Wet-Milling Characteristics of Propionate-Treated High-Moisture Maize. I. Yields and Compositions of Products[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 (as might be recovered from fermentation) 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 maize was forced-air dried (25°C) to 12% moisture and used as an untreated control. Treated maize was stored at 25°C for six months before wet milling. When the grain was treated with propionate, yields of germ were lower and contained less protein and more oil compared with untreated air-dried maize because of increased leaching of protein from germ during steeping. Starch yields increased because of propionate treatment, but residual protein levels in the recovered starch were unacceptably high. Gluten yields and purities of propionate-treated high-moisture maize were lower than those of untreated air-dried maize.

Maize is generally harvested at 22–28% moisture to minimize field losses of grain due to weather and to reduce mechanical damage to seed during harvesting. High-moisture maize needs to be artificially dried to about 15% moisture or treated with chemical preservatives to prevent fungal growth and consequent loss of quality during long-term storage. In periods of high energy costs, farmers have turned to chemical treatment instead of drying to preserve high-moisture grain.

Agents most often used to control the growth of fungi in grain are volatile organic acids, such as propionic, acetic, and isobutyric, and their salts (Sauer et al 1975). In recent years, propionic acid has become the preferred preservative for preventing fungal growth and spoilage in maize containing up to 30% moisture (Sauer and Burroughs 1974).

Conditions used in artificial drying significantly affect the wet-milling characteristics of maize (MacMasters et al 1959). High drying temperature has been linked to difficult and incomplete grinding with consequent loss of starch in by-product streams destined for livestock feeds, poor germ separation leading to low oil recovery, poor color and high free fatty acid content of the oil, and poor starch-gluten separation resulting in low starch recovery and purity. Weller (1987) and Weller et al (1988) also showed that starch recovery decreased as harvest moisture and drying temperature increased.

The effects of chemical preservatives on wet-milling characteristics of maize have not been confirmed. A number of potential disadvantages for high-moisture maize treated with propionic acid have been discussed (Freeman 1973): costs of transporting high-moisture grain are increased because of the added water; the acid is corrosive to handling, storage, and milling equipment; the level of carotenoid pigments may be reduced; and pollution problems may be increased. It also has been suggested, however, that less

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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.

steeping time may be required to achieve good wet-milling properties with propionic acid-treated high-moisture maize (Freeman 1973), and that most of the propionic acid would be extracted during early stages of countercurrent steeping. The importance of *Lactobacillus* fermentation and the role of lactic acid in starch-gluten separation have not been resolved, and the impact of propionic acid on lactic acid production during steeping is unknown. Nor is it certain whether propionic acid has the same kernel-softening effect as lactic acid. The objective of the present study was to determine the effects of propionic acid treatment on the yields of wet-milling products of propionate-treated high-moisture maize compared with those of untreated air-dried maize.

MATERIALS AND METHODS

Maize Treatment and Storage

High-moisture (25.6%) maize was treated with three forms of 1.0% propionate: propionic acid (99% pure, pH 1.7), a mixture of sodium propionate and sodium acetate acidified with HCl to the pKa of propionic acid (4.8), and the same mixture of sodium propionate and sodium acetate acidified to the natural pH of propionic acid (pH 1.7). All of the propionate treatments were made on equivalent moles of propionate by compensating for differences in molecular weight of the different forms. The latter two treatments were selected because a mixture of propionic and acetic acids might be produced via fermentation and recovered as their sodium salts. The molar ratio of propionate to acetate (5:1) in the mixtures was the ratio in which these acids might be produced by *Propionibacteria* fermentation. An untreated control lot of maize was forced-air dried at 25°C to 12% moisture.

The cleaned maize (50 kg per replicate) was sprayed with 1.0% propionate (wt propionate/wt maize) per treatment by using a ribbon mixer and a garden sprayer. The treated maize was placed in 30-gal garbage cans double-lined with polyethylene bags. The treated maize was stored at 25°C for six months before wet milling. Each propionate treatment was replicated twice.

Laboratory Wet Milling

Maize samples (300 g) were steeped countercurrently in a battery of six vessels, as described by Steinke et al (1991). The steeped maize was wet milled according to the procedures of Steinke and Johnson (1991). The recovered starch was dried in a forced-air oven at 50°C for 48 hr. The other wet-milled products (germs, coarse fiber, fine fiber, gluten, and inseparables) were dried in a forced-air oven at 60°C for at least 24 hr and then in a vacuum oven at 65°C for an additional 8 hr.

