Hydration Rates for Various Types of Mexican Maize Based on Single-Kernel Measurements

Gonzalo Ramos,[1] Marisol Pezet-Valdez,[2,3] Aileen O'Connor-Sánchez,[4] Celia Placencia,[1] and Reynaldo C. Pless[1,5]

ABSTRACT

Cereal Chem. 81(3):308–313

Hydration kinetics for sound maize kernels in liquid water, determined by single-kernel measurements for three different Mexican maize types, yielded water diffusion coefficients ordered as Celaya corn > Toluca corn > Palomero corn, at all temperatures examined. These diffusion coefficients are lower than those reported earlier for maize grains, possibly due to the fact that in the present study damaged kernels were rigorously excluded. The energies of activation determined from the Arrhenius plots were ordered as Palomero corn > Celaya corn = Toluca corn and were similar in value to those reported earlier for other maize types. Damage to the surface of the maize kernels during the hydration experiments occurs at a significant frequency. Even minor surface lacerations can strongly affect the rate of hydration of the kernels. Experiments with maize grains selectively varnished in various parts of their surface show that the entry of water into the kernels occurs predominantly through the pericarp, not through the tip cap, though the tip cap has a higher water inflow per unit area.

For large parts of the Mexican and Central American populations, and of the U.S. population of Hispanic origin, maize is the predominant starch staple, consumed almost exclusively in the form of tortillas. These are produced by brief baking of nixtamalized corn masa, which is obtained by limited cooking and subsequent steeping of whole kernels of dry white maize in an aqueous suspension of calcium hydroxide. The degree of cooking reached by the kernels during this cooking-steeping process is critical for the properties of the tortilla ultimately obtained; both overcooking and undercooking of the maize kernels during the nixtamalization process may result in an unsatisfactory masa quality (Khan et al 1982). The correct level of cooking is generally gauged in the traditional manner by a simple biting test performed on the cooked kernels by an experienced operator. This task is intrinsically difficult due to the nonquantitative nature of this test, and it is further complicated by the fact that the critical evaluation is not made at the endpoint of the entire process, but rather in midprocess. Thus, the assessment of the correct softness of the grains at the time the heating is terminated must take into account the considerable further softening that will take place during the ensuing steeping process when the corn-water-calcium hydroxide mixture slowly cools, over a period of many hours.

For these reasons, knowledge of the rate and of the ways of penetration of the various components of the nixtamalization solution into the maize kernels is of value. Recently, we studied the entrance of calcium ion into the grains under nixtamalization conditions (Zazueta et al 2002). Obviously, the penetration of water into the kernels is another important determinant in the nixtamalization process. Surprisingly, few results have been published on this subject. Ruan and Litchfield (1992) used proton magnetic resonance imaging to assess water distribution and water mobility in the interior of single maize kernels after 3 and 6 hr of room temperature steeping of the kernels in pure water. The differences observed were minor, due to the fact that the initial moisture content of the grains was relatively high (35%, wb) and did not increase much during the steeping process (to 39%, wb). A subsequent publication (Ruan et al 1992) again used proton magnetic imaging to delineate the hydration of single kernels of yellow dent corn starting from overall moisture levels (13%, w/w) which were more relevant for maize used in production processes. This work was performed mostly at 53°C and with 0.55% (w/w) of lactic acid present in the steeping liquid. The results bore out the importance of high temperature, presence of lactic acid, and low initial moisture content for a high rate of kernel hydration. The authors interpreted the preferred route of water entry to be through the tip cap to the space between germ and endosperm, then into the germ, and only later into the endosperm. Fan et al (1963) followed the global kinetics of hydration of three U.S. maize cultivars (K-4 hybrid popcorn, K-1859 hybrid dent corn, and Gold Rash sweet corn) over a wide range of temperatures and calculated the corresponding diffusion coefficients using the mathematical treatment developed by Becker (1959). This treatment, valid for a limited extent of kernel hydration, had been applied to the study of different types of wheat by Becker (1960) and by Fan et al (1961). More recently, Charan and Prasad (1996) used the same approach to determine water diffusivity in an Indian maize cultivar Hi-Starch at temperatures of 25–70°C, and to calculate, from the Arrhenius-type plot of diffusivity versus inverse absolute temperature, an energy of activation of 10.94 kcal/mol for water diffusion inside the endosperm.

We have now undertaken to carry out new experiments of this type because 1) the hydration rate measurements reported in the literature were carried out on a large number of grains used in bulk. While this is favorable in that it provides for a large statistical sample, it suffers from the defect that there is no satisfactory control of the integrity of the kernels during the experiment, and we know, from the present work, that relatively minor lesions in the kernel surface can strongly affect the kinetics of hydration. This problem can be avoided in single-kernel studies. 2) The general validity of the mathematical formalism of Becker (1959, 1960) for the case of soaking maize kernels is in doubt so long as the general route of entry of water into the kernel is not understood. 3) None of the quantitative studies so far reported refer to the types of maize commonly used in Mexico for nixtamalization.

