

ASPECTS ON BLEACHING AND TEMPO-MEDIATED OXIDATION OF WHEAT STRAW PULP FRACTIONS

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This study outlines research concerning wheat straw fines, including their impact on pulp bleachability, their modification by chemical means, and their use as a dry strength enhancer in a paper application. Results show that primary fines constituting about 23% of the whole wheat straw pulp had a large negative impact on pulp bleachability. The differences in response to bleaching were due to the different properties of the fines, *i.e.* higher kappa number, higher metal ion content, lower brightness, and lower viscosity compared to that of fibers. It was also shown that the fines fraction is more difficult to oxidize and does not reach as high fiber charge levels as that of the other fractions. However, at a dosage of ≥ 3 mmol hypochlorite/g it was possible to prepare nanofibers from wheat straw fines that showed a good strength-enhancing effect in a paper product. The fact that removal of fines from wheat straw pulps by fractionation improves bleachability and also drainage properties at the same time, while simultaneously the fines can be modified and used as a strength enhancer, is very interesting when evaluating the potential of this type of annual plant as a source for production of different paper products.

Keywords: Wheat straw; Fines; Non-wood fiber; Bleaching; TEMPO; Oxidation; Fiber properties; Strength properties; HCl method; Electron microscopy; SEM; TEM

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INTRODUCTION

With the limited availability of wood fibers in China, the Chinese pulp and paper industry is looking to use alternative fibrous resources such as non-wood plants, and therefore the interest and importance for annual plant pulping is gaining constantly. China is the largest producer of wheat in the world, and this material constitutes an interesting raw material for the manufacturing of pulps aimed for different paper products in the country.

Wheat straw is an annually renewable fiber resource with a high content of small vessels, parenchyma, and epidermal cells (representing primary fines) with many of the cell types remaining as aggregates in the final pulp. Beating breaks down these aggregates, giving an additional quantity of “so-called” secondary fines. The content of fines in wheat straw pulps differs depending on the origin of the raw material, cooking, bleaching, and beating procedures adopted. However, values between 20 and 45% have been reported in the literature (Utne and Hegbom 1992; Zhao *et al.* 1992; Rousu and Niinimäki 2007; Rousu and Hytönen 2007; Guo *et al.* 2009).

Zhao *et al.* (1992) showed that beating of wheat straw increased the water retention value (WRV) of the pulp. However, the WRV of the fiber fraction showed little change, indicating that wheat straw pulp fibers do not undergo significant fibrillation. Microscopic investigations revealed that the fibers showed little or no fibrillation, although beating increased the number of wrinkles and micro-compressions. From these results they concluded that the increase in WRV for the whole pulp is a function of the higher fines content and concomitant increase in the WRV of the fines.

It has also been reported that a high content of fines in the pulp results in a very high drainage resistance on washing and thickening filters, and on the paper machine (Rydholm 1965). Recent studies have shown that removal of fines from wheat straw pulps by fractionation can improve not only the drainability of the pulp suspension but also the mechanical and optical properties of the paper sheet, indicating that wheat straw fines are acting mainly as a filler with low bonding properties in the paper sheet (Ljusegren *et al.* 2006; Guo *et al.* 2009). This differs from hard- and softwood pulps in which the fine material is known to contribute to strength (Hthun and De Ruvo 1978; Przybysz and Czechowski 1985; Paavilainen 1990; Retulainen *et al.* 1993; Ferreira *et al.* 2000; Seth 2003).

A powerful and well known technology for preparing individual nanofibers from cellulose fibers is TEMPO-mediated oxidation of cellulose pulp fibers (Isogai and Yumiko 1998; Satio *et al.* 2007; Guimond *et al.* 2010). By using an oxidation procedure involving TEMPO, NaBr, and hypochlorite, a significant amount of carboxylate and aldehyde groups are introduced into the native cellulose, while maintaining the fibrous morphology and crystallinity. Several investigations have also shown that nanofibres prepared by this technology can improve the strength properties of a large variety of paper products (Takuya *et al.* 1999; Saito and Isogai, 2005; Duarte *et al.* 2006).

In this work, the effect of removing fines from wheat straw pulps on bleachability was studied. The possibility to modify these fines into nanofibers by chemical oxidation and its effect as a strength enhancer in paper application was also investigated.

EXPERIMENTAL

Raw Material, Fractionation, and Bleaching

Commercial wheat straw chips from Quanlin Pulp and Paper mill in Shangdong province China were Soda-AQ cooked in the laboratory. The chips were sorted by hand to remove sawdust, oversized chips, knots, and bark before cooking. The liquor-to-wood ratio was 4.5:1, containing 16% NaOH and 0.05% AQ. Cooking temperature was 153 °C for 40 minutes, and the increase in temperature from 40°C to 153 °C took 113 minutes. After cooking, the pulp was thoroughly washed, defibrated, and screened on a flat screen with slots 0.2 mm wide. Accepted pulp was dewatered in a centrifuge and subsequently homogenized. The pulp was then divided into two parts and further treated as shown in Fig. 1.

