

Effect of Lime on Gelatinization of Corn Flour and Starch¹

CORY M. BRYANT² and BRUCE R. HAMAKER^{2,3}

ABSTRACT

Cereal Chem. 74(2):171–175

Analysis of swelling power, water retention capacity, and degree of gelatinization of corn flour cooked in water with and without lime indicated, over a concentration range of 0–1% (w/v), that at low concentrations, lime increases swelling and digestibility of starch granules. Measurement of starch solubility revealed an increase in the amount of starch dissolved by lime cooking. Swelling, retention, and gelatinization exhibited maxima at or near 0.2% (w/v) lime, and then decreased as lime concentration increased. Hot-stage polarized light microscopy and differential scanning calorimetry of isolated starch revealed increasing gelatinization temperatures with

increasing lime concentrations. It is hypothesized that the high pH of the system causes starch hydroxyl groups to ionize, thereby creating binding sites for $\text{Ca}^{++}/\text{CaOH}^+$ and producing Ca-starch crosslinks. It is also suggested that, at low lime levels (<0.4%, w/v), granule crystalline regions are disrupted and the granule matrix is stretched by exchange of protons for calcium ions; when the lime level surpasses 0.4% (w/v), the granule shell becomes stabilized by Ca^{++} -starch interactions, producing stronger, more rigid granules.

A key to better understanding the formation of corn masa using the alkaline cooking process may be a better understanding of the interaction of starch and lime [$\text{Ca}(\text{OH})_2$]. The major component of the corn kernel is starch, and according to Trejo-Gonzales et al (1982), starch is responsible for the mechanical properties of the dough (masa) from lime-treated corn. Masa is produced by cooking whole corn kernels in excess water containing lime at concentrations of 0.5–2.0% (w/w) (Trejo-Gonzales et al 1982). Following the cooking step, the kernels are steeped (allowing the mixture to cool to 40°C) for 12–16 hr, followed by a washing step to remove the pericarp and excess lime. Washed kernels are then stone ground to produce masa, which may be processed to make tortillas and tortilla chip products. A fundamental understanding of the process is still lacking, resulting in an imprecise approach to its control and manipulation.

Changes due to lime cooking include weakening of kernel cell walls to facilitate pericarp removal, degradation or solubilization of the endosperm periphery, swelling of the starch granules throughout the kernel, maintenance of the granule integrity within the endosperm, and protein swelling without disruption of its position around the granules (Gomez et al 1989). Masa is composed of 52–54% moisture, 12–25% small endosperm and germ pieces, 19–31% free starch granules and cell wall fragments, and 3–4% dispersed solids and free lipids (Pflugfelder et al 1988). According to Gomez et al (1989), masa is held together by a “glue-like” mixture of dispersed solids in water (3–4% of the total wet masa), which consists of gelatinized starch, hydrated protein, lipids, and ions.

Various observers have shown that electrolytes affect the structure and swelling of starch granules (Oosten 1982, Rutenberg and Solarek 1984, Jane 1993). However, relatively few studies have focused on the action of $\text{Ca}(\text{OH})_2$ on starch. Gomez et al (1989) found decreased starch crystallinity and birefringence in corn cooked with lime. Gough and Pybus (1973) speculated that Ca^{++} ions delay gelatinization by reacting at the granule surface, causing it to swell and inhibit the supply of water to the granule interior.

The effect of lime on starch gelatinization as determined by the enzyme-susceptible starch (ESS) method has been reported. Two groups reported that 55% of the starch (550 mg of glucose/g of

starch) was gelatinized during the cooking step (Khan et al 1982, Serna-Saldivar et al 1988), whereas Gomez et al (1989) reported only a 4% loss of birefringence after this same treatment. Trejo-Gonzales et al (1982) used scanning electron microscopy (SEM) to analyze sections of corn grain that had been soaked in lime water for 0, 4, and 8 hr at room temperature. The micrographs revealed that there are differences in endosperm structure caused by soaking in lime water. They concluded that lime caused starch to gelatinize at room temperature.

Based on the calcium content of lime-treated grain as measured by atomic absorption spectrophotometry, Trejo-Gonzales et al (1982) reported that the calcium content of lime-treated corn kernels and starch isolated from lime-treated kernels was ≈ 4.5 and 2.9 times greater, respectively, than from nonlime-treated samples. They concluded that calcium is fixed or bound to the starch.

