VAPOR DIFFUSIVITY AND HYGROSCOPIC EXPANSION OF CORN KERNELS DURING ADSORPTION

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ABSTRACT
Moisture adsorption tests were conducted using two varieties of corn, locally grown K6400 and Dekalb 547, under the humid air conditions of 75, 85, and 95% relative humidity each at different temperatures of 25, 30, 35, and 40°C. Vapor diffusivity values were estimated based on the Fick's law of diffusion assuming three kernel geometries, namely, infinite slab, infinite cylinder, and sphere. From the analyses, it was found that the infinite-slab model gave the best fit for predicting the adsorption behavior of the corn kernel. Vapor diffusivity of the kernel increased with increase in the absolute temperature of the humid air and followed an Arrhenius-type relationship. However, vapor diffusivity decreased with increase in the relative humidity. The ranges of diffusivity values obtained were from $0.803 \times 10^{-6}$ to $4.318 \times 10^{-7}$ m$^2$/h for the K6400 variety and from $0.819 \times 10^{-7}$ to $4.087 \times 10^{-7}$ m$^2$/h for the Dekalb 547 variety. Hygroscopic cubical and linear expansions of corn were found to vary linearly with the moisture content in the range of 13 to 24%. Expansion in kernel thickness was the greatest followed by expansion in width and length. Greater hygroscopic expansion and higher vapor diffusivity were observed in the denser variety of corn.

INTRODUCTION
Development of fissures in corn kernels are caused by both external and internal stresses. Fissured or stress-cracked kernels are objectionable because they are quite susceptible to breakage during handling and cause problems in storage, shipping, and processing (Gunasekaran and Paulsen, 1985). Moisture and temperature gradients prevalent within the grain cause undue expansion and contraction in the grain leading to the development of internal stresses (Gunasekaran et al., 1985). In general, moisture gradients have a predominant effect on the expansion and shrinkage of grains while the effect of temperature gradients is negligible (Suuresh et al., 1975; Muthukumarappan, 1988). If the stresses developed within the kernels can be calculated accurately, better processes can be designed to reduce fissure development. However, such an estimation requires basic properties like vapor diffusivity, and coefficients of linear and cubical hygroscopic expansion of corn kernels and knowledge of how these properties interact.

Extensive research work has been done on drying of different grains with the primary focus on modeling diffusion of moisture (Steffe and Singh, 1980 a,b; Misra and Young, 1980; Suarez et al., 1981). Whitaker and Young (1972) modeled the drying behavior of peanuts and found that the cylindrical model predicted the experimental drying rate with the greatest accuracy. Misra and Young (1980) proposed a numerical solution of simultaneous moisture diffusion and shrinkage during soybean drying using the finite element technique. Walton et al. (1988) developed a diffusion-based drying model for corn in which the endosperm and germ are modeled as a sphere with the resistance of the pericarp being part of the external resistance. However, only limited information is available on diffusion of moisture during adsorption.

Steffe and Singh (1980 a,b) determined the diffusion coefficients of several rice samples during both desorption and absorption. In general, diffusion coefficients for grains depend on other physical properties and are different for different components of the grain, namely, germ, endosperm, and pericarp. Hendrickx and Tobbaken (1987) working with rice found that the diffusion coefficient of the endosperm is higher than that of the bran and that parboiled rice has a diffusivity lower than non-parboiled rice. Syarief et al. (1987) reported different diffusion coefficient data for corn kernel components during drying. From experimental investigation they concluded that the diffusion coefficient of the germ is the largest, followed by those of the floury and the horny endosperms, and then by the pericarp. Diffusion of moisture is generally enhanced by the temperature of fluid medium and has an exponential relationship with the inverse of the fluid temperature (Steffe and Singh, 1980b; Walton et al., 1988).

The objectives of this investigation were to:
- Determine vapor diffusivity of corn kernels during adsorption,
- Determine effect of temperature and relative humidity of the environment, and density of corn kernels on vapor diffusivity, and
- Determine coefficients of cubical and linear hygroscopic expansion of corn kernels when subjected to rewetting.

