Effect of Corn Wet-Milling Conditions (Sulfur Dioxide, Lactic Acid, and Steeping Temperature) on Starch Functionality[1]

D. L. SHANDERA[2] and D. S. JACKSON[3]

Cereal Chem. 73(5):632–637

ABSTRACT

Starch functional characteristics varied with wet-milled corn steeping temperature and concentrations of lactic acid and sulfur dioxide. Starch was laboratory-wet-milled from Golden Harvest 2572, a medium-hard yellow dent corn hybrid. Batch steeping levels of temperature (43 and 57°C), lactic acid concentration (0.2 and 1.5%, v/v), and sulfur dioxide concentration (0.05 and 0.30%, v/v) were assigned in a 2^3 factorial experiment. Starch milled from corn steeped with 1.5% lactic acid at 57°C had reduced Brabender Viscoamylograph pasting, shear thinning, and set-back viscosities. These starches also had increased water solubility as measured by high-performance size-exclusion chromatography. Solubilized in 90% methyl sulfoxide, starch from corn steeped at 57°C with 1.5% lactic acid or 0.30% sulfur dioxide (SO_2) had lowered resistance to shear as evident in formation of smaller molecular sized polymers. Higher differential scanning calorimetry endotherm peak start, onset, and peak maximum temperatures were observed for starch obtained from corn steeped at 57°C or with 0.2% lactic acid. Endotherms were also narrower for steeping at 57°C than at 43°C. When viewed by scanning electron microscopy, more surface irregularities were present on starch granules from corn steeped at 57°C and 1.5% lactic acid than those from corn steeped at 43°C or 0.2% lactic acid.

Corn wet-milling is the largest commercial source of starch in the United States. Corn (maize) is steeped in an aqueous solution containing sulfur dioxide (a reducing and antimicrobial agent) and lactic acid (from bacterial fermentation) before physical milling. Steeping chemicals aid starch recovery by penetrating the endosperm and disrupting the protein matrix that envelopes and binds starch granules (Cox et al 1944). Kernels are typically steeped at 45–55°C (to retard putrefactive fermentation) with 0.1–0.2% sulfur dioxide and 0.5–1.5% lactic acid for 24–40 hr.

Corn-steeping chemicals have the potential of altering chemical and physical properties of starch granules and thus affect their functionality in cooked aqueous suspensions. Modifying starch with strong acids, as in the production of thin-boiling starches, results in reduced pasting properties. Although lactic acid is considered a weak acid, a 1.5% (w/w) solution has a pH near 2.1. Commercial countercurrent and many laboratory steeping methods initially immerse corn kernels in lactic acid containing steep solution. Corn kernels absorb lactic acid concomitant with steep solution (Shandera et al 1995). Exposure of the kernel starch granules to the lactic acid at 45–55°C for 24–48 hr may cause hydrolysis of granule structures. Sulfur dioxide also reduces the pH of the steep solution by forming an ionic equilibrium with the solution (Watson 1984). Sulfur dioxide is initially absorbed during laboratory batch steeping; but in commercial countercurrent systems, steeping-solution sulfur dioxide concentrations are initially low and gradually increase during steeping.

Steeping temperatures may alter starch within the kernel. Steeping at very high temperatures can gelatinize starch and result in difficult milling properties. Moreover, starch granules undergo reversible swelling in aqueous solutions below gelatinization temperatures (Leach et al 1959), and the degree of swelling and amount of leached polysaccharides in normal maize granules increases linearly above 50°C (Tester and Morrison 1990). Heating starch in an aqueous solution at 50°C for 24 hr (similar to steeping) increases gelatinization temperatures (Kempf 1955). Heating an aqueous suspension of wheat starch for 72 hr at 40°C or at 50°C results in a narrowed gelatinization range and increased gelatinization temperature (Gough and Pybus 1971). A narrowing of gelatinization temperature range seemingly indicates increased starch crystalline homogeneity, commonly known as annealing (Zobel 1992). Increased gelatinization temperatures are a common result of annealing, but gelatinization enthalpy values (ΔH) upon annealing maize starch (50–60°C) often do not change (Knutson 1990). Some degree of annealing occurs and transforms native corn starch granules during the wet-milling process (Kruger et al 1987). Annealing has been shown to modify the structure and functional properties of starch (Fakui and Nikuni 1969, Lund 1984, Zobel et al 1988).

The functional properties of native corn kernel starch granules are likely altered by steeping conditions used for wet-mill processing. Our objective was to survey the potential effects of corn kernel steeping temperatures and concentrations of lactic acid and sulfur dioxide on the physical and functional properties of wet-milled starch.

MATERIALS AND METHODS

Starch Samples

Starch was laboratory-wet-milled from Golden Harvest 2572, a medium-hard yellow dent corn hybrid, using the method of Shandera et al (1995). Corn samples (300 g) were batch-steeped (40 hr) with circulation in Erlenmeyer flasks containing 600 ml of solution prepared from distilled water, synthetic 85% lactic acid syrup, and sodium bisulfite (Sigma Chemical Co., St. Louis, MO). Lactic acid syrup was diluted to 10% (w/w) and heated overnight at 95°C to reduce lactic polymer content (Shandera and Jackson 1993). A 2^3 factorial statistical design assigned eight corn-steeping treatment combinations of temperature (43 and 57°C), lactic acid (1.5 and 0.2%, v/v), and sulfur dioxide (0.3 and 0.05%, v/v). Steeped corn was ground using a Waring blender fitted with a blunt blade. Germs were isolated by floating. Fiber was hand-sieved. Starch was tabled on a 0.15 × 3.05 m (6 in. × 10 ft.) aluminum table inclined at 0.75% slope. Starch protein content was determined using AACC method 46-08 (N × 6.25) (AACC 1995). A reference sample of commercial unmodified normal corn starch (American Maize Products Inc., Hammond, IN) was used for starch pasting solution pH and lactic-acid thinned pasting comparisons.

