STORAGE OF CHEMICALLY PRETREATED WHEAT STRAW – A MEANS TO ENSURE QUALITY RAW MATERIAL FOR PULP PREPARATION

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The aim of this study was to evaluate effects of chemical pretreatment and storage on non-wood pulping and on pulp quality. The processes studied were hot water treatment followed by alkaline peroxide bleaching or soda cooking. The results showed that it is possible to store wheat straw outside for at least one year without significant changes in the raw material chemical composition and without adverse effects on the resulting pulp quality. The results are significant to the industry using non-woods to ensure the availability and the quality of the raw-material throughout the year in spite of the short harvesting time.

Keywords: Chemical pretreatment; Storage; Wheat straw; Hot water treatment; Soda cooking

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INTRODUCTION

Most plants grown on farms yield considerable amounts of fibrous by-products (straw or stalk) that are not consumed by people. Only a minor proportion of the fibrous products is consumed by animals. In Finland, straw is usually chopped and mulched into soil, and a minute quantity is baled for bedding or animal feed.

Conserved forage has long been a major roughage feed for ruminants, helping them to remain productive during the winter period. In Finland about 70% of the grassland area is used for silage making (Tike 2009), nowadays most for wilted silage. In silage, different grass species are preserved under anaerobic conditions at the growth stage when they possess high amounts of water soluble carbohydrates and protein (McDonald et al. 1991). To prevent disadvantageous microbial functions and fermentation, the pH is usually decreased to level 4 by using organic acids such as formic acid, earlier even mineral acids (Virtanen 1933), which are mixed into grass or cereals during the silage making (McDonald et al. 1991). For straw, caustic soda (sodium hydroxide), ammonia, and urea treatments have long been used to improve the quality of material as animal feed (Wilkinson 1984; Sundstøl and Coxworth 1984).

The use of straw for non-food production (fibre, energy, bio-composites) has been the focus of many studies (Ilvessalo-Pfäffli 1995; Papatheofanous et al. 1996; Saijonkari-Pahkala 2001; Le Digabel and Avérous 2006; Coppola et al. 2009). The main problems associated with using non-wood materials industrially are the logistics of the bulky raw material and the usually short harvesting time. Hence, the non-wood raw materials usually are stored before industrial use. If the raw material is stored outside under prevailing climate conditions, moisture and biological activity can easily cause decay of the non-wood material. Known silage methods and farming machinery could possibly be used for storing the non-wood materials for industrial use. In short, the biomass can be stored in bales without a need for extra storehouses.

The aim of this study was to evaluate the effects of chemical pretreatment and storage on wheat straw pulping and on pulp quality. The processes studied were hot water treatment followed by peroxide bleaching or soda cooking.

EXPERIMENTAL

Raw Material

Spring wheat straw harvested in 2007 (07Straw) and 2008 (08Straw) was used in the experiments. The wheat varieties were Marble in 2007 and Kruunu in 2008. The growing site for wheat was on a sandy clay field in Jokioinen, Finland (60°49'12"N, 23°28'12"E). The 07Straw was collected after threshing and cut into pieces with a laboratory cutter. The 08Straw was baled with a chopper baler, and treated with formic acid based solution one day after threshing, the targeted amount was 9 mL/kg of fresh straw. The distance between baler's knives were 8.6 cm, and the resulting straw length was 4-10 cm. Additionally, some 08Straw was collected after threshing and cut into pieces with the laboratory cutter for the minisilo experiments.

Chemical Pretreatment/Storage in Plexiglass® Acrylic Silos

Urea or formic acid was used as pretreatment/storing chemicals in Plexiglass® acrylic silo trials. The formic acid charge was 15g/kg DM, and the concentration of the used solution was 85%. The urea charge was 44g/kg DM, and the concentration of the used urea solution was 40%. The dry content of the chopped 07Straw was 74.4%. Straw and chemical were mixed carefully before weighing the mixture into the silos. The straw amount weighed was 900 g, including the weight of added acid or urea. The straw was packed with a wooden "piston" into the silos. The density of packed straw in silos was approximately 127 kg DM/m^3. Figure 1 presents the Plexiglas® acrylic silos used for the chemical pretreatment. In selected testpoints two replicates were performed.