THEORETICAL CONSIDERATIONS
A typical corn kernel is irregular in shape. Therefore, three different geometries, namely, infinite slab, infinite cylinder, and sphere were considered. The corresponding
solutions of Fick’s law of diffusion were used (Crank, 1975):

**Infinite Slab**

\[
\frac{M - M_i}{M_i - M_e} = 1 - \left(\frac{8}{\pi^2}\right) \sum_{n=0}^{\infty} \left[\left(\frac{1}{(2n+1)^2}\right) \exp\left(-\frac{(2n+1)^2 D \pi^2 t}{(4R^2)}\right)\right]
\]  

**Infinite Cylinder**

\[
\frac{M - M_i}{M_i - M_e} = 1 - \sum_{n=1}^{\infty} \left(\frac{4}{X_n^2}\right) \exp\left(-\frac{X_n^2 D \pi^2 t}{R^2}\right)
\]

**Sphere**

\[
\frac{M - M_i}{M_i - M_e} = 1 - \left(\frac{6}{\pi^2}\sum_{n=1}^{\infty} \left(\frac{1}{n^2}\right) \exp\left(-\frac{n^2 D \pi^2 t}{R^2}\right)\right)
\]

where

\[M = \text{average moisture content of the kernel at time } t(\%), \]
\[M_i = \text{average initial moisture content of the kernel (}), \]
\[M_e = \text{equilibrium moisture content of the kernel (%),} \]
\[D = \text{vapor diffusivity (m^2/h),} \]
\[t = \text{exposure time (h),} \]
\[X_n = \text{roots of the Bessel's function,} \]
\[R = \text{characteristic dimension (half-thickness for slab, radius for cylinder and sphere; m),} \]

with the following assumptions:

1. The kernel moisture content is uniform throughout its cross-section.
2. At time \( t = 0 \) the surface moisture is in equilibrium with the environment.
3. For time \( t > 0 \) the environment is maintained constantly at specified conditions.
4. The corn kernel composition is homogeneous with respect to diffusivity.
5. The kernel moisture approached equilibrium with the environment at the end of the experiment.

Coefficient of cubical expansion (\( \alpha \)) is defined as the increase in the kernel volume (\( \Delta V \)) due to increase in moisture content (\( \Delta m \)) with respect to the original volume (\( V \)). That is:

\[
\alpha = \frac{1}{V} \frac{\Delta V}{\Delta m}
\]

Coefficient of linear expansion (\( \beta \)) is defined as the increase in the characteristic dimension, length, width or thickness (\( \Delta x \)) due to increase in moisture content (\( \Delta m \)) with respect to the original dimension (\( x \)). That is:

\[
\beta = \frac{1}{x} \frac{\Delta x}{\Delta m}
\]

**MATERIALS AND METHODS**

**SAMPLE PREPARATION**

Two varieties of corn, locally grown K6400 and Dekalb 547, were used in this study. These corn varieties were grown on the Arlington Research Farm at the University of Wisconsin-Madison and combine-harvested at about 27% moisture content during Fall, 1989. The corn was dried in a laboratory dryer using the room air at a temperature of 22°C and a relative humidity (RH) of 55%. A constant airflow rate of about 2.05 m^3/min/m^2 was used. The grain bed was stirred periodically to obtain a uniform drying until the samples attained a moisture content of about 13%. The dried samples were hand-cleaned to remove the broken kernels and about 15 kg of each variety of corn was obtained. The initial moisture content of the samples were determined by the oven method (ASAE, 1988a) to be 13.4% and 13.1% for K6400 and Dekalb 547 corn, respectively. The samples were placed in sealed Ziploc bags and stored in a refrigerator maintained at 5°C and 58% RH until the experiments.

**ADSORPTION TESTS**

The adsorption tests were conducted in a controlled environment chamber (2.21 x 0.74 x 1.95m) available in the Biotron at University of Wisconsin-Madison. Four air temperatures of 25, 30, 35, and 40°C with each at three RH values of 75, 85, and 95% were selected. Temperature and RH of the air in the chamber were maintained within 0.1°C and 1.0%, respectively. Air was circulated constantly at 30 m/min during the tests. The air temperature and RH were monitored periodically using a Weston (Model TH65) thermocouple/thermometer coupled with thermocouple psychrometer. Air velocity was measured using a Hastings (Model G-11) hot-wire anemometer.

