

Physicochemical Changes in the Hull of Corn Grains during Their Alkaline Cooking

REGINO GONZÁLEZ,[†] EDILSO REGUERA,^{*,‡} LEOBARDO MENDOZA,[§]
 JUAN MANUEL FIGUEROA,[§] AND FELICIANO SÁNCHEZ-SINENCIO^{||}

Faculty of Chemistry and Institute of Materials and Reagents, University of Havana, 10400 Havana, Cuba, Center of Applied Science and Advanced Technology of IPN, Mexico, D.F., Mexico, and Department of Physics, CINVESTAV-IPN, Mexico, D.F., Mexico

The alkaline cooking of corn in a solution of Ca(OH)₂ to produce corn-based foods is oriented to make corn proteins available, to incorporate Ca to the cooked grains, and also to remove the corn hull. This process (*nixtamalization*) is known in Mexico and Guatemala from prehispanic times; however, the effect of the alkaline cooking on the corn hull remains poorly documented. In this work, the physicochemical changes that take place in the corn hull during its cooking in a saturated solution of Ca(OH)₂ were studied using infrared, X-ray diffraction, ¹³C cross-polarization/magic-angle spinning (CP/MAS) NMR, confocal imaging microscopy, differential scanning calorimetry, and thermogravimetry techniques. The main effect of this treatment on the hull is the removal of hemicelluloses and lignin, increasing the hull permeability and, as a consequence, facilitating the entry of the alkaline solution into the corn kernel. No significant changes were observed in the cellulose fiber network, which remains as native cellulose I, with a crystalline index, according to ¹³C CP/MAS NMR spectra, of 0.60. The alkaline treatment does not allow the cellulose fibers to swell and their regeneration in the form of cellulose(II). It seems any attempt to make use of the Ca binding capacity of the hull to increase the Ca availability in *nixtamalized* corn-based foods requires a separated treatment for the hull and kernel. On alkaline cooking, the hull hemicellulose fraction dissolves, losing its ability to bind Ca as a way to incorporate this element into foods elaborated from *nixtamalized* corn.

I. INTRODUCTION

In Mexico and Guatemala corn is consumed mainly as tortillas. Tortillas are prepared from mass or flours obtained through an alkaline cooking and steeping of corn grains in a saturated solution of Ca(OH)₂, a process known as *nixtamalization* and used in this region from prehispanic times (1). The *nixtamalized* corn-based food is now also extended to other countries, including the U.S. The alkaline treatment is oriented to make corn proteins available, to incorporate Ca to the cooked grain, and also to remove the hull from the corn kernel (2–4). The lime-cooking process leads to a softening of the hull and to its easy removal from the corn kernel by a simple water washing. The hull hemicelluloses contain a small fraction of lignin, a phenolic polymer, which is easily oxidized in basic media, conferring an undesirable color to the *nixtamalized* corn-based products. Otherwise, since soluble hemicelluloses behave as gums, the partial hull retention in mass and flours could result in some positive functional properties, such as thickening, emulsifying, stabilizing and extending (5, 6). Additionally, the

cellulose fraction will be a source of dietetic fiber (6). The resulting cooking liqueur (*nejayote*) is an aggressive byproduct due to its relatively high pH and content of organic matter, which finds few uses (7).

Calcium is an essential element in human nutrition. Approximately 50% of Ca intake in Mexico and Guatemala, mainly in rural regions, is provided by tortillas and other products elaborated from *nixtamalized* corn (8). In corn Ca is retained according to the following order: hull > germ > endosperm (9). In the germ, Ca is found as salts of fatty acids, due to a partial saponification of its fats during alkaline cooking, while in the endosperm it forms inclusion compounds of these salts within the amylose helical structure (9). The hull, which only represents 5% of the grain weight, shows a pronounced ability to bind Ca through its acidic groups in the hemicellulose matrix, with a retention capacity of approximately 4 mg/g (10). If the hull were preserved, the Ca availability in the resulting mass and flours (elaborated from *nixtamalized* corn) would be higher. Any attempt of technological innovation oriented to hull preservation in *nixtamalized* corn-based foods must be preceded by a detailed understanding of those chemical and physical changes that take place in the corn hull during its alkaline cooking. In this paper some of these changes are reported, which were studied using infrared (IR), ¹³C cross-polarization/magic-

* To whom correspondence should be addressed at Apartado Postal 6313, Habana 6, C.P. 10600 Habana, Cuba.

[†] Faculty of Chemistry, University of Havana.

[‡] Institute of Materials and Reagents, University of Havana.

[§] Center for Applied Science and Advanced Technology of IPN.