MATERIALS AND METHODS

The maize cultivars used were a hard white dented maize from Celaya, Mexico, with a small kernel containing both corneous and floury endosperm, a medium-size flinty white maize kernel, containing corneous and floury endosperm grown in the Toluca region, Mexico, and a small-grain orange-color popcorn maize called Palomero. The first two types are used in the preparation of nixtamal for commercial tortilla production. The initial kernel mass

---

[1] Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada del I.P.N., Unidad Querétaro, José Siurob 10, Col. Alameda, Querétaro, C.P. 76040, Mexico.

[2] Centro de Investigación en Ciencia Aplicada y Tecnología Avanzada del I.P.N., Legaria 694, Mexico, C.P. 11500, Mexico.

[3] Present address: Instituto Politécnico Nacional, Escuela Nacional de Medicina y Homeopatía, Mexico City, Mexico.

[4] CICY – Unidad de Biotecnología, Mérida, Yucatán C.P. 97200, Mexico.

[5] Corresponding author: Phone and Fax: 52-442-2129466. E-mail: Reynaldo.Pless@cicataqro.ipn.mx

Publication no. C-2004-0310-02R.

(M_0) of the grains used in this study averaged 351 mg (±17%) for the Celaya grains, 498 mg (±17%) for the Toluca grains, and 200 mg (±12%) for Palomero corn. The kernel sphericity (defined as [length × width × thickness]$^{1/3}$/major diameter) (Mohsenin 1970) determined for the three types of grain had average values of 0.72, 0.56, and 0.72, respectively. Samples of these kernels are shown in Fig. 1.

The moisture content of these grain types was determined by drying in an air oven at 103°C for 72 hr (Approved Method 44-15A, AACC 2000). For each type of corn, seven sound kernels were tested. The results were 11.2 ± 0.4% (db) for Celaya corn, 10.9 ± 0.3% for Toluca corn, and 12.1 ± 0.3% for Palomero corn.

The density of these grain types was determined based on weighing single kernels and determining their volume by the weight of the oil displaced when they were fully immersed in vegetable oil, as described by Tian et al (2001). For each type of corn, 10 separate sound kernels were evaluated and results were averaged. The densities determined were (1.28 ± 0.03) g × cm^{-3} for Celaya, (1.29 ± 0.05) g cm^{-3} for Toluca, and (1.36 ± 0.02) g cm^{-3} for Palomero.

The kernels to be used in the hydration runs were selected for integrity by visual examination. At the end of the experiment, they were again tested for integrity both by simple inspection and by immersion of the grains in an aqueous iodine-iodide test solution (12.7 g of iodine/L, 19.5 g of KI/L), checking for the dark blue coloration that indicates exposed starch. The selected kernels in dry form were weighed on an analytical balance to the nearest 0.1 mg and measured by caliper for length, width, and thickness, to the nearest 0.1 mm. The length of the kernel was measured from the crown to the border where the pericarp meets the tip cap. Before a kinetic run, the kernels were thermally equilibrated in empty plastic weighing cups held in a constant temperature bath set to the desired temperature. The run was started by transferring the kernels to weighing cups filled with distilled water, which had been preequilibrated in the constant temperature bath. After different times, the kernels were singly removed from the water with a plastic spoon, gently dabbed dry with tissue paper, rapidly weighed to the nearest 0.1 mg, and immediately reimmersed in the temperature-controlled distilled water, to continue with the kinetic run. Each weighing of a kernel took 30 sec; these weighing times were deducted from the cumulative hydration time. The kernels were weighed at 15- or 20-min intervals in the high-temperature runs (30–78°C), and at 30-min intervals in the low-temperature runs (1–20°C). Water temperature readings were taken directly inside the weighing cups holding the grains using a thermocouple calibrated to an accuracy of 0.1°C. During the hydration runs, the measured temperature never deviated by >0.5°C from the desired value.

For each kernel, its mass increase during the run was plotted against the square root of hydration time. A good linear fit, with a coefficient of determination (R^2) >0.995 and an error in the slope value of <2.5%, was generally obtained if the early data points (below t = 30 min for runs at temperatures ≤40°C, below t = 20 min for runs at higher temperatures) were disregarded. These early data points correspond to the first, rapid phase of kernel hydration and are not expected to fall on the linear part of the plot of Δ(mass) vs. √time (Becker 1960). Single-kernel hydration runs that did not result in a highly linear correlation of Δ(mass) with √time for t > 30 min were removed from consideration, as were the results obtained with a kernel after the run that showed significant surface damage in the test with the iodine-iodide solution. In all of these cases, the hydration rate for the kernel in question strongly deviated to the high side of the average rate of the kernels tested at that temperature, indicative of loss of integrity of the kernel surface. All of the kernels removed from consideration showed surface damage in the postrun test with iodine solution.

Experiments involving total or partial varnishing of the kernel surface used a fast-drying, homogeneous fingernail polish (Super Top Speed, Reddy 470, from Revlon) applied in two coats, allowing a day of air drying at room temperature after each application. In varnishing the tip cap, care was taken to assure that the entire tip cap was covered, including a narrow adjoining region of the pericarp. The final thickness of the varnish was ≈0.10 mm, estimated by examination of kernel sections under a low-power microscope equipped with a microscale. Control experiments with nail polish applied to glass slips showed hydration of the polish to be negligible (<0.1% [w/w]/hr at 30°C).

