MOISTURE SORPTION KINETICS OF SWITCHGRASS, BIG BLUESTEM, AND BROMEGRASS BIOMASS

M. Yu, C. Igathinathane, J. Hendrickson, M. Sanderson

ABSTRACT. Moisture content of biomass is the most influential factor in biomass storage. Moisture sorption kinetics control the dynamic moisture condition of the biomass, thus affecting biomass storage, processing operations, and final utilization applications. Moisture sorption characteristics of switchgrass, big bluestem, and brome grass, potential biomass feedstocks for the Northern Great Plains of the U.S., were studied. Study objectives were to determine the moisture sorption kinetics, mathematically model the sorption process using standard models, and evaluate the effect of temperature on moisture sorption. Moisture sorption experiments were conducted at temperatures of 20°C, 40°C, and 60°C and a fixed high relative humidity of 95% using a controlled-environment chamber. Standard moisture sorption kinetics models (exponential, Page, and Peleg) were used to analyze the experimental sorption characteristics of the feedstocks. Bromegrass had the highest moisture sorption rates and final moisture contents, followed by big bluestem and switchgrass. On average, at 20°C, 50% of moisture sorption completion occurred at 1.5, 1.9, and 1.7 h and 90% completion occurred at about 8.5, 13.4, and 12.8 h for switchgrass, big bluestem, and bromegrass, respectively. For the temperatures studied, on average 41% ±3%, 40% ±5%, and 39% ±1% of moisture sorption completion occurred in 1 h and 82% ±2%, 76% ±4%, and 73% ±1% completion occurred in 5 h for switchgrass, big bluestem, and brome grass, respectively. Moisture sorption rates decreased very sharply during the first hour (≥78%) from their initial values and quickly plateaued thereafter. Increase in temperature increased the moisture sorption rates for all the biomass types tested. Both the Page and Peleg models effectively described the observed sorption characteristics for the selected biomass types (R² ≥ 0.96). The Arrhenius equation adequately described the temperature dependence of the model parameters (0.77 ≤ R² ≤ 1.00). Based on this study, the Peleg model in combination with the Arrhenius equation is recommended for moisture sorption predictions. Fitted moisture sorption kinetics models, developed nomograms, and combined prediction equations (R² ≥ 0.83) form baseline data essential for storage of the selected biomass types and various handling, conditioning, and processing operations.

Keywords. Grasses, Mathematical models, Moisture relation, Renewable energy, Storage.

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switchgrass (Panicum virgatum L), big bluestem (Andropogon gerardii Vitman), and bromegrass (Bromus inermis Leyss) are high-yielding perennial grass species in the Northern Great Plains of the U.S. that can potentially be used as lignocellulosic feedstocks. Because biomass is renewable, locally grown, and environmentally friendlier than fossil fuel resources, it represents a significant feedstock source for national energy security. To meet future demands, several projections indicate that huge volumes of biomass must be processed to achieve renewable energy goals (Hess et al., 2009). Although corn stover has been proposed as a strategic feedstock both for bioenergy and bio-based applications (Pordesimo et al., 2005) and as a feedstock that would contribute a major portion of this demand (Perlack et al., 2005), other crop-based biomass types such as switchgrass, big bluestem, bromegrass, and several native grasses and crop residues are required to play a role in fulfilling the requirements.

After harvest, biomass has to be properly stored and preprocessed before it can be converted into fuels, chemicals, energy, and value-added products. During storage, transportation, and preprocessing, biomass is exposed to different environmental conditions. These conditions directly influence the moisture status of a feedstock in a dynamic manner, as the feedstock moisture adjusts in relation to the moisture present in the ambient air. Moisture sorption (increase) and desorption (decrease) occur when a feedstock is subjected to an environment, specified by its air temperature and relative humidity (RH), that is not in
equilibrium with the moisture content of the feedstock (Igathinathane et al., 2009). For example, when a low-moisture biomass is exposed to a high RH environment, the biomass moisture content increases until it attains equilibrium with the environment, corresponding to the air temperature and RH. Such moisture adjustment occurs during processing and storage.

Biomass moisture content is the most influential factor in biomass storage and preprocessing operations. Environmental conditions and elapsed time after harvest (e.g., for corn stover) alter the moisture level in biomass (Womac et al., 2005). Biomass moisture influences biochemical and microbiological activities, resulting in mass loss, fire hazards due to hot spot generation, health concerns, and overall quality, and thereby affects the conversion processes and product (Rentizelas et al., 2009). A hot and humid environment that promotes moisture gain was found to be more critical for microbial growth on corn stover than a cool and dry environment, which led to moisture loss (Igathinathane et al., 2008).

