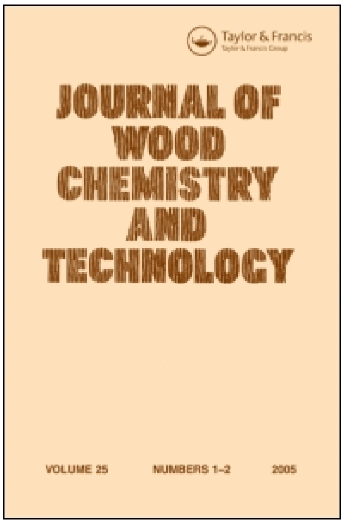

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ALKALINE SWELLING OF HEMP WOODY CORE CHIPS

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ABSTRACT

Swelling of hemp woody core chips after alkaline (peroxide) impregnation at 70 °C, as is practised in alkaline peroxide mechanical pulping (APMP) processes is examined, in relation to pulp yield and chemical composition of the chips. In contrast to wood chips, maximum swelling is attained at elevated temperature (70 °C) without chemical treatment, possibly as the result of relatively high porosity of hemp woody core cell walls. Alkaline swelling at 70 °C correlates with the xylan:lignin ratio. Swelling at ambient temperature shows some correlation with acidic group content. Apparent pore size distributions were examined, using ^{1}H NMR spin-spin relaxation. Several apparent pore size distributions could be distinguished within each sample. Elevated temperature, NaOH and peroxide addition are influencing apparent pore size distribution and total pore volume differently. Addition of peroxide results in remarkably enlarged apparent pore sizes, which emphasizes its importance (apart from bleaching) in APMP pulping, enhancing fiber flexibility and fibrillation.

INTRODUCTION

Hemp woody core may be a suitable raw material for the production of pulp of opacity and printability comparable with hardwood pulps.[1] The stem of fiber hemp (*Cannabis sativa vulgaris*, an annual dicotyledon with a height of 2-4 meters) consists of long bast fibers and a woody core. Both the papermaking potentials for bast fibers (industrially processed in France as raw material for specialty papers), as well as for woody core have been investigated on request of Dutch farmers searching for alternative crops. Alkaline peroxide mechanical pulping (APMP) can be used for production of pulp from hemp woody core, analogous to hardwood pulping.[2]

APMP is a sulfite-free alternative for conventional chemi-thermomechanical pulping (CTMP). Basically, wood chips are impregnated at 70 °C with alkaline peroxide. The advantages over CTMP processes are: improved impregnation, allowing a less critical chip size, and resulting in a lower shive content (bundles of unseparated fibers), a higher amount of longer and flexible fibers, fewer fines (fiber fragments) and a lower energy consumption. Moreover, sulfur free effluent treatment is less complicated.[2-4]

Chemical methods for upgrading strength of mechanical pulp raise the acidic group content and result in increased swelling. Impregnation of wood with aqueous sodium hydroxide solutions enhances hydration and simultaneously extracts cell wall components. Fiber walls swell when more water is absorbed than material is extracted. Both accessibility of fiber walls to aqueous reagents and ability of fibers to conform and bond during papermaking are increased.[5-8]

Wood pulp has properties of a gel, containing ionizable carboxylic acid groups (such as glucuronic acid groups, linked to the xylan backbone)[9]. In water, wood contains a higher ionic concentration (counter-ions of bound ionic groups) than the surrounding bulk water. The wood gel swells as a result of the entry of water until the osmotic pressure differential is balanced by the cohesive forces of the macromolecular network. Swelling is observed when the pH is raised, because of conversion of weak acidic groups (dissociated to a small degree) to the dissociated sodium salt form.[8,10] A plateau is found from pH 5 to 11, when carboxylate groups are fully converted to Na^+ salts. Beyond pH 11 swelling is reduced, as the ionic strength of the bulk solution diminishes the osmotic pressure differential. Similarly, swelling is reduced by the presence of salt.[8,10]

Carboxylate formation is promoted by pH and temperature elevation (saponification of carboxylic esters and alkaline degradation).[5,7,11] Alkaline peroxide initiates oxidation of lignin and formation of more carboxyl groups.[12] Oxidation of reducing-end groups and diols in carbohydrates may also result in carboxyl group formation.[13,14] Furthermore, peroxide bleached pulps display a high ionic charge in relation to acidic group content, indicating that phenolic groups in lignin become ionized.[15]

