High Moisture Corn—An Extended Preservation Trial with Ammonia

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ABSTRACT

SHELLED high-moisture corn was treated with ammonia in a trial to control microbial deterioration. Ammoniation destroyed all molds, lowered bacteria counts for up to 4 months, and modified some chemical and physical properties of this corn for 410 days at ambient temperatures ranging from 16 to 39 °C.

INTRODUCTION

Storage of high-moisture cereal grains usually results in grain deterioration due to microorganisms. For centuries, grain preservation has been accomplished by field drying to a safe moisture level. During this century, grain storage has developed around ambient air drying of ear corn, airtight silo storage, aeration and heated air drying.

With grain drying costs increasing rapidly and with limited and uncertain fuel supplies, alternative methods of preservation are being investigated. Recent studies have shown that chemicals such as volatile fatty acids and ammonia (NH₃) can serve as preservatives or antifungal agents when applied on certain high-moisture crops (Bothast et al., 1975; Hall et al., 1974; Herting and Drury, 1974; Vandergraft et al., 1975).

Application of ammonia has been reported in connection with preservation of high-moisture grain (Bothast et al., 1975; Lancaster et al., 1974), preservation of high-moisture forage (Knapp et al., 1974), aflatoxin inactivation (Brekke et al., 1977) and as a nonprotein nitrogen source to give silage a superior feeding value (Huber, 1975; Huber et al., 1973).

Preliminary studies at the Northern Regional Research Center (NRRC) pointed to a need for examination of the possible biological, chemical and physical changes that occur during long-term storage of ammoniated high-moisture corn. This paper analyzes data obtained during the 14-month indoor storage of 4,036 kg (158 bu) of 23 percent moisture corn treated initially with 1 percent aqua ammonia, which increased moisture and volatile matter content to 28 percent. As a protection against spoilage, small amounts of anhydrous ammonia were added periodically to the corn during the 14-month storage.

MATERIALS AND METHODS

Storage Bin

The corn was ammoniated in a 2.4-m long, 1.8-m wide by 2.4-m high (8 x 6 x 8 ft) closed box constructed of 1.9-cm (0.75 in.) thick plywood. All interior surfaces were coated with epoxy paint and the seams caulked. A false bottom floor consisting of hardware cloth and expanded metal mesh allowed for recirculation of the ammonia-air mixture through the corn bed.

Corn

A yellow dent hybrid corn from west-central Illinois was combined December 11, 1973, at 23 percent moisture, passed over a 0.56-cm (~14-64-in.) round hole perforated sieve to remove fines and held indoors at room temperature (ca 25 °C) for 3 days prior to ammoniation with no visible signs of deterioration.

Corn Ammoniation

Cleaned corn at 21 °C and 23 percent moisture was ammoniated December 14, 1973. A Draver regulated corn flow into a stainless-steel auger where aqua ammonia (19 percent ammonia, w/w) was sprayed onto the corn. Corn feed rate averaged 1,400 kg/h (55 bu/h) and ammonia addition was 1.02 percent based on corn dry matter. Later, five anhydrous ammonia additions of 0.26 to 0.51 percent per each addition (corn dry matter basis) were made at 28, 67, 111, 242, and 297 days after initial ammoniation. The gas was added and recirculated through the corn bed with an external blower. The total of 95 kg of ammonia added to the corn in aqua and anhydrous form amounted to 3.04 percent based on corn dry matter content.

Sampling and Determinations

Ammoniated corn in the bin was sampled by probing and corn temperatures measured with thermocouples. AACC (1971) analytical procedures were used for determination of ash, fat, glucose, starch and sucrose. Nitrogen was determined by the method of Uhl et al. (1971) and ammoniacal nitrogen by the colorimetric procedure of Uhl (1975). Fatty acid composition of petroleum ether-extracted fat was determined by gas-liquid chromatography (AOCS, 1970). Soluble solids were obtained by Standard Analytical Methods of the Members Companies of the Corn Industries Research Foundation (1965). Water-extracted ammonia (WE-NH₃) analysis followed the procedure of Lancaster et al. (1974) for "free ammonia". Moisture (hereafter meaning moisture and volatile matter) in whole corn was determined by a two-stage procedure: 25 g were dried over-
TABLE 1. EFFECT OF TIME AND CORN LEVEL ON MICROORGANISMS, AMMONIA, AND MOISTURE CONTENTS.

