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Characterization and Measurement of Corn Stover Material Properties

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Characterization and measurement of corn stover material properties

by

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Biorenewable Resources & Technology

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Abstract

The United States is beginning to replace petroleum-based fuels and chemicals with renewable sources to make the same products. One of the major petroleum products consumed in the United States is gasoline used in liquid fuel transportation. Currently, corn grain-based ethanol is the primary leader in renewable fuels, but cannot completely replace gasoline for many reasons. Therefore, cellulosic biofuels, renewable fuels derived from the cellulose in plants, have become of significant interest, due to the large quantity of cellulose on Earth.

The primary crop in Iowa is currently corn, and will likely stay that way for years to come. The infrastructure in Iowa is built around corn and soybean production, and therefore it will be very difficult to introduce a new crop for energy. Corn stover, however, is becoming more abundant as corn yields climb, and can be used to produce cellulosic biofuel. However, since corn stover has never before been harvested on a commercial scale, its material properties, and sampling techniques to measure those properties, are not well established. The four technical chapters in this thesis help to define some of corn stover's material properties, and to establish appropriate sampling techniques for these properties. The first chapter begins by assessing two different types of rapid moisture analyzing methods, as well as exploring how to obtain an accurate and representative subsample for other potential rapid analyzers. The methods developed and validated in this chapter will help to allow material properties to be measured on an industrial, large-scale corn stover harvest. The second technical chapter evaluates two sample sizes to determine the proper sample size to accurately analyze material properties of corn stover bales. This chapter outlines some guiding principles to obtain representative samples within corn stover bales. The third technical chapter examines the individual bale's variability for its material properties, moisture content and ash content. Finally, the fourth technical chapter builds on the variability of corn stover by exploring variability of moisture and ash content within a set of bales harvested from the same field. These variability chapters can aid future corn stover processing facilities in determining the number and location of samples to be taken from bales, as they're being harvested.

Chapter 1. Thesis Organization

This thesis begins with a general introduction and background, and continues with a literature review. The general introduction and background demonstrate the importance of the research conducted within this thesis. Following the literature review, the objectives for this thesis are described. The thesis will then begin with the first of four technical chapters.

The first technical chapter explores the accuracy of two rapid moisture analyzers, as well as the accuracy of subsamples from one core sample, which could be used for other rapid analysis. Rapid quality analysis is a necessity for industrial scale corn stover processing facilities, just as it is with current grain processing facilities. With the potential for variable compositions of the feedstock, rapid analysis could prove difficult.

The second technical chapter examines the question of sample size. Most industrial analytical labs take three to five gram samples of material and apply the results to the entirety of the material. With the variation of components in corn stover, stalks, cobs and leaves, there is not a high likelihood that a three to five gram sample will be representative of the entire feedstock. For a 25 million-gallon per year plant averaging 75 gallons of ethanol per ton of corn stover, and each bale averaging 1000 lbs, close to 700,000 bales will be needed. Three to five gram samples are hardly representative of a small amount of material, and will likely be less representative for a 1,000 lb bale or hundreds of these bales.

The third technical chapter focuses on quantifying ash and moisture content variability in corn stover bales and performs an in-depth experiment on several individual corn stover bales. For each of these bales, moisture content and ash content values are measured from 72 different locations within the bale, which will help map out where samples should be taken from to obtain the most representative sample from the bale.

The fourth and final technical chapter of this thesis looks at variability of moisture and ash content within a set of bales harvested from the same field. Multiple bales from 89 different fields were analyzed to determine the variation in material properties. The end goal for this experiment is to help future corn stover processing facilities know the variation within a field so they can determine how many bales to sample, per field, in order to determine the quality of the material.

This research was done in conjunction with a project sponsored by DuPont Cellulosic Ethanol. DuPont is building a 25 Million-gallon per year ethanol plant in Nevada, Iowa, to use corn stover as the primary feedstock. DuPont will contract with biomass harvesting crews and farmers, so that once the farmers have completed their grain harvest, the biomass harvesting crew can bale the corn stover from the field. As DuPont’s plant gets closer to completion, DuPont will be searching for a way to accurately measure the quality of feedstock harvested by each biomass baling crew. Thus, the research conducted for this thesis was performed to provide helpful guidance to companies, such as DuPont when measuring corn stover quality.

Chapter 2. Literature Review

2.1. Introduction and Background

In the past few years, Americans have been trying to live more sustainable lifestyles by implementing “green” initiatives such as using renewable resources to produce everyday products. Renewable resources are any natural resource that can be replenished or reproduced naturally over a couple of years (Dictionary.com, 2012). Part of the push has been government-initiated from policies, such as the Renewable Fuel Standard 2 (RFS2), which requires the United States to decrease carbon emissions, while a majority of the push has been energy and economically-driven. A large part of any society, especially a sustainable society, is in the transportation fuel sector. As fossil fuels have started to deplete, U.S. average gas prices have increased from approximately $2.00 per gallon in early 2004 to about $3.75 currently (GasBuddy.com, 2012). This takes a cut out of every American’s paycheck because we are a society that requires petroleum to fuel our lives. For example, gasoline consumption in 2011 was at 360 million gallons per day or more than one gallon per day for every person in the U.S., with current population reaching more than 305 million people (U.S. Energy Information Administration, n.d.). In order to reduce the impact of high petroleum prices, the United States has begun increasing biofuel production, with some help from the Renewable Fuel Standards’ suggested biofuel consumption levels. According to the Center for Agricultural and Rural Development (CARD), ethanol reduced the price of gasoline by an average of 89 cents in 2010 and $1.09 in 2011. Also according to CARD, in 2011, 116.7 million households used 131.2 billion gallons of gas. With the reduction of price due to ethanol, the average household spending at the pump was $1,200 less than they would have been if no ethanol had been used (Jessen, 2012).

The RFS2 requires total renewable fuel production to expand from about 13 billion gallons in 2010 to 36 billion gallons in 2022 (Schnepf & Yacobucci, October 14, 2010). Currently in the Midwest, we make first generation biofuels in the form of about 14 billion gallons of ethanol made from the starch in corn kernels (Urbanchuk, 2012). Additionally biodiesel is made from soybean oil for diesel vehicles. While making ethanol from corn is helping to make a more sustainable society and lessen the impact of high oil prices, there are many other beneficial uses for corn than biofuel production. Additionally, ethanol production from corn has been controversially blamed for the recent increases in food prices. Also, as we become more familiar with corn starch ethanol production, and begin to assess the full life cycles of corn to ethanol, questions are being raised as to whether or not corn starch ethanol is actually carbon neutral, as originally claimed (Carriquiry, et al., 2010). As the United States moves closer to sustainability, fuels must be derived from abundant biorenewable resources that are not vital to another market, such as corn is to the food market, in order to reduce our dependence on fossil fuels and make a bigger impact in the percentage of transportation fuels supplied. The biofuels from biorenewable resources that exhibit these sustainable characteristics are generally referred to as “second generation biofuels” as they strive to be more sustainable than first generation ethanol.

The next step in the process of developing second generation biofuels is to find the appropriate feedstock for biofuel conversion. When selecting a feedstock, finding one with desirable characteristics for the conversion process is crucial. Some of the desirable characteristics in a feedstock would be one that is widely abundant, is easily converted into fuel, does not cause problems to machinery in the conversion process, and produces minimal waste. The current materials being investigated as feedstock for the second-generation biofuels are lignocellulosic materials such as switchgrass, wood, Miscanthus, energy cane and agricultural residues. In the Midwest, corn and soybeans are, by far, the most abundant and profitable crops, so there will be resistance to growing any energy crop that tries to take their place. Additionally, growers in the Midwest have become increasingly familiar with, and proficient at growing these two crops, and the agricultural infrastructure of the Midwest is built to harvest and transport corn and soybeans. Nevertheless, while the implementation of new crops is unlikely, there are other very promising options.

2.2. Corn Stover as a Feedstock

As corn yield continues to climb, the amount of corn residue, or corn stover, left on the field after harvest has increased, as well. According to Xiong, et al., 2010, "corn stalk comprises roughly 75% of total agricultural residues in the U.S.A.". Corn stover generally consists of cobs, leaves, stalks, occasional corn, and soil from the harvesting and collection methods used; on some occasions, though, cobs are not included. More specifically, an article by Morissette, et. al, suggests that corn stover is comprised of "approximately 50% stalks, 22% leaves, 15% cobs, and 13% husks on a dry matter basis" (Morissette, et al., 2011). Since corn stover is so abundant in the Midwest due to the wealth of corn production, it is a very practical lignocellulosic feedstock for either thermochemical or biochemical processing. An example of the abundance of corn stover can be seen in Figure 2.1 in which some of the stover has been baled and yet an abundance of residue still remains. The bioprocessing, either thermochemical or biochemical, will use renewable plant material, or lignocellulosic material, such as corn stover, as a feedstock to produce second generation, advanced, or drop-in biofuels.

Figure 2.1. Available corn stover biomass for conversion into cellulosic ethanol.

The feedstock for each bioprocessing facility will vary by geographical region, since different crops flourish in different areas of the country. This is also beneficial so that the entire United States can benefit by using the crops that grow best in their own region. In the Midwest, the most probable feedstock appears to be corn stover, since it is abundant, and is not needed for any other purposes that substitutes do not exist. Additionally, there has been debate whether indirect land use change (ILUC) occurs with other fuels. This term stems from the idea that if a certain crop, such as corn, is desired to create more fuel, land will be taken away from somewhere else to grow the corn, therefore emitting more carbon dioxide than corn takes in (Searchinger, et al., 7 February 2008). Whether or not ILUC is actually a major factor in carbon dioxide emissions, using corn stover as a feedstock would provide the same emissions because the harvesting of corn stover requires no additional cropland. Corn stover harvest just requires taking leftover plant material from a field after the grain has been harvested. The fact that it does not require any additional land also provides an economic benefit, since two valuable products can be harvested from one piece of land and only one crop. In fact, an article by Carriquiry, et al., supports the use of residues, such as corn stover, by stating, "A major advantage of using residues for biofuel production when compared to the grain crops and dedicated energy crops is that no additional land is needed. By avoiding the competition for land, residue based biofuel production should have minimal direct impact on food prices" (Carriquiry, et al., 2010). This could help to put an end to the "Food vs. Fuel" debate, because more fuel would be derived from the biomass, and less from the grain. Therefore, the grain could be used for human consumption or for livestock feed, which ultimately results in human consumption.

There are many types of agricultural residues, so how would corn stover compare, in terms of biofuel yield, to other residues? In their working paper, Carriquiry, Du, and Timilsima, include a table showing that corn stover is not only comparable to other residues that are capable of being produced in the United States, but is very favorable. The table discussed is shown in Table 2.1, although the biofuel yield that is being referred to here is ethanol (Carriquiry, et al., 2010). Also mentioned in Carriquiry, et al.'s paper was that out of three types of agricultural residues: corn stover, sorghum straw, and barley straw; corn stover has the best potential availability around the world, by far. This is helpful to know so that, once the best practices and technologies for producing second generation biofuels from this corn stover are established, the knowledge can be used globally.

While there appear to be many benefits of using corn stover as a feedstock, there are some disadvantages, as well. The main disadvantage of corn stover is that it has a very high ash content, which translates directly to waste. This will be discussed in length later on, but it is important to note that the ash content causes economic, processing, and transportation problems. This high ash content also plays into some of the high pretreatment costs associated with corn stover conversion to cellulosic ethanol. Another disadvantage of using corn stover as a feedstock is that, when using it for biochemical conversion into cellulosic ethanol, there are not many, if any, valuable co-products. Unlike corn starch ethanol where Distiller's Dried Grains have been very popular in the cattle industry, corn stover conversion to ethanol does not produce the same type of high-value co-products, which would be able to help bring in additional profit.

Table 2.1. Composition and yields of different feedstocks (based on dry mass). Reprinted From (Carriquiry, et al., 2010). The biofuel yield refers to ethanol yield for each crop.

	Residue /crop ratio	Crop Dry Matter (%)	Lignin (%)	Carbohydrates (%)	Biofuel yield (L/kg of dry biomass)	Yield (kg/ha)	Biofuel yield (lt/ha)
Barley Straw	1.2	88.7	9.0	70.0	0.31	1,184	367
Corn Stover	1.0	86.2	18.7	58.3	0.29	1,734	503
Rice Straw	1.4	88.6	7.1	49.3	0.28	1,399	392
Sorghum straw	1.3	89.0	15.0	61.0	0.27	736	199
Wheat Straw	1.3	89.1	16.0	54.0	0.29	1,413	410
Sugarcane bagasse	0.6	26.0	14.5	67.2	0.28	11,188	3,133

According to the article by Shinners and Binversie, "Corn stover has been harvested as supplemental feed for beef and non-lactating dairy animal for decades" (Shinners & Binversie, 2007). Also, it has been utilized as bedding for cattle and swine. In these situations, the quality of the stover, mainly ash and moisture content, are not extremely significant. The reason that the ash and moisture content are not as significant is because, when used as feed, high moisture content is sometimes desirable to allow for fermentation, and it can be fed to the livestock sooner than the dry stover that is able to be stored longer.

Ash content doesn’t matter in feed because of its composition. Ash content is essentially what is left after something is burnt in the presence of oxygen. In corn stover that is baled, this consists of some plant material but mostly soil contamination.

Whereas corn harvesting technology has had time and the opportunity to mature, especially in the Midwestern United States, Shinners and Binversie mention that since there has previously been more supply of corn stover than demand, so there wasn’t an economic incentive to improve the harvesting system and study the characteristics (Shinners & Binversie, 2007). However, before corn stover is able to be used on a commercial scale for a feedstock to any type of biofuel production system, the characteristics of corn stover must be examined and investigated to determine best management practices for harvesting, and to determine what properties are bottlenecks to the system. This will also help the feedstock buyers decide which properties should be evaluated when determining the quality of the corn stover so that corn stover-based cellulosic ethanol can become a profitable industry. The unearthing of this information is so vital that in the initial press release from Dupont Danisco Cellulosic Ethanol (DDCE), they mention that they are collaborating with Pioneer Hi-Bred and Iowa State University, who both have qualified scientists to research this material, in order to gather all the information they possibly can before the commercial-scale plant is completed (DuPont Danisco Cellulosic Ethanol, 27 June 2011).

2.3. Evaluation of Probable Bioprocesses

Due to being part of a living plant at one time, corn stover has qualities that make it a practical feedstock for several bioprocesses. The thermochemical processes that would be able to use corn stover would include fast pyrolysis and gasification, and the primary biochemical process suited for corn stover is fermentation into cellulosic ethanol.

Both thermochemical processes prefer the same type of feedstock, in general, since they utilize the heating values of feedstocks to create their products. Gasification is a thermochemical process that occurs between 700-1000°C, producing thermal energy and a product called syngas (or producer’s gas). This syngas can be used to generate electric power or to synthesize fuels using catalysts or microorganisms. Fast pyrolysis is a thermochemical process that heats a feedstock, in the absence of oxygen at temperatures around 450-550°C.

The products resulting from fast pyrolysis include bio-oil, syngas, and biochar. Bio-oil can be refined to products very similar to gasoline and diesel, which could be “dropped into” our currently existing pipelines. This key quality earns these fuels the term “drop-in fuels”, as they could displace our use of petroleum. Additionally, biochar is a very carbon-rich co-product that can be applied to soil and restore the organic matter. Biochar has been shown to improve crop yields dramatically, which makes this process very promising (Brown, 2011).

Using corn stover as a feedstock for these thermochemical processes, however, is not as ideal as it may be for biochemical processes. The high ash content leads to high alkali contents from the soil contamination. The result of high alkali contents is lower yields due to higher water content in the liquids and the fact that the more alkali there is in the material, the less material there is for conversion to products (Oasmaa, et al., 2010).

The process selected for corn stover in Iowa by two companies, DuPont Danisco Cellulosic Ethanol and POET Biorefining, which have already begun construction, is biochemical processing into cellulosic ethanol. DuPont Danisco Cellulosic Ethanol (DDCE) has such high hopes for corn stover in the Midwest that it issued a press release in June of 2011 stating that they purchased land in Nevada, Iowa, to start a 27.7 MGY (million gallons per year) cellulosic ethanol plant using corn stover as a feedstock on the same land as the corn starch ethanol plant shown in Figure 2.2. They believe that local farmers will buy into the idea because it will “provide opportunities for farmers to add value to their croplands” (DuPont Danisco Cellulosic Ethanol, 27 June 2011). In an article by K. Shinners and B. Binversie, the authors go so far as to say that “Corn stover has the greatest potential as a biomass feedstock in North America, with potential annual yields of 130 Tg, producing 38.4 GL of bioethanol” (Shinners & Binversie, 2007). An article by McAloon et al., 2000, suggests that about 30% of the stover on each corn field is available to be collected and converted which would result in about 6 billion gallons of ethanol (McAloon, et al., 2000). Other sources report as high as 50%, which would be an even larger amount of ethanol produced (Morissette, et al., 2011, p. 1103). This would be a significant contribution to biofuel production, as corn grain ethanol capacity was at 12.9 MGY, and the corn stover processes have not yet even been maximized (Baker & Zahniser, 2006).

Figure 2.2. Corn stover harvesting at a field near the future site of DuPont's cellulosic ethanol plant and the current site of a corn starch ethanol plant called Lincoln Way Energy.

In terms of cost analysis, second generation ethanol plants, or lignocellulosic-based ethanol plants, can somewhat be compared with corn starch ethanol plants. However, according to McAloon et al., 2000, the lignocellulosic process costs must be assumed to be an Nth generation plant so that no first-time start-up costs will occur. This is necessary because corn ethanol processes have been well-refined and do not have those costs. In other words, this assumption puts the two types of ethanol production on relatively level playing fields for easier analysis. While each feedstock would create different costs, the general process for conversion to ethanol is approximately the same. Corn stover collection on a commercial scale is in its beginning, so collection costs have not yet been specified. In McAloon et al's article, the price of corn stover was assumed to be around $30-$40 per dry ton, while the market price of corn is currently around $5.00 per bushel (McAloon, et al., 2000). Corn stover priced at $30-$40 will probably not be realistic, but is what the authors used for this comparison. With 1 bushel of corn equal to 56 pounds, and 2000 pounds in a ton, it can be assumed that there are about 35.7 bushels in a ton. So, at $5.00 per bushel, corn is approximately $179 per ton, in comparison with the $30 to $40 of corn stover. However, the number for corn is including moisture, and the number for stover is on a dry-matter basis. Even after accounting for moisture, there is still a large enough gap to see that corn stover could be economically advantageous in terms of harvesting and collecting. In comparison, the general rule of thumb is that for every 1 ton of corn, there is about 1 dry ton of stover left on the field, so the cost to produce them could be divided somewhat equally. However, while there may be an opportunity cost to make ethanol out of corn grain, since it can be used for many other things, there is little to no opportunity cost for the stover, since it would otherwise be plowed under or used for cattle feed/bedding. Today with the current technology and machines, corn grain ethanol is estimated to cost about $1.50 per annual gallon. For about the same size of lignocellulosic plant, it is estimated that it would cost close to $4.30 per gallon, although costs are not set in stone since the feedstock would have to be transported from farther away than a smaller plant, which would have higher capital costs. The lignocellulosic plant would also cost more because of the pretreatment required to get the cellulose to a starch form that the yeast can ferment into ethanol. In addition to the pretreatment, the stover would need to be preprocessed in the form of cleaning to rid it of as much soil as possible, followed by grinding into finer pieces, and then sent through the conversion process, whereas corn grain only requires milling (McAloon, et al., 2000).

In processes that utilize corn starch as a feedstock, the quality of the corn is evaluated based on moisture content, amount of damaged kernels, amount of each component in the kernel (starch, etc), and foreign material in the grain. However, in corn stover, the two main factors affecting quality are moisture content and ash content. Moisture content will impact the type of storage needed to preserve feedstock quality. This can impact costs for the conversion facility, primarily if the facility is storing the material. The reason for this is because high moisture content will lead to higher dry matter loss, which would mean they purchased material that cannot be converted to product. Ash content causes problems with facility costs and productivity. It affects productivity due to the fact that the soil contamination in the ash will clog up and ruin machinery, causing the machines to be less efficient. Additionally, those machines will need to be cleaned and serviced more often due to the wear and tear, therefore adding costs to the facility’s already expensive process. It is for these reasons that, no matter what process, when using corn stover as a feedstock, samples will need to be taken in order to determine the quality of incoming material.

2.4. Sampling Methods

While corn stover consists of the same basic materials, cobs, stalks and leaves, each part of a field and each harvesting method is slightly different, which results in corn stover bales with varying compositions of these basic components. The variable composition can be seen in Figure 2.3. Therefore, it is difficult to put a number on the quantity of each component. Since the components of corn stover vary from one source to another, the moisture and ash properties of corn stover will tend to be variable as well. Hence, the methods in which corn stover is sampled for quality analysis are very important in order to capture properties of all the components.

Figure 2.3. Corn stover bale, showing the nonhomogeneous composition of the bale, consisting of cobs, stalks and leaves.

The sampling method will make a difference in the measurement of all properties, but especially in moisture and ash content because those properties differ for all components. For example, knowing the ash content of only the plant components of corn stover is not enough information to provide to future corn stover conversion plants since there will be soil, which contributes to ash content, intertwined with the corn stover bales. Soil tends to be brought into the corn stover bales since the material is machine-harvested, which cannot yet separate soil from plant material. Thus, the soil should be included in the sample propertie to see how it will affect a system and see what implications it has on quality. Additionally all plant components including cob, stem, and leaves, should be included in the sample since they all contain different moisture contents, which will affect the quality of the material as well.

Therefore, a standard sampling method should be established so that all moisture and ash contents from different researchers and institutions can be compared against each other. Currently, many people have examined moisture and ash contents for corn stover. However, as can be seen in the following paragraphs, every study uses different methods of sample collection, which does not allow the numbers to be compared against each other very well.

In Wang, et. al, 2011 paper, the sampling method included taking stover without cobs and grinding it to pass through a 1 mm screen. This article did not describe whether the sample was a hand-grabbed sample or one mechanically-taken from a bale of corn stover; however, since it was taken without cobs it can be assumed that it was taken as a grab sample, meaning that the sample was taken by hand. Because of natural human error, the sample may not contain a representative amount of all of the components, especially soil. In samples taken by hand, soil will not transfer to the sample’s container as easily as the rest of the components, since it has a small particle size and will fall out of the sample. Therefore, while the knowledge of the plant material’s ash content is important, it is not representative of the feedstock as it would be coming into an ethanol plant since it does not have the representative amount of soil.

In the 2010 paper by Xiong et al., which took place in China, stalks were harvested by hand and piled on a farmer’s land. Before the corn stover was sampled, a gentle shaking was done to remove impurities such as the soil. While this may be reasonable in places where hand-harvesting is still practiced, this is not practical on an industrial scale in the United States, as the corn stover would most likely be baled together for transportation efficiency, and would include soil, as mentioned previously. Therefore, industrial-sized bales ideally should be sampled to adequately represent what the corn stover conversion plants would be receiving. However, these studies are important to discover the ash content of just the stover materials, in order to learn what the ash content could be if methods were developed to remove soil.

In the book “Biorenewable Resources: Engineering New Products from Agriculture”, the author suggests that corn stover consists of 5.58% ash when a proximate analysis was done, and 6.26% when ultimate analysis was done, both on a dry weight basis (Brown, 2003).

However, a paper by Wang, et al. suggests that corn stover is 8.1% ash on a dry weight basis (Wang, et al., 2011, p. 173). The paper by Xiong et al., found ash content to be 5.863% in just the plant material, as soil was shaken out of the biomass (Xiong, et al., 2010). In the paper by McAloon et al., ash content in corn stover was listed at 6.1%; however, the sampling method was not described (McAloon, et al., 2000). As can be seen from just these four sources, ash content variation does occur. Corn stover can be harvested, baled and sampled by several different methods, which could change the composition of each bale, therefore inducing variation. The variation comes in at two different levels: variation within each bale, from top-to-bottom or left-to-right within every bale, and variation in a set of bales harvested from the same field. The field-level variation is what the stover-to-ethanol conversion plants will have a hard time adjusting to. If a conversion plant was told that the entire feedstock would be 10% ±1% ash, they would be able to develop a pretreatment process to deal with that quality of feedstock, and not worry about changing the process, since the ash content is very consistent. However, if they have some bales that are 10% ash, and some that are 25% ash on the same truckload, they will need to alter their pretreatment process while in operation to shake out more of the soil before beginning to process it.

With all of the variation of components, it is difficult for the conversion facilities know where at, in a bale, to take a sample so that they can determine the ash content of the bale. Each bale is made in the same way, but from stover collected across a field, which means that the amount of soil brought into the bale in each part of the field may be different. For example, if the windrower is on more of a slope, it may take in more soil than when it is on flat ground. Also, after a bale has been sitting in a stack for a while, the soil may fall to the bottom of the bale. Using this information, corn stover processing plants can decide where to sample so that they can get representative ash content information for the entire bale. These questions are the reason why studying sampling techniques is very critical to industrial scale harvesting of corn stover.

Many analytical laboratories will use the standard ASTM method in order to obtain a value for the ash content. However, with the large number of samples they process, they generally use machines such as the Thermogravimetric Analyzer, shown in Figure 2.4. These machines follow this standard ashing procedure, but they generally use only a small crucible to put the sample in. The crucibles they use allow for a much greater throughput since they are small and many can fit in one machine, which is ideal for industry. However, the crucibles generally hold only a few grams of corn stover, which doesn't depict the quality of an entire 1,000 pound bale. Therefore, when considering sampling methods or analyzing material property data, the size of the sample should also be taken into account.

Figure 2.4. Thermogravimetric analyzer used in industrial scale laboratories for material property analysis.

2.5. Ash Content and its Problems

Wang et al. states that "ash behavior from biomass during thermochemical conversion is one of the most important issues to be studied for the selection of a thermochemical conversion process" (Wang, et al., 2011). As alluded to earlier, ash content of biomass is considered to be the remains of a biomass sample after it is burned in the presence of oxygen. Burning a biomass material in the presence of oxygen removes the carbon from the sample, leaving only the other mineral components (Brown, 2003). Ash content can be calculated using Equation 2.1. The components of ash in a biomass sample can include elemental compounds from the plant material, such as potassium and phosphorus oxides, as well as soil. On a fast fact sheet that DuPont Danisco Cellulosic Ethanol dispersed, one fact they list is that "each bale of stover measuring 3' x 4' x 8' weighs between 1,100 and 1,700 lbs – the difference is mainly moisture and soil in the biomass." (DuPont Danisco Cellulosic Ethanol, 2011) Essentially, DDCE suggests that the ash content of just the plant material proves to be a fairly consistent number, while the biggest fluctuations lie in the amount of soil in the biomass. This is why the sampling method plays such a large role in the determination of the ash content.

Equation 2.1. Dry basis ash content calculation.

$$Ash\ Content(\%) = \frac{(Ash\ weight)}{(Dry\ weight)} \times 100$$

While the plant material, or structural ash content, is reasonably consistent, it is a valuable piece of information. One of the reasons that this is important to know is because if a harvest method is established which can eliminate or reduce soil contamination, the main source of ash would become that plant material, instead of soil remnants. Therefore, by knowing how much ash is in just the plant material, researchers studying harvest methods will have a goal to work towards, for ash content. They will be able to know the lowest level of ash they can achieve if they are able to eliminate soil contamination.