^{||} CINVESTAV-IPN.

angle spinning (CP/MAS) NMR, X-ray diffraction (XRD), confocal imaging microscopy (CIM), differential scanning calorimetry (DSC), and thermogravimetry (TG) as sensing techniques. The amount of Ca retained on the alkaline-cooked hull samples was measured using atomic absorption spectrophotometry (AAS).

II. MATERIALS AND METHODS

Corn grains (variety Toluca from Mexico) were soaked in bidistilled water and their hulls manually separated to prevent contamination from the endosperm. The collected hull was then washed with abundant bidistilled water and dried in a vacuum oven at 60 °C for 24 h. Hull samples of 2 g were cooked at 80 °C for 1 h in 50 mL of bidistilled water containing 0.2, 0.4, 0.6, 0.8, and 1.0 g of Ca(OH)₂ using 250 mL Erlenmeyer flasks. In the following these samples will be labeled as H1, H2, H3, H4, and H5, respectively. The label H0 was reserved for the original hull sample. These ranges of Ca(OH)₂ concentrations were selected according to a previous study on the hull nixtamalization kinetics (11). Once the Erlenmeyer flasks were removed from the thermostatic bath at 80 °C, they were abruptly immersed in an ice-water bath (at 0 °C) to stop the cooking process. After this treatment, the samples were washed several times with bidistilled water until total removal of the excess Ca(OH)₂.

IR spectra were run in KBr pressed disks using an FTIR spectrophotometer (Equinox 55 from Bruker). The ¹³C CP/MAS NMR spectra were recorded in a Bruker ASX300 (300 MHz) spectrometer. For Ca determination in the hull samples by AAS, a Perkin-Elmer spectrophotometer and a standard Ca solution (from Carlo Erba) were used. An estimation of the hull capacity to bind Ca was carried out by pH titration. The pH determinations were carried out at room temperature.

The samples for CIM were studied in the reflection mode (RCIM) using an inverted diaphot 200 (Nikon) attached to an MRC 1024 laser scanning confocal system (Bio-Rad) with a Kr/Ar laser at three different wavelengths (488, 568, and 647 nm). The observations were made using 40× and 100× oil immersion objectives and B1 and T1 filter blocks in the 1 and 2 scanhead positions, respectively. The images were taken using 3% laser intensity, a 6–10 Kalman factor to reduce the photomultiplier noise, and a contrast stretch to enhance the image's appearance. Photographs were recorded with a 35 mm camera fitted to an Imagerecorder Plus (Focus) device.

The DSC data were collected on a Perkin-Elmer Pyris 1 calorimeter, in the range 30–400 °C at a heating rate of 5 °C/min under a nitrogen atmosphere. Differential thermal analysis (DTA) and TG data were obtained using a Dupont DTA instrument model 1600, in an oxygen atmosphere and at a heating rate of 5 °C/min. Sample masses of 5 and 10 mg were used.

The XRD powder patterns were obtained using a Siemens D500 diffractometer operated at 30 kV and 20 mA with Cu Kα radiation ($\lambda = 1.5406 \text{ \AA}$). The samples were scanned in the 2θ range 2–60° at a step of 0.025 and a counting time of 50 s per point. The experimental patterns were compared with those reported in the PDF Data Base (12) to identify the crystalline phases in the studied hull samples.

III. RESULTS AND DISCUSSION

IR Spectra. The corn hull is composed of a saccharide matrix with a small fraction of lignin, a phenolic natural polymer present in all natural fibers. In turn, the saccharide matrix is composed of cellulose, an ordered homopolysaccharide of glucose units, which usually presents crystalline order, and of hemicelluloses, which are amorphous heteropolysaccharides. Hemicelluloses have a complex composition, with a main chain of (1→4)- β -D-xylopyranosyl units to which side chains of one to several α -L-arabinofuranosyl and D-galactopyranosyl units and uronic acid or its 4-O-methyl ester are attached (13). Often hemicelluloses are partially acetylated, with an acetyl content up to 12% (14).

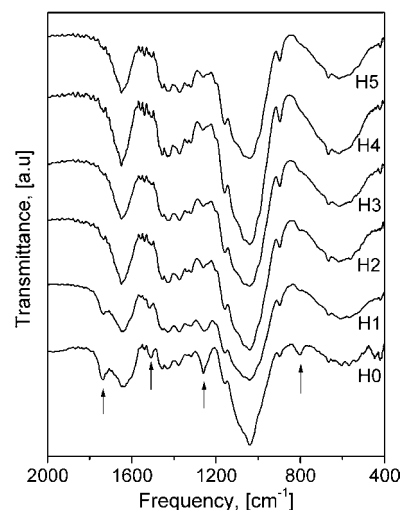


Figure 1. IR spectra (2000–400 cm⁻¹ region) of hull samples before (H0) and after (H1, H2, H3, H4, and H5) their alkaline cooking. Indicated are those IR absorption bands that can be used as sensors of the corn hull degradation during the nixtamalization process.

