## Magnesium Bisulfite and Sodium Bisulfite as Alternative Steeping Agents for Wet Milling

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Wet milling is the process by which whole corn is separated into fractions that are high in starch, protein, oil, and fiber. The initial stage of wet milling involves steeping the corn for 24–36 hr in a weak sulfurous acid solution created by adding small amounts of sulfur dioxide (1,000–2,000 ppm) to water. Steeping conditions the germ to withstand the rigors of grinding and makes it possible to separate the protein and starch of the corn endosperm.

The common methods for adding sulfur dioxide  $(SO_2)$  to the steep solution are to burn elemental sulfur or to bubble gaseous  $SO_2$  directly into the steeping solution. Both methods require gaseous  $SO_2$  to be absorbed by the steeping liquid, resulting in emissions of  $SO_2$  into the atmosphere. Because of the volatility of  $SO_2$ , its reactivity, and its inherent pungent odor, there are related health and environmental concerns, not only for the milling facility, but also for the surrounding areas. The use of magnesium bisulfite (MBS) and sodium bisulfite (NaBS) steeping agents are attractive alternatives to  $SO_2$  because they would not require any modifications to the milling process. They offer reduced  $SO_2$  emissions because they bind  $SO_2$  as a salt compound. These compounds are produced as solutions containing approximately 19–23%  $SO_2$  by weight. They can be added to the steepwater without special absorption apparatus.

The objectives of this study were to investigate MBS and NaBS steeping agents as alternatives to conventional SO<sub>2</sub> and to determine any product-yield advantages of using these alternative compounds as steeping agents in the wet-milling process.

#### MATERIALS AND METHODS

#### **Laboratory Wet-Milling Procedure**

Laboratory-scale wet milling was performed in duplicate on corn samples using the procedure of Eckhoff et al (in press), which provides yields of germ, fiber, starch, gluten, steepwater, and gluten filtrate. Each 1,000-g corn sample was passed over a 12/64-in. (4.76-mm) round-hole sieve using a reciprocating Gamet shaker and hand-inspected to remove any moldy kernels before milling. All milling yields are presented on a dry solids basis.

Rheological data were collected for selected starch samples using a Brabender Viscoamylograph according to the procedures of Shuey and Tipples (1980). Thirty-five grams of starch, 3.6 g of sodium carboxymethyl cellulose and 450 ml of buffer were mixed together to determine: onset of gelatinization, peak viscosity, and initial viscosity after heating from 50 to 95°C; viscosity after 30 min at 95°C; initial viscosity after cooling to 50°C; and final cold paste viscosity after 30 min at 50°C. Amylograph data were collected on starch from three hybrids (FR27 × FRMo17, FR618 × FR600, and FR1087 × LH123) steeped for 24 hr at 1,500 ppm concentrations of SO<sub>2</sub> and MBS solutions.

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### Effectiveness of Alternative Steeping Agents

A medium-hard hybrid of regular dent corn, FR618 × FR600, was wet-milled to investigate the effectiveness of MBS and NaBS solutions (Hydrite MBS 6310 and Hydrite NaBS solutions, respectively) obtained from the Hydrite Chemical Company, Waterloo, IA. The FR618 × FR600 hybrid had been dried at 80°C in a batch-type dryer from an initial moisture content of 26%, wet basis. This temperature is considered moderately high for drying corn and causes reduced starch and germ yields, increased fiber and gluten yields, and reduced starch quality when wet milled due to changes in steeping characteristics (Vojnovich et al 1975). Five combinations of steeping time (24 and 36 hr), steeping agent, and SO<sub>2</sub> concentration (1,000 and 2,000 ppm) were tested in duplicate (Table I). Five additional runs of time and concentration combinations (SO<sub>2</sub> at 1,000 ppm for 18, 24, and 36 hr; MBS at 3,000 ppm for 36 hr; MBS at 1,000 ppm for 18 hr) were wet-milled for comparison. However, yield data for these tests are not presented in Table I because the runs were unreplicated. To investigate potential effects of hybrid differences, six additional, unreplicated runs were made. Hybrids (FR27 imesFRMo17, FR618 × FR600, FR1087 × LH123) were steeped with 1,500 ppm of either SO<sub>2</sub> or MBS (SO<sub>2</sub> equivalent) for 24 hr.

#### RESULTS AND DISCUSSION

#### Effect of Steeping Agent on Product Yields

The average yields (Table I) from the duplicate milling runs of FR618  $\times$  FR600 hybrid corn dried at 80° C were representative of regular dent milling yields in industry (Knight 1969, Anderson and Watson 1982, May 1987). They were compared using the least significant difference method (a = 0.05). Yields from corn steeped with MBS and NaBS did not differ greatly from the yields of corn steeped using conventional SO<sub>2</sub>. There were no significant differences for the fiber, gluten, filtrate, and total recovery yield means. Yields from all the unreplicated milling runs also showed no pronounced differences between steeping agents.

