Title

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Journal

ACS Sustainable Chemistry & Engineering, 8(8)

ISSN

2168-0485

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Publication Date

2020-03-02

DOI

10.1021/acssuschemeng.9b06763

Peer reviewed

ACS Sustainable Chemistry & Engineering
pubs.acs.org/journal/ascecg
Research Article

Multiscale Characterization of Lignocellulosic Biomass Variability and Its Implications to Preprocessing and Conversion: a Case Study for Corn Stover

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Cite This: ACS Sustainable Chem. Eng. 2020, 8, 3218–3230
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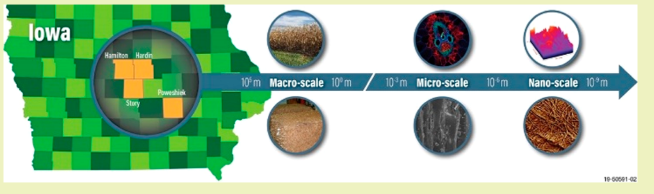

ABSTRACT: Feedstock variability that originates from biomass production and field conditions propagates through the value chain, posing a significant challenge to the emerging biorefinery industry. Variability in feedstock properties impacts feeding, handling, equipment operations, and conversion performance. Feedstock quality attributes, and their variations, are often overlooked in assessing feedstock value and utilization for conversion to fuels, chemicals, and products. This study developed and employed a multiscale analytical characterization approach coupled with data analytic methods to better understand the sources and distribution of feedstock quality variability through evaluation of 24 corn stover bales collected in 4 counties of Iowa. In total, 216 core samples were generated by sampling nine positions on each bale using a reliable bale coring process. The samples were characterized for a broad suite of physicochemical properties ranging across field and bale, macro, micro, and molecular scales. Results demonstrated that feedstock quality attributes can vary at all spatial scales and that multiple sources of variability must be considered in order to establish and manage biomass quality for conversion processes.

KEYWORDS: *Biomass variability, Multiscale characterization, Corn stover, k-means clustering, Inorganic speciation, Material attributes, Emergent properties*

INTRODUCTION

Lignocellulosic biomass holds significant promise as a viable source of sustainable and renewable transportation fuels, biochemicals, and bioproducts for domestic energy security and growth of the U.S. bioeconomy. The U.S. Department of Energy's (DOE) 2016 Billion Ton Report projected the potential for more than one billion tons of biomass in the form of agricultural and forestry, waste, energy crops, and algal materials capable of displacing approximately 30% of domestic petroleum consumption without adverse environmental effects or negative impacts to production of food and agricultural products.[1] However, feedstocks are currently assigned a monetary value based on factors that neglect variations in quality and the resulting effects on bioprocessing. For instance, variations in ash, moisture, particle size, and dimension increase energy consumption,[2] generate a significant fraction of fines, and reduce throughput,[3] which can lead to the technoeconomic failure of a biorefinery.[4] Therefore, it is crucial to develop an understanding of the multidimensional challenge caused by the myriad of inter-related and complex physicochemical attributes whose relative importance will vary with different biorefinery conversion technologies.

The realization of an industry with lignocellulosic material-based fuels, chemicals, and products hinges on an economical supply of quality biomass.[5] Initial research and development have focused primarily on the utilization of agriculturally derived feedstocks in high-biomass yielding regions, without careful consideration of their relatively low energy densities or variable composition and quality.[6] These agricultural biomass resources have inherent variability[7] that extends beyond plant species to include differences in anatomical fractions and tissue types of the same plant materials.[8−10] Prior research has demonstrated key sources of variability that stem from environmental and production factors, which affect biomass properties and, in turn, feedstock performance in downstream processes. Preliminary assessments of the compositional variability of corn stover identified a broad range of variability in structural carbohydrates, lignin, and ash for 112 maize hybrids from 52 locations in 10 states.[11] The harvest year was identified as the most significant

Received: November 12, 2019
Revised: February 2, 2020
Published: February 11, 2020

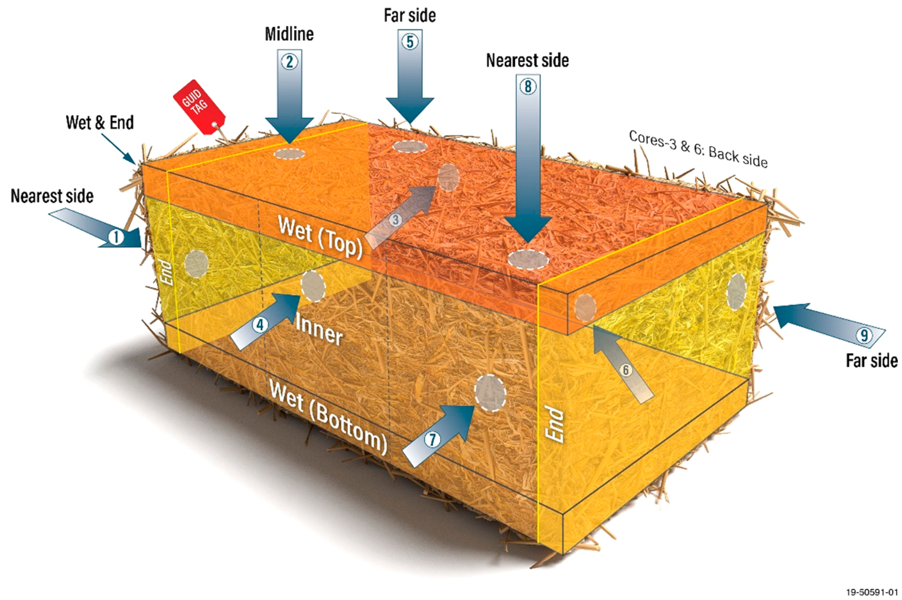

Figure 1. Illustration of bale core sample locations. Bales were cored on the bottom rather than the top if they could be identified as a bottom bale from a stack of bales to better identify wet zones and soil accumulation. Average bale dimensions were as follows: length = 247 cm; width = 124 cm; height = 90 cm; mass = 543 kg; and density = 199 kg/m^3.

factor in the compositional variation of corn stover, followed by location and variety,[12] while the harvest method has been implicated in soil accumulation that contributes to variable ash content.[13] Extreme weather events, like drought, contribute to reductions in biomass productivity,[14,15] which are further compounded by compositional variations[16,17] and changes to cell wall ultrastucture.[18] Extractable sugars accumulated in response to osmotic pressures experienced during drought are prone to degradation during chemical pretreatment[19] to the detriment of fermentation and product yields. Conditions during storage impart distinct changes over time, where high moisture coupled with oxygen exposure lead to biological degradation that results in loss of valuable carbohydrates,[20] leaving biomass depleted in fermentable components.[21] It is this complex interplay of many factors that creates significant challenges for downstream processes, which often require physically and chemically consistent feedstocks.[6,22−25]

Biomass variability has proven a formidable challenge to downstream processing in the emerging biorefining industry, impeding feeding operations and reducing conversion yields and selectivity.[26] The U.S. DOE's Bioenergy Technologies Office (BETO) assembled a team to identify the key challenges faced by the industry. These challenges centered around feedstock variability, feeding and handling of solid materials, process scale-up, and valorization of waste and coproduct streams.[4] Integrated biorefinery (IBR) development has suffered from failing to account for the structural and chemical complexity of lignocellulosic biomass, citing feedstock variability as a major operational challenge. The variations of carbohydrates and lignin cell wall compositions, extractives, moisture, ash, and soil contaminants have been noted as critical factors that impact biomass quality, process uptime, and throughput. Ultimately, characterization of the variability of available biomass feedstocks and finding methods to mitigate this variability will be required for integrated feedstock supply, preprocessing, and conversion pathways and profitable biorefineries.[4]

Given the complexity of the biomass supply chain, beginning with harvest and collection from the field, the aim of this study was to identify and understand multiple facets of biomass variability in a single species, *Zea mays*, through examination of the multiple scales at which heterogeneity exists. This case study documents a realistic range of variability of corn stover derived from 4 counties in Iowa consistent with a surrogate biorefinery supply shed in a high-yield region of the U.S. Corn Belt. Further, in addition to the characterization of feedstock attributes known or suspected to impact processing, this study employed unsupervised machine learning algorithms to extract previously overlooked features that identify and analyze regional variability of corn stover.