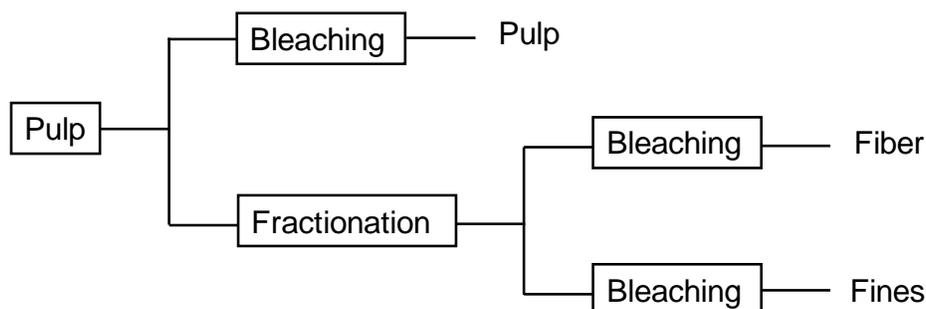


Fig. 1. Outline of the study

Fractionation of the unbleached pulp was performed at Innventia, Sweden. The pulps were diluted in water to a pulp suspension of about 0.3% and circulated through a 75 μm Cellecofilter for 180 minutes. The fine fraction was accumulated on a screen cloth with 22.4 μm pores. Thereafter, the pulps were transferred to a Büchner funnel and dewatered.

The aim of bleaching was to perform a D(EOP)D sequence with a final brightness of 80 to 90% ISO with an acceptable final pH. No pH optimization of the bleaching stages was done due to the small amount of pulp available. The conditions and chemical charges applied in the stages are outlined in Table 1. The pH and residual chemicals were analyzed after each stage. The unbleached and fully bleached pulp fractions were analyzed for brightness, kappa number, and viscosity, using ISO standard methods (ISO brightness: 2470, kappa No: 302, viscosity: 5351). The metal composition of the pulps was also determined by ICP-OES analysis after total digestion and dissolution of the samples by HNO_3 using microwave technology.

Table 1. Bleaching Conditions and Chemical Charges Applied in the Different Stages

Stage	D ₃₀	(EOP ₅)	D ₁₅
Time, min.	45	60	240
Temp., °C	70	90	70, 75
p.c., %	10	10	10
ClO ₂ , active Cl kg/t	30	-	15
H ₂ SO ₄ , kg/t	0,1.3	-	
NaOH, kg/t	0.5	11	2
Mg ²⁺ , kg/t		0.15	-
O ₂ , MPa		0.3	-
Acceptable pH range	2-4	9.5-11	3.5-4.5

TEMPO-Mediated Oxidation

Before TEMPO-mediated oxidation, an acid stage was performed at pH 3 (adjusted using HCl), at 10% consistency for 2 h at 90°C. After treatment, the pulp was washed once with deionized water at 3% consistency for 5 minutes. All filtrates were re-circulated once in order to avoid loss of fine material. The chemicals used in the oxidation procedure were as follows: TEMPO (2,2,6,6-tetramethylpiperidin-1-oxyl radical) supplied by Acros Organics, sodium bromide supplied by Scharlau, and sodium hypochlorite (~15%) supplied by Akzo Nobel Base Chemicals. The oxidation procedure was carried out at 1% pulp consistency using the methodology suggested by Kitaoka *et al.* (1999) and Saito and Isogai (2005). In principle, the never dried pulp was suspended in water containing TEMPO (0.016 g/g pulp) and NaBr (0.1 g/g pulp) with a starting pH of *ca.* 9 (adjusted with NaOH). One, 3, and 5 mmol/g sodium hypochlorite was then added quickly to the suspensions. The reaction was performed at room temperature and with the pH kept constant at pH 10 during the reaction by using 0.5 M NaOH. After treatment, the pulp was transferred to a Büchner funnel and filtered. To avoid losses of fines, the filtrate was re-circulated once. The pulp sample was washed directly after treatment with de-ionized water at 1% pulp consistency for 40 minutes. The pulp was then dewatered and the filtrate re-circulated once. The washing procedure was repeated twice.

Analytical Tools

The dimensions (length, width, shape) of fibers were measured with use of a Fibretester®. The total fiber charge measurements were conducted according to Katz *et al.* (1984) using a titration unit, 712 Conductometer, and a program from Metrohm. The water retention value (WRV) was determined according to SCAN-C 62:00.

