

ALKALINE PEROXIDE BLEACHING OF HOT WATER TREATED WHEAT STRAW

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The aim of this study was to evaluate the possibilities for chemical consumption reduction in P-P-Paa-P bleaching (P alkaline peroxide stage, Paa peracetic stage) of hot water treated straw and the effect of the wheat straw variability on the process. Papermaking fibre production from wheat straw using such a process could be implemented on a small scale if chemical consumption was low enough to eliminate the need for chemical recovery. The pulp properties obtained with this process are equal to or even superior to the properties of wheat straw soda pulp. The possibility of enhancing the first peroxide stage with oxygen and pressure was studied. The possibility for substitution of sodium hydroxide partially with sodium carbonate was also investigated. The objective was to achieve International Standardization Organization (ISO) brightness of 75%, with minimal sodium hydroxide consumption, whilst maintaining the pulp properties. The optimization of the peroxide bleaching is challenging if the final brightness target cannot be reduced. Results indicate that up to 25% of the sodium hydroxide could be substituted with sodium carbonate without losing brightness or affecting pulp properties. Another possibility is a mild alkali treatment between the hot water treatment and the bleaching sequence.

Keywords: Non-wood fibre; Wheat straw; Biorefinery; Hot water treatment; Bleachability; Pulp properties

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INTRODUCTION

The conventional way to produce wheat straw pulp on a mill scale is through the use of the soda cooking method. Evaporation and recovery of spent alkaline cooking liquor is challenging because of the high silica content of wheat straw raw material. Silica dissolves in alkaline cooking and creates well-known, serious problems in the recovery area (Boman et al. 2009). In addition, soda cooking consumes a large quantity of sodium hydroxide; usually the NaOH charge is approximately 12 to 18%. Due to these difficulties of processability and poor process economics, there is a need for a process which overcomes these deficiencies (Feng et al. 2001). A hot water treatment, where wheat straw is treated with hot water for 60 min at 120°C as a pretreatment before alkaline peroxide bleaching, is an option for wheat straw pulping. This treatment initiates a better bleachability of the straw pulp. The actual defibration of straw then occurs during the following bleaching (Leponiemi et al. 2010). Using sodium hydroxide for adjusting the conditions in alkaline peroxide bleaching is very effective, since it is a strong base. Due to the high alkalinity, however, sodium hydroxide dissolves carbohydrates,

especially hemicelluloses, from pulp, which in turn has a negative impact on the pollution load of the waste water treatment plant. Thus, replacing sodium hydroxide by a weaker alkaline compound could help to minimize carbohydrate dissolution while preserving high bleachability (Li et al. 2004).

Pan and Leary (2000) proposed sodium carbonate as an alkali source for alkaline peroxide mechanical pulping (APMP) of wheat straw. The achieved brightness and strength properties were lower as compared to the use of sodium hydroxide, but resulted in higher pulp yield and thus lower chemical costs and lower chemical oxygen demand (COD) content of spent bleaching liquors. In the APMP process the choice between NaOH and Na₂CO₃ is based on the target brightness and applied peroxide charges. The use of sodium carbonate is preferred when the peroxide charge is relatively low, e.g., about 4% on straw dry matter. In this case similar brightness levels can be achieved with Na₂CO₃ as compared to NaOH with lower peroxide consumption.

Earlier studies have shown that a hot water treatment followed by alkaline peroxide bleaching offers an interesting avenue in the search for non-wood pulping alternatives with potential to address the need for simple and economically competitive small scale pulping processes for non-wood materials. The process consumes high amounts of sodium hydroxide in bleaching with the target brightness of 75 to 80% ISO. In practice this means that the process would need some kind of chemical recovery system, unless the bleaching chemical consumption could be notably reduced (Leponiemi et al. 2010). The aim of this study was to use this simple and non-traditional process to produce chemical type wheat straw pulp with brightness of 75% ISO, instead of traditional fully bleached chemical pulp. Furthermore, the aim was to evaluate the possibilities for chemical consumption reduction in P-P-Paa-P bleaching and the effect of the wheat straw variability on the process. Since glucose and xylose are already present in the hot water treatment filtrate, they may result in additional chemical consumption or otherwise reduce the following peroxide bleaching performance. The variation in raw material was studied by comparing straws grown during different years. The objective was to achieve a brightness of 75% ISO, with minimal sodium hydroxide consumption, whilst maintaining the pulp properties. The variables studied were the pressurisation of the first peroxide (P₁) stage with oxygen, the substitution of sodium hydroxide partially with sodium carbonate, and a mild alkali treatment before the actual peroxide bleaching. In addition, the role of sugars in the bleaching stages was studied by adding glucose or xylose to the P₁ stage.

EXPERIMENTAL

Raw Material

The raw material used was air-dried wheat straw, which was cultivated by MTT (Agrifood Research Finland) and harvested during the summers of 2006 and 2007. The 2006 straw (06Straw) was chopped with a bale chopper in the winter of 2006-2007. The 2007 straw (07Straw) was chopped at the end of the threshing machine, air dried, and stored in room temperature (1st batch). Furthermore, a second batch of 07Straw was stored in an unheated barn for about two years.

The straws were screened using screens with 6 and 7 mm diameter holes. Oversized and fines fractions were removed. The standard screening method SCAN-CM 40:88 was followed with the exception of screens and the screening time, which was 30 s. The dry matter content of screened straw was determined according to the standard SCAN-CM 39:88.

Raw Material Analysis

The amount of acetone extractives was determined according to SCAN-CM 49:93. Total lignin content of the raw material was analyzed according to KCL analyzing method No. 115B:82. Quantitative determination of straw carbohydrates was implemented by total acid hydrolysis according to Sjöström et al. (1969) and Janson (1970). The monosaccharides as their alditol acetate derivatives were separated by gas chromatography using a capillary column NB-1701 and an isothermic program. The oven temperature was 210°C and the temperature for injector and detector 260°C.

Ash and multi-element determination of raw material started with drying the samples at 105°C and grinding them with a hammer mill. Then the samples were ground again with a Fritsch pulverisette grinder, dried at 105°C, and ashed at 550°C for 12 hours. For multi-element analysis the samples were dissolved by hydrogen fluoride-nitric acid. These solutions were analyzed with ICP-MS technique for multi-element contents.

Hot Water Treatment

Hot water treatment was implemented with an air heated rotating serial digester including six 2.5L autoclaves. Hot water treatment conditions are presented in Table 1.

