Effect of Selected Organic and Inorganic Acids on Corn Wet-Milling Yields[1]

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Cereal Chem. 73(1):96–98

ABSTRACT

The use of alternative organic and inorganic acid (phosphoric acid, acetic acid, citric acid, sulfuric acid, and hydrogen chloride) to replace lactic acid in corn wet-milling steeping was studied. All acids were added into steepwater at a level of 0.55% (v/v) along with 0.2% (w/v) sulfur dioxide, steeped for 24 hr, and laboratory wet-milled to measure product yields and milling characteristics. All organic and inorganic acids added in the steep solution improved the yield of starch by an average of 4.36 percentage points over that of sulfur dioxide alone, with the increased starch coming primarily from the fiber fraction. The yield of starch was highly correlated to the difference of final and initial pH of the steepwater with a correlation coefficient of 0.9174 ($P < 0.0001$). Milling characteristics including gluten filtration time, germ skimming time, and percent of fiber in germ were improved by the addition of the acids. There was no practical difference in starch protein content due to the use of different acids. Acids other than lactic acid could be added into steeping systems where lactic acid fermentation does not occur to enhance the action of sulfur dioxide, to improve the yield of starch, and to facilitate separation of starch and protein.

In conventional corn wet-milling processing, corn is countercurrently steeped for 24–40 hr with a steep solution initially containing 0.12–0.2% sulfur dioxide. As the steep solution passes through the corn, the level of sulfur dioxide in the solution decreases due to absorption by the kernel and reaction to other products. At some point in the process, the sulfur dioxide level is low enough in the steepwater to allow the naturally occurring *Lactobacillus* organisms to propagate and produce lactic acid to a level of 0.6–2.0%.

The role of lactic acid in steeping is not completely understood. However, corn wet-millers have long observed that starch yields decrease when steep conditions inhibit the production of lactic acid (Watson et al 1951). Roushdi et al (1981a) and Eckhoff and Tso (1991) reported decreased starch yields of 4–6% in batch steeping when lactic acid is not used. Other problems, including decreased gluten filtration rates and increased evaporator fouling, have been observed when lactic acid is not in the steep solution (Watson 1984).

Lactic acid acts to soften the kernel and facilitates separation of components. It increases the solubilization of endosperm protein and weakens endosperm cell walls during the steeping process (Roushdi et al 1981). Watson et al (1951) indicated that lactic acid lowered the pH of the steepwater and resulted in greater starch release. Under microscopic examination, Earp et al (1985) found holes and pits in the endosperm cell wall structure when corn was steeped with lactic acid and sulfur dioxide. Similar microscopic examination (Cox et al 1944) revealed that lactic acid accelerated the rate of moisture uptake. This result was confirmed by Ruan et al (1992) using microscopic nuclear magnetic resonance imaging technology (MRI). The objectives of this study were to determine whether organic or inorganic acids other than lactic acid could have the same result as lactic acid in increasing the yield of starch and to evaluate the changes in wet-milling characteristics caused by the use of different acids.

MATERIALS AND METHODS

Yellow dent corn (FR600 × MO17) was laboratory-dried using an ambient air tray-dryer from ≈25 to 14% (wb) moisture content. Samples (1 kg) of corn were steeped at 52°C for 24 hr with a steepwater-to-corn ratio of 2:1 (w/w) and a circulation rate of 300 ml/min. Corn was wet-milled using the laboratory procedure of Eckhoff et al (1993). The steepwater consisted of 0.2% (w/v) SO_2 produced by dissolving 5.9 g of sodium metabisulfite in 2,000 ml of water, with or without the addition of 0.55% (v/v) organic or inorganic acid (lactic acid, phosphoric acid, acetic acid, citric acid, sulfuric acid, or hydrochloric acid). Steepwater pH was measured before and after steeping. Milling characteristics assessed included the gluten filtration time and the germ skimming time. Fiber was hand-picked from the germ fraction after drying, and the percentage of fiber in the germ was calculated. Protein content of starch was measured using a Kjeldahl procedure (AACC 1983). Data were statistically analyzed by Duncan's multiple range test using the Statistical Analysis System (SAS 1994).