Dissociation of calcium hydroxide may produce monovalent [$\text{Ca}(\text{OH})^+$] or divalent (Ca^{++}) cations. Binding of calcium cations may occur to starch alkoxide groups produced by the alkaline conditions (Rutenberg and Solarek 1984).

The solubility of calcium hydroxide in water at 0°C is 0.185 g/100 mL and becomes less soluble with increasing temperature (Weast 1985). Yet preliminary work showed changing starch behavior above the saturation concentration. With this in mind, we characterized many aspects of starch behavior (gelatinization, solubility, and pasting) over a range of $\text{Ca}(\text{OH})_2$ concentrations (0.0–1.0%, w/v) with the objective of better understanding how the cation and starch granule might interact.

MATERIALS AND METHODS

Sample Preparation

Normal dent corn was obtained from Frito-Lay, Inc. (Frankfort, IN). Maize kernels were ground using a Buhler-Miag mill (model MLI-204, Minneapolis, MN) at the widest gap setting and then passed through a sample mill (Tecator Cyclotec 1093, Höganäs, Sweden) using a 0.5-mm screen. Defatted flour was prepared by washing flour with petroleum ether (1:4 flour to ether) five times. Starch was isolated from the corn using a modification of Watson's method (1964). Corn kernels were steeped overnight in 0.54% NaHSO_3 at 50°C. After decanting the soak solution, the kernels were ground in a Waring blender with 50 mM NaCl. The slurry was then passed through a 170-mesh sieve followed by shaking for 10 min in toluene (1:10, v/v), and then centrifuging at 1,000 $\times g$ for 10 min. The supernatant was discarded, and the toluene wash was repeated five times (until the toluene phase was clear). The starch was then washed with purified water (Barnstead

¹Paper 15096 from the Purdue Agricultural Experiment Station.

²Department of Food Science and the Whistler Center for Carbohydrate Research, Purdue University, 1160 Smith Hall, West Lafayette, IN 47907-1160.

³Corresponding author. E-mail: hamakerb@foodsci.purdue.edu

NANOpure II, Boston, MA) and recovered by centrifugation (1,000 × *g*, 10 min). After washing with 70% ethanol, the starch was allowed to soak in ethanol overnight. The starch was again recovered by centrifugation (1,000 × *g*, 10 min). An acetone wash (1:5 starch to acetone) completed the isolation.

Protein Content

Protein content of samples was determined by the micro-Kjeldahl method (AACC 1995). The isolated starch and defatted flour contained 0.7 and 7.7% protein, respectively.

Lime [Ca(OH)₂]

Lime [Ca(OH)₂] was obtained from Sigma Chemical Co. (C-7887, lot 14H3511, St. Louis, MO).

Sample pH Values

The pH value was determined using a pH meter equipped with a deep vessel combination electrode (Corning 125, Medfield, MS). The pH meter was calibrated at room temperature. The temperature setting was adjusted to that of the sample. pH was determined for lime-water suspensions of 0.0 to 1.0% lime, and for 10% starch-lime-water suspensions of 0.0 to 1.0% lime. Suspensions (10 mL) were placed in a boiling water bath for 3 min and then transferred to a 60°C water bath and allowed to equilibrate to 60°C. Readings were taken on four replicate samples.

Water Retention Capacity

Water retention capacity was determined according to the method of Hallgren (1985). Defatted corn flour suspensions (5.0%) with 0.0, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0% (w/v) added Ca(OH)₂ were used. Water was added to flour in preweighed centrifuge tubes at room temperature and then heated at 85°C for 15 min, with shaking at 5 and 10 min. The tubes were then centrifuged for 15 min at 1,000 × *g*, 10 min. The supernatant was decanted and the tubes were allowed to drain for 10 min at a 45° angle. The tubes were then weighed and the gain in weight was used to calculate percent gain as the water retention capacity. Experiments were performed in duplicate.

Brabender Amylography

Brabender peak viscosity, setback, temperature of initial viscosity increase, and temperature of peak viscosity were determined on 10% defatted flour-water suspensions treated with 0.0, 0.1, 0.2, 0.5, and 1.0% Ca(OH)₂ using a Brabender temperature programmed viscometer (Visco/amylo/Graph, C.W. Brabender Instruments, Inc.; South Hackensack, NJ). Samples were heated at 1.5°C/min for 48.6 min to 95°C, held at that temperature for 10 min, and then cooled for 20 min to 65°C. Samples were analyzed in triplicate.

Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) was performed using a Mettler DSC 30 with on-line Mettler TC11 TA processor (Hightstown, NJ). Data was analyzed by the Mettler TA 4000 computer program. Results were plotted on a Hewlett-Packard 7475A plotter.

Suspensions (1:3) of isolated starch-water and defatted flour-water were prepared with added 0.0, 0.1, 0.2, and 1.0% Ca(OH)₂ (w/v). Samples (10–20 mg) were then weighed into preweighed, coated aluminum, hermetic DSC sample pans (Mettler), which were sealed and allowed to equilibrate overnight. The DSC head was precooled to 25°C using liquid nitrogen. The sample pan was placed on the sample holder with an empty pan as the reference. The temperature was increased to 110°C at a scanning rate of 10°C/min. Samples were analyzed in triplicate.

Polarized Light Hot-Stage Microscopy

A polarized light microscope (Laborlux 12 POL, Leitz, Wetzlar, Germany) equipped with a Leitz 350 heating stage was used for

all experiments. Temperature was monitored by a BBC Goerz Metrawatt (Wetzlar, Germany) Metratherm 1200d thermal gauge. The onset and final temperatures of gelatinization were obtained by analysis of 5.0% (w/v) isolated corn starch samples treated with 0.0, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0% Ca(OH)₂ (w/v) and 5.0% (w/v) defatted corn flour samples treated with 0.0, 0.2 and 1.0% Ca(OH)₂ (w/v). Onset was recorded as the temperature at which the first granule was noted to lose birefringence; at final temperature >95% had lost birefringence.

Samples of defatted corn flour cooked 15 min at 85°C in 0.0, 0.1, 0.2, 0.4, 0.6, 0.8, and 1.0% (w/v) lime solution were centrifuged at 1,000 × *g*, 10 min for 15 min and the pellet was observed for evidence of birefringence. Analyses were performed in triplicate.

Degree of Gelatinization

Degree of starch gelatinization was measured using a modification of the enzymic method of Kainuma et al (1994). Flour or starch (1 g) was added to 20 mL of purified water or lime water suspension in a 75-mL test tube and heated in a boiling water bath for a specified time, vortexing every 2 min for the first 10 min. After removal from the bath, the samples were brought to 50 mL with 60°C water and homogenized. Aliquots were placed in 25-mL volumetric flasks. For the fully gelatinized reference, separate 2-mL aliquots were placed in small test tubes, gelatinized completely by treatment with 0.2 mL of 10M NaOH, swirled, and incubated in a 60°C bath for 5 min. One milliliter of 2M acetic acid was added, and the sample was vortexed. The contents of these tubes were then transferred quantitatively to 25-mL volumetric flasks. All samples were brought to volume with 0.8M acetate buffer (pH 6.0). Aliquots (4 mL) were taken from each flask and placed in screw-cap test tubes. Enzyme solution (1 mL, 0.8 IU β-amylase and 3.4 IU pullulanase) was added to each tube and the contents mixed. Unused enzyme solution was inactivated by boiling and added to a separate 4-mL sample to be used as a blank. Tubes were capped and incubated at 40°C for 30 min in a shaking water bath. The tubes were then transferred to a boiling water bath for 5 min. Contents were transferred to centrifuge tubes and centrifuged at 6,000 × *g* for 10 min. Supernatants were removed and placed in test tubes. Supernatants (1 mL) were diluted to 2 mL and analyzed by the Somogyi-Nelson method (Nelson 1944; Somogyi 1945, 1952) to measure reducing sugars. A second 0.5-mL sample of supernatant was removed, diluted to 10 mL with water, and analyzed for total sugars by the phenol-sulfuric acid method (Dubois et al 1956).

Lime-cooked samples were treated in the same way, the only difference being that lime was added to the cooking solution. Defatted corn flour suspensions (5.0%) were treated with 0.0, 0.2, 0.4, 0.6, 0.8, and 1.0% Ca(OH)₂ (w/v). The pH of lime-treated samples was measured before enzyme addition and determined to be buffered effectively by the acetate buffer. Enzyme suspensions of β-amylase (2,220 U/mg) and pullulanase (42.7 U/mg) were obtained from Megazyme Pty. Ltd. (Sydney, Australia). Samples were analyzed in duplicate.