The time of storage was varied from about 2 months to 1 year. After the period of storage, the silos were opened and the straw was washed. First, about 450 g of the straw was diluted with 10 L of deionised water, agitated, and left to settle for 30 min. Then the straw was centrifuged and washed with 20 L of deionised water while still centrifuging. The washed straw was stored in a cold storage room (+5°C) before the following experiments.

The untreated straw is not preserved at the room or cold storage temperature, if it is not air dried before storing. The straw with dry matter content of about 75% will become moulded quite rapidly in an air-proof plastic tube. Therefore, the reference points for untreated straw were excluded due to their possible health risks to the researchers and regarding the scientific value of such trials.

Fig. 1. Storage of chemically pretreated wheat straw in Plexiglass® acrylic silos. Sealing with Plexiglass® plate, lead weight, and water seal.

Chemical Pretreatment/Storage in Round Bales

Formic acid based solution AIV 2 Plus preservative from Kemira Oyj (76% formic acid, 5.5% ammoniumformate, water) was used as a pretreatment/storing chemical in the round bale trials. The straw was baled with the chopper baler and the acid was applied at the rate 9 mL/ kg of fresh straw during baling using a pump applicator attached to the baler. The density of straw in round bales was 107 kg/m^3. The dry matter content of the fresh 08Straw was 85.4%. After the baling, the straw was wrapped with 10 layers of white RaniWrap® stretch film (low-density polyethylene, width 750 mm, thickness 0.025 mm, Ab Rani Plast Oy, Finland) with 50% overlapping and 70% pre-streching.

Fig. 2. Storage of chemically pretreated wheat straw in round bales. Wrapping of the bale with white stretch film.

The raw material used for the experiments was taken after storing the bales 27, 41, and 52 weeks in an unheated barn. During the time the temperature of single days varied from -21 to +29°C according to the Finnish Meteorological Institute, and the mean temperatures are given in Table 1. After the defined time the bale was opened and the straw sample was collected evenly from the whole bale. The sample was frozen directly without washing for further use. Figure 2 illustrates the wrapping of the round bales used for chemical pretreatment.

Table 1. Weather Conditions in Jokioinen, Finland during the Round Bale Trials. Means for Daily Temperatures (Mean, Minimum and Maximum, °C) Given Monthly from October 2008 to September 2009, Jokioinen, Finnish Meteorological Institute. Baling Day 2008-09-24. Sampling Days 2009-04-03, 2009-07-07 and 2009-09-24 (Year-Mm-Dd).

Year/Month	Mean Temp. °C	Min. Temp. °C	Max. Temp. °C
2008/10	7	4	10
2008/11	1	-1	4
2008/12	0	-2	1
2009/01	-5	-8	-2
2009/02	-5	-9	-3
2009/03	-3	-6	1
2009/04	4	-1	10
2009/05	11	5	17
2009/06	13	8	19
2009/07	16	11	22
2009/08	15	10	21
2009/09	12	8	17

Temperature Sum 2073°C (base 0°C)

Chemical Pretreatment/Storage in Minisilos (glass bottles)

Formic acid or formic acid based preservative was used as a pretreatment/storing chemical in the minisilo trials. The amount of the formic acid solution (85% solution) added was the same as in the Plexiglass® acrylic silo experiment, which was 15g/kg DM acid. The formic acid based preservative charge was about the same as in the round bale experiments, 9 mL/ kg of fresh straw. The dry content of the chopped 08Straw was 85.4%. The dry content of the straw in silos was adjusted with mixture of water and preservative solution to 75%. The chemical and water were carefully mixed with the straw. Then the straw amount (32 g) was weighed into each minisilos, including the weight of water and added acid. The straw was pressed with a plastic "piston" while adding it into the silos. The density of packed straw in minisilos was 200 kg/m^3, which was higher than that of round bales or Plexiglass® Acrylic Silo experiments. This was most likely due to the slightly shorter length of the straw pieces. The storing time varied from 1 month to 1 year. Figure 3 presents the sealing of minisilos used for the chemical pretreatment.

After the defined time the silo was opened and the straw was washed. The washing started with dilution of straw with 3 L deionised water, agitation, and settling for 20 minutes. After that the straw was thickened and washed twice by diluting it with 3 L deionised water and thickening. After the last washing the straw was centrifuged and air-dried and, finally, the air dry straw was frozen in polyethylene bags. The straw from the minisilo pretreatment was used for the chemical composition analysis.

