PRESERVATION OF HIGH-MOISTURE MAIZE — A COMPARISON OF GASEOUS AND LIQUID ANHYDROUS AMMONIA WITH METHYLENE-BIS-PROPIONATE

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ABSTRACT


Freshly harvested maize (22—24% moisture) was treated with either gaseous ammonia (0.9% dry basis), liquid anhydrous ammonia (1.3% dry basis), or methylene-bis-propionate (0.8% dry basis) and stored in metal bins. All treatments initially decreased the counts of bacteria and moulds. Growth of these microorganisms was prevented throughout the 6-month storage period by methylene-bis-propionate and for 5 months by gaseous anhydrous ammonia. Liquid anhydrous ammonia prevented mould growth for 4 months, while bacterial counts increased to pretreatment numbers after 1 month but did not increase further until after 5 months’ storage. In feeding trials with steers, more efficient weight gains were obtained from the ammonia-preserved maize than from the methylene-bis-propionate preserved maize.

INTRODUCTION

In 1972—1973 field preservation trials with freshly harvested high-moisture (27%) maize, Bothast et al. (1975) reported that aqueous ammonia (5 g ammonia per kg wet maize) eliminated moulds and initially reduced bacterial counts. This research was given further impetus by Moore et al. (1973) who stressed the economic advantages of aqueous ammonia treatment over conventional drying or preservation with organic acids.

Problems encountered with aqueous ammonia-treated bunker-stored wet maize included ammonia loss during application (Lancaster et al., 1974), moisture/ammonia migration, and subsequent fungal growth, primarily

1 The mention of firm names or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.
Scopulariopsis brevicaulis Bainier (Bothast et al., 1975). The purpose of the field trials discussed in this report was to compare the efficacy of gaseous and liquid anhydrous ammonia applied to high-moisture maize in an effort to minimize the above-mentioned problems and to compare ammonia-preserved lots with organic acid-preserved high-moisture maize.

MATERIALS AND METHODS

The maize used in these trials consisted of a mixture of hybrid yellow dent varieties, freshly harvested and shelled in the autumn of 1975. Moisture content of the grain was from 22 to 24%.

A metal, circular bin 5.5 m in diameter, having an elevated slotted floor, was used for conducting the gaseous anhydrous ammonia test. This bin had been sealed (essentially gas tight) and was equipped for recirculating the ammonia—air mixture through the static bed of maize (a system used in earlier unrelated experiments). The bins used for the liquid anhydrous ammonia and methylene-bis-propionate tests were similar except that they were constructed with solid, galvanized metal floors and were not gas tight.

As the bin was being filled, four thermistors were placed equidistant in the North, South, East and West quadrants of the bin with the recording tips resting about 0.9 m from the bin wall and at mid depth of the bed to measure the temperature of the maize.

After the bin was filled, four thermowells, constructed from 0.64 cm diameter stainless steel tubing, were inserted through the bin sidewall, equidistant in the North, South, East and West quadrants with thermocouple tips resting about 1.5 m from the bin wall and about mid depth in the bed of maize.