Swelling of wood chips is enhanced by extraction. Cohesive forces in the wood gel originate from the strength of the lignocellulose matrix.[16] During growth, the cell wall is expanded by the introduction of more rigid lignin, displacing the flexible carbohydrate matrix and causing the formation of built-in stresses. Removal of material releases the stress and results in more porous cell walls and leads to both higher swelling rate and higher maximum swelling.[6,17,18] Increased swelling with lignin and carbohydrate removal was found for high yield sulfite pulps.[19]

Figure 1 illustrates that wood cell walls (figure 1A) are built up of clusters of cellulose fibrils, surrounded by lignin-hemicellulose matrix (figure 1B, after Kerr and Goring[20]). Scallan's honeycomb model for cell wall swelling[16] can also be used to visualize in more detail swelling of cellulose (figure 1C). Voids between the cellulose fibrils and within the hemicellulose-lignin matrix are accessible to water-soluble (spherical) molecules, with a

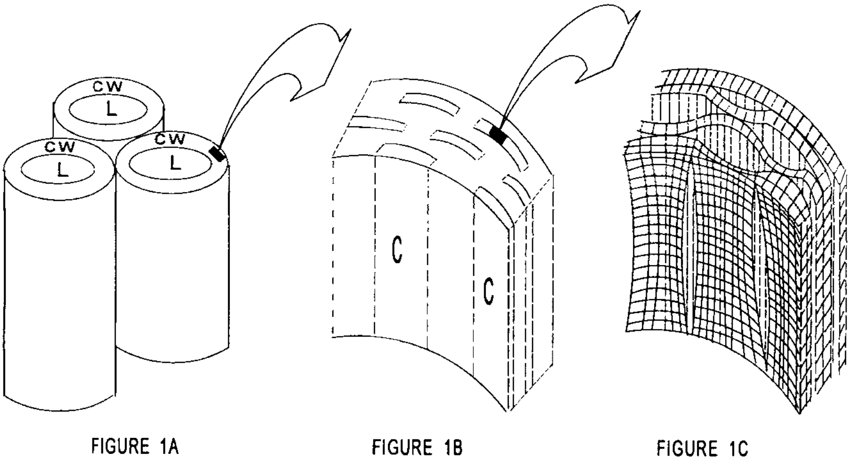


FIGURE 1A-C. 1A: Model of wood fibers (CW: cell wall, L: lumen), with 1B: fiber wall material (C: cellulose fibrils surrounded by a lignin-hemicellulose matrix, after Kerr and Goring[20]) and 1C: insight within cellulose fibrils (the honeycomb model for cell wall swelling by Scallan[16] is used to visualize swelling in more detail).

smallest diameter varying from 0.8 nm (glucose) to 14 nm (dextran 100)[17], confining the minimum distances of accessible pores (at the fiber surface).

Heating lignin-containing pulps at 70 °C and higher also enhances swelling. At this temperature wet lignin is softened, allowing hemicellulose expansion.[21-23] Hemicellulose contributes most to fiber swelling, but heating has no large impact on swelling of hemicellulose as wet hemicellulose is already softened at room temperature.[24,25]

In this article the effects of APMP impregnation conditions on pulp yield, chemical composition and swelling of hemp woody core chips are examined. Special attention is given to NaOH concentration, which has a large effect on hemicellulose content[26] and its influence on swelling. The effects of NaOH concentration at room temperature and 70 °C, and at 70 °C with peroxide addition are evaluated.

RESULTS AND DISCUSSION

1. Pulp Yield, Xylan and Lignin Fractions

The effects of impregnation on pulp yield, xylan and lignin removal are shown respectively in figures 2-4. At ambient temperature, more cell wall material is removed with higher NaOH concentrations (figure 2), however beyond 1M the rate of extraction was diminished. At 70 °C, increased amounts of material are extracted. At 70 °C and using the peroxide recipe, even more material from hemp woody core is removed. Apparently, both temperature elevation and peroxide addition promotes extractability.

The residual xylan fraction (amount on pulp multiplied with yield and divided by original xylan content) curves in figure 3 resemble the yield curves. Xylan extraction is almost complete at 70 °C, with 2M NaOH and peroxide addition. Nelson and Schuerch[27,28] found similarly for milled hardwood that higher amounts of hemicellulose could be extracted at higher temperatures.