<table>
<thead>
<tr>
<th>Day</th>
<th>Molds, microorganisms/g</th>
<th>Log bacteria count, microorganisms/g</th>
<th>Water extracted ammonia, percent d.b.</th>
<th>Corn moisture, percent, w.b.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>630,000</td>
<td>6.30*</td>
<td>0+</td>
<td>23.0</td>
</tr>
<tr>
<td>1</td>
<td>ND</td>
<td>3.47</td>
<td>0.69</td>
<td>28.0</td>
</tr>
<tr>
<td>7</td>
<td>ND</td>
<td>3.00</td>
<td>—</td>
<td>28.0</td>
</tr>
<tr>
<td>32</td>
<td>ND</td>
<td>4.87</td>
<td>0.29</td>
<td>28.0</td>
</tr>
<tr>
<td>45</td>
<td>ND</td>
<td>4.19</td>
<td>0.22</td>
<td>27.1</td>
</tr>
<tr>
<td>60</td>
<td>30</td>
<td>5.59</td>
<td>0.08</td>
<td>27.2</td>
</tr>
<tr>
<td>98</td>
<td>ND</td>
<td>5.13</td>
<td>0.28</td>
<td>27.5</td>
</tr>
<tr>
<td>146</td>
<td>ND</td>
<td>5.04</td>
<td>0.50</td>
<td>28.2</td>
</tr>
<tr>
<td>166</td>
<td>ND</td>
<td>5.00</td>
<td>0.37</td>
<td>26.1</td>
</tr>
<tr>
<td>235</td>
<td>ND</td>
<td>4.40</td>
<td>0.25</td>
<td>27.4</td>
</tr>
<tr>
<td>276</td>
<td>ND</td>
<td>5.52</td>
<td>0.19</td>
<td>24.5</td>
</tr>
<tr>
<td>355</td>
<td>ND</td>
<td>4.51</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>95 percent confidence limits</td>
<td>±0.88</td>
<td>±0.054</td>
<td>±2.04</td>
<td></td>
</tr>
<tr>
<td>Corn level location</td>
<td>Top</td>
<td>4.78*</td>
<td>0.34†</td>
<td>28.6†</td>
</tr>
<tr>
<td></td>
<td>Middle</td>
<td>4.68</td>
<td>0.26</td>
<td>26.4</td>
</tr>
<tr>
<td></td>
<td>Bottom</td>
<td>5.44</td>
<td>0.21</td>
<td>25.5</td>
</tr>
<tr>
<td>95 percent confidence limits</td>
<td>±0.54</td>
<td>±0.033</td>
<td>±1.25</td>
<td></td>
</tr>
<tr>
<td>Standard deviation(s)</td>
<td>0.71</td>
<td>0.044</td>
<td>0.65</td>
<td></td>
</tr>
</tbody>
</table>

* Variations between means in this column not significant at 5 percent level except for day zero. † Variations between means in this column significant at 1 percent level. ND = None detected.

After the initial heating and cooling, corn temperatures generally fluctuated between 22 °C and 38 °C except from May 23 to August 22 when temperatures at the bin top ranged to 47 °C. Ambient air varied from 16 °C to 39 °C throughout storage, and this was reflected in the corn temperature.

Corn moisture was increased from 23 percent to 28 percent due to addition of aqua ammonia and remained stable at 26 percent to 28 percent throughout the grain to storage day 60. About this time, a moisture gradient developed. Thereafter, moisture was greater in the corn at the bin top than at the bottom and moisture gradient between the top and bottom ranged from 1 to 7 percentage points from day 60 through day 276, then held at 7 to 8 percentage points over the last 134 days of storage. This phenomenon of moisture transfer in preserved high-moisture corn has been noted by Stewart (1975) who stated that temperature difference is the driving force for moisture migration throughout the grain mass.

