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Corn-Milling Pretreatment with Anhydrous Ammonia

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Abstract

Exposure to anhydrous ammonia has been suggested as a pretreatment for corn milling. Batches of corn were exposed to ammonia under controlled conditions. The amounts of ammonia absorbed and reacted with the corn were measured. The amounts were not more than are needed as nutritional supplement for yeast fermentation to ethanol. Loosening of the hull was observed qualitatively, and subsequent shearing in a disk mill followed by steeping for 2, 4, 6, or 8 h showed that germ could be recovered at higher yield and after a shorter steeping time compared to untreated control batches. Quality of oil was not affected by treatment with ammonia.

Index Entries: Corn; ammonia; pretreatment; milling; steeping; ethanol; fermentation.

Introduction

The corn wet-milling process begins by steeping (soaking) in water with added SO_2. Steeping may take up to 48 h in large, expensive steep tanks. This process softens the corn so that coarse grinding will release the intact germ, which can be separated and processed to recover the oil. Further grinding then permits separation of the remaining components, fiber, protein, and starch, but building a corn wet mill requires a large capital investment. By contrast, although less capital intensive, the dry-grind process for

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fuel ethanol suffers from low coproduct value. In a modification of the dry-grind process known as Quick-Germ, the germ can be recovered after 12 h of soaking to improve the coproduct credits *(1)*. Diffusion of water into the kernel during steeping or soaking is slow because the hull (pericarp) covering the kernel forms a waterproof barrier. Time required for steeping in the wet-milling process or soaking in the Quick-Germ process can be reduced if the pericarp is removed.

Alkali debranning of grains is usually done with a caustic soda solution, which loosens the hulls, so that mechanical equipment may remove and separate them from the grain *(2,3)*. A possible alternative is to expose the grain to gas-phase anhydrous ammonia. It should diffuse into the kernel more easily than liquid caustic and dissolve in the moisture that constitutes approx 15% of dry corn. Because the resulting strongly basic solution will be entirely inside the kernel, the time, temperature, and amount of base needed will be less than with caustic solution. Ammonia is also less expensive than caustic. Residual ammonia in the corn remaining after debranning and germ recovery can supply the nitrogen requirement for yeast fermentation to ethanol. Alternatively, ammonia treatment may help to separate the starch and protein from fiber in the remaining corn. The objective of the experiments reported here was to demonstrate loosening of the pericarp from whole corn using no more ammonia than needed to supply the nitrogen requirement for yeast fermentation.

Materials and Methods

A yellow dent corn hybrid (Pioneer 33A13) grown during the 2000 crop season at the Agricultural Engineering Farm, University of Illinois at Urbana-Champaign was used for the study. Corn samples were hand cleaned to remove broken corn and foreign material, packaged in plastic bags, and stored in a cold room (4°C) until processed. To measure the moisture content of corn, the sample (untreated or treated corn or dry germ) was weighed in a tared vessel, dried in a 70°C vacuum oven for 64 h, cooled in a desiccator, and weighed.

Eight batches of corn were treated with ammonia, sheared in a disk mill (Quaker City Mill, Philadelphia, PA) to tear off the pericarp and expose the endosperm, and then steeped, two batches at each of four steeping times: 2, 4, 6, and 8 h. Two conventional batches (whole corn steeped for 24 h) and two control batches (sheared without ammonia treatment and steeped for 6 h) completed the experimental design. After steeping, each sample was degermed and the yield of oil was determined.

Each treated batch started with 800 g of cleaned corn. Two 25-g samples were taken for moisture, titration, and free amino nitrogen (FAN) analysis. The remainder (approx 750 g) was weighed and placed in a bomb reactor consisting of a 10-in. (25-cm) length of 3-in. (7.6-cm)-diameter sanitary pipe, insulated, and closed with blanks on both ends. A cylinder of pure anhydrous ammonia was attached through stainless tubing to the bottom of the

reactor. The top was attached to a vacuum source through a trap of dilute sulfuric acid with phenolphthalein indicator. The reactor top was also equipped with a pressure transducer and a temperature sensor.

Before adding the corn, the reactor was warmed with a heat lamp to avoid condensation of water vapor on the cool reactor walls. After sealing the corn in the reactor, vacuum was applied. The connection to the vacuum was then closed, and a valve to the 10-psig (69-kPa) regulated ammonia source was opened and then closed exactly 6 s later. Then 20 s later, the bottom of the reactor was opened to atmosphere through a rotameter, and the connection to the vacuum was partially opened to draw 7 L/min of air through the reactor for 75 s.