Fig. 3. Chemical storing of wheat straw in minisilos. Sealing with gray rubber plug and white plastic cap.

Hot Water Treatment and Bleaching

The pretreated straw was treated with hot water using an air-heated digester equipped with six 2.5 L autoclaves as described earlier (Leponiemi et al. 2010). The treatment temperature was 120°C, and the time at temperature 60 min. Diethylene triamine pentaacetic acid (DTPA) charge in treatment was 0.2%. The bleaching sequence was based on alkaline peroxide (P) and peracetic acid (Paa): P-P-Paa-P. The procedure was also described earlier (Leponiemi et al. 2010). Bleaching conditions are shown in Table 2. After the hot water treatment and every bleaching stage the treated straw/pulp was washed. Washing was carried out by diluting the treated straw or pulp with deionised water, agitating, allowing it to settle for 2 minutes and by removing the excess water through a wire pouch. The dilution and thickening were repeated 3 times. After the last washing the straw was centrifuged to 25% consistency. After the last bleaching stage and washing, the pulp was acidified. The pulp was diluted with deionised water and dilute sulphuric acid was added, until the pH reached roughly 3.8. After 15 minutes, the final pH was between 4 and 4.5. After the acidification the pulp was washed again, as explained before. The selected testpoints were repeated to evaluate the repeatability of the trials.

Soda Cooking

The soda cooking was performed with the same air-heated digester as the hot water treatment. The cooking temperature was 160°C, and the time at cooking temperature was 60 min. The temperature was raised to 80°C within 30 min, and after that to the selected cooking temperature at a rate of 1°C/min. Liquor to straw ratio was 5 and the effective alkali varied from 12 to 16% on the straw. After soda cooking, the pulp was washed as described earlier.

Table 2. Bleaching Conditions of Hot Water Treated Straw with a P-P-Paa-P Bleaching Sequence. *

Raw material	Straw from Plexiglass acrylic silos	Straw from round bales
P1 stage		
Temperature, °C	85	85
Time, min	180	180
Consistency, %	9-10**	10
NaOH charge, % on straw	8.5	7.0
H_2O_2 charge, % on straw	5.0	4.0
P2 stage		
Temperature °C	85	85
Time, min	180	180
Consistency, %	7-10**	10
NaOH charge, % on straw	2.0	1.0
H_2O_2 charge, % on straw	2.0	2.0
Paa stage		
Temperature, °C	85	85
Time, min	60	60
Consistency, %	6-10**	10
NaOH charge, % on straw	0.2	0.2
Paa charge, % on straw	1.0	1.0
P3 stage		
Temperature, °C	85	85
Time, min	180	180
Consistency, %	5.5-10**	10
NaOH charge, % on straw	1.5	1.0
H_2O_2 charge, % on straw	2.0	2.0

* P = Alkaline peroxide stage; Paa = Peracetic Acid Stage.
** Bleaching yield was not noted in all test points, the bleaching consistency lower in these testpoints.

Analyses

Paper technical properties of hot water treated and peroxide-bleached wheat straw pulps were analyzed according to SCAN test methods. The kappa number of soda cooked wheat straw pulp was also analyzed according to the SCAN test method.

The carbohydrates and lignin composition were analysed according to the NREL/TP-510-42618 method (Sluiter et al. 2008). The monosaccharides were determined after acid hydrolysis treatment with high-performance anion-exchange chromatography with pulsed amperometric detection (HPAEC-PAD analysis). A Dionex ICS-3000 liquid chromatography and the anion-exchange column CarboPac PA20 were used for analysis. A minimum of two parallel runs with HPAEC were performed. The extractives were analyzed according to the SCAN-CM 49:93 test method.

Ash and multi-element determination of untreated straw samples started with drying the samples at 105°C and grinding the samples in a hammer mill. For multi-element analysis the samples were then ground again in a Fritsch Pulverisette grinder and dried at 105°C. Samples were ashed at 550°C for 12 hours before hydrogen fluoride-nitric acid dissolution. These solutions were analyzed with the inductively coupled plasma mass spectroscopy (ICP-MS) technique for multi-element contents. The ash content of the pretreated straw samples was analysed according to the SCAN-C6:62 test method (525°C, 4 hours).

