Sorption Kinetics of Water Vapor by Yellow Dent Corn. II. Analysis of Kinetic Data for Damaged Corn[1]

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ABSTRACT

Sorption of water vapor by sound and by damaged (broken or heat-damaged) yellow dent corn differed appreciably in rates and equilibrium moisture contents under conditions tested. Initially sorption rates decreased, in order, in broken, heat-damaged, and sound corn; then rates for heat-damaged and sound corn reversed after a certain sorption time. Equilibrium moisture contents decreased in this order: broken, sound, and heat-damaged. Sorption of water vapor on corn seemed to be controlled by a surface-adsorption mechanism early, then by a diffusion-controlling mechanism. A model describing the simultaneous adsorption and diffusion process was used to describe the entire range of the kinetic process. Parameters involved in the simultaneous adsorption-diffusion model may be used to estimate general physical quality of grain, and as a guide for grain conditioning, storage, and drying.

The importance of the sorption phenomenon while grain is conditioned, stored, and processed, has prompted numerous studies of the sorption process of water vapor by cereal grains. Among various factors that influence sorption rate, temperature and relative humidity (r.h.) are paramount (1). Another significant factor often neglected is the condition of grain. Because the sorption process is a surface phenomenon, any physical or chemical changes in surface characteristics of the grain should influence both sorption rate and hygroscopic properties. However, the sorption kinetics of water vapor by grains up to equilibrium have not been well investigated.

Therefore, the objectives of this investigation were: a) to study sorption kinetics of water vapor by sound and by damaged corn under several environmental conditions until equilibrium was reached; b) to examine the possibility of detecting corn damage by sorption rate and equilibrium moisture content; and c) to develop a mathematical model to describe sorption kinetics of water by corn up to equilibrium.

MATERIALS AND METHODS

Yellow dent corn harvested in 1969 was used. Heat-damaged samples were prepared by heating high-moisture corn (24%) in an air-oven at 125°C. for 4 hr. Broken samples were broken pieces of corn passing through a 12/64-in. round sieve but remaining on a 8/64-in. round sieve.

Samples containing various percentages of damaged corn (by weight) were

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prepared by blending known quantities of damaged kernels with sound kernels. Sound and damaged yellow corn with about 12% initial moisture content were studied under conditions shown in Table I.

A sample (20 g.) was placed in a single layer on a pan made of 200-mesh brass-wire screen. The pan was suspended from the sample loop of the CAHN Electrobalance inside the test chamber (Aminco 3-B climate-lab), where environmental conditions were controlled. A sample's weight change was traced on the strip-chart recorder until equilibrium was reached. The initial temperature of the sample was controlled to the same dry-bulb temperature of the test condition. Details on experimental setup and equipment are given in a previous paper (1).

RESULTS AND DISCUSSION

Sorption Kinetics and Equilibrium Moisture Contents

Sorption data for 100% sound, broken, and heat-damaged corn samples at 80°F.-30% r.h.; 80°F.-60% r.h.; 80°F.-70% r.h.; 80°F.-80% r.h.; and 60°F.-80% r.h. are shown in Figs. 1 through 5. Figure 1 shows a decrease in moisture (desorption) caused by vapor pressure of water in the sample being higher than that of water vapor at 80°F.-30% r.h. Sorption data for sound and various levels of broken and heat-damaged corn at 70°F.-80% r.h. are shown in Figs. 6 and 7, respectively.