Table 1. Hot Water Treatment Conditions

Temperature (°C)	120
Time (min)	60
Water:straw ratio	10:1
DTPA (% on straw)	0.2

The autoclaves were filled with the pre-determined amount of screened straw. Only then, water and DTPA were charged after thorough mixing. The target temperature of 120 °C was kept constant during the whole hot water treatment. These conditions were kept constant throughout all test runs.

The aqueous filtrate samples were stored for further analysis. Straw washing was performed by diluting the treated straw with deionised water, agitating, then leaving the mixture to settle for 2 minutes followed by removal of the excess water through a wire pouch. Dilution and thickening was repeated 3 times. Finally, the treated straw was centrifuged to ~25% consistency.

Reference Bleaching

The unpressurised bleaching stages were carried out in polyethylene bags in a water bath. Chemical charges were calculated on the initial amount of the straw. The bleaching conditions for the reference pulps and for the all other experiments, including reaction time, reaction temperature, and chemical dosage, are presented in Table 2.

Table 2. Bleaching Conditions of Reference, Pressurised P₁, Sugar Addition and Alkali Pretreatment Pulps. Consistency 10%, Temperature in P₂, Paa and P₃ stages 85°C and, Time in P₂ and P₃ Stages 180 min and in Peracetic Acid Stage 60 min. Hot Water Treatment at 120°C Followed by P-P-Paa-P Bleaching. PP₁=Pressurised P₁ Stage, APT=NaOH Pretreatment and PPT= O₂ Pressurised NaOH Pretreatment.

		Reference bleaching		Pressurised P ₁			Sugar addition			Alkali pretreatment				
		Low chem	High chem	PP ₁ 95°C 120 min	PP ₁ 105°C 60 min	PP ₁ 105°C 120 min	Low chem sugar	Medium chem sugar	High chem sugar	APT 2% NaOH	APT 2.5% NaOH, seq. P-Paa- P	PPT 3% NaOH shorter time	PPT 3% NaOH longer time	PPT 4% NaOH
Alkaline pretreatment	Pressure (bar)	-	-	-	-	-	-	-	-	-	-	3	3	3
	Time (min)	-	-	-	-	-	-	-	-	180	240	60	90	90
	NaOH (%)	-	-	-	-	-	-	-	-	2.0	2.5	3.0	3.0	4.0
P ₁	NaOH (%)	7.0	8.5	6.0	6.0	6.0	7.0	8.0	8.5	3.5	2.5	3.0	3.0	3.0
	H ₂ O ₂ (%)	4.0	5.0	4.0	4.0	4.0	4.0	5.0	5.0	3.0	3.0	2.0	2.0	2.0
	Temperature (°C)	85	85	95	105	105	85	85	85	85	85	85	85	85
	O ₂ -pressure (bar)	-	-	3	3	3	-	-	-	-	-	-	-	-
	Time (min)	60	60	120	60	120	60	60	60	60	60	60	60	60
	MgSO ₄ (%)	-	-	0.3	0.3	0.3	-	-	-	-	-	-	-	-
	DTPA (%)	-	-	0.2	0.2	0.2	-	-	-	-	-	-	-	-
	Sugar (mg/L)	-	-	-	-	-	150	150	150	-	-	-	-	-
P ₂	NaOH (%)	1.0	1.5	1.5	1.0	1.0	1.0	1.0	1.5	0.75	-	0.5	0.5	0.5
	H ₂ O ₂ (%)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	-	2.0	2.0	2.0
Paa	NaOH (%)	0.2	0.2	0.2	0.5	0.5	0.2	0.2	0.2	0.2	0.2	0.2	0.2	0.2
	Peracetic acid (%)	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
P ₃	NaOH (%)	1.0	1.5	1.0	1.0	1.0	1.0	1.5	1.5	0.75	0.75	0.75	0.75	0.75
	H ₂ O ₂ (%)	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0	2.0
Acidification	SO ₂ (%)	0.7-0.8	1.1	1.1	0.7	0.9	0.4	0.7	0.6-0.7	0.5	0.5	0.5	0.4	0.4

After each bleaching stage the pulp was washed by the dilution and thickening method, as explained above. After the last bleaching stage and wash, the pulp was acidified. The pulp was diluted with deionised water, and diluted sulphuric acid was added until the pH reached roughly 3.8. After 15 minutes, the final pH was 4 to 4.5. After acidification the pulp was washed again, as explained before.

The pulps were weighed, and dry matter content determined to define the yield after each stage. When calculating the bleaching chemical dosages for the following bleaching stage, it was assumed that there were no yield losses. Only the amount of the pulp used for defining dry matter content and ISO brightness were deducted from the original amount of pulp. However, the yield losses were taken into account when calculating the bleaching consistency.

Pressurised P₁

The pressurised P₁ stage was equipped with an air heated rotating serial digester using 2.5 litre autoclaves. O₂-pressure was 3 bars in all pressurised bleaching trials and the temperature was 95°C or 105°C. The temperature rise during heat-up period from 80°C was approximately 1°C per minute. The reaction time was 60 or 120 minutes. The conditions of the pressurised P₁ stages and the following bleaching are presented in Table 2. After bleaching the autoclaves were handled as explained in hot water treatment part.

Carbonate Bleaching

In each bleaching stage 25, 32.5, or 40% of total alkali was replaced with Na₂CO₃. The bleaching conditions were the same as in the higher chemical dosage reference bleaching.

Sugar Addition Bleaching

D(+)-glucose or D(+)-xylose was diluted in a small amount of deionised water and added to hot water treated 07Straw before chemical addition in the P₁ stage. The amount of added sugar was adjusted in order to raise the sugar level of the liquid filling of the P₁ stage. The ratio of the added sugar amount versus the total liquid filling of P₁ stage was 150 mg/L. The bleaching conditions of the sugar addition bleaching trials are presented in Table 2.

Alkali Pretreatment

A mild alkali pretreatment was performed prior to the actual P-P-Paa-P bleaching. The alkali pretreatment stage was conducted similarly to peroxide stages excluding the peroxide addition. Table 2 presents the bleaching conditions.

Screening

Pulps were screened after bleaching with a Valmet TAP03 screen with 0.25mm screen openings or with a flat screen with 0.25mm screen openings. Before screening, pulps were wet disintegrated according to standard ISO 5263, except for the number of the revolutions, which was approximately 10,000. For the second batch of pulps, the number of revolutions was 30,000.

After disintegration the pulp was diluted with deionised water to about 1%

concentration and screened. After screening, reject and accept fractions were recovered in their own containers.