Throughout storage, WE-NH$_3$ level, or "free ammonia" which Lancaster et al. (1974) stated is responsible for microbial control, served as an indicator of corn spoilage. Three days after aqua ammoniation, WE-NH$_3$ was 0.7 percent and the corn smelled strongly of ammonia; at 26 days the WE-NH$_3$ had dropped to 0.10 to 0.17 percent with very little ammonia odor noted. Each subsequent addition of ammonia raised the average WE-NH$_3$ concentration by 0.16 to 0.33 percentage points. Recycling the ammonia gas in the bin served to equalize WE-NH$_3$ content in the corn for short periods (possibly up to 2 wk), but WE-NH$_3$ values generally followed the trend of moisture contents and were often higher at the bin top than at the bottom.

RESULTS AND DISCUSSION

Storage of Ammoniated Corn

Corn temperature rose from 20 °C to 39 °C during the first 10 days after aqua ammoniation. To lower the corn temperature, room air was drawn down through the corn for 2.5 h on December 24 and this reduced the average corn temperature to 31 °C. In previous work, Bothast et al. (1975) noted a 35°C rise over a 30-day period after 27 percent moisture corn in an outdoor bin had been treated with 0.7 percent ammonia (d.b.) applied in aqua form. At that time, the initial temperature rise was attributed to a chemical reaction between ammonia and corn components, and subsequent heating was attributed to bacterial activity with possible some chemical heating.

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Microbial Activity

Microbial examination of the corn 1 day after aqua ammoniation indicated bacterial count was reduced from 2,000,000 to 3,000/g; molds were reduced from 630,000/g to a nondetectable level (Table 1). Counts on the 7-day sample agreed with the 1-day sample and the WE-NH$_3$ remained high at this time. Highest bacterial counts were observed at days 60 and 276 and WE-NH$_3$ values (0.09 to 0.19 percent) were the lowest recorded. Molds were eliminated throughout the storage period. Before ammoniation, species of Fusarium, Penicillium and Alternaria were detected on 76, 14 and 8 percent, respectively, of the corn kernels.

Statistical analysis provided no evidence of trends with time for bacteria count or corn moisture. WE-NH$_3$ was significantly variable (99 percent confidence limits) with time, obviously owing to the ammonia additions (Table 1). Corn sample depth in the bin over the same time interval was significant (99 percent confidence limit) for WE-NH$_3$ and moisture values but not for bacteria count.
Chemical Changes in Corn

Changes in corn composition occurred throughout storage (Table 2). Overall, nitrogen, ammoniacal nitrogen and soluble solids values increased by 50 percent; starch and ash remained constant; petroleum ether-extracted fat, linoleic acid in fat and sucrose were lowered.

The increase in nitrogen amounted to 21.4 kg and accounted for 22 percent of the nitrogen applied to the grain as ammonia. Ammoniacal nitrogen accounted for 15.9 kg of this increase, indicating 5.5 kg of nitrogen applied reacted with corn to produce other than ammoniacal compounds. Soluble solids increased from 6.5 to 9.5 percent; analyses of the solids residue indicated that soluble ammoniacal reaction products accounted for this change. The decrease from 2.9 to 1.3 percent in nonreducing sugars, reported as sucrose, suggests microbial activity.

Quantity of fat extracted with petroleum ether was lowered from 4.5 to 3.5 percent after 13 days and further decreased to 2.4 percent at 410 days. Similarly fat linoleic acid, an essential component for human and animal nutrition, decreased from 61 to 35 percent, after 13 days and to 17 percent at 410 days. The biological or chemical changes that caused fat degradation may have contributed to the heating which occurred in the first 10 days of this experiment and over the initial 30 days of the study by Bothast et al. (1975). More recently, Black et al. (1978) have studied the type of compounds formed by the linoleic acid-ammonia reaction and the conditions that lead to their formation.

