PERSPECTIVE

SPECIAL FOCUS: ADVANCED FEEDSTOCKS FOR ADVANCED BIOFUELS

Understanding biomass feedstock variability

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Kevin L Kenney^{*1}, William A Smith², Garold L Gresham³ & Tyler L Westover¹

If the singular goal of biomass logistics and the design of biomass feedstock supply systems is to reduce the per-ton supply cost of biomass, these systems may very well develop with ultimate unintended consequences of highly variable and reduced quality biomass feedstocks. This paper demonstrates that, due to inherent species variabilities, production conditions and differing harvest, collection and storage practices, this is a very real scenario that biomass producers and suppliers as well as conversion developers should be aware of. Biomass feedstock attributes of ash, carbohydrates, moisture and particle morphology will be discussed. We will also discuss specifications for these attributes, inherent variability of these attributes in biomass feedstocks, and approaches and solutions for reducing variability for improving feedstock quality.

Although the broad-scale use of agricultural crops and logging residues for the production of bioenergy are emergent, biomass supply systems inherit the experience of mature agriculture and logging industries. The development of the biomass supply systems on the foundation of these industries has carried with it the assumption that biomass feedstock quality specifications are the same as forage and pulpwood. This view has supported a primary focus on **feedstock logistics** to reduce the cost of feedstock supply, with relatively little emphasis on feedstock quality.

Biomass cost-to-value relationships have been a major driver behind biomass logistics research, development and demonstration. Much progress has been made in improving biomass collection and preprocessing machinery performance and efficiencies [1,2], reducing material losses throughout the supply chain [3,4], and expanding harvesting and storage operational windows [5]. However, an emphasis on feedstock quality is still lacking, with the conventional approach of merely offsetting quality-related issues by driving down logistics costs.

The emphasis of cost over quality is clearly demonstrated by the current pricing structure for biomass that assesses value on a US dollar per dry ton basis [6]. Otherwise, valuations based on dollar per clean, dry carbohydrate or dollar per clean, dry British thermal unit would exist. The overwhelming need for a low-cost, sustainable supply of biomass feedstocks is largely the driver behind this valuation, although conversion of developers' use of 'pristine' feedstocks composed of clean, homogeneous structural tissues certainly contributes to a lack of understanding of feedstock quality and specifications. Some that have scaled up to pilot-scale operations that require larger quantities of feedstock have experienced vast differences between pristine and 'field-run' feedstocks [7]. The quality of field-run biomass is impacted by inherent species variability, production conditions and differing harvest, collection and storage practices, which often differ from pristine research feedstocks that are handled very carefully from field to laboratory. Even the process of cutting biomass and laying it on the ground before collecting it introduces ash and other contaminants that can affect the overall chemical composition.

As pioneer biorefineries move from technology development and deployment to operations, and their focus changes to process optimization, experience with

¹Biofuels & Renewable Energy Technology, Idaho National Laboratory, PO Box 1625, Idaho Falls, ID 83415, USA ²Biological Systems Department, PO Box 1625, Idaho Falls, ID 83415, USA ³Interfacial Chemistry Department, PO Box 1625, Idaho Falls, ID 83415, USA *Author for correspondence: Tel.: +1 208 526 8098; Fax: +1 208 526 2639; E-mail: kevin.kenney@inl.gov



Key terms

Feedstock logistics: Operations that source and supply feedstocks to the end user, in this instance, the biorefinery.

Field-run biomass: Biomass that has been collected using commercial harvesting systems, undergone storage and represents what would be supplied at commercial scale.

Biochemical conversion: Conversion process that relies upon enzymatic activity and/or biological fermentation in at least one step to produce the final value-added product.

Lignocellulosic biomass: Plant materials rich in cellulose and

hemicellulose; may be derived from woody or herbaceous plants grown specifically for consumption or collected as residues from other operations.

Thermochemical conversion:

Conversion process that relies upon high-temperature chemical conversions such as pyrolysis, typically in the presence of catalysts, to produce the final value-added product. field-run feedstocks will move quality and specifications to the forefront. Ultimately, quality-based valuations, which include devaluation for moisture, noncarbohydrate content (e.g., ash content), as well as other contaminants or conversion inhibitors, will evolve as the importance of feedstock quality is realized. Such a valuation is also necessary to incentivize farmers and suppliers to implement best management practices that preserve biomass quality, for biorefineries to enforce best management practices, and ultimately for biomass to be traded as a commodity with definable and consistent quality measurements (e.g., specifications).

Until then, the lack of specifications should not encumber or delay feedstock development to move in this direction. Focus on supplying feedstock of consistent quality attributes will go a long way in enabling specifications, removing barriers to

accessing the USA's vast supply of biomass resources, reducing biofuel production costs and enabling a national-scale biorefining industry.

In fact, the need for consistent feedstocks will never go away as all industrial processes require consistency in raw materials to operate efficiently. Imagine the complexity of an egg sorting and packaging facility if some eggs were oval shaped and others were square. The fact that all eggs are the same shape and more or less the same size greatly enhances the efficiency of sorting and packaging. Feedstock consistency is also critical to stable and efficient biorefinery operations. Consider the economic implications if one load of feedstock yielded 90 gallons of fuel per ton and another yielded 60, or if one year the feedstock contained 10% moisture and the next year 30%.

This paper will show that this scenario is indeed within the realm of possibility given the variability inherent in biomass feedstocks without standard practices in place to provide consistent quality. We will further develop this by evaluating the variability of biomass attributes, discussing these attributes relative to general conversion specifications and describing broad solutions for addressing variability. The ultimate goal of this paper is to present a compelling perspective that informs conversion developers and empowers feedstock producers and developers who, even in the absence of the specifications, can do much to advance the biofuels industry by reducing variability and supplying feedstocks of consistent quality attributes.

Ash

At this time, no direct specifications for ash exist relative to the biochemical conversion of lignocellulosic biomass to ethanol. However, ash content has at least two indirect influences on the feedstock value to the conversion process. First, when ash content increases, especially due to the addition of a nonbiomass constituent (e.g., soil), the convertible biomass content decreases. As will be discussed later, any increase in noncarbohydrate constituent reduces the proportion of structural carbohydrates present. Second, ash - specifically soil - increases the neutralization capacity of corn stover during dilute-acid pretreatment, which reduces the conversion yields [8]. Ash has a negative impact on feedstock value for biochemical conversion; it displaces valuable carbohydrate and decreases pretreatment efficacy. For this reason, current conversion process analyses rely upon an average modeled value of approximately 5% dry basis [9].

Ash specification in pyrolysis-based thermochemical conversion processes is low – less than 1% – reflecting the negative impact of ash upon conversion [10]. Ash components impair catalysts and contribute to slag formation within the combustion processes. Elevated feedstock ash contents lead to elevated ash content and subsequent instability and corrosivity of pyrolysis oil [11]. To meet the aggressive ash specification, existing thermochemical processes rely upon debarked woody feedstocks such as hybrid poplar, willow and pine. Pilot-scale gasification has been demonstrated with herbaceous feedstocks of higher ash content - corn stover, switchgrass and wheat straw – with varying gas compositions, tar concentrations and gasifier efficiencies [12]. However, current process design and economic analyses show that higher conversion costs and maintenance requirements result from the use of herbaceous feedstocks in lieu of clean woodchips [13].

Introduction to variability

Biomass ash content generally comprises the inorganic constituents found in biomass, and it varies considerably among and within biomass materials types (Figure 1). This dataset of 840 individual samples of herbaceous biomass – predominantly corn stover, with lesser populations of *Miscanthus* and wheat straw – represents a growing library of biomass feedstock properties maintained at the Idaho National Laboratory (ID, USA). Results shown in Figure 1 are from individual samples rather than whole bales and do not necessarily represent bulk ash contents. The bars show the frequency of combined feedstock ash values within 2% bins spanning from 0 to 39% by mass; the lines indicate the frequency of ash values by individual feedstock. The majority of these samples fall into the range of 7–9%, which is above the thermochemical specification of less than 1% and the biochemical target value of 5%.

Sources of variability

Understanding biomass ash content and variability represented in Figure 1 requires that we differentiate between the sources of ash, which include structural ash associated with the plant cell walls, vascular ash associated with the plant cell extracts and introduced ash resulting from soil contamination. For distinction, structural and vascular ashes together comprise a fraction we define as 'physiological ash', which is a property of the feedstock. Introduced ash is largely a property of the feedstocks' handling meth-



Figure 1. The frequency of total ash concentrations of selected samples of three herbaceous biomass feedstocks (N = 840). Bars indicate the combined concentration frequency; lines indicate the concentration frequency by feedstock.

ods, which can entrain varying amounts of soil during logistics operations of harvest, collection, handling and storage, with harvesting methods having the greatest influence on soil contamination in baled herbaceous feedstock materials.

