in pre-dried and pre-weighed aluminum dishes and stored in the open atmosphere of the laboratory housing the calorimeter, as per the ISO 18125 method. Pellets were then placed in the oxygen bomb apparatus, sealed, and placed in the calorimeter to measure energy content. Samples of 1.0–1.2 grams were used for each replicate. The moisture content of the remaining pellets was measured and utilized in the gross energy content calculation. The reported results are an average of three experiments.

2.6.4 Moisture Absorption/Resistance

The method employed to measure moisture absorption/resistance was not a standard ISO method. A TAPPI standard room that was consistently kept at 50% relative humidity (RH) and 23°C was utilized for this experiment. Aluminum dishes and fuel pellets were dried in a 105°C oven using the ISO 18134-2 protocol. The samples were then conditioned in a desiccator to reach the temperature of the standard room for a minimum of 24 hours. Then, the dishes were filled with enough fuel pellet samples to utilize for a moisture content experiment and exposed to the 50% RH conditions of the room. The mass of the pellets was weighed in timed intervals and measured until a constant mass was obtained. The intervals of measurement were as follows (in minutes): 0, 5, 10, 15, 30, 60, 120, 180, 240, 360, 480, 720, and 1440 or until constant mass was achieved. The definition of constant mass was the same that was used in the ISO 18134-2 method. The moisture content of the samples was then measured. The change in mass of the pellets represented the moisture absorbed by the LCB or HWEed LCB pellets, and therefore, signified whether LCB or HWEed LCB were “more resistant” to moisture. The reported results are an average of three experiments.

2.6.5 Bulk Density

The bulk density of the pellets was measured using an ISO Certified bulk density container (Appendix C. Equipment Information). The container volume was recorded and verified using deionized (DI) water prior to bulk density measurements. Pellets were poured into the bulk density container from a specified height above the container. The container was then lifted vertically and dropped onto a wooden board of designated thickness. This was to imitate a “shock” to the pellets that may be encountered during shipping and handling of the materials. This procedure of lifting and dropping the container with the pellets was repeated two additional times. Any space remaining at the top of the container was filled with additional pellets and a scantling was skimmed across the top to remove excess pellets. The container was then weighed to determine the bulk density of the pellets. A moisture content following the ISO 18134-2 method was taken in conjunction with the bulk density experiment to determine the dry-bulk density of the materials. The reported results are an average of three experiments.

2.6.6 Durability

The durability of the pellets was measured using an ISO Certified rotating metal tumbler (Appendix C. Equipment Information). Pellets were first sieved with a 3.35 mm (No. 6) screen prior to the durability test. The screened sample was weighed and placed into the tumbling device. The sample was then subjected to 500 rotations at 50 rotations per minute (rpm). The sample was sieved after tumbling and weighed once more to determine the durability of the pellets. A moisture content following the ISO 18134-2 method was taken in conjunction with the durability test as per the ISO 17831 instructions. The reported results are an average of three experiments.

2.6.7 Pellet Length

The length of the pellets was measured using ISO Certified digital readout calipers. The samples were sieved with a 3.35 mm (No. 6) screen prior to sampling. Then, the diameter and length of each pellet was measured with the calipers. The mass of each pellet was measured in conjunction with the pellet dimensions and a moisture content was performed using the ISO 18134-2 method. Fifty pellets from a 30- to 40-gram sample were measured for their individual mass and dimensions.

2.6.8 Carbon Monoxide Off-Gassing

The carbon monoxide off-gassing of the pellets was measured using a non-ISO method. Approximately 3.5–4.5 kilograms of pellets per sample were examined for off-gassing properties. Each replicate contained approximately 1.2–1.5 kilograms of sample. Samples were placed into a 3.84 liter glass jar, allowing for approximately 50% headspace based upon average headspace values in prior literature studies.^{1,31,32} This was originally measured on each jar using DI water volumes for measuring the halfway point in terms of volume in the jar. Carbon monoxide sensors (Appendix C. Equipment Information) were used to detect carbon monoxide in the headspace of the jars. The sensors were programmed to record a measurement once every five minutes. The sensors were placed in the jars and the jars were sealed with Teflon tape, a lid, and parafilm (Figure 3).

For the initial trials, the jars were left in the laboratory hood with a dark curtain for 90 days. A temperature sensor (Appendix C. Equipment Information) was placed in the hood to measure temperature fluctuations. This created an ambient-condition environment to simulate a pellet storage area. This was performed for pilot scale pellets.

Figure 3. Carbon Monoxide Off-Gassing Experiment



Additional trials performed in a temperature-controlled incubator were performed for pilot scale pellets and laboratory scale pellets (Figure 4). Smaller jars were utilized for the tests in the incubator. The same carbon monoxide and temperature sensors from the ambient condition experiments were used in the temperature-controlled experiments.

Figure 4. Carbon Monoxide Off-Gassing Experiment in Temperature Controlled Conditions



3 Results and Discussion

3.1 Hot Water Extraction of Biomass Feedstocks

Initial laboratory scale experiments in the Parr Reactor showed dissolution of lignocellulosic constituents in all hot water extracted (HWEed) willow, wheat straw, and miscanthus (LCB) samples. Particularly, dissolution of lignocellulosic constituents decreased in the following order: wheat straw > miscanthus > willow. The remaining solid residue based on the starting oven-dry raw material is depicted in Table 6. The operating conditions, digester yield, and extract pH from the HWE of miscanthus from this depicted in Table 7.

Table 6. Remaining Solid Residue from Laboratory Scale Parr Reactor HWE Experiments

Biomass Sample	Pretreatment Time (Hours)	Remaining Solid Residue (% based on oven-dry mass)
Wheat Straw	2	57.2 ± 1.06
Miscanthus-2015	1	64.5 ± 0.64
Miscanthus-2015	2	60.0 ± 0.34
Miscanthus-2012	2	62.5 ± 2.53
Willow variant 9882	2	69.6 ± 0.50

Table 7. HWE of Miscanthus at the Parr, M/K, and Pilot Digester Scales

Experiments Occurred at 160°C for two hours. HWE = Hot Water Extraction.

HWE Parameters/Results	Parr Reactor	M/K Digester	Pilot Plant Digester
Biomass Particle Size (mm)	<0.60	0.42	<19.0
Biomass Loading (kg)	5 X 10 ⁻³	0.223	155.1
Water-to-Biomass Ratio	40	10	8
Digester Yield (% oven-dried [OD] Biomass)	59.9	64.7	66.9
Extract pH	3.80	3.67	3.60

This demonstrates the change in operating conditions and resulting yield and extract pH with each scale and piece of equipment utilized for HWE studies. The results from the HWE scaling experiments show a dependence on the particle size and water-to-biomass ratio utilized during the process. Even though the intermediate scale M/K Digester results provided a better estimate of the results expected in the pilot scale batch reactor compared to the laboratory scale Parr Reactor (Appendix C. Equipment Information), the

HWE results obtained from the M/K Digester and Pilot Plant Digester still show differences. While lignin removal was not influenced with further increase in biomass particle size and decrease in water amount in transition from the Parr Reactor and M/K Digester to Pilot Plant Digester, cellulose removal was diminished while the particle size of miscanthus increased, and the water-to-biomass ratio decreased in accordance with the equipment requirements. More information about the composition of miscanthus before and after HWE at the various scales can be found in Table 9.

Table 8. Operating Conditions, Digester Yield, and Extract pH of Pilot Plant Digester HWE

DSI refers to Direct Steam Injection. IHS refers to Indirect Heating System.

HWEed Sample and Parameters/Results	Miscanthus	Miscanthus	Wheat Straw	Wheat Straw	Wheat Straw	Willow	Willow
Date	1/5/16	1/12/16	3/16/16	5/16/16	5/23/16	6/6/16	6/3/21
Loading (Pounds of oven dried [OD] biomass)	341.6	335.2	199.2	200.8	206.5	538.4	594.0
Liquid to Biomass Ratio	8.0	8.0	8.0	8.0	8.0	4.5	4.3
HWE Operating Temperature (°C)	160	160	160	160	160	160	160
HWE Operating Time (Hours)	2	2	2	1	2	2	2
Heating Method	DSI	DSI	DSI	DSI	DSI	DSI + IHS	IHS
Time to Reach Operating Temperature (Minutes)	55	N/A	62	36	33	51	85
Digester Yield (% of OD Biomass)	67.07	66.82	61.45	75.14	63.62	77.50	76.47
Moisture Content of Extracted Biomass (%)	5.08	4.62	6.01	8.61	6.32	7.00	9.09
Gallons of Hydrolysate Produced	237	245	121	124	136	181	200
Extract pH	3.59	3.60	4.02	4.29	4.04	3.87	3.82

3.2 Chemical Characterization of Lignocellulosic Feedstocks and Lignin

The results of the chemical composition and characterization of miscanthus prior to Hot Water Extraction (HWE) compared to the various scales of HWE (Parr Reactor, M/K Digester, Pilot Plant Digester) can be seen in Table 9. This information supports the conclusions concerning the dependence of HWE on particle size and water-to-biomass ratio previously discussed.

Table 9. Chemical Composition of Miscanthus Before (M) and After (EM) HWE, in % OD M (EM)

Removal of lignin/cellulose is presented as a percentage of the lignin/cellulose original amount in miscanthus. ET represents ethanol. DCM represents dichloromethane. These are extraction solvents.

Chemical Constituent	M	EM_{Parr}	EM_{M/K}	EM_{Pilot}
Extractives	5.57 (ET)	4.76 (DCM)	3.03 (DCM)	3.52 (DCM)
Seifert Cellulose	39.78	60.19	58.05	57.2
Cellulose Removal	---	9.37	5.58	3.80
Klason Lignin	20.27	20.05	22.02	21.44
Acid-Soluble Lignin	1.90	1.24	1.12	1.07
Total Lignin	22.17	21.29	23.24	22.51
Lignin Removal	---	42.37	32.47	32.02
Ash	4.24	1.32	3.89	4.97/4.04

Additionally, further analysis of the chemical composition of biomass before and after HWE was examined. This characterization included the measurement of extractives content, seifert cellulose, klason lignin, acid soluble lignin (ASL), carbohydrates content, ash content, phenolic hydroxyl group content, and delignification degree (Table 10). Additional data from the Parr, M/K Digester, and pilot scale experiments can be found in Appendix B. Additional Biomass Characterization Information. Lignin recovered from the HWE process was also characterized (Table 14).

Differences in the chemical composition—specifically of xylans, lignin, and lignin-carbohydrate/xylan-complexes in miscanthus and wheat straw—resulted in opposite results regarding the removal of xylans and lignin during HWE. HWE is commonly utilized to remove xylans from xylan-rich angiosperms, such as hardwoods. Previous studies³³ have shown ~80% removal of xylans from sugar maple utilizing similar hot water extraction conditions that were employed in this research. Compared to these studies, HWE resulted in less efficient removal of xylans from wheat straw and miscanthus (~71% and ~68%, respectively). The delignification degree, however, was increased and reached ~26% for wheat straw and 32% for miscanthus, in comparison to ~16% delignification degree for willow.

The removal of inorganic content (ash) in the pilot scale experiments was less efficient than experiments in the smaller scales. More efficient deashing of biomass in the Parr Reactor scale (Table 9) could be due to a combination of using DI water, a 50-to-1 water-to-biomass ratio (compared to 8-to-1 in pilot scale [Table 8]), and smaller-mesh biomass particles that increases the surface area available for penetration and reaction.

Table 10. Characterization of LCB and Pilot-Scale HWEed LCB Biomass

All extractions were performed via Soxhlet method (T-204). DCM: dichloromethane. ET:T: ethanol: toluene (1:2). *Value is reported as a percentage of OD (oven dried). Delignification degree value is in percent (%). The phenolic hydroxyl group content is reported in mmol/g of lignin. ^Biomass extracted with DCM.

Biomass Characteristic	Willow (2016)	HWEed Willow (2016)	Miscanthus (2015)	HWEed Miscanthus (2015)	Wheat Straw (2016)	HWEed Wheat Straw (2016)
Extractives Content ^{DCM+}	1.45	5.00	1.02	3.52	2.41	4.72
Extractives Content ^{ET:T+}	3.83	9.12	5.57	8.18	6.48	8.51
Seifert Cellulose ⁺	36.94	50.62	39.78	57.20	39.14	56.91
Klason Lignin ⁺	22.50	25.58	20.27	21.44	17.24	22.16
Acid Soluble Lignin (ASL) ⁺	2.42	1.21	1.90	1.07	2.37	1.02
Total Carbohydrates Content ⁺	50.14	56.87	64.15	69.92	N/A	N/A
Ash Content ⁺	1.47	1.05	4.24	4.97/4.04	N/A	N/A
Phenolic Hydroxyl Group Content	N/A	N/A	0.64	1.38 [^]	N/A	N/A
Delignification Degree	---	16.69	---	32.02	---	26.38

Regardless of extraction solvent, the HWEed LCB had higher extractives content compared to their LCB counterparts (Table 10). Similarly, each HWEed LCB had a greater cellulose and Klason lignin content but less acid soluble lignin (ASL) (Table 10). This could be due to the dissolution of ASL susceptible in the mild pH conditions generated naturally during HWE (as seen in the HWE hydrolysate/extract pH in Table 8). While overall carbohydrate content increased after HWE (Table 10), the xylan content of the HWEed LCB was lower than the LCB (Appendix B. Additional Biomass Characterization Information).

Results from the sequential extractions using hexane, ethanol:toluene (1:2) [ET], and ethanol for fatty acid analysis (Table 11) reported a lower ET extractives content compared to the prior characterization of LCB and HWEed LCB (Table 10), except for HWEed miscanthus. HWEed miscanthus had similar values for extractives content in this research compared to previous work (8.20% versus 8.18%). The greatest differences in ET extractives content were observed with the LCB that were not hot water extracted (willow, miscanthus, and wheat straw).

The lower ET extractives values are attributed to differences in the design of the extraction procedure. The prior characterization of the LCB and HWEed LCB for extractives reported in Table 10 used only one extraction solvent (ET or DCM [dichloromethane]). However, the extractions performed for this research were sequential in which the same sample of LCB and HWEed LCB was extracted with each of the solvents. Extractives that were removed with hexane in the first round of Soxhlet extractions value after ET extraction.

Table 11. Extractives Content of LCB and HWEed LCB Utilized for Pelletizing Experiments

LCB: Lignocellulosic biomass. HWEed LCB: hot water extracted lignocellulosic biomass. Results presented as percentage of oven dried LCB/HWEed LCB. Values in parentheses represent standard deviation.

Extraction Solvent	Willow	HWEed Willow	Miscanthus	HWEed Miscanthus	Wheat Straw	HWEed Wheat Straw
Hexane	3.50 (±0.01)	4.43 (±0.55)	2.48 (±0.10)	2.74 (±0.19)	1.83 (±0.01)	3.32 (±0.01)
Ethanol:Toluene	2.89 (±0.07)	8.54 (±0.20)	4.31 (±0.10)	8.20 (±0.23)	2.81 (±0.20)	7.64 (±0.04)
Ethanol	0.33 (±0.03)	0.70 (±0.07)	0.93 (±0.04)	0.59 (±0.01)	0.98 (±0.01)	0.78 (±0.04)
<i>Total Extractives</i>	<i>6.72</i>	<i>13.67</i>	<i>7.72</i>	<i>11.53</i>	<i>5.67</i>	<i>11.74</i>

Fatty acids can be extracted from lignocellulosic biomass with non-polar solvents like hexane and polar solvents such as acetone, and these fatty acids are believed to be involved in the CO off-gassing of lignocellulosic fuel pellets in storage.¹ Therefore, it is important to note the variations in extractives content between species of LCB (willow, miscanthus, and wheat straw) and HWEed LCB. Comparing the saturated and unsaturated fatty acids found in wheat straw with extraction with hexane compared to acetone³⁴—a solvent of similar polarity to ethanol—the non-polar fractions contained a higher fatty acid concentration than the polar fractions. Considering this and the relationship of fatty acids to CO off-gassing, LCB and HWEed LCB, with greater hexane extractives content, should have higher CO off-gassing values as well.

The ET extractives content was the highest for all LCB and HWEed LCB except for willow, in which there was a higher hexane extractives content. Willow and HWEed willow contained the highest hexane extractives content compared to miscanthus, wheat straw, HWEed miscanthus, and HWEed wheat straw. Of the LCB that was not hot water extracted, miscanthus had the highest ET extractives content while willow and wheat straw had similar values (2.89% versus 2.81%). The ET extractives content of the

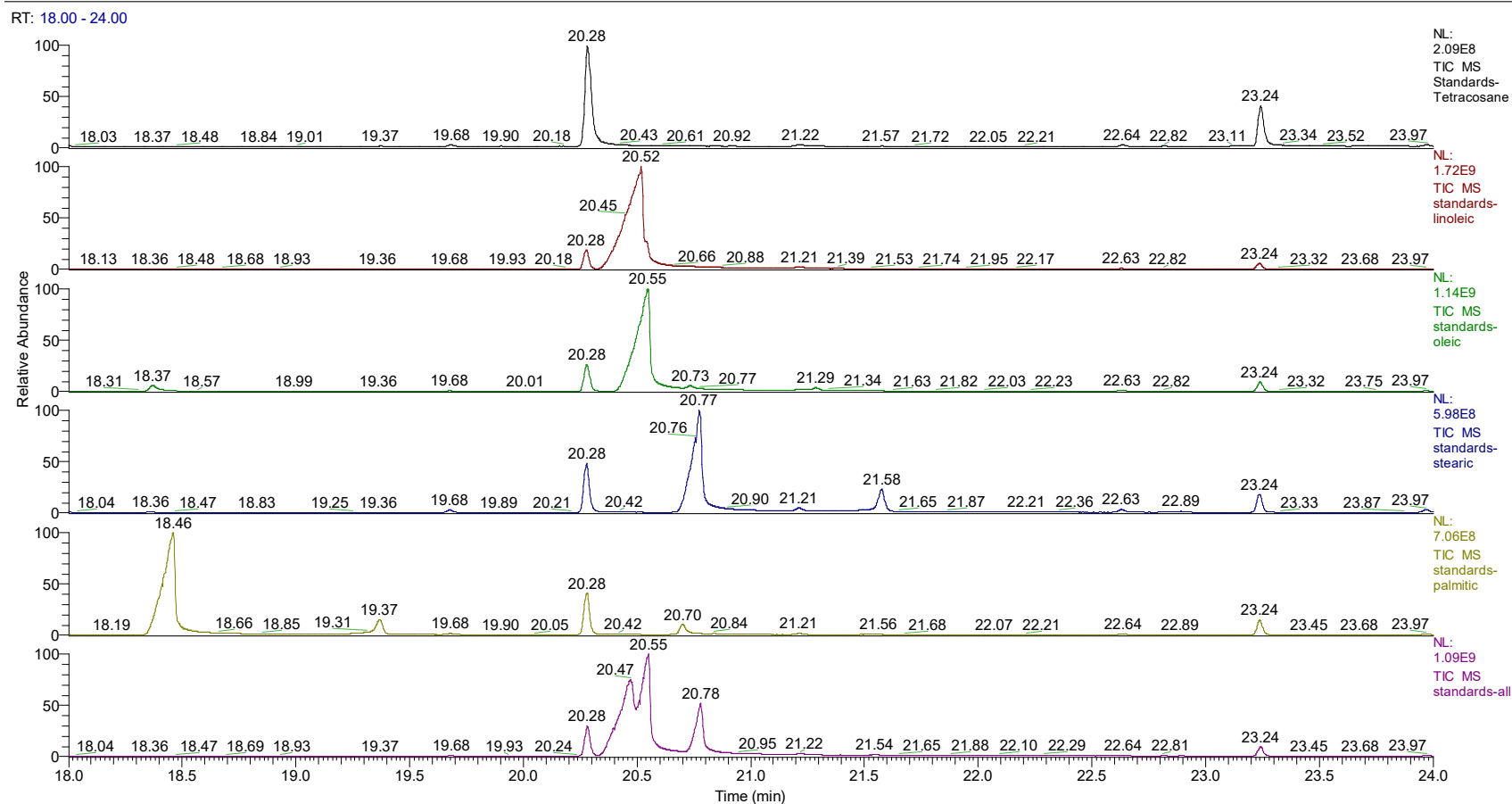
HWEed LCB were within 1% of each other, with HWEed wheat straw as the lowest in the group. Ethanol extractives accounted for the lowest percentage of the extraction solvent fractions, with miscanthus and wheat straw containing a higher ethanol extractives content compared to willow and HWEed wheat straw and HWEed willow containing a higher ethanol extractives content than HWEed miscanthus.

The presence of four fatty acids (palmitic acid, stearic acid, linoleic acid, and oleic acid) was examined with GC-MS with tetracosane as an internal standard. Standards with these four fatty acids were analyzed with GC-MS to determine retention times (Figure 5) and to develop molecular ion filters for residue analysis. Fatty acids and the tetracosane internal standard were eluted in the 18- to 24-minute range, so chromatograms were created to display peaks in that range. Then, residues of LCB and HWEed LCB from extraction with hexane, ethanol:toluene (1:2) [ET], and ethanol (thirty-six residues in total) were analyzed with GC-MS.

Figure 5. Gas Chromatogram of Fatty Acid Standards from GC-MS Analysis

Each row of the chromatogram represents a different standard.

- Row 1: Tetracosane (Internal Standard) (Elution Time: 23.24 min); Row 2: Linoleic Acid (Elution Time: 20.52 min).
- Row 3: Oleic Acid (Elution Time: 20.55 min); Row 4: Stearic Acid (Elution Time: 20.77 min); Row 5: Palmitic Acid (Elution Time: 18.48 min).
- Row 6: Combination of Tetracosane, Linoleic Acid (20.47 min), Oleic Acid (20.55 min), and Stearic Acid (20.78 min).



The area for each of the fatty acid peaks in the residues (if present) were normalized to the mass of the sample provided for analysis. This was due to the variability of the residue transferred to the GC-MS vials (11±5 mg). The fatty acid peak area that was normalized to the GC-MS sample mass was then applied to the extractives content found in one oven-dried gram of LCB or HWEed LCB based upon the reported extractives contents from the sequential Soxhlet extraction (Table 11) to compare the peak area of fatty acids in each LCB and HWEed LCB (Table 12).

In combining these two parameters, it was found that EWS had the greatest total fatty acid content (all fatty acids in all extraction solvents), with the order being EWS>WS>M>EM>EW>W. This same trend was also seen in total saturated fatty acid content across the solvent fractions. The order of LCB and HWEed LCB from highest to lowest fatty acid content shifts to EWS>M>WS>EW>EM>W when considering only unsaturated fatty acids. As such, if total fatty acid content is predictive of CO off-gassing, then pellets made from HWEed wheat straw should produce the most CO in storage while pellets made from willow should produce the least CO, which is contrary to the original hypothesis that hot water extraction would reduce emissions.