Accepts from the screening were centrifuged, homogenized, and the dry matter content was determined according to standard SCAN-C 3:78. The homogenized accepts were wet disintegrated again for sheet preparation according to ISO 5263 after the dry matter determination, except that the number of revolutions was approximately 2000. The screened accepts from the flat screen were stored as slush for sheet preparation for each of the pulps. The rejects were dried in an oven and weighed. The reject proportion was calculated as a percentage of bone dry pulp.

Pulp and Liquid Analysis

Pretreated straw samples were weighed, and their dry matter content was determined from each test point according to standard SCAN-C 3:78 to define the yield after hot water treatment. The ISO brightness after each bleaching stage was measured according to standard SCAN-C 11:75.

The carbohydrate content of selected hot water treatment and P₁ stage filtrate samples was analyzed by methanolysis according to Holmbom and Örså (1993). The gas chromatographic analysis was performed with a Hewlett-Packard 5890 gas chromatograph using a NB-30 capillary column (25 m * 32 mm I.D.). The temperature program was the following: 2 min in 100°C, 4°C/min to 200°C, and 2 min at 200°C. About 1 µL of the sample was injected via split injector (260°C) with a split ratio of 1:20. Hydrogen was used as a carrier gas, and the FID detector temperature was 290°C. The total amount of dissolved carbohydrates in the hot water treatment or bleaching filtrate was calculated based on the hot water treatment/bleaching consistency and the amount of carbohydrates in filtrate.

Filtrate samples from hot water treatment and selected bleaching stages were analyzed for organic acid anions with ion chromatograph Dionex ICS1500 and the IonPac AS9-HC column. Filtrate samples were filtered with 0.45µm filters and diluted to 100th part. The eluent was 9.0 mM Na₂CO₃, and the eluent flow rate was 1.0 mL/min. The acetate level (% on straw) was calculated based on the acetate content, which was determined via filtrate analysis with a Dionex ICS-1500 (column AS 9HC).

Paper Technical Properties

The Schopper Riegler number was determined according to standard SCAN-C 19:65. Laboratory sheets were prepared according to standard SCAN-CM 26:76. The target grammage was 60g/m². Sheets were dried between blotters in a temperature and air moisture conditioned room maintained at 23°C and with 50% relative humidity. After conditioning, the laboratory sheets were cut to 141 x 141mm sheets with a punching knife.

All paper technical properties were determined according to ISO or SCAN standard methods.

RESULTS AND DISCUSSION

Chemical Composition

Table 3 presents the chemical composition of the wheat straws used in the experiments. The total amount of sugars was over half of the wheat straw raw material, with glucose as the main component. The 06Straw had somewhat greater glucose, xylose, and arabinose share, and thus higher total sugar content than the 07Straw. The total lignin content of the 06Straw was lower than that of the 07Straw, but the soluble lignin amount was nearly the same, and the extractives content was somewhat higher in the 06Straw.

The 06Straw contained approximately 3% units less ash than the 07Straw. The amount of ash could influence ISO brightness and chemical consumption in the bleaching. Higher ash content of the 07Straw can explain part of the difference in Klason lignin. All the ash is not dissolved during acid hydrolysis, thus the undissolved part of it may be seen as somewhat increased gravimetric lignin content. The ash substances can accumulate on the fibre surfaces during bleaching and sheet preparation and therefore decrease brightness. Ash also contains metal ions, which can cause peroxide decomposition and increase the consumption of bleaching chemicals and therefore decrease bleachability.

Table 3. The Chemical Composition of Wheat Straw Raw Materials, Hardwood and Softwood.

	06Straw	07Straw	Hardwood (Alen 2000; Sixta et al. 2006)	Softwood (Alen 2000; Sixta et al. 2006)
Glucose (%)	38.4	36.6	38.3-51.3	33.0-41.7
Xylose (%)	20.1	17.4	15.1-24.9	3.3-7.6
Rhamnose (%)	0.2	0.1	0.5-0.6	0.0-0.3
Arabinose (%)	3.0	2.4	0.4-1.0	1.0-2.0
Mannose (%)	0.4	0.5	0.9-3.8	8.1-13.6
Galactose (%)	0.8	0.8	0.7-1.4	1.0-6.1
Total sugar (%)	62.9	57.8	66.0-74.4	54.4-65.2
Gravimetric lignin (%)	23.3	26.6	-	-
Total lignin			20.8-25.4	26.8-32.1
Extractives (%)	2.1	1.3	1.2-4.6	1.7-5.3
Ash (%)	6.8	9.7	0.3-1.5	0.3-1.5
Magnesium (mg/kg)	1200	1000	11-320	41-270
Silica (mg/kg)	19900	25600	10-100	10-100
Manganese (mg/kg)	11.9	13.4	2-250	25-440
Iron (mg/kg)	96.3	124.0	11-12	6-14
Copper (mg/kg)	3.5	3.4	<5	<5

The 07Straw had a clearly higher silica content compared to the 06Straw. Wet growing conditions are known to affect the amount of silica, for instance in the case of rice straw. Indeed, the summer of 2006 was very dry and the summer of 2007 was very rainy. Compared to wood, the silica and magnesium content of wheat straw is very high. The 07Straw contained somewhat smaller quantities of magnesium than the 06Straw. Wood contains only 10 to 100mg/kg silica and 10 to 320mg/kg magnesium (Alen 2000; Sixta et al. 2006). The 07Straw contained slightly more harmful metals such as iron and

manganese than did the 06Straw. Compared to wood, the iron content of wheat straw is high but the manganese content is low. One of the most important factors for successful peroxide bleaching is a relatively high magnesium / manganese molar ratio. The magnesium / manganese molar ratio for the 06Straw was 228 and 169 for the 07Straw. Both of these values exceed the appropriate level, which is over 100 (Basta et al. 1994; Lindeberg 1994).

Table 4 presents the acetate analysis results for the selected reference filtrates, performed after the hot water treatment and bleaching stages. The 06Straw was bleached with only the lower chemical dosage reference conditions, and the 07Straw was bleached with both the lower and higher chemical dosage reference conditions.

Table 4. Acetate Amount Analyzed from the Filtrates after Hot Water Treatment and Bleaching Stages in the Case of Reference Bleaching Conditions.

	Acetate amount (% of original straw)		
	06Straw Low Chem.	07Straw Low Chem.	07Straw High Chem.
Hot water treatment	0.3	0.4	0.4
P ₁	2.1	2.1	2.4
P ₂	0.1	0.2	0.2
Paa	1.2	0.7	0.7
P ₃	0.1	0.1	0.2
Total	3.8	3.5	3.9

The total amount of acetate in hot water treatment and bleaching filtrates was somewhat higher from the 06Straw than from the 07Straw with the same bleaching conditions. Slightly more acetate was released during the hot water treatment from the 07Straw but less during the bleaching compared to the 06Straw. The main part of the acetate was released in the first peroxide stage, where the sodium hydroxide charge was highest, as expected.

