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Research article

Impact of an innovated storage technology on the quality of preprocessed switchgrass bales

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Abstract: The purpose of this study was to determine the effects of three particle sizes of feedstock and two types of novel bale wraps on the quality of switchgrass by monitoring the chemical changes in cellulose, hemicellulose, lignin, extractives, and ash over a 225-day period. Using NIR (Near-infrared) modeling to predict the chemical composition of the treated biomass, differences were found in cellulose, lignin, and ash content across switchgrass bales with different particle sizes. Enclosing bales in a net and film impacted the cellulose, lignin, and ash content. Cellulose, hemicellulose, lignin, extractives, and ash were different across the 225-day storage period. A quadratic response function made better prediction about cellulose, lignin, and ash response to storage, and a linear response function best described hemicellulose and extractives response to storage. This study yields valuable information regarding the quality of switchgrass at different intervals between the start and end date of storage, which is important to conversion facilities when determining optimal storage strategies to improve quality of the biomass feedstock, based on potential output yield of a bale over time.

Keywords: chemical composition; near-infrared spectroscopy; lignocellulosic biomass quality; particle size; preprocessing; storage; switchgrass

1. Introduction

Switchgrass (*Panicum virgatum* L.) is recognized as a crop having great potential in the southeastern United States to provide feedstock for the production of bio-based fuels, power, and products [1,2]. One major challenge for a large-scale commercial switchgrass conversion facility is efficient storage of switchgrass while maintaining the quantity and quality of the feedstock given the environmental conditions of the region [3–5]. The physical and chemical quality of switchgrass may affect the efficiency of the conversion processes used to produce bio-based fuels, power and products, which directly impacts the economic viability of switchgrass processors [6].

Carbohydrates and lignin are the major components for the production of bio-based fuel, power, and products [7]. Ash may also have an important impact on the efficiency of feedstock conversion for both, thermochemical and biological conversion processes [7]. The aforementioned properties of switchgrass could change with time in storage, hence affecting the production of switchgrass-based biofuels [6]. Several studies have investigated the impacts of outdoor storage on dry matter (DM) loss of switchgrass harvested as large round or rectangular bales [8–14]. However, less is known about the compositional changes in outdoor-stored switchgrass with the exception of a few studies [5,12,13].

Wiselogel et al. [5] analyzed changes in the composition of large round bales of switchgrass stored unprotected outside for 26 weeks after harvests in October 1991 and August 1992 in Texas. Cellulose and hemicellulose content decreased, ash increased, and xylan content did not change in both 26-week storage periods. However, lignin content increased in the higher precipitation storage period after the October 1991 harvest but decreased in the lower precipitation storage period after the August 1992 harvest. Shinner et al. [12] compared ash, cellulose, and hemicellulose content for switchgrass bales stored with different wrap materials over a 311-day period in Wisconsin. Bale wrap treatments included sisal twine, plastic twine, net wrap, breathable film, and plastic film. They reported cellulose content were higher at the end of the storage period with net-wrapped bales having the highest cellulose content. Hemicellulose and ash content were higher at the end of the storage period, but did not vary by type of wrap material. Khanchi et al. [13] compared changes in cellulose, hemicellulose, and lignin for large round and large rectangular switchgrass bales stored outdoors for 180 days in Oklahoma. The experiment was conducted in 2009 and repeated in 2010. Cellulose content increased for rectangular bales in both years. By comparison, cellulose decreased for round bales in the 2009 experiment and increased in 2010. Similarly, hemicellulose and lignin content increased in one year and decreased in the other for both round and square bales. The mixed results for compositional changes over the 180 days were likely due to year-to-year weather events such as rainfall and rainfall timing.