RESULTS AND DISCUSSION

Chemical Pretreatment of the Straw with Urea or Formic Acid

The straw from the plexiglass acrylic silo treatments with urea or formic acid was washed after the pretreatment, and the pretreatment yield was estimated from the dry content of the washed straw. The yield of urea-treated straws was 91% independent of the treatment time, and the yield of formic acid treated straws was 93%, respectively. The washing yield of untreated straw was 97%; therefore, about 3% units of the yield loss in pretreatment can be explained by the loss of fines during washing.

The urea pretreatment darkened the straw due to the alkali darkening, but the formic acid pretreatment did not have an effect on the straw colour. The pH measured from the first washing filtrate remained approximately constant, regardless of pretreatment time, 8.9 for urea pretreatment and 6.7 for formic acid pretreatment. Urea is converted by bacteria on straw to ammonia, which then acts to process the straw as an alkali. The chemical treatment with alkalis softens the lignin structure (Butterworth 1985) and may modify the lignin-carbohydrate complex in straws, making the cellulose and hemicelluloses fractions more accessible. A chemical treatment with acid could be even more effective (Butterworth 1985).

Formic acid has an antibacterial effect due both to hydrogen ion concentration and to a selective bactericidal action of the undissociated acid. Formic acid lowers the pH and thus limits fermentation and reduces the degradation of proteins to ammonia. The effect of formic acid application on the chemical composition of silage varies according to the level applied, the dry matter content of the ensiled material, and the species of crop (McDonald et al. 1991). When the dry matter content is higher, the effects of the preservative are lower. The changes in the chemical composition of the raw material are therefore assumed to be limited in the studied dry matter when the dry content is greater than 70%.

After about half a year of storage of the pretreated straw the bottom and top parts of the silos were slightly mouldy. This was probably due to some air leaking through the sealings or the air left inside the straw centre. The straws from the centre part of the silo were used in the experiments, and therefore the mould probably did not affect the results.

Chemical Composition of the Pretreated Straws with Formic Acid or Formic Acid Based Preservative

The chemical pretreatment with formic acid or formic acid based preservative did not change the chemical composition of wheat straws significantly. Table 3 presents the chemical composition of the wheat straw used in the minisilo experiments and the chemical composition of the treated straws. The sugar results from separate HPAEC runs were very close to each other, the sample preparation, however, caused slight variation. Due to the preliminary nature of the findings, the need for statistically planned follow-up work is stated. Nevertheless the variation of the results in Table 3 is minute, and therefore it can be assumed that the chemical pretreatment with formic acid or formic acid based preservative does not significantly affect the chemical composition of wheat straw.

The total amount of sugars and gravimetric lignin seemed to be higher in the treated straws compared to the untreated straw. This higher organics content of the treated straws may be due to the dissolution/losses of ash and fines during the pretreatment or the following washing stage. The chemical pretreatment with formic acid or formic acid based preservative may also loosen the straw structure and thus enhance the acid hydrolysis in the chemical composition analysis. The formic acid treatment resulted in a lower pH of the washing filtrate compared to the treatment with formic acid based preservative and thus lower ash content of the treated straws. Morrison showed that formic acid silage (Morrison 1979) decreased hemicelluloses content of ryegrass 10-20% but did not affect the amounts of lignin or cellulose. In the case of lucerne silage (Morrison 1988) the formic acid decreased the cellulose content but had less effect on the hemicelluloses fraction. He explained the results by the differences in the grass structures. The dry content of these wilted silages was not mentioned but it most probably was much lower than that of the straw silages performed in the present experiments.

The chemical pretreatment of the straws was performed at a fairly high dry matter content (75%); therefore the changes in the chemical composition were expected to be somewhat limited. The chemical composition of the round bale treatments with formic acid based preservative are presented in Table 4. The results are in line with those from the minisilo experiments. The variation of the results may be due to the heterogeneity of the straws in different bales, and also the charge of formic acid based preservative may have slightly varied within the bales.

The bales treated with formic acid based preservative where not observed to be moulded by organoleptic evaluation. This is an important factor in regard to occupational health of the raw-material handlers and their exposure to fungal particles. The reference bale without chemical pretreatment was slightly mouldy after one year storage in an unheated barn. The bale expelled an excessive amount of small particles in the air during opening and also a mildewy smell was observed, despite of the high dry matter content and the shelter from the weather. However, the slight mould growth did not significantly affect the chemical composition of the straw compared to the corresponding frozen sample. On the other hand, the outdoor storage in the field has been reported to have significant effects on the chemical composition of straw. Bicho and McRae (2004) exposed Canadian wheat straw to the wheather for one year and discovered evidence of decay throughout the bales.