Determination of Moisture and Protein Contents

Moisture content was determined in duplicate by AOAC method 14.003 (AOAC 1980), and product yields were calculated on a moisture-free basis. Protein content was determined according to the macro-Kjeldahl method and by using a Kjeltec system (Tecator, Inc., Hogana, Sweden). The nitrogen conversion factor 6.25 was used to calculate the protein content.

Experimental Design and Statistical Analysis

Four samples from each treatment replicate were wet milled. Two samples were steeped for 48 hr and the other two for 24 hr. 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.

RESULTS AND DISCUSSION

Solids and Protein Contents of Light Steep Liquor

Light steep liquor is the steeping solution exiting the steeping system. Some leaching of maize solids during steeping is crucial for germ separation. With the increase of solids loss from the germs, the density of the germs decreases, and germ-separation efficiency increases. The maize treated with acidified salts and semiacidified salts had higher yields of solids in light steep liquor than untreated air-dried maize (Table I). The maize treated with pure propionic acid and untreated air-dried maize had lower yields of solids than did the other treatments. For each treatment, longer steeping time caused more solids to leach into the light steep liquor. Light steep liquor solids from propionate-treated maize contained either equivalent or more protein than those from air-dried maize. More protein (lb/bu) leached into the light steep liquor from propionate-treated maize than from air-dried maize. Longer steeping time also increased protein leaching. Protein recoveries in light steep liquor showed a trend similar to that of yields of solids.

Germ Composition and Separation

High efficiency of germ separation is important; the starch will contain high fat levels if the germ cannot be completely separated from the endosperm, making the starch prone to developing oxidized flavors during storage. Moreover, reduced yields of germ adversely affect returns because oil is the most valuable product (per unit weight basis) derived from wet milling of maize.

Table I shows the yields and compositions of germ from maize with different treatments and steeping times. In 24-hr steeping, air-dried maize, pure propionic acid-treated maize, semiacidified salts-treated maize, and acidified salts-treated maize had the highest to lowest germ yields, respectively. In 48-hr steeping, untreated air-dried maize also had significantly higher germ yield than did maize treated with acidified salts. Maize steeped for 48 hr tended toward lower germ yields.

Table I also shows that protein contents of the germs from air-dried maize were much greater than those from propionate-treated samples. Steeping time had a significant effect on protein

TABLE I
Effects of Propionate Treatments on the Mass Balance and Composition of Solids in the Light Steep Liquor, Germ, Fiber, and Mill-Starch Fractions[a]

Treatments	Steeping Time (hr)	Steep Liquor: Solids Yield[b] (%)	Steep Liquor: Protein Content[c] (%)	Steep Liquor: Protein Recovery[c] (lb/bu)	Germ: Yield[b] (%)	Germ: Protein Content[c] (%)	Germ: Oil Content[c] (%)	Fiber Yield[b] (%)	Mill-Starch Yield[b] (%)
Air-dried	24	1.16 e	33.1 bc	0.003 e	7.24 a	17.3 a	39.0 e	12.7 bc	69.8 b
	48	3.07 c	34.6 bc	0.016 cd	6.56 bc	15.6 b	43.8 b–d	10.9 e	69.9 b
Pure propionic acid	24	2.60 d	41.2 ab	0.014 d	6.74 b	8.4 d	42.2 d	13.1 a	70.6 ab
	48	3.20 c	45.2 a	0.023 c	6.40 cd	8.3 d	43.5 cd	11.6 de	71.8 a
Semiacidified salts	24	3.94 b	29.1 c	0.023 c	6.43 cd	9.2 c	43.4 cd	12.1 cd	69.7 b
	48	4.71 a	33.1 bc	0.037 b	6.30 cd	8.4 d	44.3 bc	12.9 ab	68.1 c
Acidified salts	24	4.13 b	39.0 ab	0.034 b	6.35 cd	7.2 e	46.4 a	12.2 b–d	70.3 b
	48	5.05 a	38.7 ab	0.050 a	6.21 d	7.0 e	45.7 ab	12.0 cd	69.7 b

[a] Means within the same column followed by a common letter are not significantly different according to Duncan's multiple range test at the 5% level.
[b] Percentage of total maize solids.
[c] Calculated on moisture-free basis.

