HYGROSCOPIC MOISTURE SORPTION KINETICS MODELING OF CORN STOVER AND ITS FRACTIONS

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ABSTRACT. *Corn stover, a major crop-based lignocellulosic biomass feedstock, is required to be at an optimum moisture content for efficient bioconversion processes. Environmental conditions surrounding corn stover, as in storage facilities, affect its moisture due to hygroscopic sorption or desorption. The measurement and modeling of sorption characteristics of corn stover and its leaf, husk, and stalk fractions are useful from utilization and storage standpoints, hence investigated in this article. A benchtop low-temperature humidity chamber provided the test environments of 20°C, 30°C, and 40°C at a constant 95% relative humidity. Measured sorption characteristics with three replications for each fraction were obtained from instantaneous sample masses and initial moisture contents. Observed sorption characteristics were fitted using exponential, Page, and Peleg models. Corn stover fractions displayed a rapid initial moisture uptake followed by a slower sorption rates and eventually becoming almost asymptotic after 25 h. Sorption characteristics of all corn stover fractions were significantly different ($P < 0.0001$) but not the effect of temperature ($P > 0.05$) on these fractions. The initial 30 min of sorption was found to be critical due to peak rates of sorption from storage, handling, and processing standpoints. The Page and Peleg models had comparable performance fitting the sorption curves ($R^2 \geq 0.995$), however the exponential model ($R^2 \geq 0.91$) was not found suitable because of patterned residuals. The Arrhenius type relationship ($P < 0.05$; $R^2 \geq 0.80$) explained the temperature variation of the fitted sorption model parameters. The Peleg model fitted constants, among the sorption models studied, had the best fit ($R^2 \geq 0.93$) with the Arrhenius relationship. A developed method of mass proportion, involving individual corn stover fraction dry matter ratios, predicted the whole corn stover sorption characteristics from that of its individual fractions. Sorption characteristics models of individual corn stover fractions and predicted whole corn stover including a nomogram can be used for direct and quick estimation. Developed sorption characteristics find application in several fields of corn stover biomass processing, handling, and transport.*

Keywords. *Biomass, Corn stover, Hydration, Kinetics, Models, Moisture, Sorption.*

Corn stover, among the various crop residues in the United States, ranks first based on quantity in the lignocellulosic category to be used as a feedstock for bioenergy and bioproducts applications (Jenkins and Sumner, 1986; Petrolia, 2008). For these applications, it is generally understood that the stover should be presented at an optimum moisture content. Corn stover moisture also plays an important role in its efficient storage, transport, and conversion processes. Depending on environmental conditions and elapsed time after harvest, corn stover contains moisture at varying levels (Womac et al., 2005). A kinetic model to predict the moisture present in the corn stover as a function of surrounding conditions becomes an important design and analysis tool for a successful harvest and postharvest operations.

Sorption or hydration kinetics models are broadly classified into theoretical and empirical models. Theoretical models, based on Fick's law of diffusion, are generally considered as complex – involving numerous functions and parameters, hence are not convenient for practical calculations under most situations (Maskan, 2002). However, in-depth computations should consider this approach that provides insight into the physical processes. Another approach is the new two-component internal and external resistance to moisture diffusion in tobacco of Walton and Casada (1986). On the other hand, empirical models without physical basis such as the exponential, Page (*ASABE Standards*, 2006) and Peleg (1988) model can be accurate analytical tools for prediction yet are simple to use. The Page is two-parameter exponential while the Peleg is two-parameter non-exponential model. The Peleg model has been widely used due to its simplicity and has been reported to adequately describe the hydration characteristics of various foodstuffs (Cunningham et al., 2007; Resio et al., 2006). The Page model, also simplistic, has been extensively used in drying modeling. These models can be applied to moisture sorption characteristics under hygroscopic environment, although reports on liquid water hydration are common. As noted from the literature, no biomass and not even all crops and food products that require hydration or rehydration at some stage of processing have been

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researched. As a result, there is a research gap on determining the sorption behavior for all the lignocellulosic biomass currently receiving increasing interest for biofuel or bioenergy production.

The major fractions of corn plant such as stalk, leaf, and husk, excluding the grain with cob, constitute the aboveground corn stover mass. Distribution of stalk, leaf, and husk were 72.6% [165.3% moisture content dry basis (d.b.)], 20.7% (12.2% d.b.), 6.8% (11.9% d.b.) on wet mass basis during the normal harvesting period of when grain moisture was 33.0% d.b. (Igathinathane et al., 2006). Pordesimo et al. (2004) reported 60%, 25%, and 15% on dry matter basis for stalk, leaf, and husk, respectively. Hence, sorption kinetics determination for these distinctive fractions individually encompass the total stover mass. Stalk being the dominant fraction (≈73% wet mass) of corn stover, it covers the major portion of the collectible corn stover biomass. Difficulties were experienced in collection of leaf and husk components of dry stover due to shedding and blowing off as well support the consideration of studying individual fractions. Based on the corn stover mass distribution, the sorption kinetics of corn stover can be estimated from the individual fractions as illustrated in sorption equilibrium moisture content (EMC) study of corn stover components (Igathinathane et al., 2005).