Accurate interpretation of the histogram data relative to these sources of ash is not possible without a metadata analysis that is beyond the scope of this paper. However, the following general interpretation is offered. Ash distribution is not normally distributed across samples; corn stover has a long tail containing several very high ash samples. Miscanthus appears to have a bimodal distribution, which likely reflects the limited dataset and may also represent the impact of sampling, location or environmental variables discussed below. The lower tails of the histograms represent physiological ash levels; these are the lowest levels that can be expected from these feedstock types. The upper tails of the histogram extending to very high ash contents represent the influence of soil contamination. The bulk of the histogram lying between the two tails represents real-world conditions where a certain amount of introduced ash is inevitable due windblown or rain-splashed soil becoming entrained in biomass either in the field, storage or transportation. These nominal levels need to be better understood and defined, as they are the ash levels that an end-user biorefinery or power plant will come to expect.

Physiological ash results from intrinsic biomass properties such as plant type, maturity and anatomical fractions collected [14–16] and range from as low as 0.1% in woody biomass such as debarked pine wood to as high as 25% in herbaceous crops such as rice straw (see Table 1, condensed from Appendix A of Tao et al. [16]). The ash data in Table 1 also shows how inherent ash content varies both among biomass types (e.g., herbaceous versus woody) and within biomass types based on anatomical fractions (e.g., wood versus residue and corncob versus corn stover). The data from Tao et al. confirm the visual comparisons of corn stover, wheat straw and Miscanthus ash contents in the histogram, which suggests that Miscanthus has lower inherent ash content than corn stover and wheat straw, with the latter two being similar in total ash content [16]. The data in this table also show several other interesting trends. For example, woody biomass is generally lower in ash content than herbaceous biomass; this is particularly evident in the comparison of wood (i.e., without bark, leaves and branches) to any of the herbaceous feedstocks in Table 1. Additionally, among herbaceous materials there exist large differences in ash contents - for instance, the ash content of wetland species (e.g., rice) is greater than those of more water-efficient species (e.g., Miscanthus), and ash content varies by anatomical fraction collected in the case of corncob versus whole corn stover [17].

Plant maturity also plays a major role in physiological ash content. A number of studies have shown the concentration of ash to decrease in forages as they mature [18-20]. Delaying harvest from fall until late winter to early spring further reduces ash concentrations in perennial grasses (reed canary grass [21], switchgrass [22] and *Miscanthus* [23,24]). Environmental factors such as soil

Table 1. Mean values and ranges for selected lignocellulosic biomass feedstocks.				
Feedstock	Mean ash (%) [†]	Reported range (%)		
Herbaceous				
Corncob	2.9 (13)	1.0-8.8		
Corn stover	6.6 (28)	2.9–11.4		
Miscanthus straw	3.3 (13)	1.1–9.3		
Reed canary grass	6.7 (11)	3.0-9.2		
Rice straw	17.5 (22)	7.6–25.5		
Sorghum straw	6.6 (5)	4.7–8.7		
Sugarcane bagasse	5.6 (27)	1.0–15.2		
Switchgrass straw	5.8 (21)	2.7–10.6		
Wheat straw	8.0 (50)	3.5–22.8		
Woody				
Oak residue	2.5 (5)	1.5–4.1		
Oak wood	0.6 (11)	0.2–1.3		
Pine residue	2.6 (4)	0.3-6.0		
Pine wood	1.0 (40)	0.1–6.0		
Poplar wood	2.1 (14)	0.5-4.3		
Spruce residue	4.3 (2)	2.2–6.4		
Spruce wood	0.8 (5)	0.3–1.5		
Willow residue	2.0 (1)	2.0-2.0		
Willow wood	1.5 (18)	1.0–2.3		
[†] Mean value presented with number of reported samples in parenthesis.				

costs, for disposing of inherent ash at 2.5 cents per gallon plus the cost to dispose of the additional soil, double at soil concentrations of 6.3% and triple at 12.1%, increasing the ethanol production cost by 1.2 and 2.3%, respectively. Ash contents shown in Figure 1 indicate that these levels of soil contamination are common in corn stover. The impact of soil disposal costs on ethanol production cost is modest, but represents both variability and uncertainty in total production costs. Current bioconversion research is working to reduce uncertainties around xylan pretreatment efficacy [8] and pretreatment acid loading [7], both of which impact yield and minimum ethanol selling price by roughly the same order of magnitude as our analysis of soil disposal. Thus, we can conclude that these disposal costs, though modest, are not insignificant.

type, soil water chemistry and fertilization also affect feedstock-inherent ash concentration and its elemental ash composition [24-27].

Impact of variability

The significance of biomass ash content varies depending on the tolerance of the conversion process to ash. At the very least though, soil contamination represents an additional variable operational cost to the biorefinery as it reduces pretreatment efficacy, increases wear in handling and feeding systems, and accumulates as a waste stream that requires disposal [8]. Unable to directly quantify the former, we examine the economic impact of soil-derived ash on biorefinery disposal costs. In their 2011 biochemical conversion design report, Humbird et al. estimated waste disposal costs of US\$28.86 per ton, accounting for 2.5 cents of the \$2.15 per gallon minimum ethanol selling price for a dilute-acid pretreatment, enzymatic hydrolysis and fermentation process [7]. Using this disposal cost from Humbird et al., we estimated the additional cost for soil disposal over a range of possible soil contamination levels (Figure 2) [7]. In this figure, the red line shows the disposal cost estimated by Humbird et al. for corn stover feedstock containing 5 wt% inherent ash (i.e., this assumes no soil contamination); the blue line shows the additional cost of soil disposal for introduced ash contents ranging from 2.5 to 15% [7]. The combined

Solutions to variability

Efforts to control ash concentration in biomass feedstocks must focus on both physiological ash - including vascular and structural ash - and introduced ash. Biomass selection is the most certain solution to controlling the former, while operational improvements are best suited to address the latter. Focusing on low-ash feedstock would generally favor woody biomass over herbaceous (Figure 1). Biomass fractionation – selectively removing a particular anatomical fraction or tissue takes the feedstock selection approach a step further. Note the differences in ash content between the forest residues and wood fractions in Table 1; residues contain 1.3-5.4-times the average ash content of the woods. This fractionation approach, involving debarking of woody biomass (particularly pine) is the current solution for meeting the aggressive ash specification of the thermochemical conversion processes.

An analogous improvement by anatomical fractionation occurs in herbaceous feedstock through separation of corncobs and corn stover, where the average ash content for whole stover is 2.3-times that of cobs. This type of solution through selective harvest of higher value fractions represents a trade-off between quality and economics, where the corncob makes up only 15% of the total stover dry matter [15]. Assuming that 50% of the available stover can be removed, approximately threetimes the number of acres would need to be harvested to

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collect the same mass of corncobs in a cob-only harvest as corn stover under a normal stover harvest [28].

Operational improvements through 'best management practices' that reduce soil contamination during biomass harvest will significantly reduce both the quantity and variability of biomass ash content. Single-pass and reduced-pass baling reduces soil entrainment into bales by reducing feedstock contact with the soil [29]. Additional improvements may be made by delaying the time of harvest to permit leaching of vascular ash constituent, which has an additional benefit of reducing nutrient loss from the field [30,31]. Practices such as selective cut height that reduce soil and ash-laden anatomical fractions, and single-pass harvest that reduce biomass ground contact, reduce soil contamination dramatically [29,32].

Finally, preprocessing solutions such as hot water or acid washing may provide solutions for removing ash and ash components from feedstock prior to conversion. While the study's authors did not suggest the practice for a full-scale industrial process, Das et al. reported on the effectiveness of a dilute hydrofluoric acid pretreatment for reducing ash concentrations in sugarcane bagasse from 2% (dry mass) to less than 0.05% [11]. The method was presented as a maximum effective ash removal method. Other more practical washing treatments have been used to remove alkali metals from ash to improve pyrolysis performance [33-35]. Davidsson et al. used a water and acetic acid treatment to reduce alkali metal release from wheat straw and wood wastes to levels of 30-70% of untreated material during low-temperature combustion and up to 90% at higher temperature conditions [33]. Turn et al. demonstrated an intensive ash removal process consisting of milling, mechanical dewatering and water leaching of banagrass (a tropical forage also known as elephant grass or napier grass) that removed 90% of the initial potassium, 54% of sulfur, 70% of magnesium, sodium and phosphorus and nearly all of the chlorine [35]. Ash reduction through washing or leaching may also contain tradeoffs in removal of soluble or hydrolysable components from the biomass depending on the soluble components present in the feedstock and the intensity of the wash (temperature, duration and severity). Costs associated with additional processing steps of leaching, acidification, neutralization and drying (for combustion or pyrolysis processes) may limit intensive washing to use for high-value products with the potential to offset the additional operational and capital equipment costs incurred.