The aforementioned studies provide useful insight into the composition changes of switchgrass bales during outdoor-storage but have some limitations. The aforementioned studies analyzed bales that were primarily handled using a standard agricultural hay baler. Other innovated storage technologies have been developed to reduce costs of biofuel at the plant gate [3,15,16] and mitigate other potential logistical issues with standard hay harvest and storage technologies [17]. Recently, Larson et al. [18] assessed the possibility of using a new commercial stretch-wrap baler, BaleTech 3 (BT3), to compact chopped switchgrass into a wrapped large round bale by film and net for outdoor storage. The wrapped bale has similar dimensions as an agricultural round bale but has the potential reduce DM loss. Larson et al. [18] found that BT3 may be a feasible alternative to conventional agricultural bales for chopped switchgrass. Yu et al. [14] further analyzed the DM loss in the wrapped bales and suggested that the wrapped bales by both film and net experienced less DM loss than the bales wrapped with net only. In addition, particle size is also found influential to storage DM loss in the wrapped bales. However, the compositional changes of feedstock in the BT3 bales over time were not addressed in either study, but have since been recognized as an important issue for future study [14].

Another limitation of these studies is the changes in composition between the beginning and the end of the storage period across different treatments (e.g., bale shapes, bale wrap materials), but did not examine the changes in composition at different time intervals between the start and end date of storage. Kline et al. [19] recently developed a near-infrared (NIR) multivariate model using samples from both senesced switchgrass and stored switchgrass over different days in storage to calibrate the models for major carbohydrates, extractives, lignin, and ash. They showed that using samples from senesces and storage can improve the prediction of chemical changes. Thus, more accurate information on how chemical composition varies over shorter periods of storage could be helpful for the conversion facility to determine optimal storage strategies based on potential output yield (i.e., drop in fuel) of a bale.

Thus, the objective of this study was to determine the impacts of three particles sizes of feedstock and two types of bale wraps on changes in cellulose, hemicellulose, lignin, extractives, and ash for switchgrass that was preprocessed using BT3 over a 225-day storage period. To the best of our knowledge, there have been no empirical studies that present the impacts of particle size on compositional changes during storage for switchgrass bales. Particle size could have implications for improving feedstock logistics and feasibility of the advanced biofuels industry [20]. These results could help identify important considerations when developing models for use in a large-scale biomass distribution center.

2. Materials and Method

2.1. Experiment design

Alamo switchgrass from a farm near Vonore, TN USA that was under contract with the Tennessee Biofuels Initiative was used for the study. The switchgrass was planted in 2009 and was managed following University of Tennessee fertility recommendations. Switchgrass was harvested after senescence in early February 2012 using a New Holland BB9080 large rectangular baler (1.2 × 0.9 × 2.4 m) without a cutter (New Holland Agriculture, New Holland, PA USA). Bales were moved to the Biomass Innovation Park, Vonore, TN and stored under cover. On 22-Feb-2012, switchgrass bales were broken open, the twine was removed, and the biomass was processed through a Vermeer TG5000 tub grinder (Vermeer Corporation, Pella, IA USA). After processing, switchgrass was sampled for moisture content and chemical composition and then conveyed to a BT3 baler (TLA Bale Tech LLC, South Orange, NJ USA) to be formed into large round bales (1.2 m [diameter] × 1.5 m [width]). All of the bales were wrapped in a high-density polyethylene (HDPE) 1.52 m-wide net encompassing the outside circumference, excluding the two ends, of the bale. Half of the bales were also wrapped in multiple layers of a linear low polyethylene (LLPE) 0.51 m- or 0.76 m-wide film that completely covers the bale and a has minimum tensile strength of 60 megapascals. The film created an anaerobic storage environment for the switchgrass. The pre-processed bales were weighed and stacked three bales high into storage on 23-Feb-2012 in a grass field.

The three storage treatments evaluated in the experiment were: 1) particle size of feedstock, 2) bale wrap, and 3) days in storage. The experiment was a split-split plot design with five replications. The whole plots included three particle sizes of baled switchgrass: 1) full length [~243.84 cm] (PS-1); 2) 7.62 cm (PS-2); and 3) 1.27–1.91 cm (PS-3). Particle sizes were determined and measured by the screen size on the tub grinder. Distributions of particle sizes were determined using a RO-TAP sieve analysis according to American Society of Agricultural Biological Engineers (ASABE) standards. The subplots treatments were the material the bales were wrapped in for storage: 1) wrapped using HDPE net (net), and 2) wrapped using HDPE net and LLPE film (net & film). The sub-subplots were days in storage with bales entering storage on 23-Feb-2012 and stored for 75, 150, or 225 days.

