Wet Milling of Corn Using Gaseous SO_2 Addition Before Steeping and the Effect of Lactic Acid on Steeping

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ABSTRACT

Gaseous SO_2 was applied to low-moisture corn kernels (Dekalb 636) at rates of 0.1 and 0.2% (based upon the weight of steepwater) before steeping for 6, 12, or 24 hr. These gas-treated samples were compared to a standard 48-hr control steep using the same sulfite levels. At the 0.1% treatment level, the effect of adding 0.55% lactic acid to the steepwater was studied. Starch yields of the controls were not statistically different from those of the 12-hr gaseous steeps and were lower than those of the 24-hr steeps. Brabender consistency was approximately 12% higher for the gas-treated samples at 12 hr than for the controls. The 6-hr gas-treated corn had even higher Brabender consistencies, but starch yields were decreased by approximately 3% at all treatment levels. Increasing the concentration level of gaseous SO_2 from 0.1 to 0.2% resulted in increases in starch yields of 1.44, 2.08, and 2.35% for the 6-, 12-, and 24-hr steeps, respectively. The role of lactic acid in increasing starch yields was demonstrated. Starch yields from 0.1% SO_2 plus 0.55% lactic acid were greater than those from 0.2% SO_2 without lactic acid for all steep times. Starch yields were increased by 5.64, 4.96, and 4.44% for the 6-, 12-, and 24-hr steeps, respectively, for the 0.1% treatment level. Protein contents of the starch were acceptable for all treatments (less than 0.413%).

Approximately 13% of the annual U.S. corn production is wet milled to produce food starch, ethanol, and sweetener products. The current corn wet-milling process involves steeping corn in dilute SO_2 solution (0.1–0.2%, based on the weight of steepwater) at 50–53°C for 24–38 hr, to soften the kernels and to induce chemical reactions that allow for the separation of starch and protein. The SO_2 causes the protein matrix to weaken by breaking disulfide bonds and forming soluble S-sulfoproteins, which prevent reformation of disulfide bonds (Boundy et al 1967). After steeping, the corn is ground and subsequently separated into products through a series of screening, centrifugation, and washing steps.

The rate-limiting step in steeping is the diffusion of SO_2 into the corn. Watson and Sanders (1961) found that starch release could be achieved in as little as 2–6 hr of steeping when most of the diffusion limitations were removed. Cox et al (1944) found that 8 hr was required for the SO_2 solution to completely penetrate corn kernels. After hydration, an additional 12–16 hr of steeping is required, because of the countercurrent nature of the current steeping process, to expose the kernel to sufficient levels of sulfite. Eckhoff (1983) showed that gaseous SO_2 penetrated dry corn about 100 times faster than was found for sulfurous acid by Fan et al (1965). The time required for penetration was reduced from 8 hr to 4–5 min with gaseous SO_2.

The application of gaseous SO_2 not only increases the rate of penetration into the endosperm but also increases the exposure of the endosperm to sulfur dioxide. Increased SO_2 levels have been found to increase starch yields. Watson and Sanders (1961) showed that increasing the SO_2 concentration from 0.05 to 0.2% resulted in an increased rate and extent of starch release. Cox et al (1944) found that protein dispersion was faster and starch extraction was more complete as the SO_2 concentration increased up to 0.4%. Krochta et al (1981) also showed that increasing the SO_2 concentration from 0.1 to 0.4% increased starch yield from 66.6 to 72.6%.

The main deterrent to the use of SO_2 levels above 0.2% in the steep has been concern that lactic acid fermentation would be inhibited (Watson and Sanders 1961). Lactic acid, the chief product of fermentation from soluble sugars in the steepwater solution, is reported to lower the pH value of steepwater, restrict the growth of organisms other than *Lactobacillus*, cause some softening of kernel components, and produce favorable conditions for separation of the kernel components, especially protein, after milling. However, the importance of lactic acid in steeping has never been fully established. Contrary to the assumptions made by Watson et al (1955), lactobacilli do not appear to produce the proteolytic enzymes capable of solubilizing the protein matrix, thereby enhancing starch release (Wall and Paulis 1978). Roushdi et al (1981a) found that high levels of SO_2 alone gave better starch yields than lower levels of SO_2 with lactic acid. However, in a follow-up study (Roushdi et al, 1981b), they found that steeping with lactic acid lowered protein content in starch and increased starch yield.

