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The Effect of Drying Temperature on the Composition of Biomass

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Abstract The compositional quality of different lignocellulosic feedstocks influences their performance and potential demand at a biorefinery. Many analytical protocols for determining the composition or performance characteristics of biomass involve a drying step, where the drying temperature can vary depending on the specific protocol. To get reliable data, it is important to determine the correct drying temperature to vaporize the water without negatively impacting the compositional quality of the biomass. A comparison of drying temperatures between 45 °C and 100 °C was performed using wheat straw and corn stover. Near-infrared (NIR) spectra were taken of the dried samples and compared using principal component analysis (PCA). Carbohydrates were analyzed using quantitative saccharification to determine sugar degradation. Analysis of variance was used to determine if there was a significant difference between drying at different temperatures. PCA showed an obvious separation in samples dried at different temperatures due to sample water content. However, quantitative saccharification data shows, within a 95% confidence interval, that there is no significant difference in sugar content for drying temperatures up to 100 °C for wheat straw and corn stover.

Keywords NIR · Biomass · Drying · PCA

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Introduction

Biomass products are becoming more important within energy markets than ever before. With increasing renewable energy requirements, lignocellulosic material such as corn stover and wheat straw are attractive substitutes to corn grain because of their non-food value, relatively low cost, and abundant supply [1]. Straw production alone from cereal grain in Idaho, Oregon, and Washington produce 5.73 Mt (413 gal of EtOH) of available straw, which includes total straw production minus straw returned to the field for soil quality assurance [2]. Determining the composition of each feedstock is an important step in identifying the overall value to the feedstock to a biorefinery.

Procedures for determining the composition of biomass require drying the material at a certain temperature for a period of time to remove possible interference of water on the analysis [3]. Parameters such as particle size and initial percent moisture of the biomass are essential when establishing drying temperature ranges [3]. Taking these parameters into account, it is important to identify a drying temperature that removes enough water to not interfere with the carbohydrate analytical procedure, does not degrade the carbohydrates during drying, and minimizes the drying time of the samples. Multiple drying methods such as air-drying, convection ovens, and freeze drying use a variety of temperatures and are implemented within various biomass preparations protocols [3, 4]. However, adequate drying temperature ranges for biomass other than corn stover have not been adequately addressed.

According to the National Renewable Energy Laboratory (NREL) document entitled "Preparation of Samples for Compositional Analysis"; biomass samples should be dried at 45 °C prior to compositional determination of carbohydrates [3]. While working with various feedstocks with equivalent sizes (1–2 mm) it was uncertain as to whether higher drying temperatures would have negative impacts on final carbohydrate concentrations. Similarly, while drying at 45 °C, there was a concern for possible residual moisture in the feedstock interfering with Near-infrared Analysis (NIR) and carbohydrate determination. These questions lead to this study where four drying temperatures, 45 °C, 60 °C, 85 °C, and 100 °C were used to prepare samples of corn stover and wheat straw for NIR and compositional analysis. The results of the analysis were then statistically compared to each other to determine the potential impact of drying temperature on NIR spectra and sugar composition of the feedstocks.

Materials and Methods

Wheat Straw

Wheat straw (Westbred 936) was obtained from Grant 4-D Farms (Rupert, ID). Straw was produced during the 2006 growing season. A large bail of the wheat straw, approximately a half ton, was ground to 1/4 in. minus using a tub grinder. The ground straw was stored in a supper sack and steal-storage container until it was sampled. Contents in the sack were evenly spread on a clean floor. Using random number generator sections were removed and placed in 2-gal bags [5]. One-hundred-gram samples were removed from the 2-gal bags, contents of the bag were spread on a tray, and a square metal tube with dimensions 5.08 cm × 5.08 cm × 22 cm was used to remove lines from the tray [5].

Five 100-g samples were dried at four different temperatures, 45 °C, 60 °C, 85 °C, and 100 °C, resulting in 20 total samples. All samples were dried to constant weight and then ground to 2 mm

minus using a Thompson-Wiley Mill Model 4 from Thompson Scientific. Percent moisture was determined by using the calculation found in NREL'S technical report NREL/TP-501-42621, only are samples were based on drying a 100 °C [6]. A temperature of 100 °C is sufficient at our altitude to remove all moisture. Water boils at approximately 95.5 °C at the altitude of Idaho Falls, ID. NIR spectra were taken of each sample in duplicate using a 1/4-cup sample cell. The NIR spectra were obtained using Foss NIR System model 6500. Compositional analyses were preformed at Auburn University Chemical Engineering department. Auburn University used NREL's laboratory analytical procedures for compositional analysis [3, 4, 7]. Results were produced after water extractives were removed.