Moisture sorption and desorption also occur when a product is subjected to an environment with a specific air temperature and relative humidity (RH) that is not in equilibrium with the moisture content of the product. For a sustainable supply of corn stover biomass to the processing facility, it is imperative that the biomass should be stored properly in adequate quantities to meet the demand. Similar to most agricultural materials, corn stover is hygroscopic, i.e. it will lose or gain moisture from the surrounding environment depending on the RH and temperature of the environment. Even though dry corn stover stores well, mold growth is inevitable when it is stored at high moisture content for a long period of time. From microbial growth and storage standpoints, moisture gain by corn stover from a hot and humid environment is more critical than the moisture loss in a cool and dry environment (Igathinathane et al., 2008). Thus, sorption characteristics are important information that guides estimation of moisture levels, corrective measures for enhanced storage, microbial growth assessment, and other management decisions. Establishing the maximum rate of moisture sorption from extreme air conditions with high RH, sometimes bulk storages were subjected to, such as 95% RH will provide the critical information. Therefore, the present study focuses on the hygroscopic sorption behavior of corn stover fractions in high RH conditions at different temperatures.

The objectives of this research were to 1) determine and model (using exponential, Page, and Peleg models) the sorption characteristics of corn stover fractions, 2) determine the effect of temperature on the model parameters, and 3) predict the sorption characteristics of whole corn stover from its individual fractions.

Materials and Methods

Experimental Material and Procedure

Intact corn plants (DeKalb 626; planted 21 May 2001 in Knoxville Experiment Station, Tenn.) were manually harvested (25 September 2001) and stored indoors in the air-conditioned laboratory (21°C and 50% RH) for 18 months before experiments began. This test material was actually a sub-lot from the previous years' experiments. Leaf, husk, and stalk fractions of corn stalk were separated manually and cut into pieces of about 76 mm (3 in.) length. Prepared samples were filled in aluminum foil trays (6 in. diameter, 1½ in. deep) approximately to half the depth. Mean sample mass (based on average of three replicates) for each components were approximately 8.5±0.5, 7.7±0.3, and 30.0±4.0 g for leaf, husk, and stalk, respectively. The initial moisture contents for the stover fractions (*ASAE Standards*, 2003) were determined to be 4.0%, 5.2%, and 0.88% d.b. for leaf, husk, and stalk, respectively. Unless specified otherwise, all moisture contents in the study are reported in decimal d.b., representing mass of water in sample (kg) over mass of sample dry matter (kg).

A benchtop type, low-temperature humidity chamber (Model: LHU-113; ESPEC North America, Inc., Hudsonville, Mich.) with digital control provided the desired temperature and humidity environments. Interior dimensions of the chamber were 500 mm wide × 390 mm deep × 600 mm high. Perforated flexible aluminum trays held samples in triplicate. The samples were exposed to temperatures of 20°C, 30°C, and 40°C, and to a constant RH of 95%. This RH level (95%) helps in determining maximum rate of sorption, thereby establishing the higher limits of sorption characteristics at studied temperatures. A total of 27 samples were prepared for the experiments (3 material × 3 temperatures × 3 replications). The recorded increase in mass using digital balance (±0.01 g accuracy) determined the moisture sorption characteristics of stover fractions. Mass readings were closely spaced initially and widely at later stages for a total of about 32 h, with a gap of around 15 h overnight. Cubic spline method interpolated the data for sorption rate determination.

Sorption Kinetics Models

Exponential Model

Following first-order rate kinetics, the exponential model (Sherwood, 1936; Abu-Ghannam, 1998; Casada, 2002) states that moisture sorption rate is proportional to the amount of departure of the instantaneous moisture from the final equilibrium moisture. In this study the final moisture reading was assumed as the pseudo equilibrium moisture content (PEMC) and used in the models. The PEMC was the stable moisture content of the material after sufficient time of exposure to the test environment. From preliminary studies, an exposure time of 30 to 32 h was determined to have established the PEMC in different corn stover fractions. The exponential model expressed in a form ready for model fitting with suitable limits (t = 0 to t; $M = M_0$ to M_e) as:

$$\frac{M_e - M}{M_e - M_0} = \exp(-k_e t);$$

$$M = M_e - (M_e - M_0) \times \exp(-k_e t) \qquad (1)$$

where M_e = PEMC of material selected (d.b.), M = instantaneous moisture content of the material (d.b.) at any time t, M_0 = initial moisture content of material selected (d.b.), k_e = sorption rate constant (h^{-1}) of exponential model, and t = time of sorption (h). The exponential model (eq. 1) requires two material-related constants (M_0 and M_e) to determine the unknown parameter (k_e).

Page Model

Page model (*ASABE Standards*, 2006), a common simpler approach to model thin layer drying of agricultural crops, was utilized to model the sorption characteristics of corn stover fractions. The Page model with usual notations is given as:

$$\frac{M_e - M}{M_e - M_0} = \exp(-kt^n);$$

$$M = M_e - (M_e - M_0) \times \exp(-kt^n) \quad (2)$$

where k = sorption rate constant (h^{-1}) of Page model, and n = exponent (dimensionless) of Page model. The Page model (eq. 2) requires two material-related constants (M_0 and M_e) and two parameters (k and n) to be evaluated.