The addition of sulfur dioxide gas to dry corn kernels before hydration would decrease steep time and improve starch quality. A decrease in steep time would result in the potential for expansion in land-locked facilities, a reduction in total energy utilization, and decreased capital expenditures in the building of new wet-milling plants. Modification would be required in existing plants to safely apply the gaseous sulfur dioxide to the corn. Current steep tanks could be utilized, but the addition of sulfited corn to the steeps would need to be done so as not to vent directly into the atmosphere or the steephouse.

Objectives of this research were to: 1) compare the product yields and starch quality of corn treated with gaseous SO_2 and steeped for different periods with those of standard control samples, 2) investigate the degree to which the addition of lactic acid to steepwater affects starch yield and quality, and 3) investi-

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gate how the concentration and amount of SO_2 changes in the steepwater and in the kernels during steeping.

MATERIALS AND METHODS

Experimental Design

Steep times of 6, 12, and 24 hr were evaluated for corn samples treated with gaseous SO_2 and compared to a traditional 48-hr laboratory steep. Three treatment conditions were tested at each steep time: 0.2% SO_2, 0.1% SO_2, and 0.1% SO_2 with 0.55% lactic acid. This made a total of 12 combinations of steep time, concentration levels of SO_2, and lactic acid. Two replicates were run for each condition. The concentration levels of SO_2 added were 0.4 and 0.2%, based on the weight of the corn, which corresponded to 0.214 and 0.107%, respectively, based on the weight of the steepwater (1,500 g of corn per 2,800 g of steepwater). The rounded values of 0.2 and 0.1% were used in reporting data. Statistical analysis was performed using the SAS (SAS 1982) program. Duncan's multiple range test ($P < 0.05$) was used for comparison.

Wet Milling of Corn Treated with Gaseous SO_2

Yellow dent corn lots (Dekalb 636) with initial moisture contents ranging from 13.5 to 14.5% (wb) were blended together, run through a dockage tester, and inspected visually. The lots were blended to remove the moisture variation that occurred during storage of the corn in polyethylene bags. The corn had been laboratory-dried in thin layers in ambient air from approximately 25% (wb) moisture content. Fifteen hundred grams of the corn was placed into a polyethylene bag and sealed. Gaseous SO_2 was metered through a rotameter and into the corn bag via an injection needle. The total treatment dosage was determined by the length of gas addition at a constant flow rate (1.59 g of SO_2 per minute). The corn was held in the bag for 15 min at room temperature; then it was removed from the bag and put into the steep tank.

Corn was steeped in a glass steep tank containing 2,800 ml of distilled water (with or without 0.55% lactic acid) at 50°C. The steepwater was constantly circulated at a rate of approximately 380 ml/min through tubing in a temperature-controlled water bath to maintain proper steep temperature. The steepwater was drained off and saved after steeping. The weight and pH of the steepwater were measured, and a sample of steepwater was dried to determine the weight of soluble solids. The procedure of Anderson (1963) was followed in the fractionation of the kernels and recovery of the wet-milled products.

Wet Milling of Traditionally Steeped Corn

Fifteen hundred grams of corn were placed into a glass steep tank, as described above, and 2,800 ml of distilled water (with or without 0.55% lactic acid) was recirculated through the steep at 50°C. Sulfurous acid solution was added to the steepwater to a level of 0.1 or 0.2%. After 48 hr of steeping, the steepwater was drained off and the procedure of Anderson (1963) was followed for fractionation and separation of corn components.

Analyses of Starch Quality

All starch samples were analyzed for protein content using the Kjeldahl method (AOAC 1984). A Brabender Viscoamylograph was used to measure the consistency of a 10% starch slurry made from the wet-milled starch (CPC 1987).

Determination of Concentration and Amount of SO_2 During Steeping

To investigate changes of SO_2 concentrations in corn kernels and in steepwater during steeping, 1,500 g of corn (including several 25-g samples in nylon mesh) was treated with either 0.1% gaseous SO_2 and steeped 24 hr, with 0.1% sulfurous acid and steeped 48 hr, or with 0.1% sulfurous acid and 0.55% lactic acid solution and steeped 48 hr. Corn samples and some steepwater were removed after a time to measure the water-extractable SO_2 in corn kernels and in steepwater with a direct titrimetric method (Eckhoff and Okos 1983). The corn sample was weighed after removal so that the weight of corn in the steep tank could be estimated. The appropriate amount of steepwater was removed when the corn was removed to maintain the same ratio of corn to steepwater.

RESULTS AND DISCUSSION

Results showed that steeping time could be greatly reduced when gaseous SO_2 was applied to the corn. More complete separations of corn components were obtained in those samples with added lactic acid.