Because the environmental temperature and RH as well as the time of exposure influence the moisture content of a material, the study of moisture relationships is broadly categorized into (1) equilibrium moisture content (EMC), and (2) moisture sorption/desorption kinetics. While EMC studies aim to determine the final equilibrium moisture of a material exposed to specific conditions, moisture kinetics studies aim to obtain the moisture history by determining the moisture content with respect to time.

Although EMC studies on food-related materials are numerous, biomass-related studies are limited. Some of the recent EMC research on undensified biomass feedstocks has included flax straw, hemp stalk, and reed canary grass (Nilsson et al., 2005); corn stover components (Igathinathane et al., 2005); miscanthus (Arabhosseini et al., 2010); canola straw (Chico-Santamarta et al., 2011); corn stover and big bluestem (Karunanithy et al., 2013a); switchgrass and prairie cord grass (Karunanithy et al., 2013b); and energy sorghum (Bonner and Kenney, 2013). However, the literature on moisture sorption kinetics of biomass is scarce, except for corn stover fractions (Igathinathane et al., 2009).

Understanding moisture sorption by biomass is of practical importance because it affects the resulting moisture content and subsequently influences the handling operations and the final product. Sorption kinetics control the dynamic moisture conditions of the biomass and can be modeled using kinetic models. The kinetic models developed from moisture sorption data can be used to predict the moisture content of biomass at given ambient conditions, as well as help to formulate guidelines for optimizing biomass storage and processing.

Three empirical kinetics models, namely the exponential, Page, and Peleg models, are commonly found in the literature on moisture sorption characteristics. These sorption kinetics models have been widely applied to food products. The Peleg model has been successfully used to model the sorption kinetics of several food and agricultural products, e.g., soaking of red kidney beans (Abu-Ghannam and McKenna, 1997), hydration of dried apples (Bilbao-Sáinz et al., 2005), and soaking of pasta (Cunningham et al., 2007). Igathinathane et al. (2009) adapted these three models to the moisture sorption kinetics of corn stover fractions. They observed that the initial 30 min of sorption are critical for storage, handling, and processing, as the sorption rates were highest during this period and increased the moisture content appreciably. The Page and Peleg models effectively described the observed sorption characteristics, but the exponential model did not, based on performance parameters such as sum of squared deviation and coefficient of determination. As the moisture sorption kinetics of several potential biomass feedstocks needs to be established, there is a need to fill this knowledge gap.

Moisture sorption characteristics are important information for estimating the moisture content of biomass with respect to time, for establishing corrective measures for enhanced storage, for assessing microbial growth and biomass quality, and for making other management decisions in the storage and processing of biomass feedstocks. The objectives of this research were: (1) to determine the moisture sorption characteristics of selected biomass types over a range of temperatures; (2) to mathematically model the moisture sorption kinetics with the exponential, Page, and Peleg models; and (3) to determine the effects of temperature on the moisture sorption kinetics model parameters and develop prediction models for the moisture sorption characteristics of switchgrass, big bluestem, and bromegrass.

**MATERIALS AND METHODS**

**MATERIALS AND EXPERIMENTAL PROCEDURE**

Samples of switchgrass (‘Sunburst’ variety, seeded May 2008), big bluestem (‘Bonilla’ variety, seeded May 1995), and smooth bromegrass (‘Lincoln’ variety, seeded May 2000) were harvested in early September 2012 from the USDA-ARS Northern Great Plains Research Laboratory (NGPRRL) research field plots in Mandan, North Dakota (46° 48′ 38.7″ N, 100° 55′ 1.9″ W). These grasses are perennial biomass crops and have been harvested annually after the first establishment year. The biomass samples were harvested by mechanical mower, collected without baling, and stored indoors intact as bunces. Samples were naturally dried in the air-conditioned laboratory with an average temperature of about 22.5°C.

The moisture contents of the biomass samples were determined using ASABE Standard S358.3 (ASABE Standards, 2012) following air oven drying at 103°C for 24 h in triplicate. The moisture contents determined were 4.07%, 4.44%, and 4.88% dry basis (d.b.) for switchgrass, big bluestem, and bromegrass, respectively. A total of 27 dried samples were prepared for the experiments (3 materials × 3 temperatures × 3 replications).

All moisture sorption experiments were carried out with biomass samples naturally dried to a low moisture content (<5.0% d.b.) using a controlled-environment chamber (BTX-475, ESPEC North America, Inc., Hudsonville, Mich.) that was fully programmable with a Watlow F4 controller (Watlow Controls, Winona, Minn.). A sample of harvested intact plants was chopped to about 254 mm
(10 in.) lengths, based on the tray dimensions (292 mm length × 240 mm width × 30 mm depth) to accommodate the chopped material, so that the whole plant material was used (fig. 1). About 50 g of sample, which can be conveniently held on each tray, were used for each of the three replications. Although most harvested biomass materials undergo some distortion during baling and their sorption kinetics will be different, these intact plant stalks represent the baseline sorption kinetics of the different biomass types tested. The samples were held in perforated aluminum trays (fig. 1) and loaded into the chamber. The chamber temperature was set to 20°C, 40°C, or 60°C, and a consistent relative humidity of 95% RH was used to maximize the rate of sorption. Temperature selection was partly based on the working range of the chamber as well as to mimic the wide range of possible storage and processing conditions. The constant 95% RH was the maximum level of the chamber and also represents the highest limit of the moisture sorption characteristics of the biomass. With a lower RH, the sorption characteristics are expected to be below this limit.