Peleg Model

A non-exponential empirical model originated by Peleg (1988) that has found usage in expressing moisture sorption and desorption in food materials (Cunningham et al., 2007; Resio et al., 2006) is given as:

$$M = M_0 + \frac{t}{k_1 + k_2 t} \quad (3)$$

where k_1 = Peleg model rate constant [(mass of dry matter) (mass of water)$^{-1}$ h] that is inversely related to the initial rate of water absorption, and k_2 = Peleg model capacity constant [(mass of dry matter) (mass of water)$^{-1}$] that is inversely related to EMC.

Equation 3 is already in the form amenable to model fitting. It is interesting to note that this equation needs only one material-related initial moisture content (M_0), but requires determination of two model parameters (k_1 and k_2). The Peleg model predicted EMC (M_{Pe}) in percent d.b. can be derived from equation 3 by subjecting $t \rightarrow \infty$ as

$$M_{Pe} = \left(M_0 + \frac{1}{k_2} \right) \times 100 \quad (4)$$

Rate of moisture absorption during sorption can be derived from differentiating equation 3 with respect to t, and when $t \rightarrow 0$ gives the initial rate of sorption (Resio et al., 2006) as:

$$W_0 = \left. \frac{dM}{dt} \right|_{t \rightarrow 0} = \frac{1}{k_1} \quad (5)$$

where W_0 = initial rate of moisture sorption [(mass of water) (mass of dry matter)$^{-1}$ h^{-1}].

Thus, the Peleg model has the advantage of estimating the EMC and initial sorption rate.

Temperature Dependence of Model Parameters

Several researchers employed the Arrhenius equation to explain the temperature dependence of the fitted parameters of sorption models. The variation of individual fitted models parameters (eqs. 1, 2, and 3) with temperature is quantified by the Arrhenius equation (Perry and Green, 1984), and is represented in the general form as:

$$P = A \exp\left[-\frac{E}{RT} \right] \quad (6)$$

where P = parameter modeled and takes the parameters k_e, k, n, $1/k_1$, and $1/k_2$ with consistent units, A = frequency factor of the initial hydration rate with consistent units of selected parameter P, E = activation energy (kJ mol^{-1}) of model considered, R = universal gas constant (8.314×10^{-3} kJ mol^{-1} K^{-1}), and T = absolute temperature (K). The activation energy is the minimum energy needed for the moisture transfer to initiate and proceed. Arrhenius equation sometimes should be viewed simply as a method of curve fitting (e.g. Page model dimensionless exponent, n), without the physical interpretation, wherein A and E values represent the fitted nonlinear regression constants. A combined model, incorporating the effect of temperature, capable of estimating the sorption rates of different material can be obtained by substituting individual parameter Arrhenius equation (eq. 6) back to models (eqs. 1 to 3).

Predicted Sorption Characteristics of Corn Stover

Sorption kinetic study of whole corn stover in a small laboratory setting will be difficult, although possible, because of limited available space in the benchtop humidity chamber. One way of predicting the sorption characteristics of corn stover is following the method of mass proportion of Igathinathane et al. (2005). Wherein they estimated corn stalk EMC from the mass proportion and EMC relationships of stalk skin and stalk pith components. Dry matter content were calculated using the reported wet mass proportion of stalk 72.57%, leaf 20.67%, and husk 6.76% (Igathinathane et al., 2006) and the observed initial moisture content of the components. The whole corn stover moisture from fitted sorption kinetics of individual fractions can be expressed as:

$$M_{cs} = D'_s M_s + D'_l M_l + D'_h M_h \quad (7)$$

where M_{cs} = predicted instantaneous moisture content of whole corn stover (d.b.); D'_s, D'_l, and D'_h = dry matter mass fraction of stalk, leaf, and husk in stover (dimensionless), respectively; and M_s, M_l, and M_h = instantaneous moisture content from fitted sorption kinetics of stalk, leaf, and husk (d.b.), respectively.

Kinetics Models Fitting and Data Analysis

SAS 9.1.3 (2003) model fitting procedure PROC NLIN fitted the model parameters (k_e, k, n, k_1, and k_2) of equations 1, 2, and 3. The PROC NLIN also fitted the Arrhenius equation parameters (eq. 6: A and E) using k_e, or k or n or $1/k_1$ or $1/k_2$ as dependent and T as the independent parameters. Coefficient of determination (R^2) and residuals served as a measure of models fit performance. PROC GLM performed two-way analysis of variance (ANOVA) on means of moisture contents of each material and sorption temperature to assess the differences. SAS macro (%mmaov) mixed model ANOVA (Saxton, 2003) with log transformation and Tukey-Kramer ($P < 0.05$) analyzed the mean separation among materials and temperatures of sorption.

Results and Discussion

Observed Sorption Characteristics of Corn Stover Fractions

Leaf fraction of corn stover absorbed greater quantity of moisture from the surrounding high humid air (95% RH) at all studied temperatures followed by husk and stalk (fig. 1). Being ribbonlike and very thin, thus having greater surface area per unit mass, leaf and husk fractions showed steep increase in moisture sorption during the initial stages. Both these fractions almost attained their respective PEMC within the initial 5 h of sorption. Corn stalk showed only gradual curvilinear increase initially and ultimately the sorption profile became flat after 25 h indicating PEMC. Corn stalk can be considered geometrically as elliptical frustum (Igathinathane et al., 2006) with its thick rind covering the spongy pith intact. This packed structure combined with less available surface per unit mass resisted rapid initial sorption. Although the sorption characteristic curves were grouped by material, increased environment temperature shifted the curves upwards a little demonstrating increased moisture uptake with increased temperature.