Sugars

The economics of biofuel or biopower production are tightly coupled to yield, with feedstock composition being a critical variable. For thermochemical conversion



Figure 2. Additional costs for soil disposal relative to ethanol production costs. Red line shows existing solid waste disposal costs of US\$0.0251 per gallon; blue line shows the additional disposal costs for soil contents from 2.5 to 15% (dry weight basis).

(gasification/pyrolysis) and direct combustion processes, overall energy content (the amount of energy released when a material or fuel is combusted) of biomass feedstocks is an important consideration. Although carbohydrate content is a main source of energy content in biomass, it is not an explicit specification for these conversion processes. In contrast, biochemical conversion processes are particularly sensitive to carbohydrate content, or, more specifically, structural sugars content of the feedstock material. The ratio of C5/C6 sugars and the accessibility of these sugars are also important in optimizing pretreatment and fermentation conditions.

At this time, there are few clear and explicit specifications for sugars content established by conversion technology developers or biorefineries. In development of their technoeconomic model for production of cellulosic ethanol from corn stover, Humbird *et al.* established a total structural carbohydrate specification for corn stover of 59 wt% [7]. This specification was based on the composition of a representative sample chosen from an overall sample distribution of 508 commercial corn stover samples, collected from 47 sites in eight states over a 3-year period.

Introduction to variability

In general, cellulose and hemicellulose make up approximately 60% of the total biomass dry matter, with 15–25% lignin and the remaining being 'other' compounds present, including soluble components (extractives, waxes, acids and salts), as seen in Figure 3. The soluble components strongly affect the amounts of structural constituents in the biomass [36]. This is highlighted in Figure 3 with the 'extractives and other' content varying from 5 to 35%. As a rule of thumb, all lignocellulosic biomass follow this general compositional makeup, but due to a number of factors that we will discuss, carbohydrate content of biomass feedstocks can exhibit enough variability to significantly impact biofuels yields and economics (Figure 4) [7].

The frequency histogram depicted in Figure 4 includes 684 individual samples of herbaceous biomass consisting predominantly of corn stover (n = 557), with Miscanthus (n = 80), wheat straw (n = 23) and others (n = 24) making up the remainder (the latter includes corncobs, mixed prairie grass, prairie cordgrass, sorghum, switchgrass and lodgepole pine). Results shown in this histogram are from individual samples rather than whole bales and do not necessarily represent bulk sugar concentrations. The bars show the frequency of combined feedstock glucan and xylan contents within 2% bins spanning from 39 to 66% by mass; the lines indicate the frequency of structural sugar contents by individual feedstock. Table 2 provides additional detail relative to corn stover, corncobs, Miscanthus, wheat and all of the samples combined. The concentration of structural sugars (glucan and xylan) for all feedstocks ranged from 39 to 66 wt%, with a mean of 54%. The majority of these samples fall below the 59% structural carbohydrate specification established by Humbird et al. discussed above [7].

The frequency histogram shown in Figure 4 is dominated by corn samples and, therefore, mainly demonstrates variability within corn stover compositions.



Figure 3. Range of composition of the three most prevalent components of lignocellulosic biomass dry matter: hemicellulose, cellulose and lignin. 'Extractives and other' includes, but is not limited to, such constituents as soluble sugars, protein and inorganics (ash). Reproduced with permission from [75]. This data shows variability among feedstocks as well as within feedstocks, with greatest variability exhibited by corn stover, followed by corncobs, wheat straw and *Miscanthus*.

Sources of variability

A metadata analysis of the frequency histogram data to elucidate causes and statistical differences in the data is beyond the scope of this paper. However, a review of potential sources of variability follows.

Consistent and accurate sampling of biomass is always of primary importance in biomass characterization. Most of the samples represented in the histogram were obtained from core samples collected from baled biomass. The *Miscanthus* samples are the main exception, with these samples collected by hand, not harvested using conventional harvesting equipment; this may have resulted in reduced noncarbohydrate components (such as ash and degradation products), thus increasing the relative concentration of structural sugars. The importance of sampling is highlighted in the work by Duguid *et al.*, who measured differences in wheat straw compositions from samples collected at different locations within the field, showing the importance of collecting multiple samples from randomized locations [26].

Templeton *et al.* evaluated the extent to which commercial hybrid corn stover composition varied and assessed the variation among genetic, environmental or annual influences using near-infrared spectroscopy/partial least squares multivariate modeling [36]. One of the primary conclusions of the research indicated that stover compositional variability observed could be separated into three primary factors listed in order of decreasing influence – harvest year, environment and feedstock variety.

The annual factor, or harvest year, noted by Templeton *et al.* is difficult to assess as it is inherently linked to certain environmental variables that change from year to year (e.g., weather) [36]. Assessing the annual factor and the interactions with other variables requires very tight control of experimental conditions and necessitates solid statistical design and use of experimental test plots. The annual factor may very well explain some of the variability in our data as these samples span several years, but testing and evaluation of harvest year effects are beyond the scope of this paper.

As described by Templeton *et al.*, environmental factors include uncontrollable factors such as soil type and weather, as well as controllable factors such as agronomic practices (e.g., tillage, planting data, fertilization and herbicide treatment) [36]. Agronomic practices of importance to biomass quality also include seasonal time of harvest, selection of harvesting systems and storage practices.

Harvesting practices that affect the composition of collected biomass include seasonal time of harvest as well as the specific machinery used to harvest biomass. The effect of time of harvest on the ash content of perennial grasses was discussed in the previous section. Adler et al. also showed marked differences in switchgrass carbohydrate concentrations between fall and spring harvests, with an increase in structural carbohydrates at spring harvest due to leaching of soluble components such as sugars, protein and organic acids over the winter [22]. Seasonal time of harvest also affects the composition of harvested biomass due to the loss of anatomical plant parts either naturally by abscission or by their reduced ability to withstand the forces of weather as they become dry and brittle. Shinners and Binversie noted this effect with the loss of leaves, husk and upper stalk over the course of the corn harvest season as the stover dried and became brittle [37]. Adler et al. noted a similar effect with the loss of the seed head in switchgrass and the corresponding reduction in starch content that resulted from delaying harvest from fall until spring [22].



Figure 4. Structural carbohydrate (glucan plus xylan) concentrations of biomass feedstocks, principally corn stover, *Miscanthus* and wheat straw. Bars indicate the combined concentration frequency; lines indicate the concentration frequency by feedstock. 'Other' includes samples of corncobs, mixed prairie grass, prairie cordgrass, sorghum, switchgrass and lodgepole pine.

The effect of harvest system on the composition of the collected biomass is best demonstrated with corn stover. In their investigation of corn stover harvesting systems, Prewitt *et al.* showed that collection efficiencies (the ratio of plant mass removed from the field during harvesting to the total mass available in the field) to vary widely from 32.1 to 94.5% among six systems tested [38]. Although their study did not quantify the collection efficiency of different fractions of the corn plant (e.g., stalk, cob, husk and leaves), we ourselves have noted that different systems tend to collect different stover fractions. A wheel rake, for example, which operates in contact with the ground, collects more cobs than a bar rake or a flail shredder that do not normally contact the ground. A mower, such as a flail shredder, collects lower stalk material where rakes usually do not. Collecting the stover that passes through the combine, either by dropping a windrow behind the combine or through single-pass methods, increases the amount of corncobs collected compared to methods that utilize a

Table 2. Structural carbohydrate compositions (glucan plus xylan) for corn stover, corncobs, *Miscanthus*, wheat and the combination of these, for samples shown in Figure 4.

wheat and the combination of these, for samples shown in Figure 4.					
Measurement	Combined feedstocks	Corn stover	Corncobs	Miscanthus	Wheat
Mean (%)	54	53	59	61	50
Range (%)	27	27	16	10	15
Minimum (%)	39	39	49	55	41
Maximum (%)	66	66	65	65	57
Count	684	557	14	80	23

rake or flail shredder. This variability in anatomical composition of collected stover translates to differences in carbohydrate content, as supported by studies that have shown compositional differences among anatomical fractions. In their investigation of corn stover compositional variability, Pordesimo *et al.* noted different proportions of glucan and xylan among stalk, leaf and husk fractions [15]. Duguid *et al.* reported similar characteristics of differing compositions among wheat straw anatomical fractions [39].