Product Yields

In comparison with the 48-hr controls at the same SO_2 concentration levels (Table I), the 12- and 24-hr gas-treated corn samples generally had statistically similar product yields. For 0.1% SO_2 steeps, the yields of germ, starch, and soluble solids increased while those of fiber and protein decreased with the addition of 0.55% lactic acid in most of the conditions. With the addition of lactic acid, the average of the yield values for the 12- and 24-hr treatments and the controls increased in germ, starch, and soluble solids by 0.47, 4.55, and 0.79%, respectively, while this average decreased in fiber and protein by 2.49 and 0.53%, respectively.

Starch Yields

Table I shows that the 6-hr steeps with gaseous treatments had the lowest starch yields: 61.79, 63.23, and 67.43 for 0.1%

TABLE I
Product Yields from Wet-Milled Corn Steeped Under Different Conditions[a]

Form of Sulfur Added	Steep Time (hr)	SO_2 (%)	Product Yields (%, db)				
			Germ	Fiber	Starch	Protein	Soluble Solids
Gaseous SO_2	6	0.2	7.54 a	12.63 a	63.23 f	10.03 d–g	5.52 b
		0.1	5.96 d	10.00 c–e	61.79 g	14.43 a	1.32 g
		0.1 & LA[b]	5.92 d	10.60 b–d	67.43 b	10.40 c–f	4.69 c
	12	0.2	6.59 bc	11.01 bc	66.18 c	10.15 d–f	4.62 cd
		0.1	5.73 d	11.60 ab	64.10 ef	11.31 bc	2.34 f
		0.1 & LA	6.23 b–d	9.51 d–f	69.06 a	10.78 cd	3.83 e
	24	0.2	5.92 d	9.13 e–g	67.89 b	10.70 c–e	5.49 b
		0.1	6.01 d	11.04 bc	65.54 cd	11.67 b	4.27 c–e
		0.1 & LA	6.71 b	9.15 e–g	69.98 a	9.80 e–g	4.01 de
Sulfurous acid (control)	48	0.2	5.99 d	8.82 fg	67.26 b	9.75 fg	6.17 a
		0.1	5.92 d	11.63 ab	64.87 de	9.14 g	4.53 cd
		0.1 & LA	6.12 cd	8.14 g	69.12 a	9.94 d–g	5.66 ab

[a] Each value represents the mean of two replicates; mean comparisons followed by the same letter are not significantly different ($P < 0.05$) within the same column.
[b] LA denotes 0.55% lactic acid added to the steepwater.

SO_2, 0.2% SO_2, and 0.1% SO_2 with lactic acid, respectively. They were increased by 2.31, 2.95, and 1.63 percentage points, respectively, with 12-hr steeps, and by 3.75, 4.66, and 2.55 percentage points, respectively, with 24-hr steeps. Starch yields were not statistically different between the 12-hr and control samples for the 0.1% and the 0.1% with lactic acid treatments. The 0.2% sample at 12 hr yielded statistically less starch than the control. When statistically analyzed by sulfur dioxide level and addition of lactic acid, the 24-hr samples with gaseous sulfur dioxide were statistically better than the control samples for the corn treated with 0.1% SO_2 with lactic acid or with 0.2%, even though they were not statistically different in the grouped analysis shown in Table I.

Table I also shows that corn kernels treated with 0.1% SO_2 and lactic acid had the highest starch yields, and those treated with 0.1% SO_2 had the lowest at any specific steep time. When the SO_2 concentration was increased from 0.1 to 0.2%, starch yields increased 1.44, 2.08, and 2.35% for 6-, 12-, and 24-hr steeps, respectively. Lactic acid increased starch yield more than did doubling the SO_2 concentration level. Starch yields were increased by 5.64, 4.96, and 4.44% for 6-, 12-, and 24-hr steeps, respectively. The difference between starch yields when steeping with 0.1 and 0.2% SO_2 increased as steep time increased. The largest starch yield difference between 0.1% SO_2 and 0.1% SO_2 with lactic acid occurred after 6 hr of steeping.

Some researchers and industry personnel have suggested that lactic acid fermentation in situ is more desirable in steeping than addition of lactic acid produced by an external means. Our data suggest that it is the lactic acid, regardless of how it is produced, that affects starch yield. Steinke et al (1991) reported a 6.5 percentage point increase in starch yield between batch steeping with no added lactic acid and their countercurrent steeping battery, which compares favorably with the 4–4.5 percentage point increase reported here. Their lower level of starch yield (64.9% in countercurrent steep) may account for the larger difference they observed. For Steinke et al (1991), the increase in starch yield appears to result primarily from a decrease in the fiber fraction. Our data also shows a decrease in fiber yield when lactic acid is in the steep. The lactic acid fermentation may affect the steepwater composition and other characteristics of the process, which may effect downstream-processing of the components.

