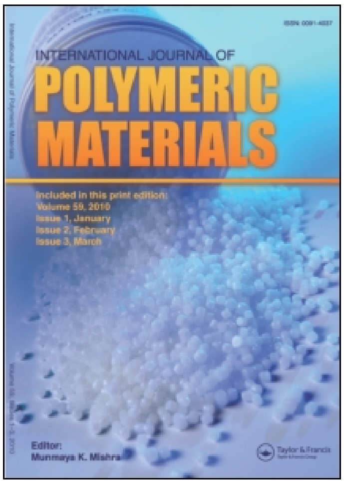

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A. Iribarren[a,b]; F. Caballero-Briones[b]; R. Castro-Rodríguez[c]; J. L. Peña[b,c]
[a] Instituto de Materiales y Reactivos, Universidad de La Habana, Cuba [b] CICATA-IPN Unidad Altamira, Altamira, Tamaulipas, México [c] Departamento de Física Aplicada, CINVESTAV-IPN Unidad Mérida, Mérida, Yucatán, México

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REACTION KINETICS OF THE CORN PERICARP DURING THE NIXTAMALIZATION

A. Iribarren
Instituto de Materiales y Reactivos, Universidad de La Habana,
Ciudad de la Habana, Cuba and CICATA-IPN Unidad
Altamira, Altamira, Tamaulipas, México

F. Caballero-Briones
CICATA-IPN Unidad Altamira,
Altamira, Tamaulipas, México

R. Castro-Rodríguez
Departamento de Física Aplicada, CINVESTAV-IPN
Unidad Mérida, Mérida, Yucatán, México

J. L. Peña
CICATA-IPN Unidad Altamira, Altamira, Tamaulipas,
México and Departamento de Física Aplicada, CINVESTAV-IPN
Unidad Mérida, Mérida, Yucatán, México

We studied by grazing incidence X-ray diffraction the behavior of the amorphous and crystalline diffractogram areas of corn pericarp samples taken during a typical nixtamalization process. The pericarp amorphous part suffers two dissolution processes, one fast, due to the dissolution of the water- and alkali-soluble parts of the pericarp, and other slow, associated with the hemicelluloses dissolution. During the steeping stage the crystalline part of the pericarp reflects the transformation of the native cellulose under the alkaline treatment into cellulose II, meanwhile, the amorphous part increases due to the alkaline cellulose transformation into amorphous II-type cellulose. Assuming first-order reactions we fitted the area behaviors in the steeping stage and found the reaction rates from native cellulose into alkaline

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Address correspondence to A. Iribarren, Instituto de Materiales y Reactivos, Universidad de La Habana, Zapata y G, Vedado, Plaza, Ciudad de la Habana 10400, Cuba. E-mail: a_iribarren@yahoo.com

cellulose and from alkaline cellulose into cellulose II to be $k_1 \cong 0.027\,min^{-1}$ *and* $k_2 \cong 0.00077\,min^{-1}$ *respectively.*

Keywords: kinetics, corn pericarp, nixtamalization

INTRODUCTION

From ancient times corn has constituted the essential nutritious base for the peoples of the Mesoamerican region. Multiple products are obtained from corn. One of these products is the tortilla, which in Mexico is consumed by all the population notwithstanding its social and economic status. Each Mexican eats an average of about 130 kg of tortillas a year [1]. To that it must be added the increasing consumption of Mexican products in the United States [2], which demands to satisfy a market with, for instance, sums dozens of billions of tortillas [3].

Dough, from which tortillas are prepared, is obtained by a method named *nixtamalization*, which consists in cooking the corn grain in a bath of water and lime, later kept for several hours steeping in the same bath, and finally washed and milled. Traditionally, dough and tortillas are home-made, or prepared in small factories named *tortillerías*. Industrially, the process includes the obtaining of corn flour by dehydration. Packaged, instantaneous flour leads to easily prepared dough by rehydration. Also packaged tortillas are available both in the Mexican and American markets. However, despite the instantaneous flour and packaged tortillas becoming very popular because of long shell-life, and ease of use, Mexican still prefer the traditionally prepared tortilla, which the industry has not been able to equal in organoleptic and structural properties.

On the other hand the physicochemical changes that take place in the corn during the *nixtamalization* process itself are not fully understood and are still under investigation [4]. A primordial importance is conferred to the corn pericarp in the obtaining of a tortilla with good properties. It has been even considered that only the pericarp might be *nixtamalized*, while the endosperm only has to be ground and incorporated into the flour [5], and that the quality of the processed corn flour is determined by the quantity of pericarp incorporated [6]. It is thought that the pericarp forms in the tortilla a framework, which contributes to give it flexibility, and mechanical and thermal resistance, as well as a particular taste. However, the effect that *nixtamalization* has on the corn pericarp has not been exhaustively studied.