Table 3. Chemical Composition of Wheat Straw and Treated Wheat Straw. Results from Minisilo Experiments

Sample	08Straw	08 Straw Formic acid				08Straw Formic acid based preservative			
Pretreatment time, months	frozen	3	6	9	12	3	6	9	12
Carbohydrates, mg/100 mg									
Glucan	37.9	43.8	43.2	42.7	42.9	43.6	43.5	42.3	42.7
Xylan	18.6	22.2	21.6	21.5	21.7	21.1	21.1	20.7	21.3
Arabinan	2.1	2.5	2.3	2.4	2.4	2.6	2.5	2.5	2.5
Galactan	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8	0.8
Mannan	0.5	0.4	0.4	0.4	0.4	0.4	0.4	0.4	0.4
Rhamnan*	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL	<DL
Total	59.8	69.8	68.3	67.8	68.1	68.6	68.3	66.6	67.7
Lignin, %									
Gravimetric lignin (ash inc.)	23.0	23.4	23.8	25.0	25.3	24.5	25.0	24.0	24.2
Gravimetric lignin (ash exc.)	18.9	19.7	18.8	20.9	20.9	19.4	19.6	19.1	19.2
Soluble lignin	3.2	1.9	1.9	1.8	1.9	2.1	2.1	2.1	2.2
Acetone extractives, %	1.72	1.65	1.65	1.67	1.74	1.56	1.62	1.87	1.77
Ash, %	8.6	6.2	6.4	6.8	7.5	8.2	7.9	7.2	7.6
Metals, mg/kg straw									
Silica	36451								
Magnesium	875								
Calcium	2291								
Potassium	14157								
Iron	97.8								
Manganese	12.2								
Copper	4.59								
Total (lignin, polysaccharides, extractives, ash), %	92.2	99.3	97.1	98.9	100.2	99.8	99.5	96.9	98.4

* <DL = under detection limit 0.1 mg/100mg

The decay caused losses in the galactan, arabinan, and ash contents, while the xylan level remained constant and lignin and glucan contents increased. These results concur with those of Collins et al. (1990), which indicate that water soluble components, such as ash and some water soluble polysaccharides, are rapidly leached from exposed straw.

Hot Water Treatment and following Peroxide Bleaching of the Pretreated Straws

The yield loss of chemical pretreatment with urea or formic acid was practically compensated in hot water treatment. The yield of hot water treatment was 95% for urea-treated straw (i.e. 86% of original straw) and 96% for formic acid-treated straw (i.e. 89% of original straw) compared to 88% of untreated straw. The bleached yield was also almost the same for pretreated and reference pulp.

The brightness of hot-water-treated and bleached pulp was affected by the pretreatment chemical and time. After 2-6 months of pretreatment time, the pulp brightness was clearly lower, as can be seen in Fig. 4. The decline in brightness in the case of formic acid treatment may be due to the lignin structure alteration caused by the acid addition (Leschinsky et al. 2008; Shiming and Lundquist 2000).

Table 4. Chemical Composition of Wheat Straw and Pretreated Wheat Straw. Results from Round Bale Experiments

Sample	08Straw frozen	08Straw outside (ref.bale)	08Straw Formic acid based preservative outside (round bales)		
Pretreatment time, months	-	12	6.3	9.4	12.0
Carbohydrates, mg/100 mg					
Glucan	37.9	40.8	43.1	41.0	43.9
Xylan	18.6	20.5	21.7	20.9	23.1
Arabinan	2.1	2.4	2.4	2.5	2.5
Galactan	0.8	0.8	0.8	0.8	0.8
Mannan	0.5	0.5	0.4	0.3	0.5
Rhamnan*	<DL	<DL	<DL	<DL	<DL
Total	59.8	65.0	68.3	65.6	70.8
Lignin, %					
Gravimetric lignin (ash inc.)	23.0	23.3	24.3	24.4	23.8
Gravimetric lignin (ash exc.)	18.9	18.9	19.2	19.5	19.1
Soluble lignin	3.2	2.3	2.2	2.1	2.1
Acetone extractives, %	1.72	1.67	1.70	1.68	1.75
Ash, %	8.6	8.9	7.7	8.4	7.7
Metals, mg/kg straw					
Silica	36451				
Magnesium	875				
Calcium	2291				
Kalium	14157				
Iron	97.8				
Manganese	12.2				
Copper	4.59				
Total (lignin, polysaccharides, extractives, ash), %	92.2	96.8	99.1	97.3	101.5