For samples extracted at 70 °C, uronic acid content was measured. Initially, hemp woody core contains a high amount of uronic acid (8.4% uronic acid on 17.6% xylan, table 1), compared with 2.2 to 6.3% for extractive-free hardwood species[29]. This may be due to residual pectic acids (extractives), that are removed with NaOH[26]. The uronic acid content in the samples treated with NaOH is lower and proportional to the xylan content, with a ratio of 0.37 ± 0.02. Peroxide treatment, up to an alkalinity of 1M, gave a ratio of 0.30 ± 0.04. It is probable that this somewhat lower ratio is the result of preferred solution of fractions with higher uronic acid contents, this explanation was also proposed for similar results with alkaline pulping.[30] The ratio at 2M NaOH is much higher, but both xylan and uronic acid contents are low, respectively 1.5% and 1.8%.

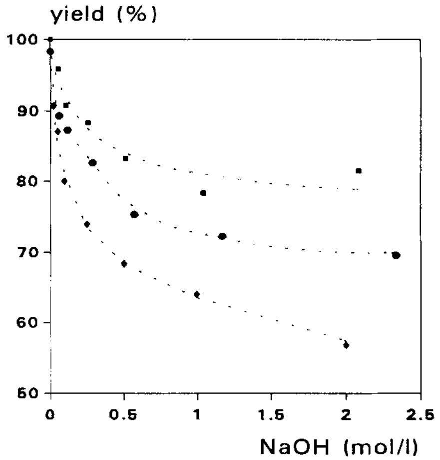


FIGURE 2

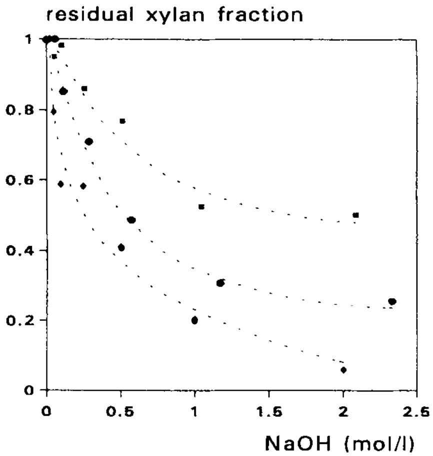
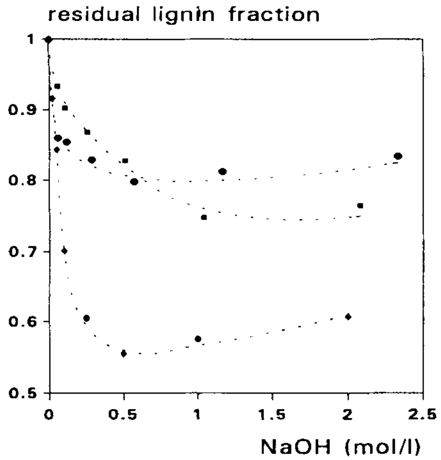


FIGURE 3



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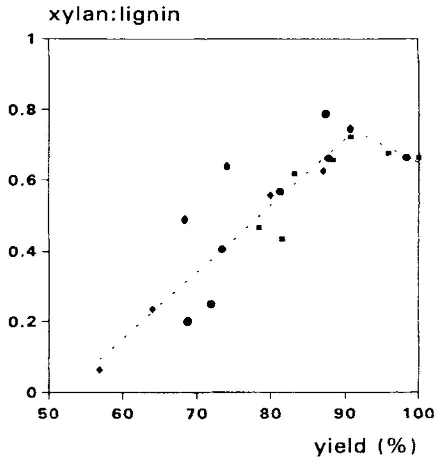

FIGURE 5

FIGURE 2: Yield for hemp woody core chips after impregnation and washing; impregnation at varying NaOH concentrations, at 20 °C (■), 70 °C (●), 70 °C with peroxide addition (♦). FIGURE 3: Xylan fraction for hemp woody core chips after impregnation and washing; impregnation at varying NaOH concentrations, symbols as in figure 2. FIGURE 4: Lignin fraction for hemp woody core chips after impregnation and washing; impregnation at varying NaOH concentrations, symbols as in figure 2. FIGURE 5: Xylan:lignin ratio for hemp woody core chips after impregnation and washing; impregnation at varying NaOH concentrations, symbols as in figure 2.