The knowledge of ash content in plant material is also a significant piece of information so the scientists who study corn genetic makeups can attempt to reduce that number, to reduce the overall ash content. However, to reduce the ash from plant material, the ash will need to be analyzed to determine what part of the plant remains in the ash, following combustion. In the article by Monti, et. al, they suggest that “leaves are generally much richer in ash than reproductive organs and stems” (Monti, et al., 2008). If this proves true, then something that could be done to reduce the ash content of just the plant material would be to reduce the leaf size. However, this would negatively affect crop growth, due to the reduced leaf area index, or available green leaf area for photosynthesizing and growing. This give and take is a delicate balance and is exactly why more studies must be done to make the most suitable corn plant for grain and stover harvest; it is also why the soil contamination part of ash content must be reduced or eliminated before structural ash content is evaluated.

The other, non-plant material, ash is soil contamination, as mentioned earlier. Soil can be brought into the biomass material by several methods. Some soil is brought onto the plant by the splash effect during rain events when the crop is in its early growing stages. This soil tends to be more difficult to remove in a pretreatment process. The main soil contamination, however, comes from various harvesting methods, such as raking the soil into the windrow that is to be baled. Additionally, sometimes the baler picks up more soil as it takes in the stover. These harvesting methods need to be adjusted to reduce soil contamination before corn stover harvest is scaled up for industrial scale ethanol production.

Soil in a biomass material poses a lot of problems to a biomass conversion plant. One significant problem with ash is that it is 100% waste. This means that it cannot be converted to a useful product and must be hauled away. As with any item, transporting it costs money. Paying money to transport an unusable material is a waste of money, and time and therefore is not economically favorable. Another way that ash content can make a biomass material economically unfavorable is the fact that the more ash that is in a truckload of biomass material, the less actual biomass content there is to convert. This results in a loss of time, money and space. However, research can be done on the ash to determine if it would have beneficial uses for on-field application in order to reduce the economic disadvantages. In DuPont's fast fact handout at their end-of-harvest gathering, they state that "There are a number of valuable co-products from the bio-refinery in addition to ethanol: lignin, high potassium ash, and sugar syrups." (DuPont Danisco Cellulosic Ethanol, 2011) Currently, one of the reasons corn starch ethanol is so profitable is because of its co-products.

Therefore, if this waste product from corn stover ethanol could be sold as a type of fertilizer or as compensation to the farmers, it would provide some economic incentives instead of economic disincentives. Monti, et. al, also discuss the high concentration of potassium and silicon in energy crops, which is also true in corn stover.

Additionally, as Wang, et. al mention in their paper, ash in biomass going through a thermochemical conversion process can cause processing problems including "sintering, agglomeration, deposition, erosion and corrosion due to the low melting point of ash in biomass feedstock" (Wang, et al., 2011). In another paper, Monti, et. al discuss the problems of slagging, corrosion and fouling for the processing equipment. Fouling, sintering, agglomeration, and deposition are all related to the accumulation of the soil from the feedstock, and clogging up the machinery. An example of the problems associated with ash is shown in Figure 2.5. This will cause problems in the processing facility and the in-field machinery because it will need to be cleaned out so that the machines can function properly.

This will cost money, adding to the economic problems associated with ash content. It will cause economic problems because of both the cost of cleaning the equipment, as well as the opportunity cost of the downtime required to clean the machines. Slagging is somewhat similar in that it “causes the formation of a glassy layer that must be removed” due to the low melting points of the alkali elements in the soil (Monti, et al., 2008). Energy crops are a rich source of silicon, which, according to the paper by Monti, et. al, wouldn’t be a problem, except that it easily reacts with the potassium or calcium which are also in the crops. It is the interaction of these elements that forms alkali silicates which have much lower melting points, allowing for slagging, and agglomeration (Monti, et al., 2008).Here, too, the removal of the slagging material will cost money, as well as the opportunity cost of the time required to clean or repair instead of producing more biofuels. Additionally, slagging causes a reduction of the heat transfer efficiency which will cause processing problems downstream (Morissette, et al., 2011). Corrosion and erosion are caused by all of the soil contamination as well as any rocks that may be in the system. The soil and rocks will take their toll on machinery, which will mean that parts will need to be replaced. So, while exact numbers have not been placed on the cost of ash or soil contamination in corn stover, the costs will be high, and therefore, soil contamination should be kept to a minimum.

Figure 2.5. Soil remaining after the combustion of a corn stover bale, demonstrating the tendency of the soil to stick together when in the presence of high temperatures.

2.6. Moisture Measurement

The measurement of moisture in biomass is also very important, just as it is important in the grain industry: in order to make storage and processing decisions. Therefore, studying the moisture content of the different components of corn stover, as well as a mixture of the components, is very important for corn-stover based cellulosic ethanol plants. One reason that it is so important is because their feedstock, like corn, will be harvested within 1-2 months of the year. Also, like corn, enough will need to be collected to feed the ethanol plant for the rest of the year, so storing lots of material is a necessity and will require much research in order to determine the best and most economical storage conditions for this feedstock. However, unlike corn, the amount of material required to feed a plant will be too large to store in grain bins. With corn, the grain is small enough to fit in aerated bins, either onsite or on the farm of one of the grain suppliers. With corn stover, though, it is made into large bales which take up a lot of room, and require large spaces to store. In fact, DDCE is stating that “sustainably harvested biomass needs will be more than 180 million tons”, which is equivalent to 90 million acres at a harvest rate of two tons per acre (DuPont Danisco Cellulosic Ethanol, 2011). All that material will need to be stored in conditions that will optimize the quality of the stover for the longest time possible. Some storage methods used for corn stover include tube-wrapping wet bales to create an anaerobic environment, placing them in a shed or barn, or storing them outside covered to protect from rain and snowfall (Shinners, et al., 2007).

Each storage condition has benefits and disadvantages related to the quality and cost of storage. The method of tube-wrapping wet bales, for example, is successful in preserving the quality, especially for high moisture material, as it is just ensiling the material. However, that method is impractical for all the bales that would need to be harvested on an industrial scale, since thousands of bales will need to be collected. Storing corn stover bales in a shed or barn provides aeration and shelter, but can cost significant amounts of money due to the size needed to store all the bales required for a corn-stover fed biofuel plant to run for a year. Storing bales outside, covered by a tarp, may require maintenance of the tarp, but may also be a very practical storage solution. It does not require the construction of a special facility just for material storage; it only requires the space for stacking the bales. However, with many different growers and conditions of feedstock, a combination of storage methods will most likely be used. Therefore, if dry matter losses, or amount of material lost, can be kept to a minimum, it may be a very effective storage solution. One of the main factors affecting dry matter loss is the initial moisture content, so bales must be sampled at the time of harvest in order to determine the storage conditions required by each set of bales (Shinners, et al., 2007). By supplying water, high initial moisture content causes dry matter loss by allowing the growth of microorganisms, which will consume the material. Therefore, the method for taking a moisture content sample is crucial to getting an accurate look at what the true moisture content is for the entire set of bales so that an estimate of how much degradation the microbes will cause.

The standard way to get the moisture content would be to take some material from the bale and dry it until it reaches a stable weight, as described in the ASABE Standard for gravimetric-based moisture content determination of forages (American Society of Agricultural and Biosystems Engineers, 1988). The moisture then can be calculated on a wet basis using Equation 2.2. While this method is very accurate because it physically dries all of the moisture out of the sample, it takes a long period of time, between 24-48 hours, to complete for corn stover. This is not practical for industrial use, as they will need to know the moisture content of a feedstock as it is harvested, or shortly after, and will not have the capacity to analyze samples from every bale for 24-48 hours. Therefore, it would be desirable to find a way to measure moisture quickly, so that cellulosic plants using corn-stover as a feedstock can stay current with moisture determination.

Equation 2.2.Wet basis moisture content calculation.

$$MoistureContent_{wet\ basis}(\%) = \frac{(Wet\ weight - dry\ weight)}{Wet\ weight} \times 100$$

For other materials, such as hay, some rapid moisture analyzers do exist. For example, the Delmhorst moisture probe (Figure 2.6) for hay is a hand-held tool that can be inserted into a bale, and the moisture can be read with the push of a single button (Delmhorst®, n.d.). However, this product has not been calibrated for materials such as corn stover that have varying compositions. These types of products would also be difficult to determine the accuracy of in that they measure the moisture by measuring electrical properties, and since the make-up of a corn stover bale is different from hay, including porosity and density, the moisture content read may not be very precise. These products also can only generally measure up to around 40% and some corn stover may have more moisture than that.

Figure 2.6. Delmhorst hay moisture probe.

In addition to hand-held rapid moisture analyzers, there are other methods to measure moisture rapidly. For some materials, a microwave oven procedure has proven to work (Cutmore, et al., 2000). Theoretically, this method should work, because it is using the same type of theory as a regular oven, just using microwaves instead to speed up the process. There are also small moisture analyzers, such as the one in Figure 2.7, that are small machines with a plate on a scale that heat a small sample of material until a stable mass is achieved. These machines follow the standard methods for gravimetric moisture content determination, since they heat the material until all of the moisture is assumed to be gone based on the fact that the weight is no longer decreasing (Ohaus, n.d.). However, the problem that could be encountered here is with a small sample size. The moisture analyzers have only a small space for the sample to be placed, so how do you choose what portions or components of the corn stover bale to put in the machine for moisture content determination? This is also something that will need further research, as it will be very influential in cellulosic ethanol plants using corn stover as a feedstock.

Figure 2.7. Small moisture analyzer.

2.7. Conclusion

As the United States and the world make a push towards a more sustainable society, the sources of energy used to fuel our societies need to become biorenewable-based. Many crops are available to be used as second-generation biofuels, but in the Midwest, corn stover, or corn residue, proves to be the most promising feedstock because of its abundance. However, corn stover does not yet have all of the desirable characteristics for an ideal cellulosic ethanol feedstock, so research must be done in order to make it a more suitable feedstock. Harvest methods, storage methods, sampling methods, and processing methods all need to be refined in order to make the most profitable and renewable product possible. Harvest methods need to be polished in order to induce the least amount of soil contamination possible, and in order to gather the material when it contains the desired amount of moisture so that it does not stimulate dry matter loss. Storage methods need to be researched and developed to keep the material at the highest quality possible for long periods of time. Sampling methods need to be standardized and refined in order to be able to compare properties against different conditions while still retaining representable data. Finally, processing methods need to be perfected so that once the corn stover has been prepared for bioprocessing, it’s a seamless process for producing fuel to ignite our sustainable society. While it may appear that corn stover-to-ethanol production has a long ways to go, much research is already underway, and the Midwest will begin to see benefits shortly. This new source of ethanol production will have its own start-up costs, but should provide many economic and environmental benefits long-term.

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Chapter 3. Overview and Objectives for Corn Stover Material Property Analysis

3.1. Overview

The United States has become increasingly interested in developing a bio-economy, or an economy based on products created from biomass materials. One backbone of an economy is its source of fuel. In a bioeconomy, a fuel should be based from biomass or renewable materials. An example of this is cellulosic ethanol, which can be produced from several different types of biomass crops such as switchgrass, Miscanthus, or corn stover. Corn stover is defined as the residue that remains in a corn field after harvest, which includes stalks, leaves, and cobs, and is the most abundant biomass feedstock in the Midwest because of the large-scale corn production. Based on its vast availability and relatively low value, corn stover is an excellent potential feedstock for cellulosic ethanol production in the Midwest.

The long range goal, or theme, of this project is to quantify material properties of industrial scale baled corn stover biomass. The objective of this project is to gain a better understanding of the characteristics and measurement techniques of corn stover properties and apply the methods to industrial biorefinery operations. The specific goals for this project include the following.

3.2. Objectives

3.2.1. Specific Goal #1: Assess the Accuracy of Subsampling and Rapid Moisture Analyzers for Commercial-Scale in Biomass Feedstock Assessment.

Rapid analysis of moisture is important for commercial scale corn stover conversion because there will be a very large quantity of corn stover to analyze during each harvest season. To determine what type of moisture analyzer should be used on a commercial-scale, various types will need to be compared to the standard oven moisture test to ensure accuracy.

3.2.2. Specific Goal #2: Determine the Influence of Sample Size and Processing on Quantifying Ash and Moisture Content in Corn Stover Bales.

Representative samples are key to discovering the true ash content of corn stover bales. The challenge with this is what size and type of sample should be taken in order to reflect the bale's properties. In order to determine this, a bale must be sampled in similar locations with different tools to analyze the difference in material properties amongst the tools.

3.2.3. Specific Goal #3: Quantifying Ash and Moisture Content Variability within Corn Stover Bales.

Ash and moisture content are properties that affect how much energy cellulosic ethanol plants can get from a feedstock because ash and water cannot be converted to ethanol, and ash must be removed before processing. The ash and moisture content also impact how the feedstock is valued. Variability is important for ethanol plants to know so they can decide where, in a bale, is the best place to take a representative sample.

3.2.4. Specific Goal #4: Analyze corn Stover Material Property Variability within a Set of Bales Harvested from the Same Field.

Determining variation of material properties, namely moisture and ash content, between bales harvested from the same field will allow industrial-scale production to design sampling procedures in order to obtain representative data for the whole field. The data from this research will then help the biomass industry determine the value of the bales and appropriately manage the inventory supply.

Chapter 4. Assessing the Accuracy of Subsampling and Rapid Moisture Analyzers for Commercial-Scale Use in Biomass Feedstock Assessment

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4.1. Abstract

Moisture content is a key property when making storage decisions for biomass. As biomass production, particularly corn stover harvesting in the Midwest, begins to escalate, the moisture content will be a value that industries need to know quickly, yet accurately. The standard procedure for determining moisture in biomass material involves drying the material in a heated oven for 24 hours or more. This procedure is too slow and intensive for industrial use. There are also other rapid moisture measuring devices, such as capacitance probes and small analyzers, used for other types of biomass. The problem, however, is that corn stover is so variable in composition that its components have different moisture holding capabilities, which may alter the capacitance probe readings. Also, small analyzers require a small sample, which means that the original representative sample of the bale will need to be ground and then subsampled in order to fit in the analyzer. The variation in moisture holding capabilities and the small sample size make it difficult to get an accurate reading with various moisture analyzers. This study tested three variations of rapid moisture analyses, and compared them to the standard oven method. The three rapid moisture testers used were a hay probe, a small scale gravimetric moisture analyzer, and a standard kitchen microwave oven. Additionally, this study tests the accuracy of subsamples compared to the entirety of the original sample.

4.2. Introduction

DuPont Cellulosic Ethanol and POET Biorefining are both constructing cellulosic ethanol plants which will use corn stover, the residue remaining after corn grain harvesting, as the primary feedstock. Similar to when grain is brought into an elevator, sampling the corn stover for moisture content is important in order to make storage decisions. In both corn grain and stover, microorganisms thrive in high moisture environments, using the moisture and

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organic material to survive. This therefore degrades the quality, as well as reduces the total dry matter available to be converted into ethanol. In fact, in Shinners, et al.'s article, "Harvest and Storage Losses Associated with Mid-size Rectangular Bales", they discuss the greater amount of dry matter loss that occurs with high moisture bales. In the article, the biomass material being discussed is hay, but the same applies with all biomass. Additionally, in corn stover especially, the degradation of material by microbes leads to heating of the biomass. This is due to the activity of microbes which use the carbohydrates in the organic material as an energy source (Shinners, et. al, 1996). While this heating has not yet to lead to self-ignition of corn stover bales, it is a potential danger, especially in the dry and dusty conditions of fall harvest.

Therefore, rapid testing of moisture content is important for commercial scale corn stover production and processing. The speed of obtaining the moisture content results will impact the processing facilities' or farmers' ability to make quick decisions about what types of storage the bale requires, or whether to reject a high moisture bale. If they cannot make these decisions quickly, they will waste money and time. The wasted money will come from essentially purchasing water if bales are not purchased on a dry weight basis. The waste of time is because the more moisture in the bales means that the baling crew will need to create more bales to account for the additional dry matter loss that will occur due to high moisture. Additionally, time will be wasted because of the low bale density. High moisture bales have less structural integrity due to the soft, spongy material. This can cause bales to break on the bottom of a stack, which results in the stack of bales to collapse. This then requires additional time and money to re-stack and clean up the mess.

There are several types of rapid moisture analyzers currently available on the market. In the hay industry, there are several types of moisture-measuring probes available, such as the Delmhorst moisture probe, shown in Figure 4.1. Probes such as these work well in the hay industry for rapid analysis of moisture in the field. These probes measure moisture by the electrical capacitance of the materials around the area of insertion. While this works well for a homogeneous material such as hay, it's accuracy in a non-homogeneous material, such as corn stover, is unknown. Corn stover bales consist of cobs, stalks, and leaves. All of these different components have different moisture holding capacities, and therefore may make it difficult to get representative bale moisture contents from a single probe reading. If the Delmhorst can be used accurately, it would greatly benefit corn stover processing facilities, as well as the harvesting crews to perform on-site moisture measurement.

Figure 4.1. Delmhorst moisture probe.

Additionally, microwave ovens have been used to measure the moisture content of forages, such as in Staples' method published by the University of Florida (Staples, 1988). The microwave works for samples of very high moisture, such as that of forages, but has not been tested with corn stover samples. Ideally, this method should work the same as an oven since the method involves drying the sample in increments until it reaches a steady mass. If this method can work, it needs to be tested for different sizes of samples, to see if the corn stover processing facilities can utilize large samples for a more representative sample.

Finally, there are many other small-scale rapid analyzers. These other rapid analyzers are the ones typically used in industrial labs. Three to five gram samples are taken from the material and put in the rapid analyzers. However, with corn stover, three to five grams is barely a trace of the entire material, and therefore will most likely not represent the entire bale, or field. Therefore, the first step to make rapid quality analysis applicable on an industrial scale would be to determine if a subsample can accurately be taken from a corn stover bale to match the ISU standard 2.5” steel coring tube’s 200-400 gram sample.

4.3. Experimental Design

4.3.1. Objective

Rapid analysis of moisture is important for commercial scale corn stover conversion because there will be a very large quantity of corn stover to analyze in a short amount of time. To determine what type of moisture analyzer should be used on a commercial-scale, various types will need to be tested against the standard oven moisture test to ensure accuracy. The objective of this study is to be able to provide a recommendation to upcoming corn stover industries on what tools they can use to test the moisture content of their material most accurately and quickly.

4.3.2. Corn Stover Supply

During the 2010 and 2011 harvest season, corn stover bales were harvested by custom harvest crews harvesting for DuPont Cellulosic Ethanol. The fields that the bales were harvested in were located around central Iowa, and were harvested using industrially applicable equipment and methods. The harvest method involved collecting the material into a windrow, using either a rake or a shredder, and then baling the material. Later, the bales were collected and stacked in the field before being transported to a satellite storage facility. A subsample of bales were weighed and sampled at Iowa State. These bales and samples from these bales were used to conduct these experiments.

4.3.3. Sampling Tools and Experimental Design

4.3.3.1. Delmhorst Probe Testing for Moisture

The instant moisture analysis was performed using a Delmhorst Hay probe, shown earlier in Figure 4.1. For this experiment, 216 independent locations in corn stover bales were sampled with a 2.5” steel coring tube with boring teeth for easy drilling, attached to a skid loader, shown taking a sample in Figure 4.2. The three bales were sampled 72 times to capture variability across the bale.

Figure 4.2. The 2.5” core sampler attached to a skid loader taking a core out of a corn stover bale.

For each location that a core sample was taken, the Delmhorst Hay probe was inserted next to where the core sample was taken. This allowed the moisture contents from the Delmhorst reading and the core sample to be analyzed equally. The core samples were dried in standard ventilated ovens using a slightly modified version of ASABE Standard S358.2, “Moisture Measurement – Forages”. The modified version included drying the core samples for 24 hours at 95°C. The samples were weighed before and after drying and moisture content was calculated on a wet basis using Equation 2.2.

A load cell was also attached to the Delmhorst Hay to ensure the insertion force of the probe remained constant. After the moisture reading in every sample location, the probe was pushed slightly harder and an insertion force was read at the point where the probe began to move. With this method, all of the readings were able to be standardized to the same insertion force.

4.3.3.2. Microwave Testing for Moisture

For the rapid testing of moisture, a microwave was also used to test its accuracy level compared to a standard ventilated drying oven. Thirty bales were sampled with a 2.5” steel coring tube. After each of these samples was taken, they were ground with one of three different screen sizes for a subsampling experiment. The core sample was then divided into as many smaller, microwavable bowls as needed, with sample sizes ranging from 6.5 to 43 grams. The average sample size was 19.2 grams. Each subsample was then placed in a microwave along with a crucible 2/3 full of water, according to the method, and microwaved at reduced power in intervals until reaching a steady mass (Staples, 1988). The water was placed in the microwave to prevent the material from combusting in the microwave. The initial microwave time listed in the original procedure was 14 minutes, but was changed to 2.5 since the corn stover was a drier material than the forages suggested in the procedure. After the initial 2.5 minutes, the sample was weighed using an electronic balance, and placed back into the microwave at 1 minute intervals until a steady mass was achieved. Finally, each sample was placed in a ventilated oven for 24 hours at 95°C in order to dry out any remaining moisture. After the 24 hours, the samples were weighed again so the microwave testing could be compared to the actual moisture. The moistures were calculated using Equation 2.2.

4.3.3.3. Subsampling for Rapid Quality Analysis

Thirty bales were sampled using the 2.5” steel coring tube shown in Figure 4.2. These samples were ground, using a small knife mill, to three different screen sizes: 6, 10, and 20 millimeters. Each of the thirty samples were then divided into as many subsamples as it took to empty out the original sample pans. The thirty samples were subsampled by hand, by taking a handful from the pan and placing it into the bowl. In grain subsampling, the material is sent through a divider funnel. However, with this experiment, there was a concern that the dust or soil from the samples would not be transferred to subsamples correctly if a divider funnel was used. The subsample weights were variable for each screen size. For the 6 mm screen, the average sample size was 25.2 grams, with a range of 16.5 - 35.5 grams. The 10 mm screen had an average sample size of 20.0 grams, with a range of 12.6 - 29.1 grams. The 20 mm screen had an average sample size of 15.5 grams, with a range of 6.5 - 43.1 grams.

Each subsample was dried using a microwave and ventilated oven at 95°C for 24 hours, recording the initial and final mass, in order to calculate moisture content on a wet basis using Equation 2.2.

Following the drying period, the subsamples were transferred into aluminum pans and then placed in a muffle furnace, which was ramped up to 570°C for 8 hours. After the 8 hours, the furnace was allowed to cool before weighing the final sample in as the "ash weight". This ashing procedure was based off of the National Renewable Energy Laboratory's procedure NREL/TP-510-42622, but altered to better suit the corn stover samples and resources available. The ash content was then calculated using Equation 2.1.

4.3.4. Statistical Analysis

Minitab 16 Statistical Software was used to complete a statistical analysis for the results of these experiments. For the Delmhorst Hay Probe testing, a Paired T-test was performed to test whether there was a significant difference between the actual oven moisture content and what the Delmhorst Hay Probe predicted it to be. For the microwave testing, a Paired can be used to determine if there is a significant difference between the moisture content achieved by the microwave and the moisture content achieved by the oven. Finally, standard deviations from the mean was used to determine the variability of the subsamples from the actual ash content of the sample. For the T-tests, an alpha-value of 0.05 was used.

4.4. Results and Discussion

4.4.1. Delmhorst Probe Testing for Moisture

The difference between the probe-predicted moisture content and the actual oven moisture content for three unique corn stover bales, each sampled 72 times, is plotted as a histogram in Figure 4.3. The average moisture for the three bales was 11.7%, 9.8%, and 11.7%, based on the oven moisture contents. The probe appeared to be much different than the oven moisture content, on both ends of the distribution. The data forms a very normal bell curve, but ranges from -3 percentage points different to near 17 percentage points different from the actual oven moisture.

Additionally, the Paired T-test was performed and the results are shown in Table 4.1. The two methods of determining moisture content are significantly different, statistically. As can be seen by the large distribution of differences, shown in Figure 4.3, the probe readings were inconsistently variable from the true oven measurement. Also, the P-value of 0.00 indicates that the Delmhorst is significantly different from the oven measurement. If the Delmhorst were to accurately read moisture content, the P-value should have resulted with no significant difference. Because of the large spread of differences, additional testing was done to explore the reason behind the variability of the Delmhorst Hay Probe to determine whether a correction factor could be used to offset the probe's reading to obtain the correct data.

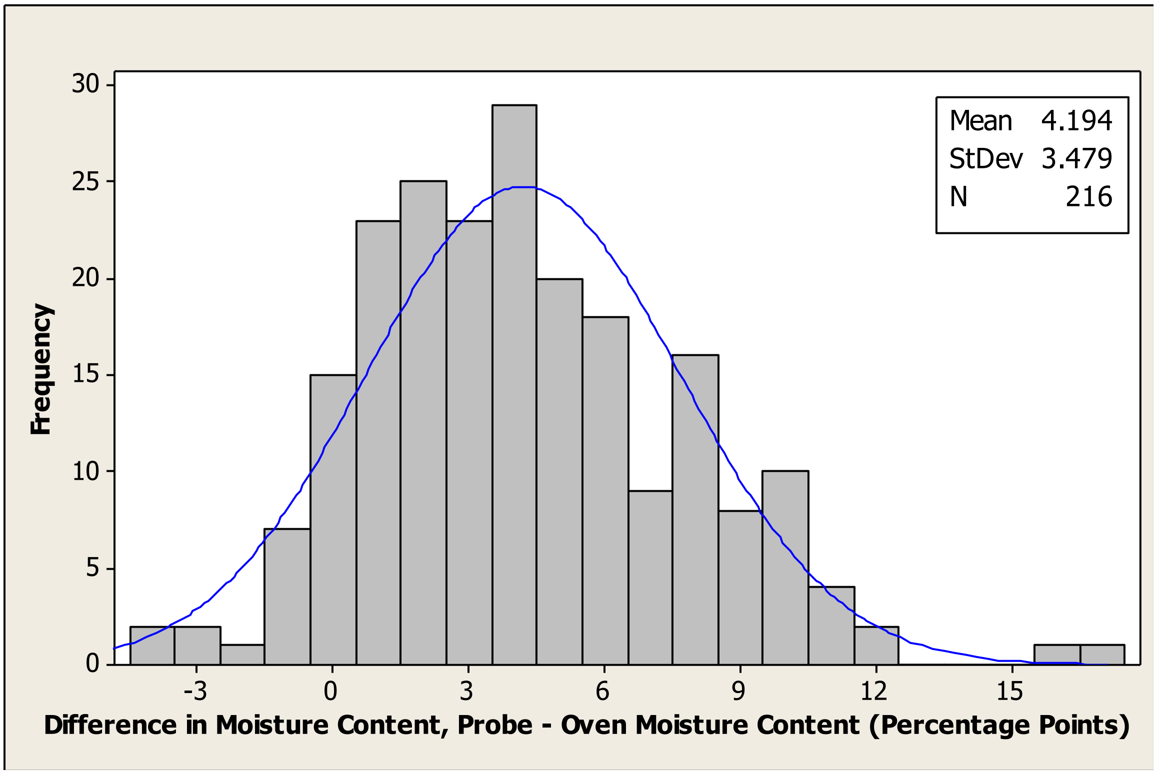

Figure 4.3. Distribution of moisture content difference between probe and oven, with the blue line representing the normal bell curve around the mean of 4.194.

Table 4.1. Paired T-test results testing the difference between the Delmhorst Hay Probe and the actual oven moisture content.