Before the start of each adsorption test, the sealed sample bags were removed from the refrigerated storage and left to equilibrate to room temperature. Any stress-cracked kernels present in the samples were removed by visual examination. Three 50-g samples of each variety were taken in perforated wire-meshed containers giving a sample depth of about 10 mm. Then the individual containers were placed over a wire-meshed platform in the controlled environment chamber facilitating air movement on all sides of the sample. For each temperature and relative humidity combination, the chamber was allowed to attain a steady-state condition before introducing the samples. The samples were removed periodically from the chamber and weighed for moisture gain determination. The tests were conducted for 48 hours during which the sample moisture content reached near-equilibrium with the chamber.

Different Fick’s law of diffusion models considering the geometry of corn as an infinite slab, an infinite cylinder, and a sphere were used for diffusivity determination. The first eight terms of all the models were considered using the non-linear, least square multivariate secant method (SAS, 1987). This was accomplished by minimizing the sum of square values. The characteristic dimensions of the kernels were determined at the initial moisture content.

*All moisture contents reported are on wet basis.*
(Table 1). The thickness and length of 100 kernels were measured using a micrometer. The average half-thickness value was used for the infinite slab model. For the infinite cylinder and sphere models, the equivalent radius of cylinder and of sphere were used. These values were computed from the average volume of 330 kernels along with the measured values of average length and thickness. The kernel volume was measured using an automated gas pycnometer (Model PYC G100A, Porous Materials, Inc.). True density of the samples were computed by determining their mass after volume measurement.

**Hygroscopic Expansion Tests**

**Volumetric Expansion.** A different set of three, 100-g samples (free from stress cracks) of each variety was used for the volumetric expansion tests. The initial volume of each sample was measured with the automated gas pycnometer mentioned above. Following this, the samples were placed in the controlled environment chamber maintained at different temperature-RH conditions used for the adsorption tests. The samples were periodically removed for volume and mass measurement. Each time the samples were removed from the chamber, they were placed in sealed Ziploc bags and left for six hours to equilibrate to room temperature before making volume and mass measurements. After each volumetric expansion measurements, the samples were discarded and a new sample was used for each subsequent test. The experiments were continued varying the time of exposure in the chamber to obtain different moisture content levels in the range of 13 to 24%.

**Linear Expansion.** The linear expansion tests were conducted at only one temperature-humidity condition (40°C and 95% RH) with a 25-g sample from each variety. From each sample, 25 kernels were randomly selected and identified by marking a number on each kernel with a felt-tip pen. Characteristic dimensions, namely length, width and thickness, were measured using a micrometer and the kernels were placed in the chamber using the perforated containers. Following the procedure used with volume measurements explained above, the linear dimensions of the marked kernels were periodically measured over a range of moisture contents.

**Results and Discussion**

**Vapor Diffusivity**

The moisture contents of the samples at the end of 48 hours of exposure to humid air conditions are presented in Table 2 along with equilibrium moisture contents predicted using modified-Henderson and Chung equations (ASAE, 1988b). There is a close agreement between the experimental and the predicted values. Since the samples attained the near-equilibrium moisture contents, moisture ratio (moisture absorbed at a given time/maximum moisture absorbed for the total time) was plotted against time of exposure for each sample as shown in figure 1. Samples exposed to higher humidity environment took a longer time to reach near-equilibrium moisture irrespective of air temperature. The increase in equilibration period indicates that the vapor diffusivity decreases (or stays constant) as the samples gain moisture throughout the adsorption phase. This phenomenon is different from that during desorption (drying) in which for some grains vapor diffusivity increases (or stays constant) with an increase in initial moisture content (Syarief et al., 1987).

The vapor diffusivity values, along with the R² values (coefficient of determination), for the different geometries at different humid air conditions are presented in Tables 3 and 4. Based on the R² values among the three models, the infinite slab geometry gave the best fit for the whole range of experimental data. In general, the vapor diffusivity decreased with increasing RH. This is due to longer exposure time needed to reach the equilibrium. On the other hand, high air temperatures enhanced diffusion resulting in high vapor diffusivities.