RESULTS AND DISCUSSION

Determination of Diffusion Coefficients for Undamaged Kernels

For the Celaya and Toluca maize types, single-kernel hydration runs were performed at 1, 10, 20, 30, 40, 50, 60, 70, and 78°C. The Palomero maize kernels were only assayed at 1, 20, 40, 60, and 78°C. For each kernel, the hydration course showed a rapid initial mass gain, up to a value of ≈10% for $\Delta M/M_0$ (where ΔM is the mass increase attendant on hydration and M_0 is the initial mass of the kernel), followed by a long-time regime in which the expected hydration kinetics were observed (i.e., where $\Delta M/M_0$ was a linear function of the square root of time). Charan and Prasad (1996) observed that for the type of maize tested in their work, this linearity holds for kernel moisture values of ≤40% (db) for runs at 25°C and for kernel moisture contents ≤60% (db) for runs performed at 70°C. In our kinetic runs, we stayed below these levels of hydration and no deviation from linearity was observed.

Figure 2A shows a typical single-kernel hydration run, performed on a grain of Toluca maize at 30°C. One observes the initial rapid rise in mass over a period of ≈20 min, followed by a long-time regime with much slower hydration kinetics. Figure 2B shows the corresponding plot of $\Delta M/M_0$ vs. √time with an extensive linear part from t = 39.5 min to t = 234.5 min. Over this time period, the linear fit to the data gives a correlation of R = 0.9997 with a slope of 0.01189 ± 0.00009 min$^{-1/2}$. From this value for the slope $\Delta(\Delta M/M_0)/\Delta(\sqrt{t})$, the linear diffusion coefficient D was calculated as 8.72×10^{-6} cm^2/min, or 0.0523×10^{-6} m^2/hr, for this particular maize grain at 30°C, based on the equation

$$\sqrt{D} = \frac{\Delta(\Delta M/M_0)}{\Delta(\sqrt{t})} \times \frac{1+m_0}{(m_S - m_0)} \times \frac{V}{S} \times \frac{\sqrt{\pi}}{2} \qquad (1)$$

Here, $\Delta(\Delta M/M_0)/\Delta(\sqrt{t})$, in units of min$^{-1/2}$, is the slope obtained from the linear fit, as described above; M_0 is the initial mass of the kernel (containing 10.9% moisture, db), V (in cm^3) and S (in cm^2) are the volume and the surface of the maize kernel in its initial state; m_0, is the initial, uniform moisture content, db, w/w (10.9% or 0.109 for Toluca maize); and m_S is the effective moisture content at the bounding surface of the immersed kernel at t > 0 (db, g/g) taken as 0.52 based on the values reported by Charan and Prasad (1996) for Hi-Starch maize (m_S = 52% db at 25°C) and by Fan et al (1963) for K-4 hybrid popcorn (m_S = 0.515 at 100°F [38°C] and m_S = 0.545 at 160°F [71°C]). As m_S and m_0 are dimensionless quantities, the units on the right side of Equation 1

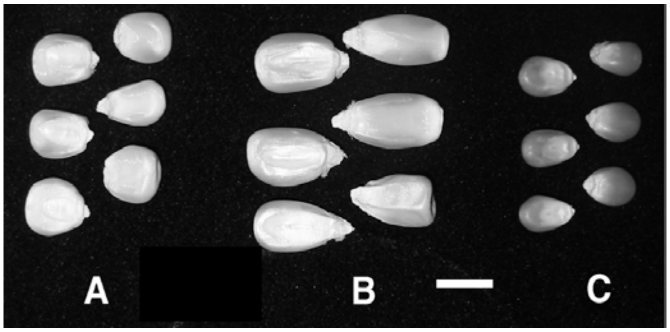

Fig. 1. Representative samples of Celaya (**A**), Toluca (**B**), and Palomero corn (**C**). Size bar = 1 cm.

reduce to cm $\min^{-1/2}$ (i.e., the right side of the equation has the correct dimension for $\sqrt{D}$). The kernel surface S was evaluated as:

$$S = \pi D_p^2 \varphi^{-1} \tag{2}$$

with D_p defined as the geometric average of length, width, and thickness of the kernel (length × width × thickness)$^{1/3}$, and the sphericity φ defined as D_p/length. Equation 2 is equivalent to $\psi = 4\pi r_v^2/S$, given by Becker (1959), or to $\varphi_S = 6v_p/D_p s_p$, given by McCabe and Smith (1976). The kernel volume V was calculated as M_0/ρ, using for ρ the value of 1.29 g cm^{-3} for Toluca corn, determined as described above. Equation 1 is equivalent to Equation 3 of Becker (1960), which reads

$$\overline{m} - m_0 = \frac{2}{\sqrt{\pi}}(m_S - m_0)\frac{S}{V}\sqrt{D}\sqrt{t} \tag{3}$$

As m_S and m_0 are dimensionless, the units on the right side of Equation 3 form the product (cm^2 × cm^{-3} × $\sqrt{(\text{cm}^2 \times \text{min}^{-1})}$ × min$^{1/2}$), which reduces to dimensionless as necessary because the left side of the equation, $\overline{m} - m_0$, is dimensionless.