The acetate released during hot water treatment was in the form of acetyl groups still attached to the xylan oligomers and as free acetate/acetic acid. The results in Table 4 describe the free acetate content of the extracts. The difference between the xylan concentration in the hot water treatment extracts of these two straws was very small (see Fig. 1). Similarly, the difference in free acetate content was also very small.

The amount of acetate released from the peracetic acid stage of the 06Straw was high compared to that of the 07Straw. The amount of released acetate from the P₂ and P₃ stages was quite low because of the low chemical charges. Increasing the sodium hydroxide charge in the bleaching increased the amount of acetate released as expected. Figure 1 presents the carbohydrate composition of the hot water treatment filtrate from the 06Straw and the 07Straw.

Hot water treatment removed twice the amount of carbohydrates from the 07Straw as from the 06Straw, but the amount of dissolved carbohydrates was still quite low. Most of the difference became from the amount of glucose and mannose released during hot water treatment.

Reference Bleaching

The reference bleaching results showed that the 06Straw was bleached more easily with similar chemical charges and required less bleaching chemicals to reach 75% ISO brightness than the 07Straw. The difference in bleachability of the straws was seen after all bleaching stages. Figure 2 shows how brightness of the reference pulps developed during bleaching. Final brightness after P₃ and acidification was 5 to 8% ISO units higher for the 06Straw than for the 07Straw. The variation of separate bleachings has been tested earlier, and the repeatability of the obtained results is very good. The final brightness may vary only by max. 0.5%. Therefore the differences in final brightness above 1% can be considered as a tangible difference.

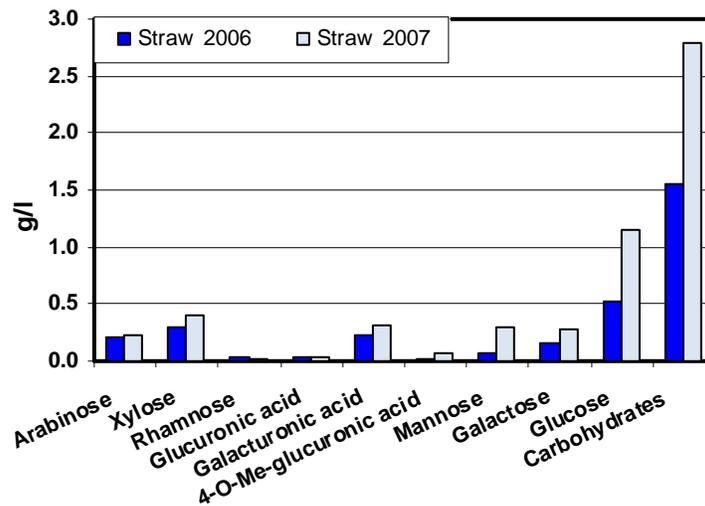


Fig. 1. Sugar content of hot water treatment filtrate from 06Straw and 07Straw by methanolysis as g/l

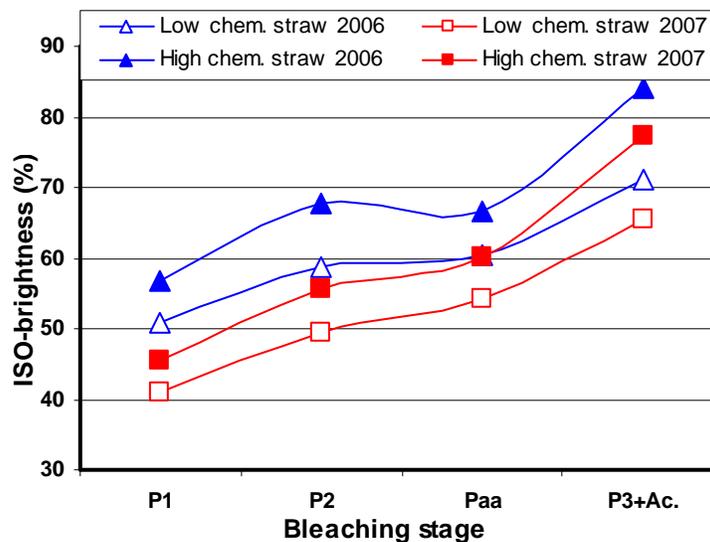


Fig. 2. Brightness of reference pulps after each bleaching stage. Raw material wheat straw 2006 and 2007. Hot water treatment of straw at 120°C for 60 min followed by P-P-Paa-P bleaching.

Figure 3 illustrates the reflectance values of the higher chemical charge reference bleaching of the hot water treated 07Straw. Compared to the pulp from the 06Straw, the pulp from the 07Straw had a clear decline and increment in the wavelength area 640 to 700nm. The drop was approximately 5% units from the level before and after the decline. When the bleaching proceeded from one stage to another, the reflectance decline decreased. The same decline was observed in all 07Straw bleaching trials. The 07Straw required a higher amount of bleaching chemicals than the 06Straw to defibrate and reach 75% ISO brightness. The difference between the 06Straw and the 07Straw chemical consumption could at least be partially explained by this difference in reflectance. The reflectance decline at the end of the measured wavelength area could mean that greyish/brownish components, possibly caused by finely dispersed inorganic deposits, exist in the pulp. Still, the possible components causing this decline in reflectance could not be identified.

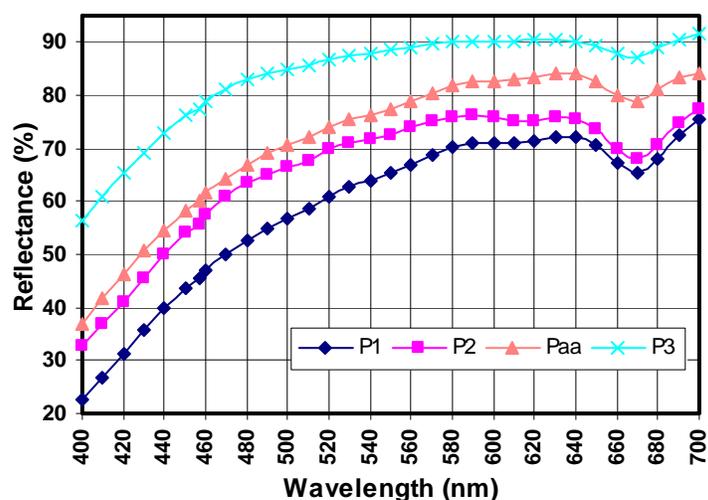


Fig. 3. Reflectance of higher chemical dosage pulp after each bleaching stage. Hot water treatment of the 2007 wheat straw (07Straw) at 120°C for 60 min followed by P-P-Paa-P bleaching.