	Estimate for difference (Probe-Oven)	**P-Value (α=0.05)**
T-Test	4.194	0.000

Figure 4.4 demonstrates how the increase in actual moisture content, as measured by the oven, affected the variation of the moisture probe from the actual moisture content. It was expected that as the moisture content increased, the difference would increase as well, showing a positive slope in a regression line. However, this plot indicates otherwise. This plot demonstrates more of a scatter, with a very slight trend downwards, indicated by the

regression fit line shown on the plot. However, with an R-squared value of only 6.3%, and a calculated Pearson correlation of -0.252 (where +1 is a perfect correlation), we can assume that the slope of the line does not accurately represent the cause of the Delmhorst probe errors.

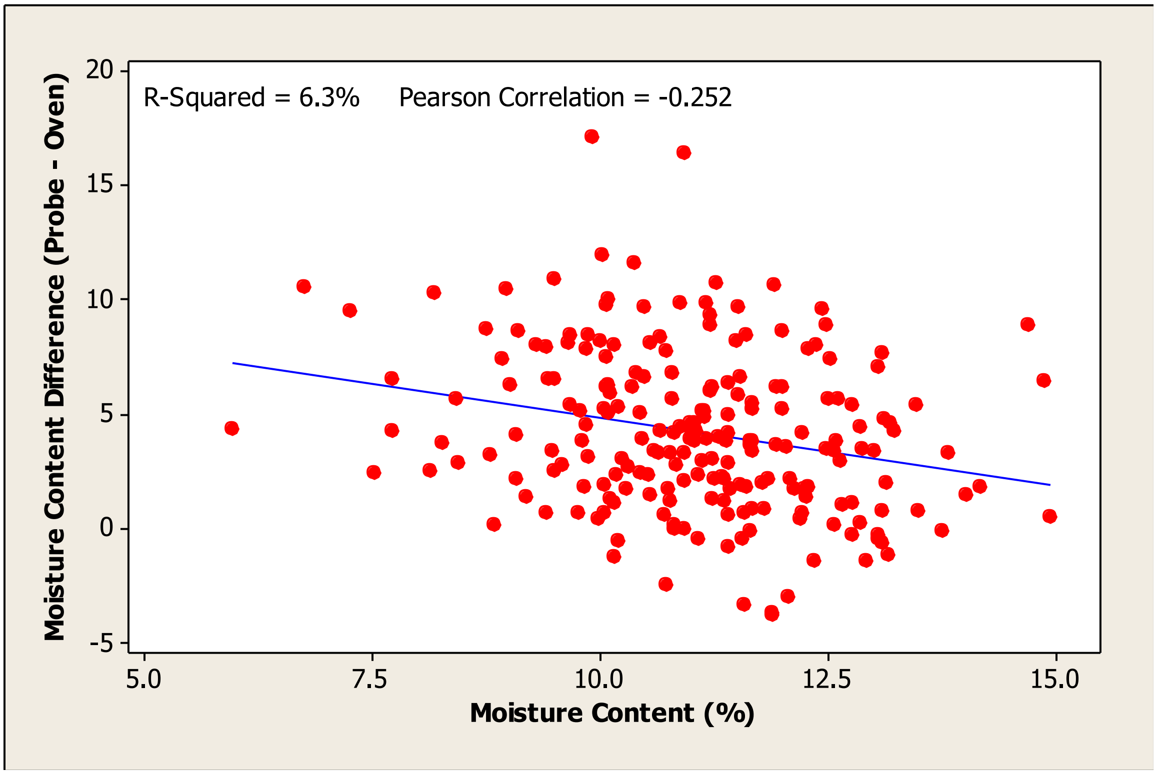

Figure 4.4. Scatterplot showing the impact of moisture content on the difference between the probe and oven results with the general trend line in blue. The R-squared value represents the trend line's ability to describe the data.

The probe was then tested using a second method which was targeted to reduce probe variability. Two high moisture bales were sampled 72 times, and five Delmhorst probe readings were taken at each sample location. The average bale moisture contents for the two bales were 28.5% and 19.3%, based on the oven moisture contents.The five readings at each location were then averaged in order to compare them to the actual oven moisture content. Figure 4.5 demonstrates the distribution of deviations of the averages from the actual moisture contents. As can be seen, the deviations from the mean of 3.915 are very large indicating that there is a large difference between the averages of what the probe read and the actual values. However, the Delmhorst probe can only read up to 40% moisture, and these wet bales had samples that were higher than that. In order to see the deviations from the actual moisture content accurately, all samples whose actual moisture content were above 40% were removed in Figure 4.6. As can be seen, the range of differences shrunk, however, the mean nearly doubled indicating that, even for the samples which were not above 40% moisture, the probe was still quite inaccurate and does not provide the required level of precision to make supply chain decisions on bales.

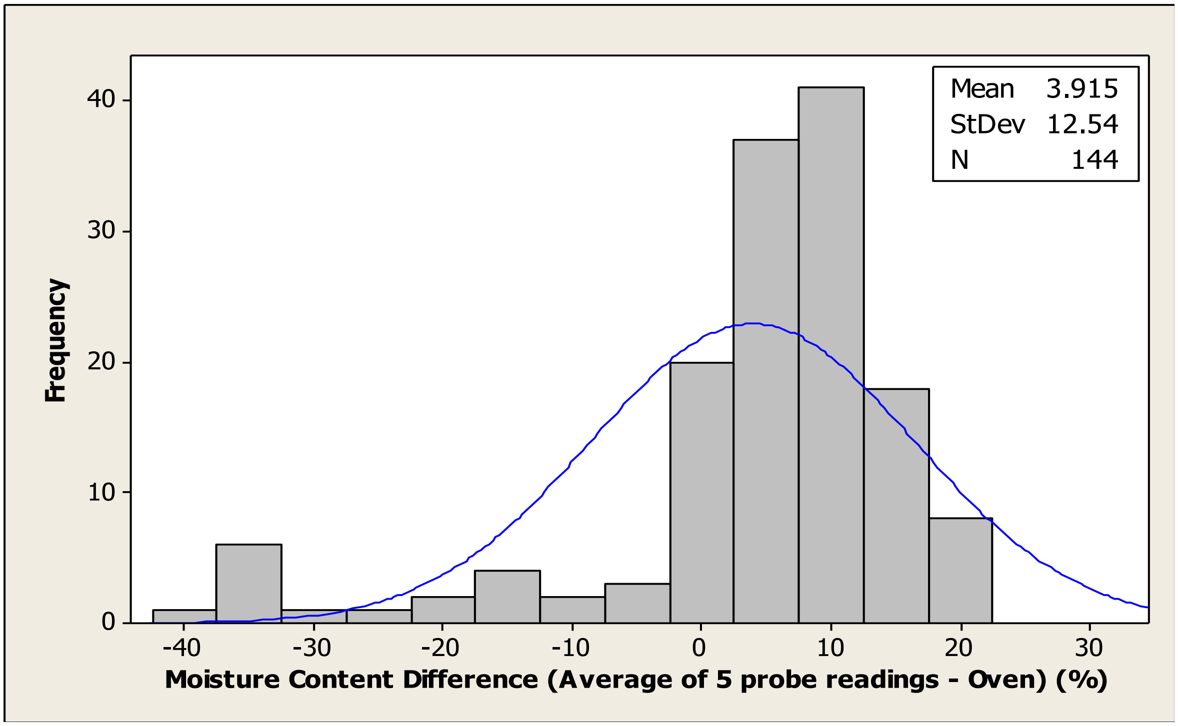

Figure 4.5. Histogram showing the distribution of the deviations of the averaged five Delmhorst probe readings from the actual value (average of 5 probe readings – oven sample). The blue line represents the normal bell curve around the mean of 3.915.

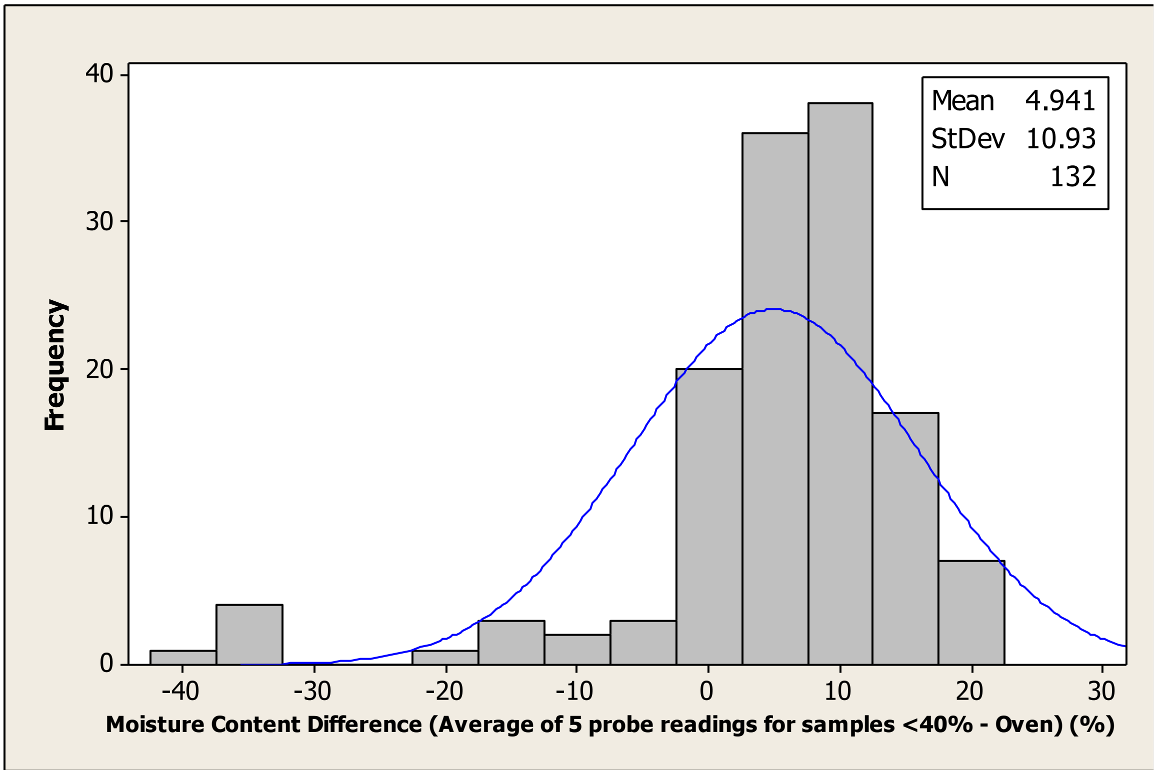

Figure 4.6. Histogram showing the distribution of the deviations of the averaged five Delmhorst probe readings from the actual value for all moisture contents below 40% actual moisture Content (average of 5 probe readings <40% moisture – oven sample). The blue line represents the normal bell curve around the mean of 4.941.

To get a visual description of how the average probe moisture content lined up with the actual oven moisture content, they were plotted in Figure 4.7. Ideally, the average would have lined up almost identically with the actual moisture content and created a perfect 45° line with a slope of one when plotted on an X-Y axis. This is because if there was a perfect correlation, for every percentage point of moisture that the average of the five probe readings increased, the oven moisture content also would have increased by one percentage point. However, the slope to this plot is 0.45, which is not ideal. Additionally, the R-squared value is 25.4, which indicates the unpredicted variability that exists with this sensor solution.

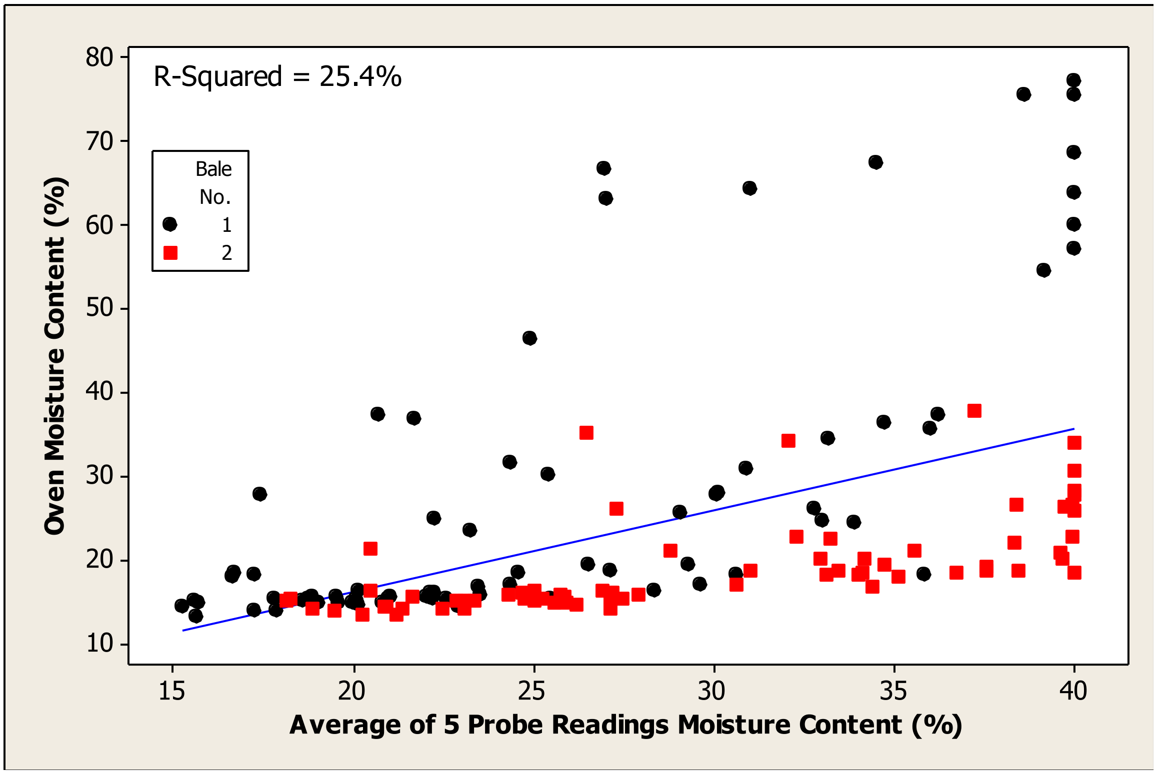

Figure 4.7. Scatterplot showing the average probe moisture content compared with the actual oven moisture content, showing the general trend line in blue. The R-squared value represents the trend line's ability to describe the data.

In conclusion, the Delmhorst probe is significantly different from the oven moisture content, and exhibits poor precision in reading the moisture content. The deviations from the actual oven moisture content are high, which means that an offset correction cannot be used to improve the accuracy of this capacitance probe. This may be because corn stover, in comparison with hay, is a much more variable product since it includes cobs, stalks and leaves. Nevertheless, the Delmhorst probe is not recommended for commercial use due to its inability to provide metrics which can be used to make supply chain decisions.

4.4.2. Microwave Testing for Moisture

Thirty bales were sampled one time, each, and the samples were divided randomly into sets of 10. The sets of 10 were then ground in a knife mill at different screen sizes: 6, 10, and 20 millimeters. Each sample was then subsampled by hand, with a mean subsample size of 19.2 grams, in order to reduce sample loss in a divider funnel. The moisture content for each subsample was recorded after it reached a stable weight, ±0.50 grams, in the microwave, and then after it dried for 24 hours in an oven. The crucible of water was refilled to the same level after every microwave experiment. The differences between these two procedures is shown below in Figure 4.8. The average difference was 4.6 percentage points, with a range between 0 and about 10 percentage points.

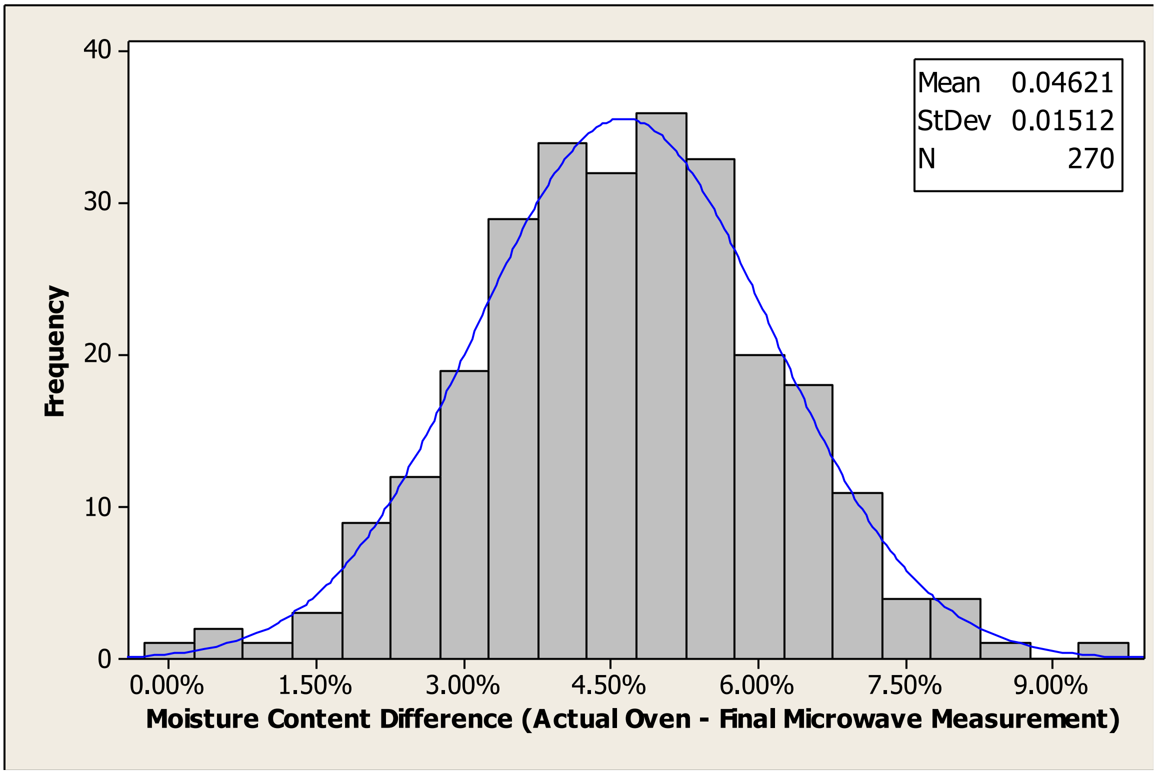

Figure 4.8. Difference between the actual oven moisture content and the final microwave reading's moisture content (actual oven measurement – final microwave measurement). Note, statistical data is in decimal format of the percent. The blue line represents the normal bell curve around the mean of 4.621.

Table 4.2. Paired T-test results for the oven moisture content vs. final microwave moisture content.

	Estimate for difference (Probe-Oven)	**P-Value (α=0.05)**
T-Test	4.621	0.000

The Paired T-test shows a significant difference between the microwave and the actual oven moisture content. This indicates that the microwave should not be used in order to rapidly test the moisture content of a sample. While the average difference is about the same as the Delmhorst probe differences, at 4.62 percentage points, the microwaved samples were very small, in order to fit into a small microwave as well as the fact that they were used for a subsampling experiment. This means that even small differences in mass proved to be large in terms of the sample size.

4.4.3. Subsampling for Rapid Quality Analysis

Since most industrial material property analyzers use very small samples, a test needed to be done to determine if subsamples could accurately reflect an entire 200-400 gram core sample. Thirty bales were sampled once, and the thirty samples were split into three groups of 10. Each group was ground in a knife mill with a different screen size, either 6, 10, or 20 millimeters. The 30 individual samples were subsampled by hand into paper bowls, as shown in Figure 4.9.

Figure 4.9. Student demonstrating the procedure for subsampling from a larger core sample.

The individual subsamples were compared against the total for the entire sample for each subsample. The differences between the full sample and each subsample are shown below in Figure 6.10 and Figure 6.11.

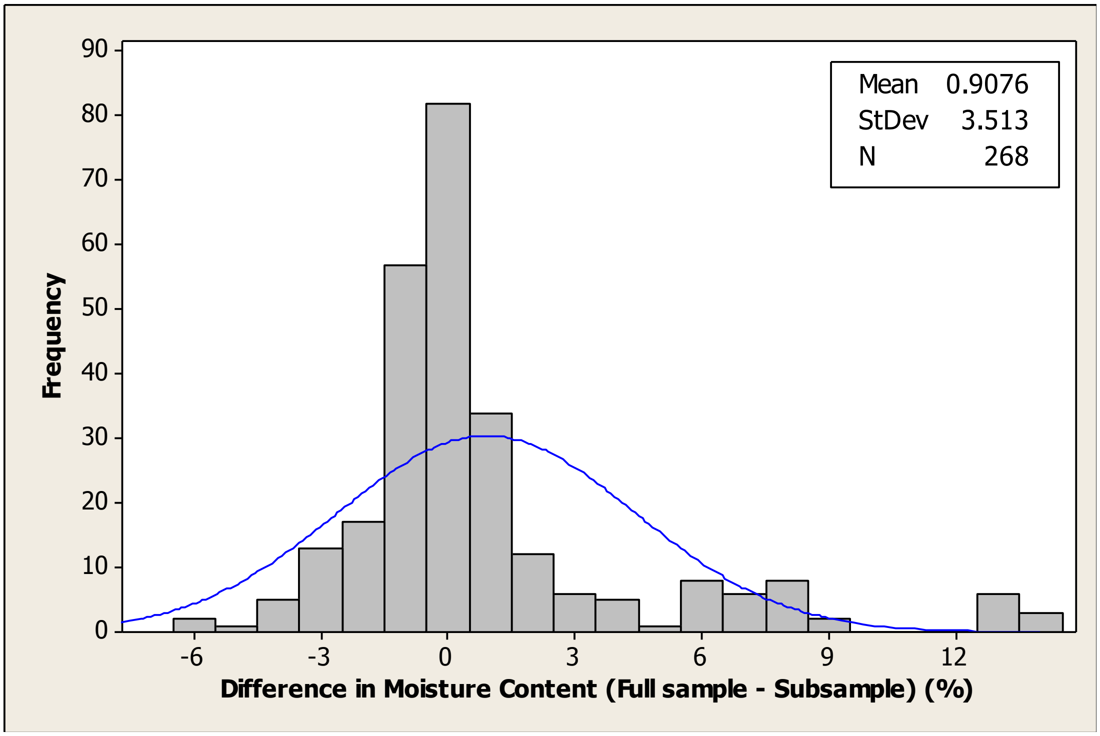

Figure 4.10. Distribution of the differences in moisture content between the full sample and each subsample (full sample – subsample). The blue line represents the normal bell curve around the mean of 0.9076.

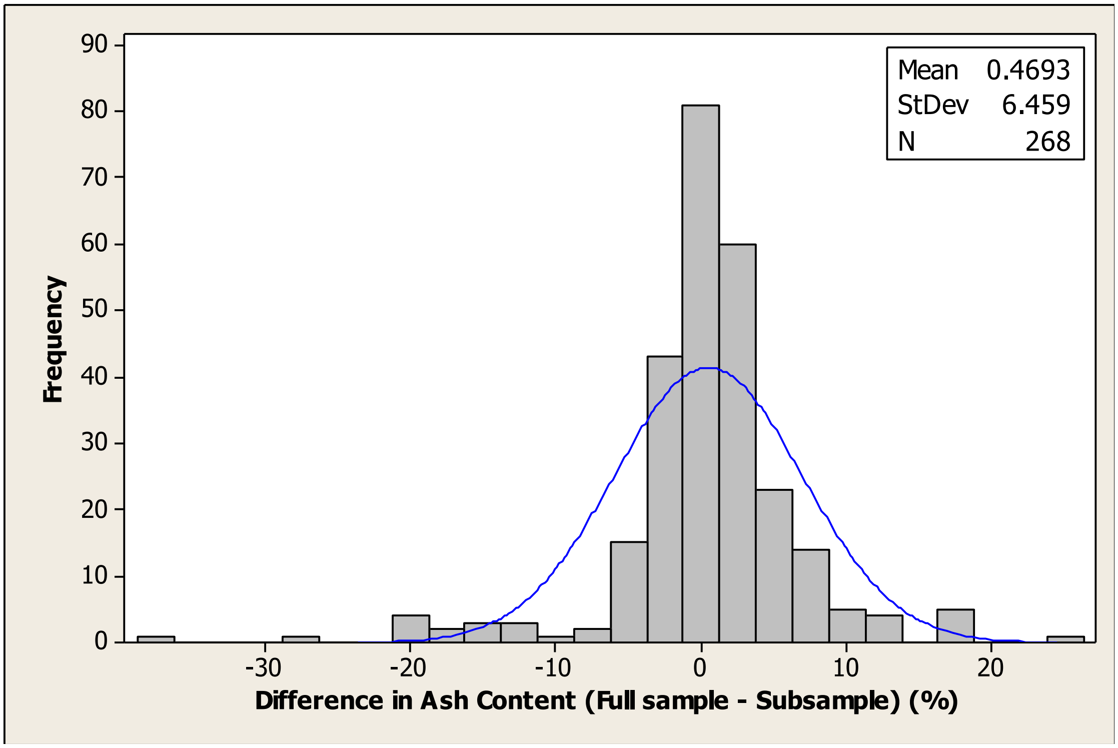

Figure 4.11. Distribution of the differences in ash content between the full sample and each subsample (full sample – subsample). The blue line represents the normal bell curve around the mean of 0.4693.

While the differences in moisture and ash content between the subsamples and the full samples have a peak around zero, the range is wide. The very negative value on the ash content difference histogram suggests that the subsamples may not have been distributed equally. In other words, the material needed to be subsampled in a more random method in order to obtain more uniform data. Most likely what happened was that, as the pan was being divided into subsamples, all of the soil contamination in the sample sifted to the bottom of the pan and ended up in the final sample or two for each pan. For moisture content, the data is pretty uniform, mostly centering on zero. This may be because the overall moisture contents of the samples were not very high, as the samples were taken from bales that had nearly a year to dry and have come to stable moisture contents.

Figure 4.12 and Figure 4.13 show the range of differences for moisture and ash content by screen size. For moisture content, it appears that the differences in moisture are statistically higher in the larger-ground material than the smaller material. A One-way ANOVA was also performed to analyze differences in screen size. The ANOVA resulted in a P-value of 0.00, indicating a significant difference in moisture content differences by screen size. The ANOVA results are shown in the Appendix. This may happen because the material that is ground smaller spends more time in the grinder, which produces heat, and thus the sample loses moisture. It may also be that since the particles are more finely ground, the samples are allowed to be more uniform. For ash content, however, screen size did not appear to make a difference, as all the confidence intervals are quite large. Additionally, the One-way ANOVA showed a P-value of 0.828 for the interaction of screen size and the interaction of ash content indicating that the screen sizes did not provide a significant difference in the accuracy of subsampling.

The conclusions that can be made from these results are that more finely ground material will have smaller differences between the subsample taken and the full sample. In general, most subsamples will provide an accurate reflection of the true moisture content for corn stover on the dry end of the moisture content spectrum. For ash content, there will be some large differences, especially if the subsamples are not taken uniformly.