For the gaseous anhydrous ammonia test, 13.1 metric tonnes of 22% moisture content maize was loaded into the bin equipped for gas recirculation. The average depth of the levelled grain was approximately 70 cm. Liquid anhydrous ammonia was drawn from the applicator tank, vaporized in propane-fired side-arm heaters to temperatures ranging from 10 to 18°C, and introduced on the suction side of a 5.6-kw Buffalo® blower delivering 9.5 m³ of air s⁻¹ at 50 cm water absolute pressure into a recirculating duct 20 cm in diameter. In previous unrelated work this blower was sized to deliver about 1 m³ air min⁻¹ tonne⁻¹ of maize and was used because of its availability. Brekke et al. (1979) demonstrated this air flow to be adequate to introduce and distribute gaseous ammonia in a static bed of maize. The pressure outlet of the blower was connected to the plenum beneath the perforated drying floor while the blower inlet (suction) was connected to the headspace of the bin to permit recycling of the gaseous ammonia—air mixture through the bed of maize. The gaseous anhydrous ammonia (9/kg maize dry matter) was introduced over a 2-h period, with the air—ammonia mixture being recirculated for 1 h after completion of ammonia addition. The blower was run for 3—4 h daily during the next 2 days to minimize free ammonia in the maize.
For the liquid ammonia test, liquid anhydrous ammonia (13 g/kg maize dry matter) was applied to 11.2 tonnes of maize of 22% moisture as it passed through a 0.15 X 15.5 m grain auger at a precalibrated rate of 66.2 kg min⁻¹. A 1.25-cm hole was drilled in the auger tube 1 m from the auger inlet and fitted with a stainless-steel pipe nipple and needle valve. Liquid anhydrous ammonia was drawn from the applicator tank through stainless-steel tubing at a measured rate, and introduced through the needle valve directly on to the maize passing through the auger. Frosting was observed on the auger for a length of about 1 m beyond the needle valve where ammonia had contacted the maize. Vaporization of ammonia continued for approximately 1 additional meter along the auger, as evidenced by condensate on the exterior surface. Some warming, indicating ammonia absorption, occurred near the upper end of the auger. Retention time of maize in the auger after ammonia contact was about 1 min. The auger head and fill hatch were covered with plastic sheeting to minimize loss of ammonia vapour during treatment.

For the methylene-bis-propionate (MBP) test, 12.8 tonnes of 24% moisture maize were delivered to a 0.15 X 4.9 m grain auger at a precalibrated rate. The MBP was metered through a control valve, rotameter, and tubing to a point 1 m from the auger inlet. Distribution of the MBP 8 g/kg maize dry matter on the maize was obtained by the mixing/blending action of maize feeding through the remainder of the auger (3.9 m).

Maize temperatures were measured by placing thermometer probes equidistant in the North, South, East and West quadrants of the bin with the recording tips inserted about 1.5 m from the bin wall about mid depth in the bed of maize.

Two replicate, composited probe samples were taken for chemical and microbiological analyses at 0, 1, 7, 14 and 28 days and, subsequently, at monthly intervals in the liquid anhydrous ammonia and methylene-bis-propionate tests. The samples were taken in the North and South quadrants of these bins about 1–1.5 m from the bin wall. Provision for sampling without entering the gaseous ammonia bin was made by burying 16 perforated plastic bottles, each filled with about 250 g of maize, at random locations in the bed at a depth of about 0.5 m, and attaching the bottles by chains to the roof ring at the fill hatch. Microbial counts of total aerobic bacteria and moulds, as well as the percentage of kernels yielding moulds after surface sterilization, were determined by the procedures of Bothast et al. (1974). Moisture determinations also were made on the probe sampling utilizing a Brabender® Rapid Moisture Tester at 130°C for 30 min. Ammoniacal nitrogen analyses were conducted according to the AOAC Method 2.040 (1960) as modified by Lancaster et al. (1974). Propionic acid analyses were conducted according to the methods described by Bothast et al. (1978).

Under a cooperative program between the University of Illinois and the Northern Regional Research Center, maize preserved in this experiment by all three treatments was compared in feedlot studies. Forty-two steers with...
an initial average weight of 308.4 kg were randomly assigned to each of the three treatments. Over 86 days, each batch of maize was given was fed to 14 steers on a 3:1 dry matter ratio of preserved maize and maize silage. Individual weights and feed consumption for each treatment were determined at 4-week intervals.

RESULTS AND DISCUSSION

Moulds and bacteria on the kernel surface of high-moisture maize were reduced or eliminated by the three treatments (Figs. 1–3). Following the gaseous anhydrous ammonia treatment, low microbial counts existed during the first 5 months of storage. However, an increase in both kernel surface moulds and bacteria was recorded in the sixth month.