■ MATERIALS AND METHODS

Corn Stover Bale Collection and Sample Preparation. Corn stover bales (n = 24) were obtained from four fields each in a different central Iowa county: Hamilton (4 bales), Hardin (6 bales), Story (6 bales), and Poweshiek (8 bales). Corn stover was baled between October 12 and 27, 2017 using an AGCO 2270XD large square baler, with the exception of Poweshiek county, where a Heston 2270XD square baler was used. Preliminary screening was performed by taking three cores per bale to select the 24 bales used in this case study; the impacts of the screening are considered in the data analysis and discussion. Selected bales were more thoroughly sampled with nine cores per bale, as adapted from prior studies[27,28] and illustrated in Figure 1. Core samples (n = 216 cores) were dried at 40 °C and milled with a 2 mm screen in a Thomas Model 4 Wiley Mill (Thomas Scientific, Swedesboro, NJ) for analysis of a suite of properties including moisture, total ash, inorganic species, structural carbohydrate, lignin. Subsequently, bales were processed through a Vermeer BG480 bale processer with a 75 mm screen then a Bliss Hammermill with a 25 mm screen at the Biomass Feedstock National User Facility (BFNUF) located at Idaho National Laboratory. Select samples were collected after the second mill, then milled to pass a 2 mm screen, and evaluated for surface topology, surface energy, and crystallinity.

Moisture and Inorganic Species Analysis. Moisture was measured gravimetrically in two steps; the first drying step was done at 40 °C for 72 h prior to milling; then, moisture and ash were measured using a LECO Thermogravimetric Analyzer 701 (St. Joseph, MI) according to ASTM D3174−04. Elemental ash analysis was determined using ASTM D6349 after milling using a Retsch ZM200 (Haan, Germany) equipped with a 0.2-screen.

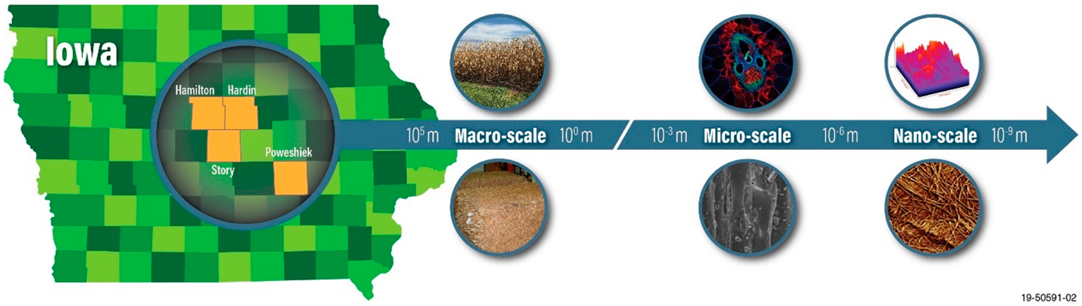

Figure 2. Feedstock variability demonstrated across various scales in this case study, from region (four counties in Iowa: Hamilton, Hardin, Poweshiek, and Story), bale, plant fractions, tissue and cell types, to surface and cell wall. The map provides locations and sources of commercial bales of corn stover for exploring regional variation across four Iowa counties used in this case study. Physicochemical and structural variability exist at multiple scales, and each scale offers unique insights to understanding the sources of variability and material attributes that impact the biomass value chain.

Fourier Transform Near-Infrared (FT-NIR)-Predicted Compositional Analysis. Samples were dried at room temperature in a desiccator for at least 72 h. Duplicate preparations of each sample were scanned at the National Renewable Energy Laboratory as described previously,[29] using a Thermo Antaris II FT-NIR with autosampler attachment and Omnic software (Thermo Scientific, Waltham, MA, USA). Spectra were collected over a range of 4000−10000 cm^{-1}. For each sample, 128 scans were averaged resulting in a single spectrum. Duplicate samples were analyzed, and the spectra were averaged prior to prediction.

Image Analysis in Visible, Red-Green-Blue (RGB) Color Space. A detailed description of the RGB image analysis can be found in the Supporting Information (SI). Images were collected from exterior cores on selected bales that appeared clean, or with evidence of biological degradation or soil accumulation. These images were subjected to colorimetric (RGB) analysis in ImageJ (https://imagej.nih.gov/ij/), and data were compared to NIRS predicted chemical composition from adjacent cores. Multiple linear regression and multinominal logistic modeling approaches were performed in JMP to assess the ability of the average red, green, and blue signature to predict the categorical quality assignments as well as the chemical composition and inorganic speciation for the stover samples.

X-ray Diffraction. XRD experiments were performed at U.S. DOE's Advanced Light Source synchrotron facility on beamline 12.2.2. located at Lawrence Berkeley National Laboratory (LBNL). Biomass samples were milled and loaded into capillary tubes from MiTeGen Crystallography. The tubes were then attached to goniometer bases that allowed for samples to be rotated along their x-axis. X-rays were emitted at a wavelength of 0.8265 Å, with a polarization factor of 0.99. Scans were conducted between 0° and 28.5° with a step size of 0.00738 2θ. Distance from sample to detector was calibrated against cerium dioxide, following the standard procedure developed at ALS beamline 12.2.2.[30] A Mar-3450 detector was utilized to measure the intensity of emitted photons and their corresponding angle (2θ). Background subtraction was performed using Dioptas online XRD powder diffraction software.[31] In order to compare data gathered from this experiment with diffractograms from the literature, the 2θ from our experiment was adjusted to match the 2θ values that would have been produced using 1.541 Å X-rays. This adjustment was performed with a few simple manipulations of Bragg's Law.[32] Samples were tested in duplicate.

Stereo Microscopy. Milled corn stover samples were imaged using a Nikon SMZ1500 stereomicroscope and captured using a Nikon DS-Fi1 CCD camera that was operated with a Nikon Digital Sight system (Nikon Instruments, Melville, NY, U.S.A.) under bright field lighting. Particle size and morphology was calculated using the *Otsu Thresholding* and *Analyze Particles* plugins in FIJI (ImageJ).