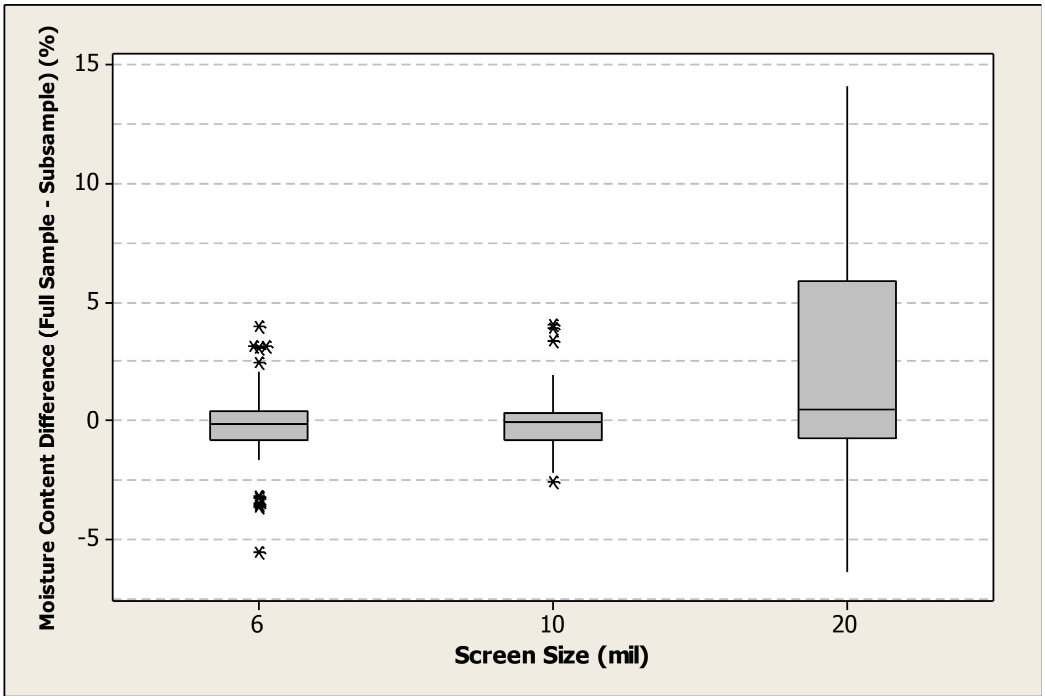

Figure 4.12. Boxplot showing the range of moisture content differences between the full sample and each subsample by screen size. The asterisks represent outliers, and the box shows the median in the middle, the third and first quartiles of the data on the outsides, and the range of the non-outliers with the extended lines.

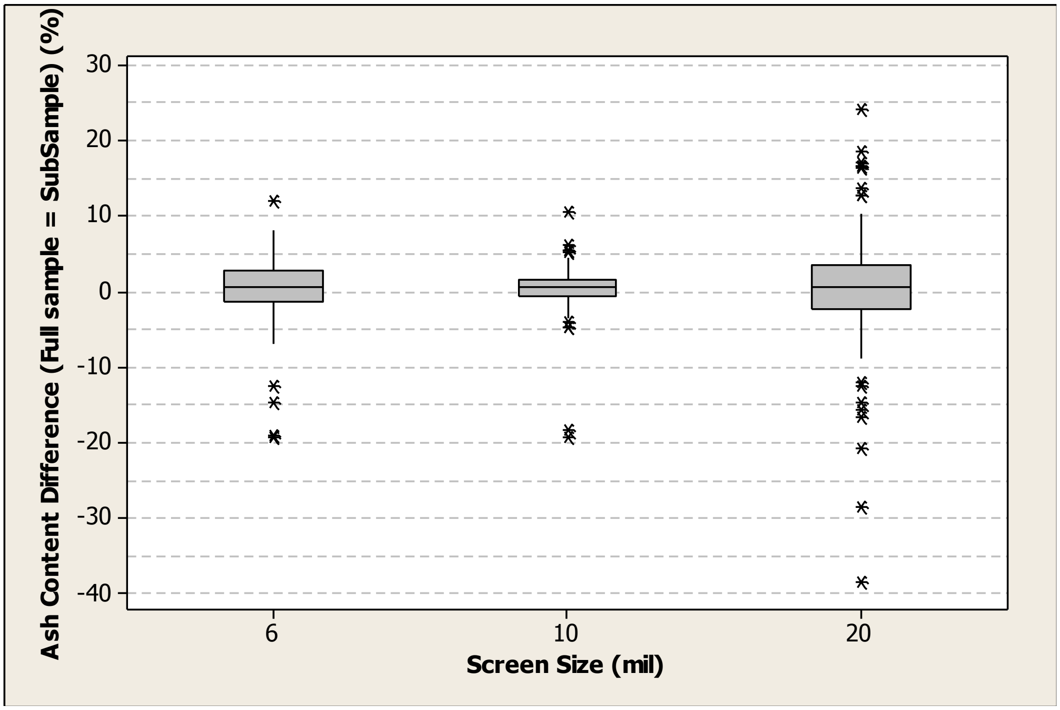

Figure 4.13. Boxplot showing the ash content differences between the full sample and each subsample by screen size. The asterisks represent outliers, while the box shows the median in the middle, the third and first quartiles of the data on the outsides, and the range of the non-outliers with the extended lines.

4.5. Conclusions

Rapid analysis of corn stover's moisture and ash content is a necessity for future corn stover processing facilities. Rapid moisture content has been achieved in the hay industry by probes, microwaves, and instruments that require subsamples. However, due to the inconsistency of corn stover, the accuracy of those tools had not been examined for corn stover. Therefore, from the experiments conducted, several conclusions can be made.

- The Delmhorst probe is significantly different from the oven moisture content, and does not appear to work well for corn stover bale moisture content measurement. The range of moisture content differences was too large to be considered accurate for commercial corn stover use. The inaccuracy was not pinpointed to a specific cause, and therefore a correction factor cannot be used to correct the data.
- Microwaves also proved to be significantly different from the oven method for testing moisture. The samples used for this experiment were small, which impacted the degree of moisture contents detected. This experiment should be carried out again with larger samples, as well as samples with higher moisture content to determine if it is accurate on a larger scale.
- Subsamples can accurately be taken from corn stover bales on the dry end of the moisture spectrum for moisture content if the material is finely ground. The subsampling experiment should be conducted again with higher moisture samples to determine if the same conclusions hold true.
- Subsamples for ash content need to be more uniformly distributed than subsampling by hand in order to obtain representative data. Soil may sift to the bottom of a sample during the grinding process, and therefore will not be reflected in subsamples taken only from the top of the material.

4.6. Acknowledgements

Funding for this project was provided by DuPont Cellulosic Ethanol, and all experiments were performed at Iowa State University's BioCentury Research Farm. All experiments were

conducted by Dr. Matthew Darr’s research team, with significant contributions from Kevin Peyton, Levi Powell, Benjamin Covington, Andrew Kissel, and Nicole Jennett.

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4.8. Appendix

4.8.1. One-way ANOVA: Difference Moisture Content versus Screen Size (mil)

The One-way ANOVA reults for the differences in moisture content by screen size are shown below:

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Source              DF      SS     MS      F      P
Screen Size (mil)    2   346.2  173.1  15.55  0.000
Error              265  2949.8   11.1
Total              267  3296.0

S = 3.336   R-Sq = 10.50%   R-Sq(adj) = 9.83%


                           Individual 95% CIs For Mean Based on Pooled StDev
Level    N    Mean  StDev    -+---------+---------+---------+--------
 6      70  -0.267  1.657    (-------*-------)
10      71  -0.072  1.223      (-------*-------)
20     127   2.103  4.591                              (-----*-----)
                             -+---------+---------+---------+--------
                           -1.0       0.0       1.0       2.0

Pooled StDev = 3.336
```

4.8.2. One-way ANOVA: Diff AC versus Screen Size (mil)

```
Source              DF       SS    MS     F      P
Screen Size (mil)    2     15.9   7.9  0.19  0.828
Error              265  11121.9  42.0
Total              267  11137.8

S = 6.478   R-Sq = 0.14%   R-Sq(adj) = 0.00%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level    N   Mean  StDev  ------+---------+---------+---------+---
 6      70  0.239  5.423  (------------------*------------------)
10      72  0.241  4.140  (------------------*------------------)
20     126  0.728  7.937             (-------------*-------------)
                          ------+---------+---------+---------+---
                             -0.80      0.00      0.80      1.60