Cross polarization/magic angle spinning (CP/MAS) ¹³C nuclear magnetic resonance (NMR) spectroscopy and spectral fitting were used to investigate the degree of pulp oxidation as well as crystallinity. After freeze drying, the wheat straw samples were packed in a zirconium oxide rotor. CP/MAS ¹³C-NMR spectra were recorded at 290 ± 1 K using a Bruker Avance AQS 300 WB instrument at 7.04 T. The MAS rate was 5 kHz. A 7 mm double air-bearing probe was used. Acquisition was performed with a CP pulse sequence, using a 4.3 ms proton 90° pulse, an 800 ms ramped (100-50%) falling contact pulse, and a 2.5 s delay between repetitions. A TPPM15 pulse sequence was used for 1H decoupling. Glycine was used for the Hartmann-Hahn matching procedure, as well as an external standard to calibrate the chemical shift scale relative to tetramethylsilane ((CH₃)₄Si). The peak of maximum intensity in the glycine carbonyl line was assigned a chemical shift of 176.03 ppm.

The HCl method (Ander *et al.* 2008; Heinemann and Ander 2011) was used to determine quantitatively dislocations and other weak points in the wheat straw pulp. In principle, the HCl method involves a short period of fiber separation in 20 mL of water in 125 mL Erlenmeyer flasks using a stirring bar followed by addition of 2N HCl to obtain 40 ml 1N acid solution at pH 0. The fiber suspension is then incubated at 80 to 82°C for 30 minutes followed by cooling and final cleavage over 30 min using a stirring bar. Final fiber washing was with a phosphate buffer at about pH 7 using a G3 glass filter. Length

weighted fiber lengths were determined in a Fibretester® at Eka Chemicals, Sweden, before and after acid treatment. Cleavage per fiber was calculated as follows:

$$\text{Cleavage per fiber} = (L_0 / L) - 1 \quad (1)$$

where L_0 is length weighted fiber lengths in mm for the control in water, and L is length weighted fiber lengths in mm for HCl-treated fibers.

The morphological appearance of the fibers, oxidized fibers, and nanofibers were visualized using fluorescence microscopy, Environmental Scanning Electron Microscopy (ESEM), and Transmission Electron Microscopy (TEM). Samples for ESEM were freeze-dried at a consistency of about 0.5% in a Heto Equipment (FD3) prior to observations.

For fluorescence microscopy, wheat straw pulps, fibers, and fractions were stained with aq. 0.01% acridine orange for 1 min., washed briefly (1 min) in distilled water, and covered with coverslips. Samples were then examined using a wide-field Leica DMRE fluorescence microscope fitted with mercury lamp and I3 513808 filter-cube (Leica, excitation 450-490 nm, emission > 515 nm). Images were digitalized using a CCD camera (Leica DC 300F) and a digital imaging system (Leica Microsystems, Wetzlar, Germany). For TEM, diluted wheat nanofiber samples in water were pipetted onto formvar coated grids and negatively stained with aq. 2% uranyl acetate. Nanofibers were examined using a Philips CM 12 TEM operated at 100kV. Images were recorded on Kodak 4489 flat film.

Strength Evaluation

To evaluate the effect of the oxidized wheat straw pulp and fractions as binder, the following procedure was followed. A furnish was prepared consisting of 90% High Temperature-Chemithermomechanical Pulp (HT-CTMP) (Freeness 700/shives 77) and 10% softwood kraft pulp (SR 26). The consistency was 0.5%, conductivity 1200 $\mu\text{s}/\text{cm}$, and pH 7. The chemicals used in the preparation of paper sheets were cationic potato starch, PearlBond 970 from Lyckeby, NP 442 (aqueous sol of anionic silica-based particles) from Eka Chemicals AB, and nanofibers prepared from different pulp fractions. All chemicals used for preparation of paper sheets in the “Dynamic sheet former” were prepared to a solution of 0.5%. The oxidized wheat straw fractions were mixed in a household mixer for 5 minutes before use. The chemical dosage and times of addition are presented in Table 2. The formation of sheets began after 60 seconds and dewatering after 90 seconds. The sheets were pressed at 10 bars for 5 minutes and thereafter dried in plan driers for 12 minutes. Thickness, grammage, tensile, and Z-strength properties were measured using standard methods according to ISO 534, ISO 536, ISO1924-2, and SCAN-P 80:98, respectively.

Table 2. Chemical Dosage and Time for Addition

Chemical/Product	Nanofibers	PB970	NP 442
Dosage, %	5	1	0.3
Time of addition (s)	0	30	45

RESULTS AND DISCUSSION

Bleaching of Wheat Straw Fractions

Three different fractions of an unbleached wheat straw pulp were collected and bleached separately using a D(EOP)D sequence. Fractionation of the unbleached pulp showed that the primary fines (< 76 μm) constituted about 23% of the total wheat straw pulp, consisting mainly of vessels, parenchyma, and epidermal cells as shown in Fig. 2 and previously described by Liu *et al.* (2005).