Steepwater solids yields were somewhat higher for longer steeping times; the yield from the 36-hr 2,000-ppm MBS steep was significantly higher than that from the 24-hr 2,000-ppm MBS steep. This is attributed to increasing amounts of solubles leaching out of the corn into the steepwater as steeping time was lengthened.

The germ yield for corn steeped for 36 hr in 2,000 ppm  $SO_2$  was similar to the MBS germ yield at the same conditions. It was significantly higher than all of the other treatments. However, the 36-hr 2,000-ppm MBS steep was statistically similar to the other MBS steeps and to the NaBS treatment. Since germ contain a large percentage of soluble material, longer steeping periods will leach more material from the germ (Fox and Eckhoff 1993). This removal of solubles causes the germ to have a lower specific gravity, making germ recovery more efficient.

Starch yield was significantly higher for the 36-hr 2,000-ppm SO<sub>2</sub> steep and significantly lower at the same conditions for the MBS steep. However, the other MBS steeping conditions were similar to the SO<sub>2</sub> steep, yielding contradictory results. In theory, the longer steeping times and higher SO<sub>2</sub> concentrations should result in higher starch yields. Comparison between Brabender amylographs using SO<sub>2</sub> or MBS showed that the MBS had no significant effect on starch pasting and viscosity characteristics.

# Effect of Steeping Agent on pH and Magnesium and Sodium Levels

Regardless of the steeping agent used, the pH level of the batch

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TABLE I Average Wet-Milling Yields (% db) of Duplicate Milling Runs for FR618 × FR600 Dried at 80°C

Fraction	Steep Agent					
	SO <sub>2</sub> (36 hr, 2,000 ppm)	MBS*				
		36 hr		24 hr	NaBS <sup>c</sup> (36 hr,	
		2,000 ppm <sup>b</sup>	1,000 ppm <sup>b</sup>	(2,000 ppm <sup>b</sup> )	2,000 ppm <sup>b</sup> )	LSD <sub>0.05</sub> d
Steepwater	4.84 ab <sup>d</sup>	5.29 a	5.13 ab	4.69 b	5.05 ab	0.460
Germ	6.71 a	6.56 ab	6.42 b	6.39 b	6.44 b	0.249
Fiber	9.36 a	8.77 a	8.56 a	9.71 a	9.92 a	1.77
Starch	65.87 a	63.10 b	64.68 ab	65.09 ab	65.16 ab	2.09
Gluten	9.77 a	11.64 a	11.08 a	10.34 a	9.60 a	2.77
Filtrate	2.38 a	2.90 a	2.63 a	2.67 a	2.31 a	0.607
Total <sup>e</sup>	98.92 a	98.25 a	98.49 a	98.87 a	98.48 a	2.24

<sup>&</sup>lt;sup>a</sup> Hydrite MBS 6310 magnesium bisulfite steeping agent.

steeps increased approximately 1 pH unit during each steeping period. However, the MBS and NaBS steeps had pH levels of 3.5-4.4 that were relatively higher than the SO<sub>2</sub> steep pH levels of 2.4-3.9. However, countercurrent steepbanks used in industry exhibit pH characteristics different from those of the batch steeps used in this study. No negative effect is anticipated because of the increase in magnesium or sodium ions in the steepwater. For a typical maximum concentration of 2,000 ppm of SO<sub>2</sub> in the steepwater, the amount of Mg or Na added to the steeping system would be 360 and 730 ppm, respectively. The amounts of Mg and Na added to the steepwater by MBS and NaBS would be within the normal range of these elements naturally occurring in corn, (900-10,000 ppm and 0-1,500 ppm for Mg and Na, respectively [Watson, 1987]). Schroder and Heiman (1970) found that the magnesium level in the steepwater solids they analyzed was 2% (20,000 ppm). They did not report the level of sodium.

#### CONCLUSIONS

MBS and NaBS steeping agents performed similarly to conventional SO2, based on wet-milling yields and Brabender amylographs. The major advantage of MBS or NaBS may be in health and safety benefits brought about by changing occupational and environmental regulations.

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<sup>&</sup>lt;sup>b</sup> Hydrite NaBS sodium bisulfite solution steeping agent.

<sup>&</sup>lt;sup>c</sup> Least significant difference for each yield mean at  $\alpha = 0.05$ .

<sup>&</sup>lt;sup>d</sup> Means followed by the same letter in the same row are not significantly different at  $\alpha = 0.05$ , as determined by the least significant difference method. Yields are averages of duplicate milling runs.

e Percentage total dry solids recovered in the milling process.