**SORPTION KINETICS MODELS**

The exponential model is given by:

\[
\frac{M_e - M}{M_e - M_0} = \exp(-k_e t)
\]

\[
M = M_e - (M_e - M_0)\exp(-k_e t)
\]

where

- \(M_e\) = pseudo-equilibrium moisture content of selected material on a dry basis (d.b.)
- \(M\) = instantaneous moisture content of material (d.b.) at any time \(t\)
- \(M_0\) = initial moisture content (d.b.)
- \(k_e\) = exponential model sorption rate constant (h\(^{-1}\))
- \(t\) = time of sorption (h).

The Page model is a two-parameter exponential model expressed as:

\[
\frac{M_e - M}{M_e - M_0} = \exp(-kt^n)
\]

\[
M = M_e - (M_e - M_0)\exp(-kt^n)
\]

where

- \(k\) = Page model sorption rate constant (h\(^{-1}\))
- \(n\) = Page model exponent (dimensionless).

Peleg (1988) proposed a simple non-exponential two-parameter sorption equation for modeling sorption as well as desorption in food materials. The Peleg model is given as:

\[
M = M_0 + \frac{t}{k_1 + k_2 t}
\]

where

- \(k_1\) = Peleg rate constant ((mass of dry matter) (mass of moisture\(^{-1}\)) h\(^{-1}\))
- \(k_2\) = Peleg capacity constant ((mass of dry matter) (mass of moisture\(^{-1}\)).

The general rate of moisture sorption \((R)\) can be obtained from the first derivative of the Peleg equation (eq. 3) as:

\[
R = \frac{dM}{dt} = \frac{k_1}{(k_1 + k_2 t)^2}
\]

The initial rate of sorption \((R_0)\) is useful information as it represents the maximum uptake of moisture, which can be obtained when \(t\) approaches 0 \((t = t_0)\) in equation 4. The initial rate of sorption, with units of (mass of moisture) (mass of dry matter\(^{-1}\) h\(^{-1}\)), is related to the Peleg rate constant \((k_1)\) and expressed as:

\[
R_0 = \frac{dM}{dt} \bigg|_{t_0} = \frac{1}{k_1}
\]

The final moisture content is also useful information as it represents the EMC after sufficient time of exposure, which can be obtained when \(t\) approaches \(\infty\) \((t = t_\infty)\) in equation 3. Thus, the Peleg model predicts the EMC from the initial moisture content. The Peleg model predicted equilibrium moisture content (PEMC) \(M_{pe}\), with units of % d.b., is expressed as:

\[
M_{pe} = M_{e |_{t_\infty}} = M_e = M_0 + \frac{1}{k_2}
\]

The Peleg model has the unique advantage of estimating...
the initial sorption rate (eq. 5) and EMC (eq. 6).

The temperature dependence of the model parameters can be represented using the Arrhenius equation:

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

(7)

where

- $P =$ parameter modeled (any of the parameters or model constants of the discussed sorption kinetics models in consistent units)
- $A =$ frequency factor of the initial sorption rate of parameter $P$ with consistent units
- $E =$ activation energy (kJ mol$^{-1}$)
- $R =$ universal gas constant ($8.314 \times 10^{-3}$ kJ mol$^{-1}$ K$^{-1}$)
- $T =$ absolute temperature (K).

The Arrhenius equation (eq. 7) is useful for evaluating the change in model constants as affected by environment temperature and thus for predicting the moisture sorption characteristics at any intermediate temperature. It can be observed that both the exponential model (eq. 1) and the Page model (eq. 2) predict the sorption characteristics based on initial and equilibrium moisture contents, which sometimes are not readily known. However, the Peleg model can predict the sorption characteristics based only on the initial moisture content, which is another advantage of the Peleg model.

**Statistical Analysis and Model Performance**

As the observed data were discrete, a cubic-spline interpolation was performed to obtain continuous data using a very close interval of 0.01 h for about 3.5 h and a slightly longer interval of 0.083 h thereafter. From the continuous interpolated data, the moisture sorption rates, the sorption kinetics with respect to time, and the time required to achieve any specified level of completion can be easily obtained.