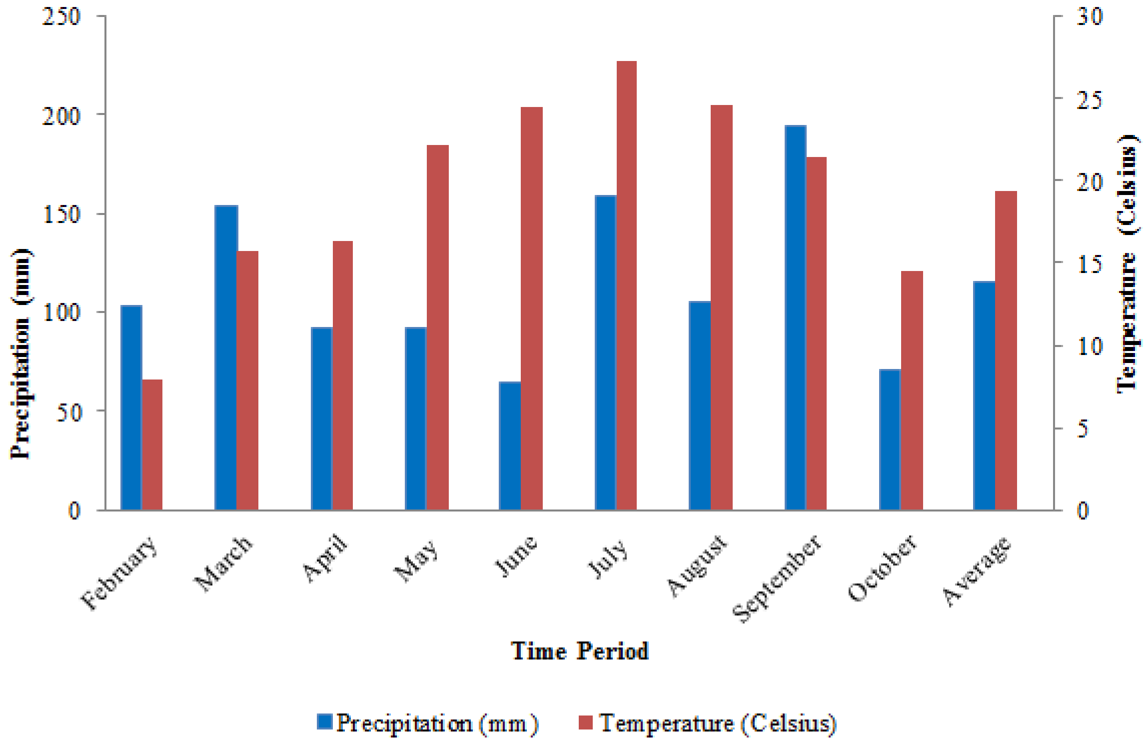

Figure 1. Monthly precipitation data (mm) from Knoxville McGhee Tyson Airport weather station in 2012.

For each storage period, 30 bales (3 particle sizes × 2 wraps × 5 replications) from the top two rows of the stacks were weighed, destroyed, and the material was randomly sampled. Therefore, a composite of 180 samples was analyzed for chemical composition—90 samples taken before placement of bales into storage and 90 samples taken after placement of bales into storage. Monthly weather data from the closest weather station are shown in Figure 1 for the timeframe of the bale storage experiment. Supplementary information about the experimental design and pictures from the experiment can be found in Yu et al. [14]. Relative to the previous studies, the experiment was conducted in a location with higher average precipitation [5,12,13].

2.2. Chemical composition analysis

The 180 switchgrass samples were analyzed by the BioEnergy Science and Technology Unit in the Center for Renewable Carbon, University of Tennessee, Knoxville for the compositional analysis. Samples were ground with a Wiley mill to 40 mesh, randomly sorted and scanned by NIR spectroscopy using an Analytical Spectral Devices (ASD) Field Spectrometer at wavelengths between 350–2,500 nanometers. A high-intensity light source housed in a scanning chamber and positioned at a right angle to the sample surface and a fiber optic oriented at 60 degrees to the sample surface were used to collect reflectance spectra. Five spectra were collected for each sample in a 10 cm dish spinning at approximately 100 rpm, with 40 scans collected and averaged into each spectrum. The reflectance spectra were transferred from the ASD to the Unscrambler® v9.0 software (CAMO, Woodbride, NJ USA), converted to absorbance, and spectral replicates were averaged to reduce the size of the spectra matrix, reducing the time required for statistical analysis. The data were also reduced by averaging the spectra that were collected at 1 nm intervals to 4 nm intervals to reduce uncertainty and the effects of noise. A mean normalization was applied and normalized spectra were submitted to a multiplicative scatter correction in order to remove scatter effects, such as those caused by light scattering due to the physical nature of the biomass particles, as opposed to chemical composition.