The properties of the unbleached and separately bleached fractions showed large differences in kappa number, brightness, and viscosity between the different fractions both before and after bleaching (Table 3). The unbleached fines fraction had a much higher kappa number, lower brightness, and lower viscosity compared to the pulp and fiber fractions. Removal of fines from the unbleached pulp decreased the kappa number by about one unit, while the brightness and viscosity increased with 5 and 500 units, respectively. With chemical dosages of active Cl 45 kg/t and H₂O₂ 5 kg/t in the D(EOP)D sequence, the final brightness of the whole pulp was 81.5% ISO, while the fiber fraction reached a brightness of 90.3% ISO. The brightness of the fines fraction increased by about 30 units during bleaching (8.8 to 38.2% ISO), indicating the much lower bleachability of this fraction. This may be explained by the much higher lignin content (kappa number) of this fraction. These results are in agreement with earlier findings by Treimanis *et al.* (2009) who studied the bleachability of surface material from birch and eucalyptus kraft pulps.

The metal ion content of the different fractions were also analysed, and results showed that the fines were rich in metal ions, especially Si but also transition metal ions such as Mn, Fe, and Cu in comparison with the other fractions (Table 4). This may also influence pulp bleachability. Thus, removal of primary fines from the wheat straw pulp prior to bleaching has a significant positive effect on bleachability.

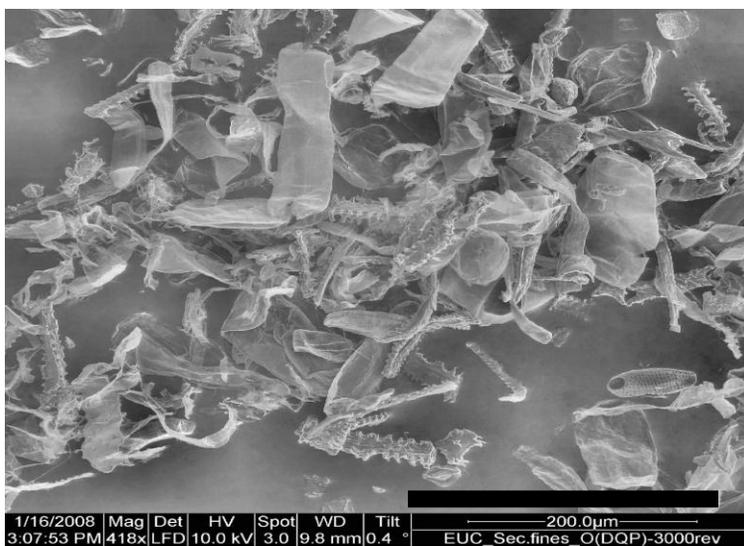


Fig. 2. ESEM image of wheat straw fines (< 76 μm)

Table 3. Properties of the Unbleached and Separately Bleached Wheat Straw Fractions

Sample	Kappa number	ISO Brightness (%)	Viscosity (dm ³ /kg)
Unbleached			
Pulp	11.9	32.4	1139
Fiber	11.0	37.7	1632
Fines	17.0	8.8	766
Bleached			
Pulp	0.83	81.5	1131
Fiber	0.38	90.3	1552
Fines	2.39	38.2	710

Table 4. Metal Ion Content of the Unbleached Wheat Straw Fractions

Metal ion (mg/kg)	Pulp	Fiber	Fines
Si	630	120	3000
Ca	270	60	130
Cu	<0.1	0.2	22
Fe	120	16	430
K	50	10	160
Mg	180	90	230
Mn	3.7	0.6	8
Na	430	370	650

TEMPO-Mediated Oxidation of Wheat Straw Fractions

The three bleached fractions – pulp, fiber, and fines – were TEMPO-oxidized with 1, 3, and 5 mmol hypochlorite/g pulp, respectively. An overview of the results on the properties of the oxidized and non-oxidized fractions is presented in Table 5. It is apparent that the WRV and total fiber charge were increased significantly for all fractions with hypochlorite addition. This is in good agreement with earlier results on chemical wood pulps (Isogai and Yumiko 1998; Saito and Isogai 2005; Saito *et al.* 2007; Guidmond *et al.* 2010). The total charge development for the pulp and fiber fraction was also faster and reached higher values compared to the fines fraction (Fig. 3). Thus, the fines fraction was more difficult to oxidize to a certain charge level. This may be explained as outlined above by the higher content of lignin and metal ions in the fines (Tables 3, 4). It is also most probable that the composition and amount of carbohydrates and extractives in the fines differ from that of the whole wheat straw pulp, as shown previously for fines from chemical soft- and hardwood pulps (Suurnäkki *et al.* 1996). Even though the total fiber charge at any given addition level was lower for the fines fraction compared to other fractions, they still had the highest WRV. This high WRV certainly created problems in the filtration and dewatering procedure.

