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SUMMARY - The main treatments of straw are presented as well as the chemical modification in straw that occurs during treatments. New methods that have been tested were described as well as the microbial approach to upgrade straw nutritive value. Attention must be paid to the improvement due to the increase in digesti-bility and or the improvement in DM intake.

RESUME - "Traitement des pailles". Les principaux traitements des pailles sont présentés en précisant leur composition chimique résultant du traitement. De nouvelles techniques microbiennes sont proposées afin d'améliorer la valeur nutritive des pailles. Il convient de discuter des effets des traitements sur l'ingestion et sur la digestibilité des pailles.

Introduction

To improve the low nutritive value of straw, and to overcome its limitations in terms of animal production, various methods of straw treatment have been tested and implemented. In order to render straws into a reasonable quality feed it should be necessary: to remove lignin, to hidrolyse cellulose, to solubilize silica or to hydrolyse the ester bond of hemicelluloses.

A certain number of treatments have been proposed so far and to obtain this goal a treatment should: a) Improve digestibility, b) be easily applicable in practice, c) be cheap, d) not introduce toxic compounds, e) not decrease the Biological value of proteins, f) maintain minerals and vitamins.

Chemical modification in straw during different treatments

The changes that take place when low quality roughages are treated with alkali are of a physical as well as chemical nature. It is well known that the materials are normally softer after chemical treatment than before the treatment. This may be one of the reasons for the higher intake found for treated material (Sundstol , 1988). Another important change that takes place during alkali treatment is a swelling of the plant cell wall. This is probably most pronounced for wet NaOH treated materials and was confirmed by Harbers et al. (1982). It may be reasonable, however, that a certain amount of moisture in the material is needed to obtain this swelling effect. When the cell wall is expanded and the surface ruptured the rumen microbes will have better access to the structural carbohydrates and consequently the digestibility is enhanced.

Treatments of straws with alkaline reagents, in particular sodium hydroxide and ammonia, has been extensively used. There is a number of chemical reactions taking place during alkali treatment.

Saponification of ester linkages between acetic acid and phenolic acids, and plysaccharides and or lignin as well as such linkages between uronic acids residues of xylans in hemicelluloses and lignin would be expected to occur during the alkaline treatment of straw material (Theander and Aman, 1984).

If the temperature is high enough, in the presence of alkali, lignin undergoes cleavage of other linkages between phenyl propane units and free phenolic groups are formed. As a result of the accompanying decrease in the molecular weight and cleavage of linkages to the hemicelluloses, an increased solubility of lignin in the alkaline solution will occur.

During alkaline treatments the hemicelluloses are expected to be partly solubilized and the cellulose to be more accessible by an alkaline swelling effect. Therefore an enrichment of cellulose is observed as the consequence of removal of hemicelluloses and lignin. Besides, the cleavage of linkages between lignin and hemicelluloses sets cellulose free. That is because cellulose is embedded in the hemicellulose-lignin complex which is destroyed by the action of the alkali.

Recent studies by Lindberg et al. (1984) indicate that xylans are partly translocated during aqueous NaOH- treatment to a position in the straw cell walls where they are more available to ruminal digestion.

Another reaction contributing to the neutralization of NaOH-treated straw is the so called "peeling reaction" by which sugar residues are released from the reducing sugar end-unit of the polysacharide and other aliphatic acids (Whistler and BeMiller, 1958).

As a conclusion one can say that alkali treatments operate not by reducing or destroying the phenolic components but by breaking specific lignin-carbohydrate linkages. Lignin free from its association with polysaccharide is solubilised when exposed at the cell wall surface and the rate of build up of an inert phenolic layer is correspondingly reduced (Chesson, 1984)

Chemical methods

Treatment with Sodium Hydroxide (NaOH)

Wet Treatment

After a first period (until 1920's) of studies on boiling straws in NaOH solution, even under pressure, Beckman and Fingerling introduced their method consisting of soaking fibrous by-products in cold NaOH solution (1-1. 5% for 12 hours) followed by washing out with water to neutrality.

Almost all the cellulose remains in the fodder while about 30 of the lignin and 10-15 of the pentosans are solubilized and washed out.

By this method the organic matter digestibility of rye straw increased from about 46 to 71 (Sundstol 1988a). During this treatmant 15-20 of the straw dry matter is lost with the rinsing water. A modified version of this method was used by the Norwegian farmers from the beginning of World War II onwards (Homb, 1984). Treatment of straw with OHNa according to the Beckman procedure was at its height in the mid-sixties and has since declined, mainly because of pollution problems (disposal of the rinsing water).