For development of predictive chemical compositional NIR model, 50 switchgrass samples were randomly selected to be the calibration sample set following methods presented in the ASTM protocol E1655-5. These samples were analyzed for quantification of compositional data following the National Renewable Energy Laboratory (NREL) standard biomass analytical procedures (wet chemistry). Each sample was first combusted at 575 °C for 24 h and measured gravimetrically for measurement of total ash content. Prior to quantification of the other structural constituents, the switchgrass samples were extracted to remove non-structural components in a Dionex (Sunnyvale, CA) Accelerated Solvent Extractor 350, following the methods described previously [21, 22]. In this process, 5 g of raw biomass with <10% moisture content was added to a 33 mL extraction cell and sequentially extracted by pressurized water then ethanol under 1500 psi, 100 °C, 5 min heating time, 7 min static time, and three static cycles. The material was then allowed to air dry to less than 10% moisture content by weight and a change in weight <1% in 24 h, determined using a sub-sample that was dried in a 105 °C convection oven for a minimum of 4 h to determine the percent of total solid.

The extractives-free material was stored in polyethylene bags at ambient temperature until further analyses were performed. The quantification of cellulose, hemicellulose, lignin, and ash in the switchgrass was performed following standard methods using three replicates [22]. The procedure was suitable for samples that do not contain extractives. A two-stage acid-catalyzed hydrolysis was performed to fractionate the sample into soluble and insoluble matter, and the two fractions were separated through vacuum filtration and ceramic fine porosity filtering crucibles. The insoluble solids fraction consisted of acid-insoluble lignin and ash. The acid-insoluble lignin was quantified gravimetrically after combustion of the residue at 575 °C for 24 h. The monomeric units of polysaccharides within the soluble liquid fraction were quantified via a Flexar high-pressure liquid chromatography (Perkin Elmer, Shelton, CT) with a refractive index detector. The system was equipped with an Aminex HPX-87P carbohydrate column (300 × 7.8 mmID, 9 µm particle size) and deashing guard column (125-0118) from Bio-Rad (Hercules, CA), using deionized water at 0.25 mL/min at 85 °C. The acid-soluble lignin content was measured using a two beam Perkin Elmer

Lambda 650 series spectrophotometer, and this value combined with the gravimetric value for acid-insoluble lignin for the total lignin content. A total of eight primary components were quantified as a mass percentage of the oven dry biomass, otherwise known as total solids (% dry basis): extractives, cellulose, hemicellulose (combined values for xylan, galactan, arabinan, and mannan), lignin, and ash.

2.3. Building PLS multivariate calibration model

After compiling the compositional data for the calibration sample set, partial-least-square (PLS) multivariate calibration model was built using Unscrambler software. PLS analysis regresses the dependent variables (the spectral data) against the independent variables (compositional constituents) for the selected calibration set of switchgrass samples, allowing for the entire spectrum to be used for the prediction of cellulose, hemicellulose, lignin, extractives, and ash. The model was generated using a full cross-validation procedure in which one sample was left out from the calibration sample set and the model was calculated based on the remaining samples. The value of the left-out data point was used for prediction, and the process was repeated with another sample from the calibration set until every sample has been left out one time. This procedure ensured that the predictive capabilities of the model were reliable and the model was not over-fitted. An overview of the technique is available in the literature [24,25]. The fit statistics of the predictive model showed the model was a robust predictor of the chemical composition.

To further validate the predictive capabilities and performance of the model a total of 10 samples, equal to 20% of samples contained within the calibration sample set, was removed from the sample population and used as validation samples to compare the measured chemical composition by wet chemistry to the NIR-predicted component data. These samples were evenly distributed along the range of the model, both by constituent value, particle size, and storage type and time. The independent validation samples were generally accurate and therefore the models were deemed acceptable for prediction of the biomass included in this study. More detail on the NIR modeling and sampling can be found in Kline et al. [19].