Pooled StDev = 6.478
```

Chapter 5. Influence of Sample Size and Processing on Quantifying Ash and Moisture Content in Corn Stover Bales

Brittany Schon[2], Dr. Matthew Darr[2]

5.1. Abstract

As the number of cellulosic ethanol plants in operation increases, there is a growing need to measure the quality of the feedstock used. The current methods used to test moisture content and ash in forages and grains are not sufficient for cellulosic ethanol plants, due to the differences in the material properties and nonhomogeneity of corn stover feedstocks. In order to test the quality of this new feedstock, the optimum sample size must be established to include all the components of this variable feedstock. In this study, side by side analyses were conducted in order to determine an adequate sample size and preprocessing steps required to achieve a representative sample of a corn stover bale. Specifically, corn stover bale core samplers of 0.75 inches and 2.5 inches were compared. The selection of these sizes was based on current commercial practices. Recommendations will be presented on optimal sampling methods to most accurately determine moisture and ash content of baled corn stover.

5.2. Introduction

As the United States moves closer towards a bioeconomy, cellulosic ethanol has become one of the most realistic and favorable biofuels to produce. Current ethanol is produced from corn starch, and has not been cleared by the Renewable Fuel Standard 2 (RFS2) as an acceptable advanced biofuel to help reach the future biofuel mandates. Corn starch ethanol is controversial because the use of corn grain for ethanol affects several markets including grain, livestock, land, and energy markets. Additionally, depending on the methods used to produce it, it can be unsustainable, and can potentially cause some pollution, and depletion of water (Schnepf & Yacobucci, October 14, 2010). Corn starch ethanol, however, was expected to reach a maximum production of around 15 billion gallons, which would only make up about 11% of US gasoline consumption. Even if all of the US corn was converted to

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ethanol, it would still not make a large dent in US gasoline consumption (Tyner, July/August 2008). Therefore, additional biofuels are needed, and as mandated by the RFS2 based on the Energy Independence and Security Act (EISA) expansions, the US must produce 36 billion gallons of renewable fuel by 2022. (US Environmental Protection Agency, 2012) Since cellulose is the most abundant resource on the planet, it makes sense to derive a biofuel from the cellulose in a plant. Cellulosic feedstocks are advantageous because they can be grown on marginal land, they can be perennial, or they are just a waste product not otherwise used for significant purposes (Schnepf & Yacobucci, October 14, 2010).

In the Midwest, two companies have announced the building of cellulosic ethanol plants, using corn stover as a feedstock. In a report prepared for Congress, Schnepf and Yacobucci mention that corn stover will be the primary feedstock of choice in the near term because of the close proximity to already-installed corn starch ethanol facilities (Schnepf & Yacobucci, October 14, 2010). In Emmetsburg, IA, POET Biorefining has begun constructing a cellulosic ethanol plant, as a part of their Project LIBERTY. Project LIBERTY is said to be up and running by late 2013, and will produce about 20 million gallons of ethanol (POET-DSM Advanced Biofuels, 2012). The other company, DuPont Cellulosic Ethanol, has already opened a small-scale cellulosic ethanol facility in Vonore, Tennessee, and has begun plans for a 27.7 MGY cellulosic ethanol plant in Nevada, Iowa (DuPont Danisco Cellulosic Ethanol, 27 June 2011).

In DuPont's case, the 27.7 million gallons per year produced will require 370,000 tons of corn stover assuming a conversion ratio of 75 gallons per ton. Initial harvest techniques have involved creating 3'x4'x8' sized bales of corn stover, weighing approximately 1,000 pounds, on average. Assuming an average weight, 740,000 bales of corn stover will be needed for this plant every year. With such a large number of corn stover bales, it will be nearly impossible to sample every bale in order to obtain material characteristics.

Corn grain has been industrially harvested for about a century, so harvesting technology has had some time to mature. Because of this, corn has become a very uniform feedstock, and sampling mechanisms have been developed for grain elevators and conversion facilities to use. This helps them to either accept or reject corn based on its quality. Corn stover harvesting, however, has really only just begun on a commercial scale. Previous corn stover harvesting has been used for applications where quality is not as important. For instance, corn stover has been used to feed cattle for decades, and has also been used as bedding (Shinners & Binversie, 2007). In those instances, it was not necessary to sample the material in order to determine the quality of the material. However, with corn stover being used as a feedstock for an ethanol process, it will need to be sampled, just as corn is, so that the facilities know how much to compensate the farmers, and so they can adjust their process settings accordingly.

Since corn stover sampling mechanisms have not been developed, the optimal size of the sample has not yet been determined. The goal would be to find the smallest sample size that can give the best reflection of the bale’s material properties. The smaller the sample size, the faster the throughput and lower the analysis cost, which leads to faster turnaround times for valuable information for making important processing decisions. However, while a smaller sample may lead to faster turnaround times, it may not be a representative sample. If the sample is not representative, then the results will bias supply chain decisions. Therefore, there is a need to find the optimum sample size to provide an accurate look at the bale’s characteristics, while minimizing sampling resources.

Currently in the forage industry, ¾” coring tubes attached to portable drills are commonly used to take samples out of bales. These samples are then used to determine material properties of the bale. Since corn stover is one material used in the forage industry and the tool is already on the market, it will be valuable to test this size of core sampler against a larger size core sampler to determine which sample provides more representative data for the bale.

5.3. Experimental Design

5.3.1. Objective

The objective of this experiment is to determine the difference between a small, commercially-available coring tube and a larger core sampler in terms of obtaining a representative sample for moisture and ash content. Representative samples are key to discovering the true ash content of corn stover bales, since ash content can be variable. The challenge with this is determining what sample size should be taken in order to portray the bale’s properties most accurately. After discovering the minimum required sample size, this information can be used in the emerging industry of cellulosic ethanol production from corn stover. In Iowa alone, two of these first-in-the-world corn stover to ethanol plants are being built. If the industries can have the knowledge of the minimum sampling size, they can optimize their analysis process by obtaining maximum throughput while maintaining quality analysis.

5.3.2. Corn Stover Bales

Large square corn stover bales were harvested during the fall of 2011 in fields near Ames, IA using standard commercial corn stover harvest methods. The bales measured 3’x4’x8’ and weighed between 900 and 1,500 lbs. depending on bale density, moisture, and ash content. The bales were put in storage immediately after harvest, either stacked under a tarp outside or placed in a stack inside a hoop barn to maintain quality. The bales were then removed in February and April 2011 for sampling experiments.

5.3.3. Sampling Tools

For this experiment, two sizes of coring machines were used, a 2.5” diameter coring tube, and a ¾” diameter coring tube. The larger coring tube was attached to the front of a skid loader in order to obtain samples. There were small teeth on the end of the coring tube to allow it to saw into the end of a bale with little resistance. This design was created by Dr. Matthew Darr’s research team at Iowa State University for sampling large corn stover bales. This large corer is shown in Figure 5.1. Depending on the components of the sample and the density of the bale, the sample size of this large corer averaged between 200 and 400 grams.

Figure 5.1. Large, 2.5" diameter coring tube attached to the front of a skid loader. The coring tube spins as it drills into the end of a bale to take a sample.

The smaller, 3/4" diameter coring tube was attached to a portable drill, which spun the tube into the bale as it cored out a sample. There were also small teeth on the end of this coring tube to allow for ease of insertion. This ¾" probe is a standard hay bale probe, and was purchased online for this experiment. The small, ¾" corer is shown in Figure 5.2. Depending on the contents of the sample taken and the density of the bale, the samples are generally 10-15 grams in weight, which is only 3-5% of the weight of the large corer. The difference in the diameter of the two probes can be seen in Figure 5.3.

Figure 5.2. Small, ¾" diameter coring tube attached to a portable drill. The coring tube drills into the end of a bale as the operator applies pressure, in order to take a sample.

Figure 5.3. Two different sizes of sampling tools were used, a large, 2.5" diameter coring tube (left) and a small, 3/4" coring tube (right). The ends of both tools have boring teeth.

5.3.4. Sampling Procedure

Within each bale, the samples were taken from the middle of the end, or “face” of the bale. This allowed the sample to cut through the cross-sectional variability which can occur due to the way the bale is produced when travelling across a field. The small core was taken from the end of the corn stover bale by going in approximately 18 inches deep, and placing the sample in an ISU sample pan, which linked the core sample to the bale it came from. The second sample was then taken with the larger, 2.5 inch corer, immediately next to where the small core was taken, also going in approximately 18 inches deep. This sample was also placed in an ISU sample pan, and was linked back to the bale’s ID so the two samples could be compared. This process of side-by-side sampling was replicated on 96 unique large square bales of corn stover randomly selected from an inventory of bales harvested in 2010.

After the samples were collected, lids were placed on the pans, and the samples were placed in a cooler to preserve the material properties until material property analysis could be completed. Initial, or “wet”, sample weights were taken soon after sampling so that all data would reflect the true vales.

5.3.5. Analytical Procedure

The ash and moisture content were analyzed to compare the large corer to the small corer. In order to get an accurate value for moisture content, the samples were dried following a procedure similar to the ASABE Standard S358.2, Moisture Measurement – Forages. Since that procedure was developed for forages instead of corn stover, Dr. Darr's research team modified the procedure to get an accurate moisture value for corn stover samples. The modified procedure included getting an initial, or "wet", weight, drying the sample in a ventilated oven at 95°C for 24 hours, and then removing the sample to record its "dry" weight. This gravimetrically measures how much moisture the sample lost, which can then be converted into a percentage of the sample that was moisture, or the moisture content. The moisture content values were calculated on a wet basis from Equation 2.2.

To obtain the ash content, the National Renewable Energy Laboratory's procedure listed in Lab Analytical Procedure: Determination of Ash in Biomass, NREL/TP-510-42622 was used as a baseline. This procedure was modified slightly, to better suit the schedule and materials available. The modified procedure included putting a dried & weighed sample in a muffle furnace, and stepping the temperature up to 570°C, letting it dwell at that temperature until it reached a stable weight, which was found to be about 8 hours, cooling down the furnace, and then recording the "ash" weight. The ash content can then be calculated gravimetrically using Equation 2.1.

5.3.6. Statistical Analysis

To analyze the results of this experiment, Minitab 16 Statistical Software was used. The null hypothesis tested was that the moisture content and the ash content values were not different between the large core samples and the small core samples. The α-value that was used was 0.05, for a confidence interval of 95%. Therefore, after performing a Paired T-Test, if the P-value was less than 0.05, the analysis would indicate that there was enough evidence to reject the null hypothesis that the means of the two sample sizes being equal. Essentially, if $p < 0.05$, the test would indicate that the difference between the two samples was not zero.

5.4. Results and Discussion

A distribution of the differences between the large and small core samples are shown in Figure 5.4 and Figure 5.5 for moisture and ash content, respectively. The large distribution of differences begins to indicate that the two sample sizes are not identical. Further analysis was then performed to verify any differences between the two sample sizes because if the sample sizes are significantly different from each other, the large corer should be used, since it usually provides a higher and more conservative ash content value, which will affect financial decisions for corn stover conversion facilities.

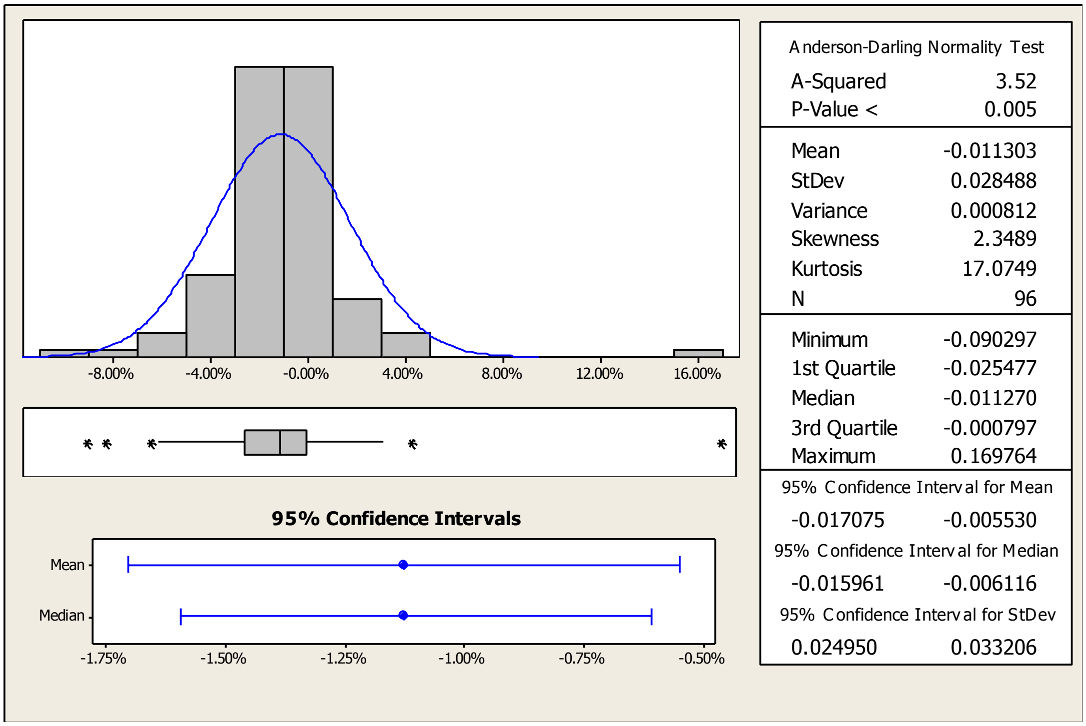
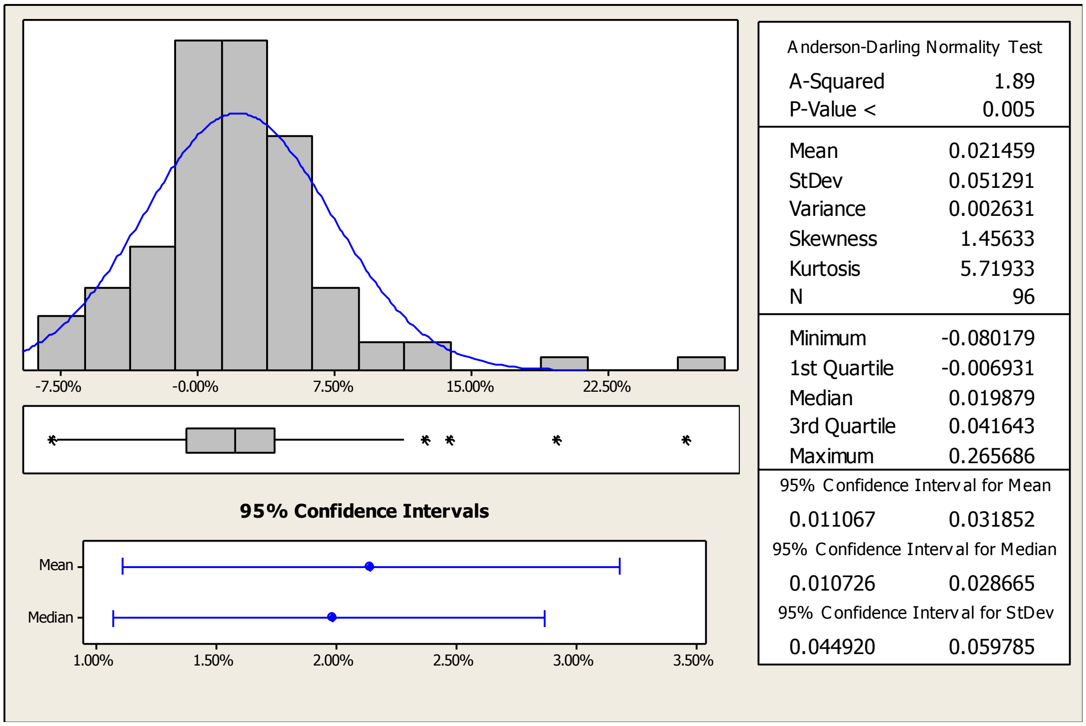


Figure 5.4. Graphical statistical summary for the difference in moisture content between the 2.5” core and the ¾” core. Note values are in decimal format. (2.5” core – ¾” core)



Anderson-Darling Normality Test	
A-Squared	1.89
P-Value <	0.005
Mean	0.021459
StDev	0.051291
Variance	0.002631
Skewness	1.45633
Kurtosis	5.71933
N	96
Minimum	-0.080179
1st Quartile	-0.006931
Median	0.019879
3rd Quartile	0.041643
Maximum	0.265686
95% Confidence Interval for Mean	
0.011067	0.031852
95% Confidence Interval for Median	
0.010726	0.028665
95% Confidence Interval for StDev	
0.044920	0.059785

Figure 5.5. Graphical statistical summary for the difference in ash content between the 2.5" core (b) and the ¾" core (s). Note values are in decimal form. (2.5" core – ¾" core)

A Paired T-test was then used to analyze the two sizes of core samplers. Table 5.1 shows the T-test results for the difference in moisture content between the two core sizes. The P-value of 0.000 is less than the alpha value of 0.05, which indicates a significant difference between the two core sizes. Different components of corn stover have different moisture holding capacities, so it is possible that the pieces of stover that the small core sample could fit held more moisture, which would make a difference. In the large core samples, there is enough material for the variability of moisture contents of the materials to average out.

The ash content two-sample t-test data is shown in Table 5.1. The P-value for this test was also below the alpha value of 0.05, at 0.000. So, while this was weaker in significance since it was closer to 0.05, it is still significantly different. This indicates that the large core sample is a higher and more conservative ash content to use. One reason that the small core sample did not provide as conservative of an ash content value is simply because it was so small. Because of the small size, less area was able to be sampled, which means that less of the true soil contamination was able to be captured in the sample. Another reason why the ash content is significantly different between core sizes may be because of the material that each probe can fit in the sample. The smaller probe does not effectively core through some of the same materials as a large probe would because of its small size. Yet another reason that the two sample sizes have significantly different ash contents is possibly because of the fact that the diameter of the large probe is larger, which covers more area of the bale, which means it has a better probability of sampling high ash content locations within the bale.

Table 5.1. Paired T-test and CI for the 2.5" and ¾" Corer. The T-test tests the difference of the 2.5" corer - the ¾" corer, or that the difference is equal to zero. P < 0.05 indicates significance.

T-Test Results		
	Moisture Results	**Ash Results**
Estimate for difference (2.5"- ¾")	-1.13%	2.15%
P-Value (α=0.05)	0.000	0.00

Production scale corn stover bales have moisture content ranges from 10-40% moisture. With the moisture content results, a difference in 1.13 percentage points is not going to cause additional trouble for the ethanol plant, because such a wide range of moisture can occur. Moisture contents of 15% and 16.13%, for example, are not practically different in biomass feedstocks. The significance of discovering moisture content will be to determine what type of storage is needed in order to prevent microbial degradation, of which 1.13 percentage points will not make a large difference, especially because the material will be allowed to ventilate and dry off during storage.

Ash content, however, is a more sensitive number since production scale ash content generally ranges from 8-15%, and it is a number that will directly relate to more waste being produced. Therefore, 2.15 percentage points of a difference is a large difference in ash content due to the small spread of data. Additionally, the additional ash content indicates, during harvest, that more material will need to be harvested to compensate for the false tonnage due to soil contamination. Finally, 2.15 percentage points of extra ash would mean that it is all going through the processing equipment, which will cause machinery problems, such as fouling, slagging and agglomeration.

The data was then split into the bales that had ash content above 10%, according to the 2.5” core sample, and bales that were equal to, or below 10% ash, which was then analyzed to see if outliers in ash content affected the differences. The break at 10% was decided based on the industry’s preference to have ash content values at or below 10%. After performing another Paired T-test for each subset of data, the results showed that the bales with lower ash content did not have enough evidence to support a difference between the ¾” core and the 2.5” core. However, the subset of data above the 10% ash mark was still statistically different between the two sizes of core samples, with a P-value of 0.02, as shown in Table 5.2.

Table 5.2. Paired T-test performed for different levels of ash content. The T-test tests the difference of the 2.5" corer minus the 3/4" corer, or that the difference is equal to zero. P<0.05 indicates significance.

T-Test Results		
	Below 10% Ash	**Above 10% Ash**
Estimate for difference (2.5”-3/4”)	0.5%	3.37%
P-Value (α=0.05)	0.307	0.000

With the current inexperience of current corn stover harvesting crews, the ash content will be more variable, and therefore will likely not fall within the industry’s desirable range 8-10% ash content. Therefore, the ¾” should not be used to acquire representative ash or moisture content data for corn stover bales. The 2.5” core sampler will provide a more conservative and representative value for the quality of the corn stover.

5.5. Conclusions

As corn stover becomes an industrial commodity, industries will want to know the quality of their incoming feedstock. Grain elevators and other industries that use corn grain as a feedstock have sample probes designed to take a prescribed random sample out of trucks. However, since corn stover collection and conversion to ethanol is a new industry, sampling methods have not yet been specified. The goal of sampling is to gain an accurate look at the important material properties of the feedstock for the facility. For corn stover, two important material properties are moisture and ash content. They affect the processing and storage capability for the material, and are what affect the quality of the stover.

This research concluded that, as a whole, a 2.5” core sampler will generally provide a larger and more conservative ash content value. This denotes that it should be used, when possible, to sample corn stover bales. However, additional conclusions can be made from this research.

- In general, moisture content values will be significantly lower in the 2.5” core samples than the small core samples. However, the estimate for the difference is only 1.13% different, which is not a significant value in practical terms of moisture content due to the wide range of production scale moisture contents. Therefore, the ¾” core samples should generally provide a nearly accurate look at moisture content.
- As mentioned previously, among all types of bales, the 2.5” core sampler will provide a more conservative estimate for ash content, and should be used when possible, due to the small core’s large average difference and the small range of production scale ash contents.
- For bales that are at industrially acceptable levels of ash content, or below 10%, the ¾” core sampler can be used to accurately measure quality. However, with corn stover harvesting for industrial purposes being relatively new, ash contents below 10% are not always common, and therefore the ¾” core sampler should not be used while the harvesting is in its beginning stages.
- For bales estimated above 10% ash content, the 2.5” core sampler should be used to provide a more accurate estimate for quality.

5.6. Acknowledgements

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Chapter 6. Quantifying Ash and Moisture Content Variability in Corn Stover Bales

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6.1. Abstract

As more cellulosic-based ethanol plants are built in the United States, the material properties of feedstock must be defined. The characterization of these material properties will help cellulosic plants determine the quality of the material and make important preprocessing and qualitative decisions for their systems. Additionally ash and moisture content, which cannot be converted into usable fuel, affect how much energy the ethanol plants can get from the feedstock. When using corn stover as a feedstock, it is generally baled, which brings in additional ash from the soil. However, the quantity and variability of each property within a bale has not been determined, making it difficult for future cellulosic ethanol plants to account for changes in the quality of an individual bale. In this study, corn stover bales were sampled intensively in order to determine the variability of material properties within a single bale. This will benefit cellulosic ethanol plants using corn stover as their feedstock by providing knowledge of the natural variability of corn stover sampling. Results will include a discussion of material property variability within a single bale and a discussion of required sampling methods to appropriately assess the ash and moisture composition of large groups of bales harvested within the same environment.

6.2. Introduction

The first ever cellulosic ethanol plants are being constructed in Iowa, using corn stover as a feedstock. Corn stover is the residue left on the field after corn grain is harvested, and is comprised of stalks, leaves, and cobs. Soil is often introduced to the bale in multi-pass harvesting systems, which harvest the stover into bales using multiple passes for windrowing and baling, as opposed to single-pass systems which bale the material immediately from the back of the combine (Webster, 2011). This soil, as well the variety of components in the feedstock, each with different moisture-holding capabilities, results in non-uniformity of

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material properties, such as moisture and ash content. Since corn stover is a residue, rather than a primary crop, the composition of the bales is not uniform, which results in material property variability. Corn stover's most common use, currently, is for animal bedding in the livestock industry. When used as bedding, material properties and quality do not have a significant impact. However, when used for biorenewable products, such as cellulosic ethanol, any material that is not able to be converted into fuel or an end product will directly reduce the feedstock value. The two key properties affecting quality in corn stover are ash content and moisture content. Neither ash nor moisture can be converted into a useful product, and therefore decrease feedstock value because more of the feedstock will need to be purchased to compensate for added waste material.