RESULTS AND DISCUSSION

Total Recovery of Solids

Total recovery of initial solids varied in this study from 97.32 to 100.40% with a standard deviation of 0.5% (Table I). There was a statistically significant difference in the total solids recovered from the samples in which no acid was added and the other samples (except acetic acid). Total recoveries of 98–99% are common with this wet-milling procedure (below 97% is deemed unacceptable). Dry solids losses are due to leakage from fiber screen, spillage during transfer of slurries between unit operations, and sampling errors in measuring volume and solids content of the steepwater and gluten filtrate. The 0.55% (v/v) added acid to the 2,000 ml of steepwater would account for a 1.1% increase in volume that would affect the total solids content, depending on the water content of the acid. Two of the samples, sulfuric acid and phosphoric acid, had recoveries slightly above 100%. The higher than 100% values may be due to the increase in solids added as acid in the steepwater or sampling error in measuring the volume and moisture content for total solids content of the steepwater and gluten filtrate.

Eckhoff et al (1993) showed a standard deviation for total solids recovery of 0.11 and 0.35% for the two groups of millers

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Publication no. C-1996-0110-03R.

studied. A recent study (Singh and Eckhoff 1995) found a standard deviation of 0.85%, with total recoveries ranging from 96.67 to 99.22% for 10 replicates of the same waxy corn hybrid.

Product Yields

The addition of any acid to the sulfur dioxide steepwater increased starch yield by a minimum of 3.55% (Table I). The largest increase in starch yield occurred when using phosphoric acid (5.75%), but it was not statistically different from that of lactic acid (4.69%). The standard deviation for starch yield was 0.48%. All acids except sulfuric acid (which had a smaller increase) had increased starch yield responses that were statistically similar to that of lactic acid. Protein contents of the resultant starches were not different from a practical perspective, although the sulfuric acid samples had statistically greater protein content (Table II).

The major difference observed between the samples steeped with sulfur dioxide alone and those with added organic or inorganic acid was in the fiber fraction. The yield of fiber for samples steeped with sulfur dioxide alone was at least 4.45 percentage points more than any of the other samples. This is consistent with the results of Roushdi et al (1981) and Eckhoff and Tso (1991), who studied the effect of lactic acid on the yield of starch. Roushdi et al (1981) and Earp et al (1985) speculated that lactic acid's ability to act on cell wall material was the reason for its importance in wet milling.

Strong inorganic acid (hydrochloric acid and sulfuric acid) resulted in low initial and final pH of the steepwater and the rise of pH values were small compare to those of samples treated with lactic acid and phosphoric acid (Table III). Initial and final pH of steepwater for sulfur dioxide alone was highest, and the pH rise was the least. Although sulfur dioxide alone had the highest initial pH and the lowest starch yield, the increase in starch yield is not directly related to the acidity of the steepwater. Sulfuric acid had the lowest initial and final pH values but had the second lowest starch yield.

Although pH alone does not appear to affect the starch yield, the difference between final pH and initial pH were highly correlated to the yield of starch. The correlation coefficient between the yield of starch and difference between final pH and initial pH was 0.9174 ($P < 0.0001$). No significant pH change was observed for samples treated with sulfur dioxide alone. However, samples treated with acids all showed a pK_a rise. No relationship could be determined between pH values of the acids and the starch yield. Further study is needed to determine the relationship of starch yield to the characteristics of specific acids.

Germ yield was not affected by the addition of different acids, although germ skimming took longer for samples steeped in sulfur dioxide alone than for samples steeped with added acid (Table II.). The most significant difference between the samples is in the amount of fiber attached to the germ. The attached fiber was hand-picked from the germ samples and accounted for almost 15% by weight of the germ fraction from the corn steeped with sulfur dioxide alone. The samples with added acid had attached fiber in germ varying from 1.78 to 6.91%.

The other major difference between samples steeped with sulfur dioxide alone and those steeped with the addition of acid is in the total amount of solubles recovered from steepwater solids and filtrate solids (Table I). For sulfur dioxide alone, the amount of solubles was low (5.04%) compared to the use of added acids (6.10 to 7.39%). This result confirms the finding of Cox et al (1944), Roushdi et al (1981), and Eckhoff and Tso (1991) that a low concentration of lactic acid in the steepwater enhances the action of sulfur dioxide to break down the protein matrix and release starch.

