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Impact of Sequential Ammonia Fiber Expansion (AFEX) Pretreatment and Pelletization on the Moisture Sorption Properties of Corn Stover

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Impact of Sequential Ammonia Fiber Expansion (AFEX) Pretreatment and Pelletization on the Moisture Sorption Properties of Corn Stover

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Abstract

Combining ammonia fiber expansion (AFEX) pretreatment with a depot processing facility is a promising option for delivering high value densified biomass to the emerging bioenergy industry. However, because the pretreatment process results in a high moisture material unsuitable for pelleting or storage (40% wet basis), the biomass must be immediately dried. If AFEX pretreatment results in a material that is difficult to dry, the economics of this already costly operation would be at risk. This work tests the nature of moisture sorption isotherms and thin-layer drying behavior of corn (*Zea mays* L.) stover at 20ºC to 60ºC before and after sequential AFEX pretreatment and pelletization to determine whether any negative impacts to material drying or storage may result from the AFEX process. The equilibrium moisture content to equilibrium relative humidity relationship for each of the materials was determined using dynamic vapor sorption isotherms and modeled with modified Chung-Pfost, modified Halsey, and modified Henderson temperature dependent models as well as the Double Log Polynomial (DLP), Peleg, and Guggenheim Anderson de Boer (GAB) temperature independent models.

Drying kinetics were quantified under thin-layer laboratory testing and modeled using the Modified Page's equation. Water activity isotherms for non-pelleted biomass were best modeled with the Peleg temperature-independent equation while isotherms for the pelleted biomass were best modeled with the Double Log Polynomial equation. Thin-layer drying results were accurately modeled with the Modified Page's equation. The results of this work indicate that AFEX pretreatment results in drying properties more favorable than or equal to that of raw corn stover, and pellets of superior physical stability in storage.

KEYWORDS: AFEX pretreatment; corn stover; water activity; drying kinetics; pelletized biomass

INTRODUCTION

The development of bioenergy from lignocellulosic feedstock has gained considerable attention in the United States (U.S.) with the expansion of the Renewable Fuels Standard in the Energy Independence and Security Act of 2007 [1] and recent startup of three commercial corn (*Zea mays* L.) stover to ethanol production facilities in the U.S. Midwest. Efficient and economical conversion of biomass to biofuels depends on effective pretreatment methods that enable successful hydrolysis of cellulose and hemicellulose for subsequent conversion to biofuels [2]. While pioneer facilities in the U.S. perform pretreatment on-site immediately before hydrolysis, this production scheme requires low bulk density baled biomass to be handled multiple times throughout the supply system, creating a high cost logistics system with a low tolerance for risk in

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feedstock supply and delivery [3]. Decoupling the process of pretreatment from the biorefinery and incorporating a densification step at distributed depots would allow high-value and high-density pretreated feedstock to enter the marketplace with enhanced opportunity for meeting the demands of multiple end users [4].

Ammonia Fiber Expansion (AFEX) is one method that could be used for chemical pretreatment of biomass at regional processing depots. AFEX treatment involves contacting moist biomass with ammonia liquid or vapor in a pressure vessel. By using volatile ammonia as the reaction medium, no liquid streams are generated and the composition of the biomass is not significantly altered, resulting in theoretical glucose yields up to 98% [5]. AFEX treatment has also been shown to mobilize lignin to the surface of the biomass, which acts as a natural binder, facilitating densification of biomass [6]. A novel design for ammonia recovery that is economically viable at the depot scale has been described by Campbell, et al. [7], improving the operational economics of biomass pretreatment. However, in order to densify the pretreated biomass, it must be immediately dried from 40% to < 15% wet basis to facilitate pelleting and prevent biological degradation. How a material is handled prior to drying can have great influence on the efficiency of drying and final material properties [8], however, no information currently exists on the sorption properties and drying kinetics of AFEX pretreated biomass to inform whether added risks or benefits may lie in this critical processing step. As discussed by Pang and Mujumdar [9], an understanding of the material properties of a biomass feedstock and the associated behavior with specific

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drying technologies is critical for ensuring bioenergy operations are efficient and cost effective.

The relationships between air temperature, relative humidity, and moisture content are necessary to understand how a material may react under specific drying and storage operations. These are developed through the relationship between equilibrium moisture content (EMC) and equilibrium relative humidity (ERH), or water activity (a_w), being expressed by mathematical models [10]. Furthermore, a drying operation or other treatment process can themselves have impacts on the final product's moisture sorption properties [11]. While these measures are predominantly used in the food industry to characterize the drying and storage properties of perishables, the bioenergy research community is beginning to relay these metrics to biomass feedstocks more routinely.