2.4. Statistical analysis of chemical composition

An analysis of variance (ANOVA) was applied to the sampled chemical composition data to determine the effects of particle size, bale wrap material, and days stored on the cellulose, hemicellulose, extractives, lignin, and ash content found in the bale as a percent of DM. Following the split-split-plot design analysis in Kuehl [26], the fixed effects included particle size, bale wrap material, days stored, and all the fixed effect interaction variables. Random effects were included for replication; particle size and replication interaction variable; and replication, particle size, and bale wrap material interaction variable. A model was estimated separately for each of the five chemical components (cellulose, hemicellulose, extractives, lignin, and ash); therefore, results are presented for five models. Mathematically, the ANOVA model is generally defined as

$$C_{ijlk} = \mu + \sum_{i=1}^{3-1}\alpha_i PS_i + \beta_j W_j + \sum_{i=1}^{3-1}\delta_{ij} PS_i W_j + \sum_{l=1}^{3-1}\gamma_l D_l + \sum_{i=1}^{3-1}\sum_{l=1}^{3-1}\lambda_{il} PS_i D_l + \sum_{l=1}^{3-1}\theta_{jl} W_j D_l + \sum_{i=1}^{3-1}\sum_{l=1}^{3-1}\omega_{ijl} PS_i W_j D_l + \nu_k + u_{ki} + \upsilon_{kij} + e_{ijlk} \quad (1)$$

where C_{ijlk} is a chemical component (% of DM) of the switchgrass (cellulose, hemicellulose, extractives, lignin, and ash) for particle size i with wrapped and stored in the jth material at the lth day for the kth replication; μ is the intercept coefficient; PS_i is an indicator variable for the ith particle size; W_j is an indicator variable for the jth wrap; D_l is an indicator variable for the lth day; α_i, β_j, δ_{ij}, γ_l, λ_{il}, θ_{jl}, and ω_{ijl} are coefficients for the different whole plots, subplots, sub-subplots, and the interaction across the treatments; $v_k \sim N(0,\sigma_v^2)$ is a random effect for the kth replication; $u_{ki} \sim N(0,\sigma_u^2)$ is a random effect for replication k and particle size i; $\upsilon_{kij} \sim N(0,\sigma_\upsilon^2)$ is a random effect for the kth replication, ith particle size wrapped and stored in the jth material; $e_{kilj} \sim N(0,\sigma_e^2)$ is the random error term. An F-test was used to determine whether chemical components were different across the fixed effects. If the F-test indicated differences across the fixed effects, pairwise comparisons were made to determine differences in chemical components across the treatments.

The model in equation (1) was estimated using the GLM procedure in SAS [27], and Tukey-Kramer method was used to make multiple comparisons across the plots, subplots, and sub-subplots. Significance was determined at $P \leq 0.05$. If the residuals from the ANOVA model violated the assumptions of normality and homoskedasticity, the data were transformed to address the non-normality and hetroskedasticity issue in the variance. Non-normality and heteroskedasticity were not found in the residuals from the models for the five chemical components.

Since data were collected for chemical composition changes over multiple storage periods, the results from the ANOVA analyses were used to identify whether a linear or quadratic response function better predicted each of the switchgrass chemical properties over storage time. The Akaike Information Criterion (AIC) and Bayesian Information Criterion (BIC) were used to determine the response function that was most appropriate for the data. The response function with the lowest AIC and BIC value was selected as the more appropriate response function [28]. The liner response function is generally defined as

$$C_{ij} = \eta_0 + \eta_{1ij} DIS + \varepsilon_{ij} \quad (2)$$

where C_{ij} is the chemical component (% of DM) for particle size i with wrapped and stored in the jth material; η_{1ij} is a coefficient; DIS is the days in storage; and $\varepsilon_{ij} \sim N(0,\sigma_\varepsilon^2)$ is the random error term. In addition, the quadratic response function is generally expressed as

$$C_{ij} = \tau_0 + \tau_{1ij} DIS + \tau_{2ij} DIS^2 + \xi_{ij} \quad (3)$$

where τ_{1ij}, and τ_{2ij} are coefficients; and $\xi_{ij} \sim N(0, \sigma_{\xi}^{2})$ are the random error term. The response functions were estimated using the GLM procedure in SAS [27].