TABLE 1
Pulp Yield, Xylan and Uronic acid content, and their ratio for chips treated at 70 °C with and without peroxide

	alkalinity as [NaOH] (mol/l)	yield (%)	xyl.[1] on pulp (%)	uronic acid[2] on pulp (%)	uronic acid: xyl. ratio
treatment at 70 °C	0	98.3	17.6	8.41	0.48
	0.059	89.3	19.9	7.07	0.36
	0.12	87.3	16.9	5.78	0.34
	0.29	82.6	14.9	5.73	0.39
	0.57	75.4	11.2	4.51	0.40
	1.2	72.3	7.35	2.69	0.37
	2.3	69.6	6.33	2.49	0.39
treatment at 70 °C with H_2O_2 addition[3]	0.020	90.8	19.7	4.77	0.24
	0.052	87.1	15.8	4.46	0.28
	0.10	80.0	12.7	4.31	0.34
	0.26	74.0	13.7	3.66	0.27
	0.51	68.4	10.4	3.18	0.31
	1.0	64.0	5.51	2.09	0.38
	2.1	56.9	1.79	1.50	0.84

1. xylose units on pulp calculated as polymer constituents (xylan)
2. uronic acid residues on pulp calculated as glucuronyl polymer constituents (e.g. glucuronic acid side groups of xylan)
3. including silicate (added for H_2O_2 stabilization, increasing alkalinity with 0.02 M)

The lignin fraction curves in figure 4 show a pattern deviating from yield and xylan fraction curves. For samples treated without peroxide a relatively high residual lignin fraction, more than 75%, remains in the chips. The effect of temperature elevation alone on lignin removal is small. Lower lignin contents were obtained after similar treatment with peroxide addition, resulting in a high xylan:lignin ratio for some samples (figure 5).

Less lignin is extracted at alkalinities of 1 and 2M, than with 0.5M NaOH at 70 °C, both with and without peroxide addition. Also, at these higher alkalinities, less lignin is extracted at 70 °C than at 20 °C. Possibly, physical factors inhibit lignin extraction at higher NaOH concentrations. The softened, rearranged lignin droplets may be enclosed in the swollen cell wall, while the more linear xylan fragments successfully find their way through the narrowed pores.

2. Acidic group content

Acidic group content was measured, as these groups are involved in hydration and swelling[8], the results are shown in figure 6.

For chips treated at ambient temperature with demineralized water only, an acidic group content of 100 mmol/kg dry pulp is found. Treating chips at ambient temperature with 0.05M NaOH raised the measured acidic group content towards 400 mmol/kg. The increase is expected, since carboxylic esters are saponified and carboxylic groups are ionized and converted to Na^+ salts.[5,7,8,10] The measured acidic group content is relatively high, compared to 170 mmol/kg reported for mechanical aspen and black spruce pulp (after treatment with 0.05M NaOH at ambient temperature).[7]

Chips treated at 70 °C with 0.05M and 0.1M NaOH (with or without peroxide addition) also show a rise of acidic group content. Lower amounts of acidic groups are found using 0.25M NaOH and higher and the samples contain less acidic groups than the chips treated at ambient temperature. This is probably the result of the extraction of (glucurono)xylan (containing most of the carboxylic groups). The values for hemp woody core at lower yields are in the range of 201 mmol/kg, reported for high yield (66%) kraft pulp.[31]

Compared to the use of NaOH only, more acidic groups are found when hydrogen peroxide is used, which was expected as the result of oxidation reactions in lignin and reducing end groups and diols in carbohy-

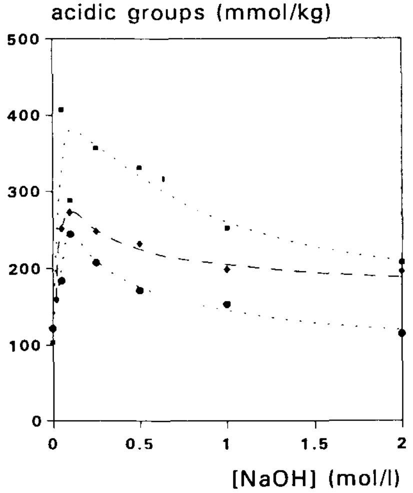

FIGURE 6

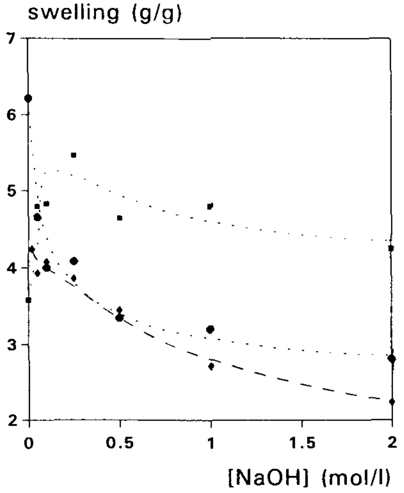

FIGURE 7

FIGURE 6: Acidic group content measured in hemp woody core chips after impregnation and washing; impregnation at varying NaOH concentrations at 20 °C (■), 70 °C (●), and 70 °C with peroxide addition (♦). FIGURE 7: Swelling measured in hemp woody core chips after impregnation and washing; impregnation at varying NaOH concentrations, symbols as in figure 6.