Corn Stover

Corn stover was obtained from Iron Horse Farms, Inc. in Imperial, Nebraska during the 2005 growing season. The corn stover was ground to 1/4 in. minus using a tub grinder. Samples were obtained and processed in the same manner as described above for wheat straw, except that after the samples were ground, they were stored at 45 °C in a convection oven overnight before NIR Spectra were taken whereas with wheat NIR, spectra were taken the same day as the samples were ground. Compositional analysis was performed at the Idaho National Laboratory. Approximately, 1.5 g of biomass was placed in an 11-ml extraction cell and ran through an ASE 200 Accelerated Solvent Extractor made by Dionex Corporation. The samples were analyzed for water extractives using the same method as NREL found within the procedure, "Determination of Extractives in Biomass" [7]. Results were produced after water extractives were removed. All drying for compositional analysis after the water extractives were removed was performed at 45 °C.

Compositional Analysis

Carbohydrate and lignin compositions were determined by quantitative saccharification [8]. A Waters high-performance liquid chromatograph with a Waters 2414 Refractive Index Detector and a Biorad Aminex HPX-87P column was used to determine carbohydrate concentrations. Carbohydrate data was processed using Empower Software build 1154. Acetic acid was determined using a Shimadzu HPLC, with a Shimadzu SPD-M10A VP Diode Array Detector, a Biorad Aminex HPX-87H column. Acetic acid data was processed with Shimadzu Class VP Version 7.2 SP1 Rev B build 14 software.

Data Processing

Spectral data was processed using Matlab R2007a a product of MathWorks. Duplicate NIR spectra were averaged together, mean-centered, and normalized to unit length. The wavelength region from 700 nm to 2,500 nm was used. A Savutzky-Golay smoothing function found in the PLS tool box (ver. 4.0 Eigen vector Research, Inc., Manson, WA) was used with the following parameters; A 15-point filter width, a second order polynomial fit, and the second derivative of the spectra were taken. Principal component analysis was performed on the modified spectra.

Analysis of variance (ANOVA) was performed to compare the samples dried at different temperatures [9]. Ash, acetyl content, K-lignin, glucose, xylose, galactose, and arabinose were compared with ANOVA for both the wheat straw and corn stover samples.

Table 1 Drying parameters for samples.

Sample	Drying time (h)	Percent moisture remaining[a]
100 °C wheat straw	3.0	0.00±0.10
85 °C wheat straw	24.1	1.70±0.08
60 °C wheat straw	72.0	3.08±0.05
45 °C wheat straw	96.3	3.74±0.10
100 °C corn stover	3.6	0.00±0.44
85 °C corn stover	24.10	0.13±0.17
60 °C corn stover	46.38	0.69±0.13
45 °C corn stover	46.30	1.92±0.39

[a] For wheat straw and corn stover, the percent moisture were respectively 6.53±0.10 and 6.36±0.44

Results and Discussion

NIR and PCA

Table 1 indicates drying times and the percent moisture for both the wheat and corn samples. The table indicates that at the higher drying temperature the more moisture was removed from the samples. While drying the wheat samples, the relative humidity ranged

