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# Effect of Sulphur Dioxide Treatment on the Quality of Wheat Straw Pretreated with Ammonia

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The effects on the nutritive value of wheat straw were studied by treatment with anhydrous ammonia (30 g/kg DM) at 20°C for 28 days and/or sulphur dioxide (40 g/kg DM) at 20°C for 3 or 7days, or 70°C for 3days.

The wheat straw was moistened with water (450 g/kg DM) prior to the treatment. Digestibility in vitro of the sample was measured by incubation with rumen liquor collected from Tokara goats fitted with rumen cannulae and fed on alfalfa hay. The results obtained were as follows :

Crude protein content was improved by 5 percent by ammoniation and increased by 12.7 percent to 14.2 percent with $NH_3 \cdot SO_2$ treatment. Contents of NDF and hemicellulose were more reduced by $NH_3 \cdot SO_2$ treatment than by ammoniation alone, however, ADF and cellulose contents were only slightly reduced by $NH_3 \cdot SO_2$ treatment. The digestibilities of DM and chemical components were increased more by $NH_3 \cdot SO_2$ treatment than by ammoniation. Digestibility of DM was negatively correlated to lignin content and positively related to lignin digestibility. A high temperature (70°C · 3 days) condition of sulphuration after ammoniation produced the highest potential digestibility of wheat straw.

## INTRODUCTION

Cereal straws are feed resources of importance to ruminants, however, low nutritive value and slow fermentation rates of straws restrict their usefulness as a ruminant feed source.

Recently, treatment of cereal straws with ammonia and sulphur dioxide has been reported to improve their nutritive value by increasing both crude protein content and dry matter digestibility (Dryden and Leng, 1986, 1988 ; Song et *al.*, 1991a, 1991b). Van Soest and McBurney (1985) comment that use of ammonia assumes that chemical linkages between carbohydrates and lignin are primarily of the ester type and thus susceptible to alkaline saponification, and that sulphur dioxide may act on such linkages.

Song et *al.* (1991a) reported that sulphuration of ammoniated rice straw gave slightly higher nutritive values compared to ammoniation alone. Song et al. (1991b) showed that the quality of ammoniated barley straw was, however, not improved further by the following sulphuration, which observation was different from the observations of Dryden and Leng (1986, 1988) who showed further improvement by sulphuration. These inconsistencies might be attributed to the differences in conditions of sulphuration and probably in species of cereal straws.

The main objective of this study was to examine the effects of sulphuration treatments of different duration and temperatures on the nutritive value of wheat straw pretreated with ammonia.

## MATERIALS AND METHODS

### Straw and its treatment

Wheat straw (japonica type, var. Nourin No. 61) was collected at the Kyushu University Farm in 1989 and dried for 48hr at 70°C, then cut into about 2-3 cm lengths. The straw was moistened with water (450 g/kg DM) and incubated at 20°C for 4days in a sealed polyvinyl jar. The prepared straw was then treated with anhydrous ammonia (0 or 30 g/kg DM) for 28days at 20°C and then treated with sulphur dioxide (0 or 40 g/kg DM) at 20°C for 3days or 7days, or 70°C for 3days. The treated straws were aired 3days to exclude excess chemicals and ground to pass through a 1 mm aperture screen.

### Analytical procedures

Crude protein content of the straw was determined by the Kjeldahl method (AOAC, 1984) and ash content by combustion at 600°C for 3hr. Cell wall components were measured by the'methods of Georing and van Soest (1970) with lignin determination by permanganate method. The acetyl bromide method (Morrison, 1972) was also applied to measure lignin. The straw digestibility *in vitro* was determined by incubation with rumen liquor (Minson and McLeod, 1972) collected from two Tokara goats fitted with rumen cannulae and fed on alfalfa hay.

### Statistical analysis

The digestibility and chemical components were examined for variance difference and the least significant difference (LSD). Linear regression was suitable for analyzing the relations between digestibility and lignin or silica.

## RESULTS AND DISCUSSION

### 1. Effects of ammoniation and different conditions of sulphuration on chemical composition of wheat straw

Table 1 shows chemical composition of wheat straw untreated, ammoniated and treated with $NH_3 \cdot SO_2$ in different duration and temperatures of sulphuration. Ammoniation of straw improved its crude protein content by 5%. Sulphuration after ammoniation increased crude protein by 14.2% with 20°C . 3days, 13.8% with 20°C . 7days and 12.7% with 70°C . 3days. Sulphites assist in the retention of volatile N by trapping NH, as ammonium sulphite or similar compounds (Buttle et al., 1974). Crude protein content was increased more with $NH_3 \cdot SO_2$ treatment than with ammoniation alone, however, crude protein content was not improved further by longer duration or higher temperature of sulphuration.