Many of the corn stover samples included in Figure 4 represent a range of harvesting systems. Some are from conventional harvesting systems similar to those discussed by Prewitt *et al.* [38] and others are experimental variations of advanced harvesting systems such as those described by Hoskinson *et al.* [32] and Karlen *et al.* [28]. Both of the latter studies evaluated prototype single-pass harvesting scenarios differentiated by cut height. These studies consistently show that stover composition changes as the different proportions of the plant are harvested, with glucan content increasing with higher proportion of lower stalk and xylan increasing with higher proportions of cob and husk fractions.

Finally, degradation and consumption of biomass carbohydrates in storage is a large source of compositional variability. Baled feedstock stored outdoors is most susceptible to dry matter loss, which does not occur uniformly among all of the measured biomass constituents, but occurs preferentially to water-soluble components and the structural components of hemicellulose and cellulose. The residual biomass is enriched in lignin and, depending upon the impact of water exposure, ash. For example, Shah et al. show increases in the lignin and cellulose fractions and decreases in the hemicellulose fraction as a result of dry matter losses in baled corn stover; dry matter losses were in the range of 5–17% [40]. The apparent enrichment in lignin and cellulose in the remaining dry matter was a result of selective degradation of hemicellulose components such as xylan. Similar compositional changes were shown to occur in baled reed canary grass and switchgrass [5]. In both these studies, hemicellulose components (C5 sugars of xylose and arabinose) were lost to a greater degree than cellulose components (glucose). When dry matter loss occurs it is not uniform throughout the bale, which creates further compositional variability within storage. Spatial differences in the loss of watersoluble extractives and xylan were reported in the outer, exposed regions of baled switchgrass [41]. As expected, the greatest compositional changes occurred in the most severely degraded regions of the bales.

Impact of variability

In a study of corn stover compositional variability, researchers at the National Renewable Energy Laboratory (CO, USA) collected and analyzed 735 commercial corn stover samples from corn fields in the US Midwest [36]. The structural sugar content (glucan and xylan) ranged from approximately 50 to 60 wt% with a mean of 59 wt%, and the sum of all structural sugars (glucan, xylan, arabinan, galactan and mannan) ranged from approximately 54 to 71 wt%. Ruth and Thomas presented the results of process modeling evaluating the effects of this corn stover variability on cellulosic ethanol vields and production costs [42]. From this analysis, they developed a correlation that showed ethanol yield to vary linearly with structural sugar content in the amount of 1.38 gallons per ton per percent structural carbohydrates. If we apply this correlation to the sugars data shown in Figure 4, the corresponding estimated ethanol yield ranges from approximately 55 to 90 gallons of ethanol per dry ton. These results are only based on glucan and xylan content, so actual yields considering total structural sugars are slightly higher. It should be noted that there are many factors that affect the conversion efficiency of carbohydrates to ethanol, and the correlation developed by Ruth and Thomas for their corn stover dataset may not apply across the different biomass types represented in Figure 4 [42]. Nonetheless, this demonstrates how variability in carbohydrate content can have significant implications in biofuel yield and economics.

Solutions to variability

Compared with other feedstock attributes such as moisture or ash, where options exist to reduce these attributes to levels desired by conversion processes, there are no explicit logistical or preprocessing options that increase intrinsic carbohydrate content of the biomass. Increasing the intrinsic carbohydrate content of biomass crops is an area of ongoing research. Rooney et al. illustrated modest increases in structural carbohydrate content of photoperiod-sensitive sorghum over that of forage and sweet sorghum [43]. Other crop genetics approaches involve improving carbohydrate conversion efficiency as a way to improve yields, with a similar effect to increasing carbohydrate content. Researchers at the Joint Bio-Energy Institute (CA, USA), for example, are working on developing biomass feedstocks with reduced lignin levels or lignin modification to reduce recalcitrance and improve sugar yields [27,44-46].

Normalizing year-to-year agronomic practices and harvesting strategies is another approach to optimize chemical composition and reduce feedstock variability as identified in the findings of Templeton *et al.* [36]. Best management practices associated with proper selection of harvest and storage systems is important in preserving biomass quality and minimizing carbohydrate variability. The timing of harvest and the selection of harvest systems should be chosen to facilitate removal of the highest quality biomass for the particular conversion process. As discussed above, this may include preference of specific plant fractions. Minimizing soil contamination during harvest, storage and handling is beneficial for reducing ash content as described above, and has the secondary benefit of increasing carbohydrate content and reducing carbohydrate variability. Finally, proper management of moisture before and during storage is critical for preserving carbohydrates through storage time [3]. Moisture-tolerant storage methods are needed that extend shelf life, maintain carbohydrate content, reduce formation of solubles and minimize variability; however, advanced storage methods must be balanced against the higher storage costs.

Formulation (or blending) is a preprocessing technology option that offers potential for upgrading the carbohydrate content of a feedstock material and reducing variability. The overarching goal of biomass formulation is to facilitate the use of consistent feedstocks composed of different and variable sources of biomass. Feedstock formulation is not a new concept in many market sectors. For example, different grades of coal are blended to reduce sulfur and nitrogen contents for power generation [47,48], grain is blended at elevators to adjust moisture content [49], animal feeds are blended to balance nutrient content [50] and high ash biomass sources are mixed with low ash coal to allow their use in biopower [51]. Tumuluru et al. also discussed the concept of biomass formulation to improve physical and chemical properties of biomass for co-firing biomass with coal [52]. Using Figure 4 as an example, sugar content variability could be significantly reduced by blending of the corn stover resource. Although the histogram was skewed toward lower sugar values, a higher percentage of high-value corn stover could be blended to normalize the mean sugar content to values above the determined mean of 54% and significantly reduce variability. Moreover, sugar content could be improved through aggregation of the corn stover with select feedstocks such as sugarcane bagasse, which as described by Betancur and Pereira has a structural carbohydrate content greater than 60% [53]. Formulation could be implemented at a preprocessing depot or at a biorefinery to meet customized process parameters and improve overall sugar content of the incoming feedstock.

Particle morphology

At some point in the supply chain, biomass must be preprocessed to reduce it to a bulk solid that can be metered into a conversion process. Particle morphology – sizes, shapes and densities – can significantly affect performance in both handling systems and conversion processes and, thus, physical properties of the biomass bulk solid are important for both biochemical and thermochemical conversion processes [54–56]. Thermochemical reaction kinetics are particularly sensitive to particle morphology, especially as reaction rates increase and residence time in the reactor decreases. It has been noted, however, that because of their greater reactivity, biomass particles can be substantially larger than coal particles in co-fired gasifiers. Biochemical conversion processes tend to be more tolerant of variability of particle morphology, with particle morphology and physical properties dictated more by requirements of the engineered systems [57,58].

Introduction to variability

In our experience of producing and supplying feedstocks in collaboration with conversion developers, we have seen a wide range of feedstock particle-size requirements. Feedstocks for fast pyrolysis are generally approximately 2 mm in size [59-61]. Feedstocks for biochemical conversion processes are varied, ranging from 6 to 75 mm in size. Often feedstock particle sizes are driven more by engineering systems than by the reaction kinetics of the conversion processes. Excessive fines are often a problem with hammer-milled feedstocks, clogging filters, reducing permeability of the bulk solid to gases and liquids, and causing problems with nuisance dust. Over-sized particles also create problems plugging air locks and pneumatic transfer lines. Often the distribution of particle sizes with a combination of fine and coarse particles is most important. For example, one of our collaborators experienced trouble with blowouts in a pressure seal of a plug flow pretreatment reactor when pretreating hammer-milled corn stover [NATIONAL RENEWABLE ENERGY LABORATORY, PERS. COMM.]. Further processing of the hammer-milled material through a knife mill of the same nominal screen size eliminated the problem. Progressive deterioration of particles as they move through multiple unit operations can also be a concern because as the amount of fines increase, the handling and conversion behavior may be detrimentally altered [62]. Thus, even if ideal specifications are achieved, care must be taken so that subsequent unit operations do not unintentionally modify material properties.