Extensive moisture sorption testing on corn stover and its individual anatomical fractions has been done to determine the feedstock's thermodynamic properties, the moisture-material binding relationship as it relates to drying energy, and even material stability in storage related to mold growth [12,13,14]. However, the work of Igathinathane et al.[9–11] was performed from initially dry samples [6 to 12% dry basis (db)]. As a result, the data does not represent the hysteresis in moisture sorption behavior that would be observed from an initially wet material. Arabhosseini, et al. [15] modeled the desorption water activity isotherms of *Miscanthus giganteus* stems and leaves from an initially wet state (near 30% db), allowing a natural initial drying hysteresis to be replicated. This hysteresis between the initial desorption and subsequent sorption cycles was shown for

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Sorghum bicolor (L.) Moench by Bonner and Kenney [16]. Acharjee, et al. [17] and Medic, et al. [18] extended their analyses beyond the moisture sorption properties of raw biomass and demonstrated that the hydrophobicity of wood chips and corn stover increases as a result of thermal pretreatment. A robust understanding of the moisture sorption relationships of AFEX pretreated biomass is critical for developing sound drying models and economic analysis of depot processing facilities.

The purpose of this research is to determine whether sequential AFEX pretreatment and pelleting of corn stover results in meaningful changes to drying and storage, respectively. Data on sorption isotherms and thin-layer drying of high moisture raw, AFEX pretreated, and pelletized corn stover is not available in the literature. This work quantifies the moisture sorption characteristics of raw and AFEX pretreated corn stover in both size reduced and pelletized formats. The objectives of this work are to: (1) describe and understand the water sorption properties of corn stover before and after AFEX pretreatment, (2) assess potential impacts to pellet stability in storage resulting from AFEX pretreatment, and (3) demonstrate and describe the drying performance of high moisture AFEX pretreated corn stover compared to untreated high moisture corn stover. This work provides important material properties for and conclusions relating to the drying of pretreated corn stover and potential implications for storage of pelletized pretreated biomass.

MATERIALS AND METHODS

Materials

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The corn stover used in this work was harvested in October of 2011 in Hamilton County, IA. Stover was windrowed using a Hiniker 5600 flail windrower and baled at 17% moisture (wet basis; wb) with a Massey Ferguson 2170XD large square baler. Bales were covered with a tarp and stored outdoors in Story County, IA, until they were shipped to Idaho National Laboratory (INL) in December, 2011. Once in Idaho, the bales were stacked on pallets and covered with tarps until October, 2012 when the bales were ground using a Vermeer BG-480 hammer mill with a 2.5 cm (1 inch) screen. Size reduced dry biomass ($\leq$15% wb) was stored in 68 kg super sack containers and housed indoors until delivery to Michigan Biotechnology Institute (MBI) for pretreatment. The non-pretreated "raw" size reduced material used in this testing was wetted to a target moisture content of 40% wb by spraying the material with a predetermined mass of deionized water and storing the wetted stover in vacuum sealed bags at 4°C for a minimum of 48 hours until use in the experiments.

Methods

Afex Pretreatment

Size reduced corn stover was AFEX treated using MBI packed-bed AFEX pilot scale reactors. The MBI pilot scale AFEX system consists of two 450 L stainless steel pressure reactors (0.43 m diameter and 3.43 m height), rated to 495 psig. Biomass was packed at about 100 kg m^{-3} packed density in cylindrical baskets made out of perforated stainless steel sheet. Baskets containing biomass were assembled into the reactors, seven baskets per reactor, and AFEX treated using a cycle of seven steps: (1) load biomass into the reactor, (2) pre-steam with atmospheric pressure saturated steam until the temperature at

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the bottom of the reactor reaches 80°C, (3) charge with ammonia vapor at 0.6 kg ammonia kg^{-1} dry biomass, (4) soak for at least 30 minutes, (5) depressurize to less than 20 psig, (6) introduce low pressure saturated steam to strip residual ammonia from the biomass, and (7) remove biomass from the reactor [7].

After AFEX treatment, a portion of the wet treated biomass (40% wb) was dried to a target moisture of 10 to 12% wb at 45°C in a forced convection oven to enable pelletization. Additional wet samples were allowed to cool to room temperature before sealing in plastic bags and shipped to INL overnight. These moist samples were then vacuum sealed and stored at 4°C until being used in the moisture sorption and thin-layer drying tests.

Biomass Pelleting

Both the raw and AFEX pretreated corn stover were pelletized by Bliss Industries, LLC at their Ponca City, OK, USA facility. The raw stover arrived at 11% moisture wb (55 kg total) while the AFEX stover arrived at 13% moisture wb (30 kg total). Both materials were ground with a hammer mill fitted with a 0.64 cm (1/4 in) screen. Pelleting was performed using a Bliss Industries (Ponca City, OK, USA) B35A-75 Pioneer pellet mill with a 0.64 cm (1/4 in) die diameter and 7.62 cm (3 in) die length (12 L/D ratio). The final pellet moisture content was 7% wb for the raw stover and 6.5% wb for the AFEX pretreated stover. The final pellet durability measured using a tumbler was 99.3% for the raw stover and 99.8% for the AFEX pretreated stover. Finished pellets were shipped to INL and stored indoors in plastic bags until use in further experiments.

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Moisture Sorption Testing

Water activity isotherms are created using a Decagon (Pullman, WA, USA) AquaSorb Isotherm Generator and Decagon AquaLab Vapor Sorption Analyzer (VSA). Both instruments have identical theory of operation and measure water activity as a function of vapor pressure through the use of a chilled mirror dew point sensor ($\pm$ 0.005 a_w) [19]. Isothermal sorption is conducted by passing an airstream [desiccant-dried for desorption (0.3 % relative humidity), and water vapor saturated for adsorption (95% relative humidity)] through the sample chamber at a fixed flow and temperature while an internal microbalance records sample mass ($\pm$ 0.1 mg). This method allows samples to be tested across a range of water activities without disturbing the testing environment or sample. All sorption tests use an airflow of 0.1 L min^{-1} and are carried out from the sample's initial water activity to a final point of 0.05 a_w for desorption and 0.90 a_w for adsorption. Only desorption isotherms are made for the size reduced samples since these materials begin at a water activity > 0.9.