After treatment, the treated corn was dumped from the reactor into a plastic container with a tight top, mixed, and weighed. Two 25-g samples were taken for moisture, titration, and FAN analysis, and two more 25-g samples were taken for immediate titration and FAN analysis. The remaining treated corn (approx 650 g) was added to 650 mL of cold tap water to quench the reaction. The time from first exposure to ammonia until quenching was 5.5 min. Ten minutes after quenching, the treated corn was sheared in the Quaker City (QCM) (Quaker City model 4E; Staub, Hatboro, PA). The QCM has a stationary and one rotating disks. The disks are corrugated and can be adjusted for gap setting. Shearing of corn kernels was done with the disk gap set to maximum (approx 3 to 4 mm).

Each batch was steeped for 2, 4, 6, 8, or 24 h in a one-half-gallon (2-L) plastic vessel fitted with a conical bottom with a stainless screen. The steep tank initially contained 650 mL of hot (70°C) tap water. The slurry of treated and sheared corn in water (control was only sheared in 650 mL of water) or 650 g of whole corn in 650 mL of water (conventional steeping) was added to the steep tank. Then 3.84 g of sodium metabisulfite and 7.15 mL of 85% lactic acid were added to give approx 2000 ppm of SO_2 and 0.55% lactic acid in the steep water. Steeping temperature (59°C) was maintained by indirect heating. A peristaltic pump circulated the steep water through a heat exchanger consisting of a 500-mm Pyrex glass Graham condenser. On the hot side of the heat exchanger, normally the cooling water jacket of the condenser, hot water was circulated from a bath maintained at no more than 70°C to avoid gelatinizing starch in the steep water.

After steeping, each batch was ground using a commercial-grade Waring blender (model 7010G; Waring, New Hartford, CT) equipped with a 15-amp motor and a 4-L container with blades that were reversed so that the leading edge of the blade was blunt. Blades were reversed so that blending would provide only shearing action and not cutting action on the corn kernels. The batch was ground for 3 min at 35% of full power, followed by 1 min at 30% of full power. These power settings on the blender were optimized for this study. Grinding at the optimum blender power setting gave, at the end of the grind, small amounts of whole kernel and minimum germ damage. After grinding, germ was skimmed by the same procedure as previously reported *(4)*.

Dry germ was weighed and samples were analyzed for moisture content. To measure total lipids, dry germ samples of approx 3 to 4 g were powdered by grinding in a mortar and pestle. This material was then ground in a blender with 150 mL of chloroform:methanol (C:M) (2:1 [v/v]) filtered through a sintered glass funnel (Coarse), and the residue on the funnel was reground with an additional 150 mL of C:M and refiltered. The extract was dried under a stream of nitrogen and redissolved in chloroform:methanol:water (10:5:3 [v/v/v]) according to the method of Folch et al. *(5)*. The lower organic layer was removed and dried under nitrogen to obtain the total lipid dry weight. The oil yield was calculated by multiplying the germ yield by the total lipid content of the germ.

Lipid extracts were analyzed by high-performance liquid chromatography according to the methods outlined in ref. *6*. A Lichrosorb SI-60 column, 250 × 4.6 mm, was purchased from Supelco (Bellfonte, PA) and operated at a flow rate of 2 mL/min using a mobile phase of hexane:isopropanol:glacial acetic acid (100:2:0.02 [v/v/v]). Detection of fatty acids and diacylglycerides was by ultraviolet detection at 206 nm. Standards consisting of oleic acid and oleic acid glycerides were used to estimate the relative amounts of each lipid class detected in these extracts.

Titration and FAN values for untreated corn measured before drying for moisture analysis were similar to values obtained after drying. Reported results are from samples measured after drying. On the other hand, titration and FAN values for treated corn analyzed immediately were higher than for treated samples analyzed after drying for moisture analysis because some of the absorbed ammonia evaporated in the vacuum oven. The difference in titration or FAN between treated samples analyzed immediately and untreated samples indicated the amount of ammonia absorbed during the treatment. The difference in titration or FAN between vacuum-dried, treated samples and untreated samples indicated the amount of ammonia that reacted with the corn to form ammonium salts or other nonvolatile products.

For titration, the sample was placed in 750 mL of deaerated, deionized water in a blender and blended for 2 min. The blended sample was transferred to a beaker on a magnetic stirrer and titrated with a pH meter to pH 7.0 using 0.2 *N* sulfuric acid (treated samples titrated immediately) or 0.1 *N* sodium hydroxide (untreated samples and treated, vacuum-dried samples). After titration, a small amount of liquid was clarified by filtration through a 0.2-μ syringe filter and analyzed for FAN by the ninhydrin method *(7)*. The FAN values for untreated samples were calculated based on a glycine standard. For treated samples, the untreated value was subtracted, and the remainder was calculated based on an ammonium chloride standard. The ninhydrin method was less sensitive to the ammonium standard than to the glycine standard by a factor of 3.45 at equimolar concentrations.