From the fiber dimensions the overall trend was for the length of all fractions to increase with hypochlorite addition. This can be explained by the straightening of the fibers during the treatment, as shown by the increase of the shape factor (Table 5). In

contrast, the fiber width showed a decrease with higher oxidation levels. These results, however, can most probably be explained by the increase in the amount of transparent material on the fiber surface, which increases with degree of oxidation and which cannot be evaluated by means of Fibertester measurements.

Figure 4 shows the morphological appearance of untreated and TEMPO-oxidized fibers. No obvious morphological differences between the untreated and TEMPO-oxidized samples can be noted, *i.e.* the structure of the fibers remained rather intact before they were subjected to mechanical treatment. This was also the case for the fine fractions, as shown in Fig. 5.

Table 5. Properties of Oxidized and Non-Oxidized Wheat Straw Fractions

Sample	NaClO charge mmol/g pulp	Length mm	Width μm	Shape factor %	WRV g/g	Charge mmol/kg
Pulp	0	0.639	19.5	90.2	2.3	35
	1	0.654	19.1	90.8	2.8	268
	3	0.690	18.7	90.8	7.3	799
	5	0.646	18.8	89.5	13.9	1110
Fiber	0	0.698	18.6	88.8	2.1	31
	1	0.711	18.0	89.9	2.2	319
	3	0.743	17.8	90.1	6.7	775
	5	0.768	17.6	89.3	9.6	1077
Fines	0	0.104	28.6	93.7	3.2	23
	1	0.105	26.7	94.2	3.3	250
	3	0.112	26.5	94.4	11.4	662
	5	0.114	26.2	94.2	14.5	824

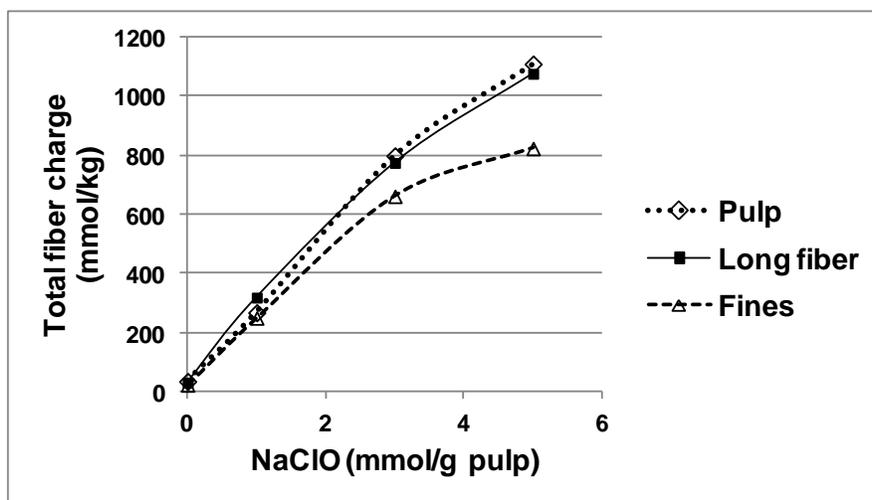


Fig. 3. Total fiber charge pulp versus the hypochlorite addition during oxidation

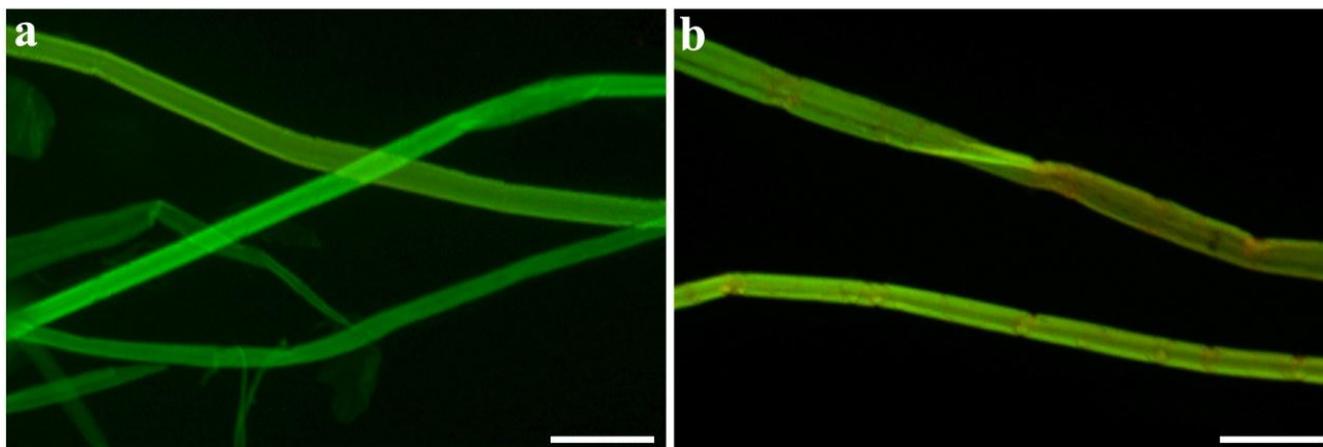


Fig. 4. Morphological appearance of a) untreated and b) TEMPO-oxidized fibers. Bars = 500 μ m