The aim of the present work is to study the kinetics of the proposed changes of the corn pericarp during the *nixtamalization*. We analyze the X-ray diffractograms taken to pericarps obtained at different *nixtamalization* times. Particularly, from the non-uniform behavior of the crystalline and amorphous areas of the pericarps, we describe the main processes that take place on the pericarp constituents and the respective reaction rates.

We confirm such behavior as due to several reactions related with hemicellulose decomposition, swelling and moistening, and the transformation of native cellulose into cellulose II.

MATERIALS AND METHODS

Composition of the Corn Pericarp

The pericarp is the external husk of the grain, covers it in all its extension, and joins with the tip cap in the grain base. It is covered by a waxy cutin that probably modulates the moisture exchange [7]. The pericarp constitutes about 5 – 6% of the grain dry weight [7], and it is formed of several continuous layers of 60 – 160 μm thickness composed mainly by about 22% of cellulose fiber and 67% of hemicellulose [7, 8]. Little amounts of starch, fat, protein and other substances are also present. Most of the hemicellulose is water-soluble (hemiB), but there also exists a water-insoluble hemicellulose (hemiA). The hemiB fraction dissolves after alkaline treatment [8, 9].

Sample Preparation and Analysis

Nixtamalization was carried out by stewing 100 g of "Maicena"-type corn in a bath containing 2 g lime (99% $Ca(OH)_2$) in 300 ml of distilled water. The bath was heated initially up to 85°C ± 3°C for 30 minutes. Afterwards, the bath was allowed to freely cool to room temperature (RT) and kept in steeping for 12 hours. From this process, some grains were taken at different times. Once extracted from the bath, the grains were rinsed in distilled water to remove the excess of alkali, and successively introduced in absolute ethanol at 50, 75 and 100% for 5 minutes. Afterwards, the ethanol excess was evaporated loading the grains in a furnace at 105°C for 1 min. The pericarp of the dehydrated grain is then removed by carefully cutting the kernel around its perimeter previously separating the tip cap in order to avoid tearing. We performed the measurements on the part of the pericarp opposite to the germ.

X-ray diffraction measurements were performed in a D5000 Siemens diffractometer using non-filtered Cu Kα radiation. The source was collimated with a slit of 0.2 mm. The detector consists of an arrangement of horizontal slits. We perform the measurements in the grazing incidence geometry, with the detector pivoting on the goniometer circle and the sample at a fixed angle of 1° with respect to the X-ray source. The measurement speed was of 0.3°/min. The pericarps were mounted and fixed on the support immediately after preparation to guarantee that they dry flat. The supports used were glass slides and the pericarps were fixed on them with a non-diffractive adhesive.

From the X-ray diffractograms, we subtract the background due to the Compton effect, taken as a straight line [10]. Once subtracted this background, the amorphous and crystalline areas of the diffractograms were estimated by using the software included in the diffractometer.

RESULTS AND DISCUSSION

Amorphous and Crystalline Areas Evolution

The diffractograms present a wide band in the region of 2θ between 19° and 24° given by the convolution of the diffraction peaks of the pericarp compounds. At the end of the *nixtamalization* only native cellulose and cellulose II remain. The amorphous region of the diffractograms is mainly due to hemicellulose.

Figure 1 shows the behaviors of the amorphous and crystalline areas of the pericarp diffractograms. With the aim of including the measurements of the raw pericarp ($t_r = 0$) we summed 1 min to each real *nixtamalization* time, *i.e.*, $t = t_r + 1$ min. The analysis of results during the cooking ($t_r \leq$ 38 min) and steeping ($t_r > 38$ min) stages will be done separately. During the cooking stage a slight diminishing in the amorphous area between the