[1]Journal Series 11340, Agricultural Research Division, Institute of Agriculture and Natural Resources, University of Nebraska-Lincoln.
[2]Graduate research assistant, Cereal/Oilseed Science & Technology Laboratory, Dept. of Food Science & Technology, University of Nebraska-Lincoln.
[3]Associate professor, Cereal/Oilseed Science & Technology Laboratory, Dept. of Food Science & Technology, University of Nebraska-Lincoln, Lincoln, NE 68583-0919. Corresponding author. E-mail: djackson@UNL.edu.

Publication no. C-1996-0806-02R.

Pasting Properties

Pasting, shear-thinning, and set-back properties were measured using a Brabender Viscoamylograph (Brabender Instruments Inc., Hackensack, NJ) (Shuey and Tipples 1982). Starch samples (35 g, dwb) in 500 ml of distilled water were pasted from 50–95°C (1.5°C/min), shear-thinned by holding at 95°C for 30 min, and cooling to 50°C (1.5°C/min) for set-back properties. Slurry pH was measured but not adjusted. Bowl rotational speed was set at 75 rpm.

Pasting properties of a lactic-acid-thinned commercial starch were also measured. Commercial starch samples (100 g) were suspended in 200 ml of 0.2% or 1.5% lactic acid solution at 43° or 57°C (similar to corn steeping) for 12 hr. Steeped starch was washed with 10 L of distilled water in two stages and isolated on the wet-milling table similarly to the wet-milled starch. A second set of steep solutions were prepared with 1.5% lactic acid and adjusted to pH 6.5 with sodium hydroxide before suspending starch to compare the effects of hydrogen ion concentration during steeping.

Enthalpic Transitions

Starch (3.75 mg) in excess water (70%) was scanned from 30 to 135°C at 5°C/min using differential scanning calorimetry (DSC) (Dupont 2000 model 910 DSC cell, TA Instruments, New Castle, DE). An empty aluminum pan was used for reference. Indium was used as a calibration standard.

Water and DMSO Solubility

High-performance size-exclusion chromatography (HPSEC) was performed following the procedure as generally outlined by Jackson (1991). HPSEC granular water solubility was measured after 0.5% starch was prepared using deionized distilled water, boiled 30 min, autoclaved 30 min at 125°C, and then stored overnight at 60°C. Molecular size profiles of starch polymers were obtained using HPSEC after boiling 0.5% starch in 90% methyl sulfoxide solution (dimethyl sulfoxide [DMSO], HPLC grade, Aldrich Chemical Co., Milwaukee, WI) for 45 min, heating for 72 hr at 90°C, and inducing shear with sonication (10 sec at 30W) (Vibra-cell V300, Sonics and Materials, Inc., Danbury, CT). All samples were filtered through 1.2-μm nylon filters (MSI, Westboro, MA), and deionized using mixed bead resin (BioRad AG 501-X8, 80 mg/ml) before size separation by HPSEC. Injected starch samples (25 μl) were eluted by deionized water at 1 ml/min through 4 KS-series Shodex Ionpak columns (Showa Denko, Tokyo, Japan) connected in series to a refractive index detector (Waters model 410, Millipore Co., Milford, MA). Solubility was calculated (dwb) using Pullulan standards (Jackson 1991).

Scanning Electron Microscopy

Starch granules to be viewed by scanning electron microscopy (SEM) were precoated with 100Å AuPd in an aluminum pan using a model Desk II cool sputterer (Denton Vacuum Inc., Cherry Hill, NJ), mounted on an aluminum stub using adhesive tape, and recoated with 200Å AuPd. Samples were viewed using a Cambridge model 90 stereoscan electron microscope (Cambridge Scientific Instruments Inc., Cambridge, England) fitted with a tungsten filament operated at 15 kV.

In addition to viewing the previously mentioned starch samples, starch was wet-milled from corn steeped at 50°C and 0.3% SO_2 (0% lactic acid) or 1.5% lactic acid (0% SO_2) to isolate the effect each chemical had on granule surface characteristics.

Statistical Analysis

Three steeping factors and the interactions were tested at two levels each in a 2^3 factorial design: temperature (43 and 57°C), lactic acid concentration (0.2 and 1.5%), and sulfur dioxide concentration (0.05 and 0.3%). DSC runs were replicated with six endotherms, amylograph runs in duplicate, and HPSEC profiles in triplicate. The significance of each factor or its interaction with other factors in influencing starch functional characteristics was determined using the general linear models (GLM) procedure in the Statistical Analysis System (SAS 1992). Additionally, mean functional characteristics were compared for each factor using Fisher's protected least significant differences in the GLM procedure ($\alpha = 0.05$) was considered significant.

RESULTS AND DISCUSSION

Pasting Viscosity

Corn-steeping conditions of temperature, lactic acid, and sulfur dioxide (SO_2) levels significantly ($P < 0.05$) affected the wet-milled starch Viscoamylograph viscosities (Table I). Reduced pasting peak viscosities, pasting at 95°C viscosities, and shear thinning viscosities (BU) resulted from using higher corn-steeping levels of temperature (57 vs. 43°C), lactic acid (1.5 vs. 0.2%), and SO_2 (0.3 vs. 0.05%) (Figs. 1–3). Pasting and shear-thinning viscosities were reduced more when steeping at 57 vs. 43°C than by higher lactic acid or SO_2 concentrations. Due to a temperature and lactic acid interaction, a higher lactic acid concentration lessened pasting viscosities to a greater magnitude at 57°C than at 43°C. Milled starch protein contents were <0.5% and not significantly different ($P < 0.05$); thus, protein content probably did not affect starch characteristics.