Scanning Electron Microscopy. Milled, corn stover samples were mounted onto aluminum stubs with carbon tape and sputter-coated with 6 nm iridium using a Cressington Sputter Coater 208 HR (Cressington Scientific Instruments, Ltd., Watford, UK). SEM micrographs were acquired with a FEI Quanta 400 FEG instrument (FEI, Hillsboro, OR, U.S.A.) operating at 15 kV using a gaseous solid-state detector (GAD) collecting secondary electrons. Surface roughness was calculated using the SurfCharJ plugin in FIJI (ImageJ).

Surface Energy. Surface energy was performed as described previously.[33,34] Surface energy measurements were estimated with a surface energy analyzer (SEA) from Surface Measurement Systems (SMS), equipped with a flame ionization detector (FID). Approximately 1 g of corn stover was packed into silanized glass columns (4 mm ID, 6 mm OD x 300 mm); packing densities measured ~0.3 g/cm^3. To ensure material packing within the column, ends were plugged with silanized glass wool provided by SMS. Dispersive surface energy and specific surface energy estimations were performed using HPLC grade n-alkanes (C7−C10), trichloromethane (monopolar Lewis acid), and ethyl acetate (monopolar Lewis base) from Sigma-Aldrich. Measurements were performed isothermally (30 °C) and at infinite dilution (a coverage of 0.005 n/nm or 0.5% monolayer coverage) with helium as the carrier gas (10 cm^3/min). The Dorris-Gray method was used to calculate the dispersive surface energy values, while the acid−base (or specific) surface energy values were calculated using the polarization method on the van Oss-Chaudhury-Good (vOCG) scale. Elution of the probes provided symmetrical peaks and were evaluated using the peak max function.

***k*-Means Clustering.** k-means clustering was performed using the Scikit-learn machine learning library in Python. The k-means clustering algorithm was run ten times with different centroid seeds, and the final number of clusters used for further analysis was chosen as the number of clusters at which the within-cluster sum-of-squared errors measured between each data point in the cluster and the cluster centroid approached its minimum value. This approach to choosing the optimal number of clusters was used to minimize within-cluster sum-of-squared errors while not overfitting the number of clusters. Each clustering was run for a maximum of 300 iterations. Data was plotted using the Matplotlib library in Python.

RESULTS AND DISCUSSION

Multiscale Characterization Approach. The complexity of lignocellulosic biomass originating from supply chain poses significant challenges to handling, preprocessing, and conversion operations. The range, magnitude, and distribution of material and quality attributes in corn stover and related impacts to integrated preprocessing and conversion are not well understood. A multiscale approach was developed and employed in this study to understand how variability of corn stover attributes originates across fields within a supply shed and how macro-scale behavior in feeding, preprocessing, and conversion is predicated upon variations in attributes at the molecular and microscale (compositional, structural, and physicochemical attributes; Figure 2). Fundamental knowledge is critical to derisking the biorefining industry and overcoming challenges related to feedstock variability from the field through final products. The sources and range of variability are highest at

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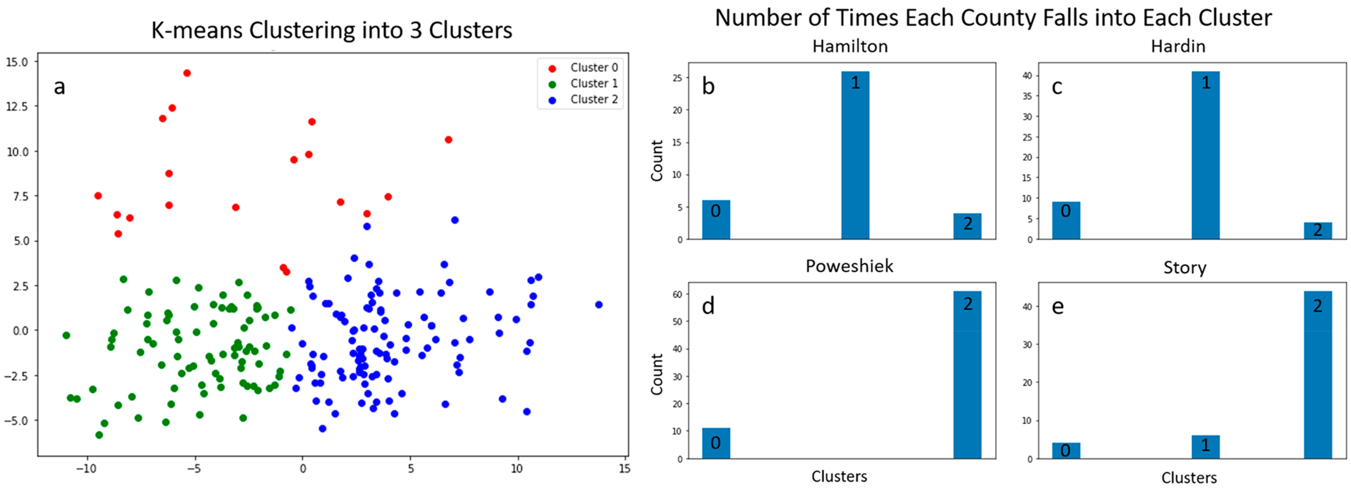

Figure 3. Clustering results using bale core data. Bale core data were clustered on glucan (%), xylan (%), lignin (%), extractives (%), ash (%, 575 °C) that were measured using near IR spectroscopy and Al_2O_3 (% w/w), CaO (% w/w), Fe_2O_3 (% w/w), K_2O (% w/w), MgO (% w/w), MnO (% w/w), Na_2O (% w/w), P_2O_5 (% w/w), SiO_2 (% w/w), TiO_2 (% w/w), SO_3 (% w/w) using *k*-means clustering. Left panel: Results of *k*-means clustering of these features into three clusters (a), indicating there are three distinct clusters with several samples overlapping data points among the clusters. For visualization purposes, clusters are displayed on a two-dimensional scatter plot of the first two principal components and color coded by cluster number. Right panel: Bar plots showing the number of times each county corresponds to each of the three clusters calculated using *k*-means clustering, indicating Hamilton (b) and Hardin (c) counties predominately fall into cluster 1 and Poweshiek (d) and Story (e) predominantly fall into cluster 2.

the regional or resource-level and propagate with modification across the value chain.

Regional/County-Level Variability: *k*-means Clustering. Understanding feedstock variability at a broad scale requires accounting for regional-scale heterogeneity.[35] Historically, most studies of biomass quality have relied upon measures that only account for bulk chemical composition, quantifying structural carbohydrates, lignin, extractives, and total ash content.[11,12,29,36−38] In the present study, *k*-means clustering was employed for retrospective examination of a multivariate data set, including organic and inorganic features ($n = 16$), using cores ($n = 216$) obtained from stover bales representing four distinct counties in Iowa.