According to IR spectra, one of the first chemical changes that takes place in the hull during its alkaline cooking is the acidic group neutralization with formation of Ca salts. The band at 1737 cm⁻¹, due to the hemicellulose uronic acids, practically has disappeared in the H2 sample (Figure 1). From pH titration we have estimated a Ca retention by the hull of approximately 4 mg/g (discussed below). The corn hull is particularly rich in phenolic acids, mainly ferulic and diferulic (14) but also trifeluric (15), and a cooperative role of these phenolic acids with the uronic ones in the hull ability to bind Ca cannot be discarded. Ferulates are present in the insoluble fiber fraction of cereal grains linking two polysaccharide chains (of arabinoxylans), providing integrity to the cell wall (15).

The small lignin fraction in the corn hull is detected as a weak-intensity IR absorption at 1509 cm⁻¹ (Figure 1), tentatively assigned to phenyl groups in lignin and by the out-of-plane δ (C–H) vibration at 801 cm⁻¹. On the alkaline treatment lignin is removed by passing to the cooking liqueur (nejayote). In the H3–H5 samples these two bands are practically absent (Figure 1). In the IR spectra of hull samples there is another absorption at 1260 cm⁻¹ (tentatively assigned to ν (C–O) from esters), which senses the hemicelluloses matrix degradation. This band decreases its intensity on alkaline cooking (Figure 1).

¹³C CP/MAS NMR Spectra. ¹³C CP/MAS NMR spectra are very informative on the hull composition and on its changes on alkaline cooking (Figure 2). In Table 1 are reported the ¹³C signals observed in the untreated hull sample (H0) and their tentative assignment. The assignment was made according to the reported signals for lignocellulosic materials (16, 17). When the carbonyl signal at 173.3 ppm is decomposed, contributions from acidic groups (the main) and from esters can be resolved. On alkaline treatment that signal is significantly reduced in intensity due to the neutralization of the uronic acidic groups and formation of their Ca salts. The aryl-O signal at 149 ppm (from lignin) disappears on alkaline cooking, which indicates that lignin has passed to the nejayote. The weak and broad signal at 116.3 ppm is also from lignin (due to its C5 in the guaiacyl unit and C3/5 in the *p*-coumaric acid ester). This signal is absent in the cooked hull. The C1 signal from the saccharide units initially is broad with a shoulder at the right side as a hemicellulose contribution. This signal sharpens when the hull is nixtamalized, showing the narrow peak of cellulose (C1) and

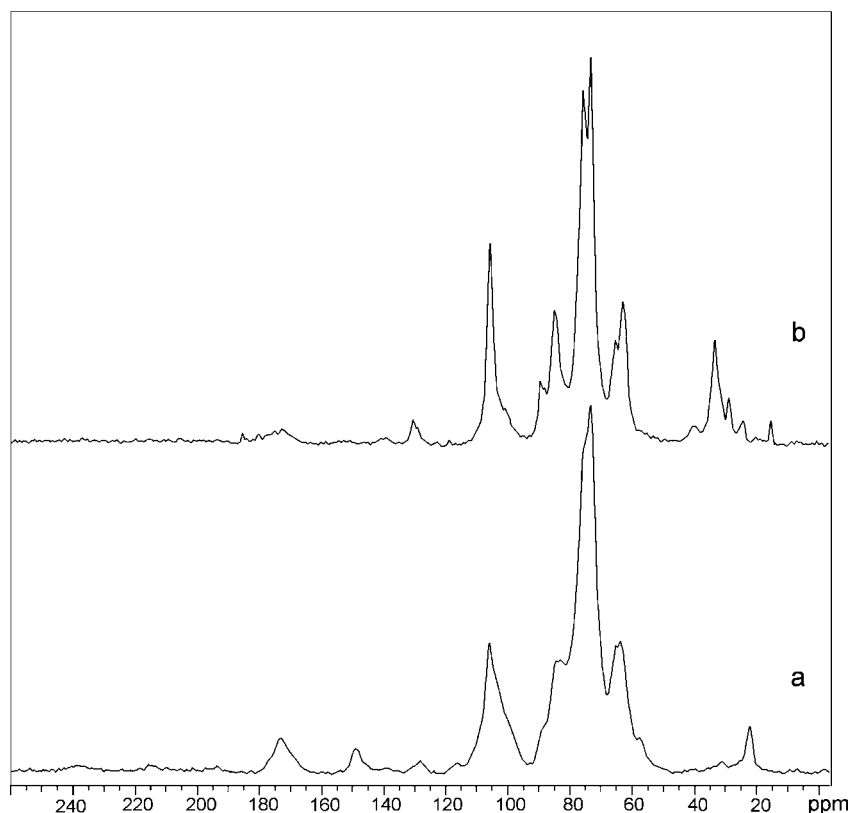


Figure 2. ^{13}C CP/MAS NMR spectra of corn hull samples before (a; H0 sample) and after (b; H2 sample) their *nixtamalization* process.