Differences observed between shear-thinned viscosity values were resultant of differences measured in pasting viscosities. Reduced shear-thinned viscosities resulting from steeping at higher levels of temperature, lactic acid, and SO_2 were similar to the differences observed in reduced pasting peak viscosity profiles (Figs. 1 and 2 vs. Fig. 3). The net loss in viscosity during shear-thinning (pasting peak minus shear thinned viscosity) did not significantly differ between steeping treatments. However, differences in the shape of the pasting peak and shear-thinning curves

TABLE I
Significance ($P < F$) of Corn Steeping Factors on Wet-Milled Starch Functionality

	Viscoamylograph Viscosity				DSC[b] Endotherm Temperature			HPSEC[c] Solubility in Water		
Steeping Factor[a]	Peak Viscosity	Viscosity at 95°C	Shear Thinning	Set-Back	Peak Start	Endotherm Onset	Peak Maximum	Total	AMP[d]	AMY[e]
Temperature (Temp)	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.052
Lactic acid (LA)	0.000	0.000	0.000	0.000	0.068	0.027	0.026	0.000	0.000	0.006
Sulfur dioxide (SO_2)	0.001	0.000	0.001	0.041	0.075	0.441	0.489	0.317	0.329	0.606
Temp × LA	0.000	0.000	0.000	0.000	0.011	0.152	0.552	0.047	0.161	0.123
Temp × SO_2	0.526	0.199	0.188	0.883	0.003	0.476	0.632	0.386	0.134	0.931
LA × SO_2	0.526	0.928	0.365	0.883	0.084	0.491	0.344	0.256	0.262	0.764
Temp × LA × SO_2	0.115	0.064	0.148	0.257	0.851	0.880	0.201	0.125	0.080	0.201

[a] Levels of temperature (43 and 57°C), lactic acid (0.2 and 1.5%, v/v), sulfur dioxide (0.05 and 0.3%, v/v) and interactions of levels.
[b] Differential scanning calorimetry.
[c] High-performance size-exclusion chromatography.
[d] Amylopectin leached from granules.
[e] Amylose leached from granules.

were observed (Fig. 4). Although the onset temperature of pasting and the rate of increase in pasting viscosity were similar between starches obtained from the different steeping treatments, those samples with lower peak-pasting viscosity plateaued earlier at their maximum (peak) pasting viscosity and began shear-thinning earlier (before 95°C was reached). This resulted in broader pasting curves and lower viscosity values when a bowl temperature of 95°C was attained (Fig. 4). Lower 95°C viscosity values were observed for starch from corn steeped at higher temperature, lactic acid, and SO_2 levels (Fig. 2). Higher steeping temperatures enhanced lactic acid effects. The temperature and lactic acid interaction caused lower viscosities at 57 vs. 43°C at each lactic acid level.

Lower set-back viscosity values were observed from using 1.5 vs. 0.2% lactic acid at either 43 or 57°C (Fig. 5). Unlike the pasting viscosity values, set-back (gelling viscosity) was affected more by lactic acid concentration than by temperature or a temperature and lactic acid interaction. Steeping at 57°C with 0.2% lactic acid resulted in a higher set-back viscosity than steeping at 43°C with 1.5% lactic acid (Fig. 5). The net amount of set-back (set-back viscosity minus shear-thinned viscosity) also was significantly influenced by temperature, lactic acid, and a temperature and lactic acid interaction. SO_2 levels did not significantly influence net amount of set-back. Pasting viscosities probably had a sequential influence on set-back values and, hence, the calculated significance of SO_2. Highest net set-backs were observed with steeping at 57°C and 0.2% lactic acid, while lowest net set-back viscosities were obtained from 57°C and 1.5% lactic acid steeps.

In summary, high levels of temperature, lactic acid, and SO_2 present during steeping reduced pasting viscosity. The net amount of shear-thinning was not affected. SO_2 concentration did not affect the net set-back viscosity, but higher levels of lactic acid lowered the net amount of set-back viscosity. A higher steeping temperature may actually increase set-back viscosity, but the temperature and lactic acid interaction resulted in the lowest set-back viscosities at 57°C and 1.5% lactic acid. Lactic acid-induced hydrolysis may explain some of the reductions in pasting properties (and an increase in HPSEC solubility). Although lactic acid is a weak acid, the exposure of the kernels to pH levels of 2.3 (at concentrations of 1.5% lactic acid) over a 40-hr steep at elevated temperatures (up to 57°C) may cause partial depolymerization of amylopectin.