The original method has now been replaced by a modification of the Dip-treatment method (Sundstol, 1981). By this method the straw is also soaked in a 1.5 solution but for 1/2 - 1h only, after which it is stored 4-6 days instead of rinsing. The organic matter digestibility of dip treated straw is increased from 45-5O% to 70-75% (Sundstol, 1988a). With this method there is no loss of dry matter and the pollution problems were greatly reduced.

Dry Treatment

The industrial procedures for dry treatment of straw with NaOH have been developed in many countries (Rexen and BachKundsen, 1984). The general procedure is that the material is desintegrated (chopped or milled) before a solution containing 200-300 g NaOH per litre is sprayed on the material. After a thorough mixing the material passes through a press thus obtaining pellets (10-25 mm in diameter) or briquettes (50 mm in diameter). The high temperature developed in the press causes an almost immediate reaction between the material and the alkali.

After leaving the press, 1-5% of the moisture evaporates off the optimal concentration of NaOH seems to be 4-6% of straw dry matter (Sunstol, 1988). This treatment may be characterized as a combination of physical and chemical treatment. Alternatively "on the farm" procedures have been developed for dry treatment of straw with sodium hydroxide. Systems where the solution is sprinkled over long form straw and thereafter mixed thoroughly or sprayed over chopped straw in a mixer wagon or even treating the straw during the process of bailing have been described (Sundstol, 1988).

However the more efficient process for dry NaOH treatment of straw seems to be the use of a machine especially designed for this purpose e.g. JF and Taarup. Straw entering the machine is first chopped into pieces of 1-5 cm in length. When the straw is leaving the chopper 4-5% of NaOH in the form of a 20-30% solution is added. The straw and the lye are thereafter well mixed as they pass through a mixing chamber before being blown into a heap for storage. The temperature increases rapidly up to 80-90° C in the centre of the heap and within a week the material is ready for feeding.

The dry treatment implies the use of small amounts of water, yet it is hazardous for the eyes and skin of the operator.

Ammonia Treatment

Amongst the other chemicals NH3 is the most suitable because, while hydrolysing the ligno-cellulosic linkages, as the other alkalis do, in addition it contributes to the nitrogen fraction. The chemical was not used in practice to a great extent until after 1970. Since then a number of methods have been developed varying according to the conditions of each country or region. Ammonia is used in pure form (anhydrous), in water solutions (aqueous) and in solid compounds, e.g. urea.

Ammonia treatment of low quality roughages was reviewed recently by Sundstol and Coxworth (1984).

Anhydrous Ammonia

The stack method for ammonia treatment of straw was developed in Norway in 1970-1975. Stack of straw are wrapped with polythylene and injected with 3% of anhydrous ammonia (Sundstol et al. 1978). The liquid ammonia evaporates gradually and the ammonia gas penetrates the stack. This method has become popular and is used in a number of European countries.

As far as concentration is concerned it is not justifiable to exceed 4% NH3 on the straw DM basis even if some little beneficial effects, from increasing the NH3 level up to 7%, are obtained (Sunstol et al. 1979). The NH3 reaction with fibrous material in much slower than that of NaOH. Like all chemical reactions it is time and temperature dependent. At temperatures near 100 °C the hidrolysis reaction is almost immediate; at 0 °C it is very slow. That means that the effect of temperature is not so relevant if the exposure time is long enough (cold climate). Moisture content is another important factor determining the effect of ammonia treatment. Anhydrous ammonia seems to exert no or little effect on upgrading straw with less than 3% moisture content (Sundstol et al. 1979). The higher the amount of water the better. Yet the optimal level of moisture seems to lie between 15 and 20% (Sundstol and Coxworth, 1984) . Even if a higher amount may give better upgrading effects, there is a greater risk of storage moulding damage.

One of the greatest advantages of the method is that ammonia has a fungicidal effect, in other words, the straw need not be dry before ammonia is added. The effect of ammonia treatment on the digestibility of straw is less than that of dip treatment with NaOH. An improvement in OMD of 10-12% units, bringing the digestibility of barley straw and oat straw up to 60-62% is common (Sundstol, 1988a). Ammonia treatment of straw can also be carried out in ovens at temperatures of about 90 °C. At such temperatures the treatment can be completed within 24h but the cost is relatively high.