drates, with formation of more carboxyl groups[12-14] and ionization of free phenolic groups in lignin.[15]

3. Fiber Swelling

After impregnation, material is removed from the hemp woody core chips and is replaced by water. Swelling occurs when the amount of water that is taken up by the fibers exceeds the amount of extracted material. The amount of water present within the fibers (w/w) has been measured with the fiber saturation point (fsp) method, which is based on the solute exclusion technique (measuring the amount of water within the fibers that is inaccessible to large dextran macromolecules).[32-34]

The results are shown in figure 7. Using demineralized water, raising the temperature to 70 °C almost doubles fiber swelling, presumably as the result of lignin softening[21-23]. Using NaOH at ambient temperature, swelling increases with concentrations up to 0.25M. Higher NaOH concentrations promote shrinkage, accompanied by material removal. At 70 °C increasing NaOH concentrations results in decreased swelling, with lower values than at ambient temperature for equal NaOH concentrations. Thus, temperature rise combined with alkaline extraction does not improve swelling of hemp woody core, in contrast with swelling of softwood or hardwood after material removal.[18,19]

Light aspenwood absorbed twice as much sulfite cooking liquor (at about 70 °C) as birchwood, which was attributed to its lower density (300 kg/m^3), compared to birch (500 kg/m^3).[33] The density of hemp woody core, 200 kg/m^3, is even lower. Thus, the described phenomena can be attributed to the originally spacious structure of hemp woody core fibers, allowing maximum absorption with demineralized water at 70 °C. Consequently, higher NaOH concentrations mainly promote extraction, accompanied by pore fusion, resulting in shrinkage.

Swelling was compared with yield, lignin or xylan contents, xylan:lignin ratio and acidic group contents. For samples treated at 70 °C under alkaline conditions, best correlation was found with xylan:lignin ratio ($r^2 = 93\%$), as is illustrated in figure 8, omitting the value found for swelling in demineralized water. This higher water absorbency of hemp woody core chips at 70 °C may be explained by the presence of hydrated pectic substances, that are dissolved with NaOH[26]. The samples treated at ambient temperature show little correlation with xylan:lignin ratio. Here, the best correlation was found with acidic group content ($r^2 = 69\%$), as is illustrated