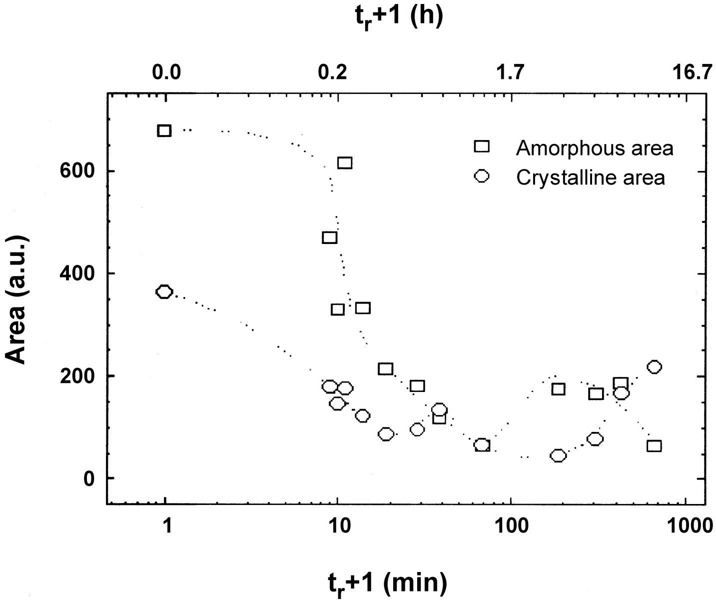

FIGURE 1 Behavior of the amorphous and crystalline areas of the pericarp diffractograms as function of the *nixtamalization* time.

raw pericarp ($t_r = 0$ min) and $t_r = 8$ min ($t = 9$ min) is observed. It is due to the attack and dissolution of the waxy cutin of the pericarp [7]. From this point, the isothermal diminishing of the amorphous area during the cooking stage, A_{AmC} was fitted by a two-exponential expression given by the equation:

$$A_{AmC} = A_1 e^{-k_{1A}(t-t_0)} + A_2 e^{-k_{2A}(t-t_0)} \tag{1}$$

The fitting values are shown in Table 1. In the Figure 2 the fitting expressions and the experimental points are plotted.

The first term represents a fast dissolution process, which is characterized by $k_{1A} = k_{rest} \cong (0.47 \pm 0.06)\,\text{min}^{-1}$ and that is associated with the

TABLE 1 Values of the amorphous-area fitting parameters during the cooking stage

Parameter	*Value*
A_1	360 ± 65
A_2	255 ± 46
$k_{1A}(\text{min}^{-1})$	0.47 ± 0.06
$k_{2A}(\text{min}^{-1})$	0.024 ± 0.004
t_0(min)	9

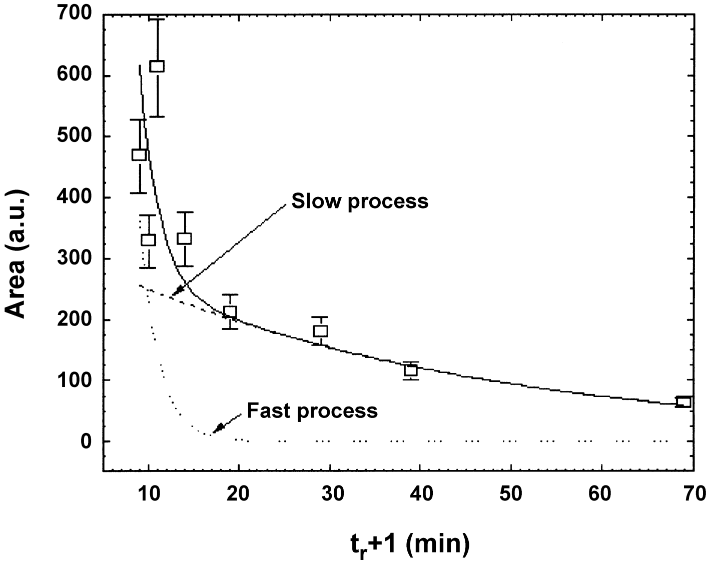

FIGURE 2 Variation of the amorphous area of the pericarp diffractograms during the cooking stage.

dissolution of hot-water-soluble pericarp components as starch and pectin, and of those alkali-soluble such as fat. The concentration of these components becomes negligible at times of about 15 min. The second term represents a slow process, associated to the alkaline dissolution of hemicelluloses [9], which is characterized by the dissolution rate $k_{2A} = k_{hemiB} \cong (0.024 \pm 0.004)\,\mathrm{min}^{-1}$.

The crystalline area shows a decrease from the raw pericarp to $t_r = 8$ min. From this point, in the isothermal conditions, the crystalline area continues diminishing but reaches a minimum value at about $t_r = 20$ min and increases again. This diminishing is explained from the moistening and swelling of the pericarp cellulose [11]. The observed maximum in the crystalline area observed at about $t_r = 38$ min, may be caused by a competition between the degradation of the chain end by extended swelling *versus* the stopping reactions.