3. Results and Discussion

3.1. ANOVA

3.1.1. Cellulose content

Cellulose content was different across particle size, wrap material, the interaction of particle size and wrap, and across days in storage ($P \leq 0.05$) (Table 1). Specifically, switchgrass bales of particle size PS-2 and PS-3 had higher content of cellulose than switchgrass baled at PS-1, which means the cellulose content increased as the particle size length decreased from PS-1 to PS-2 (Table 2). Covering the bale entirely in film increased the cellulose content to 39.8% of DM (Table 2). Shinner et al. [12] found higher cellulose content for bales wrapped in net only than bales circumferentially wrapped with a plastic film, but Khanchi et al. [13] found no difference in cellulose content between covered and uncovered bales. For the interaction of particle size and wrap material, the highest content of cellulose was found for a switchgrass bale wrapped in net and film with PS-2, and the lowest concentration of cellulose was found for switchgrass bales wrapped in net only with PS-1. Cellulose peaked at storage days 75 and 150 with increases in cellulose content to 40.8% and 40.3% of DM from day 0, respectively (Table 2). By day 225, cellulose content decreased from day 75 and 150 but was no different from day zero. Wiselogel et al. [5] found cellulose content in traditional large round bales to slightly decrease over a 26-week storage period (182 days) in Texas, which is different from what we found in this study.

Table 1. F-Test results for the fixed effects in the sugar ANOVA models.

	P-Values				
Fixed Effects	Cellulose	Hemicellulose	Extractives	Lignin	Ash
Particle Size (*PS*)	0.0075	0.0722	0.1108	0.0011	<0.0001
Wrap (*W*)	0.0069	0.0519	0.1384	<0.0001	0.0002
W x PS	0.0267	0.0037	0.0003	<0.0001	0.0011
Day (*D*)	<0.0001	0.0002	<0.0001	<0.0001	<0.0001
PS x *D*	0.3996	0.0255	0.1185	0.0158	0.1321
W x *D*	0.4756	0.5727	0.3959	0.3360	0.6550
PS x *W* x *D*	0.2295	0.6757	0.1022	0.4765	0.1043

Table 2. Expected chemical composition (in % of dry matter) across particle size, wrap, and days stored.

Treatments	Cellulose	Hemicellulose	Extractives	Lignin	Ash
Particle Size (PS)					
PS-1	39.25[b]	26.95[a]	6.03[a]	22.16[a,b]	2.94[a]
PS-2	39.72[a]	26.64[a]	5.60[a]	22.32[a]	2.41[b]
PS-3	39.79[a]	26.98[a]	5.78[a]	21.95[b]	2.21[b]
Wrap (W)					
Net	39.38[a]	26.73[a]	5.68[a]	22.36[a]	2.66[a]
Net & Film	39.79[b]	26.98[a]	5.93[a]	21.93[b]	2.38[b]
W x PS					
Net & Film x PS-1	39.39[b,c]	26.83[a]	6.13[a]	22.43[b]	2.91[a]
Net & Film x PS-2	40.20[a]	27.06[a]	5.31[b]	21.71[c]	2.09[b]
Net & Film x PS-3	39.80[a,b]	27.05[a]	6.34[a]	21.64[c]	2.16[b]
Net x PS-1	39.12[c]	27.05[a]	5.94[a]	21.87[c]	2.97[a]
Net x PS-2	39.22[b,c]	26.19[b]	5.89[a]	22.95[a]	2.74[a]
Net x PS-3	39.79[a,b]	26.91[a]	5.21[b]	22.27[b]	2.27[b]
Day (D)					
0	39.07[b]	26.87[a]	7.24[a]	21.74[b]	2.91[a]
75	40.84[a]	26.30[b]	5.41[b]	22.48[a]	2.14[b]
150	40.33[a]	26.87[a]	5.04[b]	22.73[a]	2.04[b]
225	39.13[b]	27.35[a]	5.53[b]	22.42[a]	2.23[b]
PS x D					
PS-1 x 0	38.50[c]	26.86[b,c,d]	7.92[a]	21.64[e]	3.47[a]
PS-1 x 75	40.64[a]	27.02[a,b,c,d]	5.51[c]	22.43[a,b,c,d]	2.33[b,c]
PS-1 x 150	40.33[a]	26.98[a,b,c,d]	4.99[c]	22.78[a,b,c]	2.32[b,c]
PS-1 x 225	39.05[b,c]	27.09[a,b,c,d]	5.71[c]	22.81[a,b,c]	2.57[a,b]
PS-2 x 0	39.22[b]	26.72[b,c,d]	6.92[b]	21.91[d,e]	2.75[a]
PS-2 x 75	40.99[a]	25.60[e]	5.23[c]	22.97[e]	2.22[b,c,d]
PS-2 x 150	40.31[a]	26.43[c,d]	5.10[c]	22.86[a,b]	1.92[c,d]
PS-2 x 225	39.25[b]	27.64[a]	5.15[c]	22.33[a,b,c,d]	2.11[c,d]
PS-3 x 0	39.48[b]	27.02[a,b,c,d]	6.86[b]	21.66[e]	2.51[a,b]
PS-3 x 75	40.87[a]	26.28[d,e]	5.49[c]	22.05[c,d,e]	1.88[d]
PS-3 x 150	40.36[a]	27.21[a,b,c]	5.03[c]	22.55[a,b,c,d]	1.88[d]
PS-3 x 225	39.08[b,c]	27.33[a,b]	5.73[c]	22.13[b,c,d,e]	1.98[c,d]