Residual acid levels in the amylograph starch slurries were evident. A pH of ≈4 was measured in 1.5% lactic acid samples and pH ≈5 for 0.2% samples (Table II). Although even commercial starch samples had a pH of 4.8, the starch molecule has a pKa = 12.5 and a pure solution in water should have a pH ≈6.25 (Oosten 1982). Lactic acid may be introduced into the granule during its hydration and swelling during steeping and remain as a remnant after milling. Higher steeping temperatures would cause more granule swelling and magnify these effects. We had previously reported that significantly more steep solution (including proportionately more lactic acid) is absorbed into the kernel at 57 vs. 43°C steeping (Shandera et al 1995). Sulfur dioxide had some lowering effects on starch slurry pH, but lactic acid influence was greater (Table II). Although a low starch slurry pH is generally expected to reduce pasting viscosity (Brown and Harrel 1944), adjusting the viscoamylograph starch slurries to pH 6.5 before heating did not significantly alter effects resulting from steeping (data not shown). Pasting viscosities were not reduced because of a lower pH for the amylograph starch slurry. Moreover, steeping regular commercial corn starch in 0.2 or 1.5% lactic acid solution for 12 hr at 43 or 57° (similar to corn steeping) reduced amylograph viscosities similarly to those observed from the wet-milled corn starch. However, when the lactic acid solution was adjusted to pH 6.5 with

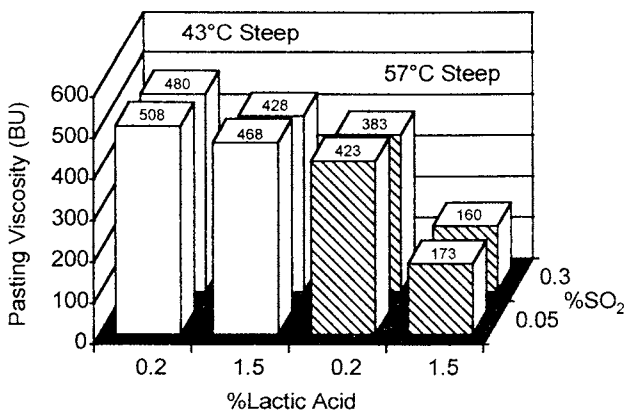

Fig. 1. Starch (35 g/500 ml) peak pasting viscosity (measured by Brabender Viscoamylograph) as affected by corn-steeping temperature, lactic acid, and sulfur dioxide (SO_2) levels.

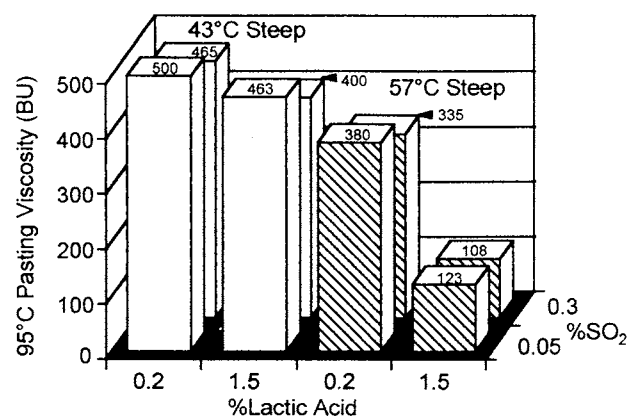

Fig. 2. Starch (35 g/500 ml) 95°C pasting viscosity (measured by Brabender Viscoamylograph) as affected by corn-steeping temperature, lactic acid, and sulfur dioxide (SO_2) levels.

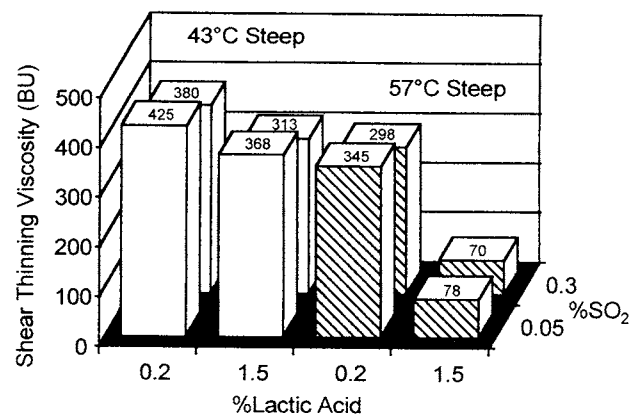

Fig. 3. Shear-thinning viscosity of starch (35 g/500 ml) (measured by Brabender Viscoamylograph at 95°C, 75 rpm, 30 min hold) as affected by corn-steeping temperature, lactic acid, and sulfur dioxide (SO_2) levels.

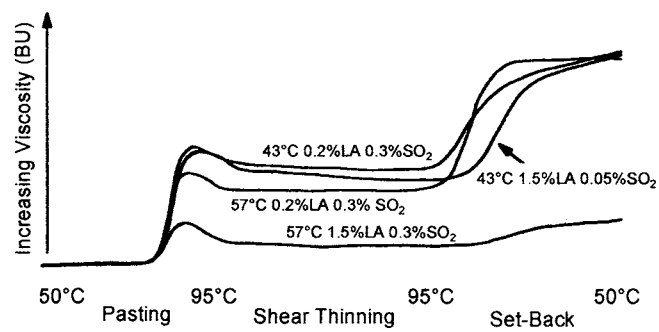

Fig. 4. Brabender Viscoamylograph viscosity profiles of starch wet-milled from corn steeped using different temperatures (°C), lactic acid concentration (%LA), and sulfur dioxide concentration(%SO_2). Reduced viscosities were observed for higher temperatures and LA concentrations.

sodium hydroxide before suspending starch and steeping, the viscosities were not significantly altered at either lactic acid level.

Granule Solubility

Starch granule solubility in water as measured by HPSEC was significantly affected by corn steeping levels of temperature, lactic acid concentration, and their interactions (Table I). Higher steeping temperature increased water solubility of starch at each lactic acid concentration, and higher levels of lactic acid increased solubility at each temperature (Fig. 6). A positive interaction between temperature and lactic acid increased the magnitude of solubility increases. The solubility of amylopectin in water increased proportionally more than amylose solubility when steeping with higher lactic acid (1.5 vs. 0.2%) and temperature (57 vs. 43°C) levels. However, the proportional solubility of amylopectin or amylose was not affected by the temperature and lactic acid interaction affecting total starch solubility. Although high shear-thinning starches tend to be more soluble (Zobel 1984), significant differences in net shear-thinning were not observed between samples. Overall trends in water solubility due to steeping levels of lactic acid and temperature were generally opposite of amylograph viscosity trends, especially for set-back viscosities (Figs. 1, 4, 6).