Neutral detergent fibre (NDF) and hemicellulose contents of the straw were each decreased by 7.3% with ammoniation, and decreased by 13.2-18.3% and 8.5-13.1% respectively with $NH_3 \cdot SO_2$ treatment. The highest decreases of NDF and hemicellulose contents resulted from sulphuration at 70°C . 3days after ammoniation. Higher temperatures caused accelerated hemicellulose degradation. Acid detergent fibre

Table **1.** Chemical composition" of wheat straw untreated and treated with ammonia and/or sulphur dioxide.

| Treatment | Control | Ammoniation (3 %) | Sulphuration (4%) after ammoniation | | |
|---|---|---|---|---|---|
| Temperature (°C) | | 20 | 20 | 20 | 70 |
| Duration (days) | | 28 | 3 | 7 | 3 |
| Dry matter | 89.73"' | 88.47' | 87.58[d] | 82.76" | 90.99[a] |
| Crude protein | 3.08" | 8.18[b] | 17.23[d] | 16.90[d] | 15.77' |
| NDF[2)] | 76.41" | 69.15[b] | 63.19' | 61.73[d] | 58.11" |
| ADF[3)] | 49.65" | 49.71" | 45.23[b] | 43.42[d] | 44.46" |
| Hemicellulose | 26.76" | 19.44[b] | 17.95' | 18.31' | 13.65[d] |
| Cellulose | 39.20[ab] | 40.29" | 36.93" | 36.13' | 38.37[b] |
| PM[4)]-lignin | 9.40" | 8.28[ab] | 8.26[ab] | 8.16[ab] | 7.45[b] |
| AB[5)]-lignin | 12.60" | 12.62" | 11.33[b] | 10.88[b] | 6.52' |
| Silica | 5.40[ab] | 5.86" | 5.32[ab] | 5.03[ab] | 5.22[ab] |

1) % dry matter basis, 2) neutral detergent fibre, 3) acid detergent fibre, 4) permanganate,
5) acetyl bromide,
6) Values with different superscripts in the same row differ significantly ($p < 0.01$).

(ADF) and cellulose contents were not affected by ammoniation, however, they were slightly reduced by treatment with $NH_3 \cdot SO_2$. Ammonia partly degraded hemicellulose, however, it might not affect cellulose (Dryden and Leng, 1988). Probably most of this "lost" hemicellulose was rendered soluble and entered the neutral-detergent solubles (Chesson, 1981).

Permanganate lignin (PML) was slightly reduced by ammoniation, however, acetyl bromide lignin (ABL) was not affected. Müller and Berger (1975) reported that lignin was increased possibly by ammonia-lignin complex formed in ammoniated straw, however, Graham and Åman (1984) showed no increase of PML content by ammoniation. Both ABL and PML decreased greatly due to the following SO, treatment with 70°C . 3days ; **9.40%** to 7.45% in PML and 12.60% to 6.52% in ABL. Sulphur dioxide might partly degrade lignin through a bleaching reaction, probably in similar to ammonium sulfide bleaching (Hart, 1969).

Silica content was little affected by treatment with NH, and $NH_3 \cdot SO_2$.

### 2. Effects of ammoniation and different conditions of sulphuration on *in vitro* digestibility of wheat straw

Table 2 shows in vitro digestibilities of DM, crude protein and cell wall components of wheat straw untreated and chemically treated. Digestibility of DM increased by about 19% with ammoniation and 28% to 39% with $NH_3 \cdot SO_2$ treatment. The highest increase of DM digestibility was found in the sulphuration with 70°C . 3days after ammoniation, showing digestibility of 88.8%.

Crude protein digestibility was improved 20-25% more with $NH_3 \cdot SO_2$ treatment than with ammoniation alone.

Cellulose digestibility was increased with ammoniation by 20% and by 27% to 36 % with $NH_3 \cdot SO_2$ treatments.

Digestibilities of lignin and silica increased by ammoniation. They further increased by $NH_3 \cdot SO_2$ treatment, and a higher temperature (70°C . 3days) gave substantially higher degradation rates of lignin and silica.

The partial solubilization of lignin in straw by alkali treatmint is well documented, and relatively weak alkali such as ammonia is unlikely to significantly alter cellulose structure (Jackson, 1977). Further digestion of cellulose depends on the prior removal of lignin, as noted by Chesson (1981). Details in lignin protecting fibrous materials from degradation is not fully known, however, there are strong indications of the existence of covalent bonds between the matrix polysaccharides and lignin (Lai and Sakanen, 1971).