In this manner, the hydration diffusion coefficients were determined for a number of grains from Celaya, Toluca, and Palomero at different temperatures. At each of the temperatures examined for each maize type 8–10 runs were performed with kernels that proved intact after the run. The plots of averaged diffusion coefficients versus temperature are shown in Fig. 3.

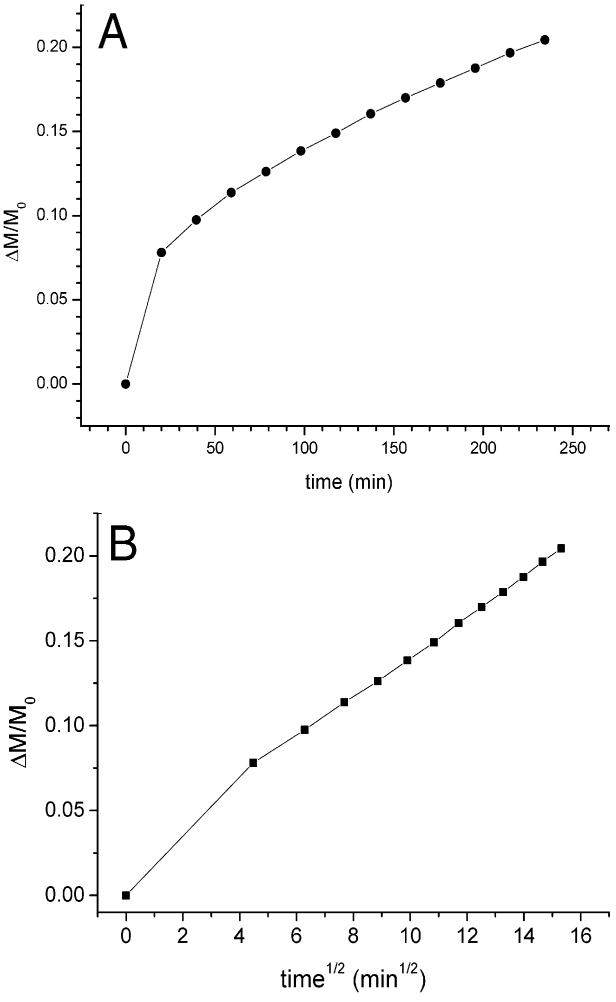

Fig. 2. Relative mass gain during hydration of a single kernel of Toluca grain (initial weight 530 mg) at 30°C plotted (**A**) against hydration time and (**B**) against the square root of hydration time.

Determination of Activation Energies

Figure 4 shows a plot of the logarithm of the averaged diffusion coefficients versus the inverse of absolute temperature. This is an Arrhenius-type plot that allows calculation of energies of activation as

$$\ln D = \ln D_0 - \frac{E_a}{RT} \tag{4}$$

from the linear fit of the data. Here, E_a is the activation energy, R is the universal gas constant 1.987 cal/mol/deg, and T is the absolute temperature in K. We chose to evaluate these data only for the temperature interval between 20 and 78°C as we found that data points for 1°C (3.648×10^{-3}/K) and 10°C (3.532×10^{-3}/K) strongly deviate from the best straight line to lower values of ln D, possibly due to the proximity of these temperatures to the melting point of water. This is also more in line with the temperature intervals used by other workers in the Arrhenius evaluation of hydration rates of cereal grains.

On this basis, we calculate activation energies of 8.77 kcal/mol (± 2.9%), 8.84 kcal/mol (± 2.8%),and 9.88 kcal/mol (± 5.5%) for Celaya, Toluca, and Palomero grains, respectively (with coefficients of determination of 0.9957, 0.9960, and 0.9939), and D_0 values of 0.171 m^2/hr (± 3.4%), 0.145 m^2/hr (± 3.3%), and 0.406 m^2/hr (± 6.7%), respectively.

Effect of Surface Damage on Hydration Rates

The susceptibility of the overall rate of hydration of the maize grains to physical damage to the grain surface was tested in simple model experiments in which the dorsal surface of the grain was pierced to a depth of ≈0.5 mm either with a fine needle or with the tip of a pointed, sharp knife blade, producing either a round lesion of ≈0.3 mm diameter or a lesion of ≈2 mm × 0.3 mm, respectively. Figure 5 shows hydration curves at 20°C for a Celaya kernel, where these lesions were introduced at the times shown in the graph. We see that three needle punctures did not affect the subsequent course of hydration for the maize kernel, but that the knife cut, even though relatively small, did expose the grain to a much more rapid penetration by water. Similar results were obtained in tests with other kernels of Celaya or Toluca corn. The accelerating effect of surface damage on the hydration of maize kernels has been demonstrated before (Ruan et al 1992), albeit for much larger lacerations (5 mm × 1 mm). Our results show that even small lacerations of the grain surface can cause a sharply elevated rate of hydration of the kernel. It is for this reason that, in the single-kernel kinetic experiments performed in the present study, the results were discarded if the time course of hydration changed