The rapid initial moisture absorption period followed by a slower rate in the later stages was commonly observed with moisture hydration and rehydration characteristics of agricultural materials (Cunningham et al., 2007; Resio et al., 2006; Maskan, 2002; and Abu-Ghannam and McKenna, 1997). It can be easily visualized that moisture uptake will be even quicker if liquid water was used for hydration than the high humid air employed in this study.

All sorption curves after 24 h proceeded almost parallel to time axis indicating the attainment of the PEMC by respective stover fractions, hence the 32 h of sorption was considered sufficient for this sorption experiments. Observed PEMC values at 20°C, 30°C, and 40°C were 35.6%, 38.7%, 39.6% d.b for leaf; 29.4%, 29.9%, and 31.0% d.b. for husk; and 24.7%, 25.2%, and 25.9% d.b. for stalk, respectively. At these temperatures of 20°C, 30°C, and 40°C, the reported (Igathinathane et al., 2005) respective EMC in the equilibrium RH range of 96%-98% were 43.6%, 36.1%, and 30.9% d.b. for leaf; husk not reported; and estimated EMC of stalks were 45.1%, 37.8%, and 30.3% d.b. It should be noted that the reported EMC values were smaller than the observed PEMC for leaf, except for 20°C, and were greater for stalk. The discrepancy can be explained by the variation in time allowed for equilibration. The EMC values obtained after 28 days while PEMC took less than 1.5 days. The PEMC values can be considered only as relatively instantaneous moisture that tend towards the EMC after sufficient time lapse, while EMC represents the ultimate limiting value. Effect of increase in environment temperature would also have contributed to the variation in both studies. Increase in temperature had slight increasing trend of PEMC and decreasing trend of EMC (type II isotherm classification). These trends can be commonly observed in numerous hydration and EMC studies of agricultural materials.

Two-way ANOVA of group-wise moisture contents means of sorption characteristics showed that materials were significantly different (df = 2; F = 334.77; $P < 0.0001$), but environment temperatures were not (df = 2; F = 4.85; P = 0.085). Further mean separation analysis among materials, assuming normal distribution of data, revealed that materials husk (estimated mean: 0.265, letter group: A) and leaf (0.298, A) were similar, while stalk (0.117, B) was significantly different ($P < 0.05$). However, the temperature-based mean groups (20°C, 0.206, A; 30°C, 0.203, A; 40°C, 0.222, A) did not produce significant difference ($P > 0.05$).

Sorption Rate Characteristics of Corn Stover Fractions

To analyze the sorption rate ($\Delta M/\Delta t$) variation, the discrete sorption characteristics data were interpolated (cubic spline interpolation) at short time intervals (Δt = 0.1 h) and plotted against time (fig. 2). Sorption rates of leaf and husk reduced very sharply during the initial period and quickly become approximately asymptotic to the time axis. Within the first 0.5 h, the sorption rate of leaf and husk almost reached the final stable values. This initial rapid sorption rate signifies that in an event of rain, where RH reaches > 95% and temperature in the range of around 30°C, the corn stover fractions will absorb moisture at the maximum rate when they are dry. In this short period of 0.5 h (1.56% of 32 h), the moisture contents of leaf, husk, and stalk were 24.2%, 26.2%, and 4.6% d.b., which were 63.8%, 87.0%, and 18.0% of their respective PEMCs. Since moisture diffusion is the accepted

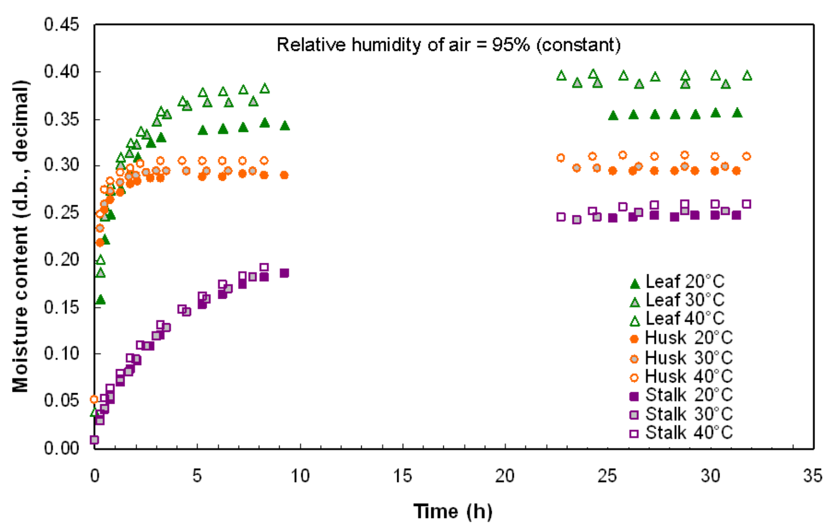

Figure 1. Observed sorption moisture contents of corn stover fractions at different temperatures.

