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2 **“Ash reduction strategies in corn stover facilitated by anatomical and size fractionation”**

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4
5 **Abstract**

6 There is growing interest internationally to produce fuels from renewable biomass
7 resources. Inorganic components of biomass feedstocks, referred to collectively as ash,
8 damage equipment and decrease yields in thermal conversion processes, and decrease
9 feedstock value for biochemical conversion processes. Decreasing the ash content of
10 feedstocks improves conversion efficiency and lowers process costs. Because physiological ash
11 is unevenly distributed in the plant, mechanical processes can be used to separate fractions of
12 the plant based on ash content. This study focuses on the ash separation that can be achieved
13 by separating corn stover by particle size and anatomical fraction. Baled corn stover was hand-
14 separated into anatomical fractions, ground to <19.1 mm, and size separated using six sieves
15 ranging from 9.5-0.150 mm. Size fractions were analyzed for total ash content and ash
16 composition. Particle size distributions observed for the anatomical fractions varied
17 considerably. Cob particles were primarily 2.0 mm or greater, while most of the sheath and husk
18 particles were 2.0 mm and smaller. Particles of leaves greater than 0.6 mm contained the
19 greatest amount of total ash, ranging from approximately 8 to 13% dry weight of the total
20 original material, while the fractions with particles smaller than 0.6 mm contained less than 2%
21 of the total ash of the original material. Based on the overall ash content and the elemental ash,
22 specific anatomical and size fractions can be separated to optimize the feedstocks being
23 delivered to biofuels conversion processes and minimize the need for more expensive ash
24 reduction treatments.

1. Introduction

Ash components in biomass feedstocks are problematic for processes that convert the feedstocks to fuels for transportation and power generation purposes. Ash causes slagging, fouling and corrosion in combustion and gasification processes for power generation [1], decreases yields for fast pyrolysis conversion to bio-oils [2], and are unusable for biochemical conversion processes. Recent work has noted that efficient methods must be devised to reduce the ash content of biomass feedstocks to reduce conversion costs and make biomass renewable energy more cost effective [3, 4].

The ash contained in harvested biomass originates from two main sources. Introduced ash is a result of dust, dirt, rocks, and other forms of inorganic contamination collected during the harvest and collection process. The differences in harvesting techniques can have a large impact on the amount of introduced ash. Multi-pass harvesting is commonly implemented and involves one pass to cut the stover and then a second pass to pick up the stover from the field for baling. Multi-pass typically collects more introduced ash than single-pass harvesting methods where the stover is cut and baled using a single piece of equipment [5]. The second source of ash in biomass is physiological ash. Plants are complex organisms comprised of many different organs and tissues, each having unique structural and chemical properties that are strongly influenced by their physiological functions. Physiological ash is naturally occurring and is contained within the plant tissues. Plants collect physiological ash components from the soil, water, and other soil amendments to be used in biological processes and consist of essential macronutrients (calcium (Ca), potassium (K), sulfur (S), magnesium (Mg), nitrogen (N), phosphorous (P)), micronutrients (zinc (Zn), iron (Fe), manganese (Mn), copper (Cu), chlorine (Cl), boron (B), molybdenum (Mo), nickel (Ni)) [6-8], and other non-essential beneficial elements (sodium (Na), silicon (Si)) [7, 9-14]. Different parts of the plant may have optimal uses

based on their unique chemical compositions and/or physical properties [15-17], because these ash elements are not uniformly distributed throughout the plant [18].