The 24 bales used for this study underwent preliminary screening on the basis of total moisture and ash content for empirical studies intended as pilot-scale assessments of corn stover variability on an integrated preprocessing and biochemical conversion pathway.[3] *k*-means clustering was initially performed using only two features—total ash and moisture content—to assess any influence that bale preselection may have contributed to the regional-scale analysis of feedstock variability. With two features and clusters set at $k = 2$ or 3, all data are intermingled (see Figure S1 in Supporting Information (SI)), suggesting that ash and moisture alone do not differentiate among bales in this study.

k-means clustering was performed using the following features: glucan (%), xylan (%), lignin (%), extractives (%), ash (%, 575 °C) were predicted using near IR spectroscopy and Al_2O_3 (% w/w), CaO (% w/w), Fe_2O_3 (% w/w), K_2O (% w/w), MgO (% w/w), MnO (% w/w), Na_2O (% w/w), P_2O_5 (% w/w), SiO_2 (% w/w), TiO_2 (% w/w), and SO_3 (% w/w) that were measured according to ASTM D6349 method. County of origin was not included as a feature in *k*-means clustering. To determine the optimal number of clusters, *k*-means clustering was first run over a range of values for the number of clusters ($k =$ 1 to 11 clusters) and the in-cluster sum of squares was calculated for each value of *k*. In-cluster sum of squares was plotted as a function of the number of clusters, and the optimal number of clusters was chosen as 3, which corresponded to the inflection point on the curve. The results are shown in Figure 3a, with data partitioned into three well-defined clusters. To further investigate the origin of the differences among the 3 clusters, the number of times each county was included in each of the clusters was counted. These data show that, based on the selected features, Hamilton and Hardin counties (Figure 3b,c) are very similar, while Poweshiek and Story (Figure 3d,e) predominantly cluster together.

Results of *k*-means clustering of 16 combined organic and inorganic features revealed a connection back to county of origin. *k*-means clustering performed with three clusters (Figure 3a) indicates that Hamilton and Hardin, which are neighboring counties, cluster together—with most features falling to cluster 1 and a few in clusters 0 and 2 (Figure 3b,c)—while Story and Poweshiek counties (Figure 3d,e), located to the south, also cluster together with most features in cluster 2 and a few others falling to 0 and 1. All counties have commonality across features with some samples in each cluster. Features of inorganic speciation, glucan, xylan, extractives, lignin, and total ash content when clustered together, with no prior knowledge of county, reflect differences in geospatial location—growth conditions, soil type and chemistry—and harvest operations. Ash content in switchgrass has been shown to be significantly affected by location[37] and landscape position;[38] for example, high ash content biomass derived from low elevation fields or floodplains may require additional preprocessing to prevent slagging in thermochemical conversion.[39] Previous studies have demonstrated the effects of harvest timing[40,41] and harvest equipment and method[13,42] on quality variations that impact sugar utilization during fermentation and the quality of convertible biomass for biochemical conversion pathways. The results indicate substantial variability exists regionally, even among counties within close proximity that are representative of a realistic, biorefinery supply shed. These findings suggest that the typical bulk measures of moisture and ash are not sufficient for understanding the complexity of feedstock variability and potential downstream impacts but important differences are

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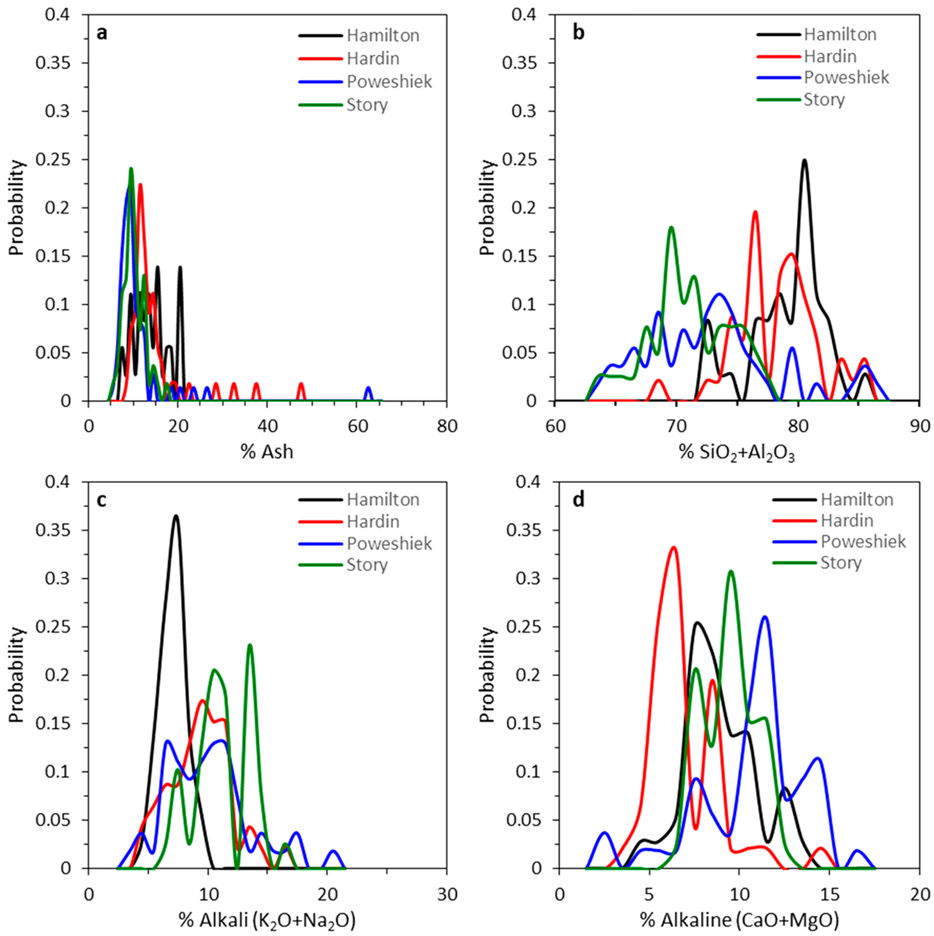

Figure 4. Probability distribution functions of inorganics measured in cores and dominant inorganic species variabilities on total ash basis in the corn stover bales collected from four counties in Iowa: (a) total ash content, (b) sum of SiO_2 and Al_2O_3, (c) alkali (K_2O, Na_2O), (d) alkaline earth metals (CaO, MgO).

manifested in the detailed measures of inorganic and organic components of biomass.

Ash and Inorganic Speciation. Currently, inorganics are treated on a bulk ash content basis with limited tracking or understanding of the impacts of individual inorganic species to preprocessing and conversion. However, *k*-means clustering results presented here suggest that total ash content was a limited descriptive feature for differentiating among bales at a regional scale. Probability distribution functions for total ash (%), combined % SiO_2 and % Al_2O_3, often derived from soil, % alkali, and %alkaline inorganic species are presented in Figure 4. Significant variability is noted in total ash content in bales measured across all four counties in this study with total inorganics ranging from about 5% to 25%; however, the distributions of total ash, particularly those for Story, Hardin and Poweshiek are not distinguishable, which further explains why total ash is not an adequate feature for uniquely differentiating (i.e., clustering) corn stover. In contrast, the distributions of inorganics are more distinct among the counties (Figure S2). Bales from Hardin and Hamilton counties were enriched in SiO_2 and Al_2O_3 on a total ash basis, suggesting increased soil accumulation,[43] relative to bales from Story and Poweshiek counties. In contrast, Story and Poweshiek counties had higher concentrations of alkaline earth metals (Ca and Mg) on a total ash basis, as compared to Hardin and Hamilton counties. Story, Hardin, and Poweshiek counties had more variable and higher alkali content than bales from Hamilton County. Inorganic species variations can be attributed to factors, like growth conditions and harvest method, although differences reported here cannot be determined from these data. Findings suggest regional differences in inorganic speciation are an important consideration for determining biorefinery process configurations and potential locations.