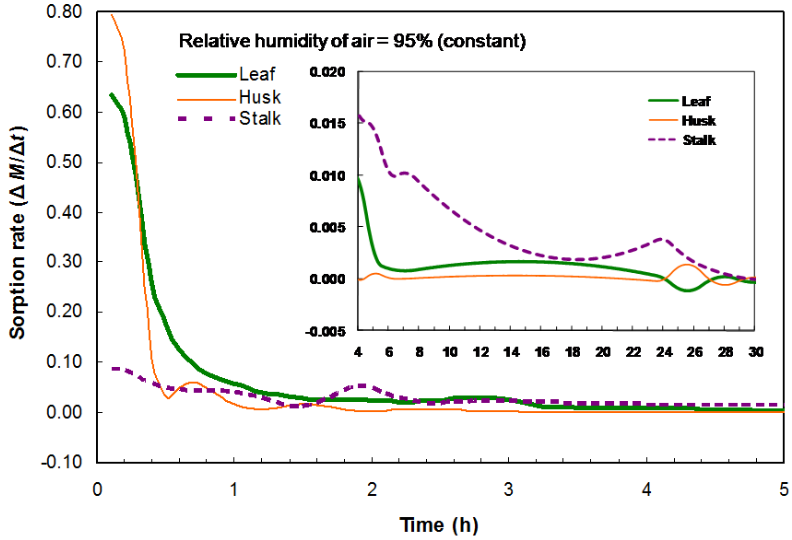

Figure 2. Typical moisture sorption rates versus time of corn stover fractions at 30°C (Insert: 4 to 30 h sorption).

mechanism of moisture transfer and moisture differential being the driving force, the initial period had greater moisture differential hence moisture diffusion was faster and vice versa.

Slow moisture uptake of stalk is clearly reflected from the flatter sorption rate profile, even at initial stages. However, the initial sorption rate was the greatest compared to rest of the period. The initial sorption rates were the greatest for husk, leaf the second, and stalk the least. Even though the initial sorption rate of husk was the greatest, after the initial period the order changed to stalk, leaf, and husk. This behavior was due to the compactness of components and available area for moisture sorption. Stalk being more compact and had less available area for moisture penetration, the sorption starts at a rate much lower than both husk and leaf and continues at a reduced rate when others have apparently reached their equilibrium moisture levels.

It appeared that all the sorption rate variation was minimized after 4 h of sorption. A close-up look of the sorption curves after the initial period (fig. 2 insert) showed the actual sorption rate variation within the narrow $\Delta M/\Delta t$ range of 0.0 to 0.02. The order of sorption rate characteristics was stalk, leaf, and husk and that order remained throughout the rest of the sorption period. Although the close-up version showed some distinct variation, it actually covered only 2.8% of the total sorption rate limits, which essentially means the sorption rates were fairly similar and equal as the rate approached zero after the initial 4 h.

Different zones of corn stover fractions sorption were visualized by plotting sorption rate against moisture content (fig. 3). Three zones of moisture uptake, namely: i) an initial relative constant high sorption rate when the moisture contents were low (≤10% d.b. for leaf and husk, and ≤2% d.b. for stalk), ii) followed by a rapid first falling rate, and iii) the final stabilization. Inexplicable small undulation in the sorption rates was observed with all fractions after the falling rate. Stalk reached its lowest stabilized sorption rates first, approaching zero, followed by husk and finally by leaf.

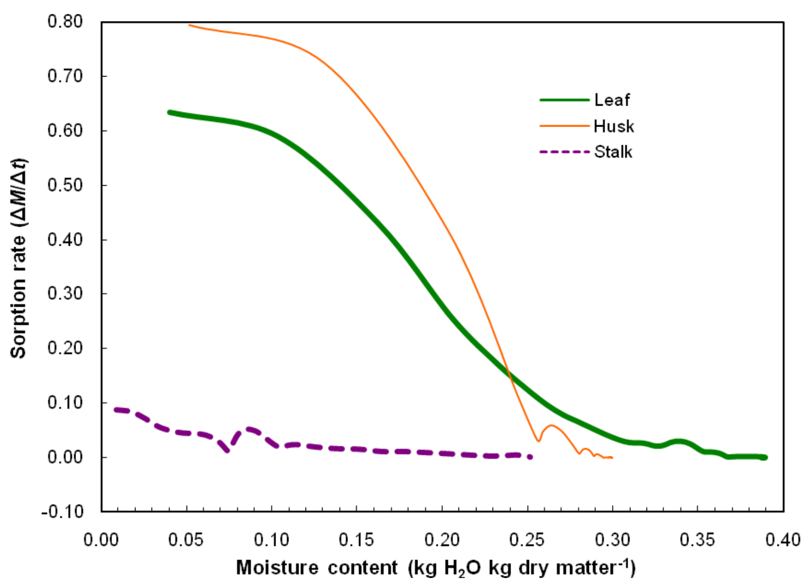

Figure 3. Typical moisture sorption rates vs. moisture content of corn stover fractions at 30°C.

Existence of increased moisture differential between the high humid environment (95% RH) and the reduced material initial moisture contents (≤5% d.b.) explains the initial increased sorption rates. Although husk started with higher rates of sorption compared to leaf, it reached the stabilized zero moisture uptake rather quickly. Initial adjustment section of the theoretical drying/hydration characteristics was not observed with all fractions of corn stover.