Table 1. ^{13}C CP/MAS NMR Chemical Shifts of Corn Hull Species before and after Alkaline Cooking^a

before alkaline cooking		after alkaline cooking	
signal, ppm	assignment	signal, ppm	assignment
173.34, br m	carbonyls (from uronic acids + esters)	173.2–185.6, br w	carbonyls (from residual acid groups + esters)
149.1, m	C in aryl-O from lignin	149.1 signal removed	
		129.4, 130.75, sh, w	aromatic C
128.2, w	aromatic C	128.2 signal removed	
116.3, br w	C5 in guaiacyl unit and C3/5 in <i>p</i> -coumaric acid ester from lignin	116.3 signal removed	
105.2, br s	C1 from hull saccharides	105.2, sh, s	C1 from cellulose(I)
101, shoulder, br m	C1 from hemicelluloses	101.1, w	C1 from residual hemicelluloses
60–90, br s, unresolved	C2–C6 from hull saccharides	63.2–89.7, sh, s, now resolved	C2–C6 from cellulose(I) + residual hemicelluloses
57.8, w	methoxyl group in guaiacyl and syringyl units from lignin	57.8 signal removed	
31.3, w br	CH ₂	31.3, appears as a shoulder	CH ₂
22.5, m, sh	acetyl groups of xylans (from hemicelluloses)	22.5 signal removed	
		15.5–39.8, m, sh	degradation products

^a s, m, or w = strong-, medium-, or weak-intensity signal; br or sh = broad or sharp signal.

residual hemicelluloses as a weak C1 signal at 101 ppm. The C2–C6 signals of saccharides appear unresolved in the native hull (H0), but they become well-resolved when hemicelluloses are removed, due to a higher crystalline order in the resulting material. The weak signal at 57.8 ppm is attributed to the methoxyl group in the guaiacyl and syringyl units from lignin. The acetyl groups of xylans (from hemicelluloses) are observed as a signal at 22.5 ppm, which is absent in the treated hull samples. The signals in the 15–40 ppm spectral region of the alkaline-cooked hull were interpreted as due to degradation products.

Comparing ^{13}C CP/MAS NMR spectra of the corn hull before and after its alkaline cooking, it is evident that when the hemicellulose and lignin fractions are removed, a material with a relatively higher crystalline order is obtained. According to

the C1–C5 signals of saccharides, that crystalline material is mainly composed of native cellulose (type I). In basic media native cellulose can be converted to cellulose(II) through a process known as *mercerization* (18), which is irreversible. It seems the *nixtamalization* conditions do not allow the cellulose fibers to swell and their regeneration in the form of cellulose(II).

The saccharide signals in the ^{13}C CP/MAS NMR spectra of the alkaline-cooked hull samples provide information on the cellulose structure. If the spectral regions 86–92 ppm (a) and 80–86 ppm (b) are integrated, the cellulose crystalline index (CrI) can be estimated according to $\text{CrI} = a/(a + b)$ (18–20), and the amorphicity index (AmI) will be $\text{AmI} = 1 - \text{CrI}$. For the hull sample H2, which is representative of a hull relatively free of hemicelluloses, the estimated values for these two

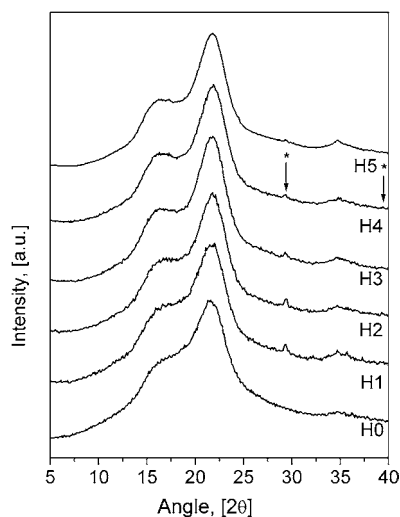


Figure 3. XRD powder patterns of corn hull samples before (H0) and after (H1, H2, H3, H4, and H5) their nixtamalization process. The cellulose network remains as native cellulose (type I). Indicated (*) are small reflections due to CaCO_3 (calcite).