Knowledge of inorganic speciation and content is central to addressing challenges around biorefinery disruptions caused by wear and deleterious impacts to thermochemical and biochemical conversion pathways. Inorganics in corn stover have been implicated in equipment damage during bioprocessing by IBRs,[4] contributing to wear through abrasive and erosion mechanisms.[44,45] A recent study reported an increase in the work of cohesion for corn stover particles corresponding with an increase in ash content,[34] highlighting the role of inorganic content and speciation in bulk solids handling challenges that relate to poor flow properties and agglomeration.[46] Alkali metals, like potassium,[47] negatively affect catalytic fast pyrolysis.[48] Water-soluble components of biomass ash, such as K, Na, Cl, and S, have been implicated in critical challenges in thermochemical conversion of solid biofuels that include fouling, slagging, corrosion, particulate emissions, and environmental contamination.[46] In biochemical pathways, inorganic species have been shown to contribute to mechanical wear during pretreatment[3,39] and reduce the efficacy of dilute acid pretreatment and xylose yields due to soil buffering capacity of the corn stover.[49] These results suggest that regional variations

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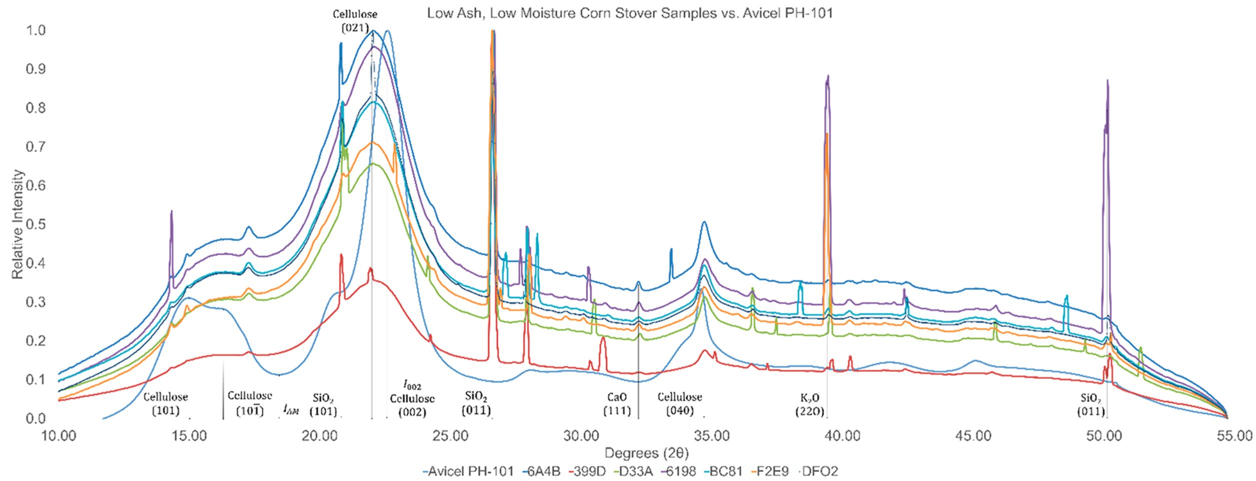

Figure 5. XRD spectra for biomass samples obtained from Story, Iowa indicated that crystallinity was similar. However, peaks indicating minerals present in the ash content of biomass can help elucidate the impact of inorganic species variabililty on feedstock quality.

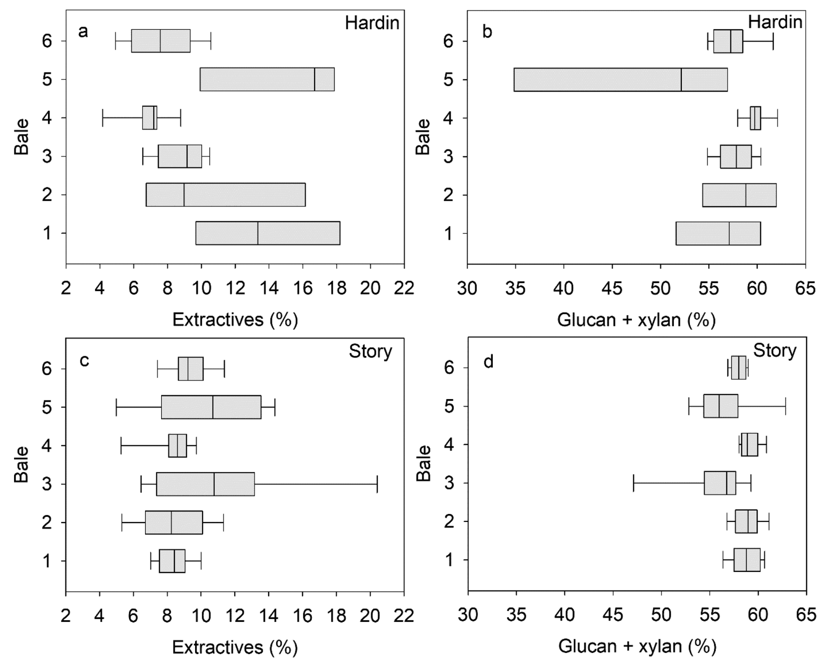

Figure 6. Distributions for (a) extractives and (b) combined glucan and xylan six bales from Hardin County. Composition for Hardin county bales was predicted with the following core samples: bales 1 and 5 − n = 4 cores; bale 2 − n = 7 cores; bales 3, 4, and 6 − n = 9 cores. Boxplots for (c) extractives and (d) combined glucan and xylan for six bales from Story County. Nine cores were sampled from each bale.

in corn stover can be revealed and potentially managed through an understanding of inorganic speciation rather than bulk compositional measures.

Spectroscopic methods, after calibration against standardized analytical techniques, have proven to be excellent methods for rapid sample analysis. We investigated X-ray diffraction as an approach to generate information on inorganic speciation along with biomass crystallinity. Figure 5 represents spectra from the various samples. All biomass types exhibited similar crystallinity indices, ranging between 44.0 and 52.66% with a standard deviation of 0.0220. Cellulose crystalline peaks were identified based on previous work on cellulose containing materials.[50] However, the spectra also provided peaks indicative of minerals. Mineral peaks were identified for SiO_2,[51] K_2O,[52] and CaO.[53] Variation of inorganic content and speciation will guide the development of integrated, analytical characterization approaches capable of discriminating between physiological and extrinsic inorganics derived from soil accumulation.

Bale-Scale Variability by County. In biorefinery operations, whole bales are received, stored as needed, deconstructed, and further milled to the desired particle size for use in conversion. A bale sampling scheme was adapted from prior studies[27,28] and used to assess composition and quality variations among bales. Variables corresponding to sampling method (core depth, location, distance from face or top) were evaluated for cores (n = 216, with n = 9 cores/bale) from bales (n = 24) corresponding to each county presented in this study. Probability density functions and distributions for each of the coring variables that were measured in this study (core depth and three core locations) are consistent for core samples from bales across all counties (SI, Figures S3−S4), indicating that the coring methodology employed here was not a source of

https://dx.doi.org/10.1021/acssuschemeng.9b06763
ACS Sustainable Chem. Eng. 2020, 8, 3218−3230

variability and did not influence or bias results. These findings provide support for a robust coring method that could readily be adopted by biomass producers or plant operators for quality and process control in a biorefinery setting. In total, 216 core samples were generated by using a reliable bale coring methodology.