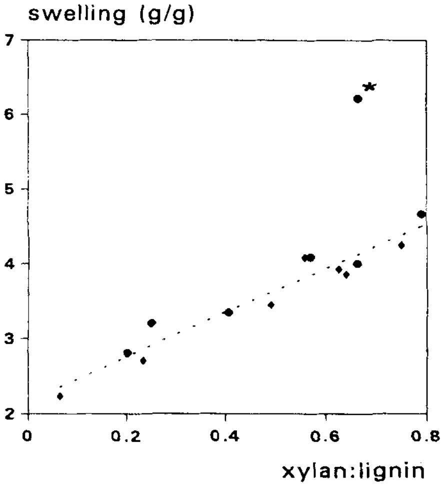

FIGURE 8

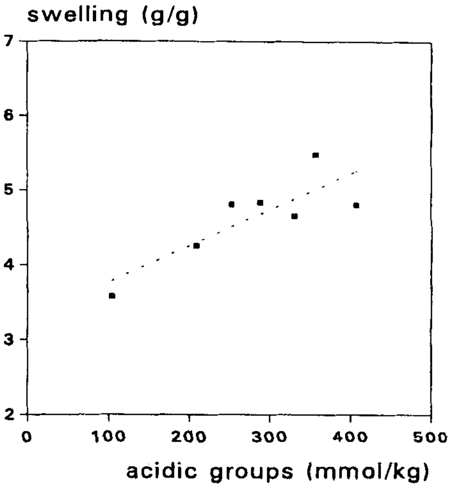

FIGURE 9

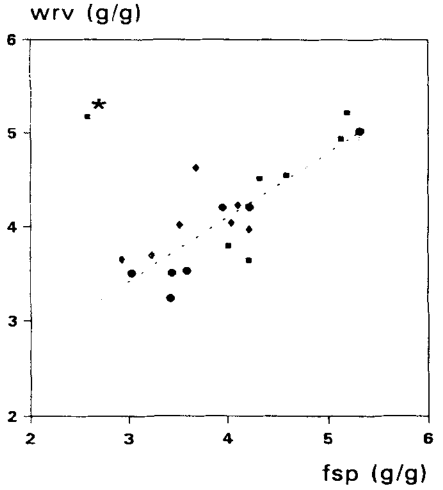

FIGURE 10

FIGURE 8. Swelling of hemp woody core chips (calculated with fsp) versus xylan:lignin ratio at 70 °C (●) and at 70 °C with peroxide addition (♦); the sample treated with demi water (●*) is excluded for regression line (....) calculation. FIGURE 9. Swelling of hemp woody core chips (calculated with fsp) versus acidic group content at 20 °C (■) and regression line (....). FIGURE 10. Wrv versus fsp; the sample treated with demi water at 20 °C (■*) is excluded for regression line (....) calculation.

in figure 9. Apparently, the effects of acidic group content are strongest at ambient temperature. While at 70 °C, when lignin is softened, xylan:lignin ratio becomes the most important factor of the features measured.

The water retention value (wrv), the water held by wet fibers after centrifuging under standard conditions[36,37], can be used as less time consuming alternative for fsp measurements.[38] A comparison of fsp and wrv for the hemp woody core samples (figure 10) shows that when no chemicals are used at ambient temperature, wrv is high and fsp is low. Possibly, at ambient temperature extractives and relatively voluminous xylan clusters cause a high wrv, but also shield cavities in the fibers, thus preventing entrance of dextran molecules (causing a low fsp). Temperature rise causes lignin softening, apparently changing the fiber structure and accessibility of pores for dextran molecules. Excluding this value resulted in a linear relationship between wrv and fsp as shown in figure 10, with $r^2=70\%$. It thus follows that for measuring alkaline swelling of hemp woody core, for values up to 5 g/g, wrv may be used as indication of fsp, with considerable care. Compared to literature values[6,7], the measured fsp and wrv are very high. Apparently, the spacious structure enables maximal utilization of water absorbing capacity (related to the high acidic groups content and the xylan:lignin ratio) within the hemp woody core fibers.

4. Pore Size Distribution

How alkaline peroxide treatment is affecting the distribution of water within the fibers, is reflected in pore size distribution.

Pore size distribution can be investigated with size exclusion chromatography, as developed by Stone and Scallan.[33] However, the method is very time consuming, while only the minimum accessible pore size distribution is evaluated. Pores within the fibers that contribute to swelling, may not necessarily be accessible from the outer surface for larger particles.

Alternatively, pore size distribution can be investigated qualitatively with ^{1}H NMR spin-spin relaxation[39], a faster method that also investigates the inner fiber wall. Spin-spin relaxation time of water molecules, T_2, increases with pore size, as molecules close to a surface have a shorter NMR relaxation time than those of an unperturbed bulk liquid. Charged molecules of a surface also affect T_2 positively.

Pore size distribution of five selected hemp woody core samples was studied with spin-spin relaxation, tables 2 and 3 showing the characteristics of the samples, with the corresponding T_2 values and relative pore volumes (calculated by integration). The most remarkable feature is that two or three separate apparent pore size distribution groups were found in each sample. As T_2 is not necessarily linearly proportional to pore size increase (chemical composition of pore wall also influences relaxation time), the observed separate apparent pore size distributions may in fact be the result of similar apparent pore size distributions, with differently charged pore walls. It is thus conceivable that different apparent pore size distributions are observed within cellulose fibrils, the surrounding lignin-hemicellulose matrix and in the middle lamella near the fiber surfaces respectively.

Supposing that apparently small pores result from lower ionic charge, the lowest T_2 is found for pores in the middle lamella, with relatively high lignin concentrations (A); higher T_2 is found for pores within cellulose (B) and the largest T_2 is found for pores in the lignin-hemicellulose matrix (C) (electrostatic repulsion of carboxylic acid groups in hemicellulose). The following explanations are based on these assumptions.

Raising the temperature (in demineralized water for samples 1 and 2, and at an alkalinity of 0.1M for samples 3 and 4) results in softened lignin and shrinkage of the apparently small pores (A, in table 3).