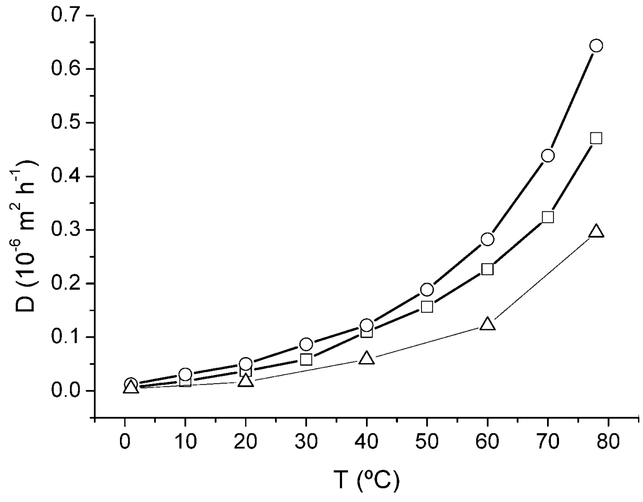

Fig. 3. Averaged diffusion coefficients in dependence of hydration temperature for Celaya (○), Toluca (□), and Palomero (△) grains.

in an abrupt manner in midrun, indicative of kernel damage occurring during the repeated handling of the kernel during the experiment. In these cases, the iodine-iodide test performed after the experiment always confirmed a laceration of the kernel in question.

Thus, kernel damage has an important effect on the rate of hydration of corn at the level of the individual maize grain and would also be expected to markedly affect the bulk rate of hydration if such kernel damage is widespread. In this context, we should note that of all the kernels used in our kinetic runs at the various temperatures, 28% were rejected in the final evaluation due to abnormal kinetics and to physical damage apparent after the run, even though all of these kernels had been carefully selected by inspection for apparent integrity at the dry kernel stage. This means that any hydration kinetics performed on bulk samples of maize would entail a considerable (and unknown) increase in the measured hydration rate due to the presence of damaged kernels in the sample. Recent work by Wang and Eckhoff (2000) shows that admixture of broken corn to sound corn in a ratio as low as 4% (w/w) already results in a detectable increase in hydration rate. This vindicates the approach of single-kernel evaluation used in the present study and posits the probability that the kinetic results reported earlier in the literature represent an overestimate in the rate of hydration of maize kernels if interpreted as relating to an ensemble of truly sound kernels.

Even after discounting the kernels with abnormal kinetics or with physical damage evident after the run, the remaining maize grains still evince considerable kernel-to-kernel variation in their hydration behavior. For instance, in the experiments conducted at 30°C, the evaluation of the water diffusion coefficients for Celaya grains and Toluca grains (with eight sound kernels in each sample) gave standard deviations of ±19% and ±20%, respectively. Similar spreads were observed in the experiments conducted at other temperatures.

Comparison of Diffusion Coefficients and Energies of Activation with Literature Values

For a comparison of hydration diffusion coefficients in maize reported by different workers, we prefer a comparison of values actually measured at intermediate temperatures (e.g., at 40°C) to a comparison of D_0 values, whose evaluation entails a long linear extrapolation to zero value for 1/T, over many orders of magnitude in D, from a linear basis in the measured temperature range which does not warrant such an extended extrapolation. This becomes obvious from the large spread in the values of D_0 listed in Table I. The data for D(40°C) in Table I show for the grains examined in the present work, descending values for the diffusion coefficients in the sequence Celaya maize – Toluca maize – Palomero maize, as was also observed at all other temperatures tested in this work. It is interesting to note that the measurements of Fan et al (1963) also showed a twofold higher diffusion coefficient for the dent corn, compared with the popcorn. However, their diffusion coefficient values are generally almost twice those observed here for the comparable grains (i.e., comparing Celaya or Toluca maize with K-1859 hybrid dent corn or comparing Palomero popcorn with K-4 hybrid popcorn). This could be ascribed either to significant intrinsic differences in diffusivity even between similar types of maize, or it may be due to a greater proportion of damaged kernels in the samples used by Fan et al (1963), who performed their measurements on bulk samples, not on single grains. The highest among the diffusion coefficients for maize listed in Table I (0.280×10^{-6} m^2/hr) is the value from Charan and Prasad (1996). This could either mean that Hi-Starch maize has a very high diffusion coefficient, or that their samples contained a large proportion of damaged kernels, though the authors state that only sound kernels were used in their experiments. All of the types of maize considered in Table I have distinctly higher diffusion coefficients compared with the other cereals reported (sorghum and wheat) but have a lower diffusivity than soybean.

Note also that the values listed in Table I for the diffusion coefficients of various types of maize grains soaking in water are comparable to the values that can be calculated from the work of Syarief et al (1987) for moisture diffusion in the drying mode for various yellow corn components: 0.54×10^{-6} m^2/hr for the germ, 0.15×10^{-6} m^2/hr for the floury endosperm, 0.11×10^{-6} m^2/hr for the corneous endosperm, 0.048×10^{-6} m^2/hr for the pericarp covering the floury endosperm, 0.032×10^{-6} m^2/hr for the pericarp covering the corneous endosperm, all at 40°C and 10% (db) moisture content.