Solubility in 90% DMSO without sonication was increased by higher levels of SO_2 and temperature (data not shown). However, starch solubility in DMSO, when exposed to shear (sonicated 10 sec after 45 min of boiling and 72 hr of heating in 90% DMSO), did not significantly differ. Steeping temperature and lactic acid levels affected the molecular size profiles obtained by HPSEC (Fig. 7). Steeping affected the amounts and molecular size of degraded starch subfractions (primarily amylopectin) induced by shear forces (sonication). Techniques used to solubilize starch granules can depolymerize amylopectin molecules and result in intermediate-sized HPSEC amylopectin peaks (Jackson 1991, Mua and Jackson 1995). Higher levels of SO_2 (0.3 vs. 0.05%) increased the larger molecular sized (intermediate A), depolymerized amylopectin peak (Fig. 7). Higher levels of lactic acid (1.5 vs. 0.2%) increased the prominence of the smaller molecular sized (intermediate B), depolymerized amylopectin peak and also increased the quantity represented by the intermediate A peak. Higher steeping temperatures (57 vs. 43°C) resulted in increased formation of these depolymerized amylopectin peaks. Additionally, primary amylopectin peaks with significantly shorter retention times (corresponding to logarithmetically shorter molecular sizes) were observed with higher steeping temperatures (57 vs. 43°C) at similar lactic acid and SO_2 concentrations. Annealing may influence the liberated sizes of amylopectin during solubilization (shearing). Molecular size profiles of water solubilized starch (boiled and autoclaved) and DMSO-boiled samples (without sonication) were generally similar between steeping conditions except for an increased prominence of a smaller molecular size amylopectin peak appearing from steeping at 57 vs. 43°C; its prominence increased with 1.5% lactic acid steeping levels. Tailing amylose peaks, indicating smaller molecular size (fragmented or depolymerized) polymers, were also observed for sonicated samples from steeping corn with 1.5% lactic acid at 57°C. The presence of these smaller fragments were also observed for nonsonicated DMSO samples

TABLE II
Amylograph Starch Slurry pH for Various Steeping Conditions[a]

Temperature	% Lactic Acid	% Sulfur Dioxide	Slurry pH
43°C	1.5	0.3	4.1
	1.5	0.05	3.9
	0.2	0.3	4.8
	0.2	0.05	4.9
57°C	1.5	0.3	4.1
	1.5	0.05	4.2
	0.2	0.3	5.0
	0.2	0.05	5.1
Commercial corn starch	...	...	4.8

[a] Laboratory-batch-steeped and wet-milled corn starch.

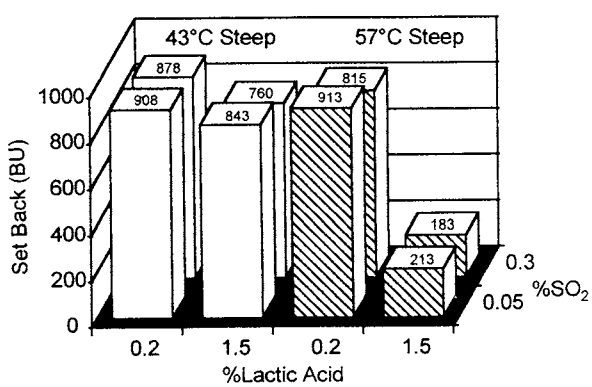

Fig. 5. Starch (35 g/500 ml) set-back viscosity (measured by Brabender Viscoamylograph) as affected by corn-steeping temperature, lactic acid, and sulfur dioxide (SO_2) levels.

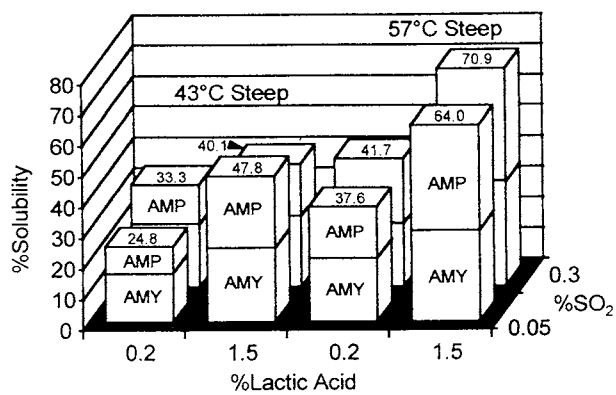

Fig. 6. Starch water solubility (0.5%) as affected by corn-steeping temperature, lactic acid, and sulfur dioxide (SO_2) levels. Total granule, amylopectin (AMP), and amylose (AMY) solubility as measured by high-performance size-exclusion chromatography (HPSEC) on boiling (30 min) and autoclaving (125°C, 30 min).