TABLE 2
Yield, Lignin, Xylan and Acidic group content.

treatment	yield (%)	lignin on start (%)	xylan on start (%)	acidic group content (mmol /kg)
1. demi water, 20 °C	100	26.1	17.4	104
2. demi water, 70 °C	98.3	26.0	17.3	122
3. 0.1M NaOH, 20 °C	90.8	23.6	17.1	288
4. 0.1M NaOH, 70 °C	87.3	22.3	14.8	245
5. 0.1M NaOH + H_2O_2, 70 °C	80.0	18.3	10.2	273

TABLE 3
FSP, Swelling, Relative Swelling, Relaxation time (T_2) and Pore Volume Distribution.

treatment	fsp (g/g)	swelling (fsp+1)* yield (g/g)	rel. swelling (3.58 = 100%) (%)	T_2 (10^{-3}s)	pore volume within sample (%)
1. demi water, 20 °C	2.58	3.58	100	A. 0.068 B. 0.142 C. 0.357	39.1 44.8 16.1
2. demi water, 70 °C	5.32	6.22	173.7	A. 0.047 B. 0.087 C. 0.197	13.6 44.3 42.1
3. 0.1M NaOH, 20 °C	4.32	4.83	134.9	A/B. 0.070 C. 0.245	78.8 21.2
4. 0.1M NaOH, 70 °C	3.59	4.00	111.7	A. 0.048 B. 0.102 C. 0.276	28.7 50.3 21.0
5. 0.1M NaOH + H_2O_2, 70 °C	4.10	4.08	114.0	A. 0.080 B. 0.204 C. 0.586	46.1 35.2 18.8

Increasing alkalinity to 0.1M (comparing samples 1 and 3 at 20 °C, and samples 2 and 4 at 70 °C) decreases yield and enlarges acidic group content (table 2), in addition effects on apparent pore size differ at 20 and 70 °C (table 3). At 20 °C more and smaller pores are formed within the lignin-hemicellulose and cellulose matrices (B,C). Pores of apparently medium size within cellulose fibrils (B) are shrunk to about the same size as those within lignin (A). At 70 °C fewer, but larger pores are formed within the lignin-hemicellulose and cellulose layers (B,C), and more of the pore volume is found within the lignin area (A).

Addition of peroxide (comparing samples 4 and 5) causes further yield loss and a decreased xylan:lignin ratio, but also results in remarkably higher T_2 and enlarged apparent pore sizes, especially in the lignin-hemicellulose and cellulose matrices. Possibly this is what makes peroxide attractive for high yield pulp production (apart from the bleaching effect), enhancing fiber flexibility and fibrillation by creating microstructure.

CONCLUSIONS

For hemp woody core, maximum swelling was found after treatment with demineralized water at 70 °C (lignin softening, without material removal). NaOH addition not only increases acidic group content, but also promotes material removal (extraction of hemicellulose). In contrast to wood species, swelling within the hemp woody core fiber is not enhanced by decreasing yield. Probably, the low density of the hemp woody core chips (in comparison with softwood and hardwood) allows relatively high water absorption, with the result that material removal does not enhance further expansion of remaining material.

Alkaline swelling of hemp woody core at 70 °C, was found to correlate with xylan:lignin ratio. At ambient temperature some correlation between swelling and acidic group content was found.

Examining pore sizes by ^1H NMR spin-spin relaxation measurements, separate pore size distribution groups were found within each sample. This previously unreported phenomenon could be a result of varying chemical and physical conditions within the hemp woody core cell wall. Smaller T_2 and apparent pores sizes are expected to be situated in the less polar lignin mass, higher T_2 and apparently bigger pores in the cellulose fibrils, and the highest T_2 and apparently biggest pores in the lignin-hemicellulose matrix (electrostatic repulsion of carboxylic groups).

Addition of peroxide results in remarkably enlarged apparent pore sizes. Possibly this combination of material removal and increased pore size is necessary for fiber separation and fibrillation.