Residual ammonia in the gaseous anhydrous ammonia-treated maize (Table II) decreased slightly over the storage period from 0.6% after 1 day to 0.4% after 6 months. Gradual reduction in residual ammonia together with increasing ambient temperatures probably accounted for the increased mould and bacterial growth toward the end of the storage period.

The average maize temperatures in both ammonia treatments (Figs. 1 and 2) showed an initial rise for the first few days of treatment, probably due to the chemical reaction of the ammonia with the maize (Bothast et al., 1975). In the gaseous anhydrous ammonia treatment there was a 5–6°C increase in recycle gas temperature due to the operation of the blower accounting for much of the initial rise in maize temperature. After the initial rise, the maize temperatures declined and then generally reflected ambient conditions.

Fig. 1. Microbial counts on gaseous anhydrous ammonia-treated maize. ND*, None detected.
Low numbers of moulds were observed through the fourth month of storage in liquid anhydrous ammonia-treated maize, but following an initial decrease, bacterial counts increased to their original level by about 40 days. These numbers were generally constant through the first 5 months of storage and then relatively high counts of both moulds and bacteria were recorded in the sixth month of storage when the maize temperature increased. Visible
mould growth (Scopulariopsis albus) occurred at the top centre of the grain bulk during the fifth month of storage.

Initially, moulds grew from approximately 80% of surface-sterilized kernels; the incidence was reduced to zero for all three treatments for the first 5 months of storage (Table I). In the sixth month, moulds (predominantly species of Scopulariopsis albus) grew from 25% of the surface-sterilized kernels from the liquid anhydrous ammonia treatment.

**TABLE I**

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Storage</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Days</td>
</tr>
<tr>
<td>Gaseous anhydrous ammonia</td>
<td>70</td>
</tr>
<tr>
<td>Liquid anhydrous ammonia</td>
<td>80</td>
</tr>
<tr>
<td>Methylene-bis-propionate</td>
<td>89</td>
</tr>
</tbody>
</table>

Bothast et al. (1978) reported that methylene-bis-propionate breaks down to propionic acid and formaldehyde when in contact with wet maize. They suggested a stoichiometric equation for this reaction in which 93% by weight of the methylene-bis-propionate is recovered as propionic acid, assuming that a complete hydrolytic reaction has taken place. The 0.5% level of propionic acid retained on the maize (Table II) was sufficient to inhibit mould and bacterial growth throughout the 6-month storage period (Fig. 3).

The most telling effect of ammonia-preserved maize was a change in colour from yellow to brown (Brekke et al., 1979). The "peppery" odour of propionic acid persisted on MBP-preserved maize throughout the storage trial.

In feedlot studies, steers gained more rapidly and efficiently on the ammoniated maize, compared to the methylene-bis-propionate-preserved maize. Performance data from these tests are summarized in Table III.

Whilst data on moisture migration and attendant microbial activity in preserved high-moisture grain have been reported (Lancaster et al., 1974; Bothast et al., 1975; Stewart, 1975; Peplinski et al., 1978), no moisture migration was noted in either gaseous anhydrous ammonia-preserved or MBP-preserved maize during a 6-months storage period; neither was there any moisture migration in the liquid anhydrous ammonia-preserved lot through the first 4 months of storage. However, during the fifth month of storage, a pocket of moisture with concomitant microbial activity was visually observed in an area about 1 m² and 0.12 m deep at the top centre of the grain mass. Except for this small localized pocket, the average moisture content of the maize
TABLE II