In the present study, the entire observed sorption characteristics dataset was used for model fitting, similar to the method used by Sopade and Obekpa (1990), Sopade et al. (1992), and Hung et al. (1993). The SAS (2003) model fitting procedure PROC NLIN was used to fit the parameters of the moisture sorption kinetics models (eqs. 1, 2, and 3) and the Arrhenius equation (eq. 7).

As various models were fitted, the model selection was carried out based on parameters that quantify the model performance in predicting the observed data. Following are the model performance parameters considered in this study, which are widely used by researchers:

$$SSD = \sum_{i=1}^{N} (M_{pred} - M_{obs})^2$$

(8)

$$RMSD = \sqrt{\frac{\sum_{i=1}^{N} (M_{pred} - M_{obs})^2}{N}}$$

(9)

$$R^2 = 1 - \frac{\sum_{i=1}^{N} (M_{obs} - M_{avg})^2}{\sum_{i=1}^{N} (M_{obs} - M_{pred})^2}$$

(10)

where

- $SSD =$ sum of squared deviation between model-predicted and observed moisture contents (decimal d.b.$)^2$
- $N =$ number of observations in the input dataset
- $M_{pred} =$ model-predicted moisture content (decimal d.b.)
- $M_{obs} =$ original or interpolated observed moisture content (decimal d.b.)
- $RMSD =$ root mean square deviation between model-predicted and observed moisture contents (decimal d.b.)
- $R^2 =$ coefficient of determination of the model (dimensionless).

The number of observed data points after interpolation for a given sorption characteristic was constant for all the models, as the total time for the sorption test, about 40 h, was maintained as constant. The total time of 40 h ensured that the moisture sorption reached stabilization, and no further moisture uptake was observable with extended exposure. Therefore, the parameter SSD, which is a larger number for better comparison, rather than RMSD, was used in the model selection in combination with $R^2$. However, for the combined model, RMSD with $R^2$ was used. A lower value of $SSD$ or $RMSD$ and a higher value of $R^2$ will lead to selection of the best-predicting model.

**Results and Discussion**

**Moisture Sorption Kinetics Results**

Table 1 presents the observed final moisture content (FMC) and PEMC values as well as the moisture sorption characteristics in terms of the time required to reach different levels of FMC (25% to 100%). The close agreement of the FMC and PEMC (deviation of -2.7% to 2.1%) demonstrates the good prediction capability of the Peleg model. It should be noted that the sorption data were obtained in about 40 h for all the biomass types and temperatures; however, the FMC might have been achieved well before 30 h because moisture equilibrium was achieved much earlier than the final observation (40 h).

The significance of the initial exposure time in increasing the moisture content of all the studied biomass types is clearly observed (table 1). The first 25% of moisture sorption happened within 35 min (0.2 to 0.6 h), 50% happened within 1.9 h, and 75% happened within 5.9 h, while 100% of moisture sorption happened within 28.9 h. On average, 100% moisture sorption completion took almost 15× the time needed for 50% completion and about twice the time needed for 90% completion. Similarly, 50% moisture sorption completion needed 3.6× the time needed for 25% completion. On average, across the temperatures studied, 41% ±3%, 40% ±5%, and 39% ±1% of sorption completion was
obtained in 1 h and 82% ±2%, 76% ±4%, and 73% ±1% was obtained in 5 h for switchgrass, big bluestem, and bromegrass, respectively.

The quicker moisture sorption during the initial period than during the final phases of moisture sorption can be explained by the temporal variation in the moisture concentration gradient, which is the driving force of the moisture diffusion mechanism. A high moisture concentration gradient in the initial stages promotes faster moisture sorption, and the absorbed moisture in turn reduces the moisture gradient and progressively resists further sorption. Thus, the initial phase of moisture sorption is critical, and about 50% of moisture sorption completion is achieved within 2 h. Similar phenomena of faster hydration and dehydration are commonly observed during the initial stages of soaking and drying, respectively, of several agricultural materials and products. The effect of increased temperature (20°C to 60°C) in reducing the time required for moisture sorption completion can also be observed (table 1). Some discrepancies seen at 60°C for big bluestem and bromegrass were possibly due to the end effect of interpolation. More observations on both sides of the middle data would have easily eliminated this issue.