EXPERIMENTAL

Presteamed hemp woody core chips, as used for APMP trials at our institute (2 g, length: 12.1 mm, width: 3.8 mm, thickness: 1.3 mm, all averages), were impregnated (after removal of air from the chips through evacuation) for 90 min with an excess of reaction liquor, using 200 ml demineralized water or NaOH (analytical grade) solution (of 0.05, 0.1, 0.25, 0.5, 1 or 2M). The experiments were carried out at ambient temperature or at 70 °C. Also a series with peroxide addition was carried out at 70 °C. The used peroxide recipe, time and temperature are based on preliminary trials and literature data[3,40]. Hemp chips were impregnated with 100 ml demineralized water. Sodium silicate (technical grade, 3 ml 36%), diethylenetriaminepenta-acetate (DTPA, 1 ml 40 g/l Dissolvine D40 technical grade), and magnesium sulfate (analytical grade, 1 ml 10 g/l) were added to a NaOH solution, with hydrogen peroxide (technical grade, 3 ml 30.4%) as the last ingredient. The amount of NaOH was adjusted, as silicate increased the alkalinity with 0.02 M. The total volume in which the chemicals were dissolved was 100 ml, which was added immediately to the 100 ml demineralized water in which the chips were impregnated and put in temperature bath at 70 °C for 90 min. The hydroxide concentrations were 0.02, 0.05, 0.1, 0.25, 0.5, 1 and 2M. DTPA is added as chelating agent, to remove trace metals that may react with peroxide ions, minimizing catalytic decomposition of hydrogen peroxide. Sodium silicate is added to buffer and stabilize the hydrogen peroxide to minimize decomposition. Magnesium sulfate is added to form a colloidal suspension of magnesium silicate, adsorbing trace metal catalysts.[40]

All data were compared with the results on a reference sample obtained by impregnation with 200 ml demineralized water for 90 min at ambient temperature (yield = 100).

The resulting chips were washed 3 times with 500 ml hot demineralized water and 3 times with cold 500 ml demineralized water, after which the chips were stored overnight in 500 ml demineralized water at 6 °C. Duplicate samples were used to determine: 1. dry matter content,[41] 2. Klason lignin[42], soluble lignin[43] and carbohydrate composition[26], 3. acidic group content[31,45], 4. uronic acid content[44] (for samples treated at 70 °C), 5. fiber saturation point (fsp)[32-34], and 6. water retention value (wrv)[36,37].

The acidic group content of the chips was measured using conductometric titration.[31,45] The chips were extensively washed in demineralized water, disintegrated in 100 ml demi water for 25 seconds (in a blender, total volume 200 ml) and were further examined in a never-dried condition. The fiberized material was converted to hydrogen form (soaked twice in 0.1 M hydrochloric acid for 45 min and washed with demineralized water), drained and dispersed in 450 ml 0.001M NaCl (in demineralized water). 2 ml 0.1M hydrochloric acid was added, after which the fiberized material was titrated under nitrogen atmosphere with 0.1M NaOH, dispensed from a microburette. Every 5 min 0.5 ml was added, which allowed sufficient time to reach equilibrium.

Fsp of the chips was determined with the solute exclusion technique, using dextran 2000 (blue dextran, as used in calibration of gel filtration columns) with an average diameter of 56 nm, concentrations of dextran 2000 solutions were determined with UV-VIS measurements at 616 nm (the wavelength at which maximum absorption was found at our laboratory, close to the value of 620 nm used by others[46,47]).

Wrv of the chips was determined after centrifuging with a centrifugal force of 900g, for 30 min.[36,37]

For swelling calculations, fsp values were used. Fsp is based on one gram of dry material, which will contain an increasing number of fibers as the yield is lowered. To judge whether swelling (increase in cell wall) occurs, the amount of solid material plus water in a fixed number of fibers must be compared.[6] For simplicity, this was measured gravimetrically instead of volumetrically (as the material density is not measured, and probably changing with material extraction). Swelling is calculated as (fsp + 1)*yield, the total amount of water added to the amount of fibers after extraction, calculated on 1g starting material.

Pore size distribution in the chips was measured qualitatively, using ^1H NMR spin-spin (T_2) relaxation measurements. The basic idea is that the molecules of water in the vicinity of a solid surface are perturbed because of the interaction with the solid surface[39]. The measurements were performed on a Bruker AMX 400 wb spectrometer, at a frequency of 400 MHz. A Carr-Purcell-Meiboom-Gill (CPMG) pulse sequence was used with a 90° pulse of 64 μs and 180° pulses of 128 μs at intervals of 200 μs. Only the maximal points of 8192 echoes per sequence were acquired resulting in a multi-exponential decay curve. To improve signal to noise ratio 8 accumulations were recorded. All experiments were performed at room temperature

(21 °C). A continuous analysis method was used to calculate values of T_2, with a computer program performing a non-linear least-square fit.[48]

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