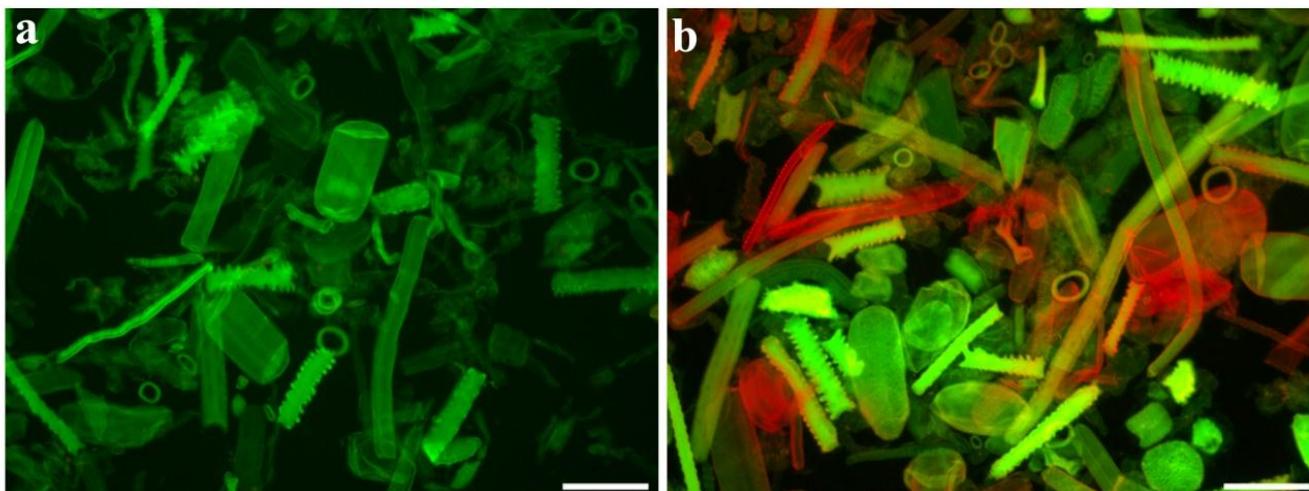


Fig. 5. Morphological appearance of a) untreated and b) TEMPO-oxidized fines. Bars = 1.0 mm

Oxidized fibers were converted into nanofibers by mixing a 0.5% fiber suspension in a house-hold mixer for five minutes. Highly viscous gels were obtained for all fractions treated with 3 and 5 mmol hypochlorite/g pulp. However, even though a significant amount of fines and fibers were converted into nanofibers during mixing, there still remained undelaminated and partially delaminated fibers and fines.

Figure 6 shows TEM-images of nanofibers prepared from pulp and fines after 5 mmol hypochlorite/t pulp treatment. The average microfibril width of nanofibers prepared from the fines was about 3.5 nm, which is somewhat less than the 4.6 nm of nanofibers prepared from the whole pulp.

Although treatment with 1 mmol hypochlorite/g created fractions with a total charge of between 220 and 300 mmol/kg, this was not enough for converting the fractions into nanofibers by only mixing.