Table 3 shows the changes with lapse of time in digestibilities *in vitro* of dry

Table 2. *In vitro* digestibilities of dry matter and chemical composition" of wheat straw untreated and treated with NH, and/or SO,.

| Treatment | Control | Ammoniation (3 %) | Sulphuration (4%) after ammoniation | | |
|---|---|---|---|---|---|
| Temperature (°C) | | 20 | 20 | 20 | 70 |
| Duration (days) | | 28 | 3 | 7 | 3 |
| Dry matter | 49.52[a4)] | 68.76[b] | 77.62' | 81.42[d] | 88.79" |
| Crude protein | 0.00" | 41.54[b] | 60.00" | 61.05[d] | 65.75" |
| Cellulose | 59.40" | 79.34[b] | 86.74" | 90.51[d] | 95.86" |
| PM[2)]-lignin | 37.80" | 46.10[b] | 61.78' | 72.39[d] | 75.70" |
| AB[3)]-lignin | 31.03" | 56.47" | 69.84' | 74.94[d] | 78.02" |
| Silica | 38.29" | 51.77[b] | 60.59' | 65.54[d] | 73.66[e] |

[1)] % dry matter basis, [2)] permanganate, [3)] acetyl bromide,
[4)] Values with different superscripts in the same row differ significantly ($p < 0.01$).

Table 3. Changes with lapse of time in digestibilities in vitro of dry matter and chemical composition') of wheat straw untreated and treated with NH, and/or SO,.

| Treatment | | Control | Ammoniation (3%) | Sulphuration (4%) after ammoniation | | |
|---|---|---|---|---|---|---|
| Temperature | (°C) | – | 20 | 20 | 20 | 70 |
| Duration | (days) | | 28 | 3 | 7 | 3 |
| Dry matter | (12h)[4)] | 15.14[a5)] | 24.68[b] | 38.16" | 43.92[d] | 51.21" |
| | (24h) | 31.55" | 48.59[b] | 68.00' | 75.23[d] | 82.69" |
| | (48h) | 49.52" | 68.76[b] | 77.62' | 81.42[d] | 88.79" |
| Crude protein | (12h) | 0.00[a] | 11.23[b] | 47.12[c] | 44.31" | 44.87' |
| | (24h) | 0.00[a] | 14.80[b] | 52.32" | 54.67[d] | 58.37" |
| | (48h) | 0.00[a] | 41.54[b] | 60.00" | 61.05[d] | 65.75" |
| Cellulose | (12h) | 18.28" | 25.88[b] | 37.79 | 46.36[d] | 53.24" |
| | (24h) | 38.29" | 57.76[b] | 78.60' | 86.68[d] | 91.70" |
| | (48h) | 59.40" | 79.34[b] | 86.74' | 90.51[d] | 95.86" |
| PM[2)]-lignin | (12h) | 2.32" | 11.67[b] | 28.09[e] | 34.27[d] | 41.39[c] |
| | (24h) | 18.37" | 25.12[b] | 55.41' | 66.05' | 73.60[d] |
| | (48h) | 37.80" | 46.10[b] | 61.78' | 72.39[c] | 75.70" |
| AB[3)]-lignin | (12h) | 6.88[a] | 17.91[b] | 27.36' | 29.66[d] | 34.61" |
| | (24h) | 19.57" | 35.18[b] | 63.25' | 66.24[d] | 73.06" |
| | (48h) | 31.03" | 56.47[b] | 69.84' | 74.94[d] | 78.02" |

[1)] % dry matter basis, [2)] permanganate, [3)] acetyl bromide, [4)] incubation time,
[5)] Values with different superscripts in the same low differ significantly ($p < 0.01$)

matter, crude protein and cell wall components. Improvement effect by ammonia and $NH_3 \cdot SO_2$ treatments already appeared by 12hr incubation. During the first 12hr incubation, cellulose was more quickly digested than any other compositions. The digestion rate of carbohydrates was initially greater than that of dry matter (Graham and _&man, 1984).

### 3. Relation of *in vitro* dry matter digestibility (IVDMD) to lignin of wheat straw untreated and chemically treated

Fig. 1 shows that IVDMD is negatively correlated to PML content ($r = -0.961$, $p <$

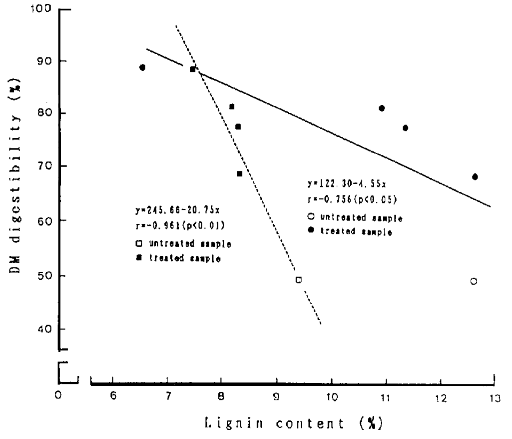


Fig. 1. Relation between in *vitro* dry matter (DM) digestibility and lignin (permanganate : □ --- ■, acetyl bromide : 0 — ●) content of wheat straw.