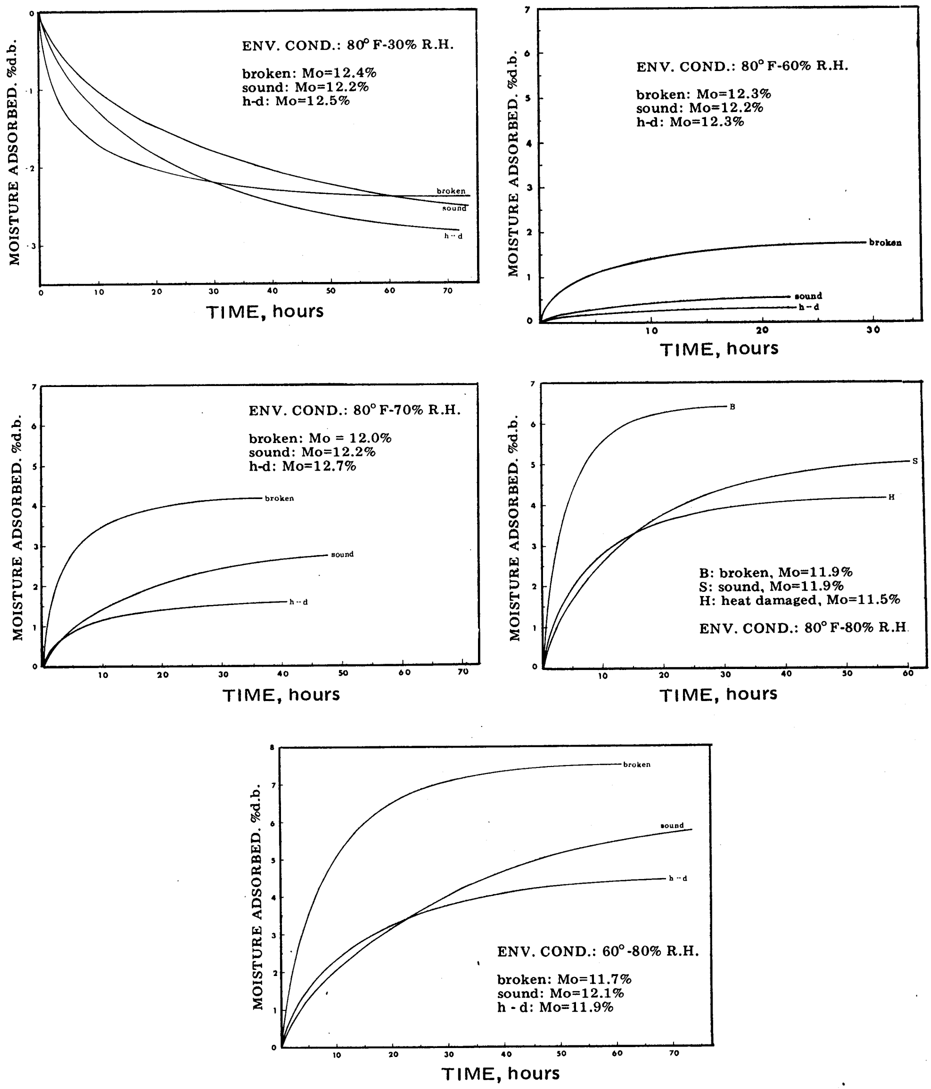
Both equilibrium moisture and sorption rates differed distinctively between sound and damaged samples. In general, damaged corn had higher sorption rates and reached equilibrium sooner than did sound samples. Equilibrium moisture contents, from high to low, were in broken, sound, and heat-damaged corn, in that order. Equilibrium moisture contents of samples blended with sound and broken or heat-damaged corn were between those of all sound or all broken or heat-damaged (Figs. 6 and 7). The rate approaching equilibrium was accelerated by increasing temperature, but equilibrium moisture content decreased as temperature increased.

Differences in rate and equilibrium moisture content among sound, broken, and heat-damaged corn samples were attributed to differences in surface characteristics of kernels. Broken kernels should have higher specific conductance than sound corn because the endosperm is exposed. Consequently, the resistance to moisture movement is considerably reduced. Also, more adsorption sites are readily available in broken kernels than in sound kernels. Artificial drying at high temperature often induces stress cracks and molecular shrinkage (2,3). Kernels with stress cracks are less resistant to moisture movement than are kernels without stress cracks. Fewer

TABLE I. ENVIRONMENTAL CONDITIONS TESTED

Type of Sample	Environmental Condition
100% Sound 100% Broken 100% Heat-damaged	80° F.-80% r.h.[a] 80° F.-70% r.h. 80° F.-60% r.h. 80° F.-30% r.h. 80° F.-80% r.h. 70° F.-80% r.h.
10, 30, and 50% Heat-damaged	70° F.-80% r.h.
10, 30, and 50% Broken	70° F.-80% r.h.

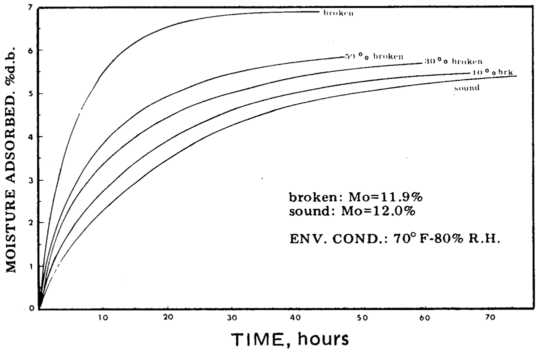
[a]r.h. = relative humidity of air.