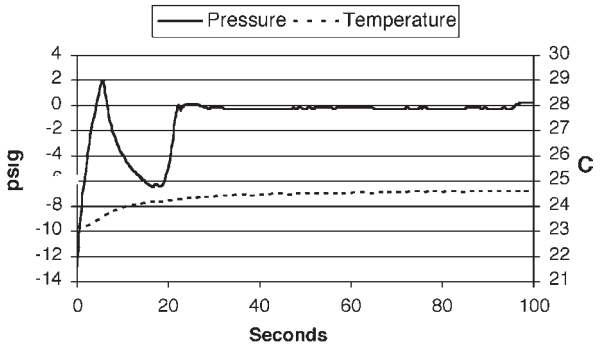

Fig. 1. Typical reactor exposure data.

Results and Discussion

The moisture content of untreated corn decreased from approx 12 to 11% during storage from the first batch to the last batch. Average moisture content of untreated corn was 11.64% and that of treated corn was 11.51%. Taking into account the fact that the weight of treated corn included approx 0.1% volatile ammonia that was counted as moisture, the actual loss of moisture on treatment was approx 0.2%.

Typical pressure and temperature data collected during the anhydrous ammonia treatment are shown in Fig. 1. The temperature increased slightly during treatment because the solution of ammonia in water is exothermic. The maximum pressure at the end of the 6-s flow of ammonia into the reactor varied from 1.3 to 5.1 psig (9–35 kPa). The minimum vacuum after closing the ammonia inlet varied from –7.9 to –5.3 psig (–54 to –37 kPa). The fact that the ammonia partial pressure of approx 0.5 atm was still decreasing when air was admitted to the reactor indicates that the corn was less than saturated with ammonia at this pressure. It may be concluded that a similar amount of ammonia would be absorbed on exposure for a similar time to a mixture of half air and half ammonia.

Preevacuation of the reactor may have removed air from pores in the kernels and thus speeded the diffusion of ammonia into those pores. However, preevacuation was necessary to provide a more even distribution of anhydrous ammonia throughout the reactor. Without such preevacuation, corn near the ammonia inlet (bottom of the reactor) would have absorbed much more ammonia than corn at the far end (top) of the reactor. On a larger scale, rapid recirculation of a mixture of air and ammonia through a moving bed of corn at atmospheric pressure should produce similar results without the need for vacuum or pressure.

Treatment resulted in a weight increase varying from 0.09 to 0.14% (average 0.12%) or approx 1 g of N/kg of corn. From the titration data (Table 1), the difference between the average of titration values for untreated corn and for treated corn sampled immediately was 71 meq/kg (0.99 g of N/kg of corn), in agreement with weight data. Titration of

Table 1
Titration Data (meq/kg)[a]

Batch	Untreated (a)	Treated, sampled immediately (b)	Total treatment (b – a)	Vacuum-dried, treated (c)	Nonvolatile treatment (c – a)
1	–37.6	33.8	71.4	–28.8	8.8
2	–38.7	37.1	75.8	–24.0	14.7
3	–37.5	15.8	53.3	–25.2	12.2
4	–38.2	41.1	79.3	–22.6	15.7
5	–33.7	42.3	76.0	–19.6	14.1
6	–36.1	29.0	65.1	–17.5	18.5
7	–34.9	38.2	73.0	–18.7	16.2
8	–34.9	37.4	72.3	–22.5	12.4
Average	–36.4	34.3	70.8	–22.4	14.1
SD	1.82	8.56	8.98	3.72	2.96
mg N/kg corn			**991**		**197**

[a]Negative numbers indicate titration with base to pH 7.0. Positive numbers indicate titration with acid to pH 7.0.

vacuum-dried, treated samples showed that most of the absorbed nitrogen was volatile. The calculated average amount of nonvolatile (reacted) ammonium was 14 meq/kg (0.20 g of N/kg of corn).

Results calculated from FAN data (Table 2) were in agreement with titration and weight data (as indicated by bold numbers in Tables 1 and 2). The average amount of FAN absorbed as ammonia in treated corn sampled immediately was 0.95 g of N/kg of corn. Of this, the amount remaining in vacuum-dried, treated samples was 0.28 g of N/kg of corn. FAN (as glycine) of untreated corn averaged 0.16 g of N/kg of corn. Assuming a mash of 25% corn, untreated corn supplies only 40 mg/L of FAN, whereas treated corn will supply approx 250 mg/L of additional FAN. This is approximately the minimum nitrogen supplementation needed for optimum yeast fermentation *(7)*.