Bale-Scale Compositional Analysis. The coring methodology described above was used to obtain a set of $n = 216$ cores ($n = 9$ cores/bale) to examine within-bale variability. Corn stover bales derived from Hardin and Story counties were selected as the focus for assessment of bale-scale compositional variability, given the notable differences in inorganic speciation revealed upon the regional or county-level clustering results. Overall, the mean and range of structural carbohydrate contents for combined glucan and xylan were similar for both Hardin (57.7%; 50.4−62.6%; $n = 42$) and Story (mean 57.8%; min. 47.1 to max. 62.8%; $n = 54$) at the county-level; lignin was similar for both counties, measuring 17.7% (14.3−20.8%; $n = 43$) and 18.0% (16.1−19.9%; $n = 54$), respectively (SI, Figure S5). Further examination of within-bale measures revealed material color changes and substantial variation in structural carbohydrates and extractives content for both counties and, in particular, Hardin County (Figure 6). Biological degradation was observed during the sampling and processing of bales derived from Hardin county; profiles of material browning consistent with biological degradation were evident on the bale exterior and cores obtained from Hardin bales 1, 2, and 5. Biological degradation occurs in response to moisture variations, aerobic and anaerobic microenvironments throughout the bale, and the associated microbial community[21] and represents an important source of within-bale heterogeneity. Evidence of biological degradation across bale sections has been linked to process upsets and reductions in throughput during bale deconstruction and milling operations.[3] Further, it was not possible to obtain FT-NIR composition predictions of all core samples obtained from Hardin bales; in bales 1 and 5, only 4 of the 9 cores were within the calibration model for prediction of composition, while in bale 2, 7 of the 9 cores were within the calibration (Figure 6a,b). These findings corroborate other reports of degradation of structural components like hemicellulose to soluble forms of C5 sugars.[21] Additionally, these results illustrate the need for robust predictive models that account for the range of variability, including moisture history and biological degradation, in realistic corn stover feedstocks.

Bale-Scale Variability Analyzed by RGB Images. Image analysis was employed as a macro-scale approach to evaluate quality of corn stover in visible, red-green-blue (RGB) space. Cores (12.7 cm) obtained from bales in this study were classified as either demonstrating evidence of biological degradation or soil accumulation (or combinations thereof), or as clean upon observation. Analysis of the red channel from these images revealed that significant variations were correlated with SiO_2 and glucan contents. Findings suggest that the red channel can yield information related to surface content of accumulated soil, primarily SiO_2, and glucan content, which changes with degree of biological degradation. Figure 7 shows sample images of material from the respective quality descriptor categories, in addition to a result of the linear regression of the measured average red signal and the predicted signal from SiO_2 and glucan. The legend indicates cores that were identified into the respective quality categories through the observational study; the apparent separation or clustering of the material quality along the intensity of the red signal was notable. Samples

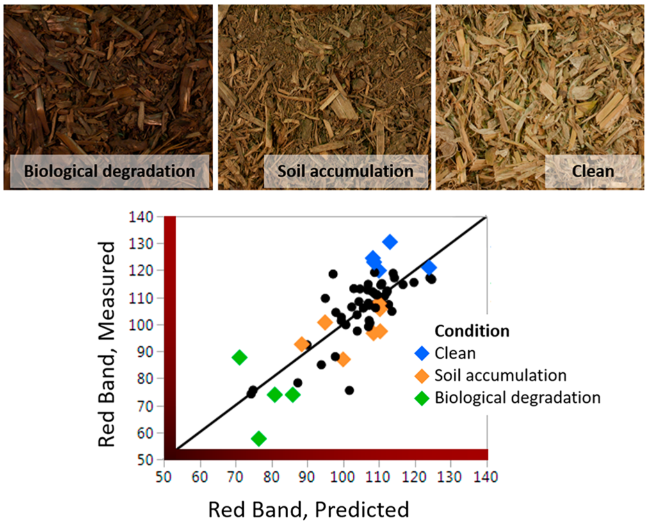

Figure 7. Image analysis of corn stover cores in red-green-blue (RGB) space enables rapid quality assessment. All samples (black circles and colored diamonds) were used in regression analysis for explaining the signal of the red channel measured from RGB image analysis using SiO_2 and glucan contents. Core samples that were identified and categorized as clean (blue diamond), noted for presence of soil accumulation (yellow diamond), or suggestive of biological degradation (green diamond) upon visual inspection demonstrate clustering of material quality related to red signal intensity.

categorized as clean clustered in a higher range of intensities (110−125) in the red channel and the biologically degraded samples clustered in lower intensities (70−90), while soil accumulated samples clustered intermediate to both.

The multinomial regression for classification of the material quality resulted in an overall accuracy of 76.2%. A differentiation among samples with evidence of biological degradation and those with combined degradation and soil accumulation yielded the largest discrepancies. Refinement of such predictive models will require a mechanistic understanding of the biological degradative processes[20] and thermo-chemical oxidative reactions that alter biomass quality attributes during storage[54] in order to deconvolute confounding signals from degradation and soil accumulation of inorganic species. Although this approach requires further development (thus model parameters are not detailed here), these qualitative results show promise for the development of rapid screening tools that could be deployed in the field or in-line for rapid assessments of quality and is the topic of future work.

To further examine particle-scale differences both among samples from different collection sites and among the bales from individual sample sites, we examined milled samples by stereomicroscopy and performed particle size distribution and morphology analysis (Figure 8). Variability across the samples collected from different counties was readily visible and directly measurable from the corn stover particles following 2-stages of milling and size reduction during preprocessing. Particles analyzed from the bales collected from Hardin county were more varied in color, size, and shape. The Story county samples were more uniform in color, particle size, and morphology across the 6 bale samples analyzed. Differences in color and particle size may be the result of variations in inorganic content and biological degradation caused by agronomic and storage practices, which warrants future investigations. These variations may also reflect different plant fractions and tissue types.

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ACS Sustainable Chem. Eng. 2020, 8, 3218−3230