The separation of biomass into fractions with the intent to target these specific properties has been widely investigated as a way to enhance conversion efficiencies. Montross and Crofcheck reported that without pretreatment, cobs, leaves, and husks produced over 300% more glucose than the stalks during a timed enzymatic hydrolysis. They suggested that anatomical fractionation could be used to increase the value of stover as a feedstock for glucose production [16]. An anatomical based selective harvest was suggested by the same group that would only collect the parts of the corn plant (cobs, leaves, and husks) that had the highest glucose potential [15]. This selective harvesting method would increase the efficiency of the enzymatic production of glucose from the stover while leaving the remainder of the biomass on the field for erosion control. Garlock et al. [17] showed that anatomical fractionation could improve theoretical ethanol yield from stover, however its effect was lower than expected. They found that their process (AFEX plus enzymatic hydrolysis) worked best with husks and leaves. It was concluded that while anatomical fractionation did prove to be beneficial, resources would be more effectively spent improving harvesting methods and optimizing biomass processing. Bootsma and Shanks [19] suggested that mechanical separation of corn stover prior to hydrolysis was not helpful, however their separations were more basic and only focused on two fractions, the pith and the fiber.

The fractionation of wheat stover has also proven to be advantageous for conversion efficiencies. Duguid et al. [20] advised that the selective harvest of wheat stover could improve ethanol production costs. They found that leaves required very little pretreatment, while nodes and internodes required a more severe pretreatment to hydrolyze the glucan and xylan to similar levels. While the levels of glucan present in the different anatomical fractions was relatively similar, the level of pretreatment required and amount of glucose produced varied

widely between anatomical fractions [21]. Jin et al. [22] found that the enzymatic sugar yield from wheat leaves was about 16% higher than that of the stems following sodium carbonate pretreatment. In a similar finding, a high leaf/stem ratio of wheat stover was found to enhance the enzymatic conversion process through higher sugar yields and lower severity pretreatment processes [23]. The selection of wheat varieties with a high leaf/stem ratio was also suggested as a method to enhance methane production from anaerobically digested wheat straw [24]. The selective harvest of wheat straw stems was proposed to reduce silica content for improved combustion characteristics [25].

In an investigation of the digestibility of corn stover in animal feed, Hansey et al. [26, 27] recommended a selective harvest of the leaves and leaf sheaths as they provided maximum conversion efficiencies in animal feed. Their work also suggested that the ethanol industry could benefit from a similar selective harvest strategy. Others, looking at stover as a feedstock for the paper industry, found that the corn stalk rind was more valuable for paper-making, having good fiber characteristics [18]. A study analyzing corn stover for use in the paper industry found that the inorganic elements that make up ash were unevenly distributed throughout the plant, with silica highest in the leaf pith and potassium and chlorine highest in the stalk rind [12]. Several of these studies have suggested selective harvest as a way to improve biomass quality, however different plant fraction are suggested for selective harvest depending upon the intended end use of the biomass, limiting the potential utilization of all the available crop. It is possible that a more efficient manner of harvest would involve the collection of all parts of the plant, with post-harvest fractionation used to generate ideal feedstocks for each end use.

While a considerable amount of work has been done related to fractionation as a means to enhance convertibility, less attention has been paid to fractionation as a method to reduce ash content in the biomass. These chemically or physically different plant tissues could benefit from ash reduction treatments tailored specifically for these properties [4]. In order to take

100 advantage of these tissue specific properties, the biomass must first be separated into these
101 different tissue types.

102 There are many factors to consider when selecting or developing methods to separate
103 biomass fractions to minimize impacts of ash on subsequent uses and end products. The first
104 concern is that the costs of reducing ash concentrations in high value product streams through
105 separations must add more value than the separations processes incur. In this consideration,
106 ash is essentially a waste product that must be dealt with at some point in the conversion
107 process. When it is included in biomass, it must be shipped, handled, and processed, even
108 though it will ultimately need to be discarded. The ash content of many biomass feedstocks can
109 exceed 10% dry weight, prompting additional biomass to be purchased, shipped, and processed
110 in order to meet production goals, thus increasing overall costs and complicating logistics.
111 Another consideration in determining methods for ash removal is the negative effects that
112 certain components of ash may have within specific conversion processes [4, 28]. In the
113 biochemical conversion platform, ash represents inert, unconvertible material that requires
114 disposal. In the pyrolysis conversion platform, the elements K, Na, Ca, and Mg can be
115 destructive to the conversion products. Nitrogen, S, and P can foul the conversion catalysts in
116 several conversion processes. Nitrogen and S are also a source of pollutants in the gasification
117 and combustion conversion process, and Si, K, Na, and Cl can be damaging to reactors
118 themselves in these same processes [28]. Depending up the selected conversion pathway,
119 certain elements at sufficiently low concentrations can be acceptable