Figs. 1–5. Sorption of water vapor by sound, by broken, and by heat-damaged (h-d) corn at: 80° F.-30% r.h. (top left); 80° F.-60% r.h. (top right); 80° F.-70% r.h. (middle left); 80° F.-80% r.h. (middle right); and 60° F.-80% r.h. (bottom).

sorption sites are available in heat-damaged kernels than in sound kernels, due to molecular shrinkage. Therefore, equilibrium was reached sooner, but with lower moisture content, by heat-damaged corn than by sound corn.

The foregoing results indicate that grain damage might be detected by differences in the rate of sorption or in equilibrium moisture; however, time required for such evaluations and difficulties in preparing a sample make the method impractical for grain grading.



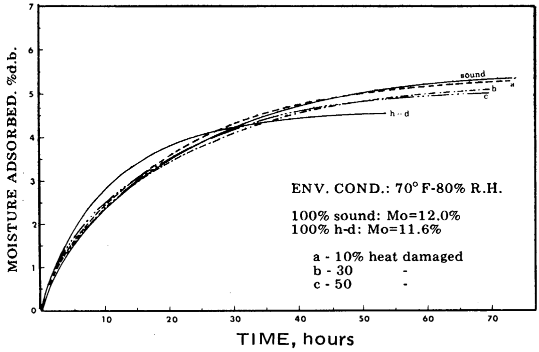


Fig. 6 (top). Sorption of water vapor by sound and by various levels of broken corn at 70° F.-80% r.h.

Fig. 7 (bottom). Sorption of water vapor by sound and by various levels of heat-damaged (h-d) corn at 70° F.-80% r.h.

Analyzing Kinetic Data

Attempts were made to correlate the kinetic data with the Elovich adsorption equation, as in a previous paper (1), and with the mass-transfer equation. Neither the Elovich equation nor the mass-transfer equation fitted the data for the entire kinetic process up to equilibrium. Kinetic data for the early stage of the kinetic process fit the Elovich equation. The diffusion model, which assumes a corn kernel as a sphere with uniform initial concentration and constant surface concentration, did not fit the range of data. In contrast to the adsorption model, the diffusion model fit the data for a later stage of the kinetic process. The analyses indicate that sorption of water vapor on corn is controlled by surface sorption mechanisms during early stages and then by a diffusion-controlling mechanism in later stages.

We assumed the sorption process of water vapor on corn to be a simultaneous diffusion and sorption process. With that assumption, we applied the following model, which described simultaneous diffusion and first-order rate processes in a porous sphere:

$$\frac{\partial M}{\partial t} = D\left(\frac{\partial^2 M}{\partial r^2} + \frac{2}{r}\frac{\partial M}{\partial r}\right) + K(M_e - M) \quad (1)$$

where M is moisture content, r is the distance from the center of the sphere, t is time, D is the diffusion coefficient, K is the rate constant, and M_e is equilibrium moisture content. The first term of the right side of equation 1 describes the diffusion process; the second term, the sorption as the first-order rate process.

Appropriate initial and boundary conditions describing the system are:

$$M = M_o \qquad \text{at } t = 0 \tag{2}$$

$$M = M_e \qquad \text{at } r = R, t > 0 \tag{3}$$

$$\frac{\partial M}{\partial r} = 0 \qquad \text{at } r = 0 \tag{4}$$

A solution of equation 1 which satisfies equations 2, 3, and 4 is:

$$M = M_e + (M_1 - M_o)\, e^{-kt} - (M_e - M_o)\, e^{-kt} \tag{5}$$

where M_1 is the solution of the equation for diffusion in the absence of sorption, that is:

$$\frac{\partial M_1}{\partial t} = D\left(\frac{\partial^2 M_1}{\partial r^2} + \frac{2}{r}\frac{\partial M_1}{\partial r}\right) \tag{6}$$

with the same initial and boundary conditions.