Another recent technique (Dale and Moreira, 1982) suggests the use of liquid NH3 mixed 50:50 with the straw and then it is made to expand rapidly. The temperature drops below 0 °C and the cell walls are broken - this enhances digestibility. It is known as Ammoniation Freeze Explosion (AFEX) . The cost is said to be not too high because liquid NH3 can be re-cycled.

When materials with high sugar content (> 5%) are treated with anhydrous ammonia at high temperatures (> 70%) the poisonous component 4-methyl imidasol can be formed which may cause hyperexcitability in farm animals and may also be transferred into the milk of dairy cows (Perdok and Leng, 1985). With pure straw, treated at low temperatures, the risk of this disturbance should be negligible.

The time required for airing, necessary to disperse extra NH3 and thus to eliminate the smell, depends on a number of factors (Sundstol and Coxwort, 1984):

- Temperature: cold climates - longer time
- Moisture of straw: high moisture - longer times
- Density of the straw: big bales of high density -longer time
- Wind: strong winds - short time.

Usually this time varies from 2-3 days up to several weeks.

As a conclusion one can say that anhydrous ammonia has the advantage of needing small amounts of NH3 and due to its gaseous nature a rapid penetration in the straw bales is ensured. However, it needs a distribution network and it must be emphasized that NH3 is dangerous and toxic.

Aqueous Ammonia

Aqueous ammonia is used commercially for straw in some countries. The advantage is that it does not need to be pressurized or it may be only slightly pressurized.

Common commercial solutions contain 25 to 33% NH3 (w/v). The treatment with aqueous NH3 has another advantage over anhydrous NH3, that no extra water must be added to dry straw. Attention must be paid if the material to be treated is wet (danger of moulding). The solution is simply poured over the stack which must be covered and sealed thereafter.

Aqueous NH3 has proved more beneficial than anhydrous NH3 because of easier transportation and handling and because a great proportion of the lignin fraction is solubilised and removed.

Urea

NH3 is formed when urea is decomposed. The ratio is roughly 2:1 (100 g urea, if completely decomposed, yield a little more than 50 g NH3).

Urea is easy to handle and to use with no health risks. It can be purchased everywhere and it is considerably cheaper than both NaOH and NH3.

Decomposition of urea into NH3 occurs spontaneously at high temperatures (over 100 °C) - otherwise it must be guided by natural ureases - if not enough enzymes are present in the fodder to be treated, more enzymes must be added (raw i.e. soybean powder), however, this would not always produce a significant improvement. Urea must not remain undecomposed in the feed as it could lead to an increased NH3 rumen production which can cause a toxic problem for the animal.

Orskov in Scotland found no effect at all in treating straws with urea (Orskov et al. 1981). The lack of positive response of urea treatment in temperate countries may be due to the moisture content (> 50%) and the high temperature (60 °C) needed for the ideal urease activity (Williams and Innes, 1983) which sometimes is difficult to obtain.

Protein Value of Ammoniated Straw

The added N is another advantage together with increased digestibility and intake, however most of this N is excreted in the faeces which according to Michalet-Doreau et al. (1990) could be due: - to the attachment of the N to the indigestible cell wall (or non digested in the rumen) or the poor utilization of this N by the rumen bacteria or to an increase of microbial N, as a consequence of an extra hind but fermentation.

Other Treatments

Recently there have been attempts to use other chemical treatment of feedstuffs to enhance digestibility. Kerley et al. (1986) reported a new chemical treatment process using alkaline hydrogen peroxide (AHP). These authors showed that NDF digestibility increased from 42.1% for sheep fed non treated straw to 81.0% for sheep fed AHP-treated straw-based diets and that digestible DM intake was increased nearly threefold when sheep were fed AHP-treated straw compared to control straw diets. Electron micrographs showed that this treatment allowed more complete bacterial colonization and more rapid degradation of the cell wall. Although the use of this treatment process will be determined by economics, the potential for practical application appears very encouraging. Ben-Ghedalia and Rubinstein (1986) evaluated the ability of another oxidizing agent, ozone, to increase the digestibility of screened manure fiber from high producing dairy cows with ozone reduced both NDF and lignin by approximately 35%. In vitro DM digestibility was increased from 36.2 to 65.2% by ozone treatment. Ozone resulted in greater improvements in digestibility than treating with 5 to 8% NaOH. Sulfur dioxide (SO2, 62.6 g/kg) was used by O'Shea and Baldwin (1986) to improve the in vitro digestibility of barley straw from 45 to 80%. This improvement was attained over a DM content range of 46 to 75% and a reaction temperature range of 60 to 70 °C. When treated straw was fed at 40% of a complete diet to lambs, in vivo straw digestibility was increased approximately 11 percentage units.

