Treating Corn With Aqua Ammonia: Effect on Meal Constituents

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ABSTRACT

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High-moisture corn was treated with aqua ammonia, stored in 1-L tightly sealed glass containers, and placed in forced draft ovens at temperatures of 37 and 60°C for six months. Control samples were treated in the same manner and stored in a cabinet at 26°C. Aqua ammonia reduced the transformation of nonreducing sugar (sucrose) to reducing sugars.

Chemical and microbial analyses of the finely ground air-dried ammoniated sample showed that carbohydrates, starch (amylose and amylopectin), and amino acids (except cystine) were preserved at 37° C and 2% ammonia while microorganisms were kept to a minimum. Amylopectin losses were observed at 60° C, however, regardless of experimental conditions.

Ammonia has great potential application in two significant areas of corn storage and treatment. First, ammonia controls mold and bacterial growth and, in sufficent quantity, can kill microorganisms (Bothast et al 1973, Nofsinger et al 1978). The ability of ammonia to control microbial growth suggests its use in low-temperature ambient air-drying of corn. Second, ammonia can effectively inactivate aflatoxin in contaminated whole corn (Brekke et al 1975, 1977). The use of ammonia in either of these applications requires information on changes in cornmeal constituents resulting from ammoniation.

MATERIALS AND METHODS

Two hundred grams of freshly harvested whole yellow dent corn (25% moisture) was added to each of 12 1-L glass containers with lids and arranged in three groups (A, B, and C) of four samples: no ammonia (control) and 0.5, 1, and 2% aqua ammonia, dry basis. The final moisture content of each ammonia sample was 29% owing to water in ammonium hydroxide solutions; the control sample was also adjusted to 29% moisture. Group A was stored in a cabinet at 26°C, group B was stored in a forced draft oven at 37°C, and group C was stored in a forced draft oven at 60°C. All containers remained tightly sealed for exactly six months. The samples were then air-dried overnight to remove free ammonia, ground in a microsample mill, and analyzed for changes in composition.

Sucrose, reducing sugars, water-soluble nitrogen, and total nitrogen were analyzed by standard AACC methods (1961). For comparison, sucrose and reducing sugar values also were obtained by gas-liquid chromatography (Sweeley et al 1963) on the alcoholic extract prepared for reducing sugar determination. Starch and amylose were determined by the method of Garcia and Wolf (1972). Starch was determined polarimetrically, and total starch by amylose was determined spectrophotometrically on a separate portion of the same solution by measuring the absorbance of the amylose-iodine complex at 615 nm. Amylopectin was obtained by difference. Purified linear starch fractions and waxy starch served as reference standards for calibration. Other workers (Lancaster and Bothast 1974, Moore et al 1973, Uhl et al 1971) have provided information regarding methods of quantitating various forms of nitrogen in ammoniated whole corn (eg, free and fixed nitrogen). Analyses of amino acids were obtained by an automatic analyzer conducted on 24-hr hydrolysates of the ground corn samples in 6N hydrochloric acid. Counts of total aerobic bacteria and fungi were determined on ground samples according to the procedure of Bothast et al (1973).

RESULTS AND DISCUSSION

At the end of six months, the control corn sample held at 26° C (group A) had a typical yellow color and a rancid odor. This was the only sample with an increased microbial count (Table I). The predominant microorganism was a yeast. The control samples from groups B and C were less rancid than the corresponding ammoniated whole corn samples, which were brown to dark brown and had a bland odor. Typical microflora was present, with no evidence of growth (Table I).

Fat and nitrogen values of the finely ground air-dried samples were determined. Fat content did not appear affected by the ammoniation process, but nitrogen values increased slightly.

Table II shows the effects of temperature and ammonia level on the six-month storage stability of reducing and nonreducing sugars. With no ammonia, nonreducing sugar dropped drastically at all temperatures. Ammonia tended to stabilize nonreducing sugar. At 1% ammonia, no loss in nonreducing sugar occurred at 60°C; at 2%, nonreducing sugar was completely stable at both 37 and 60°C. This could be a result of inhibition of kernel invertase and the absence of microbial invertase activity (Bottomley et al 1952, Olafson et al 1954).