* <DL = under detection limit 0.1 mg/100mg

Urea pretreatment reduced the brightness of hot water treated and peroxide bleached pulp even more. The colour difference was already visible in the pretreated straws. The darkening in the pretreated straws derives from the alkali darkening. The urea is converted to ammonia during the pretreatment, which then forms ammonium with water. The balance of ammonia and ammonium ions is transferred to ammonia when hydroxide ions are added in an alkaline peroxide stage. A part of the added hydroxide is consumed in this side reaction instead of the actual bleaching reaction, thus impairing the bleachability.

After about 9 months of storage, the situation changed. The bleachability of pretreated straw with both formic acid and urea was clearly improved. The better bleachability may be due to the loosened structure of wheat straw or lignin alteration. Furthermore the dissolution of sugars during the pretreatment or the hot water treatment may have a positive effect on the bleachability. Mustajoki et al. (2010) reported that the addition of glucose or xylose to the first peroxide stage of a P-P-Paa-P bleaching sequence for hot water treated wheat straw improved the pulp bleachability.

The results of straws treated with formic acid based preservative from round bale experiments showed a similar trend in the final brightness of hot water treated and peroxide bleached wheat straw pulp (Fig. 5). First the brightness decreased, but turned to increase after the above 9 months pretreatment time. The change appears after longer pretreatment time compared to the Plexiglass acrylic silo treatments. This may be due to the storage temperature: the round bales were stored in an unheated barn where the temperature was clearly lower compared to the silo experiments at room temperature.

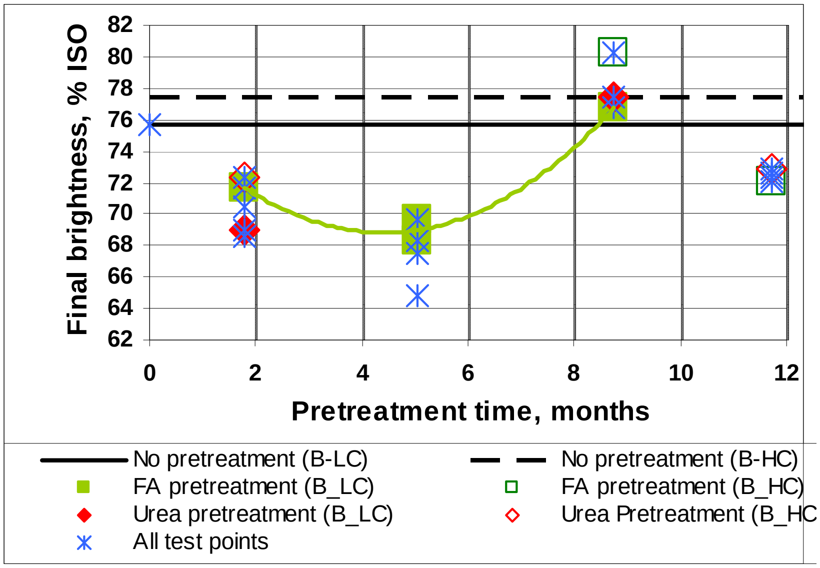

Fig. 4. Final brightness as a function of straw pretreatment time. Hot water treatment at 120°C followed by P-P-Paa-P bleaching. P = alkaline peroxide stage, Paa = peracetic acid stage. Pretreatment in Plexiglas acrylic silos. FA = Formic cid. B-LC = lower bleaching consistency (<10%), B-HC = higher bleaching consistency (10%).