In addition to the fact that more moisture in a feedstock indicates less dry material able to be converted to fuel, moisture content affects the quality of the material for a few additional reasons. Just like in corn, material with higher moisture content is at a risk to microbial action during storage, which seriously degrades the quality. Therefore, low moisture feedstock is desirable by cellulosic ethanol industries so that the material they harvested in a 1-2 month period can be stored for the duration of the year, if needed. Moisture content also affects the quality of the material because wetter material will be more difficult to grind, which will increase costs and reduce the capacity of the plant to reduce the material size due to the fact that higher moisture feedstocks require longer grinding times (Kaliyan, et al., 2012). However, in order to determine the moisture of the material, a representative sample must be taken. This is a challenge because of the variability of moisture that can occur within a bale. The moisture throughout a bale may vary due to evaporation of the moisture in the bale or absorption of moisture into the bale from the ground. Additionally, the different components of corn stover, such as cobs, stalks and leaves, have different moisture holding capacities and were harvested from different parts of a field, which results in different parts of the bale containing more moisture, depending on the components of each part of the bale (Kaliyan, et al., 2012). For these reasons, it is important to discover where the most representative sample can be taken.

Ash content is also an important property to measure because it allows corn stover conversion facilities to know how much actual biomass material they have to be converted into a fuel. A representative sample is desired so that the results reflect the entire bale. Each flake of a large square bale is made from a different part of a field and therefore can vary in composition. Therefore, there may be a higher concentration of non-structural ash, or soil contamination, in certain parts of the bale due to variation in field topography and harvesting methods. Because of this, the ash content variability within a bale must be discovered in order to locate a representative sample location.

Several studies have been performed to analyze the variability of structural components, such as xylan and glucan, among others. However, in these studies, such as the one performed by Templeton, et al., 2009, the stover samples are collected by hand harvesting stalks or stover from the field. While this will give a good look at structural properties, it does not provide an accurate look at what the quality of the stover will be like on an industrial scale. On an industrial scale, corn stover will be densified into large square bales and will most likely include soil, unless harvested via single pass, as shown in Figure 6.1.

Figure 6.1. AGCO single pass baler producing corn stover bales simultaneously with grain harvest.

Multi-pass harvesting, which is the more likely industrial practice, has several steps. After a grain-harvesting combine has gone through the field, either a rake or a shredder will come through the field and pull the material into a windrow, which will allow the baler to bale up the material later. This process can be seen in Figure 6.2. In the picture, the material is being windrowed with a shredder on the far left, and the windrow is baled up with the tractor and baler in the front. A stacker follows the baler, in this photo, to pick up bales and stack them at the edge of the field until they are moved to an off-site storage location. Since the material here touches the ground before being baled, it has a high likelihood of bringing in soil during the baling process, which will lead to higher ash contents, and more waste.

Figure 6.2. Multipass harvesting, shredder windrower on the far left, baler making bales from a windrow on the right front, and a bale stacker behind.

Currently, sampling methods have not yet been defined for corn stover bales as they would come into a cellulosic ethanol facility. In order to determine how to sample, the moisture and ash content variability of each bale must be determined, since they are very important material properties, so that the best location in each bale can be sampled to get the most representative data for the entire bale.

6.3. Experimental Design

6.3.1. Objective

The objective of this research is to measure and determine the variability of moisture and ash content in a single corn stover bale, so that a sampling location within a bale can be determined. Ash and moisture content are properties that affect how much energy the ethanol plants can get from a feedstock, because ash and water cannot be converted to ethanol, and thus must be removed. The ash and moisture content also impact how the feedstock is valued. Therefore, getting an accurate look at the moisture and ash content is important for corn stover processing facilities so they know how to value the feedstock and to alter their pretreatment processes accordingly. In order to get the accurate look at the feedstock, a representative sample needs to be taken from a representative location in the feedstock. Studying the variability of corn stover bales is important for corn stover processing facilities to know so they can decide where, in a bale, is the best place to take a representative sample.

6.3.2. Corn Stover Bales

Large, multi-pass, 4’ x 3’ x 6’ bales of corn stover were harvested in the fall of 2010 and 2011. The harvesting equipment used to harvest the bales included standard commercially available windrowing and baling equipment, such as a bar rake and a stalk chopper. As mentioned, all bales chosen for this experiment were harvested in a multi-pass system due to the fact that it is the most practical system from an industrial perspective, at the current time. The corn stover bales were put into either outside or inside storage following harvest until the time of sampling. A summary of each bale’s general information is shown in Table 6.1.

Three bales were sampled for moisture and ash content variability from both the 2010 and 2011 corn stover harvest season in central Iowa. The bales were selected to represent a random sample of typical bale properties during industrial corn stover harvesting. An additional two random bales were selected out of a high moisture storage experiment to quantify moisture content variability in high moisture bales.

Table 6.1. Summary of bales used for variability experiment.

Bale #	Year Harvested	Moisture Level	Date Sampled
1	2010	High	Summer 2011
2	2010	High	Summer 2011
3	2010	Low	Summer 2011
4	2010	Low	Summer 2011
5	2010	Low	Summer 2011
6	2011	High	Summer 2012
7	2011	Low	Summer 2012
8	2011	Low	Summer 2012

6.3.3. Sampling and Analytical Tools

In order to collect the sample from the corn stover bales, a 2.5” diameter steel coring probe with boring teeth on one end was used. The core sample length was 18” into the test bale at the desired location. This steel probe was attached to a skid loader to provide power, as it sawed into the bale, and can be seen in Figure 6.3. In addition to the probe, sample pans were needed to contain the samples. The pans were uniquely labeled for each sample, so that sample identity was preserved through the entire analytical process. Also, an electronic balance, with the unit of grams for precision, was used to measure the empty pans, and the wet, dry and ash weights of the samples taken. This allowed the moisture and ash content values to be accurate.

Figure 6.3. Steel coring tube, 2.5" in diameter, attached to a skid loader, to take samples from corn stover bales.

Analytical equipment used for this experiment included a large, ventilated Despatch dryer oven and a Thermo Scientific tabletop muffle furnace. These equipment were used to dry and ash the samples, respectively.

6.3.4. Design of Experiment

The procedure for analyzing property variability involved taking 72 total core samples each out of the eight separate test bales, for a total of 576 samples. Each bale was split into four zones, approximately 2 ft wide, along the divisions of the flakes. The four zones were not representative of anything other than different sections of a bale, harvested from different parts of a field due to the way a bale is constructed. Twelve core samples were taken on the end, or square part of each zone (locations #1-12 in Figure 6.4), and 6 from one of the sides, or the rectangular part of the zone (locations #13-18 in Figure 6.4), as shown in Figure 6.4, and one of the actual bales in Figure 6.5. The core samples were taken in the same order for each zone and each bale to ensure validity and consistency. The height of the sample from the bottom of the bale would determine its “Level”. For example samples 1-4, 13 and 14 for each zone, as shown in Figure 6.4 would be classified as “Top Level”. Samples 5-8, 15 and 16 would be the “Middle Level”, and 9-12, 17 and 18 would be the “Bottom Level”. As previously mentioned, the 432 cores from six of the bales were used for moisture and ash variability analysis, and the 144 cores from the final two bales were sampled only for moisture content variability determination as they were wetter bales than the original three and provided a different moisture level for study.

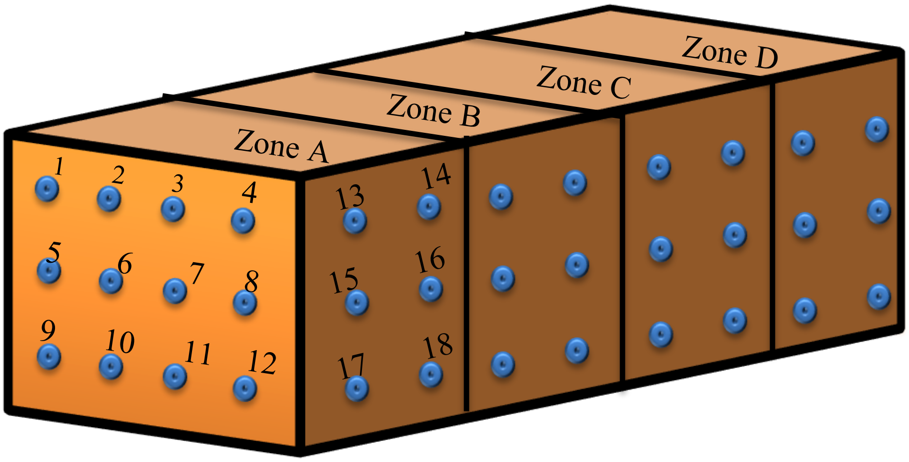

Figure 6.4. Sampling procedure for variability testing.The samples taken from Zone A were replicated for the following three zones.

Figure 6.5. One of the bales sampled for variability.

6.3.5. Analysis Procedure

The two material properties used to measure variability within the bale were moisture content and ash content. In order to get an accurate value for moisture content, the samples were dried following a procedure similar to the ASABE Standard S358.2, Moisture Measurement – Forages (American Society of Agricultural and Biosystems Engineers, 1988). Since that procedure was developed for forages instead of corn stover, the procedure was modified slightly to get an accurate moisture value for corn stover samples. The modified procedure included getting an initial, or “wet”, weight, drying the sample in a ventilated oven at 95°C for 24 hours, and then removing the sample to record its “dry” weight. This gravimetrically measures how much moisture the sample lost, which can then be converted into a percentage of the sample that was moisture, or the moisture content. The moisture content values were calculated on a wet basis from Equation 2.2.

To obtain the ash content, the National Renewable Energy Laboratory’s procedure listed in Lab Analytical Procedure: Determination of Ash in Biomass, NREL/TP-510-42622 was used as a baseline (Sluiter, et al., 2005). This procedure was modified slightly, to better suit the schedule and materials available. The modified procedure included putting a weighed, dried sample in a muffle furnace, and stepping the temperature up to 575°C, letting it dwell at that temperature until it reached a stable weight. The allotted time was found to be about 8 hours, then the sample was allowed to cool down in the furnace, and then the “ash” weight was recorded. The ash content was then calculated gravimetrically using Equation 2.1.

6.3.6. Statistical Analysis

Minitab 16 Statistical Software was used to complete a statistical analysis for the results of this experiment. Each bale would be tested separately so its results would not affect the results of another bale, since all bales were from independent treatments. The most important factors tested were the “Level” and “Zone” factors, to see if moisture tends to rise as it evaporates out of the bale, and to see if the soil falls to the bottom, creating a higher ash content at the bottom of the bale. One way ANOVAs were used to determine statistical significance for moisture content differences by vertical “Level” in the bale and ash content differences by “Zone”. Interval plots with the 95% confidence interval for the mean were also used to show individual differences within each bale, since the pooled data may become biased due to different mean values for entire bales.

6.4. Results and Discussion

6.4.1. Moisture Content Analysis Results

The plot below, Figure 6.6, shows a distribution of the moisture contents in each of the eight bales that were sampled 72 times each. In general, the bales with higher mean moisture contents had a larger variability. As can be seen in Figure 6.6, these bales with high variability had higher means than medians due to the outliers. The low variability bales had means that were very similar to medians. Another way this can be shown is in Figure 6.7. Bales with higher mean moisture contents also had high standard deviations, indicating large variability. This is further described by the 89.6% correlation between those two values.

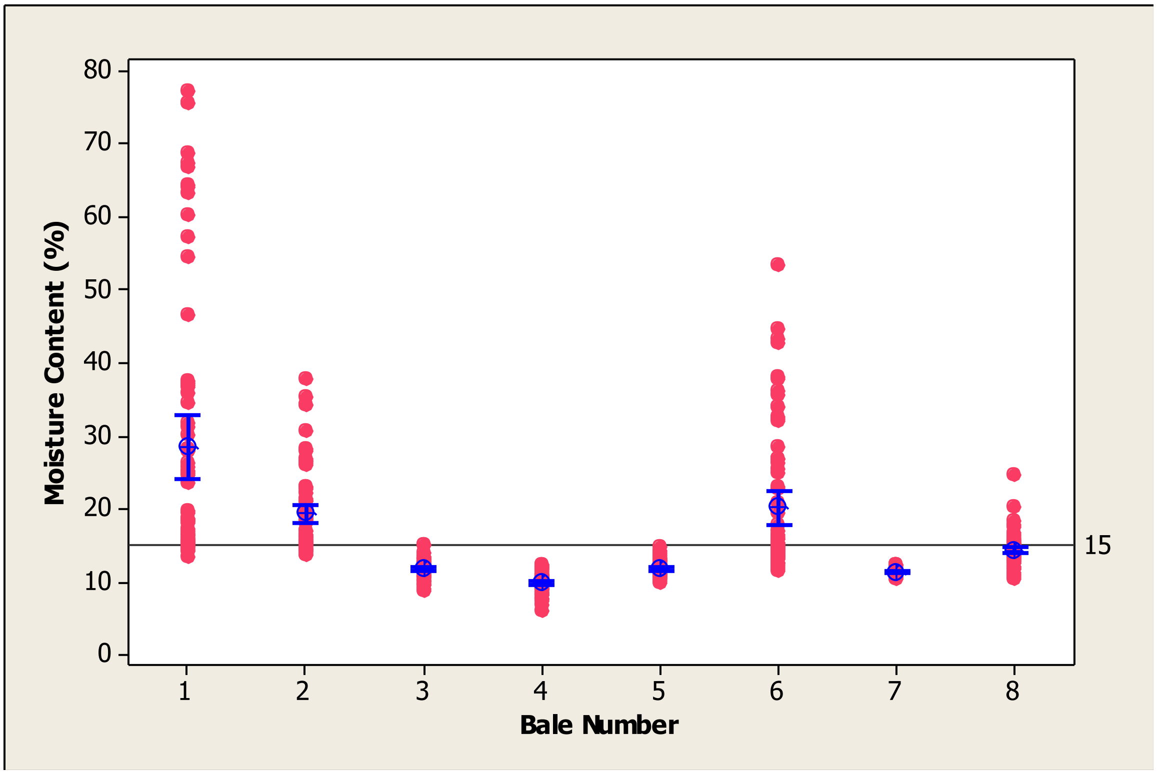

Figure 6.6. Plot showing the distributions of moisture contents throughout each bale as red dots, and the 95% confidence interval for the mean in the blue bars.

Table 6.2. Mean and standard deviation of moisture content within the bales.

Bale Number	Mean Moisture	Standard Deviation of Moisture
1	28.5	18.7
2	19.3	5.65
3	11.7	1.29
4	9.8	1.23
5	11.7	0.99
6	19.8	10.1
7	11.2	0.45
8	14.3	2.09

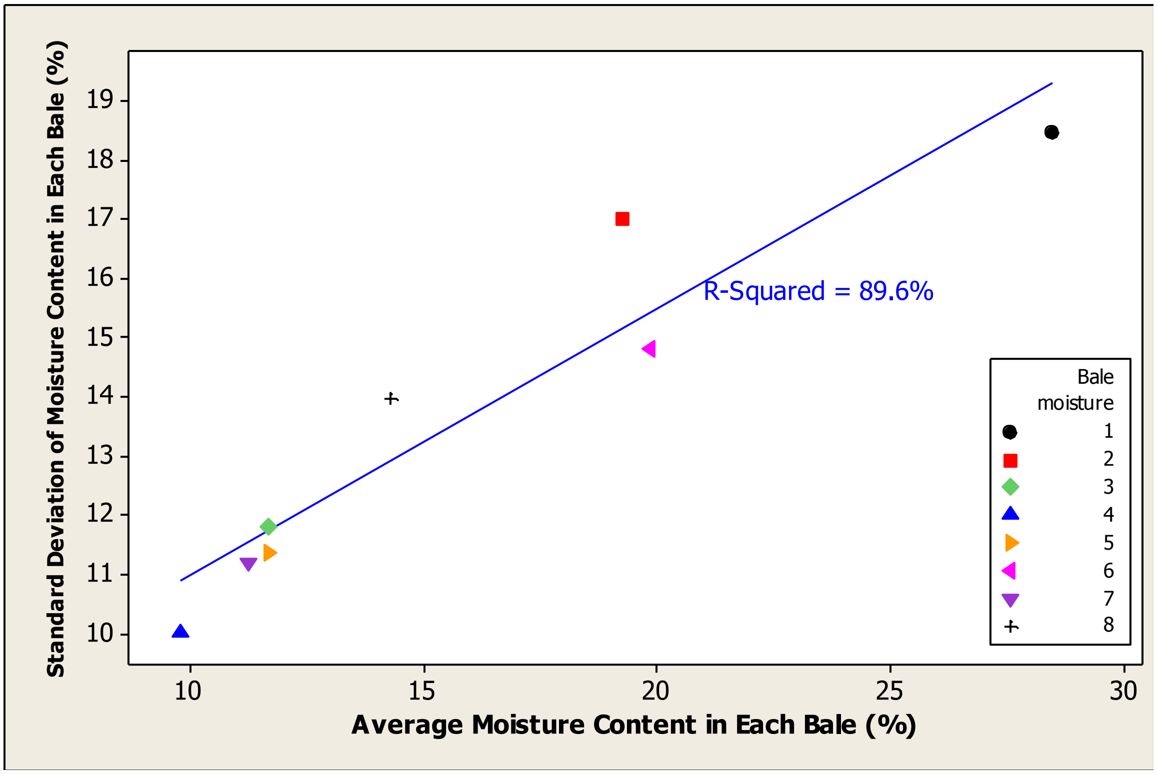

Figure 6.7. Correlation between the standard deviation and mean of moisture content, the different bales are shown by the different datapoints.

After taking a look at the spread of the data, it is important to look at where some of this variation occurs in the bale, so a sample location can be picked that will not result in a moisture content that is one of the outliers. This would be a problem because one of the outlier would be assumed to be the general moisture content throughout the bale.

The most logical place to start looking for variation would be between the three levels of samples taken in each bale, the top, middle and bottom. This is shown in Figure 6.8. A One-way ANOVA was performed for the entire data set, or for all bales together, and is shown in the Appendix. The P-value for the “Level” factor is 0.011, which is less than the alpha-value of 0.05, which means that there is a significant difference in the “level” treatment factor. Therefore, the data was analyzed graphically by level within each bale, which is shown in

Table 6.3 to see differences within individual bales.

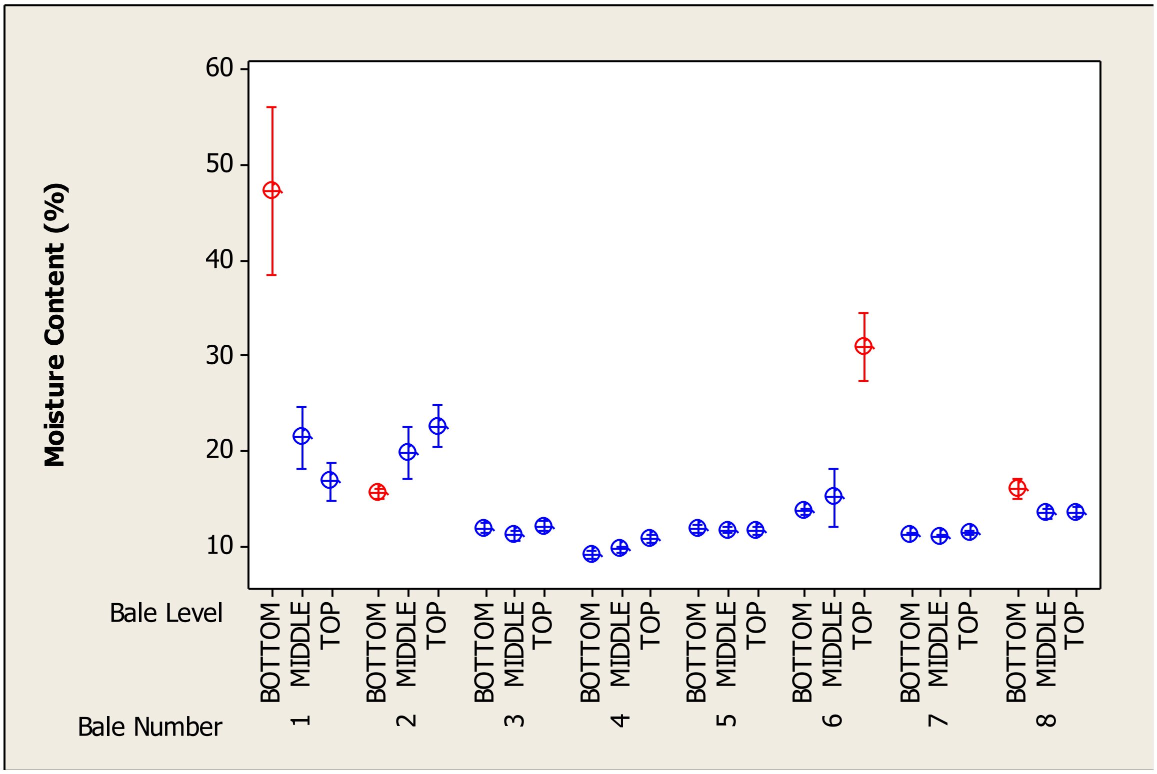

Figure 6.8. Interval plot showing where differences in 95% confidence intervals occur within the bottom, middle, and top layers of each bale. The statistical differences are highlighted in red. The circles are the mean for each level of each bale, and the bars are the 95% confidence interval for the mean.

Table 6.3. Statistical results for moisture content differences for each individual bale. Note, each grouping of A, B or C is only for each bale.

Bale Number	Vertical Level in Bale	N	Confidence Interval Lower Limit	Confidence Interval Upper Limit	Estimate	Group
1	Bottom	24	38.39	56.04	47.21	A
1	Middle	24	18.14	24.69	21.42	B
1	Top	24	14.82	18.73	16.77	B
2	Bottom	24	14.92	16.09	15.5	A
2	Middle	24	16.98	22.41	19.69	B
2	Top	24	20.34	24.85	22.6	B
3	Bottom	24	11.27	12.46	11.87	A
3	Middle	24	10.63	11.64	11.13	A
3	Top	24	11.61	12.55	12.08	A
4	Bottom	24	8.55	9.57	9.06	A
4	Middle	24	9.25	9.97	9.61	A
4	Top	24	10.35	11.18	10.75	B
5	Bottom	24	11.41	12.12	11.82	A
5	Middle	24	11.29	12.07	11.68	A
5	Top	24	11.08	12.01	11.54	A
6	Bottom	24	13.25	13.96	13.6	A
6	Middle	24	12.02	18.16	15.09	A
6	Top	24	27.24	34.4	30.82	B
7	Bottom	24	11.08	11.44	11.26	A
7	Middle	24	10.89	11.2	11.05	A
7	Top	24	11.22	11.64	11.43	A
8	Bottom	24	14.89	16.99	15.94	A
8	Middle	24	12.86	13.92	13.39	B
8	Top	24	13.03	14.05	13.54	B

It appears that there is a significant difference in the moisture content in the vertical level of the bale. After doing other tests, it was seen that no other factor provided a significant difference, such as horizontal position in the bale. However, as shown in Figure 6.9, there was some variance between different zones in each bale. A One-Way ANOVA, shown in the Appendix, showed a P-value of 0.371 when analyzing moisture content differences among zones. So, while there was some variability, there were no statistical differences.

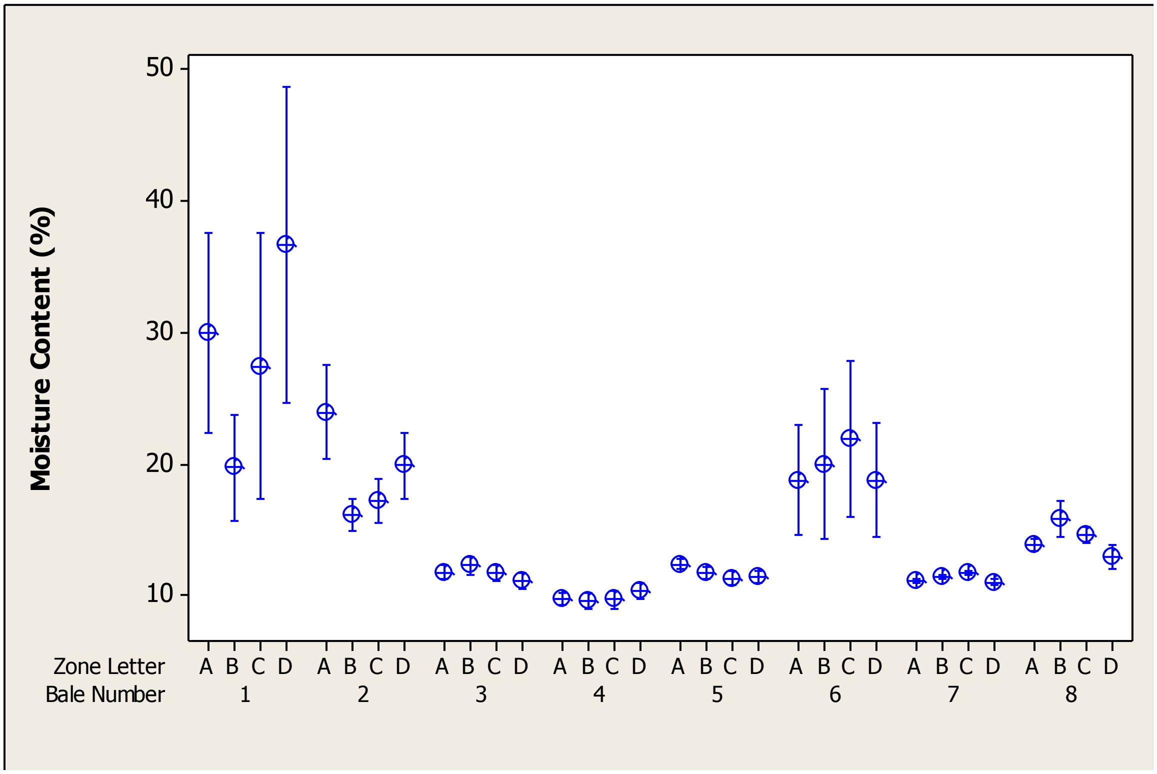

Figure 6.9. Moisture content distribution by zone in each bale. The circles show the mean for each zone, with the 95% confidence intervals for the mean shown as the bars extending from the mean.

The fact that the bottom of the bales have significantly higher moisture than the middle of the bales, and the top of the bales also have a higher mean moisture content suggests that, as moisture exits the bale, it migrates towards the outside of the bale and leaves the middle slightly drier. This is most likely because the distance from the middle of the bale to the top or bottom would be shorter than the distance from the middle to either end of the bale. Additionally, if a particular bale is on the bottom of a stack, the bottom of the bale could absorb moisture from the ground during rain events.

In terms of sampling, the most representative sample would be one taken from the middle of the bale. Figure 6.10 shows that the moisture content for the samples taken from the middle of the bale, samples 5-8 and 15-16 from Figure 6.4, are most similar to the average value for each bale. In all bales except bales 3 and 7, the average moisture content of the samples taken from the middle of the bale was closest to the average for the entire bale. Therefore, the middle of the bale will provide the most representative moisture content for the bale. Additionally, due to the fact that there is slight variability between the zones, shown earlier in Figure 6.9, it is best to take a sample from the end of a bale for representative moisture content for the bale.

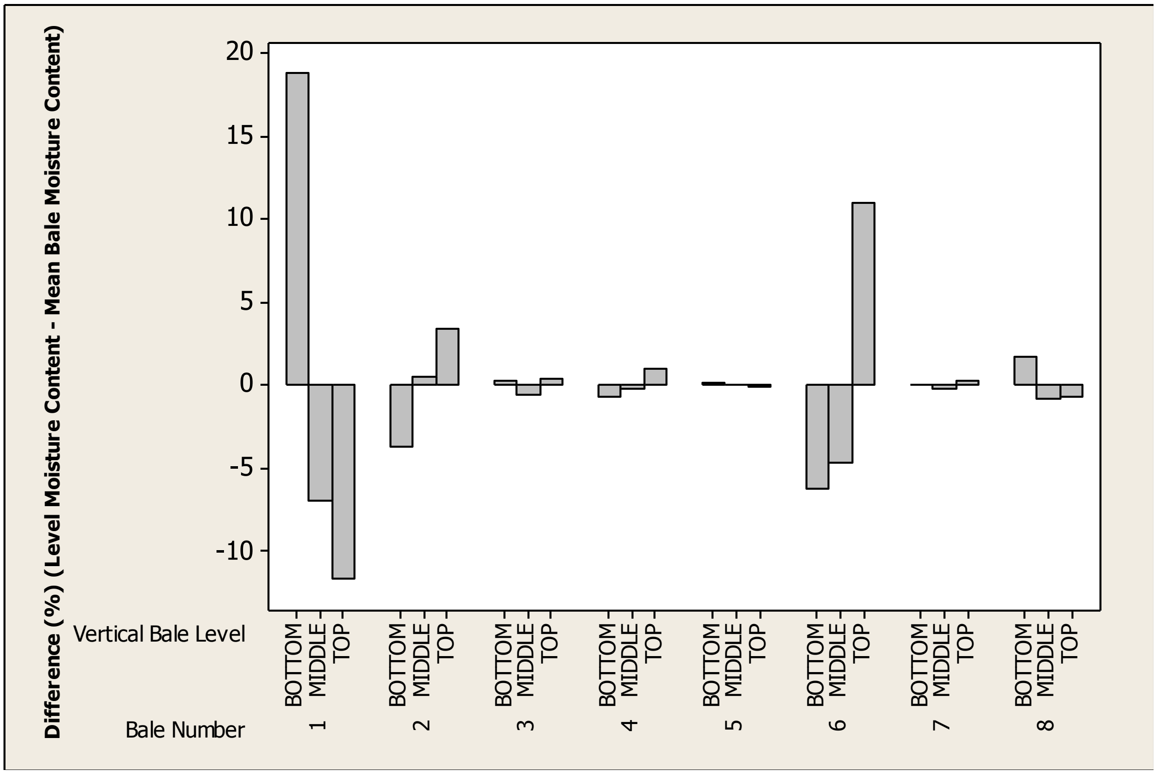

Figure 6.10. Plot showing the standard error of each level within the bale. The difference shown is the difference of the individual level in each bale subtracted from the average bale moisture.

6.4.2. Ash Content Analysis

The ash content for each of the 72 cores in the six bales sampled for moisture and ash analysis was measured and the following results are shown in Figure 6.11, separated by bale. From Figure 6.11 and Table 6.4, there appeared to be much more variability in the bales with higher average ash contents. Figure 6.12 shows this correlation between bales with a high ash content and the amount of variability within. The regression fit is 96.2%, which indicates high correlation.

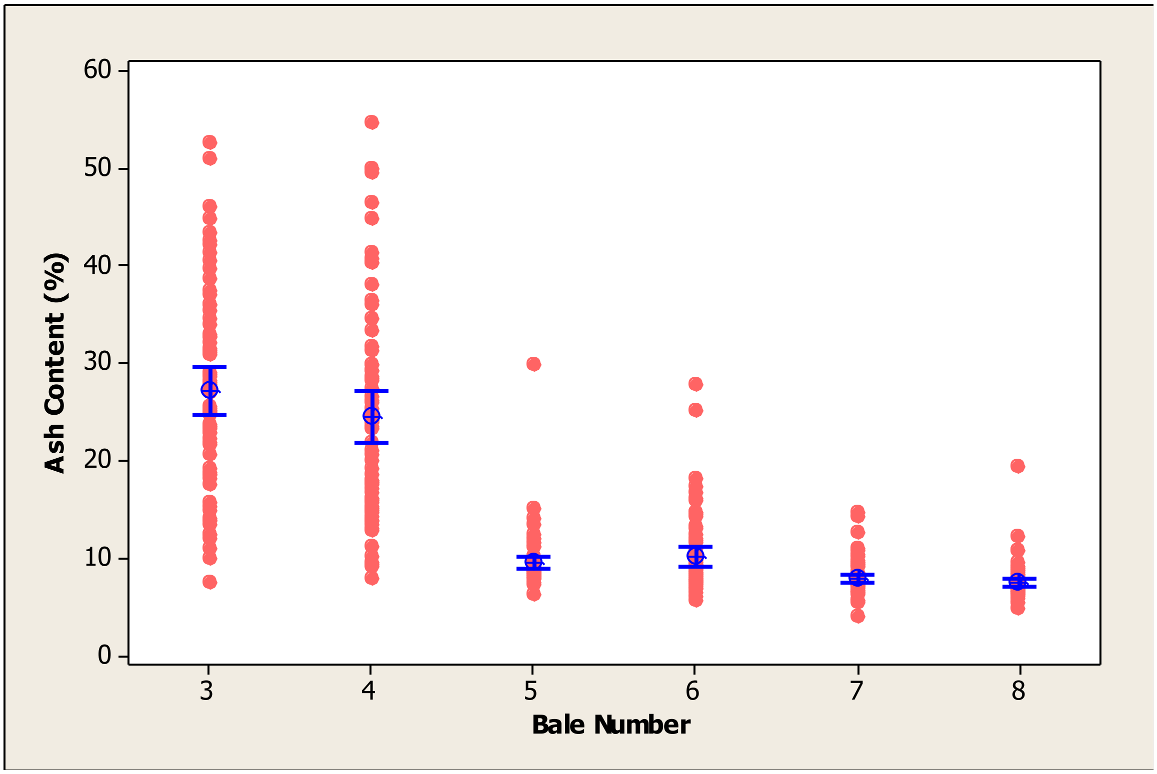

Figure 6.11. Spread of ash content data for each bale shown as the red dots, with the blue bars showing the 95% confidence interval for the mean.

Table 6.4. Mean and standard deviation of ash content in each bale.

Bale Number	Mean Ash Content	Standard Deviation of Ash Content
3	27.09	10.27
4	24.40	11.33
5	9.50	2.87
6	10.08	3.98
7	7.90	1.73
8	7.43	1.88

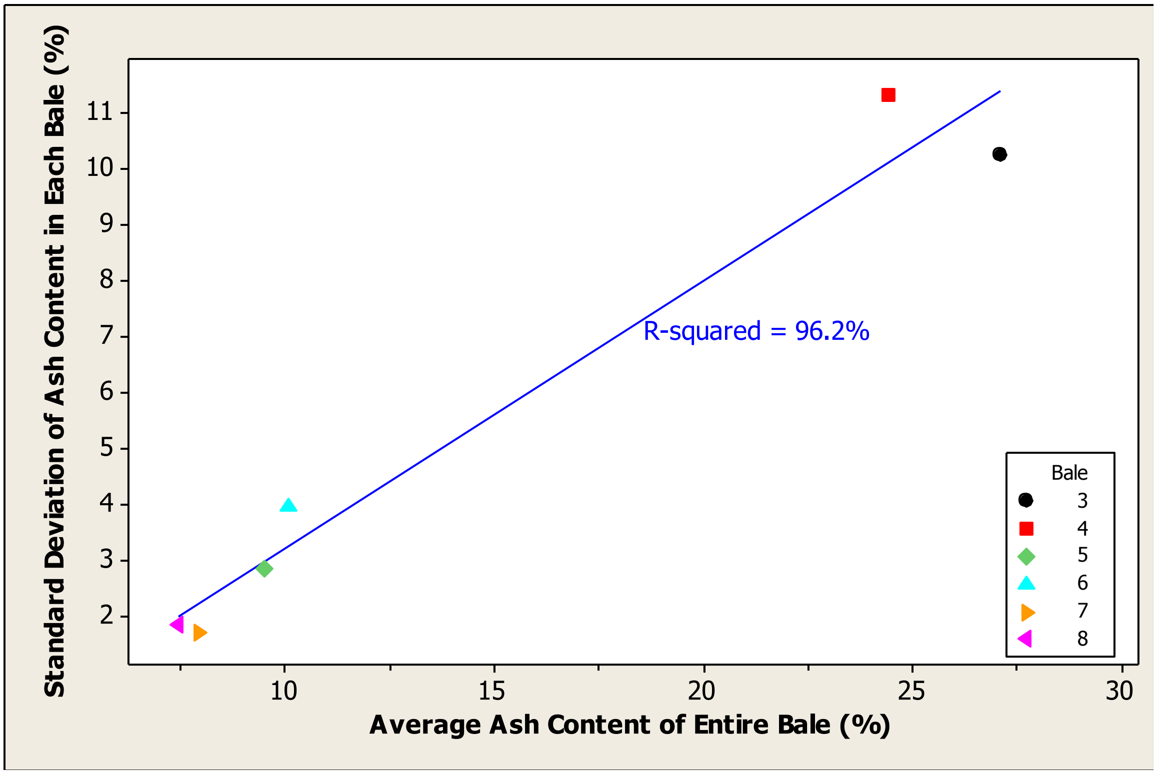

Figure 6.12. Correlation between the mean ash content and standard deviation for each bale.

Another place to look for variation is between horizontal zones in the bale, to know whether a representative sample should be taken from the end or the side of a bale. The zones are not representative of anything other than different parts of a field as the baler picked up corn stover on its pass. Figure 6.13 shows that there is some variation, or statistical differences, between zones within each bale. When pooled together, however, the differences among zones for all bales are not significant, as the P-value for the pooled data was 0.605. The One-Way ANOVA test results are shown in the Appendix of this chapter. The pooled data is biased by averaging out the high and low values for all of the bales; therefore, it is important to analyze the differences between zones in individual bales, which are shown in Figure 6.13.

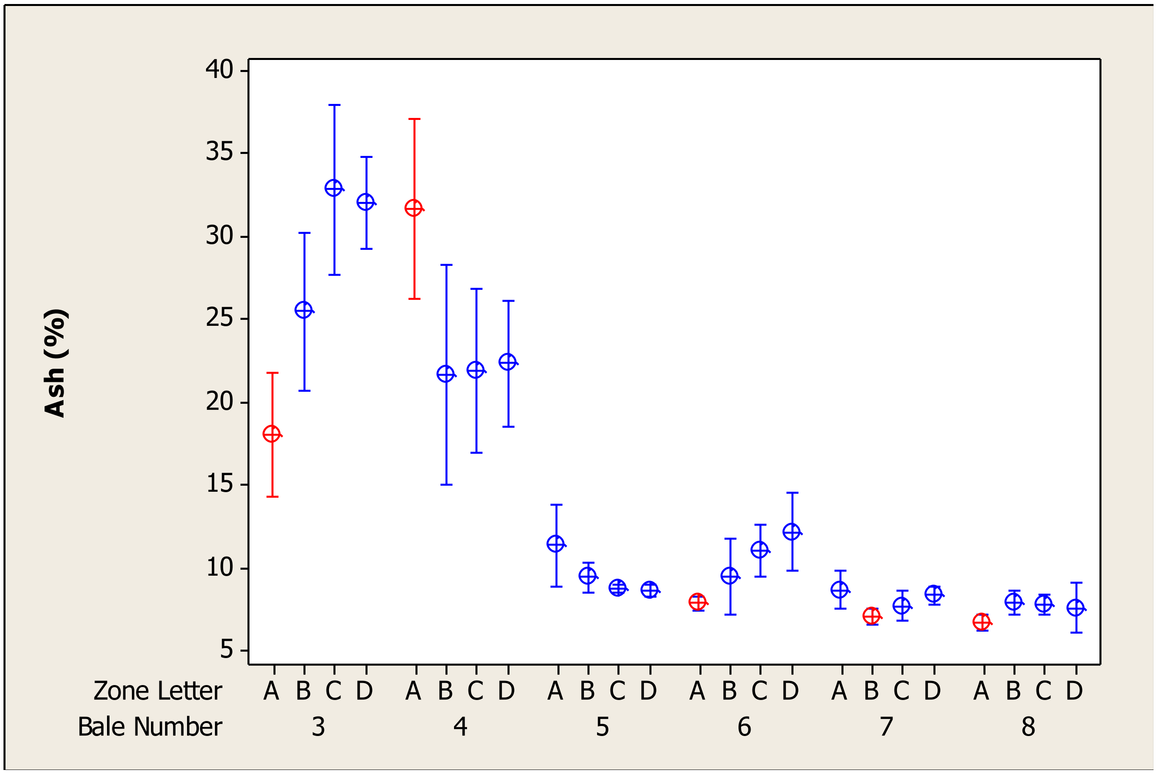

Figure 6.13. Ash content variation among zones in each individual bale. Statistical differences are shown when there are red bars within individual bales. The bars are 95% confidence intervals for the mean of each zone in each bale.

The reason for variance between zones is because each zone was made from a different part of the field, by the baler picking up a windrow along the rows of the field. Variation in ash content can occur along a pass in a field due to changes such as a change in topography causing the baler to pick up more soil. Therefore, just as with moisture, it is best to sample from the end of the bale so that the sample can include material from a greater span of the field, or more bale zones. This will increase the likelihood that the ash content of the sample will be a more representative sample in terms of material properties. The height at which the sample is taken will generally not make a large difference, as all levels are very near to the mean and median ash content values, shown in Figure 6.14. Figure 6.14 shows the difference, in percentage points, of each vertical level in each bale from the median ash content of each bale. The median was used, in this case, instead of the mean, due to some of the bales having very high outliers for ash content. This pulled up the average, which did not reflect the accuracy of the sample as well. Therefore, in most of the bales shown, the samples taken from the middle of the bale are closest to the entire bale median ash content.

Additionally, if you're analyzing the same sample for moisture and ash content, the sample should be taken from the middle of the end of the bale to get representative data for moisture, as discussed earlier.

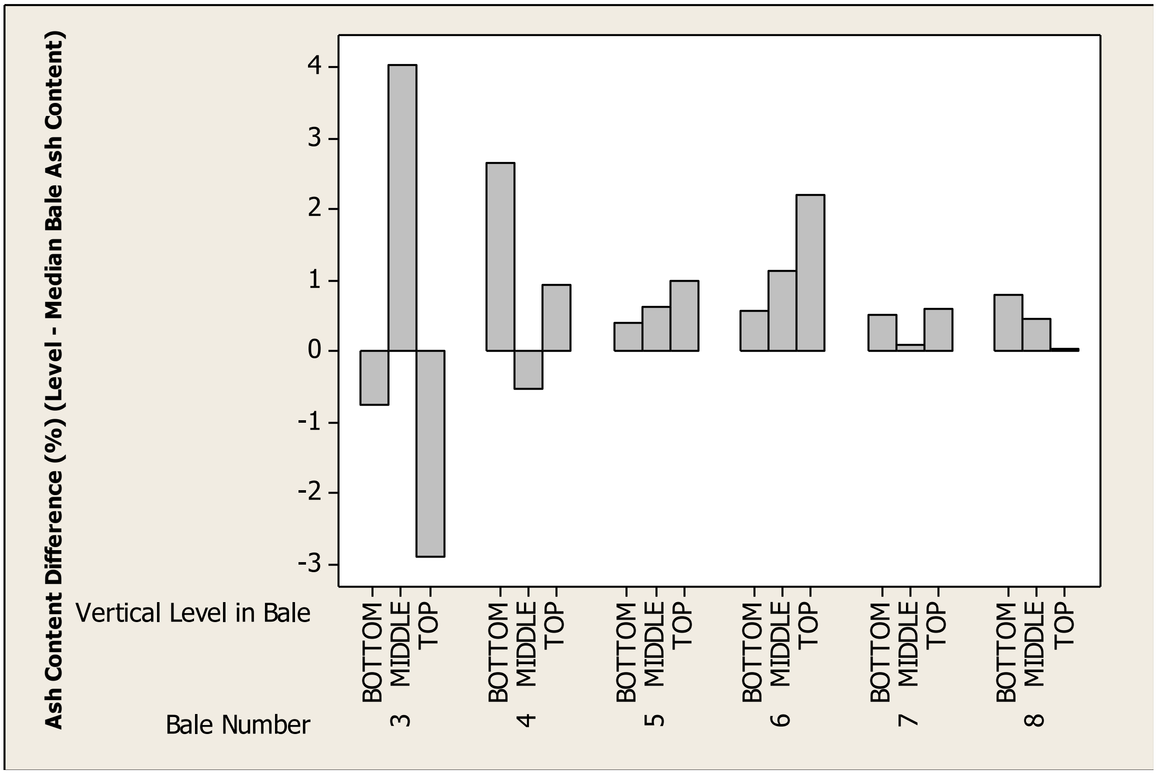

Figure 6.14. Plot showing the standard error from the median of each level within the bale. The difference shown is the difference of the individual level in each bale subtracted from the median bale ash content. The median was used since the mean was pulled high by outliers.

The standard deviation values for ash content within each bale, shown in Figure 6.15, are very high for two of the bales, and lower in the other four. The two bales that had high standard deviations were bales harvested in 2010, and were windrowed with a rake, while the other four were harvested with a stalk chopper. The standard deviations of 10.27 and 11.33 percentage points are very large standard deviations. This means that when a sample is taken, it could be 10 ash percentage points away from the average for the whole bale, therefore not giving a very representative value. The lower standard deviations are still even pretty large. The standard deviation of 2.87 percentage points means that the 67% confidence interval around the mean has a range of about six percentage points, which is a very large value in terms of ash content. Ash content, since it is all waste, is critical to measure, and therefore a difference in six percentage points could make a large difference.

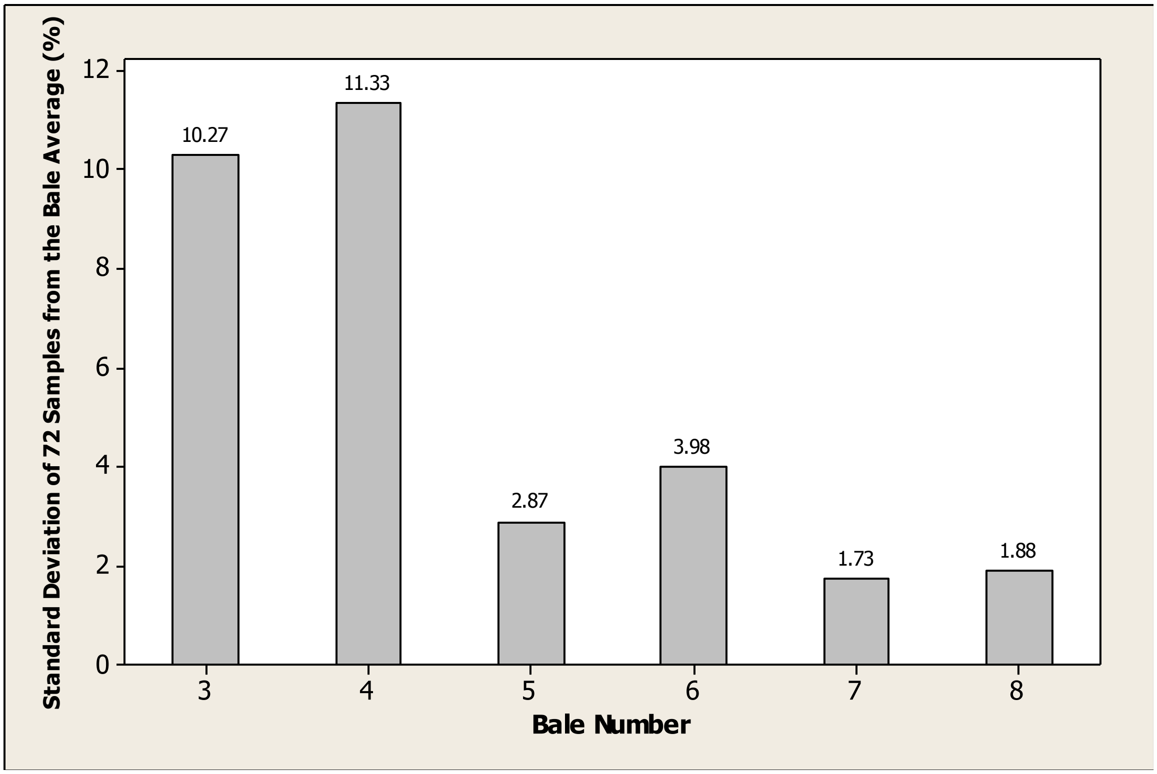

Figure 6.15. Standard deviations of ash content values within each bale.

6.5. Conclusions

Ash and moisture content are important material properties to measure to determine the quality of corn stover as a feedstock. In order to measure ash and moisture content of a bale successfully, a representative sample must be taken. The conclusions of this experiment help to map out where a sample should be taken in a bale to provide the most representative material property data.

The first important conclusion from this research is that in bales that have higher moisture content or higher ash content, the variability will also be higher. For moisture content, the two bales that had higher average moisture contents, the range of data was also very large, which indicates a larger standard deviation. The same occurs with ash content. There were two bales that had significantly higher ash contents than the others, and the spread of their data was also larger, indicating larger standard deviation. This correlation was shown in Figures 7 and 11, where mean ash content was plotted against standard deviation for each bale.

A second conclusion can be made to help with sample location. When sampling for representative data on a corn stover bale's moisture content, a sample should be taken from the middle of the end of the bale. The sample should be taken as deep into the bale as the sampler can manage, so that material is acquired from more area of the field it was baled in. The middle of the bale is more representative than the top or bottom of the bale, for moisture content, because it is not biased by moisture absorption from the ground or evaporation within the bale. The middle of the bale will provide a moisture content value closest to the average bale moisture, in most cases.

For ash content, a representative sample can be taken from the end, as well. Taking a sample from the end of the bale is more important in determining ash content, due to the variation of ash content between horizontal zones in the bale, or different parts of the field. The data for ash content isn't as variable in the vertical levels of the bale as moisture content is. However, for most bales, the middle of the bale will provide an ash content value closest to the median ash content for the entire bale, which would be the most representative value for ash content due to high outliers. If the sample is to be analyzed for moisture and ash content, the sample should be taken from the middle level on the end of the bale in order to obtain the most representative sample from the bale.

6.6. Acknowledgements

Funding for this project was provided by DuPont Cellulosic Ethanol, and all experiments were performed at Iowa State University's BioCentury Research Farm. All experiments were conducted by Dr. Matthew Darr's research team, with significant contributions from Kevin Peyton, Levi Powell, Benjamin Covington, and Andrew Kissel.

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6.8. Appendix A: Statistical Data

6.8.1. One-way ANOVA for Moisture Content Variation by Level

The results for Moisture content variation by level from Minitab are shown below:

```
Source   DF        SS     MS     F      P
Level     2     855.2  427.6  4.50  0.011
Error   573  54397.1   94.9
Total   575  55252.3

S = 9.743   R-Sq = 1.55%   R-Sq(adj) = 1.20%


                             Individual 95% CIs For Mean Based on
                             Pooled StDev
Level     N    Mean   StDev  -----+---------+---------+---------+----
BOTTOM  192  17.033  13.769                    (---------*--------)
MIDDLE  192  14.133   5.963 (--------*--------)
TOP     192  16.192   7.724               (--------*--------)
                             -----+---------+---------+---------+----
                               13.5      15.0      16.5      18.0

Pooled StDev = 9.743
```

6.8.2. One-way ANOVA: MC (%) versus Zone Letter

```
Source        DF       SS     MS     F      P
Zone Letter    3    300.8  100.3  1.05  0.371
Error        571  54616.8   95.7
Total        574  54917.6

S = 9.780   R-Sq = 0.55%   R-Sq(adj) = 0.03%


                            Individual 95% CIs For Mean Based on
                            Pooled StDev
Level    N    Mean   StDev  ---+---------+---------+---------+------
A      144  16.407   9.442              (---------*----------)
B      143  14.697   6.117  (----------*----------)
C      144  15.658  10.116         (---------*----------)
D      144  16.502  12.381              (----------*----------)
                            ---+---------+---------+---------+------
                            13.5      15.0      16.5      18.0

Pooled StDev = 9.780
```

6.8.3. One-way ANOVA: Ash (%) versus Zone Letter

The results for ash content differences among zones is shown below:

```
Source        DF     SS   MS     F      P
Zone Letter    3    203   68  0.62  0.605
Error        428  46980  110
Total        431  47182
```

```
S = 10.48   R-Sq = 0.43%   R-Sq(adj) = 0.00%


                          Individual 95% CIs For Mean Based on
                          Pooled StDev
Level    N   Mean  StDev  ---+---------+---------+---------+------
A      108  14.01  10.51     (------------*-------------)
B      108  13.48  10.06  (------------*------------)
C      108  14.96  11.17            (------------*------------)
D      108  15.15  10.13             (------------*------------)
                          ---+---------+---------+---------+------
                          12.0      13.5      15.0      16.5