Sources of variability

The performance of biomass feedstocks in handling and feeding systems depends upon many factors including particle size and shape distributions, bulk density, chemical composition of particles, moisture content, temperature, presence of trapped gases and the unique stress (i.e., compaction) history of the material. The handling performance of feedstock materials as they relate to these parameters is summarized in Table 3. Of these parameters, particle size and moisture content typically receive the most attention. Often the particle size 'specification' is based on the screen size of a laboratory mill, rather than a thorough classification of particle-size distribution. A screen size specification is often misleading because particle size is a function of many variables. For example, the type of mill has a strong impact on resulting particle morphology. Knife mills are typically used for laboratory sample preparation, whereas hammer mills are often used in high-throughput industrial-scale applications; particle morphologies differ significantly between the two [63]. Typically, it is observed that hammer mills produce materials with finer particle sizes than knife mills using the same screen size, and in both cases the mean particle size is significantly smaller than the screen size. Likewise, the particle-size distribution tends to be much tighter from a knife mill than from a hammer mill. Operational parameters such as hammer speed and geometry, as well as the material feed rate, also affect particle morphology, as do biomass material properties such as incoming particle sizes and moisture content [63].

Impact of variability

These examples illustrate that differences in particle size and shape distributions that result from different processes can play a significant role in feed systems. A landmark publication in the 1980s indicated that processes for liquids and gases typically ran at close to 90% of their design capacity, while similar processes for bulk solids tended to operate at only 40–50% of their design specification, often due to handling difficulties [64]. Plants that handled raw solid feedstocks performed the worst, achieving less than 40% of their capacity in the first year [64]. Delayed startup times and operation below the designed capacity can have serious consequences in terms of the cost of the final product and missed business opportunities.

An updated report by Merrow in 2000 indicated that performance has generally improved over the years with plants that handled raw solid feedstock operating at 77% of design capacity [64]. Importantly, however, many of the plants included in the survey handled fine powders, which have benefited from decades of intense research in the foods and pharmaceuticals industry. In addition, food and pharmaceutical powders tend to be noncohesive, have small particle sizes and distributions, high densities and low compressibilities. In contrast, feedstocks for lignocellulosic biofuels production are often cohesive, have large particle size variations, low densities and high compressibilities – causing them to arch over

Table 3. Noninclusive summary of feedstock performance aspects related to particle morphology.					
Performance aspect	Governing parameters/mechanisms	Impacts			
'Bulk solid flowability' based on unconfined shear strength	Particle–particle interactions that depend upon particle size and shape distributions, bulk density, chemical composition of particles, moisture, temperature and presence of trapped gases	 Materials with low shear strength flow under gravity without flow aids Easily flowing material: Facilitates emptying and cleaning equipment to prevent spoilage of perishable products Readily fills containers to minimize storage and transportation volumes Exerts lower stresses on storage structures Feeds uniformly for processes that requires consistent flow Tends to be easier to mix and blend If material is overly aerated, it may flow too freely and flood equipment 			
Time consolidation or caking (increase in shear strength due to prolonged storage under a compressive stress)	Time consolidation can be due to different physical, chemical or biological effects, such as crystallizations between particles, material creep that enlarges contact areas between particles, capillary condensation and fungal growth	 Loss of live storage space because material adheres to storage container walls Risk of loss of perishable material due to microbial or fungal activity Erratic flow with large dynamic forces on containing structures Material bridges or ratholes over outlet preventing flow 			
Handling properties in a slurry for enzymatic conversion	Particle-particle and particle-slurry interactions through particle shape, size and ploy dispersity	 Lower volatility resulting in increased conversion efficiency Acidity of final product bio-oil may be reduced 			
Reactivity for thermochemical and biochemical conversion processes	Particle sizes and shapes affect surface area to volume ratios	 Small particles have much greater thermochemical reaction kinetics compared with large particles, especially when the thermal conductivity of the particle is low, like biomass More reactive particles can be substantially larger than less reactive particles. For example, biomass particles can be larger than coal particles in co-fired gasifiers 			
Permeability of bulk solid to gases or liquids	Pore spaces between particles that allow gases and liquids to flow through bulk solid	 Low permeability restricts chemical access to material's interior, slowing reactions Low permeability can limit discharge rates from outlets 			

hopper openings and plug mechanical and pneumatic conveying systems.

Solutions to variability

Often, feeding and handling problems are the result of systems that are engineered without a clear picture of material variability. Designing handling and feeding systems to accommodate this variability is possible, but as the system designs become more robust, they also get more expensive. It is therefore a trade-off between capital (more robust systems) and operating expenses (down time). Relying on gravity feed, high packing densities, low moisture and consistent particle-size distributions keeps equipment designs simple and costs low, but puts higher requirements on material properties. When material properties are not sufficiently controlled to equipment design specifications, the equipment operates inefficiently and is prone to malfunction.

There are two main approaches to solving material handling problems. Either equipment systems are engineered to specific materials or material properties, or materials themselves are engineered to feed properly in specific equipment systems. The first approach is by far the most common, although a combination of both approaches is often best, especially when equipment must handle multiple feedstock materials.

This dual approach is illustrated in Figure 5, which shows how the reliability of a hypothetical handling/feeding system, such as a gravity-feed hopper or pneumatic conveyance line, is improved by a combination of a more robust engineering design and tighter control of feedstock material properties. The range of expected feedstock properties - moisture and particle size - and the corresponding design specification of our hypothetical feeding system is illustrated in the regions labeled 'expected feed' and 'system design', respectively. Variability of raw materials, which is inevitable given the diversity of sources, varieties and seasonal delivery over the course of continuous full-scale operation, often violates machinery design specifications as illustrated by the region labeled 'actual feed'. Therefore, better control and design of preprocessing operations are needed to better control material properties (e.g., particle size, shape, smoothness and moisture content). This active control of material properties, illustrated by the orange arrows in Figure 5, constrains actual feed properties to conform to the design specification. Improved equipment designs are also needed to accommodate peculiarities in feedstock properties and expand machinery performance (illustrated by blue arrows in Figure 5) to better deal with the variability in raw materials. The combination of controlling material properties and re-engineering handling and feeding equipment can result in designs in which cost and performance are both optimized.

Importantly, optimizing the feedstock properties as well as the equipment systems requires a thorough understanding of the properties of the bulk solid properties and how successive unit operations impact those properties. As noted by Bell, a common misperception is that feeding and handling problems can be addressed concurrently during start up [62]. However, retrofitting handling equipment can be very expensive and slow because the problems are usually discovered one at a time as successive pieces of equipment come online. The importance of fully characterizing all potential feedstocks and carefully controlling the handling and conversion properties to match the handling and conversion equipment is not likely to be overstated. In this process, the variability within feedstock materials can be as crucial as that between different feedstocks.

Moisture content

Feedstock moisture is likely the single most problematic biomass property affecting feedstock supply and biorefining operations. Unlike hay crops that are harvested during the time of year when field drying is a reliable approach, many herbaceous biomass crops, particularly crop residues, are harvested later in the year when field drying may not be practical or achievable [4]. Excessive moisture in herbaceous biomass requires farmers to include field drying into harvesting operations or to employ costly anaerobic storage methods to preserve it. Dry matter losses in aerobic storage increase with moisture content [65]. The threshold moisture content for safe, aerobic storage varies



Figure 5. The combined approach for solving biomass handling and feeding problems through improved system design to expand equipment performance and improved preprocessing operations that constrain feedstock properties to conform to specifications. among biomass types [4,66–68], but a moisture content of 20% (wet basis) is a generally recognized rule of thumb for limiting dry matter losses in aerobic storage to acceptable levels (5–7%) [3]. Elevated moisture contents have the potential to reduce transportation payloads, increasing the delivery cost to a biorefinery. Furthermore, the energy required for size reduction is often highly sensitive to biomass moisture content. Hammer mill grinding energy increases dramatically with increasing moisture content, while the energy required to chip wood decreases with increasing wood moisture content. Finally, biomass handling and feeding typically become more difficult with increasing moisture content as the bulk material becomes more cohesive, resulting in plugging in feeders and hoppers [69].

Different conversion processes have varying tolerance to biomass feedstock moisture. Biochemical conversion processes generally involve wet/aqueous processing, so biomass moisture content is not of significant concern for bioconversion. However, dry matter losses and degradation of biomass quality in storage are a big enough concern that moisture content in the range of 15–20% is generally recognized as a prudent specification for biochemical feedstocks processes. The efficiency and performance of thermochemical processes in general favor lower moisture contents [69]. Additional drying may be required for thermochemical conversion processes that prefer dry feedstocks; a specification as low as 10% has been identified for pyrolysis feedstocks [10].