Soluble Starch

Isolated normal corn starch-water, waxy maize starch-water, and defatted corn flour-water suspensions (5.0%) treated with 0.0–1.0% (w/v) (in increments of 0.2%) lime were placed in a boiling water bath for 15 min. Samples were centrifuged at 3,000 × *g* and the supernatant removed. The supernatants of four replicate samples were analyzed for glucose (soluble starch) content by the phenol-sulfuric acid method (Dubois et al 1956).

Statistics

The SigmaStat package (Jandel Scientific, San Rafael, CA) was used to analyze data by analysis of variance, and significant differences among means were established using the Student-Newman-Keul's test (Steel and Torrie 1983).

RESULTS

Corn samples uniformly exhibited starch behavior changes at lime concentrations both below and above the known saturation concentration of lime in water. [Solubility of $\text{Ca}(\text{OH})_2$, 0.185 g/100 mL at 0°C, decreases with increasing temperature to 0.077g/100 mL at 100°C (Weast 1985)].

pH of Samples

Figure 1 displays the effect of increasing lime concentration on the pH of lime-water and cooked corn starch-lime-water suspensions held at 60°C. Addition of 0.1% lime to water increased the pH from 7.44 to 11.59. Addition of more lime to a concentration of 1.0% increased the pH by only 0.21 units to pH 11.80. Upon cooking an isolated corn starch suspension in 0.1% lime, the pH increased to only 11.22, indicating a decrease in pH with the addition of starch to the system. Further addition of lime to 0.4% increased the pH to 11.80, where it leveled off, increasing only to 11.84 at 1.0% lime. These results indicate effective saturation of the aqueous phase with lime at concentrations ≤ 0.1 and 0.4% at 60°C in the absence and presence of corn starch, respectively.

Water Retention Capacity

Water uptake increased by the addition of lime to the cooking water (Fig. 2). Defatted flour had greatest water retention capacity at 0.1% lime concentration, from which it decreased dramatically up to a lime concentration of 0.6% and then leveled off. At lime concentrations $>0.4\%$, the uptake of water was less than that of nonlime-treated flour.

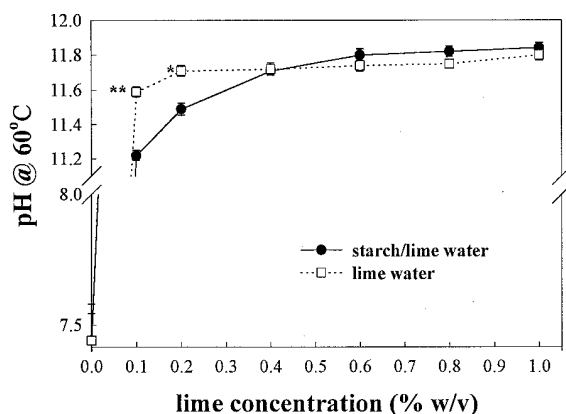


Fig. 1. pH profile of cooked corn starch-lime water and lime water suspensions. Error bars indicate standard deviation. At lime concentrations of 0.1 and 0.2% there were significant differences between treatments (** = $P < 0.001$; * = $P < 0.01$).

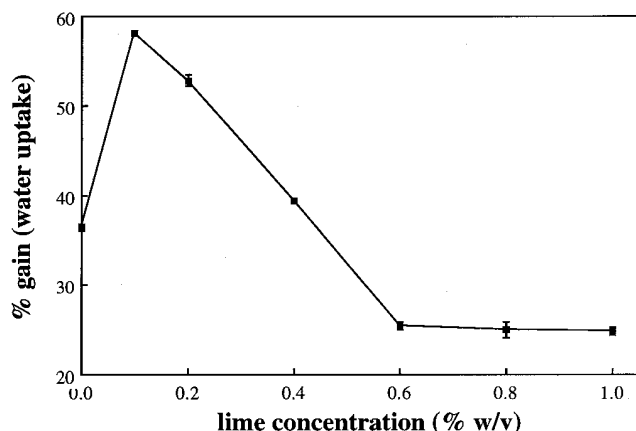


Fig. 2. Effect of lime concentration on the water retention capacity (% gain in weight) of defatted corn flour. Error bars indicate standard deviation.

Brabender Amylography

The effect of lime cooking and lime concentration on the viscosity of defatted flour-water suspensions (10%, w/v) was investigated using Brabender amylography (Fig. 3). The temperature of the initial increase in viscosity, showed some change, ranging between 67 and 73°C. The temperature of peak hot paste viscosity, which is indicative of complete gelatinization, was significantly affected by changes in lime concentration. Peak viscosity temperature decreased upon the addition of lime up to 0.5%, indicating faster granule swelling that requires less thermal energy. A further increase in lime concentration to 1.0% eliminated any apparent peak, indicating a lack of breakdown of swollen granules, slower granule swelling, and a demand for greater thermal energy to obtain equivalent swelling.