During the steeping stage the bath reaches freely room temperature. As a consequence, the amount of lime dissolved in the bath increases, due to its solubility in water is about 4 times higher at RT than at 85°C [12]. The increase in concentration and the decrease in temperature are expected to increase the swelling power of the alkaline bath [11]. Intracrystalline swelling takes place at such conditions, leading to structural transformations in the cellulose. If limited swelling takes place, it is formed a stoichiometric combination between the alkaline reagent and the cellulose, known as alkaline-cellulose. Extended swelling lead to the formation of cellulose II, and eventually, disruption of the micelles and dissolution of the cellulose chain.

In the steeping stage ($t_r > 38$ min), both the crystalline and the amorphous areas diminish, but at $t_r > 68$ min the amorphous area increases suddenly, reaches a maximum and decreases again. Meanwhile, the crystalline area reaches a minimum at $t_r \approx 188$ min, to increase again. We attribute such behavior to the structural transformation of native cellulose into cellulose II together with the sudden stopping of that process when the sample is removed from the alkaline bath. The increase of the amorphous area for $t_r \geq 68$ min during the steeping stage was initially attributed to the effect of the coexistence of three kinds of cellulose, *i.e.*, cellulose I, alkaline cellulose and cellulose II, which extend the disorder to the intracrystalline and surface regions of the cellulose matrix. The further decrease together with the increase of the crystalline area up to 188 min, show that cellulose II is already formed in the alkaline bath.

Consecutive irreversible first-order reactions [13, 14] were considered to describe the isothermal transformation process of the cellulose during the steeping stage. Considering the formation of the unstable, intermediate alkaline cellulose, we can write the general reaction $C_1 \rightarrow C_A \rightarrow C_{II}$, with rate constant k_1 for the first reaction and k_2 for the second one. C_I, C_A

and C_{II} are the time-dependent concentrations of the native cellulose, alkaline cellulose and cellulose II respectively.

Equations 2(a)–(c) describe kinetically such transformations

$$\frac{dC_I(t)}{dt} = -k_1 C_I(t), \tag{2a}$$

$$\frac{dC_A(t)}{dt} = k_1 C_I(t) - k_2 C_A(t), \tag{2b}$$

$$\frac{dC_{II}(t)}{dt} = k_2 C_A(t). \tag{2c}$$

Since before the steeping, the *nixtamalization* proceeds under low lime concentration, and it is expected that a few or no native cellulose is transformed, we assumed that the initial concentration of alkaline and II-type celluloses are zero ($C_{A0} = C_{II0} = 0$). Then the solutions of the equations are:

$$C_I(t) = C_{I0} e^{-k_1(t-t_0)}, \tag{3a}$$

$$C_{IA}(t) = \frac{C_{I0} k_1}{k_1 - k_2} \left(e^{-k_1(t-t_0)} - e^{-k_2(t-t_0)}\right), \tag{3b}$$

$$C_{II}(t) = C_{I0}\left[1 + \frac{1}{k_1 - k_2}\left(k_2 e^{-k_1(t-t_0)} - k_1 e^{-k_2(t-t_0)}\right)\right]. \tag{3c}$$

The relationship between the component concentration in reaction and their physical properties is a function of the concentration and the time [13]. In our case this correlation was made between the concentration and the X-ray diffraction amorphous, A_{amorp}, and crystalline, A_{cryst}, areas, which according to the pericarp components are given by the expressions:

$$A_{cryst}(t) = \lambda_1 C_I(t) + \lambda_2 C_A(t) + \lambda_3 C_{II}(t), \tag{4}$$

$$A_{amorp}(t) = \lambda_4 C_{amorp}(t), \tag{5}$$

where the λ_i's correspond to the proportionality constants of the concentration of each component.

The fitting of the areas in the steeping stage shows that only native cellulose and cellulose II participate in the variation of the crystalline area. The fitting values are shown in Table 2 and the fitting curve is plotted in Figure 3.

TABLE 2 Values of the crystalline-area fitting parameters during the steeping stage

Parameter	*Value*
$\lambda_1 C_{I0}$(a.u.)	134 ± 14
$\lambda_2 C_{I0}$(a.u.)	~0
$\lambda_3 C_{I0}$(a.u.)	610 ± 32
k_1(min^{-1})	0.027 ± 0.008
k_2(min^{-1})	0.00077 ± 0.00005