In contrast, reducing sugar more than doubled at the end of six months' storage for nonammoniated corn samples at all three

TABLE I
Microbial Content of Ammonia-Treated Corn^a

	Count/g			
Sample	Total Aerobic Bacteria	Total Fungi ^b 3.6×10^3		
Initial corn	3.2×10^{3}			
Group A (26°C)				
No NH ₃	3.4×10^{2}	1.2×10^{5}		
+0.5% NH ₃	4.0×10^{2}	5.5×10^{2}		
+1.0% NH ₃	2.2×10^{2}	1.1×10^{2}		
+2.0% NH ₃	4.0×10^{1}	2.0×10^{1}		
Group B (37°C)				
No NH ₃	1.0×10^{2}	2.0×10^{1}		
+0.5% NH ₃	5.0×10^{2}	4.0×10^{1}		
$+1.0\% \text{ NH}_3$	1.6×10^{2}	6.0×10^{1}		
+2.0% NH ₃	6.0×10^{1}	6.0×10^{1}		
Group C (60°C)				
No NH ₃	8.0×10^{1}	1.3×10^{2}		
+0.5% NH ₃	2.4×10^{2}	1.9×10^{2}		
+1.0% NH ₃	1.1×10^{3}	1.8×10^{2}		
+2.0% NH ₃	1.0×10^{1}	4.0×10^{1}		

^a All samples were stored for six months, then ground and analyzed. ^b Species of *Fusarium*, *Penicillium*, and *Aspergillus* were predominant on all samples except those stored at 26°C with either no or 0.5% NH₃; yeast sp. was predominant on those.

¹Mention of firm names or trade products does not imply endorsement or recommendation by the USDA over other firms or similar products not mentioned.

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TABLE II Chemical Analysis of Sugars from Ammonia-Treated Corn^a

Sample	Nonreducing Sugar as Percent Sucrose	Reducing Sugar as Percent Dextrose (Plus Reducing Substances)		
Initial corn	2.24	0.18		
Group A (26°C)				
No NH ₃	0.74	0.48		
+0.5% NH ₃	0.35	0.97		
+1.0% NH ₃	1.09	0.37		
+2.0% NH ₃	1.27	0.45		
Group B (37° C)				
No NH ₃	0.70	0.49		
+0.5% NH ₃	1.10	0.50		
+1.0% NH ₃	1.48	0.20		
+2.0% NH ₃	2.48	0.10		
Group C (60°C)				
No NH ₃	0.92	0.57		
+0.5% NH ₃	1.35	0.12		
$+1.0\% \text{ NH}_3$	2.47	0.12		
+2.0% NH ₃	2.40	0.10		

^a All samples contained about 4% fat and 9% moisture and were stored for six months. Data are reported on dry basis.

TABLE III
Amino Acid Composition of Corn Protein^a

Amino Acid	Initial Corn (0 Time) No NH ₃	37° C 0.5% NH ₃	37° C 1.0% NH ₃	60° C 2.0% NH ₃
Lysine	0.22	0.11	0.14	0.13
Histidine	0.24	0.27	0.26	0.19
Arginine	0.32	0.36	0.41	0.30
Aspartic acid	0.58	0.55	0.56	0.51
Threonine	0.34	0.33	0.33	0.28
Serine	0.44	0.44	0.43	0.35
Glutamic acid	1.64	1.64	1.66	1.63
Proline	0.84	0.83	0.83	0.78
Glycine	0.35	0.35	0.35	0.30
Alanine	0.68	0.68	0.67	0.63
Cystine	0.13	0.10	0.07	0.00
Valine	0.45	0.46	0.46	0.45
Methionine	0.17	0.15	0.16	0.14
Isoleucine	0.32	0.30	0.30	0.30
Leucine	1.12	1.08	1.09	1.09
Tyrosine	0.42	0.40	0.42	0.41
Phenylalanine	0.44	0.42	0.46	0.46

^aGrams per 100 g of corn dry weight.

temperatures. At 1 and 2% ammonia and at 37 and 60° C, on the other hand, reducing sugar content decreased and brown color increased, suggesting that a Maillard-type (nonenzymatic) browning reaction occurred (Hodge 1953, Kort 1970, Maillard 1912).

Starch content of ammoniated samples stored at 26 and 37° C did not change after six months' storage, but slight decreases in total starch and amylopectin were observed at 60° C, regardless of experimental conditions. Amylose content remained constant in all samples.

