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Research paper

Ash reduction strategies in corn stover facilitated by anatomical and size fractionation

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A B S T R A C T

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

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Abbreviations: LIBS, laser induced breakdown spectroscopy; ASTM, American Society for Testing and Materials; NREL, National Renewable Energy Laboratory; Nd:YAG, neodymium-doped yttrium aluminium garnet; NIST, National Institute of Standards and Technology.

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

There are many factors to consider when selecting or developing methods to separate biomass fractions to minimize impacts of ash on subsequent uses and end products. The first concern is that the costs of reducing ash concentrations in high value product streams through separations must add more value than the separations processes incur. In this consideration, ash is essentially a waste product that must be dealt with at some point in the conversion process. When it is included in biomass, it must be shipped, handled, and processed, even though it will ultimately need to be discarded. The ash content of many biomass feedstocks can exceed 10% dry weight, prompting additional biomass to be purchased, shipped, and processed in order to meet production goals, thus increasing overall costs and complicating logistics.

Another consideration in determining methods for ash removal is the negative effects that certain components of ash may have within specific conversion processes [4,28]. In the biochemical conversion platform, ash represents inert, unconvertible material that requires disposal. In the pyrolysis conversion platform, the elements K, Na, Ca, and Mg can be destructive to the conversion products. Nitrogen, S, and P can foul the conversion catalysts in several conversion processes. Nitrogen and S are also a source of pollutants in the gasification and combustion conversion process, and Si, K, Na, and Cl can be damaging to reactors themselves in these same processes [28]. Depending up the selected conversion pathway, certain elements at sufficiently low concentrations can be acceptable.

An understanding of the inorganic elemental composition, location, and chemical format within each plant tissue is advantageous for devising efficient ash mitigation strategies that could involve using different material fractions in processes best suited for their organic and inorganic compositions. Sodium and K are typically free ions in solution and found in the 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