TABLE II
Effects of Propionate Treatments on the Mass Balance and Composition of Solids in the Starch and Gluten Fractions[a]

Treatments	Steeping Time (hr)	Starch Yield[b] (%)	Starch Protein Content[c] (%)	Starch Recovery[c] (lb/bu)	Gluten Yield[b] (%)	Gluten Protein Content[c] (%)	Gluten Protein Recovery[c] (lb/bu)
Air-dried	24	58.4 d	0.61 d	27.5 d	5.65 a	50.2 a	1.34 a
	48	60.2 c	0.51 d	28.4 c	5.31 a	46.6 b	1.17 b
Pure propionic acid	24	61.6 bc	0.95 c	28.9 bc	4.70 bc	45.4 c	1.01 c
	48	63.6 a	1.05 bc	29.8 a	4.85 b	43.3 cd	1.00 c
Semiacidified salts	24	62.9 ab	1.24 a	29.4 ab	4.73 bc	43.0 cd	0.96 cd
	48	60.9 c	1.19 ab	28.5 c	4.40 bc	40.4 d	0.84 d
Acidified salts	24	64.3 a	1.19 ab	30.0 a	4.63 bc	40.2 d	0.84 de
	48	63.7 a	1.06 bc	29.8 a	4.27 c	41.3 d	0.83 e

[a] Means within the same column followed by a common letter are not significantly different according to Duncan's multiple range test at the 5% level.
[b] Percentage of total maize solids.
[c] Calculated on moisture-free basis.

content of germs from both air-dried maize and semiacidified salt-treated maize. Maize steeped for the shorter time yielded germs with greater protein contents. Composition differences indicated that protein was more extensively leached from germs during steeping in high-moisture maize treated with propionate than in untreated air-dried maize. Whether this difference was due to increased solubility of protein because of the propionate treatment or to reduced solubility in air-dried maize because of drying is not known.

Oil contents in the germs from propionate-treated maize were either equivalent to or greater than those from untreated air-dried maize (Table I). This difference in germ oil content reflected differences in the leaching of protein from germs. For 24-hr steeping, the oil content was inversely proportional to germ yield. No differences were observed among the treatments steeped for 48 hr. For air-dried maize, the longer steeping time resulted in higher oil contents of germs because of greater protein leaching.

There were no significant differences in total oil recovered in the germ fraction between propionate treatments. Oil recoveries in germs ranged from 1.33 lb/bu (23.8 kg/t) to 1.41 lb/bu (25.2 kg/t).

It was easier to separate germs from propionate-treated high-moisture maize and from maize steeped for longer periods than it was from other treatments. It was especially difficult to separate germs from untreated air-dried maize steeped for 24 hr, which we attributed to differences in germ densities. Because protein is denser than oil, germ density is expected to decrease as germ oil contents increase.

Improved germ separation due to propionate treatment is desirable, but increased solids in light steep liquor may cause handling problems. Increased protein leaching into light steep liquor is not desirable even though light steep liquor is eventually added back to gluten feed.

Fiber and Mill-Starch Yields

Table I compares the total fiber yield (sum of coarse and fine fiber) for each treatment. For 48-hr steeping, the untreated air-dried maize had the lowest fiber yield. For 24-hr steeping, air-dried and pure propionic acid-treated maize produced the highest fiber yields.

Mill-starch is starch-gluten solids after germ and fiber separation. Mill-starch includes starch, inseparables, gluten, and wash-water solids. Differences in yields of mill-starch between treatments were relatively small although statistically significant (Table I). For 48-hr steeping, pure propionic acid-treated maize gave the highest yield of mill-starch; semiacidified salts-treated maize had the lowest. For 24-hr steeping, there was no difference among treatments. Mill-starch yield was not affected by steeping time in either air-dried or pure propionic acid-treated maize.