Table 12. Fatty Acid Peak Areas of LCB and HWEed LCB in Each Extraction Solvent Based on Sequential Extractives Content

LCB	Linoleic Acid (C18:2 cis-9,12)	Oleic Acid (C18:2 cis-9)	Stearic Acid (C18:0)	Palmitic Acid (C16:0)
<i>Hexane Extractives</i>				
W	0.09	0.04	0.38	1.12
EW	0.07	0.05	0.49	1.63
M	0.04	0.09	0.61	1.78
EM	0.00	0.06	0.59	2.80
WS	0.34	0.54	2.64	19.37
EWS	0.59	1.60	9.93	60.94

W = Willow. M = Miscanthus. WS = Wheat Straw. E = Hot Water Extracted.

Total Fatty Acid Content defined as the sum of the fatty acid peak area in each of the three extraction solvents.

C#:# = the number of carbons in the fatty acid chain and the number of double bonded carbons (if present) to signify saturated fatty acids (0) and unsaturated fatty acids (1,2). The location of the double bonded carbons in the unsaturated fatty acids are listed as well (cis-#,#). Peak areas have been divided by 1,000,000 for ease of comparison.

* Significant figures adjusted to display non-zero fatty acid values.

Table 12 continued

LCB	Linoleic Acid (C18:2 cis-9,12)	Oleic Acid (C18:2 cis-9)	Stearic Acid (C18:0)	Palmitic Acid (C16:0)
<i>Ethanol:Toluene (1:2) Extractives</i>				
W	0.30	0.09	2.77	11.14
EW	0.71	0.34	2.99	13.15
M	3.11	0.77	4.52	26.08
EM	0.51	0.45	2.66	23.31
WS	1.13	0.04	6.09	36.32
EWS	2.74	1.44	8.46	79.78
<i>Ethanol Extractives</i>				
W	0.00	0.00	0.05	0.19
EW	0.00	0.00	0.01	0.03
M	0.00	0.00*	0.27	1.06
EM	0.00	0.00	0.04	0.12
WS	0.00	0.00*	0.21	0.85
EWS	0.00	0.00*	0.28	1.15
<i>Total Fatty Acid Content</i>				
W	0.38	0.13	3.20	12.45
EW	0.78	0.39	3.49	14.81
M	3.15	0.86	5.40	28.92
EM	0.51	0.51	3.29	26.23
WS	1.46	0.59	8.94	56.54
EWS	3.33	3.05	18.67	141.87

LCB and HWEed LCB were examined for carbon, hydrogen, nitrogen, oxygen, and sulfur content (Table 13) by Midwest Microlab (Indianapolis, IN). Samples were dried in a vacuum oven and tested in duplicate. The results of the Midwest Microlab elemental analysis of carbon, hydrogen, nitrogen, and oxygen in willow, miscanthus, and wheat straw were comparable to values found in literature (Table 13), except for the oxygen content in wheat straw. However, Midwest Microlab noted that silicon can interfere with oxygen measurement to cause higher-than-expected values. Silicon is an inorganic element found in LCB^{35,36} and can constitute 0.5% to 15% of dry plant matter.³⁶ Wheat straw has been reported to contain high amounts of silicon, ranging between 1.45%–2.5% of dry matter,^{37–39} with one study⁴⁰ reporting up to 5% silicon content in wheat straw. It is possible that this high silicon content in wheat straw interfered with the oxygen measurement, but further research and analysis into the inorganic elemental composition of LCB and HWEed LCB would be needed to support this claim as the silicon content of the LCB and HWEed LCB in this study is not known.

Table 13. Elemental Analysis of LCB and HWEed LCB

LCB	Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur
Willow	46.94 (±0.08)	5.86 (±0.04)	0.48 (±0.03)	42.55 (±0.08)	3.57 (±0.08)
HWEed Willow	49.24 (±0.02)	5.94 (±0.06)	0.39 (±0.01)	36.24 (±0.18)	1.37 (±0.06)
<i>Percent Change</i>	4.90	1.37	-19.79	-14.83	-61.71
Miscanthus	43.60 (±0.04)	5.67 (±0.02)	0.19 (±0.01)	42.07 (±0.12)	1.98 (±0.04)
HWEed Miscanthus	45.97 (±0.03)	5.77 (±0.01)	0.12 (±0.01)	26.92 [*] (---)	1.60 (±0.05)
<i>Percent Change</i>	5.45	1.85	-36.84	-36.00	-19.44
Wheat Straw	44.28 (±0.06)	5.58 (±0.04)	0.62 (±0.01)	63.39 (±0.25)	1.80 (±0.01)
HWEed Wheat Straw	46.90 (±0.08)	5.93 (±0.05)	0.52 (±0.01)	37.20 (±0.01)	1.42 (±0.01)
<i>Percent Change</i>	5.92	1.37	-16.26	-41.32	-21.11
<i>Literature Values for Elemental Analysis of LCB</i>					
Willow	47.1 ^a	6.1 ^a	0.54 ^a	44.2 ^a	0.045 ^a
Miscanthus	45.0 ^b 47.5 ^a	5.8 ^b 6.2 ^a	0.14 ^b 0.73 ^a	40.7 ^b 41.7 ^a	0.03 ^b 0.150 ^a
Wheat Straw	43.5 ^b 45.6 ^a	5.7 ^b 5.8 ^a	0.47 ^b 0.48 ^a	41.9 ^b 42.4 ^a	0.11 ^b 0.082 ^a

LCB = Lignocellulosic Biomass. HWEed = Hot Water Extracted.

Analysis performed in duplicate by Midwest Microlab. Results are a percentage of total weight of dried sample.

* Results received as a single replicate, not a duplicate.

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- b. Thy P, Yu C, Jenkins B, Lesher C. Inorganic composition and environmental impact of biomass feedstock. *Energy and Fuels*. 2013;27(7):3969–3987. doi:10.1021/ef400660u

The sulfur contents of the LCB determined by the Midwest Microlab were 13–79 times greater than the reported literature values (Table 13). The largest discrepancy was in the willow sulfur content. Sulfur is a macroelement that is needed by the plant to grow.⁴³ However, it is important to monitor as sulfur can damage boilers and other energy generating systems when utilizing lignocellulosic biomass as a fuel source.⁴¹ It is recommended to have less than 0.30% sulfur in non-woody fuel pellets⁴⁴ and less than 0.05% sulfur in woody fuel pellets.⁴⁵

One potential reason for such different values could be the method that is utilized for analysis of total sulfur content. Midwest Microlab employed the Schoniger Combustion method with titration to determine sulfur content, whereas methods such as wet digestion with nitric and perchloric acid coupled with ICP-AES (Inductively Coupled Plasma Atomic Emission Spectroscopy) have been utilized in other studies of elemental composition of lignocellulosic biomass.⁴⁶ Several studies have noted variation in the sulfur content of plant material with different determination methods.^{47,48} The difference in results between the total sulfur content utilizing the Schoniger Combustion process compared to the wet digestion process was inconsistent, with one study noting the Schoniger Combustion had lower results than wet digestion⁴⁸ and another study pointed out instances where the Schoniger Combustion method reported both a higher and lower sulfur content than the wet digestion method.⁴⁷ Regardless, it is evident that the differences in these values should not be as high as what was provided in the Midwest Microlab analysis compared to literature values. It is unclear why these results differ, and further research needs to be performed to better understand and evaluate the sulfur content in the samples.

The ratio of carbon, hydrogen, and oxygen in LCB is related to the cellulose, hemicelluloses, and lignin content in the LCB. Cellulose has a C:H:O ratio of 1:1.67:0.83.⁴⁹ While the structure of hemicelluloses and lignin in LCB varies between softwoods, hardwoods, and agricultural residues, they have an approximate C:H:O ratio as reported by Demirbas.⁴⁹ Hemicelluloses have a C:H:O ratio of 1:1.64:0.78,⁴⁹ which is similar to cellulose but slightly lower in hydrogen and oxygen content. Lignin has a C:H:O ratio of 1:1.06:0.31.⁴⁹ Cellulose and hemicelluloses have a higher degree of oxygen and hydrogen compared to lignin. As such, C:H:O ratios with lower hydrogen and oxygen values are likely to have a greater lignin content and/or a lower cellulose and hemicelluloses content.

Prior to HWE, willow had the highest carbon and hydrogen content compared to miscanthus and wheat straw. Willow had a C:H:O ratio of 1:1.49:0.68 while both miscanthus and wheat straw exhibited a higher hydrogen and oxygen ratio compared to carbon (1:1.55:0.72 and 1:1.57:1.07). However, due to the previously discussed issue with the oxygen measurement in wheat straw, this oxygen ratio should be less than 1.07. If values from the literature are used for oxygen content in wheat straw (Table 13), the ratio would be 1:1.57:0.71, which is still greater than willow.

From the characterization in Table 10, willow had the lowest cellulose and xylan content compared to miscanthus and wheat straw (M>WS>W for cellulose and WS>M>W for xylan) and the highest lignin content (W>M>WS). This is seen in the C:H:O ratio of willow having a lower amount of hydrogen and oxygen compared to miscanthus and wheat straw. If using the literature values for the oxygen content in

wheat straw, wheat straw and miscanthus had very similar C:H:O ratios. Additionally, the xylan content in wheat straw and miscanthus were similar (18.96% versus 18.26%) and the difference between their cellulose contents was not significant. Wheat straw had a lower lignin content than miscanthus despite a similar C:H:O ratio.

After HWE, the C:H:O ratio of all HWEed LCB decreased compared to LCB. HWEed willow had the C:H:O ratio with the lowest hydrogen content (1:1.44:0.55) while HWEed miscanthus had the lowest oxygen content (1:1.50:0.44). HWEed wheat straw had the highest C:H:O ratio after HWE (1:1.51:0.60). HWEed willow had the lowest cellulose and xylan content compared to HWEed miscanthus and HWEed wheat straw (EM>EWS>EW for cellulose and EM>EWS>EW for xylan) and the highest lignin content (EW>EWS>EM). HWE partially removes hemicelluloses like xylan from LCB, causing a reduction in xylan content and an increase in cellulose and lignin content (on a weight percent basis). This removal resulted in an increase in carbon and hydrogen content and decrease in oxygen content in HWEed LCB, thus affecting the C:H:O ratios.

The average increase in carbon content after HWE was $5.42 \pm 0.51\%$. Willow had the lowest percent increase in carbon content after HWE (4.90%) compared to miscanthus (5.45%) and wheat straw (5.92%), though these differences were not significant. The average change in hydrogen content after HWE was $1.53 \pm 0.28\%$. The percent change in hydrogen content for willow and wheat straw after hot water extraction was the same (1.37%) while miscanthus had a greater percent increase (1.85%). All HWEed LCB had a decreased oxygen content, with wheat straw having the greatest percent decrease (41.32%) compared to miscanthus (36.00%) and willow (14.83%). Comparatively, HWEed willow had the lowest remaining xylan content of the three HWEed LCB (EM>EWS>EW), but willow also started with the lowest xylan content compared to wheat straw and miscanthus prior to HWE.

However, HWEed wheat straw had the greatest change in cellulose, xylan, and lignin content compared to HWEed willow and HWEed miscanthus. The change in xylan content was the most similar, in which xylan in HWEed wheat straw decreased by 38.29% compared to HWEed willow (34.21%) and HWEed miscanthus (35.93%). The cellulose content increased by 46.14% in HWEed wheat straw compared to 37.03% for HWEed willow and 43.79% for HWEed miscanthus. The most significant change was in lignin content in which lignin in HWEed wheat straw increased by 14.79% compared to 7.50% for HWEed willow and 1.53% for HWEed miscanthus after the removal of hemicelluloses from HWE. The high percent decrease in oxygen content for wheat straw after HWE coincides with these changes in cellulose, xylan, and lignin content.

HWE had additional effects on the nitrogen and sulfur content as HWEed LCB had a lower nitrogen and sulfur content than LCB. HWE had the greatest effect on the removal of sulfur from willow (61.71% decrease) and was effective at removing 19.44% of sulfur from miscanthus and 21.11% of sulfur from wheat straw. Miscanthus had the greatest percent decrease in nitrogen content after HWE (36.84%) compared to willow (19.79%) and wheat straw (16.26%).

Overall, the reduction in oxygen content and increase in carbon and hydrogen content is a benefit of HWE regarding the energy content of the HWEed LCB compared to LCB. Energy content yielded from LCB increases with higher carbon and hydrogen contents and lower oxygen content.⁴⁹ The partial removal of hemicelluloses in the form of xylan alters the C:H:O ratio of HWEed LCB towards a more favorable ratio for energy generation. HWE also results in an LCB that contains a higher lignin content, which is more directly related to the energy yield from LCB according to Demirba.⁵⁰ As such, the energy content of HWEed LCB pellets is expected to be higher than LCB pellets.

The decrease in sulfur and nitrogen content after HWE is also beneficial for fuel pellets. Nitrogen oxides (NO_x) and sulfur dioxide (SO₂) are common airborne pollutants from power plants that can form ground-level ozone and particulate matter.⁵¹ This is harmful and can cause issues with the respiratory, cardiovascular, and nervous systems.⁵¹ These emissions form upon the combustion of LCB due to the nitrogen and sulfur content in the LCB.⁵² As such, using HWEed LCB for combustion should result in lower NO_x and SO₂ emissions compared to LCB, though it is not explored further in this study.

The results of the characterization of lignin recovered from the HWE of willow, miscanthus, and wheat straw can be seen in Table 14. LignoBoost lignin (ComL)—which was utilized in laboratory scale pelleting experiments—is also included based upon literature values. Additional characterization results of lignin recovered from the HWE of willow (RecL) and ComL for moisture content, ash content, and energy content can be seen in Table 15. The elemental analysis of RecL, ComL, and washed RecL can be seen in Table 16.

Table 14. Characterization of Lignin Recovered from HWE and Commercial LignoBoost Lignin

Lignin Characteristic	Recovered Willow Lignin	Recovered Miscanthus Lignin	Recovered Wheat Straw Lignin	LignoBoost Lignin ²⁴
Number Average Molecular Weight (Da)	2186 2588.98	2124 2570	2850	949
Weight Average Molecular Weight (Da)	5201.60 5962	4672 9805	12114	6772
Polydispersity Index	2.0 2.73	2.2 3.8	4.25	4.1
PhOH (mmol/g lignin)	1.97 2.29 [†]	1.96 [‡]	1.19	1.4 ^d 2.18 ^e 4.2 ^{f,A}
Klason Lignin ⁺	80.2	74.7 76.3 82.5 [*]	77.0 77.3 ⁻	91.1 ^c
Acid Soluble Lignin ⁺	4.48	4.5 [*] 4.7 4.96	3.73 ⁻	5.4 ^c
Glucan ⁺	1.19	0.60	1.99	0.12 ^c
Xylan ⁺	1.19	3.85	3.32	0.84 ^c
Total Carbohydrates ⁺	2.98	4.93 [*] 8.68	5.31	1.98 ^c
Ash Content ⁺	0.2	0.4 [*] 0.5	1.2 ⁻ 1.78	0.2-1.4 ^{g,h} 1.35 ^j 1.36 ^c
Glass Transition Temperature (T _g) (°C)	159	123	143 ⁵⁹	109 ^f 157 ^e
Higher Heating Value (MJ/kg)	22.02	23.34	23.40	26.6-27.3 ^g

⁺ Value is reported as percentage of OD (oven dried).

^{*} Lignin was washed with water pH 5 for purification.

[†] Determined with P-NMR Method.

[‡] Determined with H-NMR Method.

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Table notes are continued on the next page.

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Of the lignin-solids recovered from HWE, the Klason lignin content ranged from ~76% to ~80% of the oven dried lignin for miscanthus and willow, respectively (Table 14). Washing of miscanthus lignin samples with water (pH 5) increased the lignin content from ~76% to ~83% with a simultaneous decrease in total carbohydrate content (Table 14). All lignins were of relatively low ash content (below 0.5%), except for wheat straw (1.2% ash) (Table 14).

Table 15. Select Properties of Lignin Utilized in Pelletizing Experiments

Property	RecL	ComL
Moisture Content (%)	1.77 (±0.06)	22.26 (±0.58)
Ash Content (%)	0.41 (±0.12)	1.14 (±0.12)
Gross Calorific Value (MJ/kg)	25.5 (±0.01)	27.0 (±0.21)

RecL = Lignin recovered from hot water extraction of willow.
ComL = LignoBoost lignin obtained commercially.

Overall, RecL had a lower moisture content, ash content, and energy content compared to ComL and all differences were significant. The high moisture content of LignoBoost lignin aligns with moisture in the literature, which was reported by Abdelaziz and Hulteberg⁶⁰ to be about 30%. The ash content of RecL used for laboratory scale pelletizing was greater than the value reported for lignin recovered from the HWE of willow (0.2%) previously characterized in this work. The reason for this difference is unclear and requires further exploration. The ash content for ComL fell within the reported range of 0.2–1.4% ash for LignoBoost (Table 14).

The energy content (in the form of gross calorific value) of ComL was 5.88% higher than RecL and was consistent with the energy content reported in literature.⁵⁶ The energy content of RecL used for laboratory scale pelletizing was greater than what was previously reported for the same lignin. However, this is likely due to differences between the ISO method used for energy content analysis in this study and the American Society for Testing and Materials (ASTM) method used in previous work, or differences in calorimeter calibration and operation. This is described in detail in the Determination of Pilot Scale Pellet Properties section with the energy content of LCB and HWEed LCB pellets. Using this process of substituting EE values into the calculation of energy content from previous work (2426) into this work (2667), the energy content of RecL is closer to that reported in earlier analyses (from 25.5 MJ/ kilogram (kg) to 22.98 MJ/kg versus 22.02 MJ/kg). This also decreases the energy content of the ComL to outside of the literature range (24.20 MJ/kg versus 26.6-27.3 MJ/kg). Regardless, both RecL and ComL had higher energy contents than LCB and HWEed LCB and should increase the energy content of laboratory scale pellets when used as a binding agent.

RecL and ComL were examined for carbon, hydrogen, nitrogen, oxygen, and sulfur content (Table 16) by Midwest Microlab (Indianapolis, IN). There were discrepancies with the Midwest Microlab results. The overall analysis of the five elements in the lignin resulted in a sum of over 100% of the total weight of the dried sample for the washed RecL and the ComL, while the sum of the results for the RecL was under 100% (99.56%). This was also observed in the results for the elemental analysis of wheat straw, but was attributed to the high oxygen measurement from the potential interference of silicon in wheat straw with the testing method. However, there should not be interference with silicon affecting the measurements of lignin as lignin should not contain as much silicon as LCB like wheat straw. The results of the oxygen measurements in lignin are most likely to blame for the discrepancies in the sum of the elemental analysis.

Table 16. Elemental Analysis of Recovered Lignin and Commercial Lignin

Analysis performed in duplicate by Midwest Microlab (Appendix D). Results are % of total weight of dried sample.

Lignin	Carbon	Hydrogen	Nitrogen	Oxygen	Sulfur
Lignin recovered from HWE of Willow (ReCL)	60.22 (±0.05)	5.96 (±0.01)	1.16 (±0.00)	30.42 (±0.00)	1.80 (±0.04)
Washed ReCL	60.38 (±0.06)	5.90 (±0.08)	1.65 (±0.08)	38.05 (±0.18)	1.55 (±0.18)
<i>Percent Change</i>	<i>0.27</i>	<i>-0.92</i>	<i>41.81</i>	<i>25.08</i>	<i>-13.65</i>
Commercial LignoBoost Lignin (ComL)	63.54 (±0.03)	5.86 (±0.01)	0.14 (±0.04)	32.66 (±0.33)	2.61 (±0.11)
Literature Values for Elemental Analysis of Lignin					
Willow Lignin	55.8 ^{h, aA}	4.8 ^{h, a}	0.42 ^{i, b}	34.16 ^{i, b}	--
	59.39 ^{i, b}	5.49 ^{i, b}	1.6 ^{h, a}	37.7 ^{h, aa}	--
LignoBoost Lignin ^c	65.0 ^e	6.7 ^e	0.2 ^e	22.37 ^g	1.37 ^l
	65.23 ^j	5.59 ^g	0.09 ^k	26 ^k	1.6 ^e
	65.6 ^k	5.7 ^k	0.22 ^l	26.5 ^e	1.85 ^k
	67.3 ^g	5.83 ^j	<0.5 ^g	27.13 ^j	2-3 ^f 2.82 ^g
Hardwood Lignin ^d	59.8 ^l	6.4 ^l	--	33.7 ^l	--
Softwood Lignin ^d	63.8 ^l	6.3 ^l	--	29.9 ^l	--

- a. Ionosolv Lignin with Et₃NH HSO₄.
- b. Deep Eutectic Solvent Lignin.
- d. LignoBoost Lignin from Kraft Pulping of Softwood. ^c Procedure to Isolate Lignin was Not Disclosed.
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The values for LignoBoost (ComL) lignin were similar to literature values, with the exception of oxygen. The carbon content was slightly lower than expected and the hydrogen content was slightly higher, but the nitrogen and sulfur content fell within the expected range from the literature. However, it is important to note that the measurement of sulfur in the LCB and HWEed LCB was greater than expected, potentially due to the methods used to analyze samples for sulfur content by Midwest Microlab as previously discussed. As such, the true value of sulfur for ComL could be closer to the lower end range of the literature values, which would also contribute to the discrepancy in the sum of the elemental analysis. Additionally, the oxygen content reported from Midwest Microlab was 20.4–46.0% higher than that of the literature studies. The ComL also had a higher oxygen content than softwood lignin, which is the LCB from which the ComL was derived during the LignoBoost process.²⁴

This discrepancy that may have caused overestimates of the oxygen content was not present in the RecL. Compared to other willow lignin samples from the literature, the carbon and hydrogen content of RecL were slightly higher, the nitrogen content was within the range listed in the literature, and the oxygen content was lower than literature values. The results for the elemental analysis of the washed RecL did have similar discrepancies in the overall sum of the elemental constituents. Further, it is uncharacteristic for the washed RecL to have a higher oxygen content after washing. The process of recovering lignin from HWE involves the collection and acidification of hydrolysate rich with hemicellulosic saccharides to precipitate lignin out of the hydrolysate. The resulting lignin contains small amounts of low DP (degree of polymerization) sugars, such as monosaccharides and disaccharides, that should be removed when washing the lignin. Removal of saccharides should decrease the overall oxygen content of the lignin, which is contrary to the results of this study.