Figure 4 presents the yield of the reference bleachings after each bleaching stage of sequence P-P-Paa-P. The pulps with the lowest chemical dosage had the highest yield, as expected. Generally a yield level above 50% is considered to be advantageous. The yield reduction in the alkaline peroxide bleaching results from the dissolution of carbohydrates and ash, but also lignin is partly dissolved. Kappa number of the bleached reference pulps was 33 for the lower chemical charge bleaching and 15 for the higher chemical charge bleaching, while no significant difference was seen between the 07Straw and 06Straw. The pulp yield from the 06Straw was higher compared to the pulp from the 07Straw with the same chemical dosages. The pulp from the 07Straw showed a yield exception in the P₁ stage, which was most probably due to an error in dry matter content determination. The yield measurement is not as reproducible as the brightness but differences above 1-2% can be considered as an actual difference.

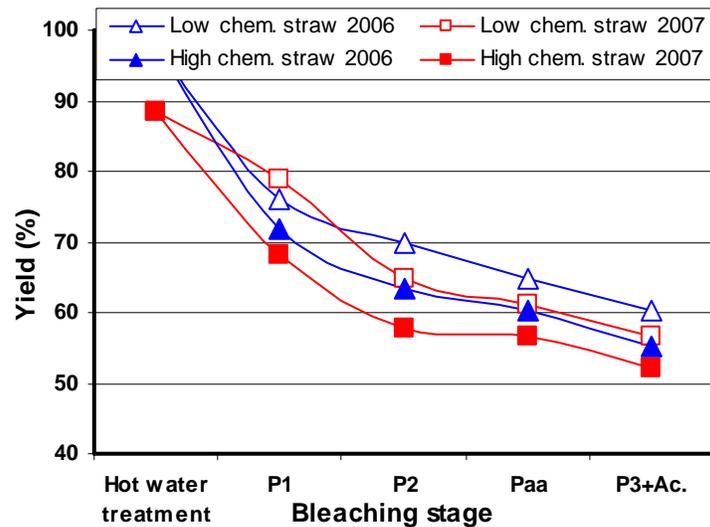


Fig. 4. Yield of reference pulps after each bleaching stage. Hot water treatment of 2007 wheat straw (07Straw) at 120°C for 60 min followed by P-P-Paa-P bleaching.

In an addition to the chemicals and the process, storage also had an effect on the pulp bleachability of the hot water treated straw. Figure 5 presents the ISO brightness of the reference pulps produced from the 07Straw after each bleaching stage. This straw was stored in two different environments: The 1st batch was stored at room temperature for approximately half a year, and the 2nd batch was stored in an unheated barn for about two years, during which time the WeatherOnline service recorded that minimum and maximum temperatures were -17 and +29°C. The longer storage time and the influence of climate may have impaired the bleachability and the bleached pulp yield (Fig. 5 and Table 6).

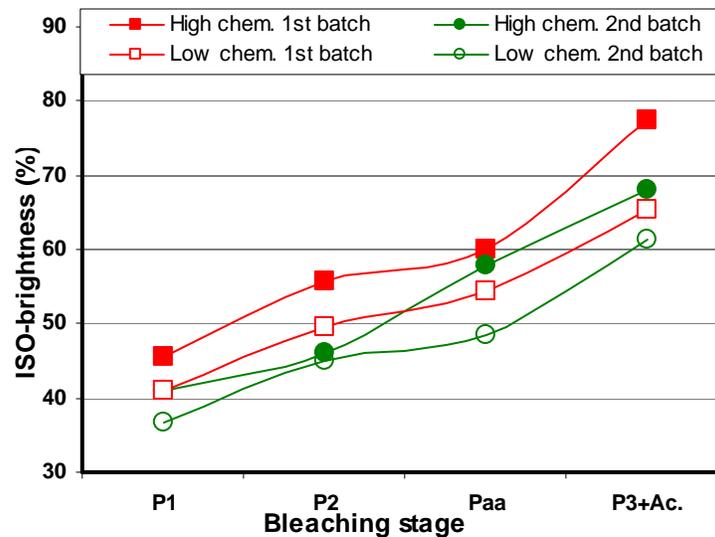


Fig. 5. Effect of storage on brightness after each bleaching stage. Hot water treatment of 2007 wheat straw (07Straw) at 120°C for 60 min followed by P-P-Paa-P bleaching. 1st straw batch stored half a year in room temperature. 2nd straw batch stored in an unheated barn for two years.

The paper technical properties of the hot water treated and peroxide bleached wheat straw pulps were relatively good. Table 5 presents the paper technical properties of the reference pulps as well as all the other bleaching trials. The pulp properties obtained were equal to or even better than the properties of wheat straw soda pulp (Leponiemi et al. 2010). The reference pulp from Straw06 had higher ISO brightness, higher light scattering coefficient, higher tensile index, higher tear index, and lower bulk than the reference pulp from Straw07 with the same bleaching conditions. This indicates that the fibres from Straw06 were probably more bonded than the fibres from Straw07.

The storage of straw in an unheated barn impaired the optical properties of the bleached pulp. The light scattering coefficient was slightly lower, as was light absorption, but opacity remained at the same level. The Schopper Riegler number of the pulp that was produced from the outside-stored straw was higher than the SR from the inside-stored straw. The bulk of these pulps was also notably lower, and the tensile index higher. This indicates that the fines content and the bondability of the pulp produced from the 2nd batch straw was increased. This may, however, just be due to longer disintegration of these pulps and not because of the storage conditions.

Pressurised P₁

O₂ pressure can be used to intensify alkaline peroxide bleaching, and because of the high chemical charges in the first P stage, it is advantageous to optimise the chemical consumption of this stage. Therefore the effect of pressurising the P₁ stage with oxygen was studied. Figure 6 illustrates the brightness of these bleachings after each bleaching stage, together with the reference pulp brightness. The raw material was from the first batch of 07Straw.