The hot paste peak viscosity was highest at 0.1% lime concentration. Further addition of lime (>0.1 to 0.5%) decreased peak viscosity from ≈ 540 to 360 BU. The highest value obtained for the viscosity at the end of the 95°C holding period and the cooling period resulted from heating flour in 1.0% lime solution. Both viscosities followed the same trend as the peak viscosity, decreasing with increasing lime concentration between 0.1 and 0.5%.

Differential Scanning Calorimetry

The effect of increasing lime concentration on changes in temperature of gelatinization of isolated starch and defatted flour suspensions was investigated by means of DSC. An effect of lime on the gelatinization temperature of defatted corn flour samples was not apparent (not shown). In the case of lime-treated corn starch

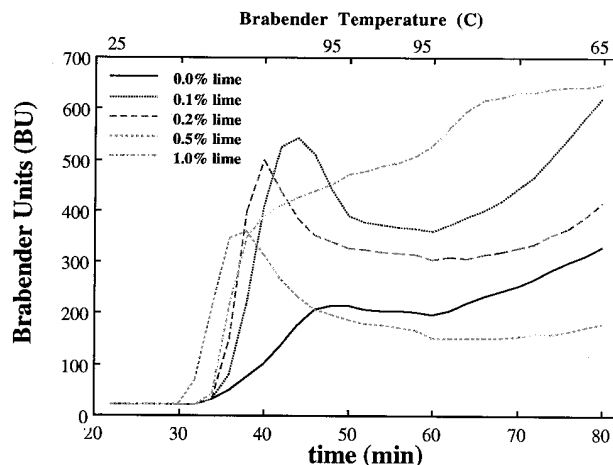


Fig. 3. Effect of lime concentration on the viscosity of defatted flour suspensions (10%, w/v) as determined by Brabender amylography.

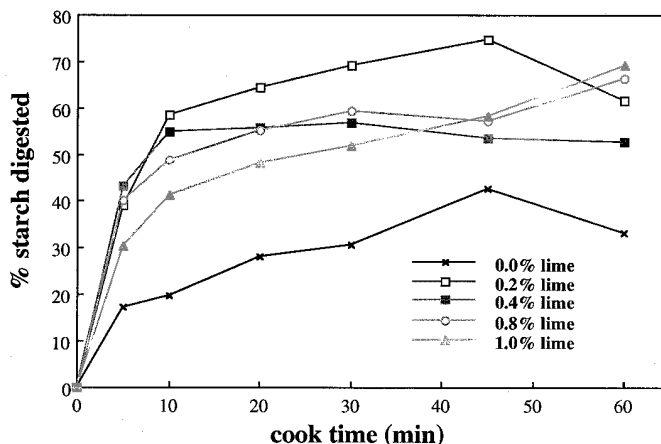


Fig. 4. Effect of lime concentration and cook time on the degree of gelatinization (the amount of starch susceptible to enzymic digestion) of suspensions of defatted corn flour (5.0%, w/v).

isolate, the gelatinization temperature increased with increasing lime concentration (Table I). Enthalpy values of the starch were approximately equal for all treatments.

Polarized Light Microscopy

The initial (onset) and final (completion) temperatures for loss of birefringence of isolated starch increased with increasing lime concentration (Table I). When starch was gelatinized in lime solutions at concentrations between 0.2 and 0.8% both temperatures increased, followed by a leveling to 1.0% concentration.

The initial and final temperatures for loss of birefringence increased due to the action of lime on defatted corn flour (not shown). However, the increase in both temperatures was much smaller than that for starch.

Pellets of centrifuged, gelatinized, defatted corn flour samples were also analyzed by polarized light microscopy (not shown). The 0.0 and 0.1% lime-cooked samples contained no intact or birefringent granules, and the sample appeared amorphous. The sample cooked in 0.2% lime also contained no birefringent granules, in addition to a small number of intact nonbirefringent granules or granule remnants. The number of these intact nonbirefringent granule remnants increased with increasing lime concentration. At concentrations of 0.8 and 1.0% lime, a small number of tiny granules were observed to retain birefringence to temperatures near 100°C.