Corn Physical Condition

The yellow dent corn changed rapidly in color upon being ammoniated. After 3 days, the color had turned to a yellow-brown hue and by 4 days to a deep-brown, stained appearance which lasted throughout storage. Dissected kernels from an 118-day sample scooped from the corn surface showed the hull to be a deep brown; the endosperm had turned cream colored while the germ section was light brown. Kernels were pliable, sticky and adhered to each other.

After the corn was sampled on the 60th day, a void remained when the probe was removed. In prior samplings, the corn would flow to fill up the free space, but this became progressively slower with successive samplings. On the 355th day, probing penetrated only 51 cm into the corn. The changing physical condition of the preserved high-moisture corn evidenced need for an in-bin stirring device to keep the grain loose, free-flowing and mixed to avoid moisture and ammonia gradients.

The 276-day sample showed differing odors and kernel hardness between bin top and bottom due to moisture and volatile matter migration. A sample taken from the top level smelled of ammonia and the kernels were soft and pliable; the middle yielded a slight ammonia odor with less kernel pliability while the sample from the bottom level had no ammonia odor and kernels were hard.

A dark-brown, pliable, plastic-like substance was observed at 270 days on the floor alongside the bin wall on the west side. This substance presumably was an ammoniation product leached from the corn. The west bin wall, which was located 1 m from an outside brick and single-pane window wall, was preferentially cooled in the evenings and acted as a condenser for warmer ammonia-water vapors inside the bin. A sample taken from an 11-kg quantity of this material gave the following analysis: 31 percent protein, 12 percent carbohydrate, 6 percent acid hydrolyzed fat, 10 percent ash, 21 percent moisture, leaving 20 percent unaccounted for, possible a polymeric substance.

Corn Removal

After 410-days storage, the corn was removed from the bin by shoveling as six separate layers, each averaging 18 to 25 cm deep. These six layers constituted about 90 percent of the corn in the bin, and ranged in moisture from 15 percent at the bottom to 24 percent at the top (Table 3). Poor flow characteristics were noted upon removal of this corn, but after the grain was broken loose, it would flow readily as corn normally does. The remaining 10 percent consisted of wet corn adhering to the north and west bin walls as a layer 10 to 15 cm thick and varying in moisture from 31 to 59 percent. Moisture transfer and condensation previously mentioned caused the high-moisture content of this corn. Samples of the wet corn obtained midway down in the bin along the north and west walls and bottled for moisture analysis contained white Phoridae larvae about 6 mm long.

The composition of grain, excluding the 10 percent of wet corn adhering to the walls, varied from bin top to bottom (Table 3). Fat, linoleic acid, and sucrose increased toward the bin bottom; moisture, WE-NH,
and soluble solids were highest at the top. Total nitrogen was slightly higher in the middle layers; starch remained constant throughout the grain bulk; ash was less only in the top layer. No aflatoxin was detected by chemical assay of the corn initially and after storage.

Corn volume was reduced by 0.44 m³ at the end of storage, an 8 percent shrinkage, while dry matter content decreased by 432 kg, a loss of 14 percent compared to original corn placed in storage. Knapp et al. (1974) showed a dry matter loss of 10 percent after holding 1 percent ammonia-treated hay for 2 months; Bothast et al. (1975) noted an unspecific dry matter loss possibly due to bacteria during storage of ammoniated corn.