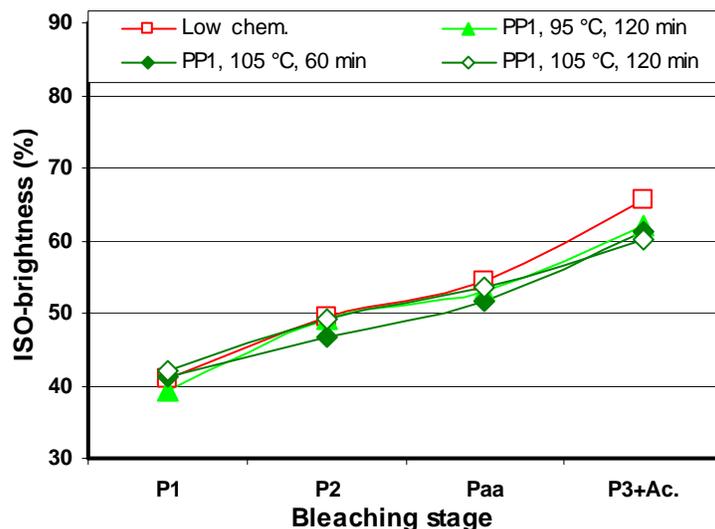


Fig. 6. Brightness of pressurised P₁ and reference bleachings after each bleaching stage. Hot water treatment of wheat straw (07Straw) at 120°C for 60 min followed by (PP₁)-P-Paa-P bleaching. PP₁ pressurised P₁ stage.

Table 5. Paper Technical Properties of Reference, Pressurised P₁, Sugar Addition and Alkali Pretreatment Bleaching Paper Sheets PP₁=Pressurised P₁ Stage, APT=NaOH Pretreatment and PPT= O₂ Pressurised NaOH Pretreatment.

	Bleaching conditions	Straw batch	SR number	Grammage (g/m ²)	Thickness (µm)	Apparent density (kg/m ³)	Bulk (m ³ /kg)	Opacity (%)	Light scatter (m ² /kg)	Light absorption (m ² /kg)	Tensile index (Nm/g)	Tear Index (Nm ² /kg)
Reference bleaching	Low chem	2006	32	58.5	93	629	1.52	71.6	23.9	0.7	63.4	4.6
	High chem	2006	30	60.8	96	636	1.53	70.3	23.1	0.5	62.4	4.4
	Low chem	1 st	32	59.0	88	668	1.54	71.1	22.4	0.8	55.9	3.9
	High chem	1 st	31	60.9	90	674	1.59	71.5	22.7	0.7	59.2	4.0
	Low chem	2 nd	34	71.8	112	639	1.56	69.7	19.7	0.3	63.9	3.6
	High chem	2 nd	43	83.9	113	743	1.35	71.2	18.8	0.2	69.8	5.4
Pressurised P ₁	PP ₁ 105°C 60 min	1 st	32	64.8	109	592	1.69	76.0	24.9	0.8	48.7	3.9
	PP ₁ 105°C 120 min	1 st	31	62.1	109	568	1.76	75.1	26.1	0.7	48.7	4.0
Carbonate	High chem, 25 % Na ₂ CO ₃	2 nd	30	67.5	99	683	1.47	68.6	21.4	0.3	58.0	4.4
	High chem, 32.5 % Na ₂ CO ₃	2 nd	29	67.7	97	696	1.44	67.9	18.4	0.3	57.8	4.6
	High chem, 40 % Na ₂ CO ₃	2 nd	32	68.5	101	679	1.47	70.5	21.5	0.4	57.8	4.6
Sugar addition	Low chem, Gluc	2 nd	47	67.9	102	669	1.50	69.5	18.8	0.4	60.3	4.7
	Low chem, Xyl	2 nd	42	67.6	99	680	1.47	68.7	18.8	0.4	63.2	4.3
	Med. chem, Gluc	1 st	31	65.2	97	675	1.48	70.7	22.6	0.4	71.1	4.2
	Med. chem, Xyl	1 st	35	65.7	97	681	1.47	67.9	20.9	0.3	70.0	4.4
	High chem, Gluc	1 st	31	64.3	93	689	1.45	74.7	28.2	0.4	60.0	4.5
	High chem, Xyl	1 st	55	66.9	100	672	1.49	70.0	21.9	0.4	73.8	3.9
Alkali pretreatment	APT 2% NaOH	2 nd	32	68.1	109	627	1.60	72.9	19.4	0.7	52.9	4.8
	APT 2.5% NaOH P-Paa-P	2 nd	57	68.3	112	609	1.64	78.2	19.0	1.4	50.8	3.4
	PPT 3% NaOH, 60 min	2 nd	49	68.7	107	644	1.55	74.9	18.6	0.9	53.5	4.7
	PPT 3% NaOH, 90 min	2 nd	30	67.7	107	684	1.46	71.6	18.3	0.6	57.0	5.3
	PPT 4% NaOH	2 nd	33	73.4	103	657	1.52	71.5	20.1	0.8	56.8	4.2

The pressurised P₁ stage was expected to intensify the peroxide bleaching and lower bleaching chemical consumption, especially that of NaOH. With the chosen, somewhat lower NaOH charge (6%), oxygen pressure in the P₁ stage did not give a clear advantage compared to the unpressurised bleaching; final brightness remained at about 3% units lower level than the reference. The NaOH charge of the reference pulp was somewhat higher. The best pressurised P₁ stage results were obtained at 95°C and 120 minutes reaction time.

Table 6 presents the yield of the pulps from the pressurised P₁ bleaching. All pulps with 6.0% NaOH charge in the P₁ stage arrived at nearly the same total yield. The yield level of the pressurised P₁ pulps was somewhat higher than the yield of the reference pulp. Due to the lower chemical concentration and shorter reaction time, less substances were dissolved during the pressurised P₁ stage than from the unpressurised stage. Despite of the higher yield level, the pulps defibrated properly. By pressurizing the first peroxide stage it was possible to reduce the NaOH charge by only about 1%.

The paper technical properties of the pressurised P₁ bleachings are presented in Table 5. The oxygen pressure in the P₁ stage and the lower chemical charge compared to the reference bleaching mostly affected the strength properties. The tensile index and the tear index of the pressurised P₁ bleaching sheets were slightly lower than those of the reference pulp. The bulk of the pulp from the pressurised bleachings was higher, which together with strength properties, is an indication of lower fibre bonding.

Table 6. Yield of Reference, Pressurised P₁ and Sugar Addition Bleachings after Each Bleaching Stage.