120 An understanding of the inorganic elemental composition, location, and chemical format
121 within each plant tissue is advantageous for devising efficient ash mitigation strategies that
122 could involve using different material fractions in processes best suited for their organic and
123 inorganic compositions. Sodium and K are typically free ions in solution and found in the
124 vascular tissues; as such, a simple water extraction of the biomass could be sufficient to remove

these elements. Calcium and Mg may be complexed as counterions with organic acids, so an acidic solvent would aid in the dissolution of these elements. Silica can be present in different forms throughout the plant [7]. The leaves and other transpiring tissues of plants typically contain higher concentrations of SiO_2 as this mineral is known to accumulate in transpiring tissues over time [29-31]. Some of these SiO_2 deposits are likely to be located in the fragile epidermal cells of transpiring tissues, and simple grinding of the tissue could be enough to liberate them. Silica is also deposited in structural tissues within the plant, including the tracheids. These deposits of SiO_2 are embedded in the tissue as Si complexes, and their removal would require the physical or chemical disassembly or disruption of the tissue structure [9, 12-14, 32, 33].

Another ash reduction method related to anatomical fractionation is particle size fractionation. Just as anatomical fractions have different ash contents as a result of their biological functionality in the plant, particle size fractions from common size reduction preprocessing techniques have also been shown to vary in ash content. When harvested biomass is ground for size reduction, the smallest size fractions typically have higher ash content than larger fractions [34-37]. Anatomical fractions have unique physical properties that are likely to cause these fractions to deconstruct differently, affecting particle size and ash distribution in deconstructed biomass. Given the variable ash content in anatomical fractions, and the potential for anatomical fractions to deconstruct in unique manners, there may be an opportunity to use size fractionation coupled with anatomical fractionation to isolate fractions that are higher or lower in total ash or specific inorganic elements. In this research, size fractionation and anatomical fractionation were used to identify opportunities for ash reduction in corn stover. Mechanical separations, including anatomical fractionation and particle size fractionation, need to be further developed for use in ash reduction.

2. Materials and Methods

2.1 Corn Stover, Anatomical Fractions

Corn stover was harvested in a multi-pass operation in Boone County, Iowa, USA (42.088175, -93.987843), during the fall of 2011. After baling, it was stored outdoors under a tarp until March 2013. Figure 1 shows the steps followed as this biomass was fractionated and processed. An aliquot was taken from the middle of the bale to avoid the edges of the bale that had been exposed to external conditions. Three complete sets of anatomical fractions (around 50 g per fraction) were manually collected from the material. The fractions included cobs, husk, leaves, sheaths, internodes and nodes. Because the sample was baled, some of the tissue in the bale could not be identified because it had been pulverized by the baling process. Only biomass pieces that could be positively identified were included in the anatomical fractions. A sample was taken from the original bale aliquot for ash analysis of the whole unfractionated sample.

2.2 Size Reduction

For particle size reduction, each of the anatomical fractions was ground through a Thomas Wiley Model 4 Mill (Ramsey, MN) until it passed through an ASTM E-11 19.1 mm (0.75 inch) sieve. For total ash analysis, an aliquot of each of these fractions was further ground through a Thomas Wiley Model 4 Mill (Ramsey, MN) until it passed through a 2 mm sieve following the same procedure as the NREL Laboratory Analytical Procedure for ash determination [38].