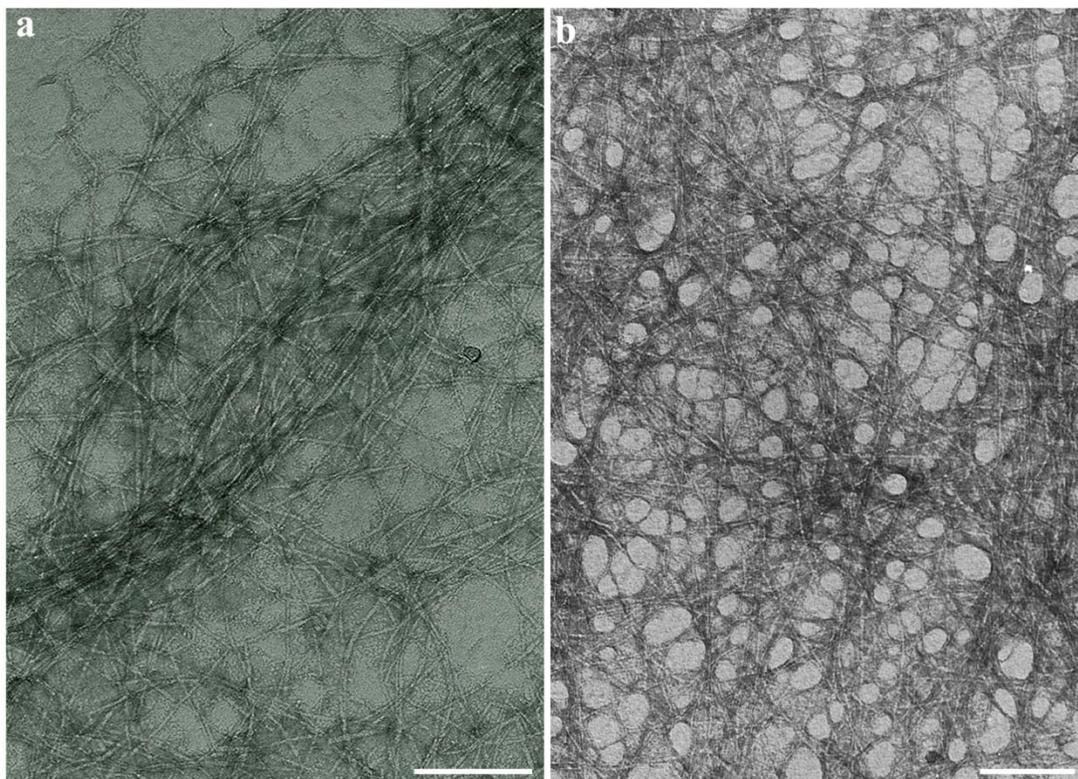


Fig. 6. TEM-images of mixed a) oxidized pulp b) oxidized fines. Bars = 100 nm

NMR analysis showed that oxidation of the wheat straw pulp using 5 mmol hypochlorite/g pulp gave an almost complete oxidation of C6 to carboxyl groups without changing the crystallinity. This means that TEMPO-mediated oxidation represents a powerful technology for preparing nanofibers from different wheat straw pulp fractions.

Furthermore, the original and TEMPO-oxidized (5 mmol/g) wheat straw pulps were also evaluated by the HCl method, which gives the number of dislocations and other weak points in the fibers (cleavage per fiber). The number of dislocations given by cleavage per fiber was 0.54 for untreated straw fibers and 0.87 for the oxidized wheat straw pulp. This increase in number of dislocations after oxidation was expected and consistent with a weakening of the fiber structure.

Effect of Oxidized Wheat Straw Fractions on Paper Properties

In this part of the study the possibility of using nanofibers prepared from fines by TEMPO-mediated oxidation as a strength enhancer in a paper application was evaluated and compared with that of other fractions. As shown in Table 6, the strength properties, both tensile index and Z-strength of the paper sheets were improved by addition of the different oxidized and mixed products. Best results were obtained for products which had been oxidized to a high degree, *i.e.* 3 and 5 mmol hypochlorite/g and where mixing converted the samples into nanofibers. The strength-enhancing effect was greatest for nanofibers prepared from the pulp and fibers; however, nanofibers from fines also

showed good improvement. Thus, the bleachability and drainage of the wheat straw pulp can be improved to a large extent by removing fines from the unbleached pulp by fractionation. This fraction may instead be modified by TEMPO-mediated oxidation and used as a strength enhancer in paper products.

Table 6. Strength Properties of the Paper Sheets

	NaClO charge mmol/g pulp	Grammage g/m ²	Density kg/m ³	Tensile index kNm/kg	Z-strength kPa
Reference		152	336	38.2	137
Pulp	1	150	367	40.1	273
	3	150	380	45.0	306
	5	152	420	48.5	387
Fiber	1	149	360	40.6	236
	3	154	372	47.6	278
	5	152	384	46.7	266
Fines	1	148	365	41.5	212
	3	151	388	45.5	305
	5	154	384	43.1	313

CONCLUSIONS

1. The primary fines constituting about 23% of the whole wheat straw pulp had a large negative impact on pulp bleachability. Differences in response to bleaching are due to the different properties of the fines, *i.e.* higher kappa number, higher metal ion content, lower brightness, and lower cellulose viscosity compared to that of the fibers.
2. The fines fraction was more difficult to oxidize and did not reach as high fiber charge levels as that of the other fractions. However, at a dosage of ≥ 3 mmol hypochlorite/g, it was possible to prepare nanofibers from the wheat straw fines that showed a good strength enhancing effect in a paper product.

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REFERENCES CITED

Ander, P., Hilden, L., and Daniel, G. (2008). "Cleavage of softwood kraft pulp fibres by HCl and cellulases," *BioResources* 3(2), 477-490.