Pelleted materials are used to create what are known as "working" isotherms. Working isotherms are comprised of separate desorption and adsorption tests from the sample's native state. These two tests are then combined to form a single isotherm that describes that material's vapor sorption behavior as changes to storage condition are made.

The moisture sorption isotherms and thin-layer drying of the size reduced materials are tested at 40°C, 50°C, and 60°C (the upper limit of the VSA) to provide data at above-ambient conditions that are more likely to be encountered in practical drying conditions.

The pelleted material sorption isotherms are conducted at lower temperatures of 20°C, 30°C, and 40°C to better replicate conditions that may be observed during storage. Tumuluru, et al. [20] indicated that these storage temperatures have a significant effect on off-gas emissions and pellet physical properties like durability. The instrument's sample cup is filled with approximately 1 g (wet weight) of the size reduced samples and 5 g of pelletized samples. All tests have three replicates per temperature. Dry mass of each sample is determined gravimetrically after drying the sample at 105°C for 24 h.

Thin-layer drying tests for the raw and AFEX treated size reduced stover are conducted using the AquaLab VSA programmed to continuously flow a desiccant-dried airstream at 100 mL/min while recording sample mass every second. The omission of water activity measurement throughout the process allows drying to continue uninterrupted and more quickly compared to the isotherm procedure. Operating temperatures, sample mass, number of replicates, and dry mass determination are the same as those used in the isotherm tests of the size reduced materials.

Data Analysis

Numerous empirical, semi-theoretical, and theoretical models have been proposed in the literature for modeling water activity isotherms for foods [21]. This work uses four common temperature dependent models identified by the American Society of Agricultural & Biological Engineers as being most applicable to agricultural products [22]:

$$\text{Modified Chung-Pfost} \quad EMC = -1/B \bullet \ln\left[\ln a_w \bullet T + C \ / \ -A\right] \qquad (1)$$

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$$\text{Modified Halsey} \quad EMC = \left[-\exp\ A + B \bullet T\ / \ln\ a_w \right] \wedge (1/C) \qquad (2)$$

$$\text{Modified Henderson} \quad EMC = \left[\ln\ 1 - a_w\ / -A\ T + B \right] \wedge (1/C) \qquad (3)$$

$$\text{Modified Oswin} \quad EMC = A + B \bullet T \bullet \left[a_w\ /\ 1 - a_w \right]^C \qquad (4)$$

Where EMC is the equilibrium moisture content (% dry basis), *T* is temperature in degrees Celsius and *A*, *B*, and *C* are empirical model coefficients unique to each model. Three temperature independent models are also used. Two of these, the Double Log Polynomial (DLP) (developed by Decagon Devices Inc.) and the Peleg [23] are empirical models designed to better capture the sigmoidal shape of isotherms.

$$\text{DLP} \quad EMC = D \bullet \ln\ -\ln\ a_w^{\ 3} + C \bullet \ln\ -\ln\ a_w^{\ 2} + B \bullet \ln\ -\ln\ a_w + A \qquad (5)$$

$$\text{Peleg} \quad EMC = A \bullet a_w^{\ B} + C \bullet a_w^{\ D} \qquad (6)$$

Where *A*, *B*, *C*, and *D* are model coefficients. The Guggenheim Anderson de Boer (GAB) [24] is a semi-theoretical model:

$$\text{GAB} \quad EMC = A \bullet B \bullet C \bullet a_w\ / \left[1 - B \bullet a_w\ \ 1 - B \bullet a_w + C \bullet B \bullet a_w \right] \qquad (7)$$

Where the parameter *A* relates to the monolayer moisture content of the material (% db), *B* relates to the material drying coefficient *k*, and *C* is an empirical model parameter.

As is the case for moisture sorption, numerous equations have also been proposed for modeling the thin-layer drying of various materials under a range of conditions [25].

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For this work, the thin-layer drying curves for the size reduced raw and AFEX pretreated stover are modeled using the Page's Modified equation [26]:

$$\text{Modified Page} \quad MR = M - M_e \;/\; M_i - M_e = \exp -kt^n \qquad (8)$$

Where MR is the moisture ratio, M is the moisture content at any time t, M_e is the equilibrium moisture content, M_i is the initial moisture content, k is the sorption rate constant, and n is an empirical parameter.

Each model is fit and analyzed using MathCad 15 (PTC; Needham, MA, USA) with nonlinear curve fitting using the Levenberg Marquardt algorithm to determine model coefficients. Model fit is assessed by the resulting residual sum of squares (RSS), coefficient of determination (R^2), and root mean squared error (RMSE). Analysis of variance was performed in JMP 10 (SAS Institute; Cary, NC, USA) using the Fit Model tool for a full factorial design with Standard Least Squares [27].