<table>
<thead>
<tr>
<th>Material</th>
<th>IMC (% d.b.)</th>
<th>T (°C)</th>
<th>Max. SD of MC (% d.b.)</th>
<th>FMC (% d.b.)</th>
<th>PEMC (% d.b.)</th>
<th>25% FMC</th>
<th>50% FMC</th>
<th>75% FMC</th>
<th>90% FMC</th>
<th>100% FMC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Switchgrass</td>
<td>4.07 ±0.12</td>
<td>20</td>
<td>1.38 ±0.08</td>
<td>19.44 ±0.15</td>
<td>19.85 ±0.17</td>
<td>0.5</td>
<td>1.5</td>
<td>4.0</td>
<td>8.5</td>
<td>28.9</td>
</tr>
<tr>
<td>Big bluestem</td>
<td>4.44 ±0.76</td>
<td>20</td>
<td>1.51 ±0.08</td>
<td>21.19 ±0.15</td>
<td>21.47 ±0.17</td>
<td>0.6</td>
<td>1.9</td>
<td>5.9</td>
<td>13.4</td>
<td>28.2</td>
</tr>
<tr>
<td>Bromegrass</td>
<td>4.88 ±0.32</td>
<td>20</td>
<td>2.00 ±0.08</td>
<td>24.82 ±0.15</td>
<td>24.52 ±0.17</td>
<td>0.6</td>
<td>1.7</td>
<td>5.4</td>
<td>12.8</td>
<td>23.7</td>
</tr>
</tbody>
</table>

[a] IMC = initial moisture content, SD = absolute standard deviation, T = temperature of environment, MC = moisture content, FMC = final moisture content, and PEMC = Peleg model predicted equilibrium moisture content (eq. 6).

**Table 1. Moisture sorption characteristics based kinetics observations of selected biomass.**

**Kinetic Moisture Sorption Characteristics of Switchgrass, Big Bluestem, and Bromegrass**

Moisture sorption characteristics, i.e., moisture content versus sorption time, exhibited typical sorption behavior at all temperatures for all three biomass types (fig. 2). All the curves showed a steep increase in moisture sorption during the initial stage (around 1 h), followed by a slower sorption rate in the later stages. Beyond this time period, the sorption curves proceeded almost parallel to the time axis. Even though the moisture sorption experiments were carried out for 40 h, the kinetic results revealed that about 30 h of exposure was sufficient for the conditions employed.

Bromegrass had higher sorption capacity than big bluestem and switchgrass. Moisture sorption increased while temperature increased for all the three feedstocks. At the same temperature, switchgrass had lower moisture sorption than big bluestem, but bromegrass had the highest moisture sorption among the three feedstocks. Bromegrass has a much softer stem with greater surface area to volume ratio and thus absorbed water more rapidly than the thicker-skinned hollow-centered switchgrass and solid-centered big bluestem filled with pith (fig. 3). However, the moisture sorption observed for bromegrass at 20°C was much lower than expected (i.e., a wider gap between 40°C and 20°C),

![Figure 2. Experimental moisture sorption kinetic curves for switchgrass, big bluestem, and bromegrass at different temperatures (plotted data points are averages of three replicates).](image-url)
obtained by plotting the moisture sorption rates (1990; Cunningham et al., 2007; Igathinathane et al., 2009). For various agricultural materials (Sopade and Obekpa, 1990; Cunningham et al., 2007; Igathinathane et al., 2009). All the sorption rate characteristic curves at other temperatures had similar trends as at 20°C for all three biomass types.

A plot of moisture sorption rate versus moisture content provides better insight into the sorption process and reveals the classical moisture sorption zones. Three distinct zones of moisture sorption were apparent (fig. 5). In the initial period, the moisture sorption exhibited a relatively constant high rate (fig. 5, zone I) when the moisture contents of the feedstocks were low. The first zone is very narrow and shows only an indication of the initial constant sorption rates. This was followed by a rapidly falling rate of moisture sorption. Zone II clearly shows this steep falling rate of moisture sorption, which accounts for the majority of moisture uptake. The final stabilization period (zone III) is representative of a much-reduced second falling-rate period. In this zone, moisture sorption occurs at a lower rate, as the material moisture content is relatively high. Such moisture sorption behavior is common in agricultural products (e.g., grains) during soaking processes (Sopade et al., 1992, 1994; Turhan et al., 2002; Pan and Tangratananavee, 2003).

A clearer separation of bromegrass from switchgrass and big bluestem is revealed in the moisture content plot (fig. 5) than in the time plot (fig. 4). When the biomass reached about 15% d.b. moisture, the sorption rate significantly decreased by 91% to 95% from the initial sorption rate. These results and knowledge of the zones of moisture sorption will be useful for preprocessing operations (e.g., feedstock moisture conditioning). To take advantage of the initial increased rate of moisture sorption, tempering, which is commonly used in drying agricultural materials, can be employed for efficient conditioning of the biomass. The tempering period equalizes the moisture gradient and improves the diffusion of moisture on subsequent exposure to a high-humidity environment, thereby reducing the moisture sorption time. High-humidity conditioning of biomass in combination with tempering is a promising area for future research in biomass moisture sorption.

**MOISTURE SORPTION KINETICS MODEL FITTING FOR SWITCHGRASS, BIG BLUESTEM, AND BROMEGRASS**

Overall, the selected models adequately described the observed water sorption characteristics, with $R^2$ values ranging from 0.83 to 0.95 for the exponential model, from 0.99 to 1.0 for the Page model, and from 0.96 to 1.0 for the Peleg model (table 2). The trend of SSD echoed the $R^2$ values, with a lower SSD indicative of higher $R^2$. Since the $R^2$ and SSD values fall in a similar range, the Peleg model seems best suited for predicting biomass sorption characteristics because of the various advantages that it offers, which were discussed earlier (e.g., PEMC determination).