Loosening of the hulls by treatment with ammonia was demonstrated qualitatively and quantitatively. Qualitatively, differences were observed during shearing in the disk mill between treated corn and the untreated controls. Shearing of ammonia-treated corn kernels resulted in more pericarp fiber removal and less broken kernel, whereas for untreated corn kernels less pericarp fiber removal and more damage to kernels (broken kernels) were observed.

Quantitatively, the effect of ammonia treatment can be seen in the oil yield data. As shown in Fig. 2, the oil yield from treated samples increased with steeping time up to 6 h. Yields at 6 and 8 h were not significantly different. Although these yields of 1.8–1.9% (corn dry wt basis) were significantly less than the 2.7% yield from conventional 24-h steeping, they

Table 2
FAN Data (mg N/kg corn)

Batch	Untreated (a)	Treated, sampled immediately (b)	Total treatment (b – a)	Vacuum-dried, treated (c)	Nonvolatile treatment (c – a)
1	158	1339	1180	483	326
2	165	Missing		495	330
3	168	Missing		414	247
4	167	1020	852	453	286
5	145	1143	999	503	358
6	169	1096	927	367	198
7	168	1065	897	400	233
8	162	1030	868	430	268
Average	163	1115	**953**	443	**280**
SD	8.2	118	122	48	54

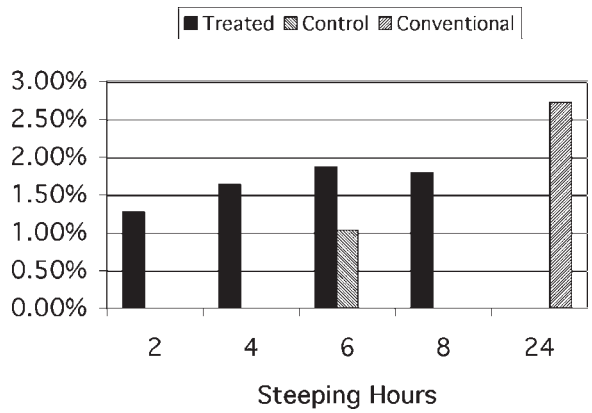

Fig. 2. Oil yield, dry corn basis. Each bar represents the average of data from two batches.

were much higher than the 1.0% yield for the control samples that were sheared without ammonia treatment and steeped for 6 h.

It can be concluded that loosening of the hulls by ammonia treatment allowed them to be torn from the kernels by coarse grinding. This allowed the germ to absorb more water during steeping and also allowed more of the soluble protein and salts in the germ to leach out. As a result, the germ in treated samples was lighter (less dense) and softer (more rubbery), so that the germ was less likely to break and more likely to float during germ recovery.

As shown in Table 3, the free fatty acid (FFA) content of total lipids extracted from germ varied from 3 to 9%. These numbers are high compared with commercial crude corn oil, which is generally from 1 to 3.5% free fatty acid *(8)*. FFAs in treated samples were less than

Table 3
Germ Yield and Oil Data, wt%, Dry Basis

Batch	Steep time (h)	Germ yield (% of corn)	Total lipids (% of germ)	FFA (% of total lipids)
1	6	6.59	25.7	2.8
2	4	5.85	29.7	3.7
3	6	6.75	30.1	4.6
4	2	5.16	25.2	4.8
5	8	6.69	31.5	4.3
6	2	4.92	25.3	3.2
7	8	6.31	23.4	3.1
8	4	5.33	28.8	4.6
Control	6	6.01	16.4	6.8
Control	6	5.95	18.1	5.4
Conventional	24	6.32	43.8	8.3
Conventional	24	6.24	43.0	9.0

in untreated controls. These data may be explained by the presence of endogenous lipase, which may be activated by steeping, but inactivated by ammonia treatment. In most samples, no partial glycerides were detected (data not shown). It can be concluded that treatment with ammonia caused no degradation of corn oil quality.

Conclusion

The techniques and apparatus for exposing whole corn kernels to anhydrous ammonia produced reliable and reproducible results. The data and qualitative observations showed that treatment with ammonia loosened the pericarp (hull), so that it could be torn off by lightly shearing in a disk mill, and that the germ could then be recovered after a short (6-h) steep. The amount of ammonia absorbed by the corn was equivalent to the minimum nitrogen supplementation required for yeast fermentation to ethanol. Ammonia treatment did not degrade the quality of the corn oil.

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