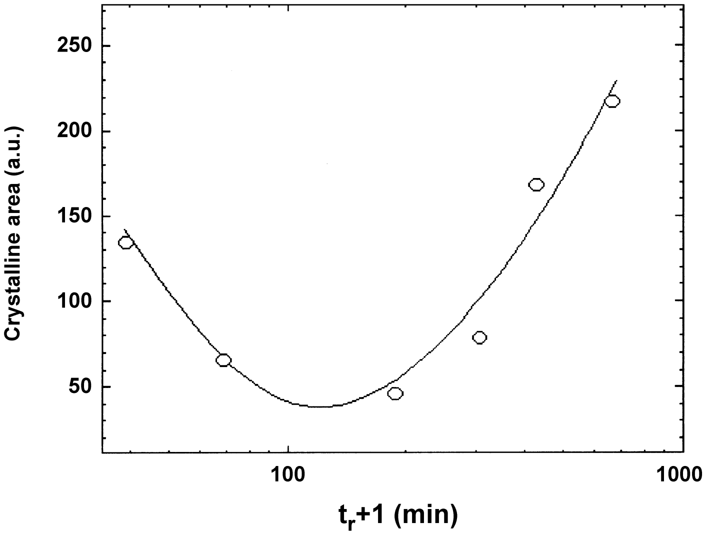

FIGURE 3 Variation of the crystalline area of the pericarp diffractograms during the steeping stage.

The behavior of the steeping-stage amorphous area was fitted considering the exponential extrapolation of the amorphous component area behavior described by the slow dissolution process in Eq. (1), which was subtracted from the experimental values. Then for $t > 39$ min the amorphous area is given by the expression:

$$A_{amorp}(t) = A_{HemiB}(t) + \lambda_5 C_A(t), \tag{6}$$

where $A_{HemiB}(t)$ is the amorphous area corresponding to the water soluble hemicellulose (HemiB) given, according to Eq. (1), by:

$$A_{HemiB}(t) = 255.1e^{-0.024\,min^{-1}(t-9\,min)}, \tag{7}$$

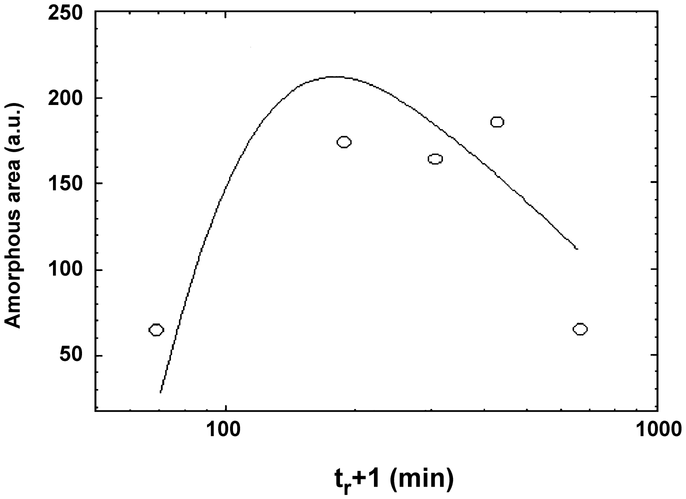

FIGURE 4 Variation of the amorphous area of the pericarp diffractograms during the steeping stage.

TABLE 3 Values of the amorphous-area fitting parameters during the steeping stage

Parameter	*Value*
$\lambda_5 C_{I0}$(a.u.)	210 ± 17
k_1(min^{-1})	0.031 ± 0.009
k_2(min^{-1})	0.0007 ± 0.0003

which is also shown in Figure 4. The fitting parameters are presented in Table 3. It is remarkable that the values of k_1 and k_2 are of the same order and coincide within their experimental errors for both the fittings.

The fitting results agree with the increment of the amorphous area for times longer than 39 min and its subsequent diminishing as shown in Figure 1. This means that the native cellulose transforms into cellulose-II structure through the alkaline cellulose if the process occurs totally in the alkaline solution, and when the sample is removed from the bath, washed and dried the alkaline cellulose does not transform into structurally ordered cellulose II as expected [11, 15], but it transforms into short-range ordered or amorphous cellulose II.

From the obtained values it can be said that the rate of transformation from native cellulose into alkaline cellulose is about 35 times higher than that from alkaline cellulose into cellulose II.

CONCLUSIONS

From X-ray diffraction measurements on corn pericarp samples taken during a typical *nixtamalization* process we studied the behavior of the crystalline and amorphous areas of the diffractograms of the pericarps taken at different processing times. Our results explain the physicochemical changes that take place during a typical *nixtamalization* process. These changes are mainly intercrystalline swelling and hemicellulosic fraction, followed by intracrystalline swelling and phase transition from cellulose I to cellulose II. From the kinetic fitting we determined the rates of dissolution of the amorphous components during the cooking stage and the reaction rates of the transformation from native cellulose into cellulose II during the steeping stage.

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