Note: Paired mean tests are performed for each level within the treatment for each chemical. If the letter is the same across all treatment levels, the numbers are not statistically different at the 0.05 level.

3.1.2. Hemicellulose content

Hemicellulose content varied across the interaction of particle size and wrap, days in storage, and the interaction of particle size and days in storage ($P \leq 0.05$) (Table 1). For hemicellulose content across the interaction of particle size and wrap material, the lowest content was for switchgrass bales wrapped in net only with PS-2, and the content of hemicellulose was not different across the other combinations of particle size and wrap (Table 2). Hemicellulose ranged between 26.3% and 27.4% of DM across the 225-day storage period and was greater at days zero, 150, and 225 than at day 75 (Table 2). Similar to cellulose, the hemicellulose content did not change over the 225-day storage period from day zero, which is different from what Wiselogel et al. [5] concluded for hemicellulose concentration. For the interaction fixed effects for particle size and days in storage, hemicellulose content was the lowest for bales with particle size PS-2 on day 75 and was highest for bales stored at particle size length PS-2 on day 225 (Table 2).

3.1.3. Extractives content

The content of extractives was different across the interaction of particle size and wrap and days in storage ($P \leq 0.05$) (Table 1). Across the interaction of particle size and wrap material, the lowest content of extractives were found for switchgrass bales wrapped in net only with PS-3 and bales wrapped in net and film with PS-2 while the content was not different across the other combinations of particle size and wrap (Table 2). Extractive content ranged was 7.24% of DM on day zero and decreased range between 5.04% and 5.53% for storage days 75 to 255 (Table 2).

3.1.4. Lignin content

Lignin content found in the switchgrass bales was different across particle size, wrap material, the interaction of particle size and wrap material, days in storage, and the interaction of particle size and days in storage ($P \leq 0.05$) (Table 1). Lignin was higher for bales with particle size PS-2 than bales with particle size PS-3, but no differences were found in lignin for bales with switchgrass length PS-1 and PS-3 (Table 2). Wrapping the bale completely with film decreased the lignin content to 21.9% of DM (Table 2). Lignin was the highest for bales wrapped in net only with switchgrass length of PS-2, and the lowest content of lignin was found in 1) bale treatments with net and film wrapping with particle size PS-2, 2) net and film wrapping with particle PS-3, and 3) net wrapping with PS-1 (Table 2). Lignin also increased from 21.7% of DM at day zero of storage to 22.2% of DM at day 225 of storage (Table 2). Wiselogel et al. [5] observed an increase in lignin content for year one of their study and a slight decrease in lignin during the second year of the study. For the interaction of particle size and days in storage, the highest content of lignin was found in bales with particle size PS-2 that have been stored for 75 days (Table 2). The lowest content of lignin was found in bales with particle size PS-1 on day zero of storage (Table 2).