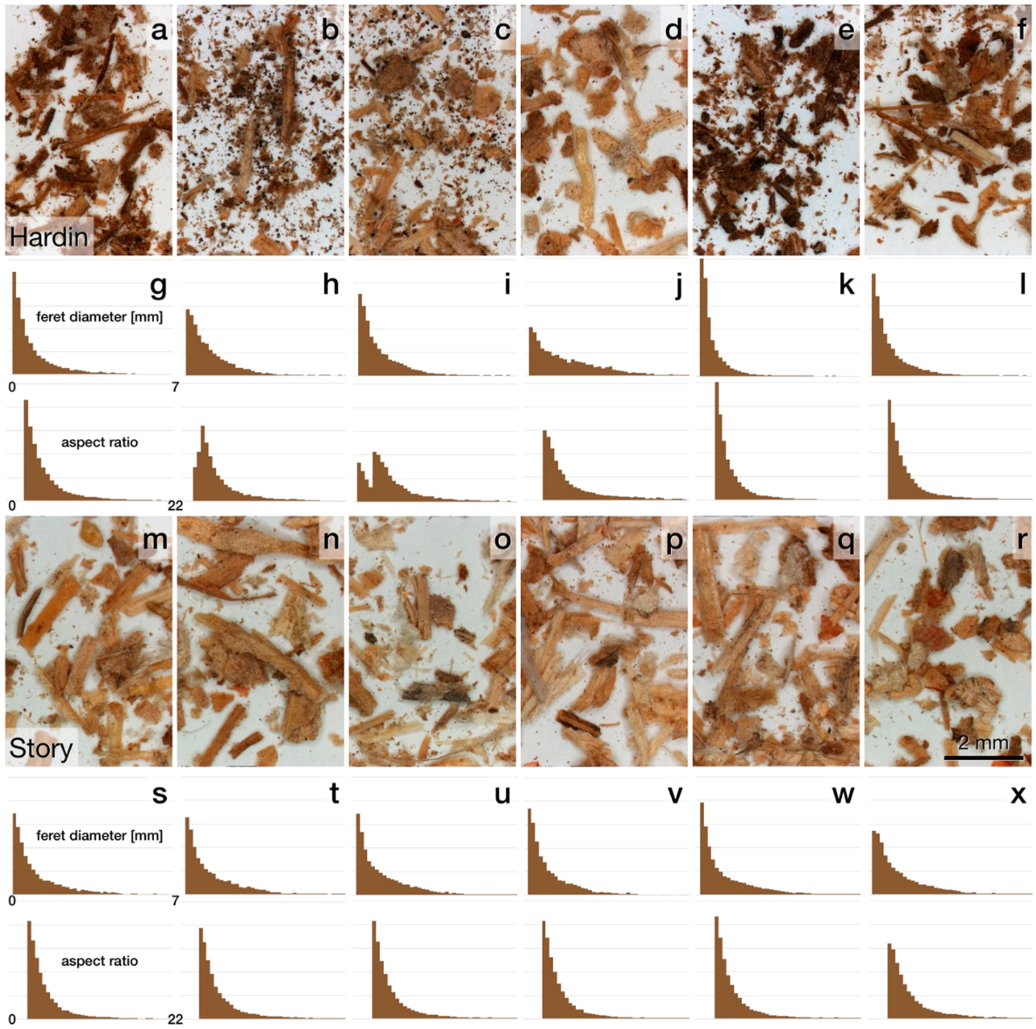

Figure 8. Stereoscope micrographs (a−f, m−r) and particle morphology (g−l, s−x) of milled, sieved corn stover particles sampled across multiple bales and bale sections. The samples collected in Hardin county displayed a greater distribution of variability in color, particle diameter, and aspect ratio both among and within the different bales than the samples collected from Story county.

Microscale Variability and Emergent Attributes. To better understand the range of variability in corn stover that exists at the microscale, we examined milled biomass particles by SEM. The micrographs in Figure 9 display a range of morphologies and surface features that are found among particles originating from different anatomical fractions or tissue types of the maize plant. This analysis demonstrates that even within a single section of a single bale from a single location examined in this study, additional variability exists. A range in surface roughness from Rq = 16 to 42 was measured from these representative images. During biomass conversion, a high surface roughness represents an increase in accessible surface area for catalysts and enzymes. For biomass conveyance, however, high surface roughness may increase interparticle friction that leads to bridging and restricts flow. Future studies will determine how this variability in surface roughness directly impacts particle flowability and conveyance.

Specific surface energy is the result of interactions between molecules with a polar nature and hydrogen bonding. Although, dispersive energy plays a role, the specific surface interactions are often the major contributor to adhesive and cohesive properties of a material. Specific surface energy was estimated using the Dong polarization method on the vOCG scale and revealed differences for Hardin and Story counties (64.1 $mJ/m^2 \pm 4.1$ and 60.7 $mJ/m^2 \pm 2.4$, respectively; $p = 0.002$); results and distributions are given in Figure 10a. Variations in specific surface energy were attributed to differences in inorganics content as a function of soil accumulation,[34] differences in surface chemistry as a result of biological degradation,[20] or in combination. Measured hydrophilicity was similar for both Hardin and Story counties (0.61 ± 0.01 and 0.60 ± 0.01, respectively), while nonparametric testing revealed a modest increase in surface area for Hardin County (1.0 ± 0.2 versus 0.8 ± 0.1 m^2/g; Rank Sum Test $p < 0.001$). Bales obtained from Hardin county showed evidence of biological degradation, which may account for the slight increase in surface area measured here and corresponding to variations in particle size noted above (Figure 8). Integrated analyses of particle morphology, surface energy, and surface mapping will enable a multimode approach to examine cellular and molecular-level properties and to elucidate impacts on handling, deconstruction, and conversion operations. The fundamental physical, chemical, and structural properties described herein represent emergent properties or features of biomass that require excessive energy inputs for size reduction in preprocessing, feeding and handling, and conversion to target products, giving rise to new

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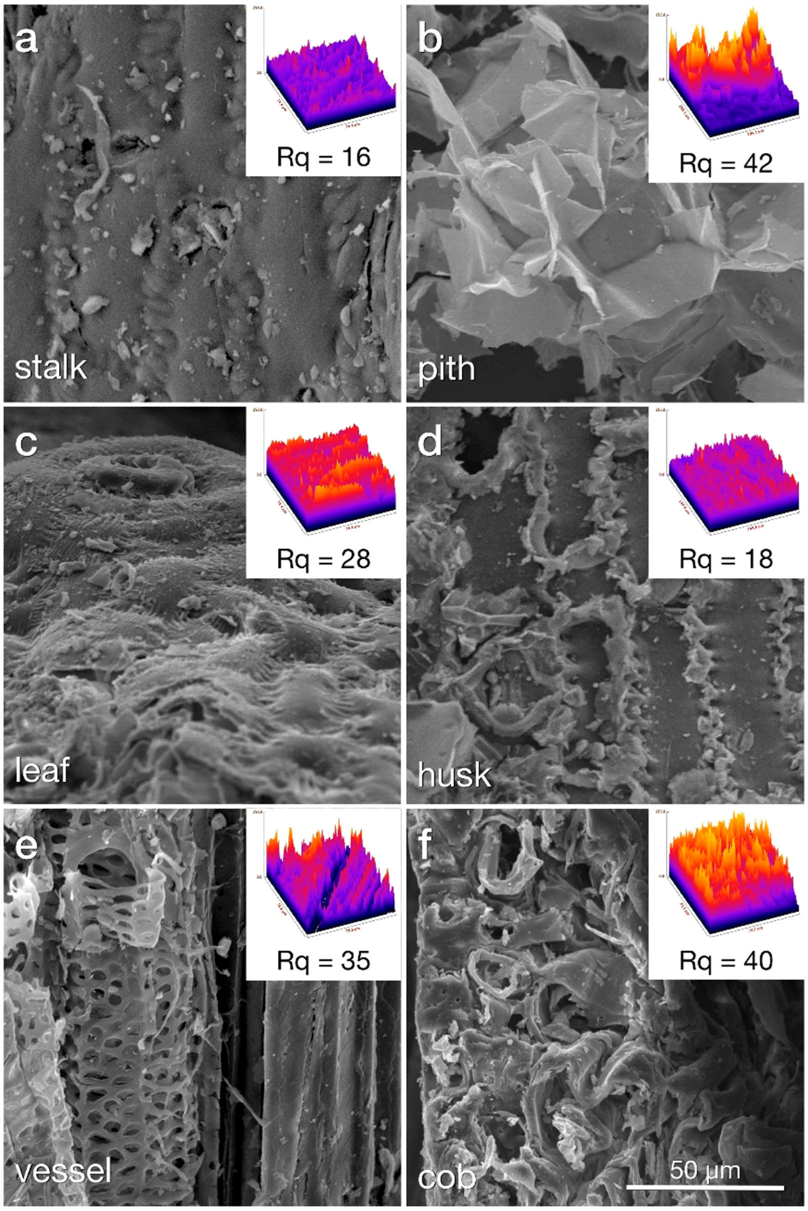