parameters are $\text{CrI} = 0.60$ and $\text{AmI} = 0.40$. From these results it is evident that the hull cellulose is a material of relatively low crystalline order. In turn, the crystalline fraction of the hull cellulose is distributed in the I_α and I_β modifications, which is usual in native cellulose. The relative fraction of I_α and I_β modifications can also be estimated from ^{13}C CP/MAS NMR spectra, integrating the spectral regions 105.4–106.4 ppm (*c*), 104.4–105.4 ppm (*d*), and 103.3–104.4 ppm (*e*) and using the relations $I_\alpha = (\text{CrI})d/(c + d + e)$ and $I_\beta = (\text{CrI})(c + e)/(c + d + e)$ (19, 20). For the studied corn hull samples the following two parameters result: $I_\alpha = 0.48$ and $I_\beta = 0.12$. The relatively small contribution of I_β modification is observed as lateral shoulders at both sides of the main C1 signal at 105.2 ppm.

XRD Powder Patterns. Figure 3 shows the XRD powder patterns of the studied hull samples. No significant changes were observed in the crystalline fraction of the hull on alkaline treatment, except the removal of the amorphous fraction (mainly hemicelluloses) to give a better resolution of the main reflections from cellulose. These patterns correspond to native cellulose-

(I) of very low crystalline order. Their main peaks can be resolved in those reflections reported for cellulose(I) (PDF 03-0226) (12). No evidence of cellulose type II is observed in these patterns, which agrees with the ^{13}C CP/MAS NMR results concerning no conversion of cellulose(I) to cellulose(II) during the nixtamalization process. A small amount of CaCO_3 (calcite) was found in the nixtamalized hull samples, which is formed in the cooked liqueur or is present in the starting $\text{Ca}(\text{OH})_2$ reagent. In air $\text{Ca}(\text{OH})_2$ is easily transformed into CaCO_3 by interaction with the environmental CO_2 .

Confocal Microscopy Study of the Alkaline-Cooked Hull Samples. Figure 4 shows a set of RCIM images representative of the corn hull before (A–C) and after (D–F) its nixtamalization process. Image A corresponds to a border region where a network of cellulose fibers and a diffuse zone rich in hemicelluloses are observed. Image B shows a cloudlike hemicellulose surface as it is observed in the fluorescence mode. In image C the cellulose–hemicellulose composite can be observed (the cellulose fibers appear in red; green-yellow regions correspond to the hemicellulose–lignin matrix). From these images (A–C) it is evident that an untreated corn hull shows a surface layer rich in hemicelluloses and lignin with short fibers of cellulose, forming a composite material. The hemicellulose–lignin matrix shows certain fluorescence properties, which can be used for its identification in the corn hull. In the RCIM fluorescent mode images the hemicellulose–lignin matrix always appears as cloudlike continuous aggregates cementing the cellulose fibers or on the untreated external hull surface as a protecting outer glaze (image B). During alkaline cooking, the surface layer on the hull is removed and the inner hull cellulose is observed as an oriented array of relatively long fibers (image D). When the alkaline attack is very pronounced, these fibers form a corrugated-like structure, sometimes with a localized hemicellulose–lignin cumulus (images E and F).

One of the aims of the alkaline cooking of corn to produce mass or flour to elaborate tortillas and other corn-based foods is the corn hull softening to increase its permeability to facilitate alkaline liqueur entry to the corn kernel. The alkaline cooking of the kernel makes corn proteins available for human nutrition. According to the above-discussed ^{13}C CP/MAS NMR and XRD results, now also supported by the RCIM images, after a certain