The vapor diffusivity values obtained from this experimental investigation compared well with other reported values for corn during drying. For example, within the 13 to 24% moisture content range, reported diffusivity values of whole kernels of corn varied from $1.529 \times 10^{-7}$ to $6.318 \times 10^{-7}$ $m^2/h$ (Chu and Hustrulid, 1968) and that of floury endosperm varied from $2.298 \times 10^{-7}$ to $9.621 \times 10^{-7}$ $m^2/h$ (Syarief et al., 1987).

Prediction of vapor diffusivity values based on absolute temperature at different RH conditions is shown in Table 5. The vapor diffusivity values followed an Arrhenius-type relationship with absolute temperature at all RH conditions.

**Table 1. Characteristic dimensions used for different corn kernel geometries in the Fick’s diffusion model**

<table>
<thead>
<tr>
<th>Kernel geometry</th>
<th>Characteristic dimension</th>
<th>Value (m)</th>
<th>K6400</th>
<th>Dekalb 547</th>
</tr>
</thead>
<tbody>
<tr>
<td>Infinite slab</td>
<td>Half-thickness</td>
<td>0.00203</td>
<td>0.00221</td>
<td></td>
</tr>
<tr>
<td>Infinite cylinder</td>
<td>Equivalent radius</td>
<td>0.00257</td>
<td>0.00258</td>
<td></td>
</tr>
<tr>
<td>Sphere</td>
<td>Equivalent radius</td>
<td>0.00388</td>
<td>0.00392</td>
<td></td>
</tr>
</tbody>
</table>

**Table 2. Equilibrium moisture contents of K6400 and Dekalb 547 variety corn samples after 48 hours of exposure to different humid environments**

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Relative humidity (%)</th>
<th>Experimental K6400</th>
<th>Experimental Dekalb 547</th>
<th>Theoretical Chung</th>
<th>Theoretical M-H*</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>75</td>
<td>15.40</td>
<td>15.66</td>
<td>14.94</td>
<td>15.12</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>17.96</td>
<td>18.15</td>
<td>17.31</td>
<td>17.41</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>20.42</td>
<td>20.58</td>
<td>21.71</td>
<td>21.22</td>
</tr>
<tr>
<td>30</td>
<td>75</td>
<td>15.41</td>
<td>16.10</td>
<td>14.57</td>
<td>14.68</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>17.46</td>
<td>18.74</td>
<td>16.96</td>
<td>16.97</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>20.60</td>
<td>21.05</td>
<td>21.40</td>
<td>20.65</td>
</tr>
<tr>
<td>35</td>
<td>75</td>
<td>15.35</td>
<td>15.46</td>
<td>14.22</td>
<td>14.27</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>17.12</td>
<td>17.56</td>
<td>16.63</td>
<td>16.46</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>21.36</td>
<td>21.88</td>
<td>21.10</td>
<td>20.11</td>
</tr>
<tr>
<td>40</td>
<td>75</td>
<td>15.27</td>
<td>15.48</td>
<td>13.90</td>
<td>13.90</td>
</tr>
<tr>
<td></td>
<td>85</td>
<td>17.07</td>
<td>17.46</td>
<td>16.33</td>
<td>16.04</td>
</tr>
<tr>
<td></td>
<td>95</td>
<td>22.78</td>
<td>23.15</td>
<td>20.84</td>
<td>19.63</td>
</tr>
</tbody>
</table>

* Based on the Chung equation (ASAE, 1988b).
† Based on the Modified-Henderson equation (ASAE, 1988b).
HYGROSCOPIC EXPANSION

Figure 2 shows the fairly linear relationship between the kernel volume and the moisture content for both the varieties. The temperature and relative humidity of the atmosphere did not have any significant effect on the volumetric expansion. Using the correlations developed between the kernel volume and moisture content, the coefficient of cubical expansion was found to be 0.0197 m³/m³/%m.c. and 0.0187 m³/m³/%m.c. for K6400 and Dekalb 547 corn, respectively.

