Wet-Milling Characteristics of Propionate-Treated High-Moisture Maize. II. Qualities of Starch and Gluten[1]

C. WANG and L. A. JOHNSON[2]

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ABSTRACT

High-moisture (25.6%) maize was treated with three forms of 1.0% propionate (weight treatments adjusted to obtain equivalent moles of propionate ion). These were propionic acid (99% pure, pH 1.7), a mixture of sodium propionate and sodium acetate acidified with HCl to the pKa of propionic acid (pH 4.8), and the same mixture of sodium propionate and sodium acetate acidified to the natural pH of propionic acid (pH 1.7). Another sample of the maize was forced-air dried (25°C) to 12% moisture content. Propionate-treated and untreated maize samples were stored at 25°C for six months before wet milling. Starch recovered from propionate-treated maize contained greater amounts of residual protein than did starch from untreated air-dried maize and was more yellow in color. Starch from propionate-treated maize had lower pasting viscosities than did starch from untreated air-dried maize, indicating partial hydrolysis. No differences in the thermal properties of the starches were observed. Gluten from propionate-treated maize contained lower concentrations of protein and was less yellow than gluten from untreated air-dried maize. Addition of a small amount of sodium chloride to the mill-starch slurry improved starch-gluten separation in propionate-treated maize.

In industrially developed countries, maize is normally harvested at 22–28% moisture and quickly dried with heated air to prevent quality deterioration by fungi. Treating maize with propionic acid or propionate salts has become a preferred alternative to drying maize during periods of high energy costs (Sauer and Burroughs 1974). The use of propionate to preserve high-moisture maize does not adversely affect feed value (Jones et al 1970), but its effect on the wet-milling properties of maize is unknown. In a companion study, Wang and Johnson (1992) showed that treatment of maize with various forms of propionate adversely affected the yields of high-value wet-milled products. The present work focuses on the qualities of starch and gluten from wet milling propionate-treated high-moisture maize and on ways to improve starch purity from propionate-treated maize.

MATERIALS AND METHODS

Treating, Storing, and Wet Milling

Methods used to treat, store, and wet mill high-moisture maize were previously described by Wang and Johnson (1992).

Color Evaluation

Colors of starch and gluten from each treatment were measured by using a Hunter colorimeter. In the Lab color unit system, *L* measures lightness, *a* measures red (+) and green (−), and *b* measures yellow (+) and blue (−). Tile LS-12414 was used for standardization.

Thermal Properties of Starch

The thermal properties of starch were determined with a Perkin-Elmer DSC7 differential scanning calorimeter (Perkin-Elmer Corp., Instrument Div., Norwalk, CT) equipped with a thermal analysis data station. About 4 mg of starch was weighed into an aluminum pan containing 8 mg of water, and this pan was hermetically sealed. The sample was heated from 30 to 120°C at the rate of 10°C/min. The enthalpy of gelatinization and onset, peak, and conclusion temperatures were calculated.

Pasting Properties of Starch

A temperature-programmed viscometer (C. W. Brabender Inc., S. Hackensack, NJ) was used to measure the starch-pasting properties of an 8% starch slurry according to the methods of Mazurs et al (1957). The slurry was heated to 95°C at the rate of 1.5°C/min, held at that temperature for 15 min, and then cooled to 50°C at 1.5°C/min.

Improving Starch-Gluten Separation from Propionate-Treated Maize

Starch-gluten separation in laboratory wet milling of propionate-treated high-moisture maize was very poor. Several approaches were explored to improve starch-gluten separation. In one treatment, the pH of 1 L of mill-starch slurry (about 16% solids content) was adjusted in 0.5 pH units over the range of 2–10. To a second sample of 1 L of mill-starch slurry (about 16% solids content), sodium chloride was gradually added (from 0.1 to 4 g). The starch-gluten separation during sedimentation was evaluated visually.

In another series, about 2 g of NaCl was added to 1 L of mill-starch (about 16% solids content) from untreated air-dried maize and pure propionic acid-treated high-moisture maize. A sample with no additional NaCl was used as a control. Three replicates of each treatment were prepared. The mill-starch was separated into starch and gluten fractions by sedimentation and centrifugation (5,860 × *g* for 30 min). The protein contents of the starch fractions were determined by macro-Kjeldahl using the nitrogen conversion factor of 6.25.

Experimental Design and Statistical Analysis

The data were analyzed by analysis of variance according to procedures of the Statistical Analysis System (SAS 1984). Duncan's multiple range test was used to compare the means at the 5% significance level.

TABLE I
Effects of Propionate on the Protein Content and Color of Starch[a]

Treatment	Steeping Time (hr)	Protein Content (%)	Hunter Color Values *L*	*a*	*b*
Air-dried	24	0.61 d	74.2 a	−0.28 ab	3.87 c
	48	0.51 d	75.9 a	−0.31 ab	3.79 c
Pure propionic acid	24	0.95 c	75.8 a	−0.33 a	3.96 bc
	48	1.05 bc	72.2 a	−0.25 b	4.12 bc
Semiacidified salts	24	1.24 a	73.3 a	−0.14 c	4.46 ab
	48	1.19 ab	73.7 a	−0.29 ab	4.82 a
Acidified salts	24	1.19 ab	71.6 a	−0.24 b	4.82 a
	48	1.06 bc	74.7 a	−0.36 b	4.81 a

[a]Means in the same column followed by a common letter are not significantly different according to Duncan's multiple range test at the 5% level.