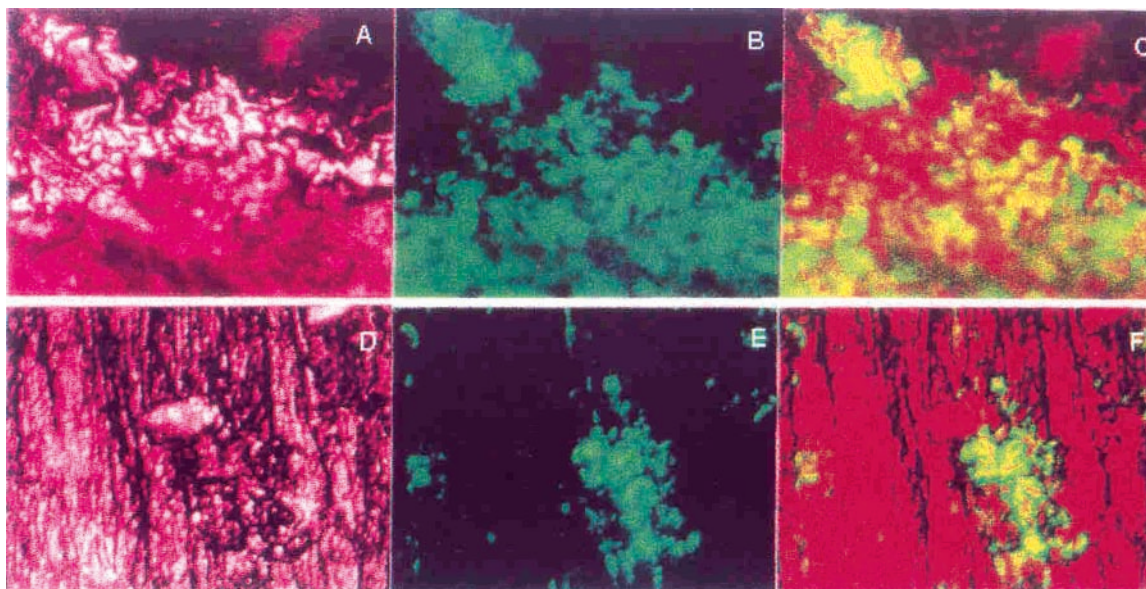


Figure 4. RCIM images representative of the corn hull before (A–C) and after (D–F) its nixtamalization process. The hemicellulose–lignin matrix is identified by its cloudlike appearance, while the cellulose fraction shows its typical structure of fibers.

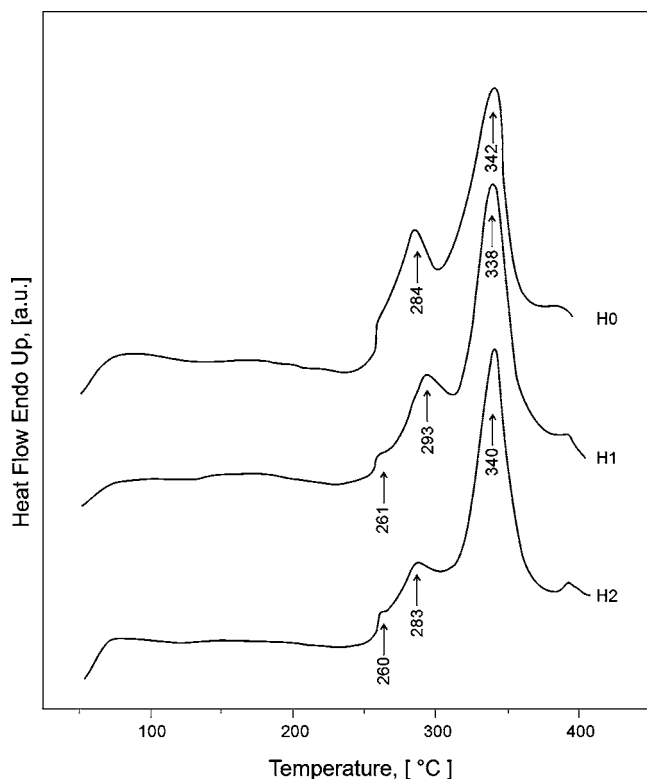


Figure 5. DSC curves of corn hull samples before (H0 sample) and after (H1 and H2 samples) their nixtamalization process.

level of alkaline treatment the residual hull, which remains attached to the corn kernel, is practically free of hemicelluloses and lignin, allowing a practically free interaction between the corn kernel and the cooking liqueur through the aleurone layer. That interaction takes place without total removal of the hull. A recent report on Ca ion diffusion in components of maize kernel during the nixtamalization process suggests a low permeability of the aleurone for the entry of water into the endosperm, when compared with the germ (21). However, the tipcap could behave as a weak physical barrier for the water diffusion, facilitating germ hydration.

DSC and TG Data. Even when hemicelluloses and cellulose have the same nature, they are polysaccharides, the higher structural order in cellulose must be detected as a higher thermal stability during the hull heating, when compared with the stability of the hemicellulose fraction. This different thermal behavior of cellulose and hemicelluloses could be used to detect their relative amount in the alkaline-cooked hull samples. **Figure 5** shows the DSC curves of the H0, H1, and H2 hull samples. The two main effects around 285 and 340 °C were interpreted as due to the hemicelluloses and cellulose decomposition processes, respectively. The small effect at 260 °C was tentatively assigned to the most disordered hemicellulose fraction. This minor effect cannot be assigned to the small lignin fraction since in the H2 sample lignin has been removed and a minor thermal effect remains. The intensity of the thermal effect around 285 °C decreases as does the amount of hemicelluloses in the alkaline-cooked hull; the higher the removed hemicellulose fraction, the smaller the thermal effect at 285 °C. The thermal effect assigned to the cellulose decomposition remains as it is observed in the native hull sample (H0) since during the nixtamalization process no significant changes take place in the cellulose component.