RESULTS AND DISCUSSION

Moisture Sorption Isotherms

Size Reduced Biomass

Desorption isotherms of the size reduced raw and AFEX pretreated corn stover are notably different from one another. The pretreated stover has consistently lower equilibrium moisture contents at equal values of water activity across the three temperatures tested (Fig. 1). These results show that the pretreated material is unable to hold an equal amount of moisture at any given equilibrium condition relative to the raw

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material. Because the energy required to dry a material increases as target moisture contents correspond to lower water activities where the binding strength of water traverses a gradient from that akin to free water to powerful and difficult to break material-to-water bonds, this result bodes well for the pretreated material's affinity to dry [28]. For example, in order to reach an equilibrium moisture content of 10% db, the water activity of the AFEX pretreated material is relatively high compared to the raw biomass; roughly 0.7 to 0.5 a_w, respectively. However, this relationship also indicates that the treated material must reach a lower moisture content to be microbially stable [the equilibrium moisture content corresponding to a water activity of 0.65 [29]]. Furthermore, the raw corn stover shows only minor temperature dependence, agreeing with the results of Igathinathane, Womac, Sokhansanj and Pordesimo [12], while the AFEX pretreated stover exhibits a noticeable decreasing trend in equilibrium moisture content with increasing temperature. Again, while this will have undesirable impacts on the biological storage stability of the AFEX pretreated material, the temperature dependence of equilibrium moisture content is indicative of increased drying efficiency at higher temperatures.

It should be noted that neither of the materials appear to behave like a naturally wet feedstock, that is to say, the process of rewetting (either through surface moisture application for the raw material or the steam exposure during pretreatment of the AFEX material) has not entirely removed the hysteresis phenomena observed between an initial desorption and a second desorption [16]. While this effect is not of particular concern for this analysis, it should be kept in mind that the "raw" material may not be fully

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representative of natively high moisture corn stover that may in fact have higher values of equilibrium moisture content than those shown here. The desorption isotherms of this work closely match the salt slurry gravimetric equilibrium moisture contents of corn stover fractions presented by Igathinathane, Womac, Sokhansanj and Pordesimo [12], supporting the case that the stover used in this work is representative of a previously dried material. Nevertheless, the two re-wetted stover samples stand as a good comparison for understanding the impact of pretreatment on the materials' thermodynamic properties without complicating factors such as native moisture content.

The Peleg model (eq 6) was found to be the best temperature independent model for describing the size reduced raw and AFEX pretreated samples within the range of 0.05 a_w to 0.9 a_w based on the highest R^2 value (mean 0.991) and lowest RSS and RMSE values (mean 174.0 and 0.69, respectively)(Table 1; Fig. 1). While all three of the models result in good fits ($R^2 \geq 0.98$; RMSE ≤ 1.2), the DLP model (eq 5) tended to accentuate the sigmoid character of the curves while the GAB model (eq 7) could only be applied to a limited range of water activities from 0.05 to 0.8. Similarly, all four of the temperature dependent models were applied to this same reduced data range to produce acceptable fits (Table 2). Inclusion of the data between 0.8 a_w and 0.9 a_w where equilibrium moisture content falls rapidly resulted in poor fits for all four of the temperature dependent models as indicated by highly patterned residuals within this range (data not shown). Of these models, the modified-Halsey (eq 2) resulted in the most faithful representation of the data and its temperature dependence.

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The reduction in the data range used for the GAB model fitting was necessary to provide reliable estimates of the monolayer moisture content (parameter *A*). The monolayer moisture content is the point at which a single layer of water molecules covers a material's surface and is widely used in the food industry as a point of premier storage stability [10]. While the feedstock handled here does not require this level of stability, the monolayer moisture content can be used to describe changes in the material's surface area due to pretreatment. Both the raw and pretreated stover display a negative relationship between monolayer moisture content and temperature (Fig. 2). Interestingly, the trends of the two materials are nearly linear and parallel to one another, though the monolayer moisture content of the raw material is higher than that of the treated material. Analysis of variance using a full factorial design confirms that both material and temperature impact monolayer moisture content (F = 147 and 20, respectively; P = <0.0001 and 0.0002, respectively), and that there is no interaction between the two effects (F = 0.1; P = 0.89). Because surface area is proportional to the monolayer moisture content, this result suggests that AFEX pretreatment lowers the water-binding surface area of corn stover. This finding is contradictory to the work of Hoover, et al. [30] where nitrogen-sorption surface area analysis was used to show increasing pore volume and surface area as a result of AFEX pretreatment. The results of the water vapor sorption analysis suggest that a portion of the pretreated material's surface area is hydrophobic, resulting in a lower apparent surface area when water is used as the adsorbent. This result is likely due to the redeposition of hydrophobic lignin to the surface of the biomass as reported by Dale, Ritchie and Marshall [6]. Despite this apparent increase in material hydrophobicity, high conversion efficiencies reported by

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Balan, Bals, Chundawat, Marshall and Dale [5] and Hoover, Tumuluru, Teymouri, Moore and Gresham [30] suggest that wet chemical assays are not negatively impacted by this behavior.