Figure 9. SEM micrographs with surface roughness inset revealing microscale heterogeneity among corn stover fractions: (a) stalk, (b) pith, (c) leaf, (d) husk, (e) vessel, (f) cob. SEM micrographs of surfaces from different milled corn stover particles from a single section of a single bale harvested from Story County, Iowa. The particles originating from different tissues of maize plant display different morphologies and variable surface roughness. Surface roughness was calculated from the images and displayed as topology profiles (insets) and Rq values.

determinants of recalcitrance.[55] These emergent properties arise from underlying physical, chemical, and structural attributes but exist and interact at a spatial scale that, we anticipate, has substantial impact on the behavior of biomass in upstream biorefinery operations that have struggled with the challenge of accommodating biomass variability.

■ CONCLUSIONS

This study utilized multiscale characterization combined with data analytic approaches to extract features that explain variability of corn stover across four, Iowa counties representing a realistic supply shed in the U.S. Corn Belt. Clustering analyses indicated that moisture and ash on a bulk compositional basis did not differentiate bales of corn stover from the fields examined here. However, *k*-means clustering performed with a combination of 16 organic and inorganic features revealed a connection back to county. Further analyses suggested that the partitioning of corn stover was driven by significant variations in inorganic speciation among the counties examined here. Though the root cause of such variations cannot be determined from these data, differences in growing conditions, production (e.g., tillage and nutrient inputs), and harvesting methods likely play a role. These data suggest that county-level differences, even within a supply shed in a high-yielding region, are an important consideration, not only for siting future biorefinery locations but also for determining optimal process configurations and operational parameters for managing variations in biomass quality. Further, this study illustrates how within-bale and within-plant variability confound the understanding of quality in the context of biorefining operations. Biological degradation and soil accumulation contribute to compositional and structural variations within a bale that have been implicated in process

https://dx.doi.org/10.1021/acssuschemeng.9b06763
ACS Sustainable Chem. Eng. 2020, 8, 3218−3230

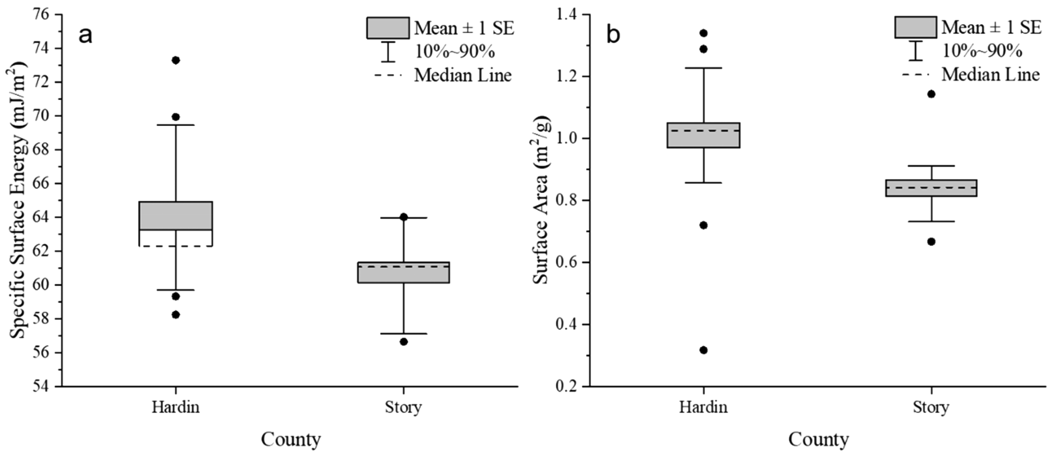

Figure 10. Distributions of specific surface energy (a) and surface area (b) with mean, standard error, median, and 10th to 90th percentiles, for milled corn stover derived from Hardin (n = 24) and Story (n = 17) counties.

upsets with reductions in throughput and conversion yield. These findings highlight the need for a fundamental understanding of biomass properties and sources that contribute to realistic variations in their distributions, including growth, production, and preprocessing factors as well as anatomical fractions and tissue types.

Here, we explored fundamental, physicochemical, and structural attributes that exist at multiple scales and represent emergent properties of biomass. The measurement of variations in the structure and composition of biomass at multiple scales is essential for translating attributes at the micro and molecular scales to behavior and recalcitrance in bioprocessing. A fundamental exploration of these features is foundational to engineer systems capable of managing variability for reliable biorefinery operations and to enable quality-based valuation required for the mobilization of domestic, diverse biomass resources and growth of the bioeconomy. Future work aims to develop a biomass-agnostic and integrated characterization approach to elucidate how feature variations relate to downstream processes, offering a predictive capability rooted in fundamental understanding of multiscale material attributes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acssuschemeng.9b06763.

Detailed information on methods for image analysis in Red-Green-Blue (RGB) color space; k-means clustering results based on features of total ash and moisture content for k = 2 and k = 3 clusters; linear discriminant analysis of inorganic features; probability distribution functions and box plot distributions of bale coring methodology employed in this study; compositional distributions across four counties in Iowa (PDF)

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https://dx.doi.org/10.1021/acssuschemeng.9b06763
ACS Sustainable Chem. Eng. 2020, 8, 3218−3230

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ACKNOWLEDGMENTS

This research was supported by the U.S. Department of Energy, Office of Energy Efficiency and Renewable Energy, Bioenergy Technologies Office, under DOE Idaho Operations Office Contract DE-AC07- 05ID14517. This research used resources of the Advanced Light Source (beamline 12.2.2), which is a DOE Office of Science User Facility under contract no. DE-AC02-05CH11231. Further, this research leveraged resources of the Biomass Feedstock National User Facility (BFNUF), which is a DOE Office of Energy Efficiency and Renewable Energy User Facility located at Idaho National Laboratory (Idaho Falls, ID). This work was authored in part by Alliance for Sustainable Energy, LLC, the manager and operator of the National Renewable Energy Laboratory for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525. This information was prepared as an account of work sponsored by an agency of the U.S. Government. Neither the U.S. Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. References herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the U.S. Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the US Government or any agency thereof. The authors would like to thank Mark Elless, Art Wiselogel, Alison Goss Eng, Beau Hoffman, Liz Moore, and Steve Thomas of the Bioenergy Technologies Office for their support on Feedstock-Conversion Interface Consortium R&D. We are grateful to numerous colleagues for their technical support: William Smith, Brad Thomas, Eric Fillerup, Rachel Colby, Kastli Schaller, Austin Murphy, Sergio Hernandez, Matt Dee, Devin Lively, Cody Scheer, Dana Scouten, Marnie Cortez, Robert Kinoshita, Pat Bonebright, Corey Landon, Craig Conner, Ning Sun, Courtney Payne, Neal Yancey, Vicki Thompson, and Daniel Campbell. AER is grateful to AAE for technical assistance.

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https://dx.doi.org/10.1021/acssuschemeng.9b06763
ACS Sustainable Chem. Eng. 2020, 8, 3218−3230