	Bleaching conditions	Straw batch	Yield (% of original straw)				
			Hot water treatment	P ₁	P ₂	Paa	P ₃ +Ac.
Reference bleaching	Low chem	2006	97.7	76.0	70.0	64.8	60.4
	High chem	2006	97.7	71.9	63.5	60.4	55.3
	Low chem	1 st	88.3	78.9	64.8	61.0	56.6
	High chem	1 st	88.3	68.2	57.8	56.7	52.0
	Low chem	2 nd	90.6	72.4	59.7	56.6	53.1
	High chem	2 nd	90.4	64.4	57.8	54.8	49.2
Pressurised P ₁	PP ₁ 95°C 120 min	1 st	90.1	76.4	66.9	65.3	58.6
	PP ₁ 105°C 60 min	1 st	89.1	73.4	70.9	66.5	59.2
	PP ₁ 105°C 120 min	1 st	90.4	76.2	67.2	66.1	60.4
Carbonate	High chem, 25 % Na ₂ CO ₃	2 nd	90.7	68.9	60.0	57.7	51.7
	High chem, 32.5 % Na ₂ CO ₃	2 nd	91.2	70.8	61.6	58.4	53.1
	High chem, 40 % Na ₂ CO ₃	2 nd	92.7	72.1	64.2	61.1	55.4
Sugar addition	Low chem, Gluc	2 nd	92.0	84.9	63.0	60.0	54.6
	Low chem, Xyl	2 nd	91.1	81.0	63.5	57.6	53.1
	Med. chem, Gluc	1 st	90.7	70.9	67.3		53.6
	Med. chem, Xyl	1 st	91.7	70.9	64.2	58.6	51.7
	High chem, Gluc	1 st	91.9	66.9	59.9	57.3	
	High chem, Xyl	1 st	92.0	71.2	59.1	56.4	50.1

Alkali Substitution with Na₂CO₃

One option to decrease NaOH consumption in peroxide bleaching is to substitute NaOH partially with Na₂CO₃. Figure 7 illustrates the brightness development of the bleachings with partial alkali substitution of NaOH with Na₂CO₃ and the corresponding reference. All these bleachings were conducted from the second batch of 07Straw. The highest brightness was achieved with the 25% Na₂CO₃ share, and it was equal to that of the reference pulp. Increasing the substitution to 40% the final brightness decreased only from 68% to 65% ISO. Sodium carbonate substitution increased the bleached yield slightly, but it may also impair the defibration if the degree of substitution is 40% or above (Table 6).

The paper technical properties of the carbonate bleaching pulps were quite close to the reference pulp (Table 5). The substitution of sodium hydroxide with sodium carbonate in the bleaching decreased the Schopper Riegler number and increased the bulk of the bleached pulp compared to the reference pulp. Strength properties, such as tensile and tear index, were also lower than those of the reference pulp. This together with a higher yield of the pulp indicated that the use of sodium carbonate as an alkali source may impair the bonding of the pulps.

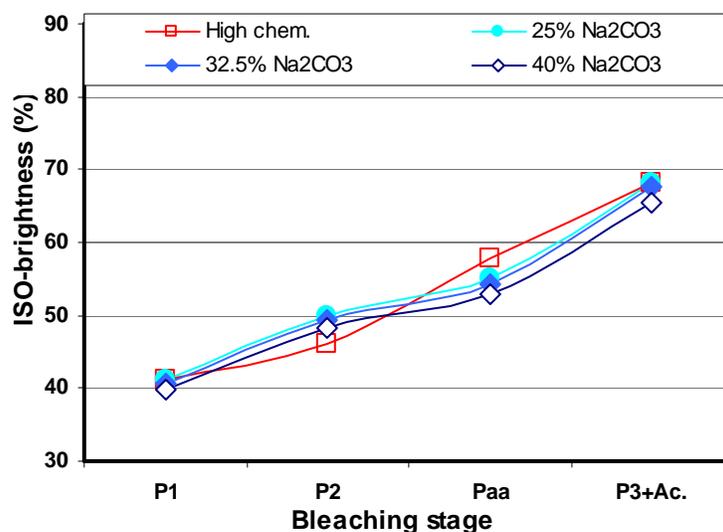


Fig. 7. Brightness of sodium carbonate substitution bleachings and reference pulp after each bleaching stage. Hot water treatment of 2007 wheat straw (07Straw) at 120°C for 60 min followed by P-P-Paa-P bleaching.

Sugar Addition

Particularly in the first alkaline peroxide stage, quite a lot of sugars dissolved because of the high alkali charge in that stage. The role of these sugars, especially glucose and xylose, was studied by adding them in the P₁ stage. The purpose of adding these sugars to the P₁ stage was to test the assumption of their negative effect on bleachability. However, glucose addition in the P₁ stage actually improved the pulp bleachability, since the final ISO brightness was 2 to 5% units higher than that of the reference pulp (Fig. 8). Xylose addition arrived at the same final brightness as the

reference pulp. The negative effect was not to be seen. This may result from the reducing sugars' possible catalyst role in alkaline peroxide bleaching (Heikkilä and Vuorinen 2000; Vuorinen and Heikkilä 2003). The yield of sugar-addition bleaching trials was on a similar level to the yield of the comparable reference pulps (Table 6).

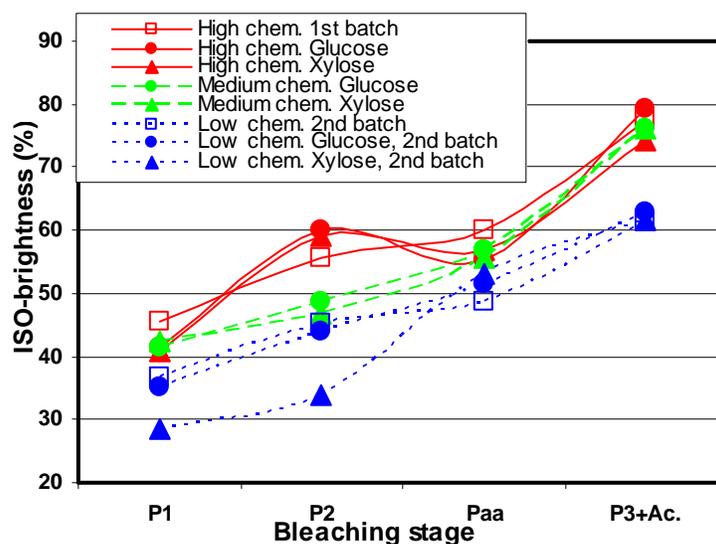


Fig. 8. Brightness of sugar addition bleachings and reference pulp after each bleaching stage. Hot water treatment of 2007 wheat straw (07Straw) at 120°C for 60 min followed by P-P-Paa-P bleaching.

Table 5 presents the paper technical properties of the sugar addition pulps. Sugar addition did not have a significant effect on the paper technical properties. Xylose addition may impair the pulp drainability.