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[2]Graduate research assistant, Department of Food Science and Human Nutrition, and professor, Center for Crops Utilization Research, respectively, Iowa State University, Ames 50011.

TABLE II
Effects of Propionate on the pH of the Steeps and the Pasting Properties[a]

Treatments	Steeping Time (hr)	pH of Steeps		Paste Viscosities (BU)	
		Range	Mean	Peak	Cooked
Air-dried	24	3.05–4.60	3.79 bc	773 bc	691 ab
	48	3.25–4.60	3.95 a	823 a	725 a
Pure propionic acid	24	3.35–4.15	3.65 c	697 d	540 d
	48	3.05–4.20	3.48 d	772 bc	646 bc
Semiacidified salts	24	3.00–4.60	3.91 ab	752 c	616 c
	48	3.20–4.60	3.79 bc	810 ab	708 ab
Acidified salts	24	2.95–4.20	3.33 e	NA[b]	NA
	48	2.90–4.00	3.23 e	NA	NA

[a]Means in the same column followed by a common letter are not significantly different according to Duncan's multiple range test at the 5% level.
[b]Not available due to insufficient sample quantity.

TABLE III
Effects of Propionate Treatment on Gluten Protein Content and Color[a]

Treatment	Steeping Time (hr)	Protein Content (%)	Hunter Color Values		
			L	*a*	*b*
Air-dried	24	50.2 a	49.8 a–c	3.30 a	15.1 a
	48	46.6 b	53.0 a	3.10 a	15.4 a
Pure propionic acid	24	45.4 cd	46.1 c	1.72 c	10.5 c
	48	43.3 cd	52.7 ab	2.21 bc	12.5 b
Semiacidified salts	24	43.0 cd	47.7 bc	2.22 bc	12.5 b
	48	40.4 d	49.2 a–c	2.18 bc	12.1 b
Acidified salts	24	40.2 d	50.0 a–c	2.29 bc	12.7 b
	48	41.3 d	45.8 c	2.55 b	11.9 b

[a]Means in the same column followed by a common letter are not significantly different according to Duncan's multiple range test at the 5% level.

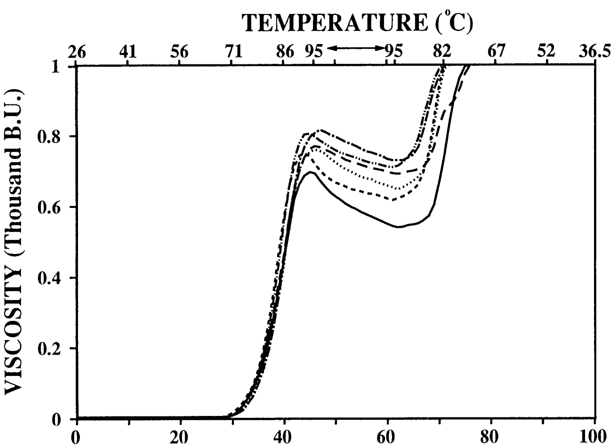

Fig. 1. Effects of propionate treatments on pasting properties of starch. —·—·— = Control, 24 hr; — — — = control, 48 hr; —··—··— = semiacidified salts, 24 hr; - - - - - = semiacidified salts, 48 hr; · · · · · = pure propionic acid, 24 hr; ———— = pure propionic acid, 48 hr.

RESULTS AND DISCUSSION

Protein Content of Recovered Starch

Protein content is a very important quality factor for industrial starch; its value needs to be as low as possible and no greater than 0.3% (Johnson 1991). Starch with a protein content greater than this value causes scumming and fouling of equipment and discolors many finished products.

The differences in protein contents among treatments were very significant (Table I). Starch from the untreated air-dried maize contained the lowest protein content, about half the protein content of the starch fraction recovered from propionate-treated high-moisture maize. There were no significant differences in protein contents of maize steeped for different times.

The separation of starch and gluten is facilitated by the difference in their respective densities, gluten having a density of 1.1 g/cm^3 and starch a density of 1.5 g/cm^3 (Watson 1984). Two explanations are possible for the poor starch-gluten separation observed in propionate-treated high-moisture maize. One possibility is reduced density of starch granules due to propionate treatment. High acidity during grain storage and/or steeping due to propionate treatment may partially hydrolyze the starch. Being more hydrophilic, the acidified starch should take up more water, which decreases starch density. Thus, lower-density starch granules would not separate easily from gluten particles because of the reduced density difference between the starch granules and the gluten. A second, but less likely, possibility is that gluten particles also are partially hydrolyzed, allowing void spaces formed during grain drying to become exposed, to absorb water, and to hydrate the gluten more. Therefore, gluten particles would increase in density and tend to settle at rates similar to those of starch granules.