Average characteristic dimensions of the kernels linearly increased with moisture content for both the varieties. Coefficients of linear hygroscopic expansion values are tabulated in Table 6. Based on these values, the expansion in kernel thickness was the greatest followed by those in width and length for both varieties.

The true density of the corn kernels (ρ, kg/m³) of both varieties was found to decrease linearly with the moisture content (M, %) as shown below.

For K6400 corn, ρ = 1258.8 − 3.0654 M
For Dekalb 547 corn, ρ = 1223.8 − 2.3015 M

CONCLUSIONS
1. An infinite slab model best predicted the adsorption behavior of corn kernels.
2. Vapor diffusivity decreased with relative humidity and varied from 0.803 x 10⁻⁶ to 4.318 x 10⁻⁶ m²/² h for K6400 variety and from 0.819 x 10⁻⁶ to 4.087 x 10⁻⁶ m²/² h for Dekalb 547 variety when vapor temperature varied from 25 to 40°C.
3. The increase in vapor diffusivity with absolute temperature followed an Arrhenius-type relationship.
4. The coefficient of cubical expansion for the K6400 variety was 0.0197 m³/m³/%m.c. and that of Dekalb 547 variety was 0.0187 m³/m³/%m.c.

TABLE 6. Arrhenius-type model for temperature dependency of vapor diffusivity

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>RH (%)</th>
<th>Model*</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>75</td>
<td>1.212 (0.992)</td>
<td>1.099 (0.985)</td>
<td>1.286 (0.982)</td>
</tr>
<tr>
<td>25</td>
<td>1.119 (0.961)</td>
<td>0.544 (0.938)</td>
<td>0.649 (0.931)</td>
</tr>
<tr>
<td>95</td>
<td>0.803 (0.985)</td>
<td>0.391 (0.969)</td>
<td>0.465 (0.968)</td>
</tr>
<tr>
<td>75</td>
<td>2.525 (0.996)</td>
<td>1.214 (0.988)</td>
<td>1.309 (0.988)</td>
</tr>
<tr>
<td>25</td>
<td>1.629 (0.989)</td>
<td>0.823 (0.976)</td>
<td>0.991 (0.975)</td>
</tr>
<tr>
<td>95</td>
<td>1.091 (0.996)</td>
<td>0.545 (0.988)</td>
<td>0.655 (0.988)</td>
</tr>
<tr>
<td>75</td>
<td>3.042 (0.998)</td>
<td>1.492 (0.995)</td>
<td>1.784 (0.995)</td>
</tr>
<tr>
<td>35</td>
<td>1.823 (0.982)</td>
<td>0.916 (0.980)</td>
<td>1.039 (0.979)</td>
</tr>
<tr>
<td>95</td>
<td>1.360 (0.995)</td>
<td>0.633 (0.985)</td>
<td>0.749 (0.985)</td>
</tr>
<tr>
<td>75</td>
<td>4.318 (0.999)</td>
<td>2.199 (0.996)</td>
<td>2.562 (0.997)</td>
</tr>
<tr>
<td>40</td>
<td>2.620 (0.998)</td>
<td>1.037 (0.993)</td>
<td>1.251 (0.993)</td>
</tr>
<tr>
<td>95</td>
<td>1.524 (0.989)</td>
<td>0.721 (0.975)</td>
<td>0.451 (0.974)</td>
</tr>
</tbody>
</table>

* R² values are given in parentheses.
5. The coefficient of linear expansion in length, width and thickness varied from 0.006 05 to 0.009 39 m/m/% m.c. for the K6400 variety and from 0.005 44 to 0.008 34 m/m/% m.c. for Dekalb 547 variety. The expansion in the thickness was the largest followed by those in width and length.

6. Of the two varieties studied, the denser variety exhibited higher coefficient of expansion (cubical and linear) and higher vapor diffusivity.

REFERENCES


Suresh, P., J.D. Mannapperuma and F.T. Wratten. 1975. Thermal and hygroscopic expansion of brown rice. Presented at the ASAE Southwest Regional Meeting, Stillwater, OK.