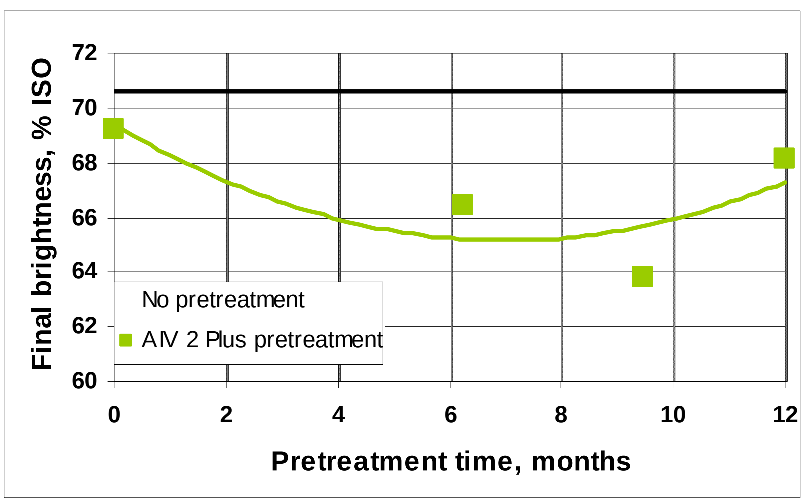

Fig. 5. Final brightness as a function of straw pretreatment time. Hot water treatment at 120°C followed by P-P-Paa-P bleaching. Pretreatment in round bales.

The chemical pretreatment did not affect the paper technical properties significantly, as is evident in Table 5 (see Appendix). Bicho and McRae (2004) reported that the field storage of Canadian wheat straw decreased pulp freeness and tear strength. In these studies, the straw bales were also frozen over the winter months and thus were less susceptible to weathering. In milder climates, moisture and heat may have a much higher impact on the paper technical properties of the produced pulp.

Soda Cooking

It is possible to combine a chemical pretreatment / storing stage also with a soda cooking process, especially if the pretreatment is performed with formic acid (Fig. 6). Urea treatment has a negative effect on the delignification due to the consumption of hydroxide ions in the side reaction of ammonium and hydroxide to ammonia. This observation suggests that the storage of straw with sodium hydroxide could be one possibility to ensure high-quality raw material to soda pulp mills and even reduce the cooking chemical consumption.

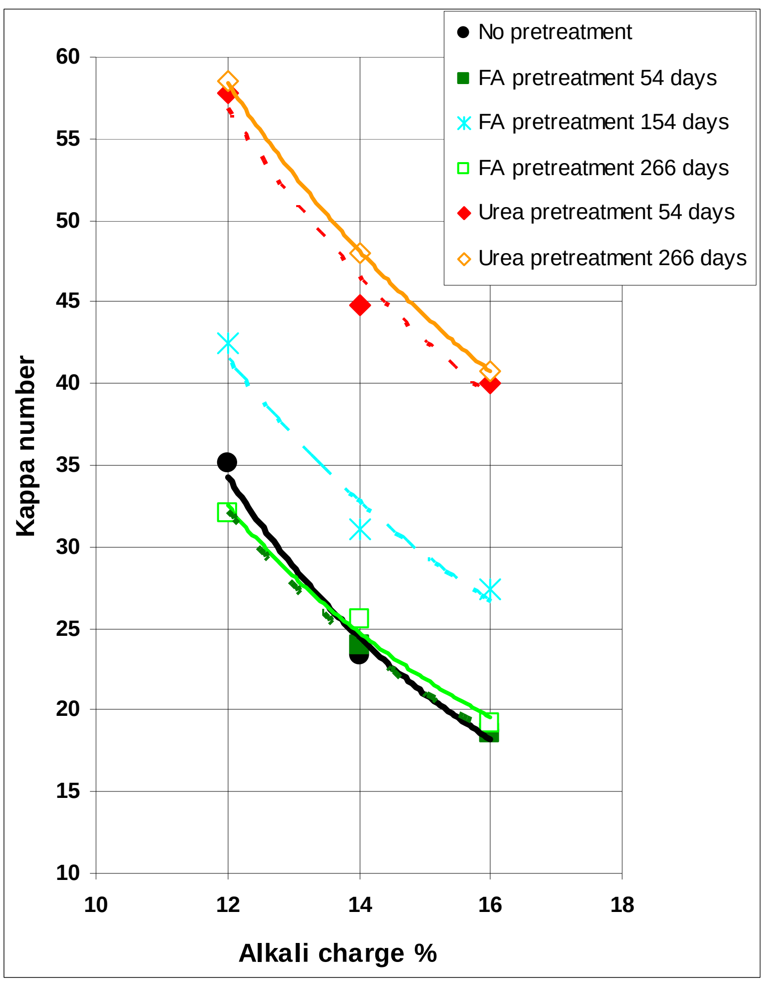

Fig. 6. Kappa number as a function of straw pretreatment time. Soda cooking at 160°C for 60 min. Pretreatment in Plexiglas® acrylic silos.