Sources of variability

Moisture content varies considerably among biomass types, regions and even year-to-year variations due to plant health and water availability. Thick-stem crops, such as forage sorghum [70], energy cane and corn stover [4,15,32] tend to be the wettest at the time of harvest, and the thick stalk also tends to make these crops difficult to field dry, especially if harvested later in the year when drying conditions are more difficult. Small-stem crops such as cereal straws, switchgrass and mixed grasses (e.g., prairie grasses) are much less resistant to dry down, and they are also harvested at the time of year when field drying is easier [5,71].

Although easily understood, moisture content is an overlooked analysis with two principal sources of variability: sampling and quantification. Sample collection must capture the range of feedstock moisture content and reflect its proportional distribution to measure bulk moisture content accurately [47]. Over-representation of either high- or low-moisture regions will skew bulk measurements accordingly. Gravimetric analyses (measurement of as-received and dried mass) are used to measure water content, but are another source of variability. Biomass drying temperatures range from 40 to 105°C, which affect the final stable material mass after drying [72,73]. Partial drying at lower temperatures produces uniformly lower moisture values and corresponding higher dry matter values than higher temperatures. However, higher temperatures can drive off volatile components such as organic acids, which results in an overestimation of feedstock moisture content. When establishing a sampling and analysis plan for biomass feedstocks it is important to select protocols that address these two sources of uncertainty.

Impact of variability

The moisture content of nonirrigated crops tends to fluctuate from year-to-year with the amount of precipitation received during the growing season. These fluctuations can be significant (Figure 6), creating challenges for growers and processors that must adapt harvest, storage and processing conditions to changing crop conditions. The data shown Figure 6 are an accurate representation of corn stover moisture contents in the Midwest corn belt in 2009 and 2010, and it paints two very different scenarios for a biorefinery. The 2010 stover crop represents a nearly-ideal scenario for both grower and processor/biorefinery alike. The majority of the crop was within a narrow distribution of moisture, low enough that field drying to safe storage levels was unnecessary. In this scenario, storage losses would be minimal, transportation costs unaffected, grinding energy low and consistent, and the resulting feedstock consistent in physical and chemical properties. The 2009 stover crop, on the other hand, sets up a scenario that a biorefinery should fear. The high grain moisture and wet field conditions experienced in 2009 slowed harvest and made field drying impractical. Consequently, stover was baled and stored at moisture contents exceeding the 20% target, resulting in high dry matter losses (20% or higher [4]) and a reduction of structural carbohydrates. To make matters worse, in this scenario, the composition and general condition of the bales continue to degrade with time, so the quality is on a general downward trend throughout year-long storage and supply of feedstock to the refinery. The bales delivered to the refinery would be more costly to preprocess, as the higher moisture content requires more energy to reduce size. Finally, the higher and variable moisture feedstock is more likely to exhibit inconsistent bulk solids properties, creating handling and feeding problems that cause the plant to operate at lower throughput. This is a bad scenario impacting the entire biofuels production chain.

Solutions to variability

There is no easy solution to this problem, although understanding and anticipating the implications of high and variable biomass moisture content goes a long way in properly preparing for and reacting to the situation. First, Understanding biomass feedstock variability Perspective

establishing best management practices to guide growers in the proper harvest and storage methods under different crop conditions is the first step. Being able to predict whether current ambient conditions will support field drying will point them in the right direction in harvesting the biomass, and will avoid additional losses and quality degradation that results from failed attempts to field dry when ambient conditions do not support such a practice. Proper storage methods too may change with biomass moisture content. Biomass harvested above 20% moisture may benefit from lower losses through anaerobic storage, although this must be balanced against the higher storage costs [3]. Biomass supply would be well served by moisture-tolerant storage systems that can control losses to acceptable and predictable levels under aerobic storage conditions. Research has shown that proper stor-

age of high moisture biomass under aerobic conditions can limit losses to acceptable levels [74], although these conditions need to be better understood to determine whether they can be replicated at commercial scale. Second, improvements in biomass size reduction to reduce the sensitivity of grinding efficiency to biomass moisture content would also be beneficial. Idaho National Laboratory data show hammer mill grinding efficiency (measured in kilowatt-h per dry ton) reductions of nearly 50% as biomass moisture increases from 10 to 25% (wet basis) [IDAHO NATIONAL LABORATORY, UNPUBLISHED DATA]. Third, the effects of moisture content on bulk solids properties need to be better understood to inform designs of handling and feeding systems that can better tolerate variabilities due to moisture.

Future perspective

Solving the problem of feedstock variability can ultimately only be achieved within the cost constraints of competitive biofuels production by contributions along the entire feedstock supply chain. Supplying high-quality feedstocks begins with the development of advanced biomass-specific harvest, collection, and storage systems and processes. Advanced harvesting systems will be sophisticated enough to balance sustainability constraints with the economics of maximizing removal rates. They will reduce, if not eliminate, the collection of undesirable constituents – whether this is foreign contaminants such as soil or certain anatomical fractions of the plant – as



Figure 6. Corn stover moisture content over 2009 and 2010 US Midwest harvest seasons (N = 339). Bars indicate the combined moisture frequency; lines indicate the moisture frequency by year.

defined by the conversion process. Advanced storage systems will effectively manage moisture to preserve dry matter and sugars, and minimize environmental risks.

Biomass quality will also benefit from science-based best management practices that educate growers and biomass suppliers on equipment and methods that promote sustainable practices, maximize quality, reduce dockage and maximize their profit in biomass supply. Biorefineries and processors will implement point-of-sale and pointof-use quality measurements that help them assess in an accurate, fast, economic and defensible manner the quality of biomass supplied to them in order to establish payment and dockage, and to select appropriate preprocessing options for preparing the biomass for conversion. The ability for processors to accurately assess quality will also provide them with the flexibility to allow their suppliers to deviate from recommended practices - in favor of alternative approaches that best suit their business - and pay according to a quality specification.

The ability for biomass processors to abdicate best management practices and accept off-spec, lower quality biomass is enabled by advanced preprocessing technologies that can transform raw biomass to on-spec feedstocks. These technologies will have the ability to remove ash – ranging from entrained soil to structural ash bound in the plant cell walls – as well as other conversion inhibitors, blend biomass of different types and qualities to a biorefinery spec, and stabilize and densify these feedstocks to specifications required of a feedstock commodity. Such an active biomass system will replace passive systems that merely react to the cost-value dynamics to eliminate the one-to-one mapping of available biomass resources to particular conversion processes, providing access to our vast biomass resources, and enabling renewable fuels and chemicals to replace the whole barrel of oil.

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Executive summary

Background

- The objective of this paper was to examine biomass feedstock attributes of ash, carbohydrates, particle morphology and moisture.
- It discusses specifications for these attributes, inherent variability of these attributes in biomass feedstocks, and approaches and solutions for reducing variability and improving feedstock.

Ash

- Biomass feedstock ash contents vary considerably due to three sources of ash: introduced ash, often associated with soil contamination during biomass harvest and collection operations; and inherent ash, which includes both vascular as well as structural ash.
- Excessive ash can cause a number of problems in biochemical and thermochemical conversion processes including increased wear in handling and processing systems, increased corrosivity and instability of pyrolysis oils, slagging and fouling in boilers and gasifiers, and increased disposal costs. The latter was estimated to increase the cost of cellulosic ethanol production over 2% due to entrained soil alone.
- Solutions to reducing ash content include feedstock selection and fractionation; best management practices to reduce, if not eliminate, the entrainment of soil; and preprocessing technologies that remove entrained soil as well as vascular or structural sources of physiological ash.

Sugars

- Biomass structural sugars vary considerably among biomass types as well as among different varieties. The loss of structural sugars during storage also introduces additional compositional variability.
- Biofuel yields through biochemical conversion processes are extremely sensitive to feedstocks structural sugar content. It was shown that
 compositional variability can reduce cellulosic ethanol yields by more than 30 gallons per dry ton.
- Feedstock selection, best management practice to preserve carbohydrates in storage, and formulation and blending are all options for reducing sugar/carbohydrate variability.

Particle morphology

- Particle morphology (size, shape and density) affects conversion efficiencies, as well as handling and feeding, with the latter being a
 particular concern. Particle morphology is very difficult to control due to the interaction of material properties and operating parameters
 of commercial size-reduction systems.
- It is estimated that feeding and handling problems due to changing and uncertain bulk solids properties can reduce plant throughputs by as much as 50%, severely influencing plant efficiencies and economics.
- Solutions to these problems involve both preprocessing technology solutions to provide consistent bulk solids properties and engineering solutions to design more robust handling and feeding systems.