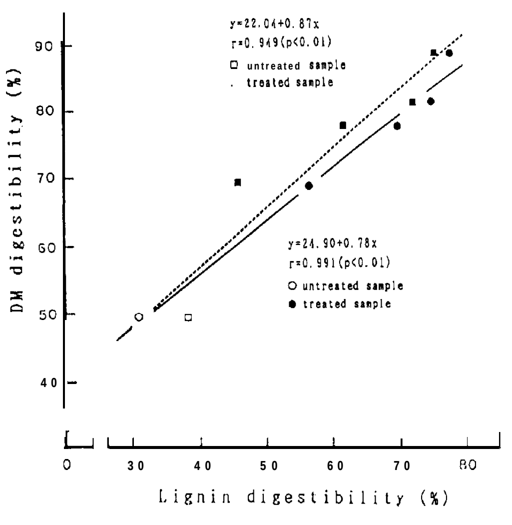


Fig. 2. Relation between *in vitro* dry matter (DM) digestibility and lignin (permanganate : □ --- ■, acetyl bromide : 0 — ● ) digestibility of wheat straw.

0.01) and ABL content (r= -0.756, NS). Lignin content was likely to be the major constraint on potential degradability of dry matter (Smith et al., 1972).

Fig. 2 shows that IVDMD is positively correlated with lignin digestibilities (PML : $r=0.992, p<0.01$ ; ABL : $r=0.991, p<0.01$).

These observations indicated that improvement in DMD was mainly due to the decreased content and increased digestibility of lignin, which had been made labile by

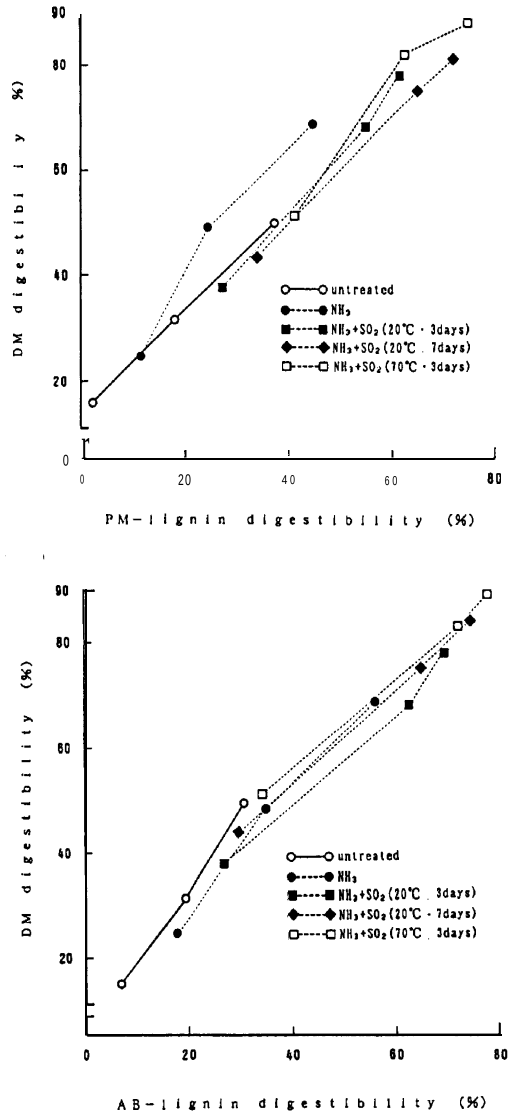


Fig. 3. Changes with lapse of time in in *vitro* dry matter (DM) digestibility and digestibilities of permanganate lignin and acetyl bromide lignin of wheat straw.

ammoniation and sulphuration. Chesson (1981) reported that when about 50% of the straw was degraded, further digestion of the cellulose and hemicellulose depended on the prior removal of lignin.

Fig. 3 shows the changes with time in IVDMD and lignin digestibility of each treatment. As lignin digestion proceeded with lapse of incubation time, DMD was also increased. About 76% of the PML and 78% of the ABL were degraded at the highest DMD values observed. Higher temperature (70°C . 3days) of sulphuration after ammoniation caused wheat straw to be potentially highly digestible, and gave the highest lignin digestibility hence the highest dry matter digestibility.

Results obtained from this study showed that appropriate application of sulphur dioxide to ammoniated wheat straw improved its nutritive value further than ammoniation alone. Treatment at higher temperature with sulphur dioxide after ammoniation greatly increased both the rate of digestion and the potentially digradable fraction of wheat straw.

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