TABLE II
Protein Contents (% db) of Starch Obtained from Wet-Milled Corn Steeped Under Different Conditions[a]

Form of Sulfur Added	Steep Time (hr)	Treatment: 0.1% SO_2 & LA[b]	0.1% SO_2	0.2% SO_2
Gaseous SO_2	6	0.278 f	0.344 b–e	0.381 a–d
	12	0.337 c–f	0.298 ef	0.405 ab
	24	0.395 a–c	0.413 a	0.366 a–d
Sulfurous acid (control)	48	0.347 b–e	0.382 a–d	0.324 d–f

[a] Each value represents the mean of two replicates. Mean comparisons followed by the same letter are not significantly different ($P < 0.05$).
[b] LA denotes 0.55% lactic acid added to the steepwater.

TABLE III
Peak Brabender Consistencies (Bu) of Starch Slurries When Steeped Under Different Conditions[a]

Form of Sulfur Added	Steep Time (hr)	Treatment: 0.1% SO_2 & LA[b]	0.1% SO_2	0.2% SO_2
Gaseous SO_2	6	1,175 aB	1,255 aA	1,130 aB
	12	1,165 aA	1,210 abA	1,060 abB
	24	1,160 aA	1,190 bA	1,030 bB
Sulfurous acid (control)	48	1,010 bB	1,070 cA	935 cC

[a] Each value represents the mean of two replicates. Mean comparisons followed by the same lowercase letters are not significantly different ($P < 0.05$) within the same column. Mean comparisons followed by the same capital letter are not significantly different ($P < 0.05$) within the same row.
[b] LA denotes 0.55% lactic acid added to the steepwater.

Starch Quality

Starch protein content and starch consistency are two important criteria in evaluating starch quality. Starch is considered to be of high quality when it has low protein content and high consistency when gelatinized.

The protein contents of the starch samples recovered in this study were lower than the average protein content in starch, 0.54%, given in Anderson (1963) for the laboratory procedure, but they were similar to those found in industrial applications (Table II). No relationship was observed between protein content and steep time, SO_2 level, application of gaseous SO_2, or addition of lactic acid.

The peak consistencies of the starch slurries, determined by use of a Brabender amylograph (Table III), demonstrate that, for the same gaseous treatment, consistency was not statistically different for 6-, 12-, and 24-hr steeps with the exception of the 24-hr steeps at 0.1 and 0.2% SO_2 levels. For the 12- and 24-hr steep times, the peak starch consistencies of the 0.1% gaseous SO_2 treatments with and without added lactic acid were not statistically different, and both produced higher consistencies than 0.2% SO_2 treatments. The consistencies from the 0.2% SO_2 treatments were approximately 4, 9, and 11% less than those from the treatments with 0.1% SO_2 and lactic acid for 6-, 12-, and 24-hr steeps, respectively. All treatments produced better consistencies than the controls. The consistencies produced by the controls were 10, 9, and 13% lower than those from the corresponding 24-hr steeps for treatments with 0.1% SO_2, 0.2% SO_2, and 0.1% SO_2 with lactic acid, respectively.

The differences observed are probably due to the uniformity of the gaseous sulfur dioxide application. The standard steep, where the SO_2 diffuses with the water into the corn kernel, may result in overexposure of the starch in the outer section of the endosperm. Longer SO_2 exposure decreases starch consistency (Schroeter 1966), probably by some acid hydrolysis of the starch. The gaseous addition distributes the SO_2 in the corn kernel in a short time (Eckhoff and Okos 1989) and provides a more uniform treatment.

Concentration and Amount of SO_2 During Steeping

Figure 1 shows the concentration changes of water-extractable SO_2 in corn kernels and in steepwater while corn was being steeped under three different conditions: 0.1% gaseous SO_2, 0.1% sulfurous acid (control), and 0.1% sulfurous acid with 0.55% lactic acid. The concentrations of SO_2 reached the highest points after steeping for 4 hr for all three treatments. At that time, the corn treated with lactic acid absorbed 300 ppm more SO_2 than the other two.