Moisture

- Biomass moisture content varies considerably among material types, and it is difficult to predict and control due to environmental conditions.
- Biomass moisture content can be extremely problematic, with the potential to affect all unit operations of feedstock supply, including handling and feeding in conversion systems.
- Solutions to moisture problems include selection of feedstocks with good dry-down characteristics, best management practices that guide proper harvest and storage under different moisture conditions, and improved preprocessing, handling and feeding systems.

References

- Papers of special note have been highlighted as:
- of interest
- of considerable interest
- Shinners KJ, Binversie BN. Whole-plant corn harvesting for biomass: comparison of single-pass and multiple-pass harvest systems. Presented at: *The ASABE Annual Meeting*. Las Vegas, NV, USA, 27–30 July 2003.
- 2 Yancey NA, Wright CT, Conner CC, Hess JR. Preprocessing moist lignocellulosic biomass for biorefinery feedstocks. Presented at: *The ASABE Annual Meeting*, Las Vegas, NV, USA, 27–30 July 2009.
- 3 Darr MJ, Shah A. Biomass storage: an update on industrial solutions for baled biomass feedstocks. *Biofuels* 3(3), 321–332 (2012).
- 4 Shinners KJ, Binversie BN, Muck RE, Weimer P. Comparison of wet and dry corn stover harvest and storage. *Biomass Bioenergy* 31(4), 211–221 (2007).
- 5 Shinners KJ, Boettcher GC, Muck RE, Weimer PJ, Casler MD. Harvest and storage of two perennial grasses as biomass feedstocks. *Trans. ASABE* 53(2), 359–370 (2010).
- 6 Sokhansanj S, Turhollow A, Cushman J, Cundiff J. Engineering aspects of collecting corn stover for bioenergy. *Biomass Bioenergy* 23(5), 347–355 (2002).
- 7 Humbird DA, Davis R, Tao L et al. Process Design and Economics for Biochemical Conversion of Lignocellulosic Biomass to Ethanol. Dilute-acid Pretreatment and Enzymatic Hydrolysis of Corn Stover. National Renewable Energy Laboratory, Golden, CO, USA (2011).
- Provides a good basis for estimating the economic consequence of corn stover sugar and ash variability.
- 8 Weiss ND, Farmer JD, Schell DJ. Impact of corn stover composition on hemicellulose conversion during dilute acid pretreatment and enzymatic cellulose digestibility of the pretreated solids. *Bioresour. Technol.* 101(2), 674–678 (2010).
- 9 Aden A, Foust T. Technoeconomic analysis of the dilute sulfuric acid and enzymatic hydrolysis process for the conversion of corn stover to ethanol. *Cellulose* 16(4), 535–545 (2009).
- 10 US Department of Energy. Biomass Multi-Year Program Plan – April 2012. US Department of Energy, Washington, DC, USA (2012).

- 11 Das P, Ganesh A, Wangikar P. Influence of pretreatment for deashing of sugarcane bagasse on pyrolysis products. *Biomass Bioenergy* 27(5), 445–457 (2004).
- 12 Carpenter DL, Bain RL, Davis RE et al. Pilot-scale gasification of corn stover, switchgrass, wheat straw, and wood: 1. Parametric study and comparison with literature. Ind. Eng. Chem. Res. 49(4), 1859–1871 (2010).
- 13 Dutta A, Talmadge M, Hensley J et al. Process Design and Economics for Conversion of Lignocellulosic Biomass to Ethanol-Thermochemical Pathway by Indirect Gasification and Mixed Alcohol Synthesis. National Renewable Energy Laboratory, Golden, CO, USA (2011).
- 14 Godin B, Ghysel F, Agneessens R et al. Cellulose, hemicelluloses, lignin, and ash contents in various lignocellulosic crops for second generation bioethanol production. *Biotechnol. Agron. Soc.* 14(2), 549–560 (2010).
- 15 Pordesimo LO, Hames BR, Sokhansanj S, Edens WC. Variation in corn stover composition and energy content with crop maturity. *Biomass Bioenergy* 28(4), 366–374 (2005).
- 16 Tao GC, Lestander TA, Geladi P, Xiong SJ. Biomass properties in association with plant species and assortments I: a synthesis based on literature data of energy properties. *Renew. Sust. Energ. Rev.* 16(5), 3481–3506 (2012).
- 17 Bakker RR, Jenkins BM. Feasibility of collecting naturally leached rice straw for thermal conversion. *Biomass Bioenergy* 25(6), 597–614 (2003).
- 18 Jorgensen U. Genotypic variation in dry matter accumulation and content of N, K and Cl in *Miscanthus* in Denmark. *Biomass Bioenergy* 12(3), 155–169 (1997).
- Madakadze IC, Stewart K, Peterson PR, Coulman BE, Smith DL. Switchgrass biomass and chemical composition for biofuel in eastern Canada. *Agron. J.* 91(4), 696–701 (1999).
- 20 Sanderson MA, Wolf DD. Switchgrass biomass composition during morphological development in diverse environments. *Crop Sci.* 35(5), 1432–1438 (1995).
- 21 Burvall J. Influence of harvest time and soil type on fuel quality in reed canary grass (*Phalaris arundinacea L*). Biomass Bioenergy 12(3), 149–154 (1997).
- 22 Adler PR, Sanderson MA, Boateng AA, Weimer PI, Jung HJG. Biomass yield and biofuel quality of switchgrass harvested in

fall or spring. Agron. J. 98(6), 1518-1525 (2006).

- 23 Lewandowski I, Kicherer A. Combustion quality of biomass: practical relevance and experiments to modify the biomass quality of *Miscanthus x giganteus. Eur. J. Agron.* 6(3–4), 163–177 (1997).
- 24 Lewandowski I, Clifton-Brown JC, Andersson B *et al.* Environment and harvest time affects the combustion qualities of *Miscanthus* genotypes. *Agron. J.* 95(5), 1274–1280 (2003).
- 25 Davidsson KO, Pettersson JBC, Nilsson R. Fertiliser influence on alkali release during straw pyrolysis. *Fuel* 81(3), 259–262 (2002).
- 26 Duguid KB, Montross MD, Radtke CW, Crofcheck CL, Shearer SA, Hoskinson RL. Screening for sugar and ethanol processing characteristics from anatomical fractions of wheat stover. *Biomass Bioenergy* 31(8), 585–592 (2007).
- 27 Jarchow ME, Liebman M, Rawat V, Anex RP. Functional group and fertilization affect the composition and bioenergy yields of prairie plants. *Glob. Change Biol. Bioenergy* 4(6), 671–679 (2012).
- 28 Karlen DL, Birell SJ, Hess JR. A five-year assessment of corn stover harvest in central Iowa, USA. *Soil Tillage Res.* 115–116, 47–55 (2011).
- 29 Shinners KJ, Bennett RG, Hoffman DS. Single- and two-pass corn grain and stover harvesting. *Trans. ASABE* 55(2), 341–350 (2012).
- 30 Bakker RR, Elbersen HW. Managing ash content and quality in herbaceous biomass: an analysis from plant to product. Presented at: *14th European Biomass Conference*. Paris, France, 17–21 October 2005.
- 31 Samson R, Mehdi B. Strategies to Reduce the Ash Content in Perennial Grasses. Resource Efficient Agricultural Production, Ste-Annede-Bellevue, QC, Canada (1998).
- 32 Hoskinson RL, Karlen DL, Birrell SJ, Radtke CW, Wilhelm WW. Engineering, nutrient removal, and feedstock conversion evaluations of four corn stover harvest scenarios. *Biomass Bioenergy* 31(2–3), 126–136 (2007).
- Good assessment of the copositional benefits of selective harvest of corn stover.
- 33 Davidsson KO, Korsgren JG, Pettersson JBC, Jaglid U. The effects of fuel washing techniques on alkali release from biomass. *Fuel* 81(2), 137–142 (2002).
- 34 Tonn B, Thumm U, Lewandowski I, Claupein W. Leaching of biomass from seminatural grasslands – effects on chemical

composition and ash high-temperature behaviour. *Biomass Bioenergy* 36, 390-403 (2012).