The energies of activation listed in Table I were all obtained from Arrhenius plots based on hydration rates determined over a fairly wide temperature range: 20–78°C in the present work, 25–70°C in the work of Charan and Prasad (1996), 0–100°C in the work of Fan et al (1963), 27–65°C in the work of Fan et al (1961), 0–70°C in the work of Becker (1960), and 20–50°C in the work of Hsu (1983). These energies of activation are taken to pertain to the process of diffusion of water within the interior of the wheat kernel, as virtually identical values for this energy of activation were determined for both water absorption and drying processes (Becker 1959, 1960). Similar values for E_a were determined for the three types of maize used in our study, with Celaya and Toluca

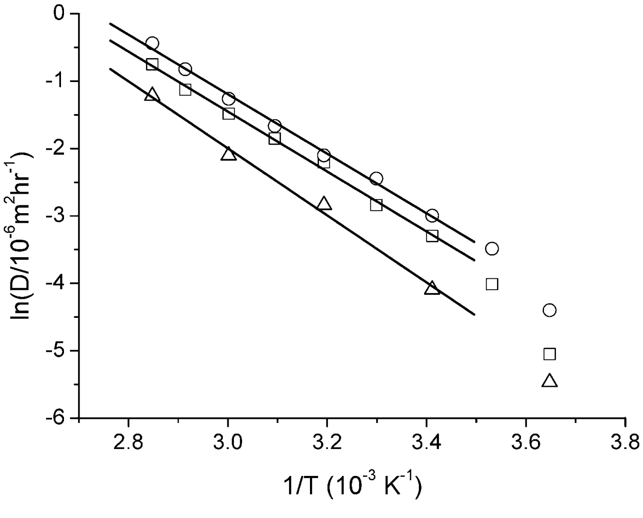

Fig. 4. Arrhenius-type plots for hydration of Celaya (○), Toluca (□), and Palomero (△) grains. Straight lines are the linear fit to the data points from 2.85×10^{-3} K^{-1} to 3.41×10^{-3} K^{-1} (78°C to 20°C).

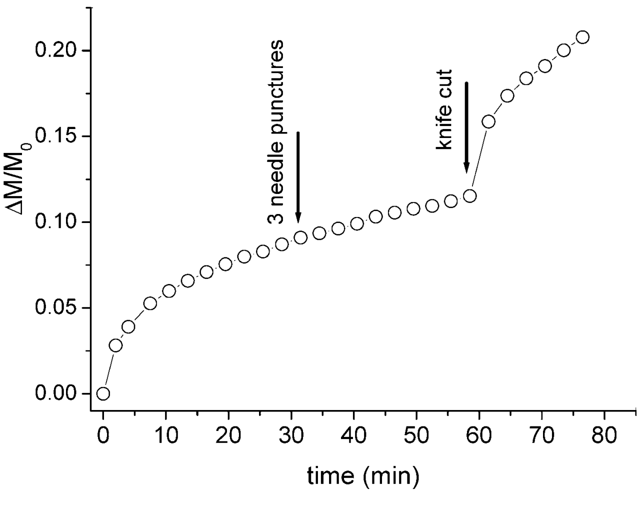

Fig. 5. Effect of surface lesions on hydration of a whole maize kernel. Progression of hydration at 20°C for a grain of Toluca corn (initial weight 433 mg). Times for introduced lesions are indicated.

grains indistinguishable in this respect, and Palomero grain giving the highest value for E_a. This is in contrast to the results of Fan et al (1963), who found that K-4 hybrid popcorn exhibited the lowest E_a value of the three maize types tested. In general, the E_a values determined in the present work are higher than the values reported by Fan et al (1963) but lower than the result of Charan and Prasad (1996), who calculated 10.94 kcal/mol for Hi-Starch maize. E_a values determined in this manner for various sorghum and wheat cultivars as well as for one soybean cultivar also fall into this general range of values: $\approx$8.4 kcal/mol for sorghum (Fan et al 1963), 10.1–11.6 kcal/mol for various wheat cultivars (Fan et al 1961), 12.3 kcal/mol for Thatcher wheat (Becker 1960), 12.45 kcal/mol for soybean (Hsu 1983). This suggests that the mechanism of water diffusion is essentially the same in these different grains.

Tests to Explore Routes of Water Entry

To test for possible preferred routes for the entry of water into the maize kernels, we performed hydration experiments using maize kernels with specific parts of their surface varnished with a fingernail polish. They were either fully varnished or varnished such as to leave only the tip cap exposed or they only had the tip cap varnished. These kernels were compared in the hydration kinetics at 30°C with unvarnished grains. Table II presents the values for $\Delta M/M_0/\Delta t$ (where M_0 is the initial mass of the unvarnished grain); that is, the rate of the percent increase in kernel mass for the time period from 40 to 100 min (for which the plot of $\Delta M/M_0$ versus time is approximately linear). For each experiment, the Table II lists the number of kernels evaluated, the range of hydration rates measured, and the average rate calculated. Even though kernel-to-kernel variation makes a strict quantitative evaluation impossible, three conclusions are warranted for both Toluca and Celaya grains.