2.3 Particle Size Separations

Each of the 19.1 mm ground fractions were separated by particle size using a RoTap RX-29 (Tyler Incorporated, Mentor, OH) into seven size fractions by the ASTM E-11 sieves: 9.5 mm, 6 mm, 2 mm, No. 30 (0.6 mm), No. 40 (0.425 mm), No. 100 (0.150 mm), and the pan (<0.150 mm). The RoTap was set for 5 minutes of shaking for each sample. Each of these particle size fractions were weighed for percent composition of the anatomical fraction. The size

fractions greater than 2 mm were ground to 2 mm with a Thomas Wiley Model 4 Mill. All size fractions were analyzed for total ash content [38].

2.4 Compositional Ash Analyses

Ash compositions of two of the sets of anatomical fractions were analyzed using a combination of inductively coupled plasma-optical emission spectrometry (ICP-OES) performed at Huffman Laboratories, Inc. (Golden, CO) and laser-induced breakdown spectroscopy (LIBS) performed at Idaho National Laboratory (INL). Sixteen of the samples were analyzed using ICP-OES at Huffman Laboratories, and the analytical results from those samples were used to create models to predict the concentration of elements of interest using specific peaks in the LIBS spectra. Both the samples and calibration standards were prepared by grinding them to minus 80 microns using a Retsch ZM200 fine grinding mill. Pellets were made for LIBS analysis by placing approximately 0.8 gram of sample powder in a 16 mm square heated pellet die and applying approximately 40 MPa pressure for one minute at 100 °C. A modified RT-100 LIBS system (Applied Spectra, Inc., Fremont, CA) was used to perform measurements. In this instrument, laser excitation was provided by a pulsed Nd:YAG laser with a wavelength of 1064 nm and a 7 ns pulse in air. The laser was capable of a maximum of 90 mJ per pulse, and was operated at 100% of maximum power. The laser focusing lens had a focal length of 15 mm. A 5-channel spectrometer system with approximately 1.5 nm resolution was used with a charge couple device (CCD). Samples were tested with a gate delay time of 1.0 μ s and a gate width of 1.0 ms. LIBS spectra were collected at 40 different sample sites (20 points on each side of each pellet).

The wavelength range from 200 nm to 1000 nm was used to identify multiple peaks for each element of interest. Each peak in the collected spectra was identified based on NIST and other spectroscopic databases. The identified peaks for each element were evaluated for use in the calibration according to signal-to-noise ratios, strength of spectral peaks, and interferences

from adjacent peaks. The peaks selected for each element were chosen to optimize linear correlations between spectral peak intensity values and measured concentration values. Univariate models were developed for elements of interest using a minimum of three separate peaks from the LIBS data, and final measured concentrations were obtained by combining the concentration estimates from the available LIBS peaks based upon measurement uncertainties based upon model fits to the element concentrations obtained from ICP-OES.

3. Results

Because the anatomical structures were disturbed during the baling process, it was not possible to measure the exact contribution of each anatomical fraction present in the bale. However, based on information available in the literature, it was estimated that the bale had the following anatomical composition: 20% cobs, 20% leaves, 10% husks, 10% sheaths, 30% internodes, and 10% nodes [39-41]. This approximate corn plant model was used to estimate the ash contributions originating from the different anatomical fractions as described below.

3.1 Particle size distribution

The quantity of biomass within each particle size class and anatomical fraction varied as shown in Figure 2. The cobs were more resistant to deconstruction than the other fractions, with a majority of the sample particle size being greater than 9.5 mm. The husks and sheaths tended to be more susceptible to deconstruction and had a more even distribution in each of the size fractions. It was somewhat surprising that leaves, given their seemingly fragile nature, had a majority of their particles in size fractions larger than 0.6 mm and made a relatively minor contribution to size fractions smaller than 0.425 mm. It is possible that due to baling process and the fragile nature of the leaf, the fraction collection methods favored portions of the leaf that were the least fragile. The more delicate and thin tissues of the leaf, which would likely make a larger contribution to the smaller size fractions, may be under-represented in this study.