Pelleted Biomass

The working isotherms for the raw and AFEX pretreated pellets are both considerably more sigmoidal in shape than those of the size reduced materials (Fig. 3). While both materials have a steep inflection on the adsorption half of the isotherms near 0.8 a_w, the raw corn stover pellets have a second pronounced inflection near 0.1 a_w on the desorption tack. Although the pretreated pellets exhibit a similar behavior at 30°C and 40°C, the relative change in moisture content is much less than what is observed in the raw pellets. This abrupt loss of moisture by the raw pellets and eventual arrival at an equilibrium moisture content equal to that of the AFEX treated pellet at 0.05 a_w indicates that the final fraction of surface bound moisture is more tightly bound in the case of the raw pellets compared to the AFEX pretreated pellets where this moisture fraction is more readily lost at higher levels of water activity.

As a result of the extreme inflections at the low and high end of the water activity range for the working isotherms, the semi-theoretical temperature dependent models all result in poor fits for the pellets, with extremely patterned residuals (data not shown). Both of the temperature independent empirical models (DLP and Peleg) are able to capture the sigmoidal shape of the working isotherms quite well (Table 3). While both models have good qualities of fit for each of the three temperatures, the DLP model more faithfully

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captures both observed inflections (Fig. 3) while the Peleg fails to capture the inflection near 0.1 a_w, resulting in patterned residuals below this point.

Neither the raw or AFEX pretreated pellets show a clear temperature dependence, with replicates from each of the three temperatures generally overlapping one another. Because of this, the empirical DLP model is insufficient for calculating thermodynamic properties of the pellets that require some form of temperature dependency. Continued research aims to develop semi-theoretical models that can adequately match the curvature of these working isotherms to better understand the impact of AFEX pretreatment on the thermodynamic properties of pelleted corn stover.

In terms of biological stability, the initial water activity near 0.4 a_w for both pellets would sufficiently inhibit microbial growth ($a_w \leq 0.65$) [29]. This stability would be retained if storage conditions prevented moisture infiltration (i.e., precipitation or condensation) and remained at a relative humidity less than 65%. If either of these conditions were not met however, material stability would be threatened. The sensitivity of the materials to moisture addition can be noticed from the slope of the working isotherms from their initial point to about 0.7 a_w. This slope is quite low for both materials (4.5 % db a_w^{-1} and 3.4 % db a_w^{-1} for the raw and AFEX pretreated pellets, respectively) indicating that small changes in pellet moisture content results in large changes in water activity. More simply put, even a small moisture addition during the storage of the pelleted materials (a 1% db increase in both cases) may lead to microbial instability if that moisture is permitted to adsorb to the stored product.

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Another important consideration with regards to storage is the physical stability of pellets when stored in high moisture conditions. It was observed that the AFEX pretreated pellets retained their shape with no visual deformation during the adsorption testing (average 3 d duration). The raw pellets on the other hand deformed during adsorption, with pellet diameter increasing by 16% and fractures forming on the pellet's surface. Furthermore, in some cases the raw pellets were observed to begin growing mold while none of the AFEX pretreated pellets had observable mold growth, despite measured water activities above 0.65 a_w (Fig. 4). This notable difference in behavior may again be caused by the repositioning of lignin during AFEX pretreatment, causing pellet surfaces to be more hydrophobic and less susceptible to microbial activity. In addition, the exposure of biomass to high temperatures and an ammonia environment encountered in AFEX pretreatment has been shown to sterilize biomass [31], potentially leading to a more microbially stable product compared to raw corn stover that has a rich native microbial community. While measures of pellet durability and microbial activity are beyond the scope of this work, these observations are an important demonstration of the realized differences in storability between the raw corn stover and AFEX pretreated corn stover pellets. Based on these findings, additional research should explore the rates of adsorption and potential degradation (both physically and chemically) of pellets stored in challenging environments to better understand storage limitations of densified feedstocks for bioenergy.

Thin-Layer Drying

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The drying curves of size reduced raw and AFEX pretreated corn stover were modeled using the Page's Modified Equation (eq 8) for moisture ratio (MR) with a good quality of fit for each material (Table 4). Both the raw and AFEX pretreated materials displayed a temperature dependency, though the raw stover appears more sensitive than the pretreated stover (Fig. 5). An analysis of variance for the factorial experiment supports a significant relationship between the drying parameter *k* and temperature (F = 7.85; P = 0.0066), but not for material (F = 1.92; P = 0.19). The failure to reject the null hypothesis of the material treatment effect is likely due to relatively large replicate-to-replicate variance within material-temperature treatments.

Using the model coefficients to construct drying curves for each material beginning at identical initial moisture contents (82% db, or 45% wb) we see that the rate of drying is greater for the AFEX pretreated stover compared to the raw stover at 40°C and 50°C early in the drying process (up to about one hour)(Fig. 6a). Beyond this point (and for the entire duration at 60°C) the raw and AFEX pretreated materials have similar rates of drying. When the rates of moisture loss are presented relative to water content, we see an improved drying rate from the AFEX pretreated stover until a moisture content near 20% db is reached at 40ºC and 50ºC (Fig. 6b). The opposite trend appears at 60ºC however, and although the magnitude of difference between the drying rates at high moisture contents is reasonably similar yet opposite between 40ºC and 60ºC, observed differences in drying performance are not similar. When considered with the drying curves in Fig. 5, the relatively high rate of drying for both materials at 60ºC has minimal impact on drying performance, whereas the much lower rates at 40ºC cause notable differences between

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the AFEX pretreated and raw corn stover samples. The drying rates are clearly temperature dependent, with peak rates near 0.5 % db min^{-1} at 40°C and 1.25 % db min^{-1} at 60°C for both materials. It should be noted that the model underestimates the rate of drying at the very early stages of drying (i.e., < 20 minutes), though the general trend of the falling rate period represents the drying behavior well.