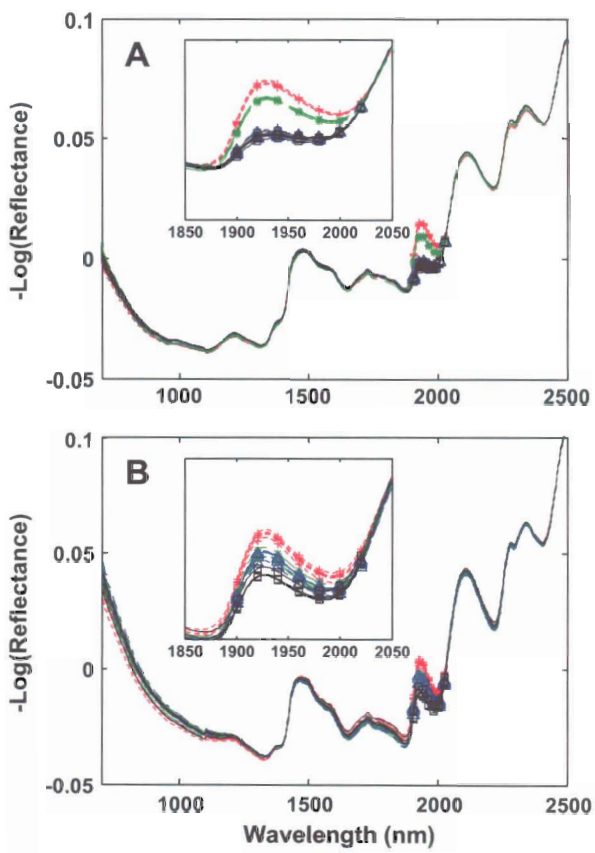

Fig. 1 Near-infrared spectra of dried wheat straw (**a**) and corn stover (**b**). Twenty spectra are shown for each sample type. Spectra have been mean-centered and normalized to unit length. Samples were dried at 100 °C (*black*), 85 °C (*blue*), 60 °C (*green*), and 45 °C (*red*)

from 28% to 55% for the first 48 h. From 48 h to 72 h, the relative humidity raised to between 80% and 90%. Between 72 h and the end of the experiment, the relative humidity was between 50% and 60%. During the drying of corn stover samples the relative humidity remained between 19% and 22%. Times for drying the wheat at 60 °C and 45 °C are longer than times for corn at the same temperatures due to an increase in humidity on the second and third days of drying making it difficult to reach a constant weight. At these lower temperatures humidity was a factor in reaching constant weight; however, this was less of a problem when drying at a higher temperature.

Figure 1 shows the NIR spectra of the wheat and the corn samples. It is evident from the spectra of both wheat and corn that there is variation from about 1,900 to 2,100 nm. This variation is associated with the combination band of water. It is also apparent that the variation is consistent with drying temperature, in that the samples dried at the same temperatures group together. The peak is higher for the lower temperatures, indicating that more water is present in the samples.

In Fig. 1a, wheat samples dried at 100 °C and 85 °C overlap. The 100 °C samples could have gained moisture from the atmosphere when they were prepared for the NIR analysis which could account for the similar NIR spectra. It may also indicate that NIR analysis is more consistent when feedstocks are dried at higher temperatures. Figure 2a shows a plot of the first principal component versus the second principal component. This figure also

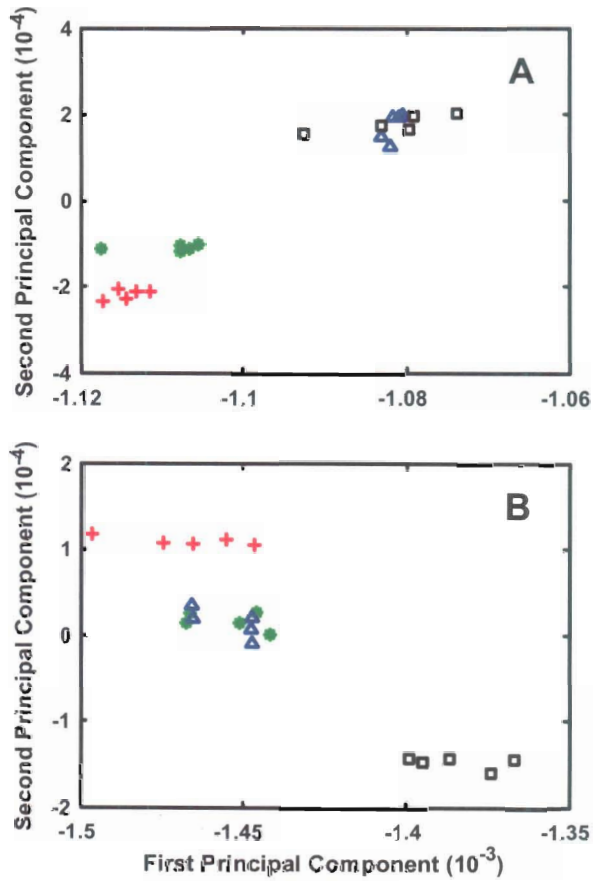

Fig. 2 Principal component analysis plots of wheat straw (**a**) and corn stover (**b**). Markers indicate samples that were dried at different temperatures, 100 °C (*empty square*), 85 °C (*empty upright triangle*), 60 °C (*asterisk*), and 45 °C (*plus sign*)

Table 2 Concentration results for wheat straw and corn stover.