A decrease in sulfur content after washing was expected for RecL. Sulfuric acid (H_2SO_4) was utilized to acidify the hydrolysate to recover the lignin from HWE of willow. The washing process gradually removes remnants of the sulfuric acid (sulfate ions) by mixing the lignin with batches of deionized water until the pH reaches a less acidic threshold. As such, the sulfur content should decrease after washing as more sulfate is removed from solution.

As discussed previously, a higher carbon and hydrogen content and a lower oxygen content improves the energy content of LCB. The energy content of lignin is 21–26.6 MJ/kg^{4,65–67} while cellulose and hemicelluloses have an energy content of 17 MJ/kg⁶⁵ and 16.63 MJ/kg⁴ due in part to the differences in carbon, hydrogen, and oxygen content. Lignin has a C:H:O ratio of 1:1.06:0.31⁴⁹ while cellulose and hemicelluloses have C:H:O ratios of 1:1.67:0.83⁴⁹ and 1:1.64:0.78⁴⁹. The average carbon to

hydrogen to oxygen ratio (C:H:O) of HWEed LCB (1:1.48:0.53) was lower than LCB (1:1.54:0.83). The contribution from wheat straw to the average C:H:O ratio of LCB, however, skewed this value due to a potential interference with the oxygen measurement. If literature values from Table 13 are utilized for the oxygen content of wheat straw in this calculation, the C:H:O ratio would be 1:1.54:0.71, which is still higher than HWEed LCB.

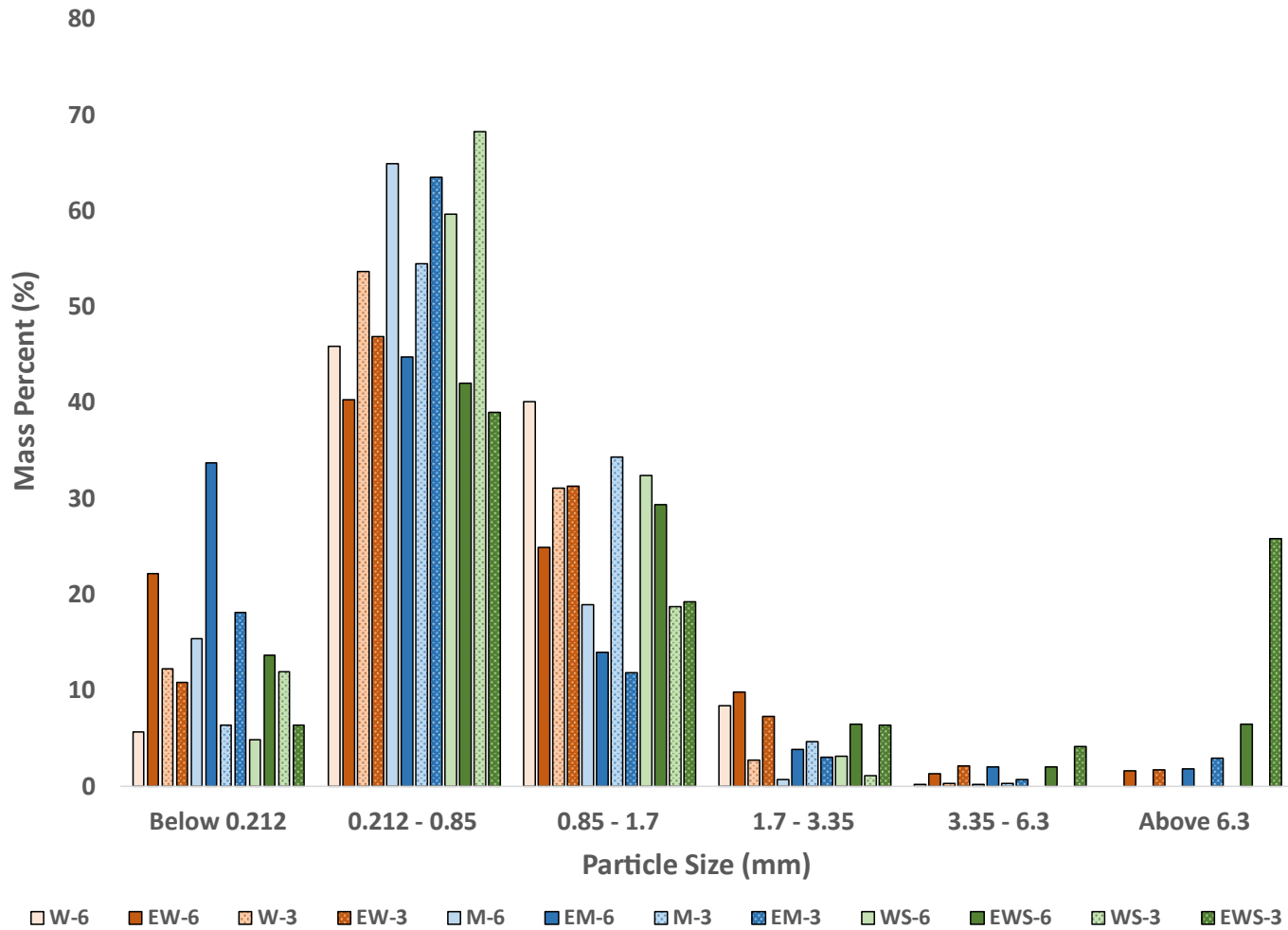
Comparatively, all lignin samples had a lower C:H:O ratio than the LCB and HWEed LCB, which is the expected result. ComL had the lowest hydrogen ratio (1:1.10:0.39), while RecL had the lowest oxygen ratio (1:1.18:0.38), with washed RecL containing a lower hydrogen but higher oxygen content (1:1.16:0.47). Compared to the literature C:H:O ratio of lignin, all lignin samples had a higher C:H:O ratio. However, it is important to note that the oxygen results for the ComL and washed RecL were uncharacteristically high, as previously discussed. As such, the oxygen ratios of the lignin samples are anticipated to be closer to that of the literature value than the results of the Midwest Microlab analysis.

3.3 Pelletization of Biomass Feedstocks

Each LCB and HWEed LCB was hammermilled prior to pelletizing with screens containing either a 6 mm or 3 mm mesh. The particle size distribution of the hammermilled LCB and HWEed LCB was examined with an oscillating screen and their mass percent distribution into different fractions are reported below (Figure 6, Table 18, Table 19). The average particle size of each hammermilled LCB and HWEed LCB are reported in Table 17.

Regardless of the screen size, each of the HWEed LCB reported a mass fraction above 6.3 mm. Upon further visual inspection, it was found that the HWEed LCB particles—while smaller than 6.3 mm—would aggregate on top of the screen and form a “fluffy” bundle of LCB despite the oscillations. Hot water extraction removes a portion of the hemicelluloses, lignin, and ash from the LCB, resulting in a chip or material that is lower in density,³³ which can make it difficult to feed through gravity-based systems. The lower density and observed propensity to entangle with itself—as seen in this particle size distribution test—was also observed to cause issues with pelletizing of the HWEed LCB.

Figure 6. Particle Size Distribution of LCB Hammermilled with 6-mm and 3-mm Screens



W = Willow. M = Miscanthus. WS = Wheat Straw. E = Hot Water Extracted.

6/3 = Pellets made from Biomass Hammermilled with 6/3 mm screen. Results are average of two replicates.

* Indicates only one replicate was performed.

Table 17. Average Particle Size of Hammermilled LCB and HWEed LCB

W-6	EW-6	M-6	EM-6	WS-6	EWS-6
0.712 (±0.002)	0.557 (±0.002)	0.459 (±0.002)	0.410 (±0.003)	0.601 (±0.002)	0.616 (±0.002)
W-3	EW-3	M-3	EM-3	WS-3	EWS-3
0.557 (±0.002)	0.643 (±0.002)	0.626 (±0.002)	0.440 (±0.002)	0.474 (±0.002)	0.681 (±0.002)

W = Willow. M = Miscanthus. WS = Wheat Straw. E = Hot Water Extracted.
6/3 = Pellets made from Biomass Hammermilled with 6/3 mm screen. Average particle size is presented in mm.

Table 18. Particle Size Distribution of Lignocellulosic Biomass Ground with 6-mm Hammermill Screen

Fraction / Sieve Size (mm)	W-6	EW-6	M-6	EM-6	WS-6	EWS-6
Above 6.3	0.00	1.61	0.00	1.81	0.00	6.48
3.35-6.3	0.16 ⁺	1.29	0.16 ⁺	1.98	0.00 ⁺	2.05
1.7-3.35	8.37	9.76	0.66 ⁺	3.79 ⁺	3.09 ⁺	6.48
0.85-1.7	40.06	24.92	18.90 ⁺	13.98	32.43	29.35
0.212-0.85	45.81	40.23	64.88	44.75	59.62	41.98
Below 0.212	5.60	22.18 ⁺	15.41	33.70 ⁺	4.87	13.65
Moisture Content (%)	7.49 (±0.08)	5.63 (±0.08)	7.23 (±0.04)	5.75 (±0.01)	7.38 (±0.23)	4.63 (±0.10)

Values are the mass percent of the fraction from the total mass of the sample.

W = Willow. M = Miscanthus. WS = Wheat Straw. E = Hot Water Extracted.

Moisture contents of the LCB and HWEed LCB are provided as per ISO 17827.

⁺ Represents fractions within the recommended distribution range, based on Kaliyan and Morey.⁹

Table 19. Particle Size Distribution of Lignocellulosic Biomass Ground with 3-mm Hammermill Screen

Fraction / Sieve Size (mm)	W-3	EW-3	M-3	EM-3	WS-3	EWS-3
Above 6.3	0.00	1.73	0.00	2.90	0.00	25.75
3.35-6.3	0.32 ⁺	2.06	0.31 ⁺	0.65	0.00 ⁺	4.18
1.7-3.35	2.74 ⁺	7.29	4.65 ⁺	3.04 ⁺	1.13 ⁺	6.35
0.85-1.7	31.08	31.31	34.25	11.83	18.71 ⁺	19.23
0.212-0.85	53.62 ⁺	46.83	54.44 ⁺	63.45	68.22	38.96
Below 0.212	12.24	10.77	6.36	18.14	11.94	6.35
Moisture Content (%)	6.28 (±0.09)	5.10 (±0.09)	6.22 (±0.03)	5.03 (±0.16)	6.82 (±0.11)	5.11 (±0.27)

Values are the mass percent of the fraction from the total mass of the sample.

W = Willow. M = Miscanthus. WS = Wheat Straw. E = Hot Water Extracted.

Moisture contents of the LCB and HWEed LCB are provided as per ISO 17827.

⁺ Represents fractions within the recommended distribution range, based on Kaliyan and Morey.⁹

During pilot scale pelletizing, EW-6, EWS-6, EW-3, and EWS-3 caught on itself when travelling up the feed auger and would not fall to the exit chute to the horizontal feed/mix auger. This caused the feed auger to overflow with material and shift off its axis, which threatened the integrity of the equipment. This resulted in the need to remove the exit chute and feed the material by hand into the horizontal feed/mix auger as it would not flow via normal operation.

Similar issues were observed with the laboratory scale pelletizer in which areas that required gravity to drop the HWEed LCB material from one section of the equipment to the next (feed hopper, mixing chamber, feed chute from main auger to die) would frequently clog with material and pause operation of the pelletizer. The feed hopper required constant monitoring and mixing by hand to ensure the HWEed LCB would fall into the feed auger instead of forming a fluffy layer over the auger that prevented particles from dropping into the screw. This created unfavorable flow characteristics for HWEed LCB, which could be a deterrent to utilizing this material for pelletizing.

These issues with the “flowability” of hydrothermally treated LCB were observed in a study by Adapa⁶⁸ on the pelletizing of four straw materials (barley straw, canary straw, oak straw, and wheat straw) that were treated with steam explosion compared to straws that were not pretreated. Adapa⁶⁸ observed similar issues with clogging and the flowability of the steam exploded materials that resulted in the inability to pelletize the material in certain applications. Adapa⁶⁸ attributed this in part to the lower bulk density

of the steam-exploded straw compared to untreated straw and reported that blends of steam-exploded material with untreated material at hammermill screen size of 0.8 mm could produce pellets. Increasing the hammermill screen size of the steam-exploded material, however, incurred flowability issues even in the blends.

Kaliyan and Morey⁹ suggested that the particle size distribution of lignocellulosic biomass should have a specific proportion of different particle size fractions for optimum pelletizing (Table 19). While the sieve sizes utilized in the particle size distribution tests in this research were not the exact fractions listed by Kaliyan and Morey,⁹ comparisons between their “ideal” distribution and that of the LCB and HWEed LCB used in this research can be made (Table 18, Table 19).

For the 3.0 mm sieve size recommendation (up to 1% of material retained on the screen), examination of the 3.35 mm sieve size fractions can be made. Willow, miscanthus, and wheat straw—regardless of the hammermill screen utilized (6 or 3 mm)—all satisfied this fraction recommendation. EM-3 also satisfied this suggestion when looking only at the 3.35 mm sieve, but EM-3 also had 2.90% of material retained on the 6.3 mm screen. All HWEed LCB had greater than 1% of material retained on the 3.35 mm screen, and all had a portion retained on the 6.3 mm screen as discussed prior.

Examining the 1.7 mm sieve fraction can provide insight into the 2.0 mm sieve-fraction recommendation from Kaliyan and Morey⁹ (up to 5%). Similarly, all LCB except for W-6 aligned with the recommended sieve fraction size. EM-3 and EM-6 also satisfied the suggested fraction size. The recommended material retention for the 1.0 mm sieve size is “around 20%,” and when compared to the 0.85 mm sieve fraction, only M-6, WS-3, and EWS-3 were within a 2% range of this target. EM-6 and EM-3 were below this recommendation by more than 5%, while all other LCB and HWEed LCB were above this suggestion by at least 4%.

The 0.5 mm and 0.25 mm sieve fractions suggestions (“around 30%” and “around 24%”) can be combined to compare to the 0.212 mm screen utilized in this research (for a value of 54%). W-3 and M-3 were the closest to this target (53.62% and 54.44%), while all other LCB and HWEed LCB were outside of this range by 4% or more (either above or below).

Finally, the fraction recommendation of “not less than 20%” for particles below 0.25 mm can be compared to the “below 0.212 mm” sieve in this research. Interestingly, only EW-6 and EM-6 had fractions above this suggested percentage (22.18% and 33.70%). EM-3 was close to this specification (18.14%), but the rest of the LCB and HWEed LCB were 15.41% or below. W-6 and WS-6 had the lowest fraction percentages (5.60% and 4.87%), while M-3 and EWS-3 were nearly the same (6.36% and 6.35%).

Overall, M-6, M-3, W-3, and WS-3 had the most fractions of weight percentages in the suggested ranges. It is possible that HWEed LCB could have a closer distribution to that of LCB; however, the issue of HWEed LCB retaining on the 6.3 mm sieve interfered with this measurement. In the calculation of average particle size for each LCB and HWEed LCB, the fraction above the 6.3 mm sieve was disregarded due to this interfering issue. Future work could explore a better method for examining the true particle size distribution and average particle size of HWEed LCB that addresses this entangling behavior.

Of the LCB and HWEed LCB, W-6 had the highest average particle size (0.712 ± 0.002 mm), which can be seen in the higher weight fractions in the 0.85–1.7 mm and 1.7–3.35 mm bins (Figure 6). EM-3 had the smallest average particle size (0.410 ± 0.002 mm) and the largest weight percent in the <0.212 mm weight fraction of all LCB and HWEed LCB. The average particle size of LCB was not statistically significant to HWEed LCB (0.572 ± 0.096 mm versus 0.558 ± 0.111 mm). This is also seen when comparing LCB-6 to HWEed LCB-6 (0.591 ± 0.127 mm versus 0.527 ± 0.106 mm) and LCB-3 to HWEed LCB-3 (0.553 ± 0.076 mm versus 0.588 ± 0.129 mm). There was no significance between LCB-6 and LCB-3 as well as HWEed LCB-6 and HWEed LCB-3. Among the LCB, the average particle size from highest to lowest was W-6 > M-3 > WS-6 > W-3 > WS-3 > M-6, while HWEed LCB had an order of EWS-3 > EW-3 > EWS-6 > EW-6 > EM-3 > EM-6.

Pelletization presented unique issues with the use of hot water extracted (HWEed) biomass.

HWEed willow, wheat straw, and miscanthus (HWEed LCB) had issues with flow characteristics in both pelletizers. During pilot scale production, four samples (HWEed willow [6 mm and 3 mm particle size screen] and HWEed wheat straw [6 mm and 3 mm]) had to be hand-fed due to clogging in the feed auger of the pelletizer. This impacted the production and quality of the pellets due to variability in the feed flow. The HWEed miscanthus did not present these flow problems. However, considerable

amounts of water were needed to make pellets from the 3 mm HWEed willow and 3 mm HWEed miscanthus pellets. Due to this and low air-drying exposure time, these samples had higher moisture contents and resulting properties that were uncharacteristic to the other HWEed LCB pellets. Additionally, despite multiple runs the pilot scale pelletizer did not produce pellets from 3 mm particle size miscanthus (no-HWE). As such, some results from the pilot scale pelletization experiments were disregarded and will be readdressed with laboratory scale pelletization studies.

Overall, 161 kilograms of 6 mm particle size pellets and 104 kilograms of 3 mm particle size pellets were made with the pilot scale pelletizer (Table 20). The production rate amongst samples that did not require handfeeding showed that HWEed LCB had a greater production rate than LCB. However, due to the need to handfeed four out of six HWEed samples, it is not a conclusive result. Additionally, the environment of the pilot scale pelletizer changed between the 6 mm particle size pelletizing and the 3 mm particle size pelletizing due to the location of the pelletizer. Specifically, the ambient temperature of the pelletizer and surrounding area was much lower during the latter operations, which may have impacted the productivity of the pelletizer and the potential need for more water during processing. Controlling the environment and minimizing variability in the laboratory scale pelletizing operations will provide insight into the impact of HWE on production rate of pellets.

Table 20. Production Results from Pilot Scale Pelletizing Operations

LCB or HWEed LCB and Particle Size	Production Rate (kg/hr)	Mass Produced (kg)	Samples Hand-fed?
6 mm Willow	10.8	26.9	No
6 mm HWE Willow	17.6	30.9	Yes
6 mm Miscanthus	12.6	31.4	No
6 mm HWE Miscanthus	16.1	26.9	No
6 mm Wheat Straw	10.3	20.5	No
6 mm HWE Wheat Straw	10.9	24.5	Yes
3 mm Willow	6	20.4	No
3 mm HWE Willow	2.9	38.2	Yes
3 mm Miscanthus	N/A	N/A	N/A
3 mm HWE Miscanthus	9.3	21.7	No
3 mm Wheat Straw	8.2	21.8	No
3 mm HWE Wheat Straw	5.6	23.4	Yes

However, similar flow issues occur with the laboratory scale pelletizer. The utilization of equipment management techniques such as manually stirring the feed hopper, using smaller hammermill screen sizes (in this case, 3 mm and 1 mm), monitoring the auger exit shoot for clogging, and installing a pump to control water flow to the unit were implemented to improve the pelletizing capabilities of the laboratory scale pelletizer.

3.4 Determination of Pilot Scale Pellet Properties

As seen in the Executive Summary (Figure S-1), hot water extraction (HWE) affected pellet properties compared to lignocellulosic biomass pellets that were not hot water extracted. However, the anticipated effects varied depending upon the property for pilot scale pellets (Table 21 and Table 22).

There were inconsistencies in the results that both supported and disputed anticipated impacts of HWE. It was anticipated that durability and pellet length would improve with HWE given the higher lignin content of HWE biomass (Table 21) as lignin acts as a binding agent in pelletizing.^{9,57,66,69} It was also anticipated that HWE pellets would have a lower bulk density due to the removal of hemicelluloses. However, the results showed conflicting trends. When testing to determine whether pellet length had an impact on this variability, a distinct trend or relationship could not reasonably be obtained based upon the data (Figure 7, Figure 8). This was examined by plotting these properties versus the pellet length.

Some differences, such as the mixed results regarding durability, pellet length, and bulk density, may be attributed to the variation in production properties of the pellets during pilot scale pelletizing operations. This was discussed previously in the “Pelletization of Biomass Feedstocks” section. Attempts to minimize variability in the feedstock biomass, operating parameters, and equipment environment in laboratory scale pelletizing will provide insight into the true impact of hot water extraction as a pretreatment process on these fuel pellet properties, if such stabilization can be obtained. Despite this, there were still consistent differences in pellet properties regarding the HWE effect (Table 21 and Table 22).

Table 21. Pellet Properties of LCB and HWEed LCB 6 mm Hammermill Biomass from Pilot Scale Pelletization

Pellet Property/ LCB or HWEed LCB	Willow	HWEed Willow	Miscanthus	HWEed Miscanthus	Wheat Straw	HWEed Wheat Straw	Commercial
Moisture Content (%) ^a	7.67 (0.04)	9.08 (0.09)	9.04 (0.09)	7.03 (0.04)	10.57 (0.11)	8.50 (0.06)	4.80 (0.05)
Ash Content (% %, Dry Basis)	2.59 (0.13)	1.88 ⁺ (0.10)	4.20 (0.60)	3.89 (0.54)	4.63 (0.54)	3.80 ⁺ (0.09)	0.52 (0.05)
Gross Calorific Value (MJ/kg)	24.0 (0.04)	24.9 ⁺ (0.04)	22.9 (0.06)	23.5 ⁺ (0.05)	23.1 (0.07)	23.8 ⁺ (0.07)	24.5 (0.05)
Bulk Density (kg/m ³ , Dry Basis)	623 (2)	623 (1)	550 (3)	657 ⁺ (3)	542 (2)	649 ⁺ (3)	615 (4)
Durability (Index/ Dimensionless)	96.6 (0.2)	90.7 ⁺ (0.2)	92.4 (0.5)	93.9 ⁺ (0.2)	96.9 (0.5)	91.7 ⁺ (0.3)	98.8 (0.03)
Pellet Length (mm)	13.71 (3.44)	14.01 (4.73)	15.90 (4.73)	12.44 ⁺ (3.27)	15.14 (4.23)	14.35 (4.87)	17.34 (3.76)
Moisture Absorption (% Moisture Gained)	6.94 (0.03)	5.06 ⁺ (0.01)	6.23 (0.03)	5.23 ⁺ (0.07)	7.09 (0.04)	5.40 ⁺ (0.03)	6.39 (0.04)
CO Emissions [Day 3 Peak] (ppm)	23 (5)	92 ⁺ (6)	21 (3)	34 ⁺ (6)	36 (7)	66 ⁺ (2)	133 (6)

Statistical analysis performed with ANOVA [Analysis of Variance] in MiniTab Software using One-Way ANOVA (Tukey, $\alpha=0.05$). Values are averages of three replicates for each test, except pellet length, which is an average of fifty pellets for each sample.

^a Represents moisture content of samples after pelletizing and sealed storage in cold room.