Sorption rate characteristic curves of other temperatures of 20°C and 40°C (not shown) had similar trends to 30°C (figs. 2 and 3), as the sorption characteristics were similar among temperatures (fig. 1). These results indicate that undue moisture increase and possible mold attack thereafter can be avoided if the RH and temperature of the air are not very high. Rain events may present situations of high RH, which call for exercising adequate precautionary measures. An in-field evaluation of whole corn stover moisture relations after two different rain events of 1.52 mm and less revealed that the peak moisture increase of corn stover under a shelter tent as well as in open field occurred over a period of time varying from the same day to two days after the rain (Womac et al., 2005). The observed delay in attaining peak moistures after rain events can be attributed to difference in varying field weather conditions (15±4°C and 79±9% RH) and single measurement per day on field as opposed to constant conditions in humidity chamber (20°C to 40°C and 95% RH) and regular monitoring in laboratory, among other variables. Shinners et al. (2007) also reported similar delays in attaining the peak moisture contents for field-stored flail shredded and chopped corn stover laid flat and in windrows after rain events up to 8 mm. It was reported that increased temperature and RH also favors the growth of mold on corn stover; a temperature of 20°C and RH of 97.6% will give 15 mold-free days, while an increased temperature of 40°C with even at a reduced RH of 89% gave only 10 mold-free days (Igathinathane et al., 2008).

Sorption Model Fitting Results

Comparison of Fitted Sorption Models

Overall, all the selected models adequately (P < 0.0001) described the observed sorption characteristics (table 1). However, both the Page ($0.996 \le R^2 \le 0.999$; $4.4\times10^{-5} \le$ SSD $\le 55\times10^{-5}$) and Peleg ($0.995 \le R^2 \le 1.0$; $2\times10^{-5} \le$ SSD $\le 67\times10^{-5}$) models were better than the exponential model ($0.908 \le R^2 \le 0.990$; $124\times10^{-5} \le$ SSD $\le 1271\times10^{-5}$). Analysis of exponential model residuals revealed a clear sinusoidal pattern (not shown) consisting of exactly one trough and one crest for all fractions and temperatures. Whereas, the residuals of both the Page and Peleg models showed sinusoidal pattern they crossed the zero residual line more often and were randomly distributed. The exponential model therefore cannot be recommended for sorption prediction of corn stover fractions because of the systematic pattern in combination with increased magnitude of residuals.

Both sorption constants (k_e and k) of exponential and Page models of husk were the greatest followed by leaf and stalk, but Page model n followed an opposite trend with materials. These constants indicate the ease of moisture sorption among the corn stover fractions, with higher values signifying quicker moisture uptake. The sorption constants (k_e and k) increased with temperature of air, and this trend was commonly observed in moisture sorption of agricultural materials. However, n values showed decreasing trend with increase in temperature.

A lower value of the Peleg model rate constant (k_1) related to mass transfer rate, indicated higher initial moisture absorption rate (Turhan et al., 2002). This can be clearly seen in husk fraction, a less compact material, combined with increased temperatures (table 1). Both the Peleg model k_1 and k_2 showed inverse variation with temperature. The Peleg model capacity factor (k_2) is related to the maximum water absorption capacity, with a lower value indicating increased water absorption capacity (Turhan et al., 2002). This explains the observed k_2 values at increased temperatures (table 1). It has been suggested that k_2 can be considered to be independent of temperature and a mean value be used for prediction (Peleg, 1988; Sopade et al., 1992). However, an appreciable mean absolute deviation from the predicted and observed sorption characteristics (*leaf*: 1.49 – 7.73 times; *husk*: 1.59 – 6.70 times; and *stalk*: 1.00 – 1.13 times) were observed between constant and variable k_2 in this study. Thus the usage of variable k_2 values for prediction of hygroscopic sorption moistures of corn stover fractions leads to better predictions. Pan and Tangratanavalee (2003) also confirmed

Table 1. Fitted exponential, Page, and Peleg models and their performance parameters, and Peleg model estimated saturation moisture content and initial moisture sorption rate of corn stover fractions.

		Exponential Model[a]			Page Model[b]				Peleg Model[b]					
Material	T (°C)	k_e (h^{-1})	R^2	SSD[c] ($\times10^{-5}$)	k (h^{-1})	n	R^2	SSD ($\times10^{-5}$)	k_1	k_2	R^2	SSD ($\times10^{-5}$)	M_{Pe} (% d.b.)	W_0
Leaf	20	1.3192	0.954	591	1.2091	0.5825	0.996	55	1.2603	3.1218	0.998	20	36.02	0.7935
	30	1.3401	0.908	1271	1.2307	0.5029	0.997	37	1.0725	2.8694	0.995	64	38.84	0.9324
	40	1.4791	0.926	1111	1.2570	0.4931	0.999	21	1.0008	2.7912	0.996	64	39.82	0.9992
Husk	20	3.9447	0.975	145	2.2482	0.4369	0.998	14	0.4561	4.1201	0.999	4	29.44	2.1925
	30	4.4610	0.977	133	2.4319	0.4251	0.999	4.4	0.3726	4.0351	1.000	2	29.95	2.6838
	40	4.7441	0.978	140	2.4378	0.3654	0.999	9.2	0.3160	3.8738	1.000	3	30.98	3.1646
Stalk	20	0.1804	0.990	136	0.2366	0.8268	0.998	29	17.2625	3.6178	0.999	20	28.52	0.0579
	30	0.1900	0.990	124	0.2450	0.8127	0.999	17	16.4855	3.5727	0.998	22	28.87	0.0607
	40	0.1935	0.981	263	0.2781	0.7583	0.997	37	14.6063	3.5368	0.995	67	29.15	0.0685