The drying rate behavior of both materials reflects the isotherm findings discussed previously, principally that the AFEX pretreatment has minor positive benefits on the drying rate of corn stover. The time required to reach a range of moisture contents can be easily calculated and compared between materials using the thin-drying models. For example, if we assume both materials begin at 82% db moisture, the AFEX pretreated stover requires on average 19% less time to reach a moisture content between 25% db and 10% db than the raw stover at 40°C. However, this difference is no longer apparent by 60°C.

Overall the results of this testing demonstrate that drying technologies suitable for conventional high moisture biomass would be suitable for AFEX pretreated corn stover. When comparing the two materials the treated corn stover dries more favorably at lower temperatures than the untreated stover as a result of lower equilibrium moisture contents compared to raw stover, though higher temperatures intuitively result in increased drying rates. In high temperature forced-air drying it is likely that there is no beneficial effect from AFEX pretreatment. However, low temperature drying may be of interest if the high temperatures encountered in a rotary drum dryer (i.e., >200°C) result in (1) unfavorable

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chemical or physical changes to the material or (2) unacceptable levels of volatiles for air quality permitting. Economics of the drying process should be explored to determine if these concerns merit further review.

Our further studies on the sorption data obtained from this work will include calculation of the isosteric heat of sorption using Clausious-Clapeyron equation, develop a computer model to understand the temperature dependent sorption characteristics using the finite control volume method using vapor pressure as the driving potential, and derive diffusion coefficients from the physically well-established sorption isotherms.

CONCLUSIONS

The scale-up of AFEX pretreatment systems to the depot level depends on the ability to efficiently dry biomass for pelleting. The results of this work demonstrate a decreased equilibrium moisture content to water activity relationship and improved rates of drying as a result of AFEX pretreatment. As a result, drying operations suitable for raw corn stover are expected to perform similarly or better with AFEX pretreated stover. Observational evidence of pellet degradation indicates that the pretreated pellets are more resilient under humid conditions than raw pellets despite a lower equilibrium moisture content to water activity relationship. This finding has direct impacts on pellet shelf-life and value within a commodity system. Ongoing research will use the results and models presented here to better understand the physical and chemical drying properties of AFEX pretreated biomass.

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TABLE 1 Temperature independent model parameters for the desorption isotherms of size reduced raw and AFEX pretreated corn stover. Model parameters are derived from three replicates within each treatment.

		Model Parameters				Fit Parameters		
Material	Temperature (°C)	*A*	*B*	*C*	*D*	RSS	R^2	RMSE
		DLP Model (0.05 to 0.9 a_w)						
Raw	40	8.602	-4.444	1.019	-1.370	146.6	0.987	0.84
	50	8.251	-3.885	1.122	-1.878	168.3	0.990	0.80
	60	7.271	-3.427	0.807	-2.105	57.7	0.997	0.51
AFEX Pretreated	40	6.955	-2.247	0.383	-2.304	619.4	0.979	1.21
	50	5.984	-2.562	1.056	-1.407	50.3	0.995	0.43
	60	5.068	-2.432	0.625	-1.366	57.1	0.992	0.48
		Peleg Model (0.05 to 0.9 a_w)						
Raw	40	15.564	0.549	63.701	9.137	155.5	0.987	0.87
	50	15.24	0.561	85.666	10.06	162.	0.99	0.78

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		9			9	4	1	
	60	14.542	0.633	94.887	11.014	28.5	0.998	0.36
AFEX Pretreated	40	12.381	0.507	104.153	12.045	574.2	0.981	1.16
	50	10.145	0.472	61.631	9.305	62.7	0.994	0.49
	60	9.529	0.583	57.107	9.950	60.4	0.992	0.50
		GAB Model (0.05 to 0.8 a_w)						
Raw	40	6.157	0.884	24.473	-	62.4	0.989	0.45
	50	5.730	0.916	30.791	-	50.6	0.988	0.46
	60	5.170	0.925	20.782	-	13.3	0.996	0.26
AFEX Pretreated	40	4.637	0.925	56.235	-	103.4	0.975	0.54
	50	3.928	0.944	67.852	-	26.1	0.989	0.33
	60	3.433	0.942	30.708	-	14.0	0.992	0.25

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TABLE 2 Temperature dependent model parameters for the size reduced raw and AFEX pretreated corn stover. Models fitted from 0.05 a_w to 0.8 a_w and 40°C to 60°C. Model parameters are derived from three replicates within each treatment.