⁺ Represents statistically significant difference between LCB and HWEed LCB based on ANOVA analysis. Moisture Content was not statistically compared.

Table 22. Pellet Properties of LCB and HWEed LCB 3 mm Hammermill Biomass from Pilot Scale Pelletization

Pellet Property/ LCB or HWEed LCB	Willow	HWEed Willow	Miscanthus	HWEed Miscanthus	Wheat Straw	HWEed Wheat Straw	Commercial
Moisture Content (%) ^a	9.45 (0.11)	16.69 (0.24)	- -	23.10 (0.10)	7.06 (0.11)	9.36 (0.11)	4.80 (0.05)
Ash Content (%, Dry Basis)	1.97 (0.30)	1.85 (0.36)	- -	4.92 (0.20)	4.49 (0.25)	3.98 (0.25)	0.52 (0.05)
Gross Calorific Value (MJ/kg, Dry Basis)	24.2 (0.04)	24.8 ⁺ (0.23)	- -	23.4 (0.04)	23.1 (0.04)	24.3 ⁺ (0.11)	24.5 (0.04)
Bulk Density (kg/m ³ , Dry Basis)	582 (6)	498 (1)	- -	458 (3)	589 (1)	572 (1)	615 (4)
Durability (Index/ Dimensionless)	91.8 (1.0)	89.8 (1.2)	- -	91.6 (0.5)	94.0 (0.2)	84.9 ⁺ (1.0)	98.8 (0.03)
Pellet Length (mm)	18.97 (5.07)	16.00 ⁺ (5.30)	- -	14.85 (5.08)	18.66 (7.10)	13.35 ⁺ (4.61)	17.34 (3.76)
Moisture Absorption (% Moisture Gained)	6.99 (0.03)	5.69 ⁺ (0.01)	- -	5.73 (0.07)	7.12 (0.02)	5.51 ⁺ (0.07)	6.39 (0.04)
CO Emissions [Day 3 Peak] parts per million (ppm)	59 (9)	- -	- -	- -	82 (18)	98 (6)	133 (6)

Statistical analysis performed with ANOVA [Analysis of Variance] in MiniTab Software using One-Way ANOVA (Tukey, $\alpha=0.05$). Values are averages of three replicates for each test, except pellet length, which is an average of fifty pellets for each sample.

^a Represents moisture content of samples after pelletizing and sealed storage in cold room.

⁺ Represents statistically significant difference between LCB and HWEed LCB based on ANOVA analysis. Moisture Content was not statistically compared.

Figure 7. Pellet Length of Fuel Pellets Compared to Bulk Density of Fuel Pellets

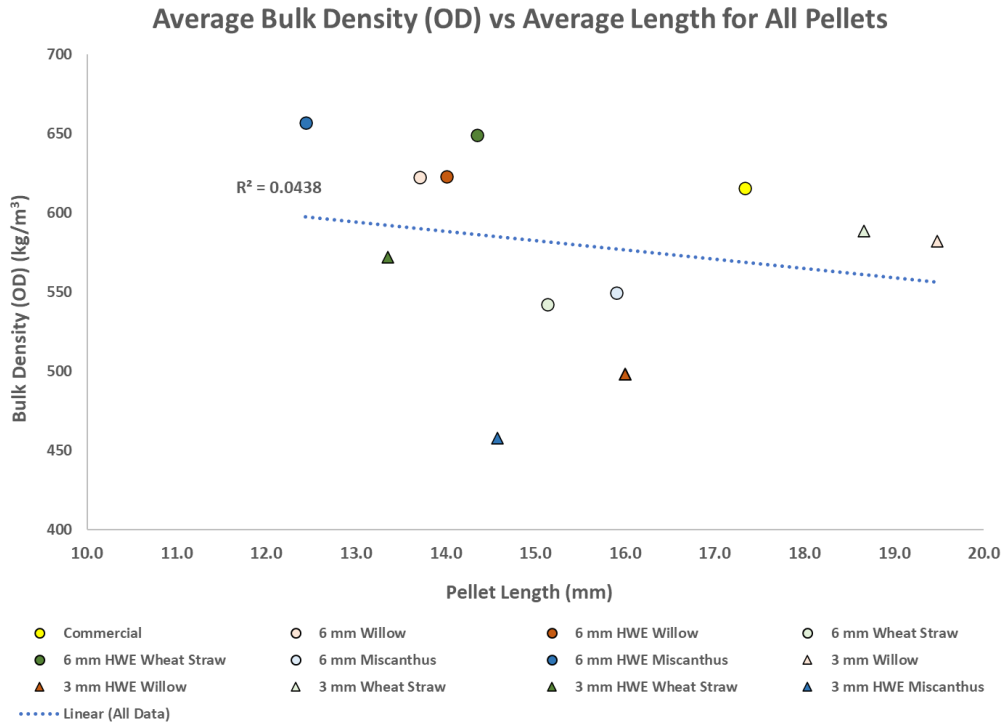
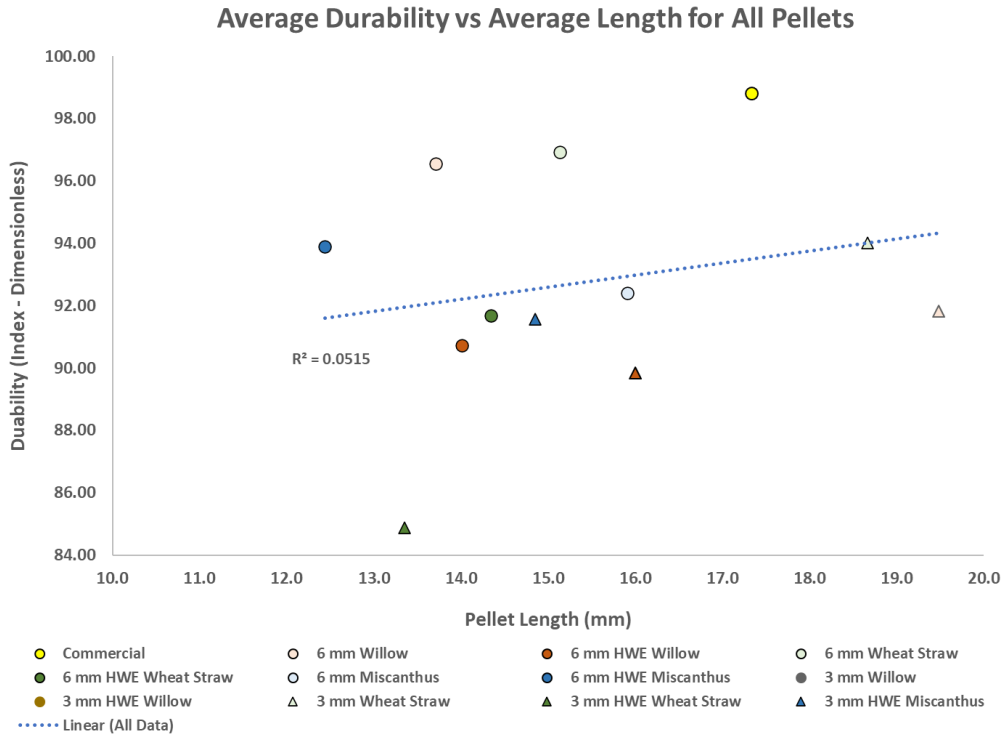


Figure 8. Pellet Length of Fuel Pellets Compared to Durability of Fuel Pellets



As anticipated based on previous literature,⁴ the ash content of the HWEed LCB pellets was lower than the LCB pellets made with the 6 mm hammermill screen material. In the case of willow and wheat straw, this difference was statistically significant (Table 21). However, ash values for all pellets are not comparable to commercially available pellets, which have an ash content lower than 1% (Table 21). This could be due to ash added during harvesting and processing and the nature of the materials (shrubs/grasses compared to a hardwood/softwood blend). Additionally, previous studies⁴⁶ indicate that varying bark content can contribute to a higher ash content in willow compared to debarked willow both with and without HWE (depending on the bark composition and cultivar). The willow utilized in this study was not debarked, and therefore this could have impacted the ash content of the LCB and HWEed LCB willow pellets. Similar trends were seen with the ash content of pellets made with the 3 mm hammermill screen material (Table 22). However, the differences in ash content were not statistically significant.

The energy content (calorific value) of HWEed LCB pellets made with the 6 mm hammermill screen material was consistently higher than that of LCB pellets (Table 21). This was also true of the HWEed LCB pellets made with the 3 mm hammermill screen material (Table 22). In each case, the HWEed LCB pellet exhibited statistically significant differences in energy content. This is attributed to the removal of hemicelluloses during the HWE process and the increase in lignin content (Table 10). The average energy content of polysaccharides is 17.5-17.7 MJ/kg,^{65,67} while the average energy content of lignin is 21–26.6 MJ/kg^{4,65-67}. Cellulose has an average energy content of approximately 17 MJ/kg while hemicelluloses have an average of approximately 16.63 MJ/kg.⁴ by removing hemicelluloses with HWE, the energy content of the HWEed LCB improves since other components have a higher energy content.⁴⁶ In the case of HWEed willow pellets, this value was higher than commercial pellets as well. HWE significantly improved the energy content of miscanthus and wheat straw, indicating that HWE may be beneficial for energy-related changes in the biomass.

However, the energy content observed in the LCB and HWEed LCB pellets is greater than what was expected according to the literature on the energy content of lignocellulosic materials. The reported energy content of HWEed LCB should not exceed the average energy content of lignin alone as HWEed LCB contains components with lower heating values than lignin (such as cellulose and hemicelluloses) that would reduce the overall energy content of the HWEed LCB. The higher heating value of willow was reported in the literature to be 18.9–19.3 MJ/kg⁴⁶ and 19.52 MJ/kg⁷⁰ for pellets made from willow. Miscanthus was reported to have a higher heating value of 18.6 MJ/kg⁴ with pellets made from

miscanthus ranging from 16.85–18.59 MJ/kg.^{70,71} Wheat straw had a higher heating value of 17.5 MJ/kg⁶⁵ while pellets made from wheat straw have been reported to have a higher heating value of 18.83 MJ/kg.⁷⁰ However, the reported energy content of HWEed willow, HWEed miscanthus, and HWEed wheat straw in the literature was 19.7–20.4 MJ/kg,⁴⁶ 19.51–20.1 MJ/kg,⁴ and 19.01 MJ/kg,⁷² These values were higher than LCB. Further, if the results of the elemental analysis of the LCB and HWEed LCB from Midwest Microlab (Table 13) were utilized to calculate the higher heating value of LCB and HWEed LCB with the equation from Demirbas,⁷³ a similar trend can be seen in the energy content (Table 23).

Table 23. Higher Heating Value of LCB and HWEed LCB Calculated from Elemental Analysis

LCB = Lignocellulosic Biomass. HWEed = Hot Water Extracted.

Higher Heating Value calculated with Data from Elemental Analysis (Table 13) and Equation from Demirbas.⁷³

The pellet adjustment to the higher heating values derives from work by Quinones et. al.⁷⁴ that reported an average increase in energy content of 9.97% between ground LCB and pelletized LCB.

LCB/HWEed LCB	Calculated Higher Heating Value (MJ/kg)	Calculated Higher Heating Value with Pellet Adjustment (MJ/kg)
Willow	17.4	19.1
HWEed Willow	19.3	21.2
Miscanthus	16.2	17.8
HWEed Miscanthus	19.5	21.4
Wheat Straw	16.6	18.3
HWEed Wheat Straw	18.3	20.1

One potential explanation for the difference in energy content values between what was measured and what was expected was the programming of the calorimeter utilized for gross calorific value measurements. The general equation used by the calorimeter to determine the energy content of a sample is as follows:

Equation 1.
$$H_c = \frac{WT - e_1 - e_2 - e_3}{m}$$

Where:

H_c = gross heat of combustion

T = observed temperature rise

W = energy equivalent of calorimeter being used

e_1 , e_2 , and e_3 = correction values for the heat produced by burning nitrogen in the atmosphere of the bomb, heat produced from the formation of sulfuric acid, and heat produced from the heating wire and cotton thread

M = mass of sample

Different acid multiplier and sulfur multiplier values were utilized between the ASTM method and ISO method on the calorimeter, the former of which is the default of the calorimeter and the latter of which was programmed into the calorimeter for the measurement of pellet energy content. However, these corrections would result in a lower calorific value for the fuel pellets under the ISO method than the ASTM method (Appendix A. Modifications to Testing Methods for the differences in the program settings). The energy equivalent—W or EE value—was determined through the calibration of the calorimeter to benzoic acid. Upon examining the calibration performed for previous measurements of LCB and HWEed LCB and the calibration performed for fuel pellet analysis, the EE values were different (2425.96 versus 2895.23). Although the calibration for the fuel pellet analysis was more in line with the benzoic acid energy content (11,364 Btu/pound) based upon the reported energy content values from calibration, this higher EE value resulted in uncharacteristic calorific values for the pellets. Recalculating the gross calorific values with the alternative EE value yields results more in line with expectations from literature (table here). Regardless of this adjustment, the trend of HWEed LCB pellets demonstrating a higher energy content than LCB pellets was consistent.

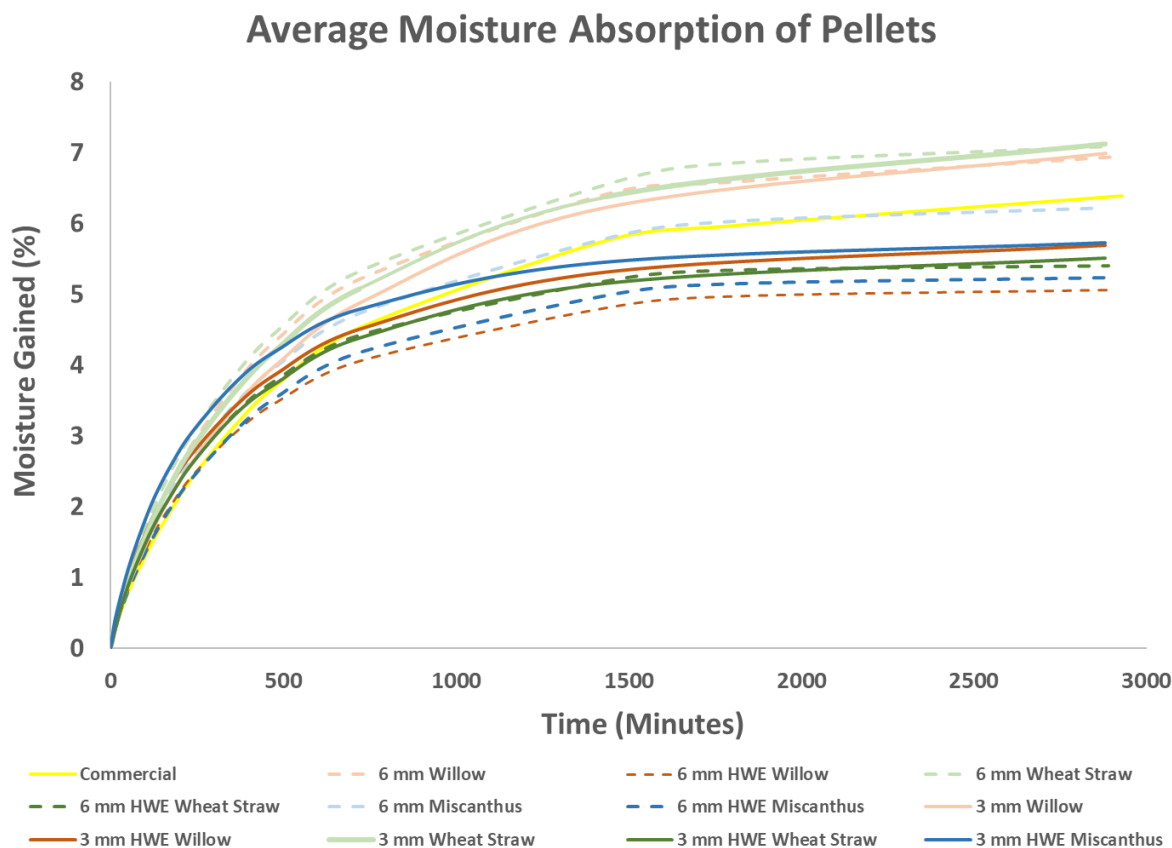
Table 24. Alternate Gross Calorific Value (Energy Content) of Pilot Scale Pellets

Energy Content = MJ/kg

Hammermill Screen Size/ LCB or HWEed LCB	Willow	HWEed Willow	Miscanthus	HWEed Miscanthus	Wheat Straw	HWEed Wheat Straw	Commercial
6 mm Hammermill Screen Pellets	19.8 (0.03)	20.5 (0.04)	19.1 (0.06)	19.6 (0.03)	18.9 (0.07)	19.4 (0.05)	20.2 (0.04)
3 mm Hammermill Screen Pellets	20.0 (0.04)	20.5 (0.18)	- (-)	19.1 (0.02)	19.1 (0.03)	20.0 (0.11)	

The moisture absorption or resistance of the pellets also followed anticipated trends. In each case, the HWEed LCB pellets exhibited statistically significant differences in moisture absorption and absorbed less moisture in a controlled humidity environment compared to their LCB counterparts. This effect was observed throughout all samples, regardless of particle size (Figure 9). All HWEed LCB pellets outperformed commercially available pellets in this property.

Figure 9. Percent Moisture Gained/Absorbed by Pellets in TAPPI Conditioning Room



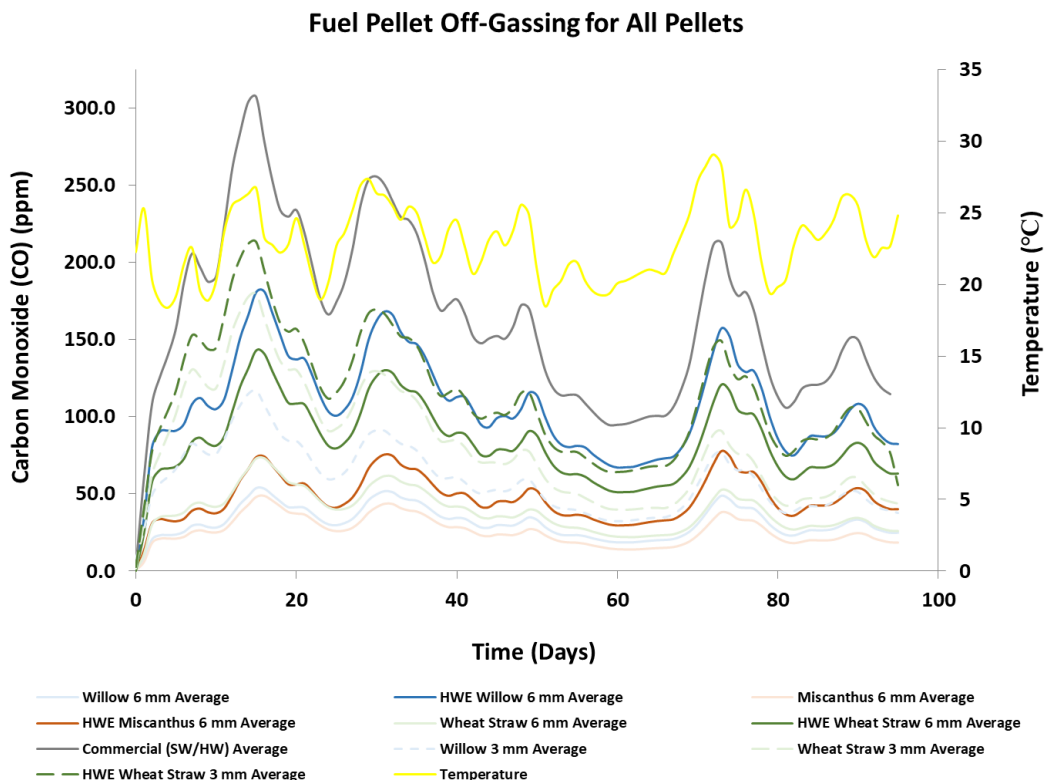
The difference between HWEed LCB and LCB pellets is most likely attributed to the removal of hydrophilic hemicelluloses during HWE and an increase in less-hydrophilic lignin content (Table 10). This could indicate that HWEed LCB pellets will be less encumbered by ambient moisture conditions in storage facilities prior to energy combustion. This could also have implications on transportation costs regarding the shipment of material versus paying for shipping moisture. However, conflicting bulk density results indicate that the degree of this impact is still unknown.

The effect of HWE on carbon monoxide off-gassing disputed the hypothesis. It was anticipated that the removal of hemicelluloses with HWE—particularly xylans as these were the basis of experiments on the mechanism of fuel pellet off-gassing¹—would result in a lower carbon monoxide off-gassing value. However, in every case, off-gassing values were higher with HWEed LCB pellets than with LCB pellets (Table 21, Figure 10). In all cases of 6 mm particle size pellets, this difference was statistically significant (Table 21).

Values for 3 mm HWEed willow and 3 mm HWEed miscanthus pellets were not included in the data set. This was due to very high pellet moisture contents (16.7% and 23.1%, respectively). The moisture content values for these HWEed samples are high compared to the moisture content of other samples in this study (average 8.26% across all other samples [commercial pellets, 6 mm LCB and HWEed LCB pellets, 3 mm willow and wheat straw pellets, and 3 mm HWEed wheat straw pellets]) and compared to literature. It is common practice to pelletize most biomass types with a moisture content that does not exceed 10–12%.⁷⁵ In several studies of hardwood, softwood, shrub willow, wheat straw, and miscanthus pellets, the moisture content of the pellets did not exceed 14%, with a range of moisture contents from 3–13.46%.^{10,11,31,70,71,76–79} It is possible that the high moisture content of the 3 mm HWEed willow and 3 mm HWEed miscanthus caused uncharacteristic behavior in the off-gassing properties, potentially due to biological growth.

In every case, however, the experimental pellets outperformed the commercially available pellets in carbon monoxide off-gassing. This aligns with expectations based upon previous literature^{1,31} that indicated softwood and softwood-blend pellets would produce more carbon monoxide than hardwood pellets.