CONCLUSIONS

1. It is possible to integrate the chemical pretreatment stage / storing of straw or other non-woods with an existing pulping process. The chemical storing ensures more homogenous raw material resources throughout the year to mills that utilize non-wood materials. Furthermore, no large storing houses are required; hence the straws can be stored on farms with existing equipment.
2. The storage of chemically pretreated straw could also be integrated with energy processes or other processes that utilize non-woods as a raw-material. The uniform raw material is a relevant issue to these mills as well.
3. Formic acid is a potential preservative, but formic acid based preservative could also be used as a preservative if it is otherwise available on the farms.
4. Urea is not such a desired storing chemical, as it increases the sodium hydroxide consumption in the following process. This manifests itself as decreased pulp bleachability of hot water treated straw or as an increased kappa number of soda cooked pulp.
5. Due to the preliminary nature of this study, the chemical charges in the pretreatment are to be systematically optimised and their effects evaluated in further studies. The use of other possible chemicals, such as sodium hydroxide should also be investigated.
6. The storage of pretreated straw did not significantly affect the chemical composition of the straws or the paper technical properties of the produced pulps. If the storage time is very short, and the straws can be protected from the weather, the chemical process may not be the most advantageous option.

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APPENDIX

Table 5. Paper Technical Properties of Hot Water Treated and Peroxide Bleached Pulps. Pretreatment with Urea, Formic (Plexiglass Acrylic Silo Experiments) or Formic Acid Based Preservative (Round Bale Experiments).

Pretreatment chemical	07Straw Ref.	07Straw Urea (room temp.)			07Straw Formic acid (room temp.)				08Straw Ref.	08Straw Formic acid based preservative (outside)		
Pretreatment time, months	0	8.7	11.7*	11.7*	5.1	8.7	8.7*	11.7*	0	6.3	9.4	12
ISO brightness %	75.7	77.4	77.3	77.0	69.0	76.7	80.3	74.8	70.6	66.4	63.8	68.1
SR	50	41	36	42	37	40	40	43	35	24	32	40
Grammage, g/m^2	61.4	64.0	63.5	63.6	63.5	64.8	63.9	62.8	63.0	63.2	67.5	65.3
Thickness, µm	86	101	90	88	88	102	100	93	101	92	98	102
Apparent density, kg/m^3	714	637	706	725	724	634	640	672	664	689	692	637
Bulk, m^3/t	1.40	1.57	1.42	1.38	1.38	1.58	1.56	1.49	1.51	1.45	1.45	1.57
Opacity, %	66.6				70.0					67.5	67.8	70.4
Light scattering coeff., m^2/kg	21.5				20.5					21.2	18.9	21.8
Roughness, ml/min	1800	2250	2036	2050	1771	2116	2128	2040	1796	2721	1662	2023
Air permeance, ml/min	35.0	32.0	25.6	24.2	25.3	32.0	32.0	25.2	66.2	70.2	27.4	29.4
Tensile index Nm/g	71.9	65.0	74.6	76.9	75.2	63.4	63.5	71.0	86.7	90.6	86.6	82.0
Tensile stiffness index, MNm/kg	7.5	6.7	6.8	7.4	7.3	7.1	6.6	6.7	6.9	6.3	6.5	7.3
Stretch, %	2.2	2.6	3.7	3.3	2.4	2.0	2.3	3.1	2.8	3.2	2.9	2.6
Tensile energy, mJ/g	1049	1150	1850	1798	1053	853	1002	1475	1298	1435	1283	1256
Burst index, $kPam^2/g$	3.9	4.4	5.1	5.2	3.8	4.7	4.8	6.1	5.7	4.3	4.3	4.4
Tear index, Nm^2/kg	3.9	3.8	3.7	3.8	3.8	4.3	4.5	4.2	4.3	4.1	4.0	4.1

*Higher consistency in bleaching