Gluten yields varied from 8.21 to 9.82%, and three groups of statistically different treatments were observed (Table I). The highest gluten yield was for samples with lactic acid and sulfuric acid. A second group contained hydrochloric acid alone, while the third group included the other four treatments. The most significant finding was the time required for gluten filtration (Table II). The samples with sulfur dioxide alone required over 900 min to complete filtration while all samples with added acid completed filtration in 40–45 min. No appearance differences were observed between samples, but it is speculated that the added acids altered the protein conformation, resulting in the observed differences in protein filtration. Fox (1993) found that the addition of starch to gluten slurry did not significantly decrease filtration rates indicating that the higher gluten filtration times observed for samples steeped in sulfur dioxide alone were not caused by the lower starch yield of the samples.

Acetic acid is not recommended for use in commercial systems because of a detectable odor that carried through the whole process into the final products. No other odor or color problems were observed for any of the other acids.

CONCLUSIONS

The addition of organic and inorganic acids (phosphoric acid, acetic acid, citric acid, sulfuric acid, and hydrogen chloride) into

TABLE I
Wet Milling Yields (%)from Corn Steeped in 0.2% Sulfur Dioxide and 0.55% of Various Organic or Inorganic Acids[a]

Acid	Starch	Fiber	Germ	Gluten	Filtrate Solids	Total Solids Recovery
None	59.12d	18.63a	6.33a	8.21c	2.51c	97.32d
Lactic	63.81ab	12.74d	6.38a	9.67a	3.05bc	99.47ab
Phosphoric	64.87a	13.05cd	6.56a	8.77bc	3.12b	100.29ab
Acetic	62.93bc	14.05bc	6.38a	8.25c	3.11b	98.14cd
Citric	62.96bc	14.00bc	6.56a	8.71bc	3.30b	99.49ab
Hydrochloric	63.64bc	13.88bc	6.69a	8.84b	3.19b	99.14bc
Sulfuric	62.67c	14.18b	6.36a	9.82a	3.90a	100.40a

[a] Means with the same letter in the same column are not significantly different at $P < 0.05$.

TABLE II
Milling Characteristics of Corn Steeped in 0.2% Sulfur Dioxide and 0.55% of Various Organic or Inorganic Acids[a]

Acid	Protein Content in Starch (%)	Fiber in Germ (%)	Germ Skimming (min)	Gluten Filtration (min)
None	0.29b	14.79a	25a	900a
Lactic	0.31b	1.78b	15c	45b
Phosphoric	0.29b	3.36b	15b	45b
Acetic	0.30b	6.91b	20b	45b
Citric	0.31b	5.52b	20b	45b
Hydrochloric	0.32b	5.68b	15c	40c
Sulfuric	0.36a	5.82b	20b	40c

[a] Means with the same letter in the same column are not significantly different at $P < 0.05$.

TABLE III
Changes of pH of Steepwater Before and After Steeping[a]

Acid	pH of Steepwater Before Steeping	pH of Steepwater After Steeping	Rise in Steepwater pH
None	5.93a	5.86a	–0.07d
Lactic	2.93c	4.34c	1.41ab
Phosphoric	2.07d	4.58b	2.51a
Acetic	3.50b	4.59b	1.09bc
Citric	2.92c	4.20c	1.28bc
Hydrochloric	1.66e	2.87e	1.21bc
Sulfuric	1.28e	1.67e	0.39c

[a] Means with the same letter in the same column are not significantly different at $P < 0.05$.

steepwater can increase the yield of starch in a manner similar to that of lactic acid. All acids studied increased the amount of starch recovered by an average of 4.36 percentage points, with the increase in starch yield primarily coming from the fiber fraction. The highest starch yield was obtained using phosphoric acid, but it was not significantly different from samples with lactic acid. The increase in starch yield is highly correlated to the difference of final and initial pH of the steepwater with a correlation coefficient of 0.9174 ($P < 0.0001$). The addition of all acids improved milling characteristics. Acids eased germ separation and increased the rate of gluten filtration. Due to odor in the final products, acetic acid is not recommended for industrial use.

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[Received May 22, 1995. Accepted September 14, 1995.]