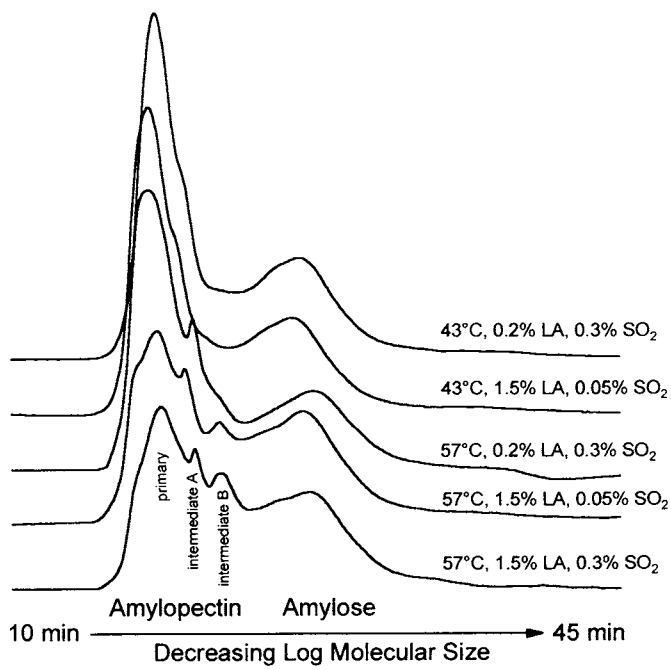

Fig. 7. High-performance size-exclusion chromatography profiles of starch wet-milled from corn steeped at various levels of temperature (°C), lactic acid (%LA), and sulfur dioxide (%SO_2). Starch was heated in dimethyl sulfoxide and sonicated for 10 sec.

and water-boiled samples from higher steeping temperature and lactic acid levels. The presence of these smaller molecular size fractions indicates that lactic acid has enhanced depolymerization effects at higher steeping temperatures. Amylopectin was also more susceptible to partial depolymerization with application of shear (Fig. 7). Corn-steeping temperature and chemical concentrations influence the solvent solubility of milled starch and granular susceptibility to shear forces.

DSC Endotherm Temperatures

Enthalpic transitions of starch gelatinization (in excess water) were monitored as described by Stevens et al (1971). DSC peak start, endotherm onset, and peak maximum temperatures were higher for starch milled from corn steeped at 57 vs. 43°C (Table I, Figs. 8–10). Additionally, significantly lower endotherm onset and lower maximum temperatures simultaneously occurred at the higher concentration (1.5 vs. 0.2%) of lactic acid. The lower endotherm melting temperatures suggests the properties of an acid-modified starch (Wootton and Bamunuarachchi 1979). Lactic acid and sulfur dioxide effects on peak start temperature were mainly dependent on steeping temperature. SO_2 levels did not affect onset or maximum temperatures. Endotherm enthalpies (ΔH) and peak end temperatures did not differ significantly with steeping treatments. Because our DSC cell analyzes a small amount of sample (≈3.8 mg, dwb), and it may not have detected differences in gelatinization enthalpies. However, detectable changes may not have occurred (Knutson 1990).

Due to the consistent influence of steeping temperature on starch functionality measured previously, endotherm peak widths (peak end temperature minus peak start temperature) were also analyzed. Peak widths were significantly influenced by temperature, temperature and lactic acid, and lactic acid and SO_2 interactions. Peak widths averaged over each temperature were significantly higher for steeping at 43°C (16.41°C) than at 57°C (13.25°C). The temperature range from peak start to endotherm onset were also significantly higher for 43°C (2.99°C) than 57°C (2.24°C) with an additional significant influence of temperature and SO_2 (wider widths were present at lower SO_2 levels). The temperature difference between peak start and peak maximum was also significantly higher for 43°C steeping (7.97°C) than for 57°C (6.13°C). Differences were greater for lower SO_2 levels (at $P < 0.06$). Temperature and SO_2 and lactic acid and SO_2 interactions also significantly affected the peak start to peak maximum difference. The significant increases in the temperature ranges at lower SO_2 levels (0.05 vs. 0.3%) were attributable to SO_2 raising peak start temperatures (Table I, Fig. 8).

Elevation of corn-steeping temperature elevating from initial starch gelatinization temperature (peak start) and a decreased range of gelatinization (peak start minus peak end) suggests an altering of crystalline structure. Temperature was the only significant factor affecting the range between endotherm peak end temperature (which did not significantly differ) to endotherm onset or maximum temperatures. Steeping at 43°C resulted in a larger difference in onset to end temperatures than at 57°C steeping (13.42 vs. 11.00°C, respectively). Additionally, a greater difference was also observed for maximum to end temperatures at 43°C (8.44°C) than at 57°C (7.11°C). As only temperature influenced the range of onset and peak maximum temperatures to peak end temperature, steeping temperature primarily shifts these two characteristic peak measurements, perhaps caused by granule annealing. Gough and Pybus (1971) and Knutson (1990) observed such a range narrowing and increase of gelatinization temperature for annealed starch (50°C). Kruger et al (1987) reported that annealing occurs at wet-milling temperatures; rises in endotherm temperatures were also observed when steeping starch in excess water at 50 to 60°C. Peak start temperature, however, is also affected by steeping concentrations of lactic acid and SO_2. The granular effect of SO_2 in raising peak start temperatures is not clear.

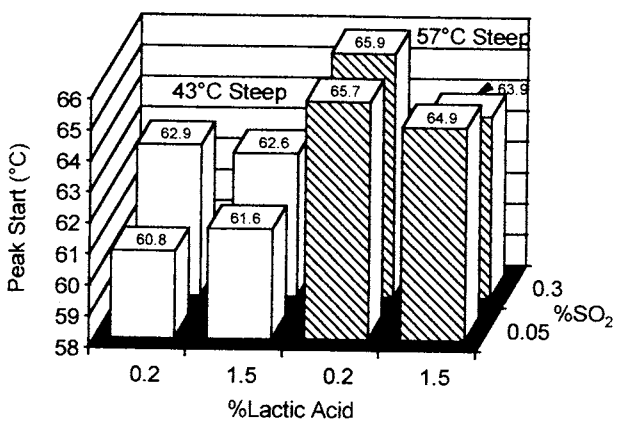

Fig. 8. Differential scanning calorimetry endotherm (5°C/min, excess water) peak start temperature of starch as affected by corn-steeping temperature, lactic acid, and sulfur dioxide (SO_2) levels.