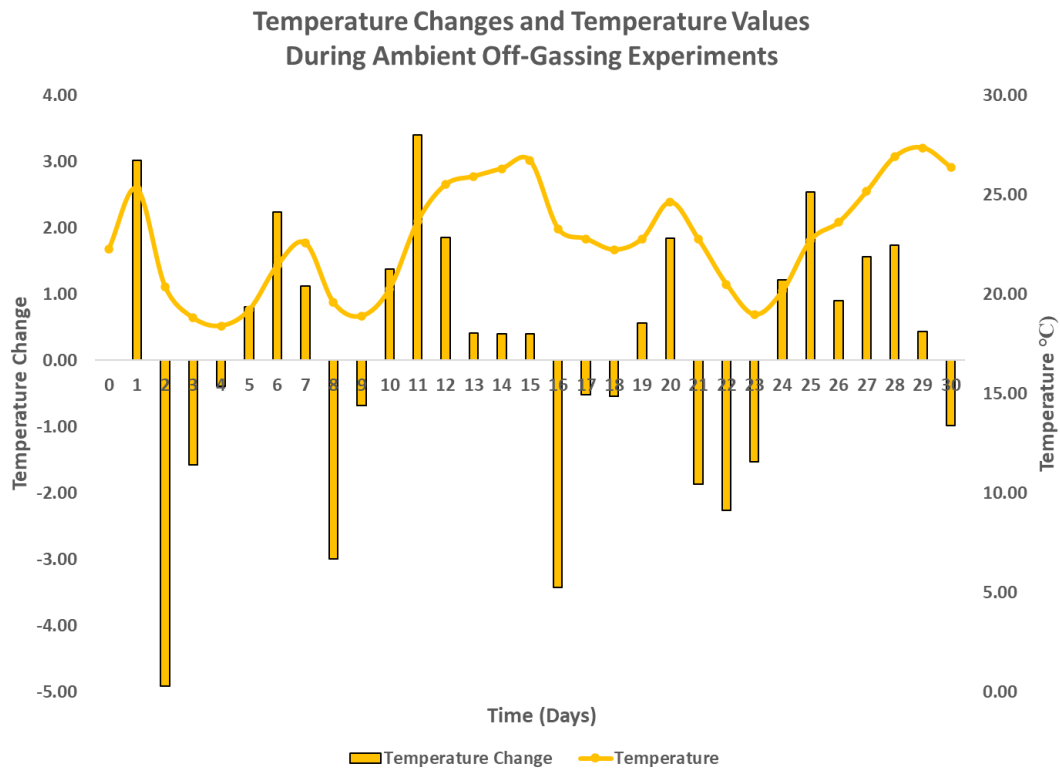
Figure 10. Carbon Monoxide Off-Gassing of Fuel Pellets



In this experiment, sample jars were stored in ambient conditions over a 90+ day period. In this time, temperature fluctuations occurred and an observable impact of temperature change on the recorded off-gassing value was observed. Previous studies^{1,31} have examined off-gassing characteristics in controlled temperature conditions, showing limited fluctuations in off-gassing values. Other studies examining ambient storage bins,^{15,80,81} however, display similar fluctuating carbon monoxide values as the ambient trial in this study.

These rising and falling values do not provide a sense of the “true” impact of HWE on off-gassing properties independent of temperature influence. However, carbon monoxide production uninfluenced by temperature change can still be observed in the ambient condition data. This is seen when examining the change in temperature compared to the change in off-gassing value (Figure 11, Figure 12).

Figure 11. Change in Temperature and Temperature Values During Ambient Off-Gassing Experiments



In this figure, the change in temperature is plotted as a bar graph to indicate the direction and severity of the change each day. Alongside this is the value of the temperature recorded each day along a plotted line to visualize the fluctuation in conditions. As can be seen, the slope and value between two points on the plotted line is affiliated with its respective bar plot; when a bar is short, the change between one point and another is small. When it is large, the change is greater to the point where the slope may even change direction and display a lower temperature value.

When plotting these same temperature-change bars with the off-gassing-change bars of each 6 mm particle size sample and its respective carbon monoxide values as a line, the influence of temperature fluctuations on the reading can be seen. During the first few days of CO off-gassing, the temperature changed rather rapidly within a range of nearly 7°C. However, the change in off-gassing values does not seem to be impacted by the swing in temperature and consistently increases despite a temperature drop. It wasn't until Day 3 that a noticeable effect of temperature on the recorded off-gassing value occurred. It was at this point in each of the 6 mm particle size samples that the data began to plateau before following a temperature trend where the change in carbon monoxide reading increased or decreased based upon the trend in temperature (Figure 12, Figure 13, Figure 14). As such, the values at Day 3 of the ambient off-gassing experiment were taken as the "true" off-gassing values and utilized for statistical analysis. This "peak" of production was compared in a separate temperature trial on commercial pellets to confirm that similar trends were observed in ambient conditions and this peak observation aligned with the peaking and plateauing of pellets in a controlled environment.

Figure 12. Changes in Off-Gassing Values for Willow Compared to Temperature Changes in Ambient Conditions

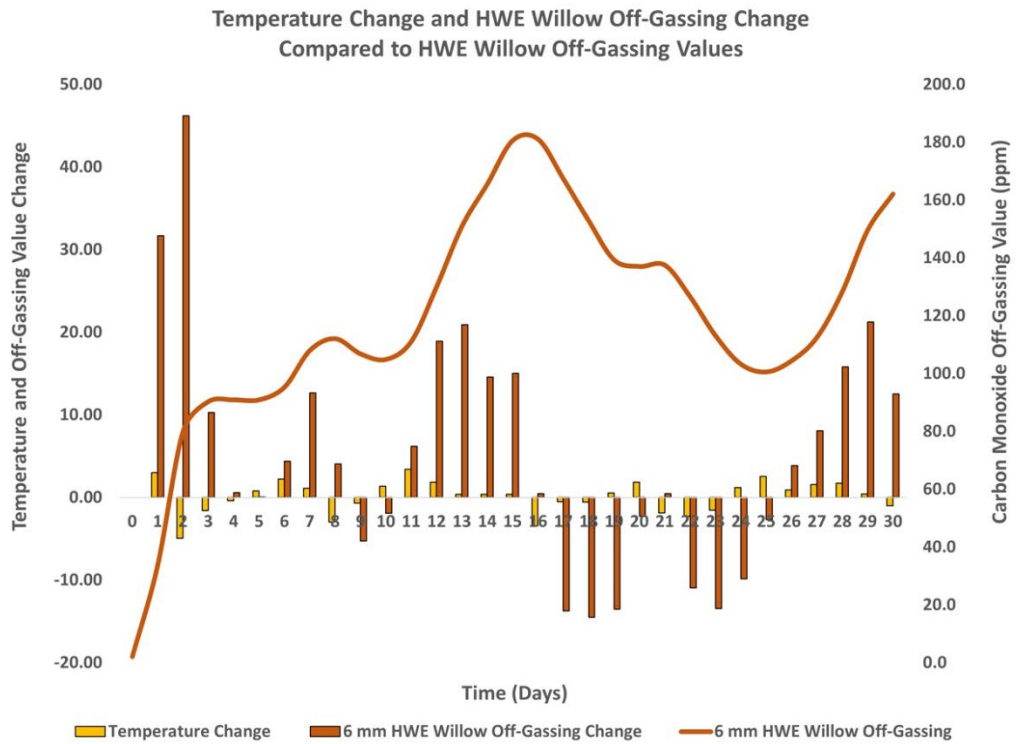
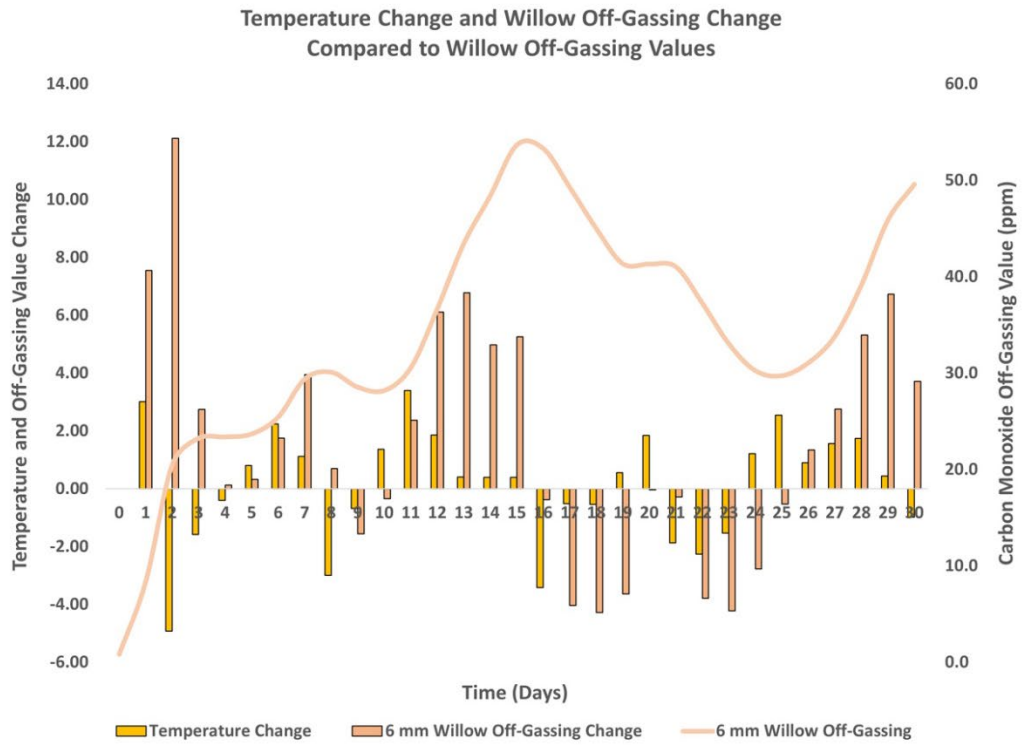


Figure 13. Changes in Off-Gassing Values for Miscanthus Compared to Temperature Changes in Ambient Conditions

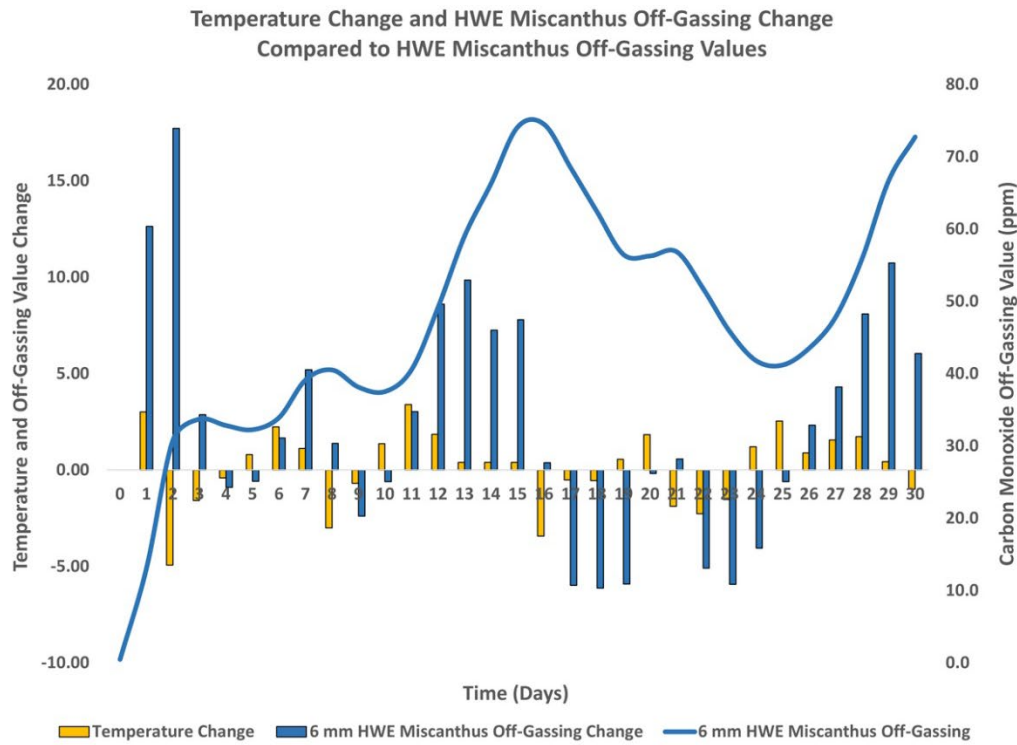
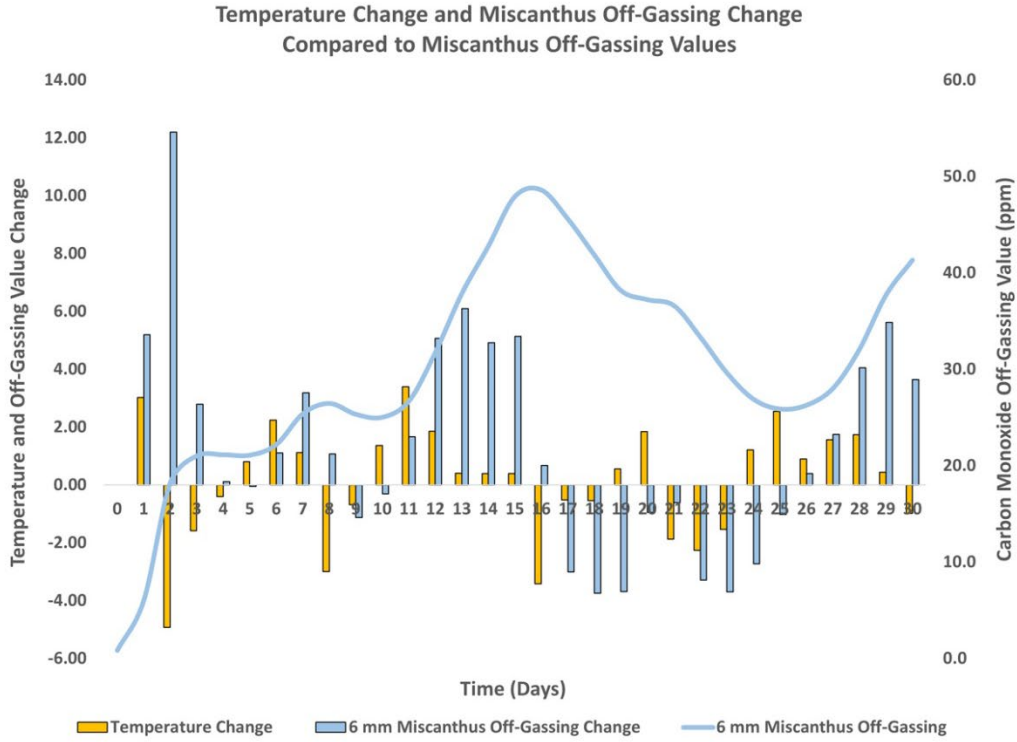
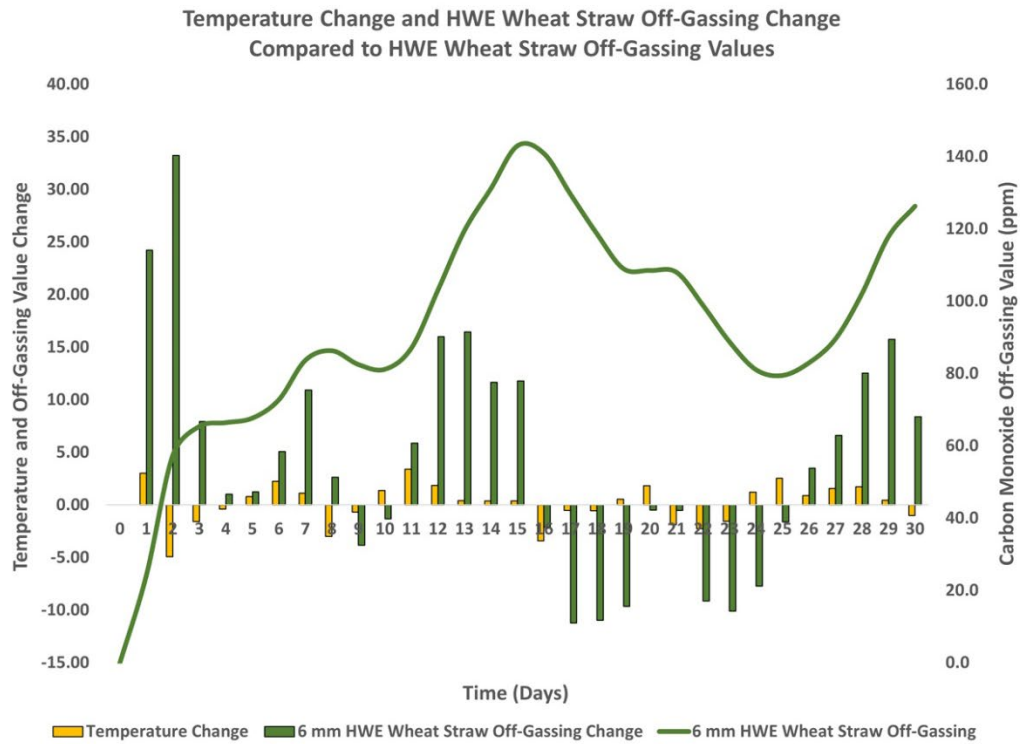
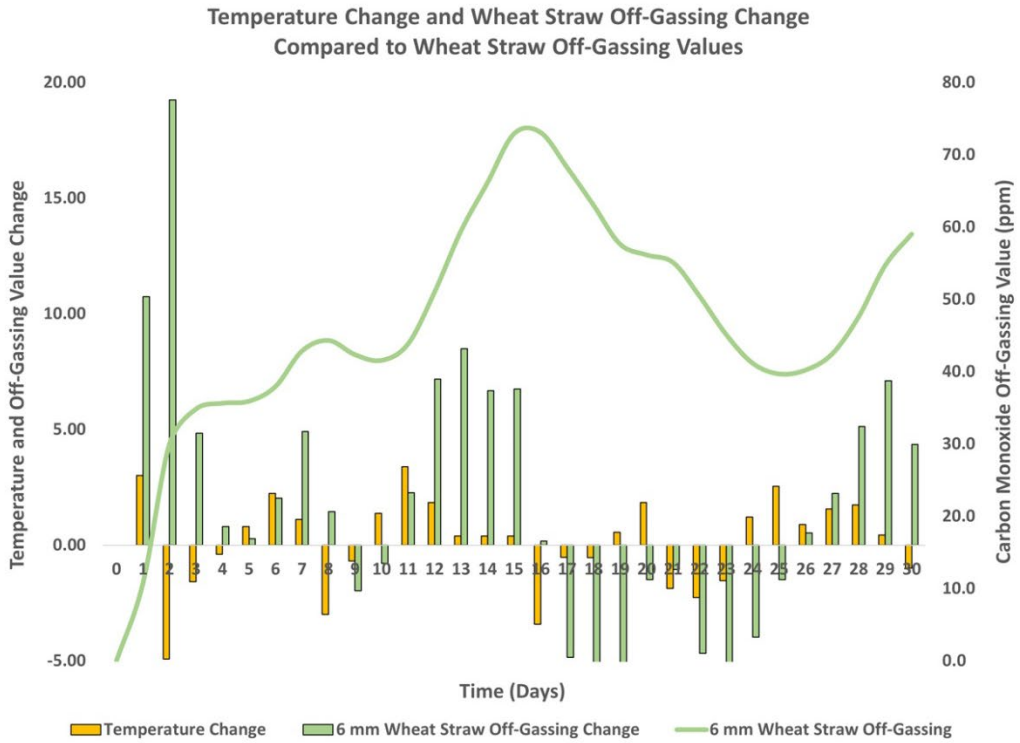
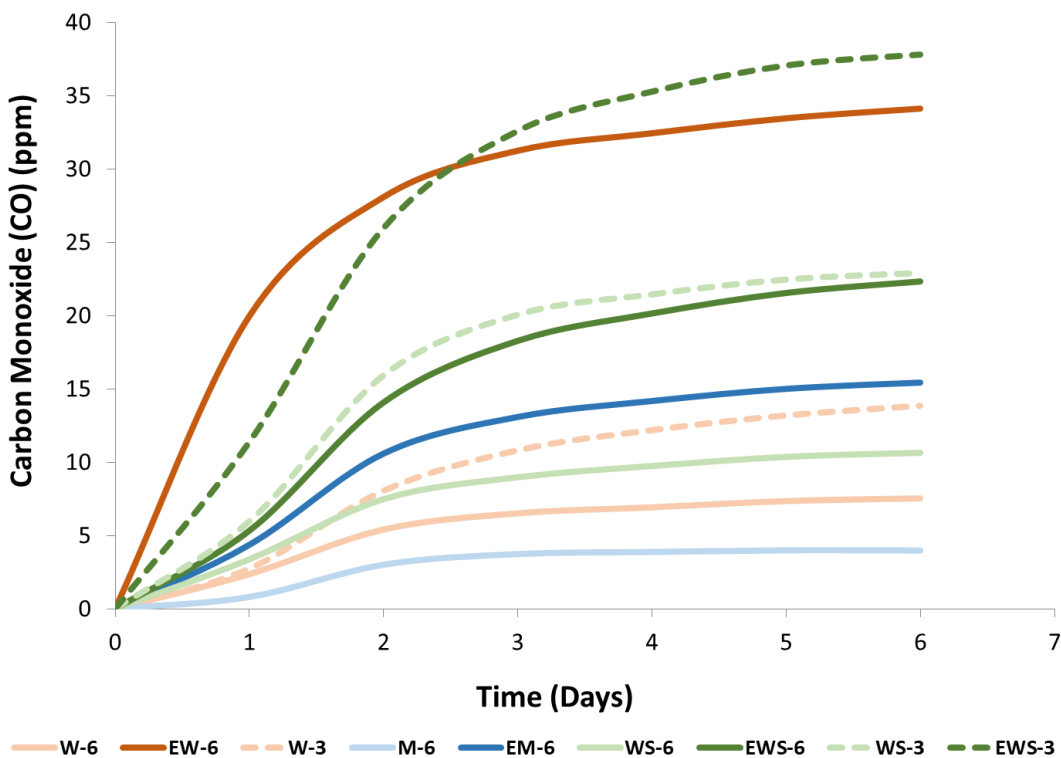


Figure 14. Changes in Off-Gassing Values for Wheat Straw Compared to Temperature Changes in Ambient Conditions



Similar CO emissions trends were observed in the CO off-gassing of pilot-scale pellets in controlled temperature conditions. The pellets were placed in sealed jars in an incubator that was operated at $22.37 \pm 0.40^\circ\text{C}$. The HWEed LCB pellets had higher concentrations of CO during the testing period than LCB pellets (Figure 15), with an average of 27 ± 10 parts per million (ppm) for HWEed LCB pellets and 12 ± 7 ppm for LCB pellets. This difference was not significant. LCB pellets and HWEed LCB pellets made from the 3 mm hammermill screen also emitted more CO than LCB pellets and HWEed LCB pellets made from the 6 mm screen in the controlled temperature trials (18 ± 6 ppm and 37 ppm versus 8 ± 4 ppm and 24 ± 10 ppm). Like the pilot scale pellet trials in ambient conditions, the HWEed LCB pellets made from the 3 mm hammermill screen are only represented by HWEed wheat straw. The difference between the HWEed LCB pellets and LCB pellets made from the 6 mm hammermill screen was significant.