Degree of Gelatinization

Figure 4 shows that the amount of digestible starch increased (based on the β -amylase-pullulanase method) when cooked in the presence of lime. Defatted flour cooked in a 0.2% lime solution resulted in the greatest starch digestibility. Concentrations >0.2% exhibited increased digestibility, but to a lesser extent. In the presence of 0.2–0.8% lime, >75% of the starch susceptible to enzyme digestion was produced in the first 10 min of heating in a 100°C bath. Cooking in 1.0% lime decreased this to 65%, and cooking without lime resulted in <50% of the gelatinization occurring in the first 10 min.

Soluble Starch

Starch solubilized after cooking and assayed as glucose in the supernatant peaked at 0.2% lime for both the isolated starch and defatted corn flour samples (Fig. 5). However, the peak was at 0.4% lime for waxy maize starch. The increase in amount of starch solubilized over that in the nonlime treated samples dropped significantly with increasing lime concentration to 0.8% and then leveled to 1.0%.

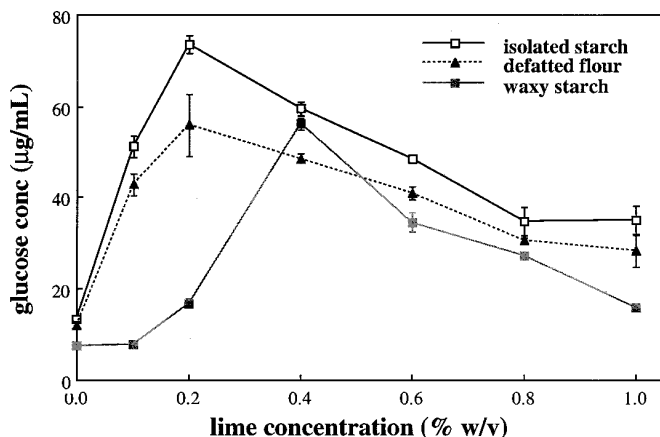


Fig. 5. Effect of lime concentration on the assayable glucose content of the supernatant of isolated corn starch, waxy corn starch, and defatted corn flour suspensions (10%, w/v) cooked 15 min. Error bars indicate standard deviation.

Results show that the effect of lime on the gelatinization properties of corn starch is a complex and concentration dependent phenomenon. With increasing lime concentration, two distinct trends in the gelatinization pattern were apparent: the first occurring between 0.0 and \approx 0.4% lime, and the second occurring at >0.4% lime. When cooked in low concentrations of lime (<0.4%), starch granules were more susceptible to enzyme attack, held more water, swelled to a greater extent, solubilized more, and produced greater viscosity as compared to samples cooked in water. Conversely, when treated with higher lime concentrations (>0.4%), the granules appeared to be stabilized and the trends reversed. The gelatinization properties of corn starch varied with changing lime concentration at concentrations above the saturation concentration [0.185 g/100 mL at 0°C to 0.077 g/100 mL at 100°C (Weast 1985)]. We interpret this to mean that lime is consumed and bound by starch.

The decrease in pH due to the addition of starch to a lime-water system, (5.0% starch, <0.4% lime), even though slight, indicates that flour binds Ca^{++} or $\text{Ca}(\text{OH})^+$ (Fig. 1). The pH of lime water was almost at its maximum at a concentration of 0.1% lime (60°C), indicating that maximum solubility of lime is nearly reached at this level. This was not true of the starch-water system, where the pH did not approach maximum until the lime level reached 0.4%, indicating that the starch is nearly saturated with lime at this concentration. Due to the high pH of the system, some starch hydroxyl groups should have ionized (Rendleman 1966, Oosten 1982, Rutenberg and Solarek 1984), making them sites for interaction with the Ca^{++} or CaOH^+ of dissociated $\text{Ca}(\text{OH})_2$, thereby shifting the equilibrium and allowing greater solubilization of lime.

At lime concentrations of 0.1–0.2%, water retention reached a maximum level, while at concentrations >0.2% retention decreased until, at >0.4%, it was less than that of nonlime-treated flour (Fig. 2). We postulate that Ca^{++} - and $\text{Ca}(\text{OH})^+$ -starch interactions are responsible for this phenomena. The reversal in water retention may be due to the saturation of the starch hydroxyl sites with cations. At low lime concentrations, crystalline regions are likely to be disrupted by alkali, and as suggested by Oosten (1983), the granule matrix is stretched by the replacement of protons with cations, thereby increasing the granule volume. At higher concentrations, Ca^{++} ions act to stabilize the granules and increase their rigidity, decreasing their volume. Oosten (1982) suggests that divalent cations bind tightly with starch molecules actually causing water holding capacity to decrease. It appears that a certain cation concentration (\approx 0.4% lime) is required for this to occur.