SEM

Granules obtained from corn that was intensively steeped (57°C, 1.5% lactic acid, 0.3% SO_2) had surfaces with many ridges and were generally etched and rough (Fig. 11). These granules also showed a translucent edge or ghostlike appearance. Samples steeped at 57°C or with 1.5% lactic acid were more prone to show these characteristics. Alternatively, granules obtained from corn less intensively steeped (43°C, 0.2% lactic acid, 0.3% SO_2)

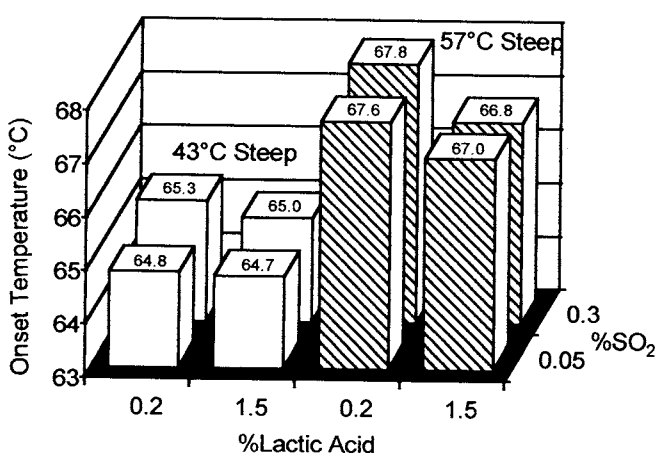

Fig. 9. Differential scanning calorimetry endotherm (5°C/min, excess water) onset temperature of starch as affected by corn-steeping temperature, lactic acid, and sulfur dioxide (SO_2) levels.

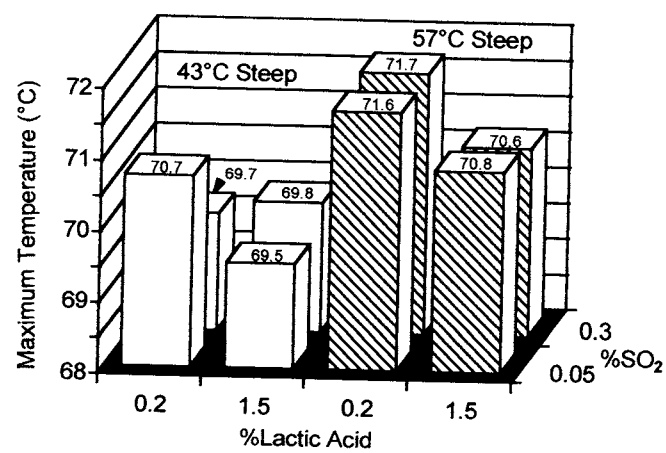

Fig. 10. Differential scanning calorimetry endotherm (5°C/min, excess water) peak maximum temperature of starch as affected by corn-steeping temperature, lactic acid, and sulfur dioxide (SO_2) levels.

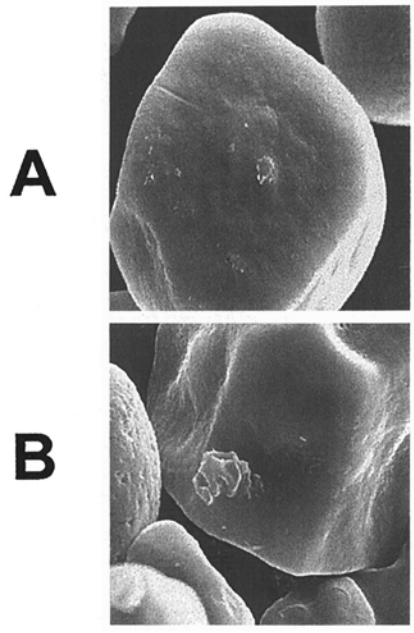

Fig. 11. Scanning electron micrographs (magnification 6,000×) of starch wet-milled from corn steeped at: **A**, 43°C, 0.2% lactic acid, 0.05% sulfur dioxide; **B,** 57°C, 1.5% lactic acid, 0.3% sulfur dioxide. Granules in sample **B** appeared more etched, textured, and somewhat larger than those in **A**.

showed less surface roughness. These granules also seemed somewhat smaller and rounder in character (subjectively quantified). However, there is considerable variability in the sizes and shapes (round, polyhedral, zein dented) of maize starch granules. Polyhedral granules seemed more prone to etching and surface irregularities than the smaller, smoother round granules.

Granules from corn steeped with 0.3% SO_2 and 0% lactic acid at 50°C had relatively smooth surfaces but were more easily damaged (cracking) upon prolonged exposure to the electron beam (which causes heating). Alternatively, samples wet-milled from corn steeped with 1.5% lactic acid alone (50°C) were more prone to shrivel into raisinlike structures before beam damage induced cracking. This was especially evident in the aforementioned (amylograph tested) samples of commercial corn starch steeped in 1.5% lactic acid.