Pooled StDev = 10.48
```

Chapter 7. Variability of Corn Stover Material Properties within a Set of Bales Harvested from the Same Field

Brittany Schon[4], Dr. Matthew Darr[4]

7.1. Abstract

The construction of two cellulosic ethanol plants is currently underway in Iowa. The primary feedstock for these cellulosic ethanol plants will be corn stover, or the residue left after corn grain is harvested. The corn stover is harvested in the form of bales, and usually stored in storage stacks. Stacks can be made in hoop barns, for indoor storage, or be covered with a tarp, for outdoor storage. However, in order for the companies to reimburse the harvesters or to make processing decisions later on, they will need to know the quality of the feedstock, primarily moisture and ash content. With as many bales as will need to be harvested, not every bale can be sampled for quality. Therefore, the determination of ash and moisture content variability between multiple bales harvested in one field is a valuable factor. The results of this study will provide an assessment of the variability of material properties so informed decisions can be made how many bales need to be sampled per field, or per stack.

7.2. Introduction

Corn stover has been selected as the primary cellulosic feedstock for cellulosic ethanol plants in the Midwest. Currently, two cellulosic plants are under construction in Iowa. One plant is under construction by POET Biorefining under their Project Liberty. It is being built in Emmetsburg, IA and will have local farmers harvest their own corn stover to bring into the plant. They will accept all shapes and sizes of bales, and will reimburse the farmers. The quality metrics they will abide by include docking $5 per bone dry ton for moistures 35-50%, and reject bales above 50% moisture. In terms of ash content, POET will dock $10 per bone dry ton for stover with 15-25% ash, and reject bales with above 25% ash (POET-DSM Advanced Biofuels, 2012). DuPont Danisco Cellulosic Ethanol (DDCE) is the other company that will be constructing a cellulosic plant in the next few years. Their plant will be

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[4] Graduate Student and Major Professor, respectfully, Agricultural and Biosystems Engineering Department, Iowa State University.

located in Nevada, IA, adjacent to the current Lincoln Way Energy corn ethanol plant. Different from POET, DuPont will contract with farmers so that they can bring in a custom harvesting crew to harvest their corn stover bales, and will be using large square bales.

Moving forward, both companies will want to get material property data as soon after harvesting as possible, so they can make storage and/or processing decisions. POET, for example, will want to know material property data so they know if they need to dock the farmer for any bad quality stover, or even reject the stover. The important factor to make an informed decision on bale quality, is how best to sample a truckload or bales, or a stack of bales in a field, in order to obtain representative information for them all. At first glance, this problem looks minor due to the fact that the hay industry already exists. Corn stover, though, while it can be baled, is not a consistent material, such as grass hay. Corn stover has cobs, stalks, leaves, and contains soil contamination, which all have different material characteristics. These things all contribute to variability in bales, which affect how the ethanol facilities receive their feedstock. In order to determine how best to take a representative sample, the variability of different bales from the same field must be determined. After the variability is determined, recommendations can be made on the number of samples per field to take to get an estimate of material properties.

Moisture content and ash content are important to measure, as they both affect the quality of the material. Moisture content allows for the growth of microbes, which will consume the biomass and create less available feedstock. Additionally, the presence of moisture means that there is less feedstock to be converted, which results in the need to harvest more material, or more acres. The harvesting of more material than originally intended requires additional resources, such as time and money that were not originally allotted. Additionally, in the case of DuPont, if the material that they paid their crews to harvest is high moisture, it essentially means they paid their crews to harvest water. This is clearly a waste of money and time.

Ash content is an important metric because it affects everything from machine efficiency and functionality to biomass quality to processing equipment functionality and efficiency. There are two main types of ash content: structural and non-structural ash. The structural ash is embedded in the plant material, and does not have much of an impact on machinery or equipment. It is mainly just a source of waste that will contain small amounts of silica, potassium and phosphorus. The non-structural ash content comes from soil introduced into the machinery, biomass material, and processing equipment, and is what causes the efficiency loss and loss of equipment functionality. It also is the largest contributor to the waste in multi-pass harvesting systems. The soil contamination will begin causing problems in the windrowing stage of harvest. The soil can come from the plant components flinging up the soil they are entangled with, or from rootballs, due to the windrower including stalks that are still firmly planted in the soil. Since topography, amount of stalks, and soil type can change throughout a field, variability tends to occur and brings into question what the variability of ash content in bales throughout a field can be. This variability will be important to quantify so processing facilities know how many samples to take from a truckload of bales, all coming from one field, in order to get the most representative ash content value for the whole truckload. That ash content value, then, will be important for the facilities to know so they know how much to reimburse or dock the harvester’s compensation for each field of bales because the ash content value is a direct correlation to the quality of the biomass. This biomass quality affects how much product you can get from the raw material, which is why waste percentage, or ash content, needs to be docked from compensation. Finally, the soil contamination in the ash content will cause processing equipment functionality and efficiency problems at the processing facility, as well. The problems arise because high temperatures during thermochemical conversions cause the alkali silicates and sulfates in the material to deposit on the walls of the equipment and leave behind a sticky residue, due to the alkali low melting points (Wang, et al., 2011).

The variability of ash and moisture content in bales within a field is not something that has been investigated previously, yet it is a very important metric to consider during the scaling up of industrial corn stover harvesting. Even though the same process and equipment will be used throughout the field, the natural environmental variability will cause material property variability within the set of bales harvested. This variability is something that processing facilities will need to know in order to adjust their processes accordingly.

7.3. Experimental Design

7.3.1. Objective

Knowing the variation of material properties, namely moisture and ash content, between bales harvested from the same field will allow industrial-scale production to determine how many samples they need to take in order to obtain representative data for the whole field. This data will then help the biomass industry determine the value of the bales.

7.3.2. Corn Stover Supply

During the 2011 harvest season, 89 fields were harvested by custom harvest crews harvesting for DuPont Cellulosic Ethanol, with a target of 2.0 tons harvested per acre. This resulted in hundreds of bales produced per field. These fields were located around central Iowa, and were harvested using industrially applicable methods. The harvest method involved collecting the material into a windrow, using either a rake or a shredder, and then baling the material. Later, the bales were collected and stacked in the field before being transported to a satellite storage facility. A summary of each field, the windrowing method, and the number of bales sampled in each field is shown in Table 7.1. The information from these bales is the data that was used for this research.

7.3.3. Sampling Tools and Procedure

In order to sample bales in the field, a sampling rig was designed. This sampling system was an attachment to a tractor that could weigh a bale by picking it up with its forks. Following the weighing, the operator would lower the coring device and drill out a core sample with a 2.5” diameter steel coring tube with boring teeth on the end. Pictures of the device can be seen in Figure 7.1 and Figure 7.2. Aluminum pans were used to collect the corn stover samples and process them through the analytical lab.

Table 7.1. Field summary list.

Field	Windrower	Number of Samples
1	Rake	6
2	Shredder	9
3	Rake	3
4	Shredder	10
5	Shredder	10
6	Shredder	10
7	Shredder	9
8	Shredder	38
9	Rake	23
10	Rake	9
11	Shredder	10
12	Shredder	10
13	Shredder	10
14	Shredder	9
15	Rake	9
16	Rake	10
17	Shredder	8
18	Shredder	10
19	Rake	9
20	Shredder	10
21	Rake	10
22	Shredder	10
23	Rake	3
24	Shredder	13
25	Rake	10
26	Rake	5
27	Shredder	5
28	Rake	6
29	Rake	15
30	Shredder	20
31	Shredder	10
32	Shredder	18
33	Shredder	18
34	Shredder	10
35	Shredder	8
36	Shredder	20
37	Rake	20
38	Rake	18
39	Shredder	20
40	Shredder	10
41	Shredder	37
42	Rake	18
43	Shredder	10
44	Shredder	41
45	Rake	36
46	Shredder	10
47	Shredder	9
48	Shredder	10
49	Rake	5
50	Shredder	19
51	Shredder	40
52	Shredder	20
53	Rake	37
54	Shredder	21
55	Shredder	22
56	Shredder	21
57	Shredder	4
58	Rake	22
59	Rake	4
60	Shredder	10
61	Shredder	10
62	Rake	39
63	Shredder	39
64	Shredder	10
65	Shredder	10
66	Shredder	38
67	Shredder	37
68	Rake	10
69	Rake	10
70	Shredder	10
71	Shredder	10
72	Rake	8
73	Rake	7
74	Rake	8
75	Shredder	9
76	Shredder	8
77	Shredder	8
78	Rake	9
79	Rake	9
80	Rake	10
81	Rake	10
82	Rake	29
83	Shredder	35
84	Rake	27
85	Shredder	29
86	Shredder	15
87	Rake	9
88	Rake	10
89	Rake	10

Figure 7.1. Field sampling tool in the process of sampling a bale.

Figure 7.2. Close-up view of the field sampling tool. The forks used to weigh the bale are below, with the coring probe currently up, out of use.

7.3.4. Analytical Tools and Procedure

The analytical tools used for this research include an electronic balance, large, ventilated Despatch drying ovens and Thermo Scientific muffle furnaces. The electronic balance was first used to get the initial or “wet weight” of the sample. The large, ventilated ovens were then used to dry the samples down for 24 hours at 95°C, and then the samples were weighed in again to record their dry weight. This drying period was based off of the ASABE Standard S358.2 “Moisture Measurement – Forages”, but slightly altered to better suit industrial corn stover samples. The moisture content was then able to be calculated using Equation 2.2.

Following the drying period, the sample was then put in the muffle furnace, which was ramped up to 570°C for 8 hours. After the 8 hours, the furnace was allowed to cool before weighing the final sample in as the “ash weight”. This ashing procedure was based off of the National Renewable Energy Laboratory’s procedure NREL/TP-510-42622, but altered to better suit the corn stover samples and resources available. The ash content was then calculated using Equation 2.1.

7.3.5. Statistical Analysis

Minitab 16 Statistical Software was used to analyze the results of this experiment. Normality plots were used with the full data set of moisture and ash contents to determine if statistical plots can be made using the assumption that the data was normal. The moisture content data was fairly normal, while the ash data was not. The ash data was then limited to samples below 20% ash, since the industrial standard will not accept ash levels above that level. The variability was tested by analyzing standard deviations from the data. The standard deviations within each field were plotted using histograms to show the variability.

7.4. Results and Discussion

In order to analyze variability within a field, since averages and variance will be used, the sample data needs to be analyzed for normality. A normality plot of all the 2011 field samples, Figure 7.3, shows the data to be mostly normal, although a slight right-tailed skew. The slight right-tailed skew, most likely, results from high moisture samples that were harvested at the beginning of the season. As the season progresses, the corn stover will begin to dry, and create a more normal distribution. Eventually the corn stover stabilizes around 15%, which is when the bulk of harvest occurs. The distribution of moisture contents can be seen in Figure 7.4.

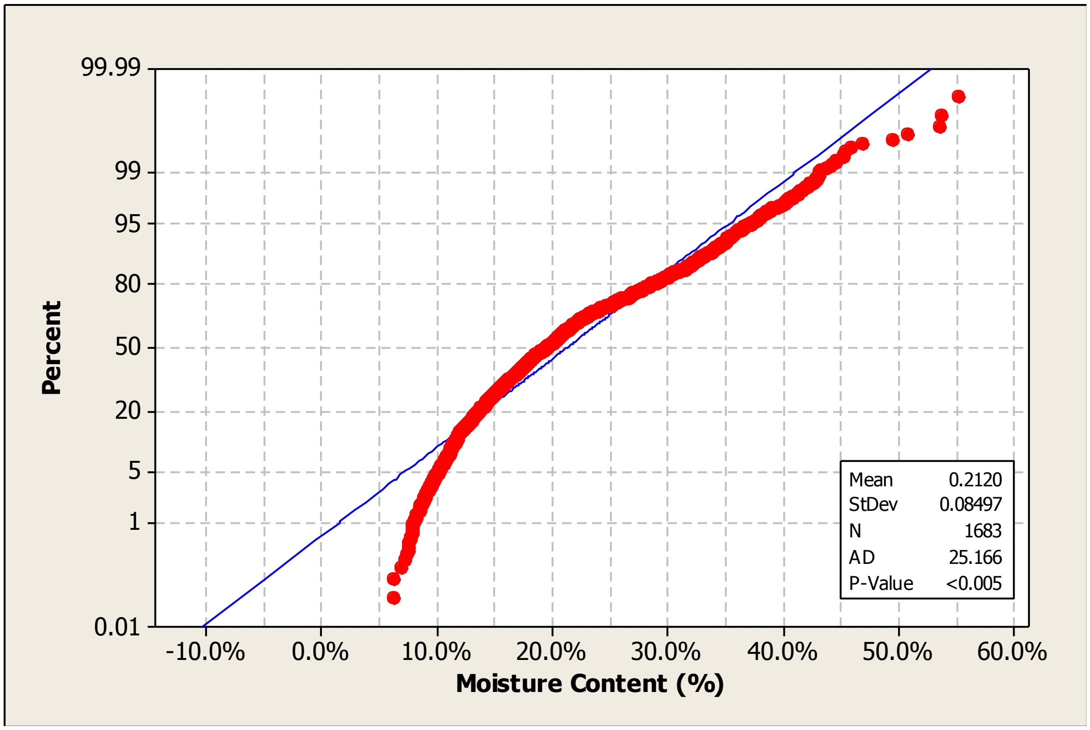

Figure 7.3. Normality plot of moisture content across all samples taken in fields. The blue line indicates perfect normality, while the red dots show the distribution of the data.

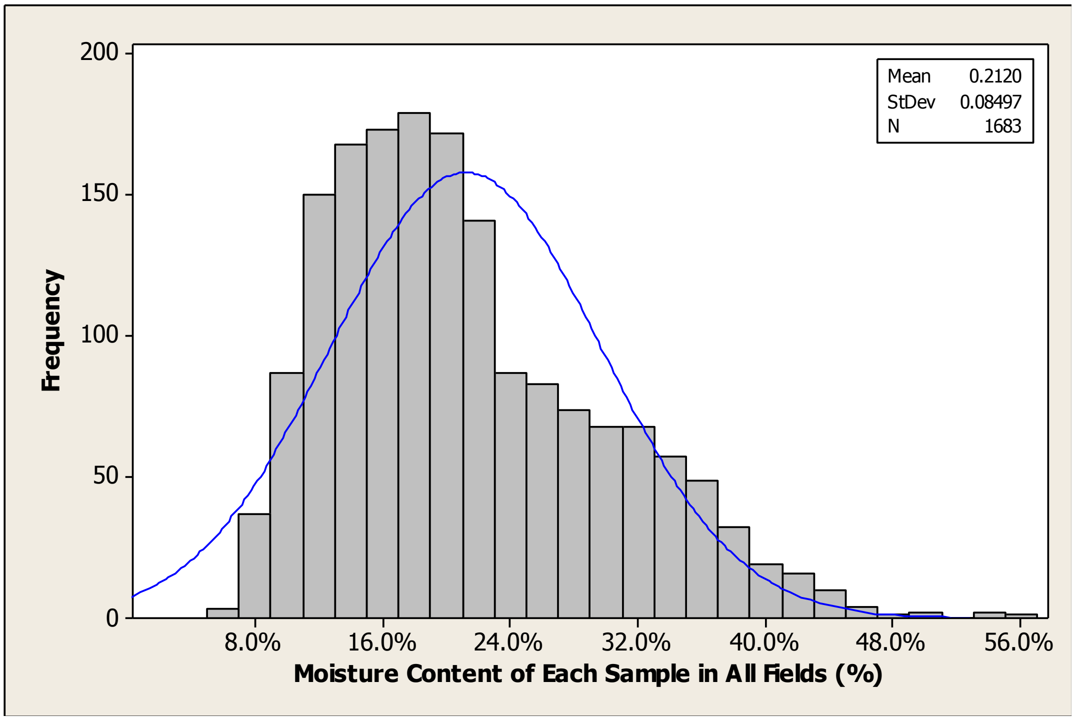

Figure 7.4. Distribution of moisture content values from 2011 harvested corn stover samples. The right-tailed skew is most likely due to early season high-moisture samples. N represents number of samples. The blue line represents the normal bell curve around the mean.

Looking at the ash content values from all 2011 samples, there is a prominent right-tailed skew, and the normality plot reflects this, as can be seen in Figure 7.5. The next step, then, was to decipher why the data was not normally distributed. It was discovered that most of the points in the right tail were from a early season fields and experimental fields, in which machinery settings were still being adjusted, therefore inducing more soil contamination and not operating in steady state. However, once normal harvest machinery settings were achieved later in the season, the ash content values were lower. Additionally, when corn stover processing facilities begin to open, they will reject corn stover bales with high ash contents, which means that harvesting crews will begin to take less soil into the bales, therefore creating a smaller range than this initial large-scale production. Therefore, we can attempt to limit the range of data to be below 20% ash. This produces much more normal data, as shown in Figure 7.6. This is a more normal plot because it follows the theoretical normal distribution line, more closely. In other words, the deviations of the individual data from the theoretical line are smaller, on average, in Figure 7.6 than in Figure 7.5.

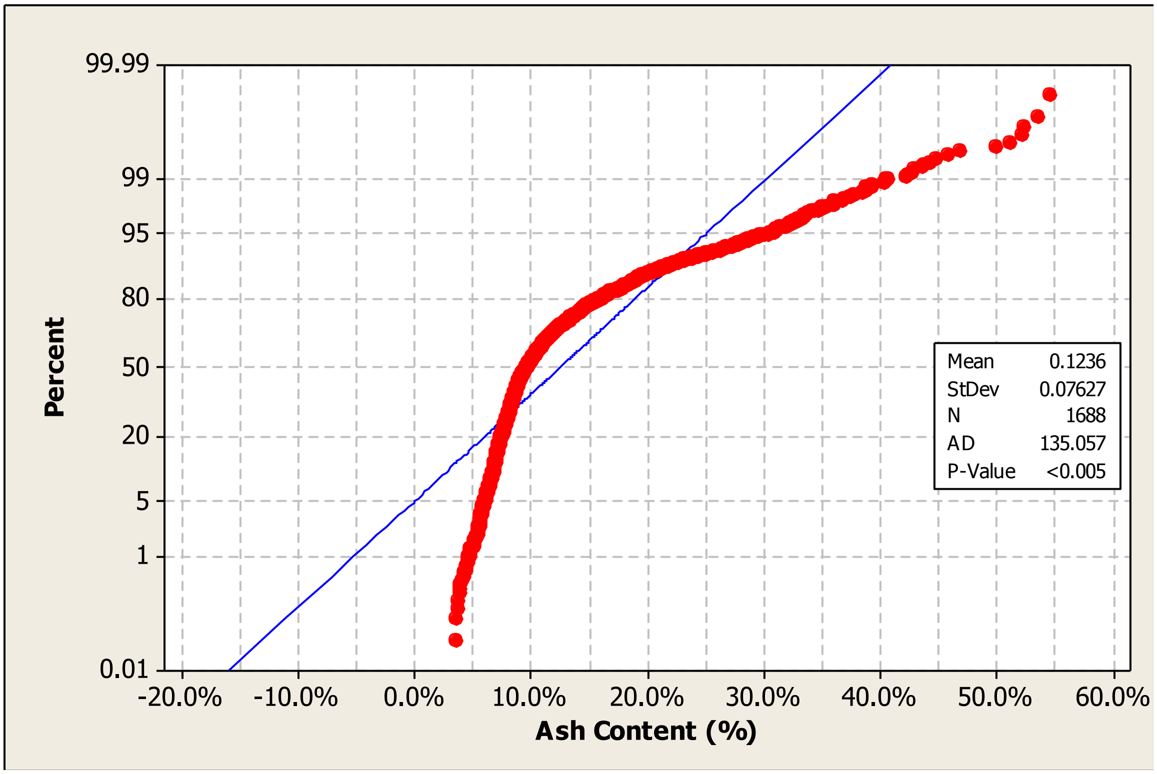

Figure 7.5. Normality plot for ash content data for 2011 corn stover harvest samples. The blue line indicates perfect normality, while the red dots show the distribution of the data.

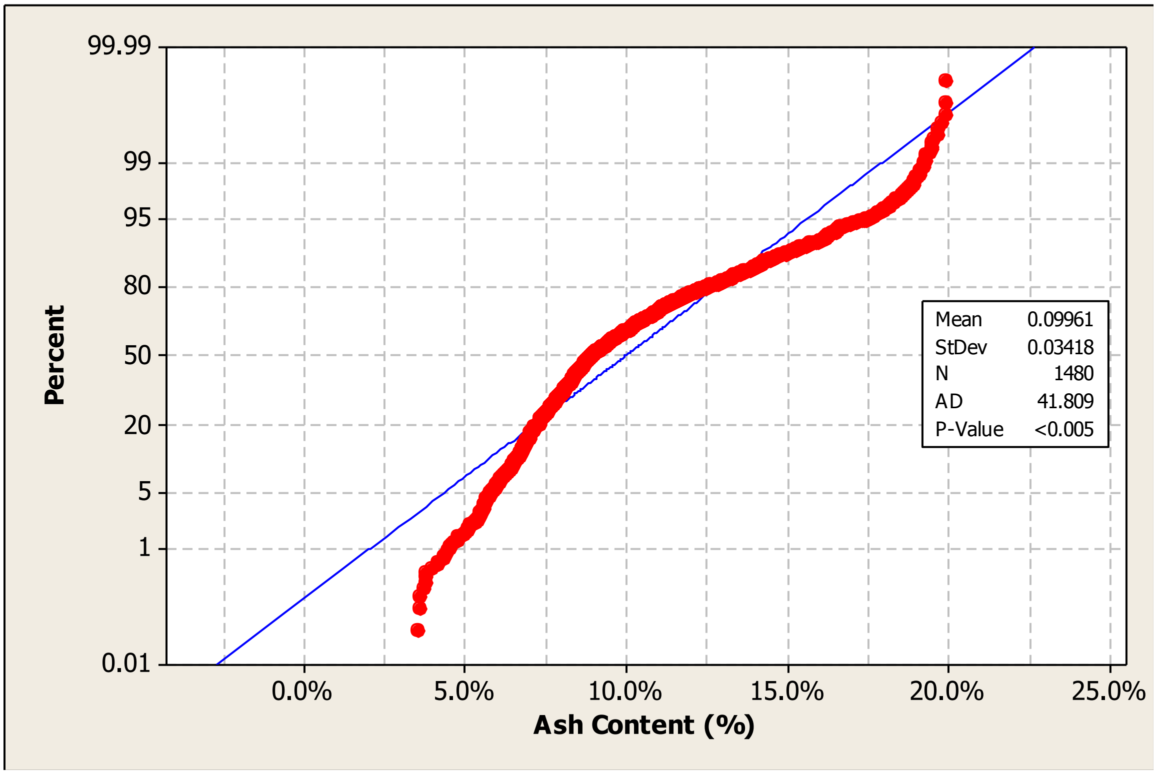

Figure 7.6. Normality plot for ash content data for 2011 corn stover harvest samples below 20% ash. The blue line indicates perfect normality, while the red dots show the distribution of the data.

7.4.1. Moisture Content Variability

For 89 different fields, the standard deviation was calculated of moisture contents within the samples taken from each field. The distribution of the standard deviations or the variation among fields is plotted in Figure 7.7. The standard deviations range from about 1 to 12 percentage points, which is a wide range for moisture content values across the span of one field. The next step is to analyze some possible contributing factors to the variation in moisture content throughout a field.

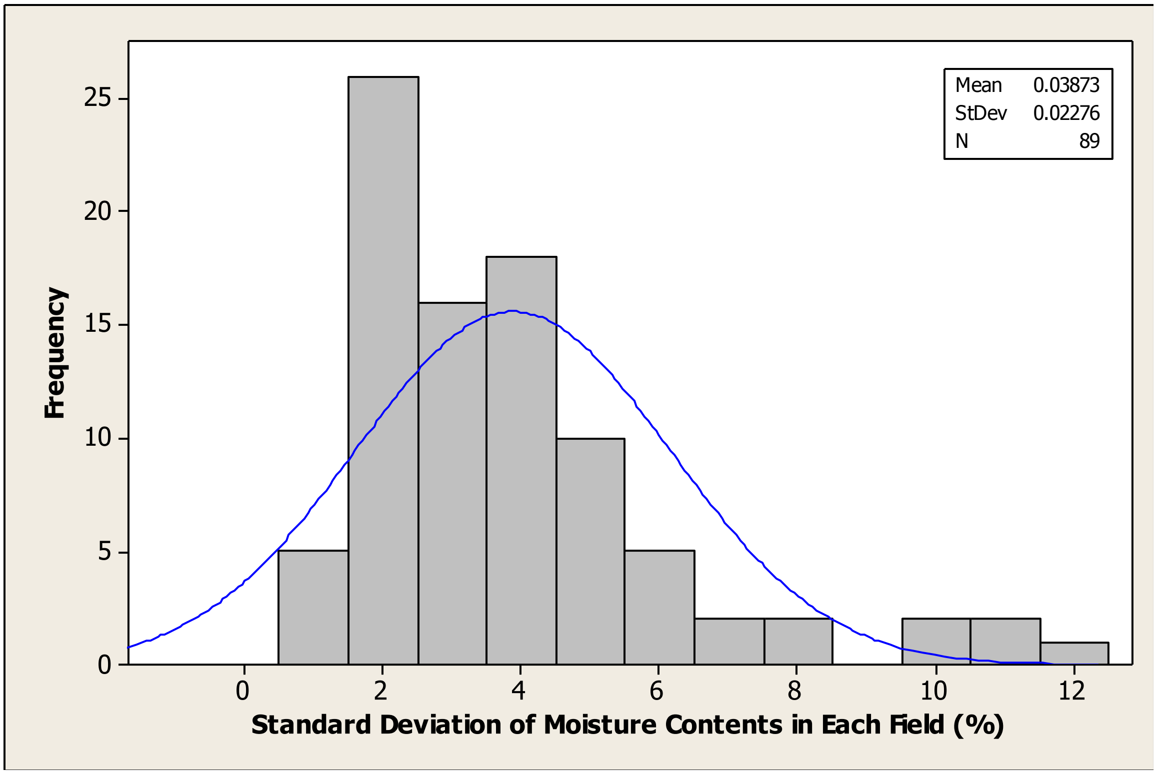

Figure 7.7. Distribution of standard deviations from the mean of field moisture contents. N represents the number of fields displayed in the histogram. Note, X axis values are in decimal form. The blue line represents the normal bell curve around the mean.

One thing that can be looked at to discover some reasons behind the variation is moisture content variability throughout the season. Due to the fact that each field was harvested and sampled generally within the same day or two, time can help to decipher if variability is caused by timing in the season and if the variability in field moisture content shrinks throughout a the season. As can be seen from Figure 7.8**,** the standard deviation of moisture contents within a field decreased with time, during harvest. In other words, field moisture content variability decreased as harvest progressed. Additionally, Figure 7.9 shows the moisture contents in each field as the season progressed. Based on this plot, moisture content and variability of moisture content did decrease with time.

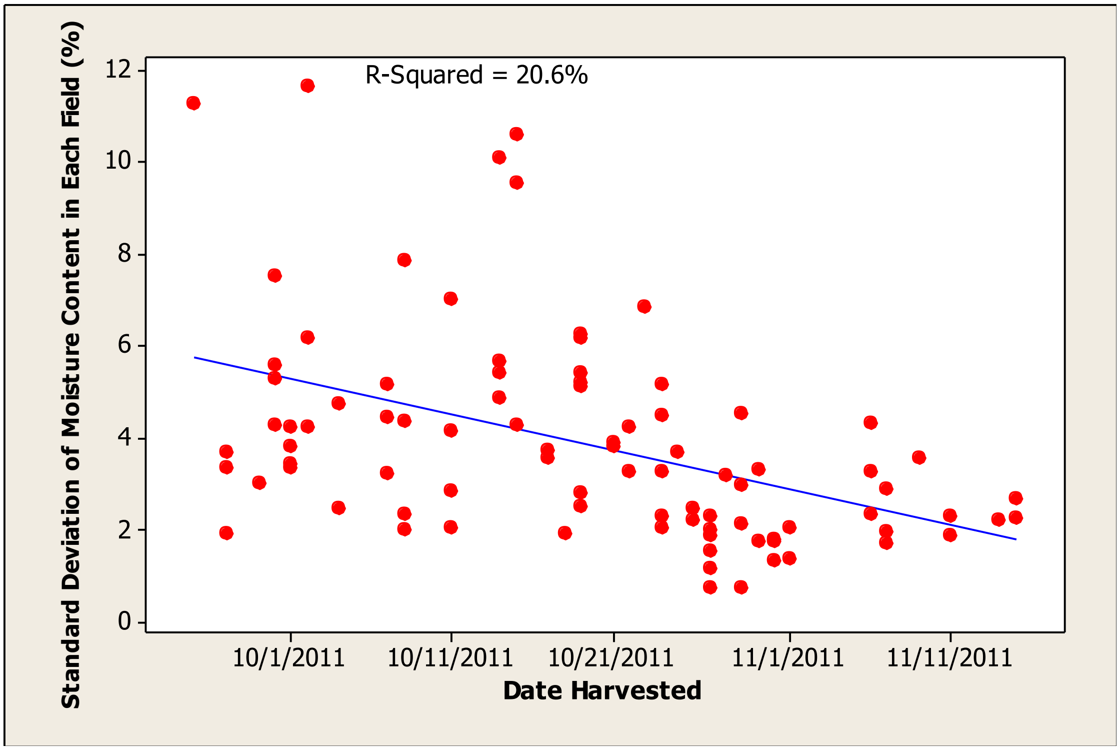

Figure 7.8. Scatterplot showing standard deviation of moisture content values within fields as the harvest season progresses. The blue line shows the general trend of the data.

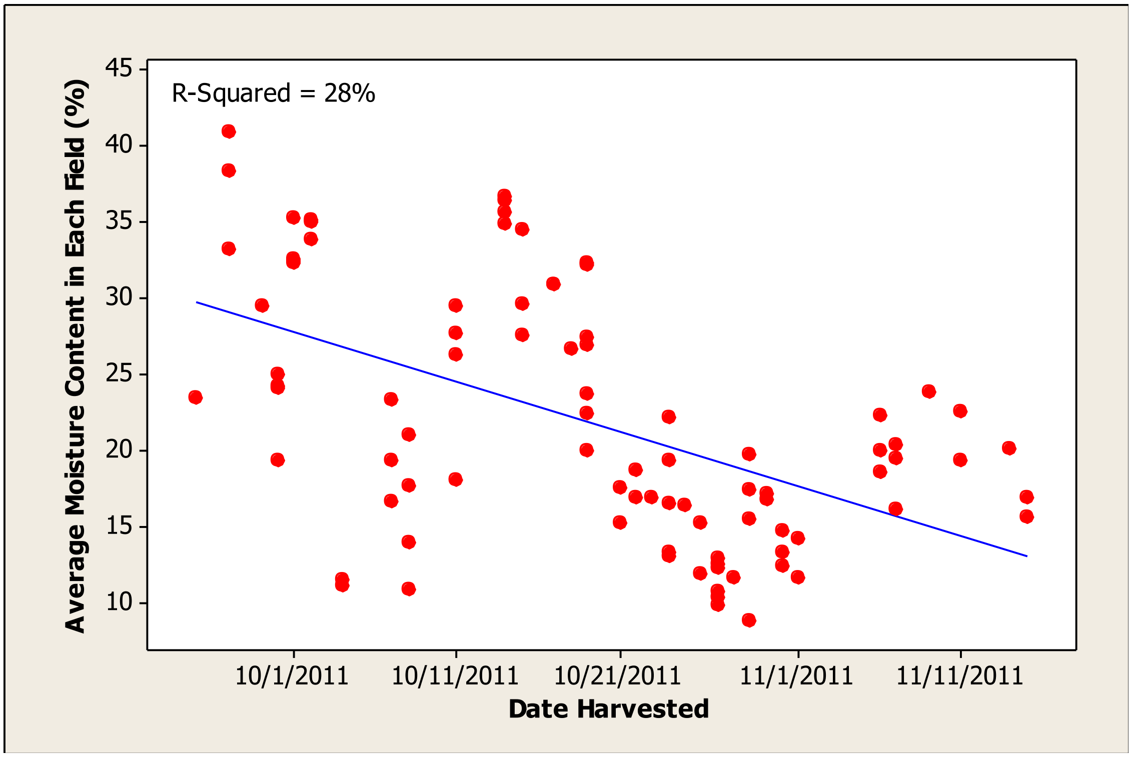

Figure 7.9. Scatterplot showing the average moisture contents in each field as the season progressed. The blue line shows the general trend of the data.

7.4.2. Ash Content Variability

The distribution of the standard deviations from the mean ash content for 89 fields is shown in Figure 7.10. The standard deviations range from about 0.4 percentage points to about 4.4 percentage points away from the mean for each field. Given the fact that this data is capped off at 20% ash content, a 4.4 percentage point difference in ash content values throughout a field is incredibly variable. The ash content value, as discussed in the introduction section, is a very influential value since it directly affects waste, and therefore affects incentive pay for the harvester. Therefore, the large variability is an important factor when sampling to determine the quality of a set of bales. The next step is to attempt to identify the cause for some of the variability, which can help future harvesters make better choices for harvesting the corn stover.

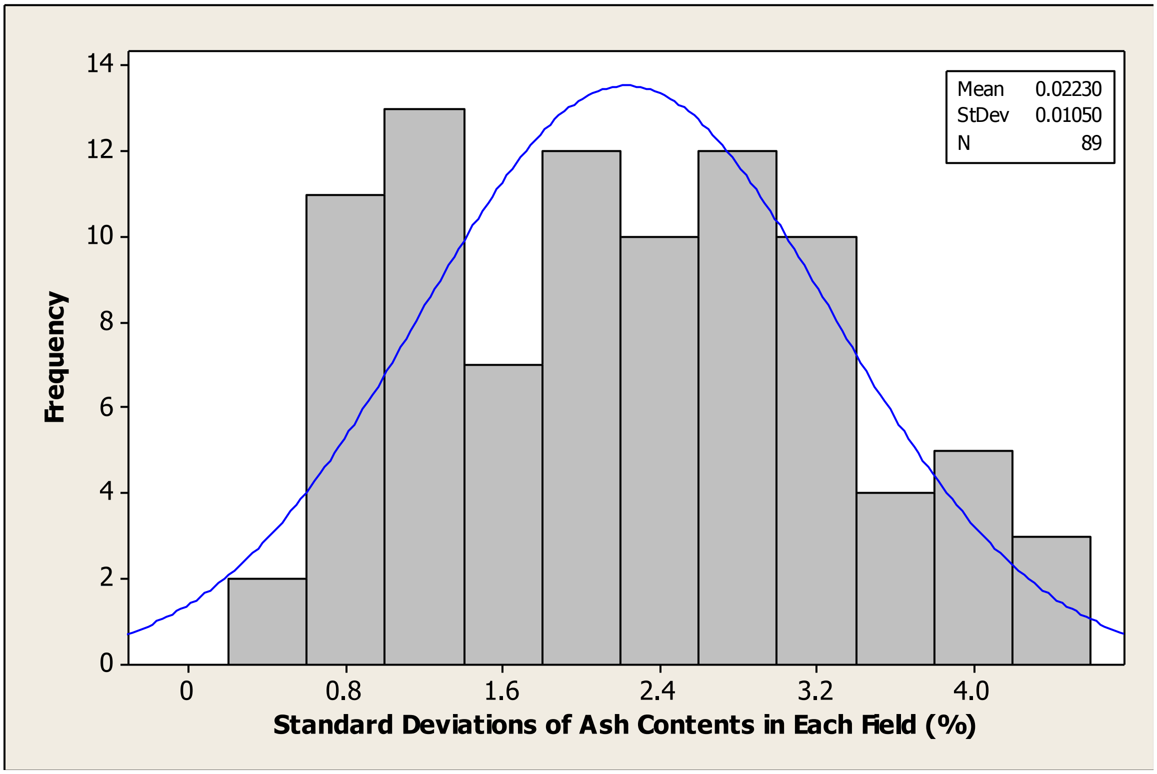

Figure 7.10. Distribution of standard deviations from the mean of field ash contents. N represents the number of fields displayed in the histogram. Note, X axis values are in decimal form.

Just as with moisture content, ash content variability could change throughout the season. As harvesting crews become more familiar with the machinery and more adaptable to topography, the variability of ash content could shrink. Also, as the soil and plants start to dry out as the season progresses, the windrowers and balers might have a harder time pulling in clumps of soil, since dry soil is not as adhesive as wet soil. On the contrary, as the soil gets drier, it becomes more easily airborne in the form of dust, which can gather in balers and windrowers. Looking at Figure 7.11 and Figure 7.12, there does not appear to be a trend indicating that variation, or the confidence intervals, lessens as the season progresses. Additionally, the mean and median values do not form a general trend in any direction, as indicated by the low R-squared value of 1.3%.

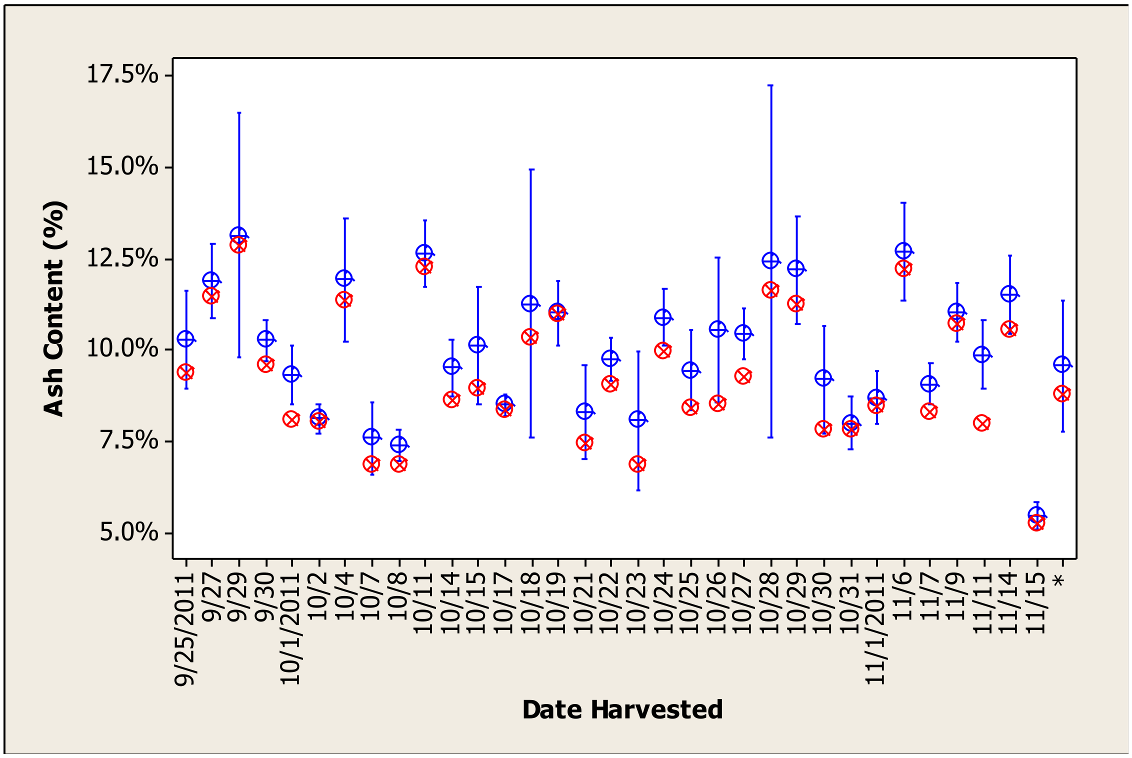

Figure 7.11. Interval plot showing the variability of ash content values each day throughout the harvest season. Mean symbol with confidence interval is in blue, median is in red.

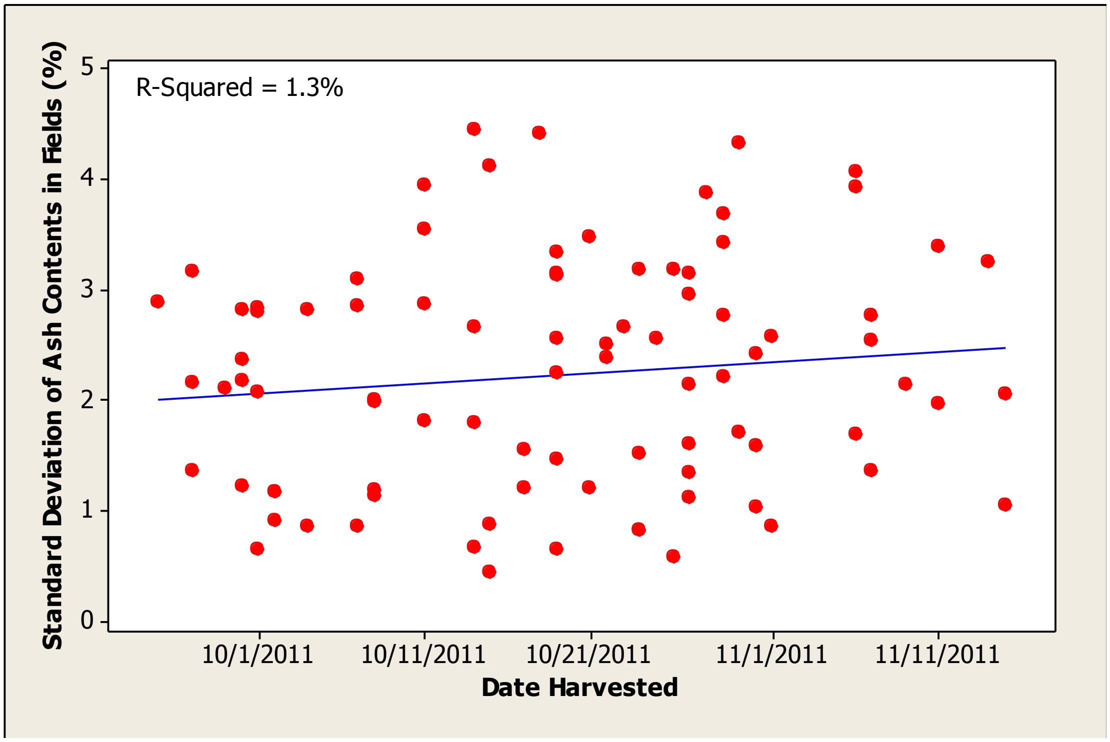

Figure 7.12. Standard deviation of ash contents in fields as the season progressed.

7.5. Number of Samples per Field

Using the variability data, the number of samples to be taken in each field to obtain representative quality data on fields can be calculated. The number of samples is a vital piece of information for industries to know what sort of sample throughput they will need to process in order to keep up with the harvest crews in order. Additionally, knowing the number of fields to sample per field can minimize supply chain risk. This is because obtaining the correct values for moisture and ash content which will allow industries to make the correct informed decisions for storage and transportation using the sample size calculation equation Equation 7.1.

Equation 7.1. Sample size calculation equation.

$$n = \left(2 \times z_{\alpha/2} \times \frac{\sigma}{w}\right)^2$$

Where:
n = Number of samples to take per field
Z = Area under the normal curve (1.96 for an α=.05)
σ = Standard deviation of data
w = Interval width

Since moisture content lessens and stabilizes as the season progresses, the important factor to use for sample size calculations would be the values related to ash content. Figure 7.13 shows a range of desired precision levels, based on industrial standards, and the sample number required. Since 2011 fields showed an average of 2.23% standard deviation, the standard deviation used in the equation would be 2.23, and if the precision is desired only within ±5 percentage points of the actual mean, the sample size should be around 1 per field.

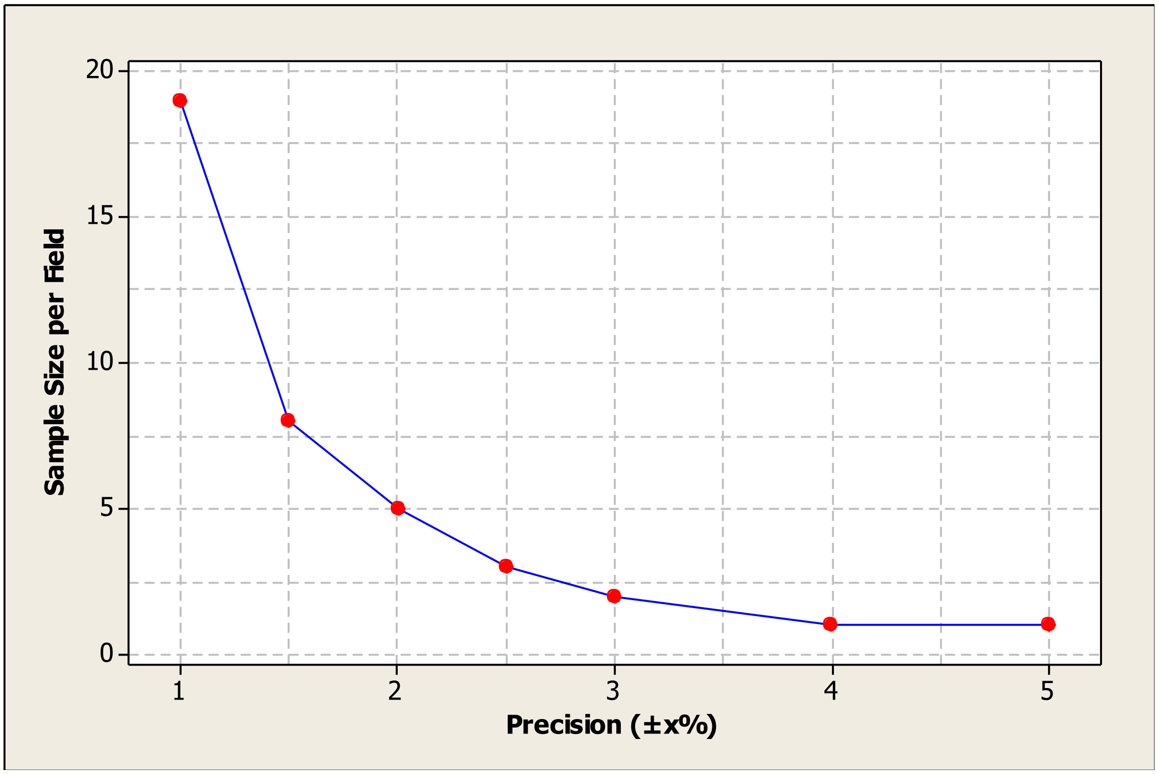

Figure 7.13. Plot showing required number of samples to take in each field, using the mean standard deviation for ash content of 2.23% and desired level of precision.

7.6. Conclusions

Moisture and ash content are very important material properties when determining the quality of corn stover as a feedstock. Moisture content can vary across a season, but generally fields are harvested within a day or two. Ash contents can vary throughout a field due to changes in topography, plant genetics or soil type.

For these reasons, it is important to know the variation of these properties in different bales harvested from the same field. Moisture content does vary considerably, with a range of standard deviations between 1 and 12 percentage points away from the mean. However, as the season progresses, moisture content variation within a field appears to shrink. This indicates that, in order to get a representative moisture content value for material harvested from the same field, more samples may need to be taken in the early part of the season in order to achieve a mean moisture content nearest the true field average. Additionally, it has been concluded that bales made from shredded material have higher average moisture contents, most likely due to cutting fresh plant material into windrows.

Ash content, though this data was capped at 20% due to selecting only industrially applicable scenarios, also varies a fair amount. According to the 2011 data, ash content variation did not appear to lessen throughout the course of a harvest season. Sample number was calculated based on desired precision level based on ash content values, using the maximum variability from 2011 field data. If ash content data is desired to be within ±5 percentage points of the actual field average for ash content, with a maximum variability of 2%, 30 samples should be taken from each field.

7.7. Acknowledgements

Funding for this project was provided by DuPont Cellulosic Ethanol, and all experiments were performed at Iowa State University's BioCentury Research Farm or in fields contracted by DuPont Cellulosic Ethanol. All experiments were conducted by Dr. Matthew Darr's research team, with significant contributions from Kevin Peyton, Benjamin Covington, Levi Powell , Andrew Kissel, and Nicole Jennett.

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Chapter 8. General Conclusions

As corn stover becomes a commonly harvested commodity to use in cellulosic ethanol plants, the sampling type, size and methods, as well as variability must be quantified. In order for material quality testing to become industrially applicable, moisture and ash content values will need to be analyzed quickly, so that informed decisions can be made regarding storage and processing of the material. In the first chapter, two types of rapid moisture analyzers were tested, as well as a test to determine if a subsample could accurately be taken from a large sample of corn stover. The two types of rapid moisture testing methods that were tested include a standard hay capacitance moisture probe, the Delmhorst Hay Probe, and microwave testing. While the Delmhorst Probe is commonly used in hay and forage, it should not be used in testing the moisture content of corn stover bales. The probe was inaccurate and imprecise, without a consistent correction factor. Microwave testing for moisture also proved to be inaccurate. However, the samples used for this experiment were small, which impacted the degree of moisture contents detected. The microwave experiment should be carried out again with larger samples, as well as samples with higher moisture content to determine if it is accurate on a larger scale. If it is accurate on a large scale, the microwave would be an excellent method for testing moisture, as it is a very rapid measurement technique. Additionally, other rapid analyzers require small samples in order to test the moisture and ash content. Therefore, a test was conducted to determine whether representative subsamples can be taken from a 200-400 gram sample of corn stover. It was determined that, for moisture content, subsamples can accurately be taken for low moisture samples. This test should be repeated with higher moisture samples to determine if they, too, can be accurate. Subsamples for ash content, however, need to be more uniformly distributed than subsampling by hand in order to obtain representative data. Soil tends to sift to the bottom of a sample during the grinding process, and therefore will not be reflected in subsamples taken only from the top of the material. Therefore, this test should be repeated, using a divider funnel to separate the material, to see if the results differ from hand sampling.

The question of original sample size is also one that will be important to corn stover processing facilities. If smaller samples can be taken, then the sample throughput can be faster, thus increasing the timeliness for getting results. In the sample size chapter, samples were taken side-by-side in 96 corn stover bales, with a ¾” core sampler and a 2.5” core sampler and analyzed for differences in moisture and ash content. In general, moisture content values will be significantly lower in the 2.5” core samples than the small core samples. However, the estimate for the difference is only 1.13% different, which is not a significant value in practical terms of moisture content. Therefore, the ¾” core samples will generally provide a nearly accurate look at moisture content, and the 2.5” core sample will not be practically different than the smaller sample. For ash content, however, the larger, 2.5” core sample will provide a more conservative estimate of the average bale ash content; therefore, the 2.5” core sampler should be used when possible. For bales that are at industrially acceptable levels of ash content, or below 10%, the ¾” core sampler can be used to accurately measure quality. However, with industrial harvesting of corn stover being relatively new, ash contents below 10% are not always common, and therefore the ¾” core sampler should not be used while the harvesting is in its beginning stages, but rather the 2.5” core sampler should be used.

Variability in corn stover poses a challenge to sampling, in that the best location and appropriate number of samples to take can be greatly affect by variability. Corn stover bales have variable moisture and ash content due to the heterogeneous mixture of materials in the bale. If moisture or ash content resides primarily in one part of a bale, a sample that does not include, or only includes that part of the bale will not be completely representative. Eight bales were sampled 72 times each, and it was determined that for both moisture and ash content, samples should be taken from the middle of the end of the bale in order to obtain the most representative sample for the bale. Sampling from the middle of the bale will help to avoid biased moisture contents due to evaporation or absorption of moisture from the ground. Sampling from the end of the bale will allow the sample to reflect more lengthwise area of the bale, which represents more area of the field, due to the way the bale is created.

In addition to variability in individual bales, corn stover processing facilities will need to know the variability of moisture and ash content within a set of bales harvested from the same field. This will allow the facilities to know how many samples they need to take from each field in order to make an informed decision on bale quality. It was determined that windrower type influences variability. Rakes, for instance, will provide material with higher variability. Additionally, shredders will generally provide higher moisture material. However, as the harvesting season progresses, the variability of moisture content will gradually decrease, and therefore the higher moisture material will not matter greatly. Using the field variability data from 2011 harvested fields, the number of samples needed to take in each field can be determined, if given a desired precision level. For example, in a field with a maximum ash content variability of ±3%, with a desired precision of ±5%, 45 samples should be taken. This is a very high sample number, however, so processing facilities may want to allow lower precision levels.

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