Figure 15. Carbon Monoxide Off-Gassing from Pilot Scale Pellets in Controlled Temperature



W = Willow. M = Miscanthus. WS = Wheat Straw. E = Hot Water Extracted.

6/3 = Pellets made from Biomass Hammermilled with 6/3 mm Screen.

Pellets were stored in an incubator at a temperature of $22.37 \pm 0.40^\circ\text{C}$.

The behavior of the CO emissions in the controlled temperatures trials aligned to that observed in the literature.^{1,31} Typically, in controlled temperatures and sealed containers, the CO off gassed and accumulated in the container to a certain point. Then the rate of production declined until a complete plateau was reached, the accumulation of the CO continued at a slower pace, or the CO emission values slowly decreased.

The commercial pellets emitted more CO than the pilot scale pellets (152 ppm). This value was omitted in Figure 15 due to clustering of the lower value data. The high CO emission values for commercial pellets compared to pilot scale pellets was expected. This is due to the softwood content of the pellets. Soto-Garcia et. al.³¹ examined the CO off-gassing characteristics of pellets made from hardwood, softwood, and hardwood/softwood blends and reported the CO emission values to be softwood>hardwood/softwood>hardwood. This was attributed to the higher extractives/fatty acid content in softwood compared to hardwood and hardwood/softwood blends upon further analysis by Rahman and Hopke.¹

Selected properties of lignocellulosics and pelletized lignocellulosics from literature can be seen in Table 25 to compare to current research results. There is little data available for pellets made from HWEed LCB (willow, miscanthus, and wheat straw) regarding properties such as bulk density, durability, and carbon monoxide off-gassing, hence the inherent value and novelty to this research. Moisture absorption was not included in the table due to the method utilized in this research compared to other methods. Pellet length was not included as it is infrequently reported in pellet data, regardless of the LCB.

Table 25. Select Biomass and Pellet Properties from Literature

Biomass Property	Willow	HWEed Willow	Miscanthus	HWEed Miscanthus	Wheat Straw	HWEed Wheat Straw
Ash Content (%)	1.34 ^{A-m} 1.47 ^{A-b} 1.6 ^{A-c,d} 2-3 ^{A-k} 1.27-2.23 ^{A-g} ~1.45 ^{B-n} 2.22 ^{B-h}	0.84-1.66 ^{A-g} 1.05 ^{A-b} ~0.73 ^{B-n}	1.6 ^{A-d} 2 ^{A-o} 2.7-3 ^{A-p} 2.2-3.2 ^{A-p} 4.24 ^{A-a} 2.2 ^{B-ii} 3.56 ^{B-h}	1.32-4.97 ^{A-a}	3.11 ^{A-e} 3.7 ^{A-i} 6.4-7.1 ^{A-p} 6.6 ^{A-f} 7.88 ^{A-l} 3.31-3.72 ^{B-e} 6.49 ^{B-h}	2.6 ^{A-j}
Energy Content (MJ/kg)	~18.9-19.3 ^{A-g} 19.52 ^{B-h} ~16.5 ^{B-n}	~19.7-20.4 ^{A-g} ~17.6 ^{B-n}	18.6 ^{A-a} 18.59 ^{B-h} 16.85 ^{B-i}	19.51-20.1 ^{A-a}	18.48 ^{A-j} 18.83 ^{B-h}	19.01 ^{A-j}
Bulk Density (kg/m ³)	654.8 ^{B-h} ~622 ^{B-n}	~690 ^{B-n}	612.5 ^{B-h} 624 ^{B-i}	N/A	525-649 ^{B-E} 637.2 ^{B-h}	N/A
Durability (Index/Dimensionless)	85.5-89.1 ^{B-k} 97.3 ^{B-h}	N/A	95.3 ^{B-h} 97.8 ^{B-i}	N/A	96.1 ^{B-h} 96.6-98.3 ^{B-e}	N/A

This includes information about biomass in general (A) and pellets from the representative biomass (B). *Represents Lower Heating/Net Energy Value. +Represents Higher Heating/Gross Energy Value. N/A represents information that is not available in the literature.

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Table notes are continued on the next page.

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Similar trends in ash content and energy content between LCB and HWEed LCB can be observed between literature values and the results of this research. Overall, ash content decreased, and energy content increased after HWE. All pellets made in this study had higher energy contents than those cited in literature. Ash values for pellets made from miscanthus, HWEed miscanthus, and wheat straw fell within the range of the general literature values. Miscanthus pellets in this study had a higher ash content than literature pellets but was still within unpelletized miscanthus values. Ash content in pellets made from HWEed wheat straw in this study was higher than literature values. The ash content of pellets made from willow and HWEed willow in this research was higher than reported ash values in literature. This could be attributed to the bark content of the willow used in this study (as this research did not use debarked willow), and to the difference in testing procedure, depending on the reference. Methods employing higher furnace temperatures (such as TAPPI T-413²¹ with a maximum temperature of 900°C) result in a lower ash value than those with lower maximum temperatures (such as the ISO 18122 used in this research).

No clear trend was comparable between literature values and this current research, partly due to lack of data. However, the bulk density of willow pellets and wheat straw pellets from this research fell within the range presented in the literature. The bulk density of pellets made from miscanthus and HWEed willow in this research was lower than that of the literature. Pellet durability was also comparable. The durability of pellets made from willow and wheat straw in this research fell within the range of values reported in literature while pellets made from miscanthus had a lower durability value compared to the literature.

3.5 Determination of Laboratory Scale Pellet Properties

RecL and ComL were utilized as binding agents in the production of willow pellets. Willow hammermilled with a 3 mm screen (W-3) and a 1 mm screen (W-1) was utilized to make pellets, though lignin was added only to the W-1 feedstock (W-1-RecL and W-1-ComL). This was due to the operational performance of the W-1 compared to the W-3. The W-1 presented fewer issues regarding flow through the pelletizer and less need for adjustments during the pelletizing process. Lignin was added to the feedstock in powder form at 5% weight of the W-1 feedstock. The pellets were characterized for moisture content, ash content, energy content, bulk density, durability, pellet length, moisture absorption, and carbon monoxide off-gassing.

Table 26. Properties of Laboratory Scale Pellets with Lignin as a Binder

Pellet Property	W-3	W-1	W-1-RecL	W-1-ComL	Commercial
Moisture Content (%) ^a	6.88 (0.05)	7.43 (0.05)	7.06 (0.06)	7.24 (0.15)	7.94 (0.17)
Ash Content (% _{Dry Basis})	2.07 (0.11)	3.57 ⁺ (0.29)	3.18 (0.33)	3.72 (0.36)	0.41 (0.09)
Gross Calorific Value (MJ/kg, Dry Basis)	22.3 (0.11)	22.2 (0.05)	22.5 [*] (0.04)	22.6 [*] (0.02)	22.4 (0.05)
Bulk Density (kg/m ³ , Dry Basis)	586 (9)	612 ⁺ (1)	642 [*] (9)	633 [*] (1)	537 (4)
Durability (Index/Dimensionless)	84.6 (0.7)	90.4 ⁺ (0.5)	95.4 [*] (1.0)	95.2 [*] (0.1)	98.7 (0.2)
Pellet Length (mm)	15.45 (4.19)	16.43 (4.91)	17.89 (4.58)	17.95 (4.80)	17.09 (2.56)
Moisture Absorption (% Moisture Gained)	2.80 (0.02)	2.64 ⁺ (0.02)	2.50 [*] (0.05)	2.62 ⁻ (0.01)	2.61 (0.15)
CO Emissions [Maximum Peak] (ppm)	39 (2)	55 (13)	32 (4)	39 (4)	36 (4)

W = Willow. 3/1 = Pellets made from biomass that was hammermilled with a 3/1 mm screen.

RecL = Lignin Recovered from the Hot Water Extraction of Willow.

ComL = Commercial Lignin (LignoBoost).

Values are averages of three replicates for each test, except pellet length, which is an average of fifty pellets.

Values in parentheses are standard deviations.

^a Represents moisture content of samples after pelletizing, air-drying overnight and sealed storage in cold room.

^{*} Symbolic superscripts represent statistically significant differences based on Pairwise ANOVA analysis of Two Means (One-Way ANOVA [Tukey, $\alpha=0.05$]). Moisture Content was not statistically compared.

⁺ Significance between W-3 and W-1. ^{*} Significance between W-1 and W-1-RecL or W-1-ComL.

⁻ Significance between W-1-RecL and W-1-ComL.

Overall, pellets with additional lignin binder (W-L) had a lower moisture content, higher bulk density, higher durability, higher average pellet length, less moisture absorption, and lower CO emissions than W-1 pellets (Table 26). Compared to the W-1 pellets, the addition of RecL had a greater positive effect on the moisture content, ash content, bulk density, durability, moisture absorption, and CO emissions than the addition of ComL. However, ComL improved gross calorific value (energy content) and pellet length compared to W-1 pellets more than RecL did.

The moisture content, ash content, moisture absorption, and CO emissions of W-1-RecL pellets were lower than W-1-ComL pellets, which are desirable pellet traits. Additionally, the bulk density and durability of W-1-RecL pellets were higher than W-1-ComL pellets. The W-1-ComL pellets had a higher energy content and an average longer pellet than W-1-RecL pellets. While energy content, bulk density, and durability significantly improved between W-L and W-1 pellets, only the moisture absorption between W-1-RecL and W-1-ComL pellets was significant.

These improvements in the W-1-RecL pellets compared to W-1-ComL were influenced by the properties of the lignin utilized. RecL had a significantly lower moisture content than ComL ($1.77\pm 0.06\%$ versus $22.26\pm 0.58\%$), which introduces less additional moisture to the feedstock during pelletizing. The ash content of RecL was also significantly lower than ComL ($0.41\pm 0.12\%$ versus $1.14\pm 0.12\%$), which can explain the difference in ash content for the W-1-RecL pellets and the W-1-ComL pellets.

The energy content of ComL was significantly higher than RecL (27.0 ± 0.21 versus 25.5 ± 0.01 MJ/kg). This was expected when comparing the total lignin (Klason + acid soluble lignin) and total carbohydrates (glucose, xylose, etc.) in RecL and literature values of ComL (Table 14). ComL has a higher total lignin content (96.5%) and a lower total carbohydrate content (1.98%) compared to RecL (84.68% and 2.98%). As discussed prior, higher oxygen content (such as from carbohydrates) reduces the energy content of the sample.

The moisture content of the laboratory scale pellets was measured with ISO 18134⁸⁶ after cooling the pellets overnight and storing them sealed in a cold room (4°C). Overall, the observed effect of lignin addition on the moisture content of the pellets supported the hypothesized effect: the pellets with lignin added as a binding agent would have a lower moisture content than the pellets without additional lignin. All laboratory scale pellets had a lower moisture content than the commercial pellets (COM-B).

The W-1 pellets had a greater moisture content than the W-3 pellets, with a percent difference of 7.00%. This is attributed to water addition during the pelletizing operation, in which the W-1 pellets required a higher water flow than the W-3 pellets (0.30 mL/s compared to 0.25 mL/s). A restart of the pelletizing process occurred between the first batch of W-1 pellets and the lignin pellets. However, once pelletizing conditions (water flowrate and feedstock flowrate) were established for W-1, the pelletizing of W-1-RecL feedstock began. During this time, the same water flowrate for W-1 was maintained to produce W-1-RecL and W-1-ComL pellets, but the feedstock flowrate was adjusted to prevent overloading the pelletizer, with the order of flowrate being $W-1 > W-1-RecL > W-1-ComL$. When the W-1-ComL feedstock was switched into the pelletizer, excess steam was produced that put a strain on the pelletizer. This adjustment in the flowrate of the W-1-ComL feedstock was to accommodate the high moisture content of the ComL (Table 15) that was mixed with W-1.

The ash content of the pellets was measured with ISO 18122.⁸⁷ The process of milling the willow with the 1 mm screen required two passes through the hammermill: one with the 3 mm screen and once again with the 1 mm screen. This caused more interaction with the metal components in the hammermill and can increase the ash content of the material due to abrasion, as observed by Theerarattananoon et.al.¹¹ Accordingly, the W-1 pellets had a significantly higher ash content than W-3 pellets with a 72.43% difference in the ash content.

The W-1-RecL pellets had a lower ash content than W-1 pellets (12.26% difference). This was expected due to the measured ash content of RecL ($0.41 \pm 0.12\%$). Blends are often utilized in lignocellulosic feedstocks to reduce the ash content, as seen in studies of blending different ratios of hot water extracted material⁸³ or bark free material.⁴⁶ When adding lignin as a binding agent, a portion of willow in the feedstock is displaced, resulting in an overall composition of W-1-RecL pellets having a lower ash content. This does not explain the increase in ash content of the W-1-ComL pellets considering the measured ash of ComL was $1.14 \pm 0.12\%$. All laboratory scale pellets had a significantly higher ash content than the COM-B pellets.

The energy content of the fuel pellets was measured with ISO 18125²⁶ to determine the gross calorific value at constant volume of the pellets. The measurement of energy content for RecL, ComL, and the laboratory scale pellets utilized the same calibration and programming settings (whereas the pilot scale pellets were tested with parameters (such as EE) that were from a previous calibration). The observed effect of adding lignin as a binding agent on the energy content of pellets supported the hypothesized effect: adding lignin increases the energy content of the pellets.

The W-1-L pellets had a higher average energy content than the W-1, W-3, and COM-B pellets (22.52 ± 0.04 MJ/kg versus 22.25 ± 0.06 MJ/kg and 22.39 ± 0.05). The energy content of RecL and ComL were 25.5 ± 0.01 and 27.0 ± 0.21 MJ/kg. Accordingly, the energy content of W-1-ComL pellets increased more than W-1-RecL pellets. The addition of 5% RecL and 5% ComL increased the energy content of the resulting pellets by 1.26% and 1.53%.

The bulk density of the pellets was measured with ISO 17828.⁸⁸ Overall, the observed effect of adding lignin as a binding agent on the bulk density of the pellets supported the hypothesized effect: adding lignin to feedstock increases the bulk density of the pellets made from that feedstock.

The average moisture-free bulk density of W-1-L pellets was higher than W-3/W-1 pellets (638 ± 6 kg/m³ versus 599 ± 18 kg/m³). W-1-RecL pellets and W-1-ComL pellets had a similar percent increase in bulk density compared to W-1 pellets (4.9% and 5.1%), and both were statistically significant to W-1 pellets based. The bulk density of W-1-RecL pellets was higher than W-1-ComL pellets, but this was not statistically significant. Hammermill screen size also affected the bulk density of the willow pellets. The bulk density of W-1 pellets was greater than W-3 pellets, with a 4.2% increase in the bulk density. This effect was only observed with the wheat straw pellets (WS-6 and WS-3) in the pilot scale pelletizing experiments. However, in a study by Theerarattanannon et. al.¹¹ on the pelletizing of wheat straw, corner stover, big bluestem, and sorghum stalk, the bulk density of the pellets increased with increasing average particle size.

The moisture-free bulk density of COM-B pellets (537 kg/m³) was lower than what was expected compared to the previous batch of commercial pellets from the pilot scale studies (615 kg/m³). This could be attributed to the age of the pellets as the commercial pellets utilized in this test were not as fresh as those utilized in the pilot scale experiments. This has occurred in literature as well. One study by Soto-Garcia et. al.³¹ measured the bulk density and CO off-gassing value of aged hardwood, softwood, and hardwood/softwood blended pellets and found that both the bulk density and CO emissions decrease as pellets aged in storage.

The durability of the pellets was measured with ISO 17831.⁸⁹ It was hypothesized that adding lignin would increase the durability of fuel pellets due to participation of lignin in the binding and bridging of LCB particles during pelletizing. Overall, the average durability of the W-1-L pellets (95.3 ± 0.1) was higher compared to W-1/W-3 pellets (87.5 ± 4.1). Adding 5% RecL and 5% ComL increased the

durability by 5.5% and 5.3%. The increase in durability between W-1 and W-1-L pellets was statistically significant. Although W-1-RecL pellets had a higher durability than W-1-ComL pellets, it was not a statistically significant difference.

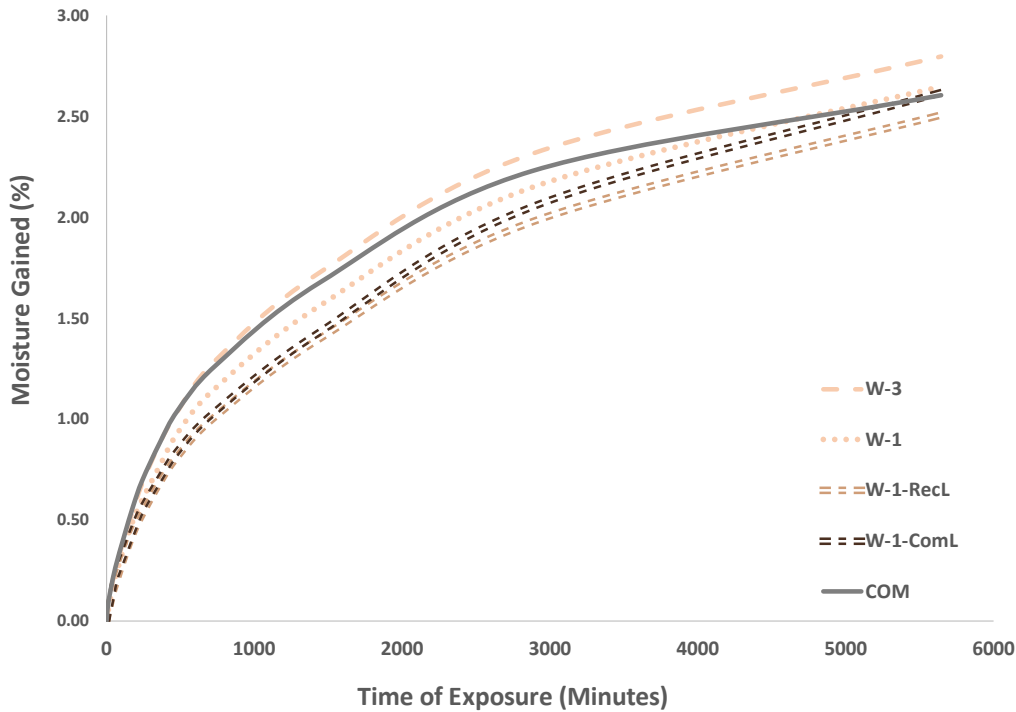
The durability of W-1 pellets was significantly higher than W-3 pellets. The effect of hammermill screen size on the durability of pellets in the literature, however, is variable. In the study by Theerarattananoon et. al.,¹¹ wheat straw, corn stover, big bluestem, and sorghum stalk was hammermilled with 6.5 mm and 3.2 mm screens. The durability of the pellets made with the 3.2 mm corn stover was greater than the pellets made with 6.5 mm corn stover. However, the reverse was true for the other three LCB.

The length of the pellets was measured with ISO 17829⁹⁰ an average pellet length was determined. The pellets utilized in pellet length measurements can be seen in (Figure 16). It was hypothesized that adding lignin to the pellets would increase the pellet length due to enhanced binding and bridging of LCB particles with lignin during pelletizing. Overall, the average length of W-1-L pellets (17.92 ± 0.04 mm) was longer than W-3/W-1 pellets (15.94 ± 0.69). The addition of 5% RecL and 5% ComL increased the pellet length by 8.89% and 9.25%. This effect was not statistically significant. The average pellet length of W-1 pellets was longer than W-3 pellets, indicating a potential hammermill screen size effect. However, this difference was not statistically significant. The average pellet length of W-1-RecL and W-1-ComL pellets were comparable with commercial pellets as well.

Moisture absorption was measured by exposing oven-dried pellets to a TAPPI conditioning room. These experiments were conducted at 71°F/21.7°C and $18 \pm 2\%$ relative humidity. The hypothesized effect of lignin on the moisture absorption of fuel pellets was that adding lignin to the feedstock would result in pellets that would absorb less moisture from the ambient conditions. This is due to the less hydrophilic nature of lignin compared to cellulose and hemicelluloses, which are more hydrophilic in nature.⁹¹

Overall, the W-1-RecL and W-1-ComL pellets absorbed less moisture than W-1 and W-3 pellets (Figure 16). The W-1-RecL absorbed the least moisture from the atmosphere compared to the other pellet samples. There was a 5.30% decrease in the moisture absorbed by W-1-RecL while W-1-ComL only exhibited a 0.80% decrease in moisture absorbed compared to W-1 pellets. This is contrary to expectations when considering the total lignin content and total carbohydrate content of RecL (84.48% and 2.98%)⁵ and ComL (96.5% and 1.98%).²⁴

Figure 16. Moisture Absorption Curves for Laboratory Scale Pellets



W = Willow. 3/1 = Pellets made from Biomass Hammersed with 3/1 mm Screen.

COM-B = Commercial Pellets.

Recl = Lignin Recovered from Hot Water Extraction of Willow.

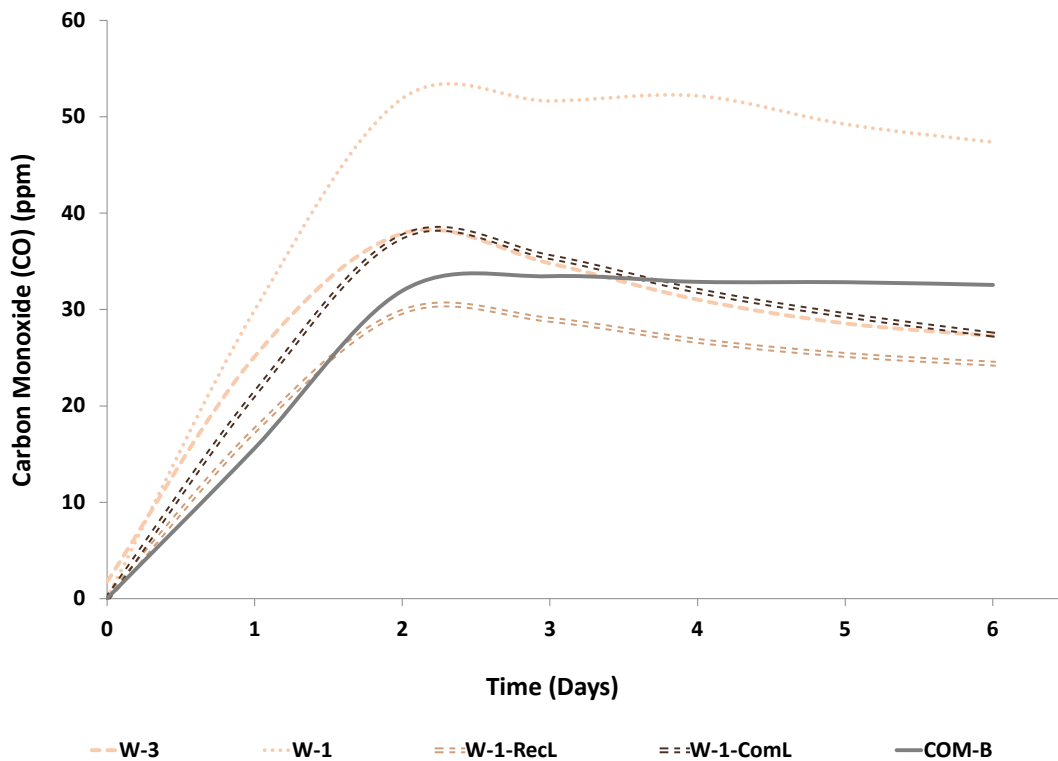
ComL = Commercial Lignin (LignoBoost). Temperature: 71°F/21.7°C. Relative Humidity: 18±2%.