**SUMMARY AND CONCLUSIONS**

Ammoniation completely eliminated mold growth while bacterial counts were lowered during storage of 4,036 kg (158 bu) of high-moisture corn. The freshly harvested yellow-dent corn at 23 percent moisture was treated with 1 percent ammonia (corn dry matter basis) added as aqua ammonia, which also raised the corn moisture to 27-28 percent. The corn was stored indoors in a covered plywood bin. To prevent spoilage, ammonia gas was added periodically to the corn over the following 14-month storage; a total of 3 percent ammonia was added in both aqua and anhydrous form. A rapid rise in corn temperature from 20 to 39 °C, of undetermined but possibly of chemical origin, was noted during the first 10 days. At this time, the grain was cooled by aeration; thereafter corn temperatures ranged from 20 to 47 °C as ambient air varied from 16 to 39 °C. Corn color changed to brown after 14 days; kernels caked and exhibited poor flow characteristics after 60 days. Ammoniation increased the non-protein nitrogen content by a 0.68 percentage point, a quantity which may increase the nutritional value of the corn for ruminant feed. Petroleum ether extracted fat was lowered from 4.5 percent to 2.4 percent while inolico acid content of fat decreased from 61 to 17 percent. Starch and ash values remained constant but nonreducing sugars decreased by 55 percent. A volume shrinkage of 8 percent, a dry matter loss of 14 percent, and the fact that corn temperatures were constantly higher than the ambient air suggest bacterial activity as the cause of these changes.

This research has shown that ammonia acts as a lasting fungistat while only temporarily checking bacterial growth. The increase in corn nonprotein nitrogen will be of benefit in feeding ruminants while the reduction in ether-extracted fat may lower corn energy values.

**TABLE 3. CHEMICAL ANALYSIS OF CORN REMOVED FROM STORAGE BY LAYERS.**

<table>
<thead>
<tr>
<th>Layer</th>
<th>Moisture, percent</th>
<th>WE-NH₃, percent d.b.</th>
<th>Total nitrogen, percent d.b.</th>
<th>Fat extracted, percent d.b.</th>
<th>Linoleic acid, percent d.b.</th>
<th>Starch, percent d.b.</th>
<th>Non-reducing sugars, percent d.b.</th>
<th>Ash, percent d.b.</th>
<th>Soluble solids, percent d.b.</th>
<th>Proportion of corn, percent</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>23.0</td>
<td>0.3</td>
<td>2.1</td>
<td>2.0</td>
<td>1.2</td>
<td>74.0</td>
<td>1.4</td>
<td>1.1</td>
<td>13.0</td>
<td>10.0</td>
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<tr>
<td>2</td>
<td>24.0</td>
<td>0.3</td>
<td>2.3</td>
<td>2.1</td>
<td>1.1</td>
<td>74.0</td>
<td>1.6</td>
<td>1.4</td>
<td>12.0</td>
<td>15.0</td>
</tr>
<tr>
<td>3</td>
<td>20.0</td>
<td>0.2</td>
<td>2.2</td>
<td>2.3</td>
<td>1.2</td>
<td>74.0</td>
<td>1.6</td>
<td>1.4</td>
<td>15.0</td>
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<td>4</td>
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<td>1.4</td>
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<td>2.3</td>
<td>1.5</td>
<td>74.0</td>
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<td>6</td>
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<td>0.2</td>
<td>2.1</td>
<td>2.7</td>
<td>2.1</td>
<td>75.0</td>
<td>1.8</td>
<td>1.4</td>
<td>7.0</td>
<td>17.0</td>
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<tr>
<td>Average</td>
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<td>0.2</td>
<td>2.2</td>
<td>2.3</td>
<td>1.5</td>
<td>74.0</td>
<td>1.7</td>
<td>1.4</td>
<td>10.0</td>
<td>90.0</td>
</tr>
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</table>

*Excluding high-moisture corn adhering to bin walls.

†Layer 1 is top, 6 is bottom.

‡As percent of extracted fat.

Corn odor and water-extracted ammonia level can be used as indicators of corn condition. We believe ammonia can be used by the procedure described as a preservative for short-term storage, ca 2 to 4 wk, of high-moisture corn. Based upon our results, experimental work was undertaken wherein for long-term storage, high-moisture corn was dried with ambient air in conjunction with intermittent application of small quantities of gaseous ammonia. Results from these trials have been reported by Nofsinger et al. (1976).

**REFERENCES**


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