		Model Parameters			Fit Parameters			
Model	Material	*A*	*B*	*C*	RSS	R^2	RMSE	Residuals
Mod. Chung Pfost	Raw	492.988	0.165	68.971	602.1	0.957	0.97	Patterned
	AFEX Pretreated	178.977	0.222	-7.463	472.8	0.944	0.83	Patterned
Mod. Halsey	Raw	3.661	-8.33E-03	1.572	146.1	0.989	0.48	Normal
	AFEX Pretreated	4.027	-0.023	1.599	83.8	0.99	0.35	Normal
Mod. Henderson	Raw	1.09E-04	1.640	78.170	538.9	0.961	0.92	Patterned
	AFEX Pretreated	4.65E-04	1.743	-10.912	435.6	0.948	0.80	Patterned
Mod. Oswin	Raw	13.104	-0.054	2.243	238.4	0.983	0.61	Normal
	AFEX Pretreated	13.927	-0.120	2.331	212.2	0.975	0.56	Normal

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TABLE 3 Model parameters for working isotherms of pelleted raw and AFEX pretreated corn stover using the DLP and Peleg models at each of the three test temperatures per material. Model parameters are derived from three replicates within each treatment.

		Model Parameters				Fit Parameters		
Material	Temperature (°C)	*A*	*B*	*C*	*D*	RSS	R^2	RMSE
		DLP Model (0.05 to 0.9 a_w)						
Raw Pellets	20	7.778	-0.427	-1.100	-1.442	244.0	0.941	0.84
	30	7.720	-1.467	-0.340	-1.079	25.4	0.997	0.28
	40	7.529	-1.290	-0.890	-1.120	18.9	0.996	0.27
AFEX Pretreated Pellets	20	6.292	-0.559	-0.326	-0.627	101.0	0.892	0.60
	30	5.845	-0.156	-0.356	-1.133	76.0	0.974	0.51
	40	5.763	-0.349	-0.560	-1.285	94.6	0.958	0.60
		Peleg Model (0.05 to 0.9 a_w)						
Raw Pellets	20	9.290	0.209	59.516	16.023	254.6	0.939	0.86
	30	9.93	0.249	34.76	10.46	25.2	0.99	0.28

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		0		0	0		7	
	40	9.562	0.256	32.215	11.961	28.6	0.993	0.33
AFEX Pretreated Pellets	20	7.515	0.165	40.796	17.436	88.3	0.906	0.56
	30	6.893	0.158	48.528	14.248	70.5	0.976	0.49
	40	7.051	0.206	50.472	13.792	89.7	0.960	0.58

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TABLE 4 Thin-layer drying model fit parameters for the Modified Page's equation for size reduced raw and AFEX pretreated corn stover. Model parameters are derived from three replicates within each treatment.

Material	Temperature, °C	*k*	*n*	RSS	R^2	RMSE
Raw	40	0.001285	1.396	4.41	1.000	0.044
	50	0.002124	1.380	3.40	1.000	0.042
	60	0.008863	1.259	4.01	1.000	0.044
AFEX Pretreated	40	0.002689	1.308	1.88	1.000	0.029
	50	0.006683	1.240	2.70	1.000	0.037
	60	0.008076	1.249	3.54	1.000	0.039

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FIGURE 1. Desorption isotherms for size reduced raw corn stover and AFEX pretreated corn stover across the three test temperatures. Data series are composite sets of three replicates per treatment and fitted with the Peleg model.

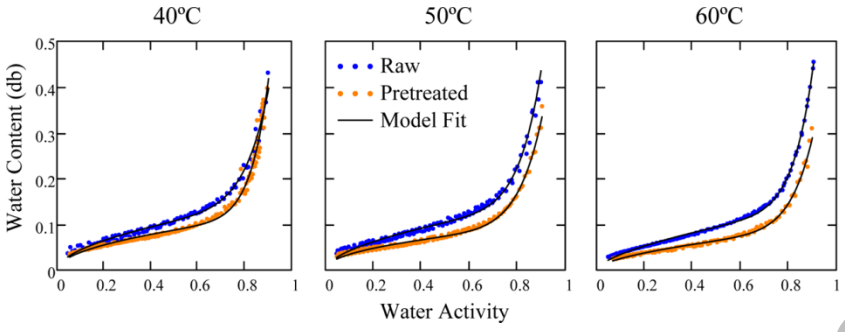

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FIGURE 2. Monolayer moisture content of raw and AFEX pretreated corn stover using the GAB model. Error bars represent the 95% confidence interval of the mean, *n*=3.

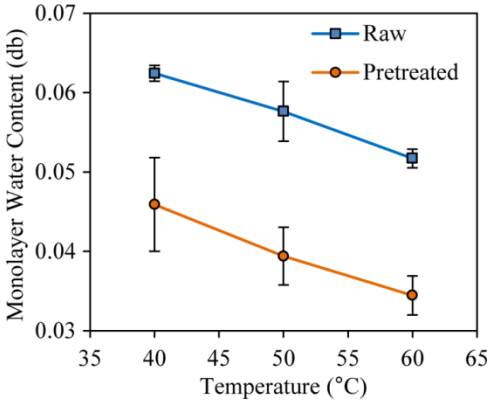

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FIGURE 3. Working isotherms for pelleted raw and AFEX pretreated corn stover across the three test temperatures. Each series consists of three adsorption and three desorption replicates combined and fitted with the DLP model.