Laboratory scale pellets absorbed less moisture than pilot scale pellets when comparing willow (W-3) and commercial pellets. W-3 pilot scale pellets and commercial pellets absorbed 6.99% and 6.39% moisture compared to laboratory W-3 and commercial pellets (2.80% and 2.61%). However, this is most likely due to the difference in operating parameters during the moisture absorption test. Pilot scale pellets were tested in an atmosphere at 50% relative humidity, whereas laboratory scale pellets were exposed to only 18% relative humidity. This procedure utilizes the equilibrium moisture that the LCB reaches when exposed to humidity. As such, it is expected that the laboratory scale pellets would absorb less moisture than pilot scale pellets.

The difference in moisture absorption of W-1-RecL pellets and W-1 pellets, as well as W-1-RecL and W-1-ComL, were statistically significant. There is a significant difference in the moisture absorption of W-1 and W-3 pellets in which W-3 pellets absorbed 6.06% more moisture than W-1 pellets. This is contrary to the perspective of how hammermill screen size affects moisture absorption that was observed in the pilot scale experiments. The W-1-RecL pellets were the only pellets to absorb less moisture than commercial pellets.

CO off-gassing was measured in temperature-controlled conditions. It was hypothesized that adding lignin would reduce CO emissions based upon the mechanism of CO off-gassing in fuel pellets proposed by Rahman and Hopke.¹ The hypothesized mechanism involves the autoxidation of fatty acids in the lignocellulosic biomass to generate hydroxyl radicals that then react with hemicelluloses to form CO.

Figure 17. Carbon Monoxide Off-Gassing from Laboratory Scale Pellets with Lignin Added as a Binding Agent



W = Willow. 3/1 = Pellets made from Biomass Hammermilled with 3/1 mm Screen.

COM-B = Commercial Pellets.

RecL = Lignin Recovered from Hot Water Extraction of Willow.

ComL = Commercial Lignin (LignoBoost). Pellets were stored in an incubator at a temperature of $21.61 \pm 0.66^\circ\text{C}$.

Overall, the average CO emissions of W-1-L pellets (35.25 ± 5.30 ppm) were lower than CO emissions from W-3/W-1 pellets (47.13 ± 11.14 ppm) (Figure 17). An addition of 5% RecL and 5% ComL decreased CO off-gassing values by 42.73% and 29.09%. Similar to the CO off-gassing of pilot scale pellets, a hammermill screen size effect was also observed in the laboratory scale pellets. The CO emissions of W-3 pellets were less than W-1 pellets by 28.64%. However, there was only a small difference in the CO emissions of W-1-RecL and W-1-ComL despite the potential differences in radical scavenging potential.

The CO emissions of the commercial pellets (COM-B) were uncharacteristically low compared to previous data collected through this research project. As mentioned previously, this could be attributed to the age of the pellets as they were not freshly purchased at the time of the testing. Emissions were much higher in fresh commercial (COM) pellets (150 ppm) compared to the COM-B (35 ppm).

There were no statistically significant differences between the pairs of pellet treatments. Regardless, the CO off-gassing characteristics of pellets with lignin added as a binder will have important implications for future work and the utilization of lignin in pelletizing applications.

3.6 Initial Economic Analysis

The following is an initial outline for the economic analysis of this research. It considers the entirety of the process, from the acquisition of materials to the eventual delivery of a theoretical retailer.

**Future updates will expand upon this analysis.

3.6.1 Economic Analysis of Hot Water Extraction of Wood Chips for Pellet Production

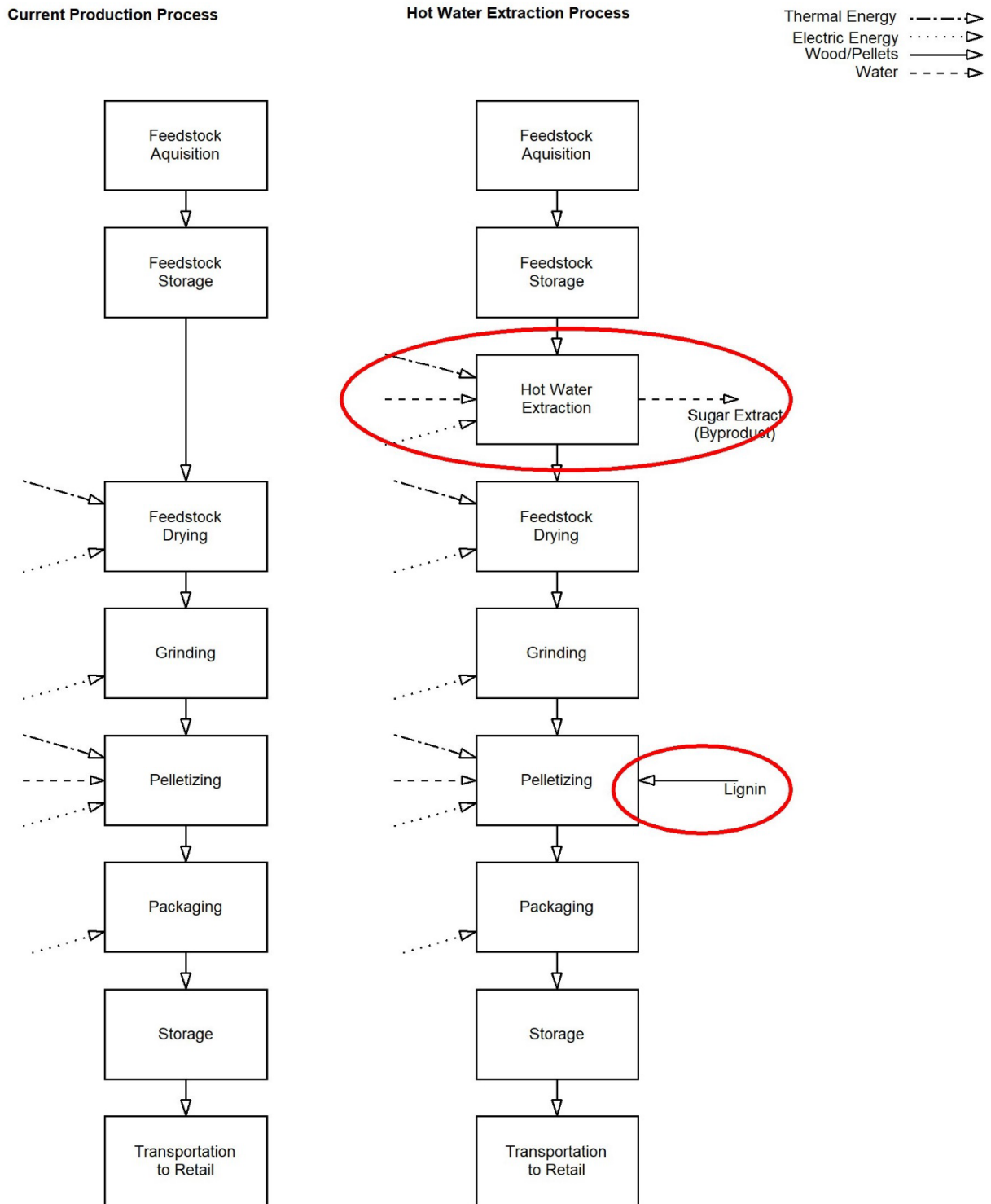
The attached diagram (Figure 18) shows the anticipated process changes as a result of the technology being developed. As noted, the hot-water extraction process is inserted between the feedstock storage and the drying process. In addition, lignin can be added to the pelletizing process. The anticipated economic changes that are being considered are summarized below (Table 27).

Table 27. Anticipated Economic Changes on Pellet Production Due to Hot Water Extraction

Parameter	Anticipated Economic Change
Feedstock Acquisition	No Significant Changes
Feed Stock Storage	No Significant Changes
Hot Water Extraction	Thermal Costs, Water and Other Utility Costs, Electric Energy Costs, Sugar Extract (Byproduct) Revenue, Equipment Costs, Maintenance Costs, Labor Costs
Feedback Drying	Thermal Costs Due to Changes in Moisture Content
Grinding	Energy Costs Due to Changes in Chip Properties
Pelletizing	Energy Costs Due to Changes in Chip Properties, Lignin Addition Costs, Equipment Costs, Maintenance Costs, Labor Costs
Packaging	No Significant Changes
Storage	No Significant Changes
Transportation	No Significant Changes
Pellet Property Changes	Higher Heat Value Changes, Ash Changes, Durability Changes

Figure 18. Outline of Factors to be Considered in Analyzing the Economic Analysis of Research

This includes thermal energy, electrical energy, water, and products.



4 Conclusions

Overall, this research has examined the effect of hot water extraction (HWE) on the chemical composition of three lignocellulosics (willow, wheat straw, and miscanthus) and fuel pellets made from these lignocellulosics (LCB) with a pilot scale flat die pelletizer. HWE removed hemicelluloses from the LCB, particularly xylans, and resulted in a lower carbohydrate content (though cellulose content was higher after HWE). HWEed LCB also had a lower ash content, higher energy value, and a higher lignin content. The same trend of lower ash and higher energy content was observed in fuel pellets made from HWEed LCB compared to pellets made from LCB. This impact of HWE on the ash and energy content of LCB was also observed in literature studies.

Pellets made from HWEed LCB exhibited more resistance to moisture absorption compared to pellets made from LCB due to the removal of hydrophilic hemicelluloses. The impact of HWE on durability, bulk density, and pellet length were inconclusive and more work is needed to examine these properties in laboratory scale studies. Some of these properties of the fuel pellets made in this research fell within literature values (when available), but others were outside of the reported literature. The carbon monoxide off-gassing of the HWEed LCB pellets was consistently greater than the LCB pellets, despite the hypothesis that removal of hemicelluloses would reduce emissions.¹ However, these emission values were still lower than commercially available pellets made from a softwood/hardwood blend.

Pellets made from willow that had lignin as an additional binding agent exhibited improved mechanical properties, with higher bulk density and durability than pellets without additional lignin. The average pellet length of pellets with lignin binder was also higher. The pellets with lignin binder absorbed less moisture and had an overall lower moisture content after pelletizing and cooling. CO emissions in pellets with lignin binder were lower than pellets without lignin binder. The ash content of the pellets varied when adding lignin, as the ash decreased for pellets with lignin recovered from the HWE of willow but increased for pellets with commercially available LignoBoost lignin as an additional binder.

5 References

5.1 References Utilized for Overall Summary of Fuel Pellet Research Project Figure

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6 Research Products (Publications, Presentations, Posters, etc.)

6.1 Peer-Reviewed Publications

Nagardeolekar, A., Ovadias, M., and Bujanovic, B. (2020): “Willow lignin recovered from hot-water extraction for the production of hydrogels and thermoplastic blends,” *ChemSusChem* 13: 4702-4721

Wang, K.-T., Jing, C., Wood, C., Nagardeolekar, A., Kohen, N., Dongre, P., Amidon, T.E., and Bujanovic, B.M. (2018): “Toward complete utilization of miscanthus in a hot-water extraction-based biorefinery,” *Energies*, 11 (1): 39.

6.2 Thesis and Dissertation Publications

Elniski, Autumn. Spring 2023, PhD Thesis: “The Effect of Hot Water Extraction of Lignocellulosic Biomass and Recovered Lignin Addition on Fuel Pellet Properties,” SUNY-ESF, Syracuse, NY; Major Professors Bujanovic and Scott

Aditi Nagardeolekar, Summer 2020, PhD Thesis: “Studies of Lignin-based Gels as Sorbents,” SUNY-ESF, Syracuse, NY; Major Professor Bujanovic

Prajakta Dongre, Spring 2018, PhD Thesis: “Characterization and utilization of hot-water extracted lignin for formaldehyde-free resin applications,” SUNY-ESF, Syracuse, NY; Co-Major Professors Bujanovic and Amidon

Mathew J. Ovadias, Fall 2019, MS Thesis: “Lignin thermoplastic blends: Biorefinery willow lignin and polylactic acid,” SUNY-ESF, Syracuse, NY; Major Professor Bujanovic

Chengyan Jing, Spring 2017, MS Thesis: “Lignin content in xylan-rich lignocellulosics before and after hot-water extraction: Klason lignin and acetyl bromide methods,” SUNY-ESF, Syracuse, NY; Major Professor Bujanovic

Derek B. Corbett, Spring 2016, MS Thesis: “Recovery of Lignin from Hot-Water Extracts of Sugar Maple: Valorization by Catalytic Fast Pyrolysis,” SUNY-ESF, Syracuse, NY; Major Professor Bujanovic

6.3 Conference Presentations

Elniski, A. Bujanovic, B. (2022): “The Effects of Hot Water Extraction of Lignocellulosic Biomass on Fuel Pellet Properties,” TAPPI Intern. Bioenergy and Bioproducts Conf. (IBBC), Sess. 5, 10/30-11/2, Providence, RI

Nagardeolekar, A.; Ovadias, M.; Wang, K.T.; Wood, C.; Amidon, T.; Bujanovic, B. (2019) “Valorization of willow lignin recovered in a pilot-scale biorefinery based on hot-water extraction,” Int Bioenergy Bioproducts Conf. by the Technical Association of Pulp and Paper Industry (IBBC-TAPPI), 10/27-10/30, St. Louis, MO.: IBBC Sess. 4: Biorefinery Technology, oral pres.

Ovadias, M., Bujanovic, B. (2019): “Lignin-based thermoplastic blends: Biorefinery willow lignin and PLA,” 258th ACS, Symp. on Lignin-based Bioproducts, August, 25-26, San Diego, CA, oral pres. #2.

Nagardeolekar, A., Ovadias, M., Wang, K., Wood, C.D., Bujanovic, B. (2019): “Hydrogels and thermoplastic blends from willow lignin recovered from pilot-scale hot-water extraction,” ACS NERM (NE Reg. Meeting), Sess: Aerogels: Remarkable materials for diverse applications, 6/23-26, Saratoga, NY, oral pres. #59.

Elniski, A., Dongre, P., Nagardeolekar, A., Ovadias, M., Bujanovic, B. (2019): “Valorization of hot-water extracted lignin from different angiosperms” Sess.: Bioproducts, 6/9-12, 2019, Thunder Bay, Ontario, Canada

Nagardeolekar, A. Bujanovic, B. (2018): “Lignin recovered from hot-water extracts of angiosperms: Lignin-based hydrogels,” TAPPI Intern. Bioenergy and Bioproducts Conf. (IBBC), Sess. 5, 10/28-31, Portland, OR

Nagardeolekar, A; Dongre, D; Wang, K; Jing, C; Wood, C; Elniski, A; Amidon, T; Bujanovic, B. (2017): “Lignin recovered from hot-water extracts of Angiosperm-based biomass produced in 65 ft³ digester,” TAPPI-Intern. Bioenergy and Bioproducts Conf. (IBBC), November 2017, Norfolk, VA

Nagardeolekar, A.; Dongre, P.; Wang, K.; Jing, C.; Wood, C.; Elniski, A.; Amidon, T.; Bujanovic, B. (2017): “Lignin as a by-product of hot-water extraction: potential increase in the value of biorefineries based on angiosperms,” 17th Syracuse CoE Symp, Syracuse, NY, 10/4, 2017; Sess. B.3. Biorefineries, Biofuels and Bioproducts; Biljana Bujanovic, Sess. Moderator

Dongre, P., Nagardeolekar, A., Wang, K.-T., Jing, C., Wood, C., Kohan, N., Amidon, T., and Bujanovic, B. (2017): “Use of Angiosperm Lignocellulosics in a Biorefinery Based on Hot Water Extraction: Willow, Miscanthus, and Wheat Straw” Intern. Conf. on Biomass Conversion and Renewable Materials, 8/15-17, 2017, Syracuse, NY (in abstract)

Nagardeolekar, A., Wang, K-T., Jing, C., Dongre, P., Wood, C., Amidon, T., and Bujanovic, B. (2017): “Prospects of complete utilization of Miscanthus in a biorefinery based on hot water extraction,” 1st Intern. Forest Bioref. Conf., May 9-11, Thunder Bay, Ontario, CA

6.4 Posters

Nagardeolekar, A. and Bujanovic, B. (2018): “Lignin based hydrogels: Novel applications of lignin isolated from hot-water extracts of angiosperms,” 10th Ann. NY State Biotechn. Symp., 5-17-18, 2018, Syracuse, NY

6.5 Miscellaneous

- Four Minute Thesis Competition, SUNY-ESF, 4/28/22
- Creative Undergraduate Biomass Chemical Engineering and Science Experience, 7/21/18, Syracuse, NY
- 16th Annual Syracuse COE Symposium, 9/21/2016
- 8th Annual CNY Biotechnology Symposium, 5/19-5/20, 2016, Syracuse, NY
- 2016 SUNY-ESF Student Spotlight on Graduate Research, 4/12/2016, Syracuse, NY

6.6 Educational Productions

Utilization of biomass (pretreated with hot water extraction and untreated biomass) in the following courses for student learning and research:

- Introduction to Lignocellulosics (PSE 223)
- Fiber Processing (PSE 350)
- Pulping and Bleaching Processes (PSE 450)

Guest Lectures and Pelletizing Trials

- Fiber Processing (PSE 350): Spring 2018, Spring 2019, Spring 2020, Spring 2021, Spring 2022

Appendix A. Modifications to Testing Methods

A.1 Moisture Content (ISO 18134-2)

Dishes were pre-dried in a 105 °C oven for 24 hours prior to testing or until constant mass was achieved. Dishes were cooled in a desiccator instead of immediately weighed and weighed to the nearest 0.1 g.

The procedure noted that test portion samples should be 300 grams minimum but given the small size of the dishes (5.6 cm diameter, 20 gram sample maximum for the dishes), and limited amount of pellet sample, this number was modified to no less than ten grams per replicate.

After heating, samples were placed in a desiccator instead of immediately weighed. Once the samples cooled, samples and dishes were weighed.

A.2 Ash Content (ISO 18122)

Crucibles and test portions were removed from the oven and placed in a desiccator to cool instead of immediately weighed.

A.3 Energy Content (Gross Energy Value at Constant Volume) (ISO 18125)

This method determined the absolute value of the specific energy of combustion, in joules, for unit mass of a solid biofuel burned in oxygen in a calorimetric bomb under the conditions specified. Specifically, the gross energy value was determined for various fuel pellet treatments.

This property was tested with a modified version of ISO 18125. The instrument used was a Parr 6200 isoperibol oxygen bomb calorimeter following pre-October 2010 operation. The calorimeter operated automatically regarding measurement of parameters like temperature rise and energy value calculations.

The oxygen pressure from the storage tank to the calorimeter was set between 350-400 psi, which is slightly lower than operating parameters for the 6200 Parr according to the manual (which states to set pressure at 450 psi). This was due to past testing with the calorimeter to ensure proper calorimeter operation. The ISO method stated to ensure the bomb is filled to 3 MPa (435 psi) of pressure. However, the operating manual also stated that lower filling pressures can be used so long as the pressure does not exceed 600 psi (page 5-1).

The sample size did not to exceed the range of 0.6-1.2 grams based upon the 6200 Parr manual (page 1-1). The ISO method requires a sample of 1.0 g +/- 0.2 grams. The Parr manual implied that materials can be utilized in the reactor without grinding and compressing into a pellet (page 5-6) and noted that fibrous materials sometimes do not pellet well. The ISO 18125 method stated that, due to the low density of solid biofuels, they are to be tested in pellet form (page 7) or can be tested in powder form in a closed combustion bag or capsule. However, the fuel pellets used in this measurement are already in pellet form and therefore don't need to deal with compression issues or powdered forms.

Unlike the 6200 Parr and ISO 18125 methods, the fuel pellets were not ground to a specific mesh and compressed into a pellet. Instead, the pellets were tested in the metal crucible as-is.

The mass of the pellet samples was selected to be within the 0.8-1.2 grams range for energy testing.

Prior to testing the fuel pellets for gross energy content, the pellets were conditioned to constant mass in the laboratory atmosphere and humidity. This is required by the ISO 18125 (page 7).

Other specifications include the following:

- Parr Ignition Threads (Item No. 845DD2) used
- Parr Heat Wires (Item No. 840DD2) used
- The following corrections placed under Thermochemical Corrections:
 - Fixed Fuse: On – 15.0 Calories (Default)
 - Fixed Acid: On – 10.0 Calories (Default)
 - Fixed Sulfur: On – 0.0 Calories (Default)
 - Use Offset Correction (ISO): On [this is set for ISO 1928]
 - Acid is Nitric Only: On
 - Acid Multiplier: 0.154 (instead of 0.0709 – Default Value) [this is set for ISO 1928]
 - Sulfur Value is Percent: Off (instead of On – Default Value) [this is set for ISO 1928]
 - Sulfur Multiplier: 0.1 (instead of 0.6238 – Default Value) [this is set for ISO 1928]
 - User Offset Value (On) [this is set for ISO 1928]

- Offset Value: -43.5 (instead of 0.0 – Default Value) [this is set for ISO 1928]
- Hydrogen Multiplier: 50.68 (Default)
- Fixed Hydrogen: Off (Default)
- Dry Calculation: Off (Default)
- Fixed Moisture: Off (Default)
- Moisture Multiplier: 5.83 (Default)

For lignin testing, lignin was utilized in a powder form and had to be formed into pellets with the pellet press for energy testing, compared to the fuel pellets which were already in pellet form and tested as is. Lignin was also tested at the as-received moisture content whereas pellets were placed in the laboratory that housed the calorimeter to reach an equilibrium with the calorimeter.

A.4 Bulk Density (ISO 17828)

The ISO method called for the test portion volume to exceed the volume of the measuring container by a minimum of 30%. In this instance, the minimum volume would be 6.5 Liters of material. However, for the already off-gassed materials, approximately 5-5.5L of sample was available. Therefore, an initial bulk density on the off-gassed material was performed with an exception to this part of the method.

A.5 Durability (ISO 17831)

A screen with a 3.35 mm mesh size (No. 6) was utilized instead of a 3.15 mm screen.