The solution of equation 6 with initial and boundary conditions given is:

$$\frac{M_1 - M_o}{M_e - M_o} = 1 + \frac{2R}{\pi r} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \, \mathrm{SIN}\frac{n\pi r}{R}\, e^{-\bar{D}n^2 t} \tag{7}$$

where

$$\bar{D} = \frac{D\pi^2}{R^2} \tag{8}$$

Substituting equation 7 into equation 5 yields:

$$\frac{M - M_o}{M_e - M_o} = 1 + \frac{2R}{\pi r} e^{-kt} \sum_{n=1}^{\infty} \frac{(-1)^n}{n} \, \mathrm{SIN}\frac{n\pi r}{R}\, e^{-\bar{D}n^2 t} \tag{9}$$

The average moisture content obtained by integrating equation 9 over an entire sphere is:

$$\frac{\bar{M} - M_o}{M_e - M_o} = 1 - \frac{6}{\pi^2} e^{-kt} \sum_{n=1}^{\infty} \frac{1}{n^2} e^{-\bar{D}n^2 t} \tag{10}$$

The kinetic data were analyzed by equation 10, using an IBM 360 digital computer. Two parameters, K and $\bar{D}$ in equation 10, were found by using Bard's parameter estimation method (4). The results of parameters estimated for various conditions are given in Table II, which shows differences in parameters between sound and damaged kernels under various conditions. Theoretical data were generated by equation 10 (with parameters estimated for various conditions) and were compared with corresponding experimental data. An example of the results of analysis based on equation 10 for sound, broken, and heat-damaged corn at 70°F.-80% r.h. is shown in Fig. 8. Figure 8 and other results show that the model

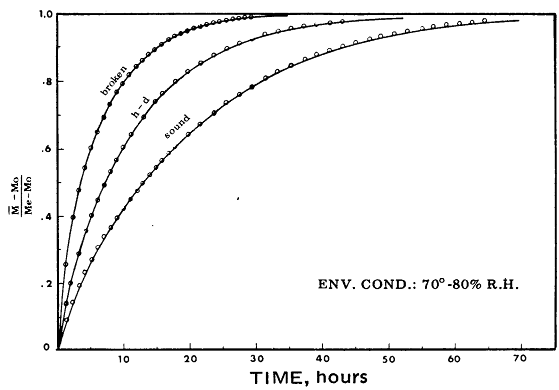


Fig. 8. Experimental sorption data (straight line) and data generated by equation 10 (circles) compared.

TABLE II. VALUES OF PARAMETERS IN SIMULTANEOUS DIFFUSION AND SORPTION MODEL EQUATION[a]

Sample	Environmental Condition	M_o % d.b.	K hr.$^{-1}$	$\bar{D}$ hr.$^{-1}$	M_e % d.b.
Sound	80° F.-80% r.h.	11.9	0.0590	0.00346	16.95
h-d	80° F.-80% r.h.	11.5	0.0437	0.03241	15.68
Broken	80° F.-80% r.h.	11.9	0.1237	0.04338	18.24
Sound	80° F.-70% r.h.	12.2	0.0586	0.00440	14.93
h-d	80° F.-70% r.h.	12.7	0.0220	0.06958	14.21
Broken	80° F.-70% r.h.	12.0	0.0164	0.12570	16.13
Sound	70° F.-80% r.h.	12.0	0.0463	0.00175	17.21
h-d	70° F.-80% r.h.	11.6	0.0706	0.00694	16.12
Broken	70° F.-80% r.h.	11.9	0.0997	0.02949	18.76
Sound	60° F.-80% r.h.	12.1	0.0400	0.00099	17.91
h-d	60° F.-80% r.h.	11.9	0.0402	0.01197	16.25
Broken	60° F.-80% r.h.	11.7	0.0580	0.02408	19.21
10% h-d	70° F.-80% r.h.	11.8	0.0444	0.00335	17.20
30% h-d	70° F.-80% r.h.	11.8	0.0461	0.00428	16.90
50% h-d	70° F.-80% r.h.	11.9	0.0424	0.00583	17.00
10% Broken	70° F.-80% r.h.	11.9	0.0422	0.00876	17.27
30% Broken	70° F.-80% r.h.	12.0	0.0298	0.02852	17.70
50% Broken	70° F.-80% r.h.	12.0	0.0516	0.02511	17.80

[a]For symbols, see text; h-d = heat-damaged; r.h. = relative humidity of the air.

based on simultaneous diffusion and sorption (Equation 10) fits the experimental kinetic data well over the entire range.

Therefore, equation 10 should be useful in describing kinetic behaviors of various corn samples at different environmental conditions and for generating data with sparse experimental data.

General physical quality of grain could be estimated by comparing either equilibrium moisture content or the two parameters–sorption-rate constant, and diffusion coefficient–of a sound sample and a damaged sample. The results reported here should provide useful information and a guide to use in conditioning, storing, and drying grain.

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