- 35 Turn SQ, Kinoshita CM, Ishimura DM. Removal of inorganic constituents of biomass feedstocks by mechanical dewatering and leaching. *Biomass Bioenergy* 12(4), 241–252 (1997).
- 36 Templeton DW, Sluiter AD, Hayward TK, Hames BR, Thomas SR. Assessing corn stover composition and sources of variability via NIRS. *Cellulose* 16(4), 621–639 (2009).
- Excellent study on corn stover compositional variablity.
- 37 Shinners KJ, Binversie BN. Fractional yield and moisture of corn stover biomass produced in the Northern US Corn Belt. *Biomass Bioenergy* 31(8), 576–584 (2007).
- 38 Prewitt RM, Montross MD, Shearer SA et al. Corn stover availability and collection efficiency using typical hay equipment. Trans. ASABE 50(3), 705–711 (2007).
- 39 Duguid KB, Montross MD, Radtke CW, Crofcheck CL, Wendt LM, Shearer SA. Effect of anatomical fractionation on the enzymatic hydrolysis of acid and alkaline pretreated corn stover. *Bioresour. Technol.* 100(21), 5189–5195 (2009).
- Good assessment of the copositional benefits of selective harvest of corn stover.
- 40 Shah A, Darr MJ, Webster K, Hoffman C. Outdoor storage characteristics of singlepass large square corn stover bales in Iowa. *Energies* 4(10), 1687–1695 (2011).
- 41 Wiselogel AE, Agblevor FA, Johnson DK, Deutch S, Fennell JA, Sanderson MA. Compositional changes during storage of large round switchgrass bales. *Bioresour. Technol.* 56(1), 103–109 (1996).
- 42 Ruth ML, Thomas SR. The effect of corn stover composition on ethanol process economics. Presented at: *The 25th Symposium on Biotechnology for Fuels and Chemicals*, Breckenridge, CO, USA, 4–7 May 2003.
- Excellent study on corn stover compositional variability.
- 43 Rooney WL, Blumenthal J, Bean B, Mullet JE. Designing sorghum as a dedicated bioenergy feedstock. *Biofuel. Bioprod. Bior.* 1(2), 147–157 (2007).
- 44 Chen F, Dixon RA. Lignin modification improves fermentable sugar yields for biofuel production. *Nat. Biotechnol.* 25(7), 759–761 (2007).
- 45 Reddy MSS, Chen F, Shadle G, Jackson L, Aljoe H, Dixon RA. Targeted down-

regulation of cytochrome P450 enzymes for forage quality improvement in alfalfa (*Medicago sativa L.*). *Proc. Natl Acad. Sci.* USA 102(46), 16573–16578 (2005).

- 46 Smith WA, Bonner IJ, Kenney KL, Wendt LM. Practical considerations of moisture in baled biomass feedstocks. *Biofuels* 4(1), 95–110 (2013).
- 47 Boavida D, Abelha P, Gulyurtlu I, Valentim B, Lemos De Sousa MJ. A study on coal blending for reducing NO_x and N₂O levels during fluidized bed combustion. *Clean Air* 5, 175–191 (2004).
- 48 Shih J-S, Frey HC. Coal blending optimization under uncertainty. *Eur.* J. Oper. Res. 83(3), 452–465 (1995).
- 49 Hill LD. Grain Grades and Standards: Historical Issues Shaping the Future. University of Illinois Press, Champaign, IL, USA (1990).
- 50 Reddy DV, Krishna N. Precision animal nutrition: a tool for economic and ecofriendly animal production in ruminants. *Livest. Res. Rural Dev.* 21(3), 36 (2009).
- 51 Sami M, Annamalai K, Wooldridge M. Co-firing of coal and biomass fuel blends. *Prog. Energ. Combust.* 27(2), 171–214 (2001).
- 52 Tumuluru JS, Hess JR, Boardman RD, Wright CT, Westover TL. Formulation, pretreatment, and densification options to improve biomass specifications for co-firing high percentages with coal. *Ind. Biotechnol.* 8(3), 113–132 (2012).
- 53 Betancur GJ, Pereira N. Sugar cane bagasse as feedstock for second generation ethanol production. Part I: diluted acid pretreatment optimization. *Electron. J. Biotechn.* 13(3) (2010).
- 54 Bitra VSP, Womac AR, Chevanan N et al. Direct mechanical energy measures of hammer mill comminution of switchgrass, wheat straw, and corn stover and analysis of their particle size distributions. *Powder Technol.* 193(1), 32–45 (2009).
- 55 Igathinathane C, Womac AR, Sokhansanj S, Narayan S. Size reduction of high- and lowmoisture corn stalks by linear knife grid system. *Biomass Bioenergy* 33(4), 547–557 (2009).
- 56 Mani S, Tabil LG, Sokhansanj S. Grinding performance and physical properties of wheat and barley straws, corn stover and switchgrass. *Biomass Bioenergy* 27(4), 339–352 (2004).
- 57 Dibble CJ, Shatova TA, Jorgenson JL, Stickel JJ. Particle morphology characterization and manipulation in

biomass slurries and the effect on rheological properties and enzymatic conversion. *Biotechnol. Prog.* 27(6), 1751– 1759 (2011).

- 58 van Walsum GP, Allen SG, Spencer MJ, Laser MS, Antal MJ, Lynd LR. Conversion of lignocellulosics pretreated with liquid hot water to ethanol. *Appl. Biochem. Biotechnol.* 57–58(1), 157–170 (1996).
- 59 Bridgwater AV. Principles and practice of biomass fast pyrolysis processes for liquids. J. Anal. Appl. Pyrolysis 51(1–2), 3–22 (1999).
- 60 Jones SB, Valkenburg C, Walton CW et al. Production of Gasoline and Diesel from Biomass via Fast Pyrolysis, Hydrotreating and Hydrocracking: A Design Case. Pacific Northwest National Laboratory, Richland, WA, USA (2009).
- 61 Mohan D, Pittman CU, Steele PH. Pyrolysis of wood/biomass for bio-oil: a critical review. *Energy Fuels* 20(3), 848–889 (2006).
- 62 Bell TA. Challenges in the scale-up of particulate processes – an industrial perspective. *Powder Technol.* 150(2), 60–71 (2005).
- Excellent overview of the potential impact of bulk solids handling problems.
- 63 Miao Z, Grift TE, Hansen AC, Ting KC. Energy requirement for comminution of biomass in relation to particle physical properties. *Ind. Crops Prod.* 33(2), 504–513 (2011).
- 64 Merrow EW. Problems and progress in particle processing. *Chem. Innov.* January, 35–41 (2000).
- Excellent overview of the potential impact of bulk solids handling problems.
- 65 Emery IR, Mosier NS. The impact of dry matter loss during herbaceous biomass storage on net greenhouse gas emissions from biofuels production. *Biomass Bioenergy* 39, 237–246 (2012).
- 66 Coble CG, Egg R. Dry matter losses during hay production and storage of sweet sorghum used for methane production. *Biomass* 14(3), 209–217 (1987).
- 67 Jirjis R. Storage and drying of wood fuel. Biomass Bioenergy 9(1-5), 181-190 (1995).
- 68 Sanderson MA, Egg RP, Wiselogel AE. Biomass losses during harvest and storage of switchgrass. *Biomass Bioenergy* 12(2), 107–114 (1997).
- 69 Dai J, Cui H, Grace JR. Biomass feeding for thermochemical reactors. *Prog. Energ. Combust.* 38(5), 716–736 (2012).
- 70 Zegada-Lizarazu W, Monti A. Are we ready to cultivate sweet sorghum as a bioenergy

feedstock? A review on field management practices. *Biomass Bioenergy* 40, 1–12 (2012).

- 71 Hess JR, Kenney KL, Ovard LP, Searcy EM, Wright CT. Commodity-Scale Production of an Infrastructure-Compatible Bulk Solid from Herbaceous Lignocellulosic Biomass. Uniform-Format Bioenergy Feedstock Supply System Design Report Series. Idaho National Laboratory, Idaho Falls, ID, USA (2009).
- 72 Sluiter A, Hames B, Hyman D et al. Determination of Total Solids in Biomass and Total Dissolved Solids in Liquid Process Samples. Laboratory Analytical Procedure (LAP). National Renewable Energy Laboratory, Golden, CO, USA (2008).
- 73 Undersander D, Mertens DR, Thiex N. Forage Analyses Procedures. National Forage Testing Association, Omaha, NE, USA (1993).
- 74 Shinners KJ, Wepner AD, Muck RE, Weimer PJ. Aerobic and anaerobic storage of single-pass, chopped corn stover. *Bioenerg. Res.* 4(1), 61–75 (2011).
- 75 Lee D, Owens VN, Boe A, Jeranyama P. Composition of Herbaceous Biomass Feedstocks. South Dakota State University, Brookings, SD, USA (2007).