Residual preservative material in maize

<table>
<thead>
<tr>
<th>Time</th>
<th>Gaseous anhydrous ammonia (%) d.b.</th>
<th>Liquid anhydrous ammonia (%) d.b.</th>
<th>Methylene-bis-propionate (%) d.b.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>as added</td>
<td>0.9</td>
<td>1.3</td>
</tr>
<tr>
<td>1 day</td>
<td>0.63</td>
<td>0.29</td>
<td>0.79</td>
</tr>
<tr>
<td>7 days</td>
<td>0.61</td>
<td>0.28</td>
<td>0.74</td>
</tr>
<tr>
<td>14 days</td>
<td>0.56</td>
<td>0.26</td>
<td>0.72</td>
</tr>
<tr>
<td>28 days</td>
<td>0.48</td>
<td>0.24</td>
<td>0.38</td>
</tr>
<tr>
<td>2 months</td>
<td>0.57</td>
<td>0.29</td>
<td>0.54</td>
</tr>
<tr>
<td>3 months</td>
<td>0.54</td>
<td>0.31</td>
<td>0.46</td>
</tr>
<tr>
<td>4 months</td>
<td>0.54</td>
<td>0.32</td>
<td>0.47</td>
</tr>
<tr>
<td>5 months</td>
<td>0.48</td>
<td>0.30</td>
<td>0.46</td>
</tr>
<tr>
<td>6 months</td>
<td>0.41</td>
<td>0.29</td>
<td>0.52</td>
</tr>
</tbody>
</table>

*This value represents the stoichiometric amount of propionic acid added to the maize as methylene-bis-propionate, assuming a complete hydrolytic conversion of methylene-bis-propionate to propionic acid and formaldehyde.

TABLE III

Feedlot performance*

<table>
<thead>
<tr>
<th>Maize treatment</th>
<th>Gaseous anhydrous ammonia (kg head⁻¹ day⁻¹)</th>
<th>Liquid anhydrous ammonia (kg day⁻¹)</th>
<th>Methylene-bis-propionate (kg feed kg⁻¹ gain⁻¹)</th>
<th>S.E.**</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dry matter consumption</td>
<td>8.25</td>
<td>7.93</td>
<td>7.49</td>
<td>0.35</td>
</tr>
<tr>
<td>Average daily gain</td>
<td>1.24a</td>
<td>1.17ab</td>
<td>1.02b</td>
<td>0.06</td>
</tr>
<tr>
<td>Feed efficiency</td>
<td>6.65</td>
<td>6.78</td>
<td>7.34</td>
<td>0.70</td>
</tr>
</tbody>
</table>

*Forty-two steers with an initial average weight of 308.4 kg were randomly assigned to each of the three treatments. Over 86 days, each batch of maize was given to 14 steers on 3:1 dry matter ratio of maize and maize silage.

**Standard error of the mean. Two means with no letter in common differ significantly at the 0.5 level.
remained unchanged throughout the storage period in maize treated by all three methods.

Lancaster et al. (1974) reported ammonia/moisture gradients to be a problem in previous field trials. Limited funding prevented us from optimally matching the quantities of maize preserved with the equipment employed. However, the ammonia application technique explored in these experiments, while not completely eliminating problems of moisture/ammonia migration, is worthy of further investigation and study. In the gaseous anhydrous ammonia test employing a gas-tight recirculation system, the problems of moisture migration and ammonia loss could be essentially eliminated. While it is true the cost to equip a circular metal bin with a gas-tight recirculating system is expensive, the procedure could be applied in high-moisture maize grain gas-tight silos if uniform, accurate, application methods can be developed. Anhydrous ammonia is now being used on forage silage to increase the nonprotein nitrogen level for ruminant consumption (Huber et al., 1973; Huber, 1975; Anonymous, 1977). While the increases in nutritive value have been abundantly documented in the literature, the microbiocidal benefits have been mentioned only in passing.

In the liquid anhydrous ammonia test, we feel that the application technique described in this report may have aided in more uniformly distributing the preservative material on the grain compared to applying an aqueous solution of ammonia used in the earlier studies of Bothast et al. (1975). In addition, the quantity of preservative material handled was significantly less. The obvious advantage of using liquid anhydrous ammonia rather than an aqueous ammonia solution is the elimination of additional water being added to grain already high in moisture content. We feel the significant loss of ammonia experienced in this test could be substantially reduced by placing the treated grain in a gas-tight silo. More experimentation and research is needed to minimize handling problems and attendant gas losses.

REFERENCES