The TG curve of the studied material also informs us of its relative composition. The TG curves of the hull samples show three regions of weight loss (**Figure 6**). The weight loss up to 106 °C, 5.2%, was interpreted as a dehydration process. Then, at 227 °C a pronounced weight loss assigned to hemicellulose decomposition begins. Above 300 °C an inflection in the TG curves is observed, which indicates the beginning of the cellulose decomposition process. On hemicellulose removal, that inflection shifts toward higher temperatures. For the H1–H3 samples, the maximum change in the slope of the TG curves is observed close to 300 °C, approximately the temperature at which the inflection in the TG curve for the H0 sample was observed. In the H1–H3 samples the observed weight loss is mainly due to cellulose decomposition because these samples are poor in hemicelluloses. These results from TG curves are in agreement with those observed in the DSC experiments. Both thermal methods can be used to obtain information on the relative hull composition.

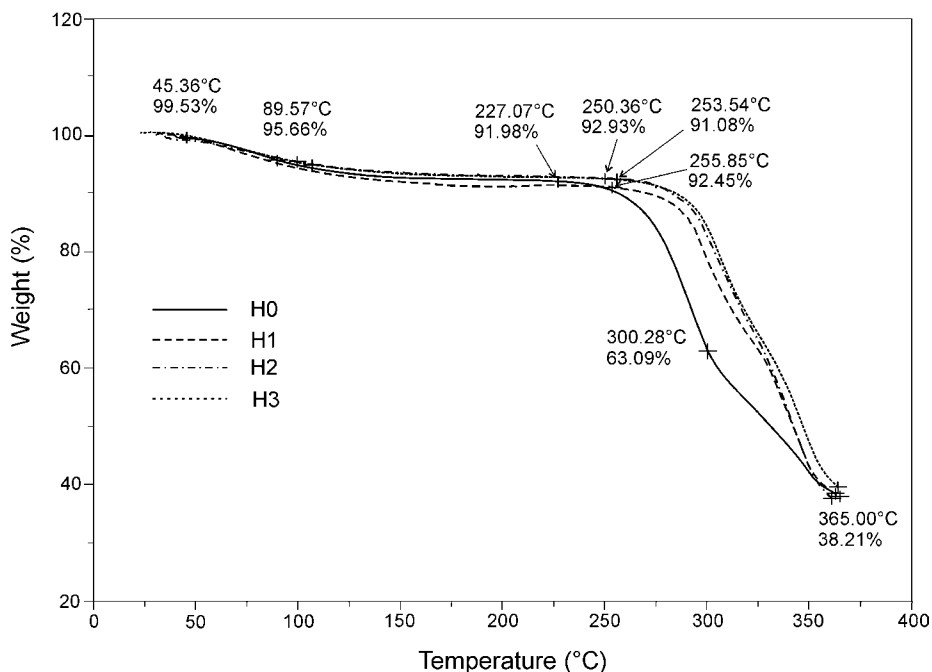


Figure 6. TG curves of corn hull samples before (H0 sample) and after (H1 and H2 samples) their nixtamalization process.

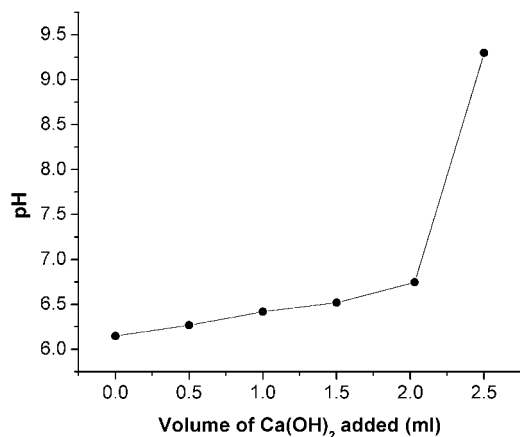


Figure 7. pH variation when a hull sample was immersed in distilled water (neutral) and then when drops of a standard solution of $\text{Ca}(\text{OH})_2$ were added. That behavior results from the hull acidic character.