Visual examination of flour samples cooked at lime concentrations >0.6% revealed samples that appeared dry and ungelatinized. This may be due to increased granule rigidity caused by

TABLE I
Thermal Characteristics of Starch Cooked in Lime Solution as Determined by Differential Scanning Calorimetry (DSC) and Hot-Stage Microscopy^{a,b}

% Lime	DSC			Hot-Stage	
	T_o	T_p	T_c	T_o	T_c
0.0	62.9a	69.3a	77.6a	61.5a	71.2a
0.1	66.1b	72.4b	80.6b	65.5b	74.5b
0.2	66.9b	73.0b	81.5b	65.0b	72.0a
0.4	69.4c	75.3c	83.1c	69.0c	75.5b
0.6	69.5c	75.5c	82.8c	75.2d	84.8c
0.8	70.0c	76.6c	84.1c	81.0e	87.1d
1.0	72.1d	79.2d	92.0d	81.5e	87.5d

^a Mean values followed by the same letter within a column were not statistically different at $P < 0.05$.

^b T_o , T_p , and T_c = onset, peak, and completion temperatures, respectively.

Ca⁺⁺-starch interactions that stabilize granules and reduce water retention. Lower starch solubilization at high lime concentrations may also indicate crosslinking by cations.

The extent of maximum granule swelling increased by lime cooking at concentrations up to 0.5% (Fig. 3). Above 0.5%, more thermal energy was required to swell to point of rupture. Cooking in 1.0% lime appeared to inhibit the rupture of granules as indicated by the fact that there was no loss in viscosity. This characteristic is similar to that of crosslinked starches (Rutemberg and Solarek 1984).

DSC and polarized light microscopy data indicated that the gelatinization temperature of starch is increased with increasing lime concentration (Table I). The DSC peak temperature of the starch sample increased significantly with increasing lime concentration from ≈68°C at 0.0% to ≈78°C at 1.0% lime. The defatted flour sample showed a less dramatic response to lime treatment. These findings were supported by polarized-light microscopy, which showed a significant increase in both the onset and final temperatures of gelatinization in the starch sample with increasing lime concentration; yet among the defatted flour samples only negligible differences were found. At increasing lime concentrations, Ca⁺⁺-starch interactions could produce granules with increased structural integrity.

The amount of enzyme digestible starch upon lime cooking (Fig. 4) was in agreement with results reported by Khan et al (1982) and Serna-Saldivar et al (1988). The increase in digestible starch, which appeared to peak at ≈0.2%, may be due to the disruption of associated regions of the granule interior that provides enzymes greater access to starch molecules. We attribute the decreasing trend in solubility at lime concentrations >0.2% to the increased structural integrity of the granule due to Ca⁺⁺ starch interaction. Lime cooking increased the amount of starch solubilized, which would also contribute to starch digestibility. The lower solubility of defatted flour can be attributed to the decrease in starch content of flour versus that of isolated starch. At low lime concentrations, the low solubility of waxy maize starch suggests that amylose comprises most of the solubilized starch in normal corn starch.

CONCLUSIONS

Ca(OH)₂ is consumed and bound by starch granules upon treatment of starch with lime. The high pH of the alkaline system appears to promote starch hydroxyl group ionization, thus creating opportunity for interaction between Ca⁺⁺ or CaOH⁺ and starch molecules. Ionization of starch hydroxyl groups would lower the pH of the solution, thereby increasing the solubility of lime. Starch gelatinization indicators, such as enzyme digestion, water retention capacity, starch solubility, and gelatinization temperature, are increased by addition of lime at levels between 0 and ≈0.4–0.5%, peaking at 0.2%. At levels >0.4–0.5%, most of these properties are retarded by the presence of lime (digestion, water retention, and solubility), while gelatinization temperature is further elevated. We postulate that, at low lime levels, the granule matrix is stretched by exchange of protons with Ca⁺⁺ or CaOH⁺ ions. When the lime level surpasses 0.4%, the granule shell becomes stabilized by calcium-starch interactions producing stronger, more rigid granules. We also speculate that at 1.0% lime starch granules are essentially crosslinked, producing breakdown-resistant granules with high viscosity forming potential.