3.2 Total ash content

The actual ash content measured from the whole stover was 12.7%. After manual fractionation of the anatomical parts, the estimated ash content calculated from the anatomical parts was $4.9 \pm 0.1\%$ (Table 1), less than half the actual ash value. The difference between these two values was likely due to how the individual fractions were collected. As anatomical fractions were manually collected, only plant material that could be positively identified as a specific anatomical fraction was included in the anatomical fraction sample. This selection process likely minimized the introduction of dirt or dust into the samples [21]. Also, as aforementioned, some of the material was pulverized during the baling process and the remaining identifiable plant material could have been biased towards lower ash results. The finding that over 7% of the ash in this multi-pass bale is from introduced soil and dust and is easily removed is in agreement with results that are typically observed in baled corn stover materials that are analyzed at Idaho National Laboratory. It is notable that the total ash content of this material (4.9%) appears to meet the current ash specification for the biochemical conversion platform, which is currently 5% [1]. However, as shown by Kenney et al [4], total ash content in biomass is highly variable, with well over 50% of the available corn stover having ash contents that exceed 5%. The discussion below focuses on economical methods to isolate fractions of material that are suitable for biochemical and thermochemical conversion processes.

3.3 Ash removal by size fractionation alone

Methods to separate biomass particles based upon size are simple and cost effective to implement, so this method is attractive for ash separation and reduction requirements. The ash content of the size fractions and their contributions to the total mass is shown in Table 2. As expected, the smallest size fractions contained the highest concentrations of ash for all samples. Approximately 50% of the total mass is contained in the 9.5 mm and 6.0 mm fractions which have a combined ash content of 3.9% on a dry weight basis. Approximately 95% of the

mass is contained in the 0.425 mm and larger fractions, which have a combined ash content of 4.6% on a dry weight basis. Although separation would not be needed for this particular sample in order to achieve an ash specification of 5% [3], these results show that separation can be an effective method to achieve specifications for other stover materials that may have higher ash contents [4]. The exact amount of material that would need to be separated in order to meet conversion specifications for different processes would depend upon the ash content and composition of the available stover material, which can vary dramatically.

3.4 Selective ash reduction

The ash content for each size class can also be separated by the contributions from the individual anatomical fractions, as shown in Figure 3. Particles of leaves with sizes greater than 0.6 mm contained the greatest amount of total ash, with values ranging from approximately 8 to 13% dry weight of the total original material, while all of the anatomical fractions with particles smaller than 0.6 mm contained less than 2% of the total ash of the original material. The contributions of leaves, husks, sheaths and internodes were similar for the smallest size fractions (< 0.6 mm), while nodes and cobs of the smallest size fractions made no measureable contribution to the overall ash content of the fraction. This information, in conjunction with the anatomical particle size distributions, can be used to develop strategies to identify samples which if removed from the bulk biomass, present the best opportunities for the removal of ash in significant quantities.

For example, the smallest size fractions were shown to have the highest ash contents, yet removal of these fractions makes very little difference in total ash content because of the limited amount of material present in these fractions. In order to maximize the reduction of ash while minimizing the loss of organic matter, anatomical size fractions with the highest ash content were removed sequentially and the resulting ash content of the whole sample was recalculated, as shown in Table 3. Removal of fractions with ash content over 20% (0.4% of

total mass) resulted in a minor decrease in ash content. The most dramatic drop in ash content occurred when fractions with ash content over 8% were removed. While these removed fractions represented 20% of the total mass, they contained over 31% of the ash in the whole sample, reducing the ash content of the remaining sample to 3.3%. Achieving an ash content of approximately 3% opens opportunities to use these materials in combustion, gasification, and fast pyrolysis conversion processes [42].