Sample	Cellulose (%)	Hemicellulose (%)	K-Lignin (%)	Acetate (%)	Ash (%)	Acid-Soluble Lignin (%)
100 °C wheat straw	38.13±0.75	28.68±0.93	19.47±1.78	3.10±0.94	10.37±0.60	1.21±0.003
85 °C wheat straw	38.65±0.45	28.58±0.46	18.22±0.94	2.93±0.73	9.22±0.90	1.26±0.003
60 °C wheat straw	38.42±0.96	28.69±0.38	18.51±0.89	3.36±0.62	8.96±1.18	1.26±0.003
45 °C wheat straw	39.39±0.64	29.26±0.64	18.82±2.52	3.07±0.80	8.92±0.44	1.11±0.003
100 °C corn stover	39.82±0.75	21.75±0.55	18.04±0.36	2.24±0.05	8.70±0.62	
85 °C corn stover	40.25±0.47	22.21±0.26	18.13±0.23	2.26±0.06	9.01±0.71	
60 °C corn stover	40.22±0.25	22.31±0.21	17.91±0.19	2.25±0.06	8.99±0.65	
45 °C corn stover	40.37±0.62	22.32±0.37	17.84±0.26	2.19±0.06	8.86±0.52	

Compositional analysis for wheat straw samples were conducted at Auburn University where acid-soluble lignin was determined. Corn stover compositional analysis was performed at the Idaho National Laboratory and acid-soluble lignin was not determined

demonstrates that the samples dried at 100 °C and 85 °C overlap and samples dried at 60 °C and 45 °C are clearly separated in principal component (PC) space.

As with wheat, corn samples show spatial separation based on drying temperature (Fig. 1b). Corn samples dried at 85 °C and 60 °C tended to group closer together in both the NIR spectra (Fig. 1b) and the PC plot (Fig. 2b). Spectra of corn samples in Fig. 1b show more variation between drying temperature that do the wheat sample in Fig. 1a. This may be due to the fact that wheat samples were ran the same day that they were dried and ground whereas, corn samples were stored at 45 °C overnight before running NIR spectra. Figure 2b indicates that samples dried at 100 °C and 45 °C could be clearly separated from each other and from the 85 °C and 60 °C samples. The 85 °C and 60 °C samples were not separated in the PC space. The 85 °C and 60 °C samples may be separated with improved sample treatment such as, grinding the samples before drying and taking NIR spectra as soon as possible. Thus, further detailed analyses would be necessary to determine the exact reasons of the PCA groupings.

Compositional Analysis

Table 2 presents the average percent concentration from the compositional analysis of the wheat and corn samples. Hemicellulose contents were estimated as the sums of the non-glucan anhydro-sugars in the straw, including the xylan, galactan, arabinan, and mannan, measured in the compositional analyses. The ranges are the standard deviation of the five replicate samples dried that same temperature. From a general look at the data in the table all values look similar.

ANOVA was performed on the data to determine if there was a significant difference at a 95% confidence interval between the different drying temperatures. Results form the ANOVA analyses are in Table 3. The F-critical value is 3.24 for degrees of freedom 1=3

Table 3 Analysis of variance F test value.

Sample	Cellulose	Hemicellulose	K-lignin	Acetate	Ash
Wheat straw	2.76	1.15	0.51	0.27	3.38
Corn stover	0.91	2.67	1.25	1.38	0.26

α=0.05, df_1=3, df_2=16, F-critical value=3.24

and degrees of freedom 2=16. As indicated in Table 2 there is no significant difference in any of the data at a 95% confidence interval except for the ash concentration in wheat. Table 2 shows that the concentration of ash in wheat decreases as temperature decreases. Intuitively, this is what can be expected, as the sample loses more moisture the percent ash concentration should go up because the water has been removed from the sample. So the fact that there is a significant difference is ash concentration could be expected. With corn stover, however, it is uncertain why there is not a significant difference in ash concentration relative to wheat straw. One suggestion might be that it requires higher temperatures to remove bound water where corn stover-bound water is removed at lower temperatures. Further research should be done to determine a conclusive answer as to why there is a significant difference in the ash concentration in the wheat straw samples but not in the corn stover.

Conclusion

The results of this analysis indicate that there is no significant difference in the composition of wheat straw and corn stover when dried at temperatures up to 100 °C for non-pretreated biomass. It is also evident that at lower temperatures, relative humidity can affect the analytical weights of a sample. Thus, biomass should be dried at higher temperatures to eliminate errors due to humidity. It is also evident that at lower temperatures, relative humidity can affect the analytical weights of a sample during drying. High-temperature drying can affect biomass water uptake prior to NIR and other analyses. These analyses were performed on non-pretreated biomass and may not be applicable for these applications.

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