3.1.5. Ash content

Ash content was found to be different across particle size, wrap material, interaction of particle size and wrap material, and days in storage ($P \leq 0.05$) (Table 1). Switchgrass bales with particle size

PS-1 had higher ash than bales with particle size PS-2 and PS-3 (Table 2). Covering the bales completely in film along with the net wrap decreased the ash content (Table 2). The interaction of particle size and wrap material showed bales wrapped in net and film with particle size PS-2, wrapped in net and film with particle size PS-3, and wrapped in net with particle size PS-3 was found to have lower amounts of ash than the other fixed effects included in these interactions. Wiselogel et al. [5] found ash content to increase over a 26-week storage period in large round bales in Texas; however, the ash content in the densified and wrapped bales of this present study was the highest at day zero and decreased by 0.7% over the 225-day storage period, thus providing a low ash feedstock for thermochemical conversion processes. Specifically, the 75 days bales show a significant decrease in ash with little change in carbohydrates content, making these bales ideal for thermochemical conversion with minimized catalytic reactions while maintaining a quality carbohydrate-rich feedstock for biochemical processes.

3.2. Response function

Chemical composition response to days in storage was estimated and parameter estimates are presented in Table 3. Using the AIC and BIC criteria, the quadratic functional form was found to better predict the content of cellulose, lignin, and ash response to storage length, while the linear functional form was the most appropriate to model the content of hemicellulose and extractives response to storage. Cellulose and lignin content was found to be increasing at a decreasing rate, while ash content declined at an increasing rate. Hemicellulose increased linearly with storage days, and extractive content decreased linearly with storage days. Compositional response to days in storage has never been conducted for switchgrass bales in the previous research, which makes the findings from this study an extension to the current literature.

Table 3. Parameter estimates for chemical level (as a % of dry matter) response function to days stored.

Fixed Effects	Cellulose	Hemicellulose	Extractives	Lignin	Ash
Linear					
β_0	39.42***	26.73***	6.9831***	21.84***	2.80***
β_1	0.002**	0.002**	−0.009***	0.004***	−0.004***
AIC	612.3	520.2	596.6	392.6	348.9
BIC	611.6	519.4	595.9	391.8	347.7
Quadratic					
β_0	39.10***	26.85***	7.23***	21.74***	2.91***
β_1	0.030***	−0.008***	−0.031***	0.014***	−0.013***
β_2	−0.0001***	0.00005***	0.00010***	−0.00005***	0.00004***
AIC	569.0	528.1	578.2	384.3	339.3
BIC	568.3	527.4	577.5	383.5	338.1

4. Conclusion

The objective of this research was to determine the influence of three particles sizes of feedstock and two types of bale wraps on changes in cellulose, hemicellulose, extractives, lignin, and ash for switchgrass that was preprocessed using BT3 over a 225-day storage period at 75-day sampling intervals. There have been no empirical studies that present the impacts of particle size on compositional changes during storage for switchgrass bales that we have found in the literature. Particle size could have implications for improving feedstock logistics and feasibility of the advanced biofuels industry.

Particle size, wrap material, and days stored were found to impact cellulose, hemicellulose, extractives, lignin, and ash content across switchgrass bales. Differences were found in cellulose, lignin, and ash content across switchgrass bales with different particle sizes. Enclosing bales in a net and film impacted the cellulose, lignin, and ash content. Cellulose and hemicellulose content were not different across the 225-day storage period, and lignin concentrations increased from day zero to day 225. Response functions to storage days were estimated to predict the chemical composition over time. A quadratic response function made better predictions for cellulose, lignin, and ash response to storage, and a linear response function best described hemicellulose and extractives response to storage.

A limitation of this study is only having one year of data. Replicating this experiment over time would provide more robust results. Overall, the preferred storage method from this study a biorefinery would likely select will depend on several factors such as output, land constraints, and storage capacity constraints. Future research could investigate optimal storage methods considering DM loss and chemical changes for the different storage method while considering biorefinery constraints.

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Conflict of Interest

All authors declare no conflict of interest.

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