Alkali Pretreatment

The alkali charge of the first peroxide stage was high, and organic substances were dissolved in abundance. These organic substances react further by consuming alkali. The idea of implementing an alkali pretreatment prior to the actual alkaline peroxide bleaching was to reduce sodium hydroxide consumption as much as possible in the following P stages while still being able to produce suitable fibres for paper making. The total NaOH consumption can be reduced from a level of 9 – 11.5% to 6 – 7%. The effect of such a reduction was a clearly lower final ISO brightness (15 to 24% units) and a higher yield (1.2-11.1% units) compared to the reference pulp. However, the alkali charge was not sufficient to defibrate the straw as well as in the case of the reference pulp. If a moderate mechanical treatment was to be combined with this bleaching and the brightness was not the main issue, then a pulp with acceptable properties could be achieved.

Figure 9 presents the ISO brightness and Fig. 10 presents the yield of the alkali-pretreated pulps and the reference as a function of NaOH consumption. The raw material of all alkali pretreatment bleachings was from the second batch of 07Straw, which was stored for two years in an unheated barn. The best response was probably achieved with

atmospheric alkali pretreatment followed by the bleaching with sufficient alkali charge of about 5% NaOH on the original straw. The pressure in the alkali pretreatment did not significantly improve the final brightness of the pulp.

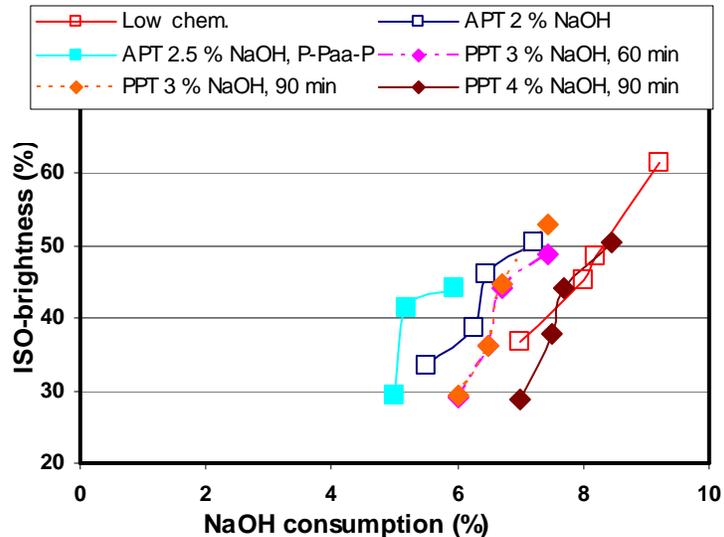


Fig. 9. Brightness of alkali pretreatment bleachings and reference pulp as a function of NaOH consumption. Hot water treatment of 2007 wheat straw (07Straw) at 120°C for 60 min followed by APT/PPT-P-P-Paa-P bleaching. APT alkali pretreatment, PPT pressurised alkali pretreatment.

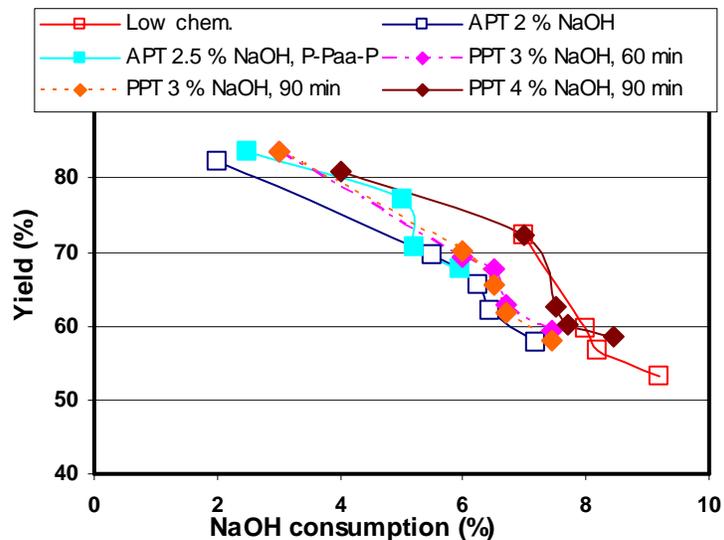


Fig. 10. Yield of alkali pretreatment bleachings and reference pulp as a function of NaOH consumption. Hot water treatment of 2007 wheat straw (07Straw) at 120°C for 60 min followed by APT/PPT-P-P-Paa-P bleaching. APT alkali pretreatment, PPT pressurised alkali pretreatment.

The reduction of sodium hydroxide consumption by an alkali pretreatment stage did not impair the pulp properties significantly, even though the yield of these pulps was higher and the bondability and thus the tensile index lower (Table 5). The short bleaching

sequence P-Paa-P was not long enough to defibrate the pulp properly, and this may result in poorer pulp properties.

CONCLUSIONS

1. The minimization of sodium hydroxide consumption in the peroxide bleaching of the hot water treated wheat straw is challenging. Straws grown during different years have a different chemical composition, and therefore, the amount of chemicals required in bleaching varies. The 2006 straw (06Straw) required less chemical to be bleached to 75% ISO brightness than the 2007 straw (07Straw).
2. Replacing NaOH with Na₂CO₃ is possible with a 25 to 40% share of total alkali. If the Na₂CO₃ share is 25%, the pulp properties are similar to the reference pulp properties. With higher sodium carbonate shares, the brightness is slightly lower than that of the reference pulp brightness.
3. It is possible to reduce the total alkali consumption of the alkaline peroxide bleaching of hot water treated straw by about 40% if an alkaline pretreatment stage is implemented prior to bleaching. This of course means also a clear reduction of 15 to 20% units in the final brightness, but the pulp properties are still acceptable. Therefore an alkali pretreatment and peroxide bleaching combined with a moderate mechanical treatment could be an acceptable possibility to minimise chemical consumption if the reduction of brightness is acceptable.
4. Sugar addition in the P₁ stage had an interesting influence on brightness. Glucose addition to the first peroxide stage delivered a higher brightness than that of the reference pulp. The reason for this may be that the reducing sugars act as catalysts in alkaline peroxide bleaching.
5. The oxygen pressure in the P₁ stage did not give a clear advantage compared to the unpressurised bleaching.
6. The most prevalent findings of this study indicate that the quality of pulp produced from wheat straw, when processed through the hot water treatment, and alkaline peroxide bleaching is satisfactory. If, however, the final application requires a high brightness level, this type of pulp may not be the most suitable one, due to the required amount of chemicals to attain such high brightness levels. Despite this disadvantage, wheat straw pulps have several applications, such as writing and printing papers, and packaging materials, where it can be regarded as the pulp of choice.

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