Results of research reported by Nolte et al. (1987) suggest that treatment of wheat straw with alkaline solution of wood ashes effectively improves fiber utilization by ruminants. Wheat straw was soaked in alkaline solution prepared from wood ashes. General observations included improvements in the digestibility of DM, NDF and ADF when the alkali soluble wood ashtreated straw was compared With either NaOH-treated or untreated straw. Alexander et al. (1987) reported that Sulfur dioxide (S02), ozone and alkaline hydrogen peroxide selectively degraded phenolic material without modifying the carbohydrate content of the straw. The degradability of ozone-treated straw was substantially increased whereas S02 treatment had a lesser effect and treatment with alkaline hydrogen peroxide was largely ineffective.

Miron and Ben-Ghedalia (1987) studied the effect of increasing fermentability of wheat straw by S02 or by S02 and cellulase on several nutritional parameters in sheep. They reported that the content of cell solubles in the straw was increased by the S02 treatment and further increased by the combined SO2-cellulase treatment. The increase in the content of rapidly fermentable sugars of the straw was associated with a gradual decrease in the proportion of ruminal acetic acid and an increase in butyric acid. Overall, the authors suggest that it is possible to convert straw into a highly fermentable material by a combined treatment of SO2 and cellulase, but for N metabolism the combination is not superior to the S02-treated material.

Ground wheat straw was treated with 0, 2, 4 and 6% ethanolamine and stored for four days at 40 °C, Flachowsky et al. (1988). Ethanolamine treatment resulted in a decrease in fiber content and an increase in "in situ" digestibility.

Several of these treatments are still to be proved or at least tested and some, like the chlorine based oxidisers, depress digestibility.

At present it seems that no effective alternatives to Sodium hydroxide or to Ammonia are possible.

Microbial methods

Microbial treatment methods for improvement of poor quality forages and roughages has not been used in practice to date, but it may prove to be one of the most promising in the future. The main problem in biological upgrading poor quality materials is to find suitable microorganisms which decompose lignin without using too much of the hemicellulose and the cellulose.

Zadrazil (1984), reviewing microbial conversion of poor quality products into feed, concludes that in vitro digestibility of fungal substrates decreases at the beginning of colonization by white rot fungi and increases afterwards. During incubation the contents of soluble substances (partly sugars) increase.

The increase in digestibility depends on the fungal species, cultivation time, temperature, water/air ratio in the substrate, and on the preparation, bulk density and composition of the substrate. In vitro digestibility of lignocellulose by white fungi is decreased by addition of inorganic nitrogen.

Not surprisingly, cellulase and hemicellulase enzymes are ineffective in the initial degradation of such lignified cell walls. However, a single lignase, produced by the soft-rot fungus *Phanerochaete chrysosporium* is capable of causing a high degree of depolymerisation (Tien and Kirk, 1983). The enzyme acts like a peroxidase and causes a free radical-mediated cleavage of carbon-carbon bonds which require hydrogen peroxide or oxygen (Kersten et al, 1985). At present, the levels of lignase produced by basidiomycete fungi are not sufficient for the biological pre-treatment of straw to be a commercial proposition. However, with the use of recombinant DNA engineering techniques, it is conceivably possible to modify the lignase genes and thus the proteins, to increase their efficiency and stability. With regard to this objective, several research groups have now cloned and sequenced the lignin gene from *Phanerochaete chrysosporium* (Tien and Tu, 1987; Zhang et al, 1986), a pre-requisite for future manipulation of the gene.

Other "fermentation" processes have also been tried for the upgrading of low quality products (Seal and Eggins, 1976), but if the "fermentation" process cannot be controlled, the quality of the product cannot be guaranteed and even toxic substances may be formed.

It may be concluded, however, that with sufficient knowledge of the biology of higher fungi and solid-state fermentation a low-cost technology for the conversion of lignocelluloses could be developed (Zadrazil, 1984).

Concluding remarks

Many methods have also been developed in which the material undergoes a combination of physical and chemical treatment.

Straw may also be "ensiled" with other chemicals such as NaOH, Ca(OH)2 etc. at a relatively-high moisture content. No practical method for microbial treatment of fibrous materials has been developed yet, but the scope for such a method may prove to be great. The improvement in digestibility is frequently used to express the effectiveness of straw treatment however, in most cases, this improvement is accompanied by a significant increase in the straw intake.

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