Yields and Protein Contents of Starch

Table II compares the yields, recoveries, and protein contents

TABLE III
Effects of Propionate Treatments on the Mass Balance and Composition of Solids in the Inseparables and Wash-Water Fractions[a]

Treatments	Steeping Time (hr)	Inseparables Yield[b] (%)	Wash Water Solids Yield[b] (%)	Wash Water Protein Content[c] (%)
Air-dried	24	5.66 a	2.35 a	0.11 a
	48	4.39 ab	2.15 b	0.10 b
Pure propionic acid	24	4.24 ab	1.78 c	0.10 ab
	48	3.31 bc	1.43 de	0.06 d
Semiacidified salts	24	2.05 cd	1.63 cd	0.08 c
	48	2.73 cd	1.31 e	0.06 d
Acidified salts	24	1.43 d	1.74 c	0.08 c
	48	1.71 d	1.27 e	0.05 d

[a] Means within the same column followed by a common letter are not significantly different according to Duncan's multiple range test at the 5% level.
[b] Percentage of total maize solids.
[c] Calculated on moisture-free basis.

of the starch fraction recovered from propionate-treated maize with those recovered from the untreated air-dried control. At both steeping times, propionate-treated high-moisture maize gave higher starch yields and recoveries than did untreated air-dried maize. Maize treated with the acidified salts mixture gave the highest starch yield. For pure propionic acid-treated maize and untreated air-dried maize, longer steeping times gave higher starch yields.

Reducing the steeping time of air-dried maize from 48 to 24 hr increased the protein content of the starch. Reducing the steeping time of propionate-treated maize did not significantly affect the protein contents of the recovered starches.

The higher starch yields and recoveries from the propionate-treated samples were partly due to lower amounts of inseparables (Table III) and to poorer starch-gluten separation, as indicated by the higher protein contents of the starch. The protein contents of the starches from propionate-treated maize were nearly twice that of the untreated air-dried control. Higher levels of protein contents of starch than are typically achieved today (< 0.3%) would generally be unacceptable to the wet-milling industry (Johnson 1991). The poorer starch-gluten separation may have been due to poor *Lactobacillus* fermentation, to inadequate lactic acid production, or to protein denaturation caused by prolonged exposure to highly acidic propionic acid.

We did not observe attached gluten particles nor unacceptable grinding properties in any of the propionate treatments. However, we did observe that both starch and gluten tended to settle at nearly the same rates when propionate-treated maize was wet milled.

Wash-Water Solids Recovery

For both steeping times, the yields of wash-water solids in untreated air-dried maize were significantly greater than the yields of solids from all propionate-treated high-moisture maize samples (Table III). There were no differences among the three propionate treatments. For each treatment, maize steeped for 24 hr had higher yields of solids in wash water than did maize steeped for 48 hr. Propionate-treated maize gave wash water with lower protein contents, as did longer steeping time. Fewer solids in wash water were associated with greater yields of starch and gluten.

Yields and Protein Contents of Inseparables

Table III compares the yields of the inseparable fractions (often referred to as "squeegee"). For both steeping times, untreated air-dried maize had the highest amount of inseparables, and acidified salts-treated maize had the lowest. Protein contents of the inseparables averaged about 4% and were not significantly different.

Yields and Protein Contents of Gluten

Table II compares the yields and protein contents for the gluten fractions and the protein recoveries of propionate-treated maize with those of untreated air-dried maize. For both steeping times, untreated air-dried maize had the highest gluten yields and protein recoveries. Generally, no significant difference was found in gluten yields between the two steeping times, although the recovery of protein sometimes decreased at the longer steeping time. Protein contents of the gluten showed a similar trend, as did gluten yield. The gluten from untreated air-dried maize had the greatest protein content. Gluten from untreated air-dried maize steeped for 24 hr had greater protein content than the same maize steeped for 48 hr. Steeping time did not affect the protein contents of gluten from propionate-treated maize.

Propionate treatment of high-moisture maize decreased gluten yield and protein recovery because the endosperm gluten was solubilized more completely during steeping. Propionate treatment reduced the protein content of gluten because of poor starch-gluten separation, resulting in high starch contamination.

CONCLUSIONS

Treatment of maize with propionate to reduce drying costs adversely affected milling properties, especially starch-gluten separation and product yields. The treatments increased starch yield, but at the cost of lower purity. Thus, we conclude that it is not practical to wet mill propionate-treated maize. The yields of germs, gluten, and inseparables from propionate-treated high-moisture maize were lower than those from untreated air-dried maize. At 24-hr steeping, germ separations of propionate-treated high-moisture maize were easier than those of untreated air-dried maize.

The effects of propionate treatment were much more adverse than we had anticipated. Perhaps the adverse effects were due to the reduced lactic acid production and insufficient kernel softening resulting from the natural *Lactobacillus* fermentation during steeping or to the denaturation of maize protein and/or changes in starch resulting from exposure to higher than normal acidities during storage and steeping.

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