- Duarte, A. P., Martins, S., Abrantes, C., Ismael, I. M., Simones, R., and Figueiredo, J. A. (2006). "Improvement of bleached kraft pulp properties by cellulose oxidation," *Papel* 76-82.
- Ferreira, P. J., Martins, A. A., and Figueiredo, M. M. (2000). "Primary and secondary fines from *Eucalyptus globulus* kraft pulps. Characterization and influence," *Paperi ja Puu- Paper and Timber* 82(6), 403-408.
- Guimond, R., Chabot, B., and Daneault, C. (2010). "Production of cellulose nanofibers by TEMPO-mediated oxidation of unbeaten kraft pulp," 96th Annual meeting 2010/96e Congr s annuel 2010, pp. 161-167.
- Guo, S., Heijnesson-Hult n, A., Basta, J., and Greschik, T. (2009). "Pulp and fiber characterization of wheat straw and Eucalyptus pulp - A comparison," *BioResources* 4(3), 1006-1016.
- Heinemann, S., and Ander, P. (2011). "Standard pulp and paper tests," In Fine Structure of Papermaking Fibres, COST Action E54. "Characterisation of the fine structure and properties of papermaking fibres using new technologies," Ander, P., Bauer, W., Heinemann S., Kallio P., Passas R., and Treimanis, A. (eds.), Swedish University of Agricultural Sciences. ISBN 978-91-576-9007-4, pp. 211-232.
- Hthun, M., and De Ruvo, A. (1978). "The implication of the fines fraction for the properties of bleached kraft sheet," *Svensk Papperstidning* 81(16), 507-510.
- Isogai, A., and Yumiko, K. (1998). "Preparation of polyuronic acid from cellulose by TEMPO-mediated oxidation," *Cellulose* 5(3), 153-164.
- Katz, S., Beatson, R. P., and Scallan, A. M. (1984). "The determination of strong and weak acidic groups in sulfite pulps," *Svensk Papperstidning* 87(6), R48-R53.
- Kitaoka, T., Isogai, A., and Onabe, F. (1999). "Chemical modification of pulp fibers by TEMPO-mediated oxidation," *Nordic Pulp Paper Res. J.* 14(4). 279-284.
- Liu, R., Yu, H., and Huang, Y. (2005). "Structure and morphology of cellulose in wheat straw," *Cellulose* 12, 25-34.
- Ljusegren, I., Wiberg, B., Tubek Lindblom, A., and Persson, T. (2006). "Papermaking potential of Scandinavian softwood pulp together with non-wood pulp," New Technologies in Non-wood Fiber Pulping and Papermaking, 5th INWFPPC, Guangzhou, China, pp. 281-286.
- Paavilainen, L. (1990). "Importance of particle size-fibre length and fines-for the characterization of softwood kraft pulp," *Paperi ja Puu* 72(5), 516-526.
- Przybysz, K., and Czechowski, J. (1985). "The effect of pulp fines on the drying process and paper strength properties," *Cellulose Chemistry and Technology* 19(2), 197-209.
- Retulainen, E., Luukko, K., Fagerholm, K., Pere, J., Laine, J., and Paulapuro, H. (1993). "Papermaking quality of fines from different pulps: The effect of size, shape and chemical composition," *APPITA J.* 55(6), 457-460.
- Rousu, P., and Hyt nen, K. (2007) "The role of non-wood fines constituents on pulp and paper properties," TAPPI EPE 2007.
- Rousu, P., and Niinim ki, J. (2007). "Nonwood pulp constitutes Part II-Combined use of Bauer-McNett apparatus and optical analyser," *APPITA J.* 60(3), 222-227.
- Rydholm, S. A. (1965). *Pulping Processes*, Wiley, New York, Preprint 1985 (facsimile edition) Robert E. Krieger, Malabar, FL, pp.1270.

- Saito, T., and Isogai, A. (2005). "A novel method to improve wet strength of paper," *Tappi J.* 4(3), 3-8.
- Saito, T., Kimura, S., Nishiyama, Y., and Isogai, A. (2007). "Cellulose nanofibers prepared by TEMPO-mediated oxidation of native cellulose," *Biomacromolecules* 8(8), 2485-2491.
- Seth, R. S. (2003). "The measurement and significance of fines – Their addition to pulp improves sheet consolidation," *Pulp & Paper Canada* T47 104(2), 4-44.
- Suurnäkki, A., Heijnesson Hultén, A., Buchert, J., Viikari, L., and Westermark, U. (1996). "Chemical characterization of the surface layers of unbleached pine and birch kraft pulp fibers," *J. Pulp Paper Sci.* 22(2), 43-47.
- Takuya, K., Isogai, A., and Onabe, F. (1999). "Chemical modification of pulp fibers by TEMPO-mediated oxidation," *Nordic Pulp Paper Res. J.* 279-284.
- Treimanis, A., Grinfelds, U., and Skute, M. (2009). "Are the pulp fiber wall surface layers the most resistant ones towards bleaching?" *BioResources* 4(2), 554-565.
- Utne, B., and Hegbom, L. (1992). "Microscopy studies of wheat and rice straw as raw materials for the pulp and paper industry," Proc. Second Int. Nonwood Fibre Pulping and Papermaking Conf, Shanghai, P.R. China.
- Zhao, X., Ödberg, L., and Risinger, G. (1992). "Beating of wheat-straw pulp: dissolved carbohydrates and lignins, fiber swelling and fines generation," *Tappi J.* 75(1), 153-16.

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