When a two-way analysis of variance was run on amino acids as grams per 100 g of corn dry weight, cystine showed the only significant variation associated with temperature or ammoniation level (Table III). The cystine value decreased as the ammonia level and temperature increased. An apparent decline in lysine was not

significant when tested against variations based on the number of runs in the experiment. However, the lysine value is probably valid because of the known involvement of lysine in the browning reaction

Other workers (Bothast et al 1973; Brekke et al 1975, 1977; Nofsinger et al 1977) have shown that ammonia at the 0.5% level is a potent fungicide and inactivates aflatoxin under conditions of ammoniation similar to those we have described. Our studies reveal additional information regarding ammoniation and storage of high-moisture corn, ie, ammonia appears to stabilize nonreducing sugars. At 1% ammonia and 60°C, nonreducing sugars are completely stable. At 2% ammonia, nonreducing sugars are completely stable at both 37 and 60°C, owing at least in part to low activity of invertase naturally present in the kernel or to low microbial invertase. Low values of reducing sugars are due both to a low level of sucrose inversion and to participation in the browning reaction.

Although these data cannot be extrapolated to long-term food storage in general, the information should be useful in storage and nutritional studies similar to those reported in a recent review by Labuza (1972).

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LITERATURE CITED

- AMERICAN ASSOCIATION OF CEREAL CHEMISTS. Approved Methods of the AACC. Methods 46-12, 80-50, and 80-60, approved April 1961. The Association: St. Paul, MN.
- BOTHAST, R. J., LANCASTER, E. B., and HESSELTINE, C. W. 1973. Ammonia kills spoilage molds in corn. J. Dairy Sci. 56:241.
- BOTTOMLEY, R. A., CHRISTENSEN, C. M., and GEDDES, W. F. 1952. Grain storage studies. X. The influence of aeration, time, and moisture content on fat acidity, nonreducing sugars, and mold flora of stored yellow corn. Cereal Chem. 29:53.
- BREKKE, O. L., PEPLINSKI, A. J., and LANCASTER, E. B. 1977. Aflatoxin inactivation in corn by aqua ammonia. Trans. ASAE. 20(6):1161.
- BREKKE, O. L., SINNHUBER, R. O., PEPLINSKI, A. J., WALES, J. H., PUTMAN, G. B., LEE, D. J., and CIEGLER, A. 1977. Aflatoxin in corn: Ammonia inactivation and bioassay with rainbow trout. Appl. Environ. Microbiol. 34:34.
- GARCIA, W. J., and WOLF, M. J. 1972. Polarimetric determination of starch in corn with dimethyl sulfoxide as a solvent. Cereal Chem. 49:298. HODGE, J. E. 1953. Chemistry and browning reactions in model systems.

J. Agric. Food Chem. 1:928.

- KORT, M. J. 1970. Reactions of free sugars with aqueous ammonia. Adv. Carbohydr. Chem. Biochem. 25:311.
- LABUZA, T. P. 1972. Nutrient losses during drying and storage of dehydrated foods. Crit. Rev. Food Technol. 3(2):217.
- LANCASTER, E. B., and BOTHAST, R. J. 1974. Treating corn with ammonia: Behavior of corn-water-ammonia system. Trans. ASAE 17(2):331
- MAILLARD, L. G. 1912. Action des acides amines sur les sucres; formation des melanoides par voie methodique. Compes Rendus 154:66.
- MOORE, C. A., LANCASTER, E. B., and BOTHAST, R. J. 1973. Aqua ammonia's economical potential as a preservative for stored high-moisture corn. Econ. Res. Serv., USDA, ERS-535, 19 pp.
- NOFSINGER, G. W., BOTHAST, R. J., LANCASTER, E. B., and BAGLEY, E. B. 1977. Ammonia-supplemented ambient temperature drying of high-moisture corn. Trans. ASAE 20(6):1151.
- OLAFSON, J. H., CHRISTENSEN, C. M., and GEDDES, W. F. 1954. Grain storage studies. XV. Influence of moisture content, commercial grade, and maturity on the respiration and chemical deterioration of corn. Cereal Chem. 31:333.
- SWEELEY, C. C., BENTLEY, R., MAKITA, M., and WALLS, D. D. 1963. Gas-liquid chromatography of trimethylsilyl derivatives of sugars and related compounds. J. Am. Chem. Soc. 85:2497.
- UHL, D. E., LANCASTER, E. B., and VOJNOVICH, C. 1971. Automation of nitrogen analysis of grain products. Anal. Chem. 43:990.

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