The findings presented here are not meant to be directly applied to those occurring within the corn kernel during masa processing. However, the data does show an optimum change in starch behavior at a lime level similar to that used by the corn masa indus-

try, and we feel our results act as a good indicator of the chemistry occurring around the periphery of the kernel where water is more abundant and gelatinization takes place.

ACKNOWLEDGMENTS

We thank Frito-Lay, Inc. for partial support of this project.

LITERATURE CITED

- AMERICAN ASSOCIATION OF CEREAL CHEMISTS. 1995. Approved Methods of the AACC, 9th ed. The Association: St. Paul, MN.
- AOAC. 1984. Association of Official Analytical Chemists Official Methods of Analysis, 14th ed. The Association: Arlington, VA.
- DUBOIS, M., GILLES, K. A., HAMILTON, J. K., REBERS, P. A., and SMITH, F. 1956. Colorimetric method for determination of sugars and related substances. *Anal. Chem.* 28:350-356.
- GOMEZ, M. H., McDONOUGH, C. M., ROONEY, L. W., and WANISKA, R. D. 1989. Changes in corn and sorghum during nixtamalization and tortilla baking. *J. Food Sci.* 54:330-336.
- GOUGH, B. M., and PYBUS, J. N. 1973. Effect of metal cations on the swelling and gelatinization behaviour of large wheat starch granules. *Starch/Staerke* 25:123-130.
- HALLGREN, L. 1985. Physical and Structural Properties of Cereals, Sorghum in Particular, in Relation to Milling Methods and Product Use, Vol. 1. Carlsberg Research Laboratory, Technical University of Denmark: Copenhagen.
- JANE, J. 1993. Mechanism of starch gelatinization in neutral salt solutions. *Starch/Staerke* 45:161-166.
- KAINUMA, K. 1994. Determination of the degree of gelatinization and retrogradation of starch. *Meth. Carbohydr. Chem.* 10:137-141.
- 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.
- NELSON, N. 1944. A photometric adaptation of the somogyi method for the determination of glucose. *J. Biol. Chem.* 153:375-380.
- OOSTEN, B. J. 1982. Tentative hypothesis to explain how electrolytes affect the gelatinization temperature of starches in water. *Starch/Staerke* 34:233-239.
- OOSTEN, B. J. 1983. Explanations for phenomena arising from starch-electrolytes interactions. *Starch/Staerke* 35:166-169.
- PFLUGFELDER, R. L., ROONEY, L. W., and WANISKA, R. D. 1988. Fractionation and composition of commercial corn masa. *Cereal Chem.* 65: 262-266.
- RENDLEMAN, J. A., JR. 1966. Complexes of alkali metals and alkaline-earth metals with carbohydrates. Pages 209-271 in: *Advances in Carbohydrate Chemistry*, Vol. 21. Academic Press: New York.
- RUTENBERG, M. W., and SOLAREK, D. 1984. Starch derivatives: Production and uses. Pages 312-388 in: *Starch: Chemistry and Technology*, 2nd ed. R. L. Whistler, J. N. BeMiller, and E. F. Paschall, eds. Academic Press: Orlando, FL.
- SERNA-SALDIVAR, S. O., TELLEZ-GIRON, A., and ROONEY, L. W. 1988. Production of tortilla chips from sorghum and maize. *J. Cereal Sci.* 8:275-284.
- SOMOGYI, M. 1945. A new reagent for the determination of sugars. *J. Biol. Chem.* 160:61-68.
- SOMOGYI, M. 1952. Notes on sugar determination. *J. Biol. Chem.* 195:19-23.
- STEEL, R. G. D., and TORRIE, J. H. 1980. Principles and Procedures of Statistics, A Biometrical Approach. McGraw-Hill: New York.
- TREJO-GONZALES, A., FERIA-MORALES, A., and WILD-ALTAMIRANO, C. 1982. The role of lime in the alkaline treatment of corn for tortilla production. Pages 245-263 in: *Modification of Proteins: Food, Nutritional, and Pharmacological Aspects*. Advances in Chemistry, Series 198. R. E. Feeney and J. R. Whitaker, eds. Am. Chem. Soc.: Washington, DC.
- WATSON, S. A. 1964. Whole starch. Pages 3-5 in: *Corn Starch. Methods Carbohydr. Chem.*, 4. Academic Press: New York.
- WEAST, R. C. 1985. CRC Handbook of Chemistry and Physics, 66th ed. CRC Press: Boca Raton, FL.