[a] Residuals show clear sinusoidal pattern with one trough and one crest about zero line.
[b] Residuals although showed some sinusoidal pattern, but were randomly distributed.
[c] SSD sum of squared deviation from observed and predicted characteristics.
Units: k_1 is (mass of dry matter) (mass of water)$^{-1}$ h; k_2 is (mass of dry matter) (mass of water)$^{-1}$; W_0 is (mass of water) (mass of dry matter)$^{-1}$ h^{-1}.

the application of variable k_2 to mean k_2 with soybean soaking.

The predicted data of the Page and Peleg models fitted better than the exponential model with observed sorption characteristics. Typical observed and predicted characteristics at 30°C illustrate this observation (fig. 4). Similar predictive behavior of these models was also observed at other temperatures (20°C and 40°C) of sorption (not shown).

Saturation Moisture Content and Initial Sorption Rate from Peleg Model

The Peleg model predicted EMC (M_{Pe}) of corn stover fractions ranged from 28.5% to 39.8% d.b. (table 1). For similar air conditions in static EMC study, Igathinathane et al. (2005) reported EMC values ranging from 30.5% to 32.7% d.b. for corn leaf and estimated values ranging from 30.3% to 34.2% d.b. for corn stalk. Compared to reported experimental results, the M_{Pe} values showed some overestimation. Furthermore, the effect of temperature in moisture sorption of both these studies showed opposite trends. One of the reasons for the observed deviations may be due to the difference in nature of the experiments; static (salt solution in desiccators) in EMC determination and dynamic (climate chamber) in this sorption study.

The Peleg model predicted initial sorption rates (W_0) varied from 0.058 to 3.165 (mass of water) (mass of dry matter)$^{-1}$ h^{-1} for the materials studied (table 1). The W_0 values signify the theoretical maximum rate of sorption of the material that happens immediately ($t \rightarrow 0$) when a dry material is introduced to a high humidity environment. It will be difficult to measure W_0 values and validate the prediction, unless sorption measurements were made at very close time intervals preferably by automatic systems. However, the estimates of W_0 may be acceptable as the Peleg model produced better performance for all the materials and temperatures studied, since the prediction only mathematically extended the observed trend. The W_0 values of different materials corroborate the moisture sorption property signified by other Peleg model constants discussed earlier (k_1 and k_2).

Temperature Dependence of Models Constants

Arrhenius equations fitted constants of sorption models constants are tabulated for different materials in table 2. Although only three temperatures were used for the fit, the fitted models were significant ($P < 0.05$) and R^2 values were greater than 0.8. Arrhenius model constants (A and E) were the greatest for husk followed by leaf and stalk. This means husk requires or absorbs more energy from the surrounding environment than stalk to initiate the moisture sorption. It can be observed from the fitted results (table 2) that the Peleg model constants fit the Arrhenius equation properly ($R^2 \geq$ 0.929). Hence, the Peleg model is better qualified to predict the sorption characteristics of corn stover fractions and whole corn stover at intermediate temperatures. While the Arrhenius constants explain the variation of model parameters with temperature, they can also be employed to predict sorption model parameters at any unknown intermediate temperature between the studied 20°C to 40°C.

Predicted Sorption Characteristics of Whole Corn Stover Using Peleg and Arrhenius Models

Assuming unit wet mass of corn stover and using the initial moisture contents of the stover fractions and mass proportions already given, the dry matter mass fractions of stalk, leaf, and husk were evaluated as 0.7323, 0.2023, and 0.0654, respectively. Utilizing these values in equation 7 after obtaining instantaneous moistures from the Peleg model (eq. 3) with the constants (k_1 and k_2) derived from Arrhenius equation (table 2), the whole corn stover sorption characteristics at intermediate temperatures between 20°C to 40°C with constant 95% RH can be estimated accurately. However, figure 5 (obtained using the aforementioned procedure) showing the whole corn stover sorption characteristics at 20°C to 40°C in steps of 5°C can be used as a quick estimation nomogram.

The whole corn stover predicted characteristics resemble more the stalk fraction (figs. 1 and 5) because of its greater mass fraction (73.23% dry matter). However, the moisture increasing effect of other fractions, mostly by leaf (20.23% dry matter) was also evident. This can be seen as the predicted moisture content of whole corn stover at all temperatures beyond 15 h was above 25.0% d.b., while for the individual stalk fraction the moisture contents were approximately less

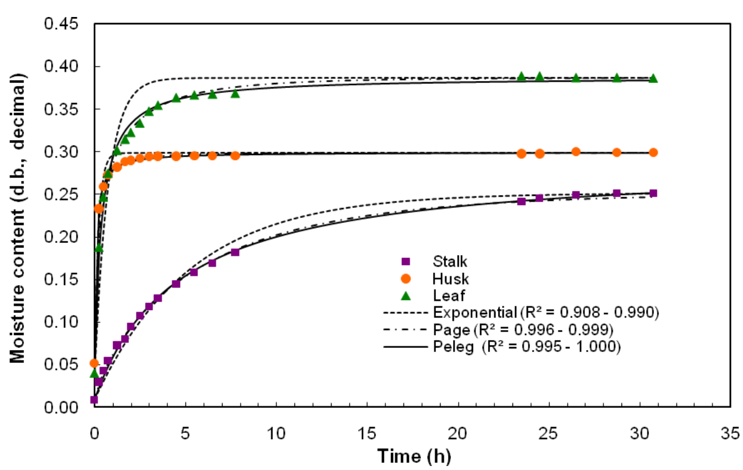

Figure 4. Typical exponential, Page, and Peleg models fitting of sorption data of corn stover fractions at 30°C.