1. The fingernail polish is an effective sealant (reducing the rate of water penetration to the kernel by $\approx$20-fold for Toluca grains and by $\approx$50-fold for Celaya grains, for fully varnished kernels).
2. Entry of water through the tip cap occurs only to a minor though significant extent ($\approx$15% or less of the rate for the unvarnished kernels). Still, considering the small area of the tip cap (less than one-twentieth of the area of the pericarp), this means that the flow per unit area is much larger for the tip cap than for the pericarp.
3. Most of the hydration occurs through the pericarp, as seen in data for grains with the tip cap sealed with varnish. In this comparison, the average hydration rate was similar to that observed for the unvarnished kernels.

Similar conclusions were drawn from the evaluation of the hydration curves over the first 40 min of the experiment (data not shown), during which the rapid initial rise in kernel mass occurs.

The differences in hydration behavior observed in these experiments clearly show that water enters the grain mainly through the pericarp not through the tip cap, though the latter pathway is also significant. This conclusion is similar to that drawn for maize kernels under nixtamalization conditions in a more qualitative study reported by Muñoz Hernández (1998).

The fact that most of the water enters the grain through the pericarp provides some justification for the use of the formalism, first proposed by Becker (1959, 1960) for the wheat kernel, which models the hydration process as a uniform concentric penetration of water from the entire kernel surface. Nonetheless, it is obvious that this model can only represent a rough approximation to reality given the high flow density through the tip cap compared with the pericarp and the various anisotropies and asymmetries inherent to the kernel.

TABLE I
Comparison of Kinetic Parameters for Hydration of Different Types of Grains in Liquid Water

Grain	D_0 (m^2 hr^{-1})	D (40°C) (10^{-6} m^2 hr^{-1})	E_a (kcal/mol)	Reference
Celaya maize	0.171	0.122	8.77	This work
Toluca maize	0.145	0.110	8.84	This work
Palomero popcorn	0.406	0.059	9.88	This work
"Hi-Starch" maize	15.274	0.280	10.94	Charan and Prasad(1996)
K-1859 hybrid dent corn	0.0388	0.199[a]	7.578	Fan et al (1963)
K-4 hybrid popcorn	0.0055	0.091[a]	6.853	Fan et al (1963)
Gold Rash sweet corn	0.0307	0.061[a]	8.167	Fan et al (1963)
Atlas sorgo sorghum	0.0223	0.0294[a]	8.424	Fan et al (1963)
White kafir sorghum	0.0161	0.0243[a]	8.339	Fan et al (1963)
Vernum wheat	0.684	0.0180	10.1[c]	Fan et al (1961)
Brevor wheat	0.212	0.0191	11.6[c]	Fan et al (1961)
Seneca wheat	0.360	0.0274[b]	10.2[c]	Fan et al (1961)
Ponca wheat	1.692	0.0258[b]	11.2[c]	Fan et al (1961)
Thatcher wheat	10.8	0.0281[d]	12.3	Becker (1960)
Amsoy 71 soybean		0.389[e]	12.45[e]	Hsu (1983)

[a] Values back-calculated from the kinetic data of Fan et al (1963).
[b] Values back-calculated from the kinetic data of Fan et al (1961).
[c] For $T < 65$°C.
[d] Value back-calculated from the kinetic data of Becker (1960).
[e] For soybeans starting with zero water content.

TABLE II
Hydration Kinetics at 30°C for Maize Kernel Surfaces Varnished in Specific Parts

	No. of Grains Tested	$\triangle M/M_0/\triangle t$ (mass%/hr)[a]	Average Range
Celaya kernels			
Unvarnished	4	4.72	3.86–5.18
Fully varnished	3	0.10	0.05–0.14
Varnished, except for tipcap	4	0.79	0.59–1.24
Only the tipcap varnished	4	4.17	3.13–5.82
Toluca kernels			
Unvarnished	4	3.82	3.66–4.06
Fully varnished	3	0.19	0.13–0.27
Varnished, except for tipcap	5	0.58	0.49–0.74
Only the tipcap varnished	4	3.95	3.26–4.46

[a] Slope of linear approximation to data curve M/M_0 vs. time for 40–100 min.

At first sight, these results may appear to conflict with the report by Ruan et al (1992) that steepwater first moves into the maize kernel through the tip cap. This dichotomy cannot be explained on the basis that the experiments were performed in different pH conditions (0.55% aqueous lactic acid in the work of Ruan et al [1992], strongly basic conditions in the experiments of Muñoz Hernández [1998], neutral water in the present work), because the study of Dailey (2000) on the hydration rates of germ and of endosperm in whole yellow corn found no significant differences between hydration in neutral water and in water containing SO_2 or lactic acid. Rather, the apparent contradiction between our present results and the earlier work is resolved if we consider that the results of Ruan et al (1992) reflect the distribution of water in the kernel in terms of *local concentrations*, while our experiments with varnished maize grains assess the *global contribution* of water entry through the pericarp and through the tip cap. Thus, the results reported in our present work and in the earlier reports are compatible. In terms of overall water entry, hydration through the pericarp is preponderant, but the entry of water through the tip cap is also significant, and given the very small area of the tip cap, the flow of water per unit area is much larger in this structure. This leads to a higher local concentration of water in the part of the grain adjacent to the tip cap. As a result, water first becomes detectable by spectroscopic methods (Ruan et al 1992) specifically in these regions. This is similar to observations made by magnetic resonance imaging techniques for hydration of barley grains (McEntyre et al 1998) and by autoradiographic techniques for hydration of wheat grains (Stenvert and Kingswood 1976). The capacity of the maize tip for rapid conduction of small molecules has also been documented for gaseous sulfur dioxide, where the early entry of the gas through the tip cap was visualized essentially as a negative signal in a subsequent staining with iodine (Eckhoff and Okos 1987).