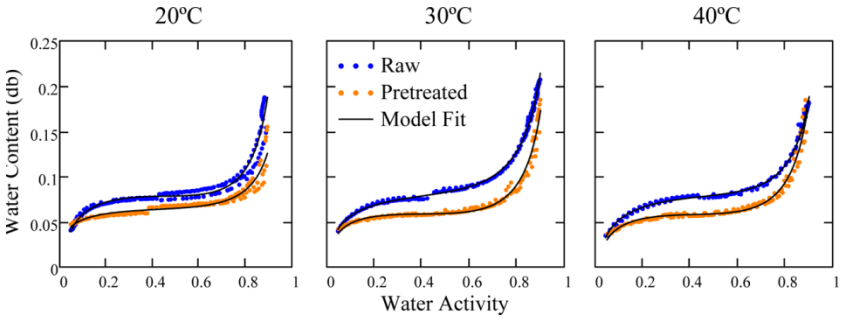

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FIGURE 4. Pellets following adsorption under 95% relative humidity conditions. (Left) AFEX pretreated pellets with no visible deformation or mold growth. (Right) Raw corn stover pellets showing swelling, surface fractures, and mold growth.

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FIGURE 5. Moisture Ratio (MR) drying curves for raw and AFEX pretreated corn stover fitted using the Page's Modified equation comparing (a) the effect of temperature and (b) material. Each data series is derived from three replicates per treatment.

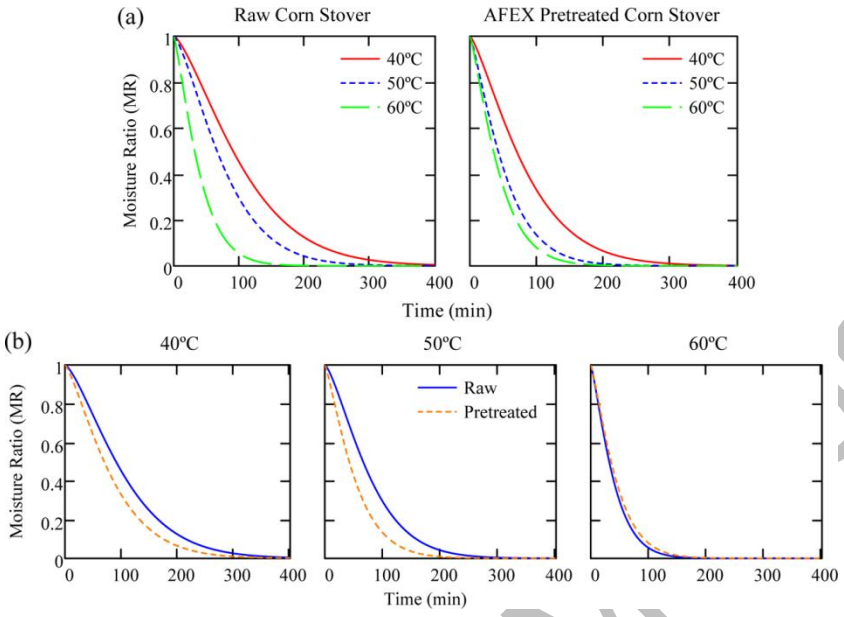

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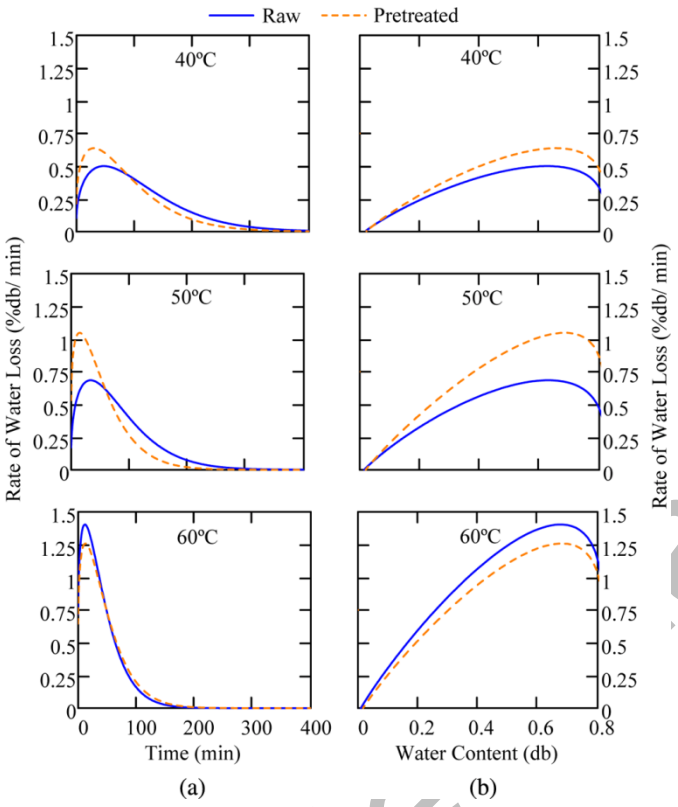
FIGURE 6. Rates of thin-layer drying beginning from an initial moisture content of 82% db for raw and AFEX pretreated corn stover modeled with the Modified Page equation relative to (a) time and (b) moisture content.



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