Retention of Ca by the Corn Hull. The corn hull has an acidic character. When a hull sample without a previous treatment is immersed in distilled water (neutral), a decrease in its pH is observed (Figure 7). As already mentioned, hemicelluloses have acidic groups (uronic and phenolic) which are responsible for that behavior. If drops of a solution of $\text{Ca}(\text{OH})_2$ are added to that acidic aqueous medium, a slow increase in its pH is observed up to pH 7, where all the accessible acidic groups become neutralized. A further addition of $\text{Ca}(\text{OH})_2$ solution leads to a sudden increase in the pH value of that aqueous medium. From the amount of $\text{Ca}(\text{OH})_2$ required to neutralize a given mass of hull in neutral water, its Ca binding capacity can be calculated, which was 4 mg/g for the hull sample used to obtain the pH titration curve shown in Figure 7. For a hull containing 50% hemicelluloses with 7% uronic acid, a Ca retention capacity of 3.6 mg/g has been estimated,⁶ which is in excellent agreement with our estimation considering that the phenolic acidic groups could also be complexing Ca(II) ions. For short cooking times Ca is retained in corn grains according to hull > germ > endosperm (10, 21). This order results from the acidic character of hemicelluloses. When the alkaline treatment is prolonged and hemicelluloses dissolve, passing to the nejayote, Ca is preferentially retained by the germ due to a partial saponification of its fats, forming calcium salts of fatty acids (9).

The kinetics of the degradation of the corn hull during its nixtamalization depends on three factors: the pH of the solution and the temperature and time of cooking. Two parameters are effective for following the hull degradation process: the change in the viscosity of the cooking liqueur due to the dissolution of the hemicellulose–lignin matrix and the weight loss of the hull sample. Our previous results using these parameters as sensors can be summarized as follows (11): the hull degradation rate strongly depends on the amount of $\text{Ca}(\text{OH})_2$ and becomes appreciable when more than 10% $\text{Ca}(\text{OH})_2$ is used, the cooking liquor viscosity significantly increases when the temperature reaches at least 80 °C, and under these conditions ($\text{Ca}(\text{OH})_2$ concentration and temperature) the hull degradation becomes detectable after 10 min of treatment. Below 5% $\text{Ca}(\text{OH})_2$ the nixtamalization process leads to a decrease in the solution pH due to the consumption of OH^- by the hull, but above 20% $\text{Ca}(\text{OH})_2$ there is a sufficient amount of nondissolved calcium hydroxide to restore the amount of OH^- consumed, maintaining the solution pH at a constant level. In this sense the solution pH is not always a good sensor of the processes involved in the hull degradation; it serves to sense the first stage of the

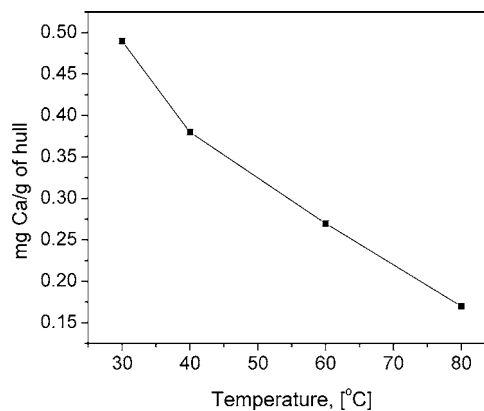


Figure 8. Degradation of the corn hull with the temperature of cooking as detected by the amount of Ca contained in the nondissolved hull fraction, mainly composed of native cellulose.

alkaline solution–hull interaction at relatively low $\text{Ca}(\text{OH})_2$ concentration. Figure 8 shows the hull degradation behavior according to the concentration of Ca measured (by AAS) in the nondissolved hull fraction for different temperatures of cooking in a solution with an initial concentration of 10% $\text{Ca}(\text{OH})_2$ maintained for 60 min in the thermostatic bath following a rapid cooling at 0 °C. As expected, the hull degradation leads to a rapid decrease in the ability of the nondissolved hull because it is mainly composed of cellulose without groups able to complex Ca. A small amount of Ca is always found in the hull of nixtamalized corn grains, but it is mainly in the form of CaCO_3 (calcite), as an occluded phase within the cellulose network and detected in the corresponding XRD patterns (Figure 3).

Conclusions. During cooking of the corn hull in a lime solution its hemicellulose and lignin fractions become soluble, passing to the cooking liqueur (nejayote). In the lime solution the acidic groups of hemicelluloses are rapidly neutralized, retaining Ca on the hull, but then, when hemicelluloses and lignin are removed, these Ca ligand species also go to the cooking liqueur, reducing the amount of Ca on the hull fraction that remains undissolved. This adhered fraction is mainly composed of native cellulose (type I). The nixtamalization conditions do not allow the cellulose fibers to swell and their regeneration in the form of cellulose(II). It seems any attempt to make use of the Ca binding capacity of the hull to increase the Ca availability in nixtamalized corn-based foods and, at the same time, remove the undesirable color sources (mainly lignin) requires a separated alkaline cooking of the hull and kernel. The soaking process of the corn kernel in the hot lime solution needs the hull to be removed, which in this treatment passes to the cooking liqueur, generating an aggressive byproduct and losing those functional properties that are inherent to the hull nature, for instance, the ability to retain Ca and act a source of dietary fibers.

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