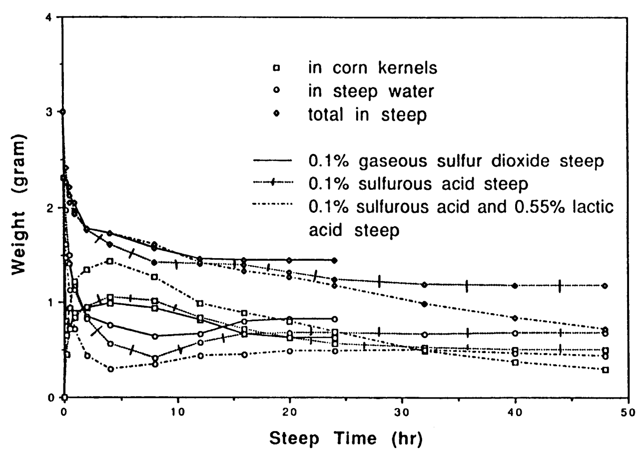

Fig. 1. Concentrations of water-extractable SO_2 in corn kernels and steepwater during steeping under different conditions.

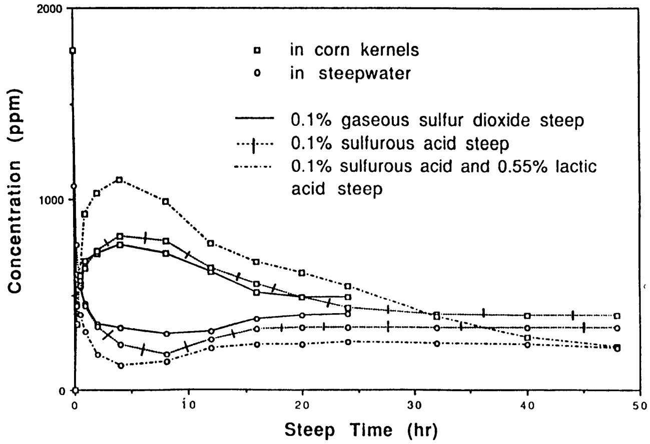

Fig. 2. Weights of water-extractable SO_2 in corn kernels and steepwater during steeping under different conditions.

After a 48-hr steep, the concentrations of SO_2 in corn kernels and in steepwater were 175 and 110 ppm less, respectively, when lactic acid was added to 0.1% sulfurous acid.

Figure 2 presents weight changes of SO_2 in corn kernels, in steepwater, and total in steep. The weight of SO_2 was determined with the concentration shown in Figure 1, and the weights of corn kernels and steepwater were estimated from the removed samples, as previously described. For the same steep time, the total amounts of SO_2 were about the same when corn kernels were treated with gaseous SO_2 and sulfurous acid alone. The total amount of water-extractable SO_2 remained constant after 16–20 hr when gaseous SO_2 was applied, and it took 32–40 hr to reach a steady value when 0.1% sulfurous acid alone was applied.

Figure 2 also shows that from a total of 3 g of water-extractable SO_2 at the beginning of steeping, the total for the treatment with lactic acid remained 0.7 g while the total for the 0.1% sulfurous acid treatment remained 1.2 g after a 48-hr steep. The difference in total amount of water-extractable SO_2 between the two treatments was getting larger after 24 hr. The difference may be caused by the lactic acid, which lowers the pH of the steep and thus reduces the amount of water-extractable SO_2.

The amount of sulfur dioxide in the corn kernel after steeping in a conventional steep battery is determined by the level of sulfur dioxide added to the steepwater. Since the system is countercurrent, the corn is exposed to the highest levels of sulfur dioxide just before being sent to the mill for grinding. Current starch washing procedures are adequate to ensure low residual sulfite in the starch. Since the down-stream processing of the corn into starch would not be changed by the use of gaseous sulfur dioxide, no increase in residual sulfite in the starch or other products should occur.

CONCLUSIONS

The application of gaseous SO_2 in corn wet milling by treating corn kernels before steeping could significantly save steep time. Product yields of a 12-hr steep with gaseous SO_2 treatment were similar to those of a 48-hr standard steep. Both the increase in the concentration level of gaseous SO_2 and the addition of lactic acid resulted in an increase in the starch yield. Due to the reduction of steep time, consistencies of starch slurries recovered from gaseous SO_2 treatments were increased significantly as compared to those of the controls. No effect was found on the protein content in starch made by the applications of gaseous SO_2 and lactic acid. The addition of lactic acid was found to increase starch yields by 4–5 percentage points. The role of the lactic acid in steeping is not clearly understood, but it does appear to affect starch yield.

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