3.5 Elemental Ash Analysis

As described in section 2.4, a combination of inductively coupled plasma-optical emission spectrometry (ICP-OES) and laser-induced breakdown spectroscopy (LIBS) was used to quantify the concentrations of specific elements in the anatomical size fractions. The results of these analyses are shown in Figures 4a-4d. The uncertainty in the measured concentration of each element of interest (U_{EOI}) has contributions from the anatomical fractionation that was performed by hand $U_{EOI, Sets1-2}$ and also from calibration and natural variation of the LIBS instrument $U_{EOI, LIBS}$. The uncertainty for each element of interest was estimated as

$$U_{EOI} = \sqrt{(U_{EOI, Sets1-2})^2 + (U_{EOI, LIBS})^2} \quad \text{Eq. 1}$$

where $U_{EOI, Sets1-2}$ is estimated using the difference between measured values obtained from the two replicate sets of samples that were prepared and analyzed, and $U_{EOI, LIBS}$ is estimated using the difference between values obtained using OES and LIBS for samples that were analyzed by both methods. In most cases, the uncertainty associated with hand fractionation was two to three times greater than that of the LIBS measurements.

There was an uneven distribution of ash components among both anatomical fractions and size fractions. Silicon was the most plentiful ash element found in each sample and had a maximum concentration of approximately 6% in husk pan fraction and approximately 3-5% in most of the leaf fractions. Potassium, calcium, magnesium and phosphorus were also present in

the samples in relatively high concentrations. It was found that the concentrations of silicon tended to increase as the particle size decreased for all anatomical fractions except the nodes, revealing that the use of size fractionation can selectively isolate this element for specific conversion processes. The “pan” fraction was only available in sufficient quantities for elemental ash analysis for the husks, and silicon concentrations in this fraction were more than three times higher than the next smallest size fraction and higher than any measured leaf fraction (Figure 4c). Given the lower silicon concentration of the husks, it is possible that silicon is easily liberated from the epidermal tissues of husks during processing. The elemental distribution information in Figures 4a-4d can also be utilized to contour chemical treatments for specific elemental removal (e.g. acid or base wash, chelating agents) in different size and anatomical fractions.

4. Discussion

The fractionation or selective harvest of biomass feedstocks for quality improvement is not a new concept, and it has been considered by several industries, including biofuel, pulp and paper, and animal feed. The end use of the biomass determines the characteristics deemed to be valuable in each industry, and the desired fraction of the biomass is not always the same. A variety of biomass separation methods may be necessary to meet the diverse needs of these industries. For ash reduction, it was found that size separations and anatomical fractionation could be used together to maximize ash removal.

Because the desired fraction is not always the same, selective harvest may not be the best approach to supplying sufficient quantities of optimal feedstocks to each industry. Rather, post-harvest fractionation methods should be developed to make use of all of the biomass that is collected. Post-harvest fractionation also provides opportunities for tissue specific treatments for ash reduction or quality improvement. Using the information gathered in this research, it could be possible to isolate specific size or anatomical fractions to achieve desired reductions in

whole ash content or specific inorganic elements of ash. As an example, the ash content of whole leaves of corn stover and their size fractions were shown to be higher than that of any other anatomical fraction. It has also been shown that leaves require very little pretreatment prior to enzymatic conversion [20, 21]. Leaves could be isolated from the biomass for a quick reduction in ash content. Once isolated, additional ash removal steps (e.g. leaching) that were optimized for the leaf tissue could be used to bring ash levels down to a more acceptable level. Leaves showed elevated levels of calcium (9,000-11,000mg kg⁻¹) and magnesium (4,000-5,000mg kg⁻¹), so the leaching solutions could be optimized for removal of these alkaline earth metals. In addition to providing a reduction in ash content, the removal of alkaline earth metals would enhance the quality of this biomass for thermochemical conversion processes. For example, switchgrass with an ash content of 4% has been identified as an attractive additive in feedstock formulations for fast pyrolysis conversion because it reduces demand of other feedstocks in order to minimize overall formulation costs [42].

5. Conclusions

In this work it has been demonstrated that mechanical separations, including anatomical and size fractionation, provide opportunities for quality improvement and ash reduction. Using basic size and/or anatomical fractionation, fractions with low ash contents suitable for multiple fuels conversion processes can be obtained. The total amount of high-ash material is also reduced, such that the amount of material that may require additional treatment for ash removal can be reduced dramatically, depending upon the ash content of the original material. Additional gains in ash reduction or reduction in specific elements of ash could be realized by using size separations and anatomical fractionation in tandem.