CONCLUSIONS

Starch physiochemical and functional properties, as measured by amylograph, DSC, HPSEC, or viewed by SEM, are affected by corn kernel steeping conditions. Corn-steeping levels of temperature, lactic acid concentration, and sulfur dioxide concentration affected functional properties. The impact of sulfur dioxide was limited to lowering pasting viscosities and raising DSC peak start temperatures. This impact, however, was not as great as those of temperature or lactic acid. Elevated steeping temperatures partially annealed native starch granules within the steeping kernels. Lactic acid has an acid-thinning effect on granules. This acid-thinning effect is likely due to amylopectin depolymerization, as evident in reduced pasting viscosities. Higher steeping temperatures probably magnify the effect of lactic acid by increasing reaction rates, affecting polymer states, and by increasing the amount of lactic acid absorbed with steep solution into the corn kernel.

The relative time difference in exposure of kernels to lactic acid and sulfur dioxide during batch steeping and countercurrent systems, may cause different results in commercial countercurrent steeping systems. Lactic acid is initially absorbed proportionally with water during countercurrent steeping and may have a large impact on the kernel interior. However, the presence of leached corn solubles and operator regulation of steep pH may alter the effects of lactic acid. Simultaneously, kernels in commercial systems are initially exposed to minimal sulfur dioxide concentrations that gradually increase during steeping. Further study is required to detail how temperature, lactic acid, SO_2, and their interactions change starch polymers and granules.

LITERATURE CITED

AMERICAN ASSOCIATION OF CEREAL CHEMISTS. 1995. Approved Methods of the AACC, 9th ed. The Association: St. Paul, MN.

BROWN, R. O., and HARREL, C. G. 1944. The use of the amylograph in the cereal laboratory. Cereal Chem. 21:360-364.

COX, M. J., MacMASTERS, M. M., and HILBERT, G. E. 1944. Effects of the sulfurous acid steep in corn wet milling. Cereal Chem. 21:447-465.

FAKUI, T., and NEKUNI, Z. 1969. Heat-moisture treatment of cereal starch observed by x-ray diffraction. Agri. Biol. Chem. 33:460-462.

GOUGH, B. M., and PYBUS, J. N. 1971. Effect on the gelatinization temperature of wheat starch granules of prolonged treatment with water at 50°C. Staerke 23:210-212.

JACKSON, D. S. 1991. Solubility behavior of granular corn starches in methyl sulfoxide (DMSO) as measured by higher performance size exclusion chromatography. Starch/Staerke 43:422-424.

KEMPF, W. 1955. Gelatinization temperature behavior by different starches. Staerke 7:161-169.

KNUTSON, C. A. 1990. Annealing of maize starches at elevated temperatures. Cereal Chem. 67:376-384.

KRUGER, B. R., KNUTSON, C. A., INGLETT, G. E., and WALKER, C. W. 1987. A differential scanning calorimetry study on the effect of annealing on the gelatinization behavior of corn starch. J. Food Sci. 52:715-719.

LEACH, H. W., McCOWEN, L. D., and SCHOCH, T. J. 1959. Structure of the starch granule. I. Swelling and solubility patterns of various starches. Cereal Chem. 36:534-544.

LUND, D. B. 1984. Influence of time, temperature, moisture, ingrdients and processing conditions on starch gelatinization. Crit. Rev. Food Sci. Nutr. 20:249-252.

MUA, J. P. and JACKSON, D. S. 1995. Gelatinization and solubility properties of commercial oat starch. Starch/Staerke 47:2-7.

OOSTEN, B. J. 1982. Tentative hypothesis to explain how electrolytes affect the gelatinization temperature of starches in water. Starch/Starke 34:233-239.

SAS. 1992. Proprietary software, vers 6.08. SAS Institute: Cary, NC.

SHANDERA, D. L., and JACKSON, D. S. 1993. A simplified method for measurement of lactic acid and sulfur dioxide in corn wet milling steep water. Starch/Staerke 45:351-354.

SHANDERA, D. L., PARKHURST, A. M., and JACKSON, D. S. 1995. Interactions of sulfur dioxide, lactic acid, and temperature during simulated corn wet milling. Cereal Chem. 72:371-378.

SHUEY, W. C., and TIPPLES, K. H. 1982. Uses and applications (of the amylograph). Pages 16-23 in: The Amylograph Handbook. Am. Assoc. Cereal Chem.: St. Paul, MN.

STEVENS, D. J., and ELTON, G. A. H. 1971. Thermal properties of the starch/water system. I. Measurement of heat of gelatinisation by differential scanning calorimetry. Staerke 23:8-11.

TESTER, R. F., and MORRISON, W. R. 1990. Swelling and gelatinization of cereal starches. I. Effects of amylopectin, amylose, and lipids. Cereal Chem. 67:551-557.

WATSON, S. A. 1984. Starch production. Pages 285-309 in: Starch: Chemistry and Technology. R. L. Whistler, J. N. BeMiller, and E. F. Paschall, eds. Academic Press: Orlando FL.

WOOTTON, M., and BANUNUARACHCHI, A. 1979. Application of differential scanning calorimetry to starch gelatinization. I. Commercial native and modified starches. Starch/Starke 31:201-204.

ZOBEL , H. F., YOUNG, S. N., and ROCCA, L. A. 1988. An x-ray diffraction study. Cereal Chem. 65:443-446

ZOBEL, H. F. 1984. Gelatinization of starch and mechanical properties of starch pastes. Pages 285-309 in: Starch: Chemistry and Technology. R. L. Whistler, J. N. BeMiller, and E. F. Paschall, eds. Academic Press: Orlando FL.

ZOBEL, H. F. 1992. Starch granule structure. Pages 1-36 in: Developments in Carbohydrate Chemistry. R. J. Alexander and H. F. Zobel, eds. Am. Assoc. Cereal Chem. St. Paul, MN.

[Received November 6, 1995. Accepted May 13, 1996.]