Table 2. Arrhenius type relationship fitted constants of models parameters of corn stover fractions.

Material	Exponential Model k_e							
	A (h^{-1})	E (kJ mol^{-1})	R^2	P > F				
Leaf	8.0857	4.4567	0.845	0.020				
Husk	68.6241	6.9350	0.970	0.013				
Stalk	0.5403	2.6604	0.937	0.007				
	Page Model k				Page Model n			
	A (d.b. h^{-1})	E (kJ mol^{-1})	R^2	P > F	A (d.b.)	E (kJ mol^{-1})	R^2	P > F
Leaf	2.2201	1.4830	0.995	0.001	0.0372	-6.6686	0.863	0.028
Husk	7.9451	3.0451	0.800	0.017	0.0312	-6.4762	0.839	0.031
Stalk	3.1170	6.3282	0.897	0.023	0.2226	-3.2175	0.877	0.013
	Peleg Model $1/k_1$				Peleg Model $1/k_2$			
	A (d.b. h^{-1})	E (kJ mol^{-1})	R^2	P > F	A (d.b.)	E (kJ mol^{-1})	R^2	P > F
Leaf	27.3499	8.5857	0.955	0.020	1.8260	4.2186	0.929	0.013
Husk	660.0000	13.8954	0.998	0.006	0.6369	2.3603	0.960	0.005
Stalk	0.8264	6.5150	0.931	0.019	0.3942	0.8643	0.998	0.0004

than 25.0% d.b. over the entire studied time of sorption (fig. 1). This demonstrates the moisture contribution of leaf and husk in increasing the moisture of the whole corn stover sorption characteristics.

Further research is required to determine the sorption characteristics of intact whole corn stover both with high humid environment and with liquid water to determine the sorption and hydration directly. The fitted Peleg model and the outlined method of mass proportions aid in prediction of absorbed moisture in corn stover fractions and whole corn stover as a function of time. The fitted models, the developed nomogram, and the various results from this study comprise data essential for corn stover quality assessment, storage life evaluation, transportation and logistics, and process and storage systems design, among other applications.

Conclusions

Hygroscopic sorption characteristics of dry corn stover leaf, husk, and stalk fractions were significantly different ($P < 0.0001$) under high relative humidity air conditions (95% RH; 20°C to 40°C). Corn stover fractions absorbed moisture initially at rapid rate, slowed down gradually, finally followed by a slower and negligible rate change after 25 h. The initial 30 min of sorption is critical from storage, handling, and processing standpoints, as the corn stover fractions absorbed moistures at the highest rate producing significant levels of absorbed moisture. Both the Page ($R^2 \geq 0.996$) and Peleg ($R^2 \geq 0.995$) models effectively described the observed sorption characteristics of corn stover fractions, but the exponential model was not found suitable. Arrhenius-type relationships adequately explained the temperature variation of model parameters ($P < 0.01$; $R^2 \geq 0.80$ for Page and ≥ 0.93 for Peleg models) that can be utilized to determine the model parameters at any intermediate temperatures. The predicted sorption characteristics of whole corn stover resembled the stalk sorption characteristics owing to its increased mass fraction (73.23%). The Peleg model in combination with the Arrhenius equation is recommended for sorption prediction of corn stover and similar lignocellulosic biomass.

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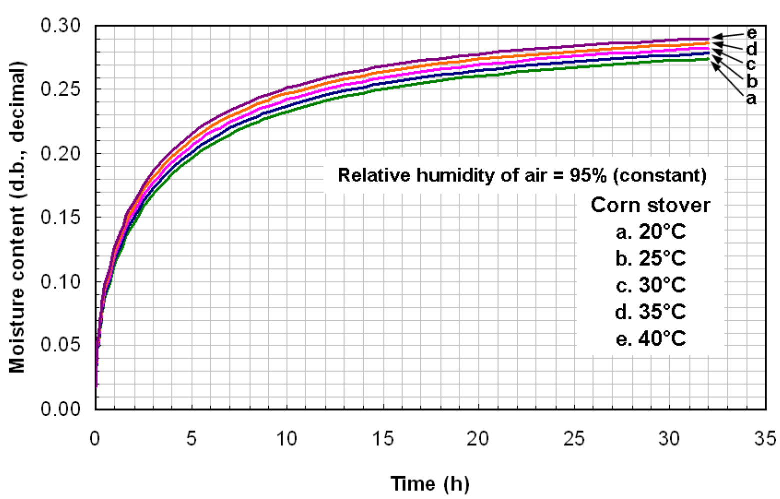

Figure 5. Predicted sorption characteristics of whole corn stover based on Peleg model at different temperatures.

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