A.6 Pellet Dimensions (ISO 17829)

A screen with a 3.35 mm mesh size (No. 6) was utilized instead of a 3.15 mm screen. The mass and diameter of each pellet was measured instead of the diameter of just 10 pellets, contrary to the method.

A.7 Particle Size Distribution (ISO 17827)

This method was modified for two reasons. First, the range of particle sizes examined in this experiment was approximately 6 mm to less than 1 mm. The combination of these procedures allowed for the testing of this range for the hammermilled samples.

Second, in ISO 17827-2 (Vibrating screen method using sieves of aperture of 3.15 mm and below), the method required the use of a vibratory screen for particle sizes below 3.15 mm, which would be needed for the samples hammermilled with the 1 mm and 3 mm screens, as well as the 6 mm screen to a degree. However, the sieving screens available for this range of particle sizes are utilized in an oscillating testing system. Therefore, part of the procedure from ISO 17827-1 (Oscillating screen method using sieves with apertures of 3.15 mm and above) was incorporated for the use of an oscillating screen.

For each replicate, 30 g of sample was spread evenly over the mesh of the top sieve. This was also a modification to the method, which called for 50 g of sample. Due to the sample availability, this sample size was modified and the time for oscillation was adjusted in ratio to the sample size from the method.

A.8 Moisture Content (TAPPI Standard T-412)

The moisture content of lignocellulosic biomass samples using this method was determined in accordance with TAPPI Standard T-412²⁵, which required heating of samples at 105 °C. For lignin, samples were not dried in a 105°C oven. Instead, lignin was dried in a vacuum oven set to 40±5°C.

Appendix B. Additional Biomass Characterization Information

Table B-1. Extractives Content

Sample	Method	Solvent			
		Acetone/H ₂ O	DCM	EtOH	EtOH/ Toluene
SM ₂₀₁₂	Soxhlet	1.98	0.67	3.09	2.83
ESM ₂₀₁₂ MK	Soxhlet	10.25	5.26	11.15	11.69
W ₂₀₁₂	Soxhlet	2.88	1.64	3.77	3.95
W ₂₀₁₆	Soxhlet	2.95	1.45		3.83
EW ₂₀₁₂ MK	Soxhlet	7.82	4.48	9.35	11.92
EW ₂₀₁₆ pilot	Soxhlet		5.00		9.12
MS ₂₀₁₅	Soxhlet		1.02		5.57
EMS ₂₀₁₅ parr	Soxhlet		4.76		
EMS ₂₀₁₅ MK	Soxhlet		3.03		
EMS ₂₀₁₅ pilot	Soxhlet		3.52		8.18
EMS ₂₀₁₅ pilot(>20)	Soxhlet		2.89		
EMS ₂₀₁₅ pilot(<20)	Soxhlet		5.93		
WS ₂₀₁₆	Soxhlet	3.68	2.41	4.55	6.48
EWS ₂₀₁₆ pilot (1hr)	Soxhlet		2.55		7.26
EWS ₂₀₁₆ pilot (2hr)	Soxhlet	8.00	4.72	9.31	8.51

Table B-2. Seifert Cellulose

Sample	Seifert Cellulose (% of O.D)
MS ₂₀₁₅	39.78 ± 0.32
EMS ₂₀₁₅ parr	60.19 ± 0.61
EMS ₂₀₁₅ MK	58.05 ± 0.44
EMS ₂₀₁₅ pilot	57.20 ± 0.51
EMS ₂₀₁₅ pilot (>20)	58.31 ± 0.76
EMS ₂₀₁₅ pilot (<20)	62.79 ± 0.50
WS ₂₀₁₆	39.14 ± 1.04
EWS ₂₀₁₆ parr	57.81 ± 0.42
EWS ₂₀₁₆ pilot (1hr)	41.71 ± 0.29
EWS ₂₀₁₆ pilot (2hr)	56.91 ± 0.12
W _{sx64}	38.32 ± 1.39
W ₂₀₁₆	36.94 ± 0.03
EW ₂₀₁₆ pilot	± 0.57

Table B-3. Lignin

Sample	Klason (% of O.D)	ASL (% of O.D)	Total (% of O.D)
WS ₂₀₁₃	14.05 ± 0.32	1.79 ± 0.06	15.83 ± 0.28
WS ₂₀₁₆	17.24 ± 0.58	2.37 ± 0.09	19.60 ± 0.64
EWS _{2013parr}	12.22 ± 0.56	1.02 ± 0.14	13.24 ± 0.70
EWS _{2016pilot (2hr)}	22.16 ± 0.81	0.92 ± 0.02	23.08 ± 0.81
MS ₂₀₁₂	12.00 ± 0.50	1.77 ± 0.11	13.77 ± 0.44
MS ₂₀₁₅	20.27 ± 0.26	1.90 ± 0.06	22.17 ± 0.29
EMS _{2012parr}	20.76 ± 0.51	1.42 ± 0.08	22.18 ± 0.57
EMS _{2015parr}	20.05 ± 0.04	1.24 ± 0.07	21.30 ± 0.03
EMS _{2015MK}	22.02 ± 0.12	1.12 ± 0.03	23.13 ± 0.14
EMS _{2015pilot}	21.44 ± 0.49	1.07 ± 0.05	22.51 ± 0.45
EMS _{2015pilot (>20)}	21.57 ± 0.28	0.99 ± 0.04	22.57 ± 0.25
EMS _{2015pilot (<20)}	21.16 ± 0.47	1.17 ± 0.11	22.33 ± 0.52
EMS _{2015MK Recl}	77.91 ± 0.52	3.88 ± 0.01	81.79 ± 0.51
EMS _{2015pilot Recl}	74.73 ± 0.56	4.71 ± 0.19	79.44 ± 0.37
W ₂₀₁₆	22.50 ± 0.06	2.42 ± 0.22	24.92 ± 0.16
EW _{2016pilot}	25.58 ± 0.10	1.21 ± 0.07	26.79 ± 0.12
EW _{9882parr}	25.21 ± 0.46	1.09 ± 0.04	26.29 ± 0.42
EW _{sx64parr}	23.05 ± 1.03	1.14 ± 0.02	24.19 ± 1.01

WS and MS: extracted by ET. W: extracted by AW. Hot-water extracted samples: extracted by DCM.

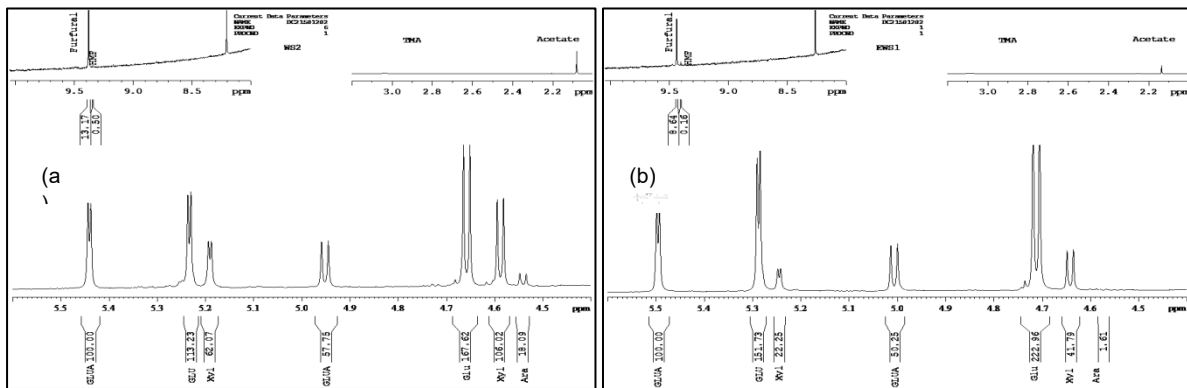
Table B-4. D.D (Delignification Degree)

Sample	HWE Yield (%)	Total lignin (%)	D. D (%)
WS ₂₀₁₃	---	15.83 ± 0.28	---
WS ₂₀₁₆	---	19.60 ± 0.64	---
EWS _{2013parr}	57.16 ± 1.06	13.24 ± 0.70	52.20 ± 2.53
EWS _{2016pilot (2hr)}	62.54 ± 1.54	23.08 ± 0.81	26.38 ± 2.59
MS ₂₀₁₅	---	22.17 ± 0.29	---
EMS _{2015parr}	59.98 ± 0.34	21.30 ± 0.03	42.37 ± 0.09
EMS _{2015MK}	64.70	23.13 ± 0.14	32.47 ± 0.41
EMS _{2015pilot}	66.95 ± 0.18	22.51 ± 0.45	32.02 ± 1.36
W ₂₀₁₆	---	24.92 ± 0.16	---
EW _{2016pilot}	77.50	26.79 ± 0.12	± 0.38

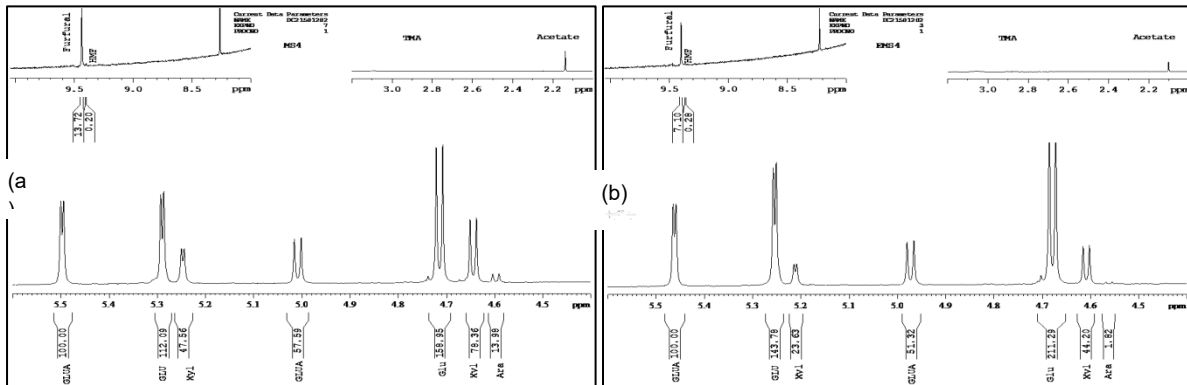
Table B-5. Carbohydrates

Sample (% of O.D)	Glu	Xyl	Ara	Furfural	HMF	Acetate	Total Carbo.
WS ₂₀₁₃	42.93	21.59	2.05	1.05	0.05	0.10	67.77
EWS _{2013parr}	66.98	9.78	0.25	0.73	0.03	0.04	77.81
MS ₂₀₁₅	41.54	20.75	1.45	0.31	0.00	0.11	64.15
EMS _{2015parr}	58.02	13.31	0.26	0.18	0.00	0.06	71.83
EMS _{2015MK}	59.93	10.89	0.13	0.20	0.00	0.05	71.20
EMS _{2015pilot}	56.00	13.30	0.26	0.30	0.00	0.06	69.92
EMS _{2015pilot (>20)}	53.60	9.99	0.26	0.16	0.00	0.04	64.06
EMS _{2015pilot (<20)}	55.85	9.97	0.26	0.31	0.00	0.04	66.43
W ₂₀₁₆	36.13	12.59	0.47	0.00	0.83	0.13	50.14
EW _{2016pilot}	48.15	8.28	0.00	0.00	0.36	0.07	56.87

These results are being checked and are not included in this discussion; underestimated sugars through H-NMR measurements.



¹ H NMR spectrum of original (a) and hot-water-extracted (b) wheat straw 40% sulfuric acid hydrolysate.



¹ H NMR spectrum of original (a) and hot-water-extracted (b) miscanthus 40% sulfuric acid hydrolysate.

Table B-6. Ash

Sample	Ash (% of O.D)
MS ₂₀₁₅	4.24 ± 0.07
EMS _{2015parr}	1.32 ± 0.47
EMS _{2015MK}	3.89 ± 0.10
EMS _{2015pilot}	4.97 ± 0.02
EMS _{2015pilot}	4.04 ± 0.02
W ₂₀₁₆	1.47 ± 0.01
EW _{2016pilot}	± 0.04

Table B-7. PhOH (Phenolic Hydroxyl Group Content)

Sample	PhOH (mmol/g lignin)
AW_W ₉₈₈₂	0.36 ± 0.00
DCM_EW ₉₈₈₂	1.69 ± 0.00
ET_MS ₂₀₁₅	0.64 ± 0.01
DCM_EMS _{2015parr}	1.38 ± 0.02
DCM_EMS _{2015MK}	1.47 ± 0.07
DCM_EMS _{2015pilot}	1.38 ± 0.18
EMS _{2015MK} Recl	1.96 ± 0.01
EMS _{2015pilot} Recl	1.96 ± 0.02
AW_SM	0.3 ± 0.01
DCM_ESM	1.50 ± 0.01

Table B-8. Recovered Lignin Characteristics

Lignin recovered from hot-water extracts of wheat straw (WS), Miscanthus (MS) and willow (pilot plant experiments studies); Sugar maple included for comparative purposes: chemical composition.

Lignin Sample	% OD lignin							Total
	Lignin		Ash	Arabinan	Glucan	Xylan	Mannan	
	Klason	Acid-soluble						
MS	76.3	4.96	0.5	1.16	1.16	6.36	-	90.44
MS*	82.5	4.50	0.4	0.48	0.60	3.85	-	92.33
WS	77.3	3.73	1.2	0.66	1.99	3.32	-	88.20
W	80.2	4.48	0.2	-	1.19	1.19	0.60	87.86
SM	80.2	5.8	0.04	0.15	0.59	5.59	0.43	92.80

* this lignin was washed with water pH5 for purification.

Appendix C. Equipment Information

This appendix has information pertaining to selected equipment used in this research project. Some equipment is omitted, such as ovens, furnaces, and balances.

C.1 Hot Water Extraction Vessels

The Parr Reactor used in Hot Water Extraction experiments is a Parr (300 cm³ 4560 Mini bench top reactor) from Parr Instrument Company, (Moline, IL, USA).⁴

The M/K Digester used in Hot Water Extraction experiments is an M/K (4 L) from M/K Systems Inc., (Peabody, MA, USA).⁴

The Pilot Digester used in Hot Water Extraction experiments is a Struthers-Well (65 ft³) stainless lined batch digester, (Santa Fe Springs, CA, USA).⁴

C.2 Grinding and Pelletizing Equipment

The Laboratory Scale Hammermill utilized for grinding biomass to 6 mm, 3 mm, and 1 mm particle size is a Mini Hammermill from Farm Feed Systems Ltd., (Cinderford, UK). The 6 mm and 3 mm screens were provided by Farm Feed Systems while the 1 mm screen was custom made by Procore-Peerless Inc. (Buffalo, NY).

The Laboratory Scale Pelletizer is a Mini Pellet Mill (advertised capacity 20-100 kg/h) from Farm Feed Systems Ltd., (Cinderford, UK). The pelletizer was equipped with three compression ring dies (low compression, medium compression, and high compression), all of which have 6 mm pellet die holes.

A Pilot Scale Hammermill was also utilized for grinding 6 mm biomass. The Pilot Scale Pelletizer is a flat die pelletizer with 6 mm diameter pellet die holes. Both are from Lawson Mills Biomass Solutions (now Kovo Novak, division of Kesir Industrial, Canada).

C.3 Biomass Characterization Equipment

C.3.1 Carbohydrate Analysis

Filtrates from the carbohydrate analysis process were examined with ¹H-NMR using an AVANCE III 600 spectrometer (600 MHz ¹H frequency) from Bruker, (Billerica, MA, USA) equipped with a 5 mm Cryo Prodigy BBO z-gradient probe.⁴ Data was acquired and processed in TOPSPIN v3.2 Bruker BioSpin.

C.3.2 Klason Lignin and Acid Soluble Lignin

The modified Klason lignin method was utilized with a Branson 3510 sonicator.⁴

C.3.3 Gas Chromatography—Mass Spectroscopy for Fatty Acid Analysis

Extracts were analyzed by gas chromatography coupled to a high resolution Orbitrap mass spectrometer (HR-GC-MS, Thermo Scientific Exactive Orbitrap coupled to a Trace 1310 Gas Chromatograph) located at the Analytical & Technical Services (ATS) at SUNY-ESF. A Thermo Scientific TG-5SILMS fused silica capillary column (30 m length, 0.25 mm inner diameter, 0.2 μL film) was utilized for the analysis. The samples were analyzed in the EI (electron effect) mode with the Electron Energy 70.00 eV. Mass spectroscopy spectra were collected in full scan mode from m/z (mass to charge ratio) 50 to 600 amu with a resolution of 60,000. Spectra were analyzed using Thermo Xcalibur (v.4.2.47) and library searches were done using NIST (National Institute of Standards and Technology) Mass Spectral Search program (version 2.3 build May 4, 2017). The initial program settings were determined based upon literature analyzing fatty acids in lignocellulosic biomass^{22,23,34,92} and were tested with the sample standards. The programming was then adjusted to create GC-MS operating conditions for the extractive samples and the sample standards analysis. The injection volume for each sample was 1 μL.

Table C-1. GC-MS Equipment and Operation Specifications

Equipment or Property	Equipment Information or Property Value
GC-MS	Thermo Scientific Exactive Orbitrap coupled to Trace 1310 Gas Chromatograph
Column	Thermo Scientific TG-5SILMS
Column Properties	30 m length, 0.25 mm inner diameter, 0.2 μL film
Carrier Gas	Helium
Carrier Gas Flow Rate	1.2 mL/min
Split Ratio	Splitless
Initial Temperature	80°C (Initial Hold of 2 minutes)
Temperature Rate	8°C/min
Final Temperature	300°C (Held for 10 minutes)
Injector Temperature	280°C

C.3.4 Particle Size Distribution

Particle size distribution was measured in a W.S. Tyler RX-812 Coarse Sieve Shaker (Mentor, OH) that utilized 12-inch (30.5 cm) diameter sieves of various mesh sizes (Table 29).

Table C-2. Aperture/Mesh Sizes for Particle Size Distribution Determination

ISO 17827-2 Recommended Aperture Size (MM)	W.S. Tyler RX-812 Screen (Metric Equivalent [MM])	W.S. Tyler RX-812 Screen (Mesh Number)
5.6	6.3	1/4"
4.0	-	-
3.15	3.35	6
2.8	-	-
2.0	1.7	12
1.4	-	-
1.0	0.850	20
0.5	-	-
0.25	0.212	70

C.3.5 Pellet Characterization Equipment

C.3.5.1 *Energy Content*

A Parr 6200 Oxygen Bomb Calorimeter with a 1108 Oxygen Combustion Bomb and a Parr 6510 Water Handling System from Parr Instrument Company, (Moline, IL, USA).

C.3.5.2 *Durability*

A TUMBLER 100 R Durability Tester (designed for specification under ISO 17831-1 and EN 15210-1) from the Bioenergy Institute (Vienna, Austria) was utilized for durability testing.

C.3.5.3 *Bulk Density*

A 5 L Steel Bulk Density Cylinder Tester (designed for specification under ISO 17828 and EN 15103) from the Bioenergy Institute (Vienna, Austria) was utilized for bulk density testing.

C.3.5.4 *Pellet Length*

A Stainless-Steel Digital Caliper (designed for specification under ISO 17829 and EN 16127) from the Bioenergy Institute (Vienna, Austria) was utilized for pellet length testing.

C.3.5.5 Carbon Monoxide Off-Gassing

EasyLog EL-USB-CO sensors were utilized for measuring carbon monoxide for off-gassing experiments. These sensors are USB sensors with a 0-1000 ppm sensitivity range and were utilized in other CO studies.¹

EasyLog EL-SIE-1 sensors were utilized for measure temperature in off-gassing experiments. These sensors are USB sensors with a digital display and a -18°C-55°C sensitivity range.

A Fisher Scientific Isotemp Low Temperature Incubator (Model Number 13-987-626) was utilized for laboratory scale off-gassing measurements as well as other temperature studies in the off-gassing experiments.

Appendix D. Midwest Microlab Testing Procedures

The home landing page for the Midwest Microlab can be found at <https://www.midwestlab.com>.

The information provided below for each of the elemental tests are general overviews of the testing method listed on the Midwest Microlab website at the time of testing.

D.1 Carbon, Hydrogen, and Nitrogen Content

The carbon content of the lignocellulosic biomass and recovered lignin samples was determined with a method that is an upgraded form of a testing method research in Switzerland. It involved the combustion of the sample in ultra-pure oxygen at 990°C in a closed system. The gasses were then passed through copper to remove excess oxygen and silver salts to remove halogens, phosphorous, and sulfur. Water was removed, and then carbon dioxide and nitrogen gas were removed. Sensing was performed after each removal.

D.2 Oxygen Content

The oxygen content of the lignocellulosic biomass and recovered lignin samples was determined via pyrolysis. The sample was inserted into a pyrolysis tube that is backswept to remove residual air that may have occurred during the insertion process. The sample was then pyrolyzed at 1000°C in the presence of purified carbon. The resulting carbon monoxide gas was passed through copper heated at 670°C to remove sulfur. Additional traps removed hydrochloric acid and hydrobromic acid. The carbon monoxide was then oxidized to carbon dioxide and trapped in a preweighed Ascarite tube. The weight change was utilized to calculate the amount of oxygen present within the sample.

D.3 Sulfur Content

The sulfur content of the lignocellulosic biomass and recovered lignin samples was determined via Schoniger Combustion. The solid sample was weighed into ashless paper and inserted into a platinum stopper. This was fitted to a flask that is charged with reactants and oxygen. During combustion, the sulfur present was oxidized from sulfur dioxide to sulfur trioxide. The resulting liquid was removed and titrated to determine the sulfur content.

Appendix E. Pilot and Laboratory Scale Pellets from Pellet Length Analysis

Figure E-1 Pilot Scale and Laboratory Scale Pellets from Pellet Length Measurements

W = Willow. M = Miscanthus. WS = Wheat Straw. E = Hot Water Extracted. COM = Commercial Pellets.
6/3/1 = Pellets made from Biomass Hammermilled with 6/3/1 mm Screen.
ReL = Lignin Recovered from Hot Water Extraction of Willow. ComL = Commercial Lignin (LignoBoost)

Pilot Scale Pellets



W-6



EW-6



W-3



EW-3



M-6



EM-6



EM-3



COM



WS-6



EWS-6



WS-3



EWS-3

Table E-1 Continued

Laboratory Scale Pellets



W-3



W-1



W-1-Recl



W-1-ComL



COM

NYSERDA, a public benefit corporation, offers objective information and analysis, innovative programs, technical expertise, and support to help New Yorkers increase energy efficiency, save money, use renewable energy, and reduce reliance on fossil fuels. NYSERDA professionals work to protect the environment and create clean-energy jobs. NYSERDA has been developing partnerships to advance innovative energy solutions in New York State since 1975.

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