For all three tested biomass types, the exponential model constant ($k_e$) and the Page model constant ($k_w$) were close.

**Figure 3. Cross-sections and longitudinal sections of switchgrass, big bluestem, and bromegrass stems showing their morphological characteristics (ruler graduations = 1/16 in.).**
Both sorption constants ($k_e$ and $k$) increased with increasing temperature from 20°C to 60°C, except for the exponential model of bromegrass. With the exponential model (eq. 1), the shape of the observed sorption kinetics influences the value of $k_e$. It can be shown that a smaller $k_e$ value (e.g., $k_e = 0.1$) represents a gradual increase of moisture sorption with less time for moisture stabilization, while a larger $k_e$ value (e.g., $k_e = 0.4$) represents a steep increase accompanied by an increased moisture stabilization period. Thus, the moisture sorption characteristics of bromegrass at 20°C, showing a steep increase for a shorter time followed by an increased stabilization period, had a higher $k_e$ value (0.429) than the sorption characteristics at increased temperatures, which displayed a gradually increasing trend ($k_e = 0.397$ and 0.421). The difference in the shapes of these characteristic curves was also evident from the increased separation of 20°C from the other temperatures. The similar shapes of the moisture sorption characteristic curves for the other tested feedstocks were the reason for the observed increase of $k_e$ with temperature. However, the Page model parameter $n$ showed an opposite trend of decreasing value with increasing temperature, which is similar to previous results for corn stover (Igathinathane et al., 2009). Overall, bromegrass had the lowest values for sorption constants $k_e$ and $k$ compared with switchgrass and big bluestem (table 2). A lower value means a slower approach to moisture equilibrium, and vice versa. This can be seen in figure 2. At around 10 h, both switchgrass and big bluestem almost approached their equilibrium moisture levels, while bromegrass was still below the final moisture level. However, the placement of the sorption characteristics was predominantly based on the final moisture content achieved (EMC); hence, bromegrass with EMC around 30% d.b. was above big bluestem and switchgrass.
Table 2. Exponential, Page, and Peleg moisture sorption kinetics model fitting and performance parameters for selected biomass.\(^{[a]}\)

<table>
<thead>
<tr>
<th>Model and Material</th>
<th>T (°C)</th>
<th>(k_1) ±SD (h(^{-1}))</th>
<th>(k_2) ±SD</th>
<th>Model Fitting and Performance Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Exponential model</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Switchgrass</td>
<td>20</td>
<td>0.4765 ±0.0416</td>
<td>1910</td>
<td>0.95</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.6243 ±0.0706</td>
<td>2844</td>
<td>0.93</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.6797 ±0.0853</td>
<td>3732</td>
<td>0.92</td>
</tr>
<tr>
<td>Big bluestem</td>
<td>20</td>
<td>0.3804 ±0.0384</td>
<td>5732</td>
<td>0.92</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.5592 ±0.0826</td>
<td>8787</td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.6129 ±0.0811</td>
<td>7405</td>
<td>0.86</td>
</tr>
<tr>
<td>Bromegrass</td>
<td>20</td>
<td>0.4290 ±0.0511</td>
<td>7576</td>
<td>0.91</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>0.3974 ±0.0513</td>
<td>10904</td>
<td>0.87</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>0.4211 ±0.0564</td>
<td>26573</td>
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<tr>
<td>Page model</td>
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<td>Switchgrass</td>
<td>20</td>
<td>0.6050 ±0.0039</td>
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<td>0.7430 ±0.0151</td>
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<td></td>
<td>60</td>
<td>0.7768 ±0.0116</td>
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<tr>
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<td>0.7358 ±0.0162</td>
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<tr>
<td></td>
<td>60</td>
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<td>1924</td>
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<tr>
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<td>60</td>
<td>4.7516 ±0.4195</td>
<td>655</td>
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<td>60</td>
<td>4.3322 ±0.5493</td>
<td>7927</td>
<td>0.96</td>
</tr>
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</table>

\(^{[a]}\) T = temperature of environment; \(k_1\) = exponential model constant (eq. 1); SD = standard deviation; SSD = sum of squared deviation between experimental and predicted data; \(R^2\) = coefficient of determination; \(k_1\) and \(k_2\) = Page model constants (eq. 2); \(k_1\) and \(k_2\) = Peleg model constants (eq. 3) with units of ((mass of dry matter) (mass of moisture)\(^{-1}\)) h (mass of dry matter) (mass of moisture)\(^{-1}\), respectively; \(R_0\) = initial rate of sorption (eq. 5) with units of (mass of moisture) (mass of dry matter)\(^{-1}\) h\(^{-1}\); and \(M_e\) = Peleg model predicted equilibrium moisture content (% d.b., eq. 6).