Selective harvest of anatomical fractions is a solution for quality improvement that has been considered, and this would be effective if the methods for selective harvest existed, the desired anatomical fraction was known prior to harvest and collection, and the biomass was

being collected for a single customer or process. As a consequence, total biomass yields would be lower, which would be detrimental to the costs of harvest and the total supply of biomass available. Further development of post-harvest fractionation methods would enable maximum harvest yield and biomass utilization and could generate multiple product streams with specific chemical or structural properties for a variety of different end uses.

6. Acknowledgements

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Anatomical Fraction	% of Plant Mass*	Ash Content
Leaves	20%	10.4 ± 0.5%
Sheath	10%	6.9 ± 0.2%
Nodes	10%	4.0 ± 0.3%
Husk	10%	3.7 ± 0.2%
Internode	30%	3.5 ± 0.2%
Cob	20%	1.5 ± 0.2%
Composite Total	100%	4.9 ± 0.1%

Table 1: Contribution of anatomical fractions to total plant mass and ash content of these anatomical fractions. Ash content is reported as mean ± 1 SD, *n* = 3. *Percentages of plant mass were estimated based upon values found in the literature.

Size Fraction	% of Total Mass	Ash content
9.5mm	31.0 ± 4.2%	3.5 ± 0.4%
6.0mm	18.8 ± 3.7%	4.6 ± 0.9%
2.0mm	27.5 ± 1.4%	5.1 ± 0.5%
0.6mm	14.4 ± 6.0%	5.9 ± 0.2%
0.425mm	3.5 ± 0.9%	4.8 ± 0.7%
0.150mm	3.9 ± 0.9%	7.5 ± 2.5%
<0.150mm (pan)	0.8 ± 0.2%	22.5 ± 10.8%

Table 2: Particle size distribution of corn stover ground to ¼” mesh and the ash content of these size fractions. The mass reported refers to the material that was retained on top of each sieve after separation. All values are reported as mean ± 1 SD, *n* = 3.

% Ash of removed samples	% Biomass remaining	% Ash of remaining biomass
None	100%	4.9%
> 20%	99.7%	4.8%
> 10%	94.7%	4.4%
> 8%	79.2%	3.3%
> 7%	78.5%	3.1%
> 6%	69.3%	2.9%
> 5%	68.2%	2.8%

Table 3: Using a combination of size and anatomical fractionation, fractions containing the highest ash content were sequentially removed from the bulk sample and the ash content of the remaining sample was calculated.

Figure 1: Flow diagram of experimental design for ash analysis of anatomical fractions and particle size fractions. *only samples that were >2mm were ground down to 2mm in order to get a homogeneous representative sample for ash analysis.

Figure 2: Particle size distribution among anatomical fractions. Error bars represent 1 standard deviation, $n = 3$.

Figure 3: Ash distribution within anatomical and size fractions. Error bars represent 1 standard deviation, $n = 3$.

Figure 4a: Corn stover size fraction magnesium (Mg) concentrations. Error bars represent the uncertainty in the measured concentration of each element of interest (U_{EOI}), $n = 3$ on all measurements except husk-pan, where $n = 1$.

Figure 4b: Corn stover size fraction calcium (Ca) concentrations. Error bars represent the uncertainty in the measured concentration of each element of interest (U_{EOI}), $n = 3$ on all measurements except husk-pan, where $n = 1$.

Figure 4c: Corn stover size fraction silicon (Si) concentrations. Error bars represent the uncertainty in the measured concentration of each element of interest (U_{EOI}), $n = 3$ on all measurements except husk-pan, where $n = 1$.

Figure 4d: Corn stover size fraction potassium (K) concentrations. Error bars represent the uncertainty in the measured concentration of each element of interest (U_{EOI}), $n = 3$ on all measurements except husk-pan, where $n = 1$.