CONCLUSIONS

Hydration experiments can be conducted successfully on single maize kernels, which allows collection of hydration rate data unaffected by the presence of broken kernels, in contrast to the kinetics obtained with bulk samples. Small surface lacerations can significantly affect the rate of hydration of a given kernel. Even for sound kernels, grain-to-grain variation in hydration rate is significant, pointing to the need for testing several maize kernels, even in simple biting tests performed during nixtamalization.

For the three types of Mexican maize examined in this study, water diffusion coefficients calculated from the rate data were similar (though lower) to those reported previously for various types of maize. The difference may be due to only sound kernels being considered in the present evaluation. The energies of activation derived from the temperature dependence of the hydration rates for the three maize types tested in this study were similar to those previously reported for various maize types.

Entry of water into the maize kernels during steeping occurs predominantly through the pericarp, though the pathway through the tip cap is also significant.

ACKNOWLEDGMENTS

This work was carried out with support from CGPI grant No. 20010300, from the Instituto Politécnico Nacional.

LITERATURE CITED

American Association of Cereal Chemists. 2000. Approved Methods of the AACC, 10th Ed. Method 44-15A. The Association: St. Paul, MN.

Becker, H. A. 1959. A study of diffusion in solids of arbitrary shape, with application to the drying of the wheat kernel. J. Appl. Polym. Sci. 1:212-226.

Becker, H. A. 1960. On the absorption of liquid water by the wheat kernel. Cereal Chem. 37:309-323.

Charan, R., and Prasad, S. 1996. Moisture diffusion during hydration of maize. J. Food Sci. Technol. 33:384-388.

Dailey, O. D. 2000. Variability in water absorption of germ and endosperm during laboratory steeping of yellow corn hybrid. Cereal Chem. 77:721-723.

Eckhoff, S. R., and Okos, M. R. 1989. Diffusion of gaseous sulfur dioxide into corn grain. Cereal Chem. 66:30-33.

Fan, L., Chung, D. S., and Shellenberger, J. A. 1961. Diffusion coefficients of water in wheat kernels. Cereal Chem. 38:540-548.

Fan, L., Chu, P., and Shellenberger, J. A. 1963. Diffusion of water in kernels of corn and sorghum. Cereal Chem. 40:303-313.

Hsu, K. H. 1983. Effect of temperature on water diffusion in soybean. J. Food Sci. 48:1364-1365.

Khan, M. N., Des Rosiers, M. C., Rooney, L. W., Morgan, R. G., and Sweat, V. E. 1982. Corn tortillas: Evaluation of corn cooking procedures. Cereal Chem. 59:279-284.

McCabe, W. L., and Smith, J. 1976. Unit Operations of Chemical Engineering, 3rd Ed. McGraw-Hill: New York.

McEntyre, E., Ruan, R., and Fulcher, R. G. 1998. Comparison of water absorption patterns in two barley cultivars, using magnetic resonance imaging. Cereal Chem. 75:792-795.

Mohsenin, N. N. 1970. Physical Properties of Plant and Animal Materials. Gordon and Breach: New York.

Muñoz Hernández, R. A. 1998. Aplicación de la técnica fotoacústica en el estudio de biopolímeros y sistemas de dos capas, Doctoral thesis. CINVESTAV, Instituto Politécnico Nacional: Mexico.

Ruan, R., and Litchfield, J. B. 1992. Determination of water distribution and mobility inside maize kernels during steeping using magnetic resonance imaging. Cereal Chem. 69:13-17.

Ruan, R., Litchfield, J. B., and Eckhoff, S. R. 1992. Simultaneous and nondestructive measurement of transient moisture profiles and structural changes in corn kernels during steeping using microscopic nuclear magnetic resonance imaging. Cereal Chem. 69:600-606.

Stenvert, N. L., and Kingswood, K. 1976. An autoradiographic demonstration of the penetration of water into wheat during tempering. Cereal Chem. 53:141-149.

Syarief, A. M., Gustafson, R. J., and Morey, R. V. 1987. Moisture diffusion coefficients for yellow-dent corn components. Trans. ASAE 30:522-528.

Tian, Y., Buriak, P., and Eckhoff, S. R. 2001. Effect of hybrid and physical properties of individual popcorn kernels on expansion volumes. Cereal Chem. 78:578-582.

Wang, D., and Eckhoff, S. R. 2000. Effect of broken corn levels on water absorption and steepwater characteristics. Cereal Chem. 77:525-528.

Zazueta, C., Ramos, G., Fernández-Muñoz, J. L., Rodríguez, M. E., Acevedo-Hernández, G., and Pless, R. C. 2002. A radioisotopic study of the entry of calcium ion into the maize kernel during nixtamalization. Cereal Chem. 79:500-503.

[Received April 15, 2003. Accepted November 30, 2003.]