Constants \(k_1\) and \(k_2\) in the Peleg model for switchgrass, big bluestem, and bromegrass both showed an inverse trend with temperature (table 2). A similar trend was observed for corn stover (Igathinathane et al., 2009), amaranth grain (Resio et al., 2006), and pasta (Cunningham et al., 2007). A reverse trend of these model constants with temperature was also reported for wheat (Maskan, 2002) and chickpea (Turhan et al., 2002). Constant \(k_1\) is related to the mass transfer rate: the lower the value of \(k_1\), the higher the initial sorption rate, indicating the increased sorption rate at increased temperature. Constant \(k_2\) is a capacity factor that is related to the maximum achievable FMC, and hence related to PEMC: the lower the value of \(k_2\), the higher the moisture holding potential, as explained in equation 6, resulting in increased PEMC (Peleg, 1988; Sopade and Obekpa, 1990). This explains why constant \(k_2\) decreased as temperature increased (table 1). Bromegrass had smaller values of constants \(k_1\) and \(k_2\) compared to big bluestem and switchgrass, which indicated that bromegrass had a greater initial moisture content and higher water sorption capacity than big bluestem and switchgrass.

Moisture sorption characteristics predicted by the exponential, Page, and Peleg models for switchgrass, big bluestem, and bromegrass at 20°C with the experimental data are plotted in figure 6 to visualize the model performances. The predicted values from the Page and Peleg models were close to the experimental moisture content values, but the predicted values from the exponential model deviated from the experimental values at about 4 h and beyond. The Peleg model values were the best fit to the experimental values. Similar trends were observed for big bluestem and bromegrass at the other temperatures. Therefore, the Peleg model appeared best suited for moisture sorption prediction for switchgrass, big bluestem, and bromegrass because of its good performance and other capabilities, such as prediction of moisture content without initial moisture content, and determination of initial rate of sorption and PEMC.

**Temperature Dependence of Moisture Sorption Kinetics Model Constants**

Following the Arrhenius equation (eq. 7), the temperature dependence of the sorption kinetics model constants was evaluated, and the determined frequency factor (\(A\)) and activation energy (\(E\)) values for the exponential, Page, and Peleg models were obtained (table 3). Overall, the activation energy values for bromegrass were the lowest, followed by switchgrass and big bluestem. This trend indicates that the model parameters for bromegrass tended to be the most temperature sensitive compared to switchgrass and big bluestem. This finding suggests that increasing the temperature of the sorption process would affect the sorption behavior of bromegrass more than switchgrass and big bluestem.
Workable equations for predicting moisture sorption characteristics (using the models considered) at any intermediate temperature in the range of 20°C ≤ T ≤ 60°C can be reconstructed using the Arrhenius model constants (table 3). Therefore, it is possible to develop prediction nomograms of moisture sorption characteristics using these prediction equations. Moisture sorption prediction nomograms for switchgrass, big bluestem, and brome-grass at five temperatures including two intermediate temperatures (30°C and 50°C) were developed (fig. 7) based on estimates from the Peleg model (table 3).

It should be observed that the prediction characteristics are smoother than the experimental data (fig. 2) because the prediction characteristics are the result of mathematical sorption kinetics models. The spread or separation of the sorption characteristic curves was more pronounced for bromegrass, followed by big bluestem, while switchgrass had the least separation with respect to sorption temperature. This spread indicates the effect of temperature on the sorption process; bromegrass was highly influenced by temperature, while switchgrass was the least influenced.

These nomograms provide an easy-to-use tool for visualizing sorption characteristics as well as providing quick evaluation of biomass moisture content at a given time, or vice versa, during the sorption process. For intermediate temperatures that were not plotted, it would be possible to estimate the sorption characteristics by observing the trend while knowing the limits of the bordering characteristics. These nomograms were derived to present the maximum limit with a constant 95% RH; thus, for <95% RH, the moisture levels will be lower than these limits. Developing nomograms for such reduced RH values needs further research, but the procedure outlined can be readily applied. Further research is also required to determine moisture sorption at lower temperatures (e.g., freezing) to meet Midwestern environmental demands.

**PREDICTION NOMOGRAMS FOR KINETIC MOISTURE SORPTION CHARACTERISTICS**

Workable equations for predicting moisture sorption characteristics (using the models considered) at any intermediate temperature in the range of 20°C ≤ T ≤ 60°C can be reconstructed using the Arrhenius model constants (table 3). Therefore, it is possible to develop prediction nomograms of moisture sorption characteristics using these prediction equations. Moisture sorption prediction nomograms for switchgrass, big bluestem, and bromegrass at five temperatures including two intermediate temperatures (30°C and 50°C) were developed (fig. 7) based on estimates from the Peleg model (table 3).