Any hydrolysis of starch or protein likely occurred during storage of propionate-treated maize rather than during steeping. The acidity profiles in the steeps were not greatly different (Table II), although mean steeping pHs were significantly more acid in propionic acid-treated and acidified salts-treated maize than in either air-dried or semiacidified salts-treated maize.

Colors of Starch and Gluten

Tables I and III show the colors of gluten and starch, respectively, as measured by the Hunter colorimeter. Differences among treatments in *L* and *a* values were not as significant as those in *b* values. The propionate treatments significantly affected the colors of both starch and gluten. Because of lower protein content (Table III) and rapid degradation of carotenoids in propionate-treated high-moisture maize, gluten from this maize was less yellow than gluten from air-dried maize. Because of its greater gluten contamination, starch from the propionate-treated high-moisture maize was more yellow than starch from air-dried maize.

Thermal Properties of Recovered Starch

There were no significant differences among treatments for gelatinization onset, peak, and conclusion temperatures and for enthalpy. The lack of significant differences in enthalpy indicated that the starch granules were still intact.

Pasting Properties of Recovered Starch

Figure 1 shows the viscoamylograph patterns of starch samples from untreated air-dried maize, pure propionic acid-treated maize, and semiacidified salt-treated maize. The patterns were different among treatments and between the two steeping times. Differences were especially obvious for peak (at 96°C) and cooked (before the slurry began to cool) viscosities (Table II).

In both 48- and 24-hr steepings, the starch from the untreated

TABLE IV
Effect of NaCl Addition on Starch-Gluten Separation

Amount of NaCl (g/300 g of corn)	Concentration (%)	Separation Observed
0.2	0.02	Extremely poor
0.5	0.05	Extremely poor
1.0	0.10	Poor
1.5	0.15	Moderately poor
2.0	0.20	Good
2.5	0.25	Good
3.0	0.30	Good

air-dried maize had the highest peak and cooked viscosities, followed by the starch from semiacidified salts-treated maize. The starch from pure propionic acid-treated maize had the lowest viscosities. There were also significant differences between the two steeping times for starch samples from maize treated with pure propionic acid and that treated with semiacidified salts. The starch from 24-hr steeping had significantly greater peak and cooked viscosities than did the starch from 48-hr steeping.

The propionate treatments, especially pure propionic acid treatment, yielded starch with lower starch-pasting viscosities. Longer steeping time also produced lower pasting viscosities. Propionate treatments slightly, but significantly, reduced the pH in the steeping vessels (Table II). Acid modification (hydrolysis of starch in amorphous areas of the granule) usually decreases pasting viscosities of starch without destroying the granular structure (Rohwer and Klem 1984). It is improbable that the increased acidity of the steeping was sufficient to modify the starch. It seems more likely that propionic acid modified the starch during grain storage.

Methods to Improve Starch-Gluten Separation

No improvement in starch-gluten separation was observed when the pH of the mill-starch slurry was adjusted. Additions of small amounts of NaCl to the mill-starch slurry, however, significantly improved starch-gluten separation (Table IV). Density of the slurry was checked by using a hydrometer, but no significant change in density (1.049–1.050 g/cm^3) was observed over the range of NaCl concentrations evaluated.

Addition of NaCl significantly reduced the protein contents of the recovered starches from both air-dried maize and pure propionic acid-treated high-moisture maize. The addition of 2 g of NaCl per 300 g of maize reduced the protein contents of starches from pure propionic acid-treated high-moisture maize and air-dried maize from 0.84 to 0.44% and from 0.59 to 0.53%, respectively.

The mechanism for the improved separation is not understood. The increased ionic strength due to the addition of NaCl in the mill-starch slurry may have caused the starch granules and/or gluten particles to lose different amounts of associated water, causing the densities of starch granules to increase and/or those of gluten particles to decrease. However, further studies are needed to understand why added salt enhanced starch-gluten separations.

CONCLUSIONS

Treatment with propionate to preserve high-moisture maize adversely affected the qualities of starch and gluten recovered in wet milling. Detrimental effects occurred at both 24- and 48-hr steepings; thus, it was not possible to mitigate these effects and to take advantage of the high moisture content already present in propionate-treated maize to reduce steeping time. High-moisture maize treated with propionate exhibited very poor starch-gluten separation characteristics. Addition of sodium chloride significantly improved starch-gluten separation. Without added NaCl, starch from propionate-treated high-moisture maize had poor starch-gluten separation and high protein content.

Starch from propionate-treated maize was more yellow than starch from air-dried maize. Gluten from propionate-treated maize was less yellow than gluten from untreated air-dried maize. Starch from high-moisture maize treated with more acidic solutions of propionate (pure propionic acid) had lower pasting viscosities than did starch from high-moisture maize treated with less acidic solutions of propionate (semiacidified) and air-dried maize. No differences in thermal properties of the starch due to propionate treatment were observed.

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