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**COMBINED PREDICTION EQUATIONS FOR KINETIC MOISTURE SORPTION CHARACTERISTICS**

It would be convenient to have a single combined moisture sorption prediction equation that can evaluate the sorption characteristics from the basic input variables of time and temperature. Using the Peleg model (eq. 3) with model
Figure 7. Moisture sorption kinetics prediction nomograms for selected biomass types at various studied and interpolated temperatures.

Switchgrass

Big Bluestem

Bromegrass

Relative humidity of air = 95% (constant)
constants $k_1$ and $k_2$ expressed in terms of frequency factor of initial sorption rate ($A$) and activation energy ($E$) of the Arrhenius equation for the selected biomass (Table 3), the following combined equations were derived for the selected biomass types for temperatures ranging from 20°C to 60°C at constant 95% RH:

$$M_{\text{Switchgrass}} = \frac{1}{t \times e^T} \left[ \frac{1}{200.21} - 1.34254 \right] + \frac{1}{t \times e^T} \left[ \frac{1}{162.33} - 0.1417 \right]$$

$$M_{\text{Bigbluestem}} = \frac{1}{t \times e^T} \left[ \frac{1}{356.92} - 1.203427 \right] + \frac{1}{t \times e^T} \left[ \frac{1}{1677.35} - 0.0254 \right]$$

$$M_{\text{Bromegrass}} = \frac{1}{t \times e^T} \left[ \frac{1}{661.25} - 1.47152 \right] + \frac{1}{t \times e^T} \left[ \frac{1}{820.80} - 0.3693 \right]$$

where

- $M_{\text{Switchgrass}}, M_{\text{Bigbluestem}}, M_{\text{Bromegrass}} =$ instantaneous moisture content of switchgrass, big bluestem, and bromegrass (decimal d.b.), respectively
- $t =$ time of sorption (h)
- $T =$ absolute temperature of the environment (K)
- $R^2 =$ coefficient of determination of the combined prediction model
- RMSD = root mean squared deviation between observed and combined prediction model data
- $N =$ number of observations.

These combined prediction equations (eqs. 11 through 13) have the advantage of accurately predicting the sorption moisture contents at any intermediate temperature (20°C ≤ $T$ ≤ 60°C) compared to that obtained from the nomograms (Fig. 7). The performance of the combined equations was good, with $R^2$ ≥ 0.83. These equations generate nomograms at any desired temperature. These equations can be readily added to various modeling systems that require prediction of moisture sorption for biomass subjected to a storage environment. Similar combined equations can be developed for other temperature and relative humidity values, as well as for other biomass types, following the procedure outlined in this research.

**CONCLUSIONS**

Based on this moisture sorption kinetics study with harvested intact biomass, bromegrass had the highest moisture sorption rate, the highest final moisture content, and required a longer time to reach equilibrium than big bluestem, followed by switchgrass. The cellulose and lignin contents, obtained from the literature, corroborate this order of the moisture sorption characteristics of the biomass types, with higher cellulose and lower lignin contents representing the quickest sorption rates and greatest final moisture contents. On average, at 20°C and 95% RH, 50% of moisture sorption completion occurred at 1.5, 1.9, and 1.7 h and 90% completion occurred at about 8.5, 13.4, and 12.8 h for switchgrass, big bluestem, and bromegrass, respectively. For all the temperatures studied, on average, 41% ±3%, 40% ±5%, and 39% ±1% of sorption completion occurred in 1 h and 82% ±2%, 76% ±4%, and 73% ±1% occurred in 5 h for switchgrass, big bluestem, and bromegrass, respectively. During the first hour at 20°C, moisture sorption rates fell sharply from their highest initial levels by about 79.0%, 78%, and 88% for switchgrass, big bluestem, and bromegrass, respectively, and quickly become approximately asymptotic to the time axis. The initial time of exposure resulted in substantial moisture uptake, and the moisture sorption rate increased with increasing temperature.

Both the Page and Peleg models effectively described ($R^2 > 0.95$) the observed sorption characteristics of the biomass types tested. The exponential model was less efficient, with $R^2$ values ranging from 0.82 to 0.95. The Peleg model in combination with the Arrhenius equation is recommended for moisture sorption prediction at any intermediate temperature between 20°C to 60°C for the selected biomass types. A combination of these equations could also be expected to perform adequately for other biomass feedstocks and other environmental variables of practical importance. Fitted moisture sorption kinetics models, developed nomograms, and combined prediction equations, as well as the results from this study, form baseline data essential for the selected biomass storage life; the quality of biomass during storage, transportation, and logistics; and the design and efficient operation of processing, handling, and storage systems.

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**REFERENCES**


