The hemicellulose composition of pulp fibers and their ability to endure mechanical treatment

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ABSTRACT: Two pulps of different hemicellulose content were subjected to high-intensity shear forces in a laboratory mixer to damage the fibers. The ability of the fibers to resist the mechanical treatment was evaluated by comparing their strength to that of undamaged pulps.

The study showed that pulp produced at high hydroxide ion concentration, which resulted in lower xylan and higher glucomannan content, was sensitive to mechanical treatment. The pulp strength decreased, evaluated as tear versus tensile index and as rewetted zero-span tensile index. Pulp with a higher xylan and lower glucomannan content could be subjected to mechanical treatment without losing strength.

Application: By choosing the appropriate cooking parameters, a pulp with a certain carbohydrate composition can be obtained. The carbohydrate composition of pulp fibers influences their ability to resist mechanical damage.

The superior strength of laboratory-cooked pulp compared with corresponding industrially produced pulp is well known. The concept of "strength delivery" quantifies the strength of mill pulp as a percentage of the strength of laboratory-cooked pulp. The strength delivery of softwood kraft pulps is reported to range from 65% to 85% [1-6], measured as tear index at a given tensile index.

Many studies have shown that pulp inside the digester is stronger than pulp discharged from the digester [1-4, 7, 8]. It has been possible to assess the loss in strength caused by discharge by comparing the strengths of pulp in baskets hung in the digester and discharged pulp. Fibers are mechanically damaged as they pass through blow-line valves and pumps [2, 3, 9]. High temperature when blowing the pulp has a detrimental effect on pulp strength [9, 10]. However, high temperature is not the only hazard encountered by fibers, as damage occurred even when the discharge temperature was below 100ºC [7]. Chemical degradation of cellulose has been ruled out as a reason for the strength loss, as it could not be related to losses in pulp viscosity [3].

One apparent difference between the fibers of laboratory-cooked and mill pulp is the shape of the fibers. Mill pulp fibers are more curled, with more kinks and dislocations [2, 3, 6, 11, 12]. Such fiber deformations reduce the strength of the pulp [12-16]. Straight fibers can bear a load along their entire length, whereas curled fibers are not as efficient in load transfer. Fiber deformations increase along the fiber line, from brown stock to bleached pulp [12, 17, 18]. The length of mill pulp fibers and fiber strength (measured as zero-span tensile strength) has been shown to be somewhat inferior to that of corresponding laboratory pulps [6].

Exposing cooked chips to mixing at the end of an alkaline cook decreases tear strength and rewetted zero span strength [19]. The deterioration in strength was attributed to an increased size of the pores in the fiber wall as the mechanical action separates the fibril aggregates of the fiber wall [20]. This gives fewer bonds between fibrils in the fiber wall, which results in an inferior fiber strength. Medium consistency handling of pulp introduces curl to fibers [14, 15]. The decrease in pulp strength continues through the bleach plant as well, as shown in a survey by Fahey [21].

The survey could not assess whether chemically degraded parts of fibers are more susceptible to damage from mechanical action or mechanically damaged parts are more susceptible to chemical degradation. Nevertheless, it seems unavoidable that fibers will be damaged as they are transported to and treated in each process step involved in transforming wood to fully bleached pulp. However, pulp can lose strength in several places along the fiber line. In a scenario involving strong unbleached pulp from Mill A and weaker unbleached pulp from Mill B, the pulps on their way through the fiber line may lose strength to different extents, so that in the bleached state pulp B ends up as the stronger pulp. Reports of such cases can be found in the literature [22, 23]. A

more uniform cooking has been claimed to give pulp with lesser tendency to acquire damage [24]. Spruce fibers have been shown to be more damaged and lose strength more than pine fibers when subjected to mechanical treatment [25].

Different pulp fibers have different abilities to endure mechanical treatment and it would be of interest to determine what properties make fibers resilient. The hypothesis for the investigation in this paper is that the hemicellulose composition of the pulp affects its ability to resist mechanical treatment. By choosing the suitable cooking conditions, pulp can be obtained with a hemicellulose composition that ensures durable fibers.

EXPERIMENTAL

Pulping for carbohydrate composition survey

Spruce chips from the Hallsta pulp mill were air dried before screening in a laboratory chip screen, using a chip fraction between 2 mm and 6 mm in thickness. We performed further screening by hand, removing over-thick chips and chips containing knots and bark. We charged 25 g of chips (oven dry weight) in steel autoclaves of 1 L in volume. The autoclaves were evacuated for 30 min before the cooking liquor was charged. The white liquor used in the experiments was made from appropriate amounts of stock solutions of sodium hydroxide and sodium hydrogen sulfide and diluted with deionized water. To have constant concentrations of cooking chemicals, we used a liquor-to-wood ratio of 75:1. We obtained the total sodium ion concentration of 2 mol/L by sodium chloride addition. The autoclaves were placed in a glycol bath at a temperature of 70ºC and ramped by 1ºC/min. In each set of cooking parameters, the H-factor was varied to get three pulp samples with kappa numbers ranging from approximately 35 down to 20.

The delignified chips were washed for about 12 h with deionized water and thereafter defibrated in a water-jet NAF defibrator. The pulps were centrifuged to a dry solid content of between 25% and 30%.

	Low [OH-]	High [OH-]
[OH-] mol/L	0.3	1.0
[HS-] mol/L	0.2	0.2
[Na+] mol/L	2.0	2.0
Liquor-to-wood, L/kg	30:1	30:1
Temperature, ºC	164	147
Cooking time, h	4	4
H-factor	2500	520

I. Conditions in the cooks.

Pulping for strength testing

Each cooking batch was 700 g moisture-free chips. The chips were cooked at a high liquor-to-wood ratio, 30 L/kg. NaCl was added to the cooking liquor to reach a sodium ion concentration of 2 mol/L. For chemical charges, cooking temperatures, and H-factors, see **Table I**.

Conditions in the cooks

We performed pulping in a forced-circulation laboratory digester. After charging with chips and closing the digester, we steamed the chips for 5 min. The circulation of the cooking liquor was then started and the increase in temperature was approximately 1ºC/min until the desired cooking temperature was reached. Emptying the digester of the black liquor and cooling with deionized water terminated the cooking.

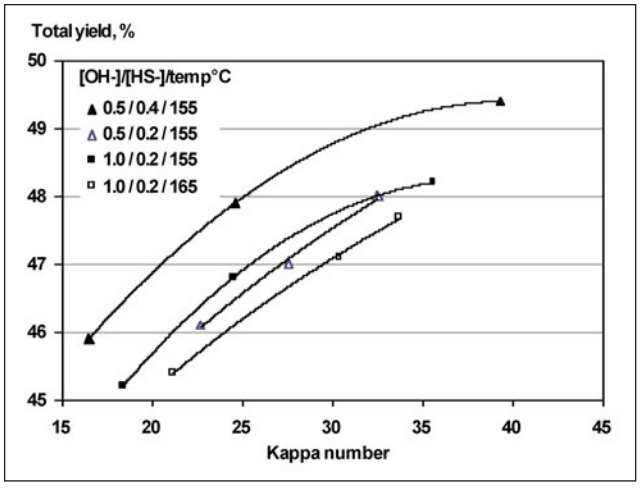
The delignified chips were washed in the digester for 12 h with deionized water and thereafter defibrated in a water-jet NAF defibrator. The pulp was centrifuged to a dry solid content between 25% and 30%.

We simulated the mechanical action encountered by fibers in industrial processing, for example in pumps and dewatering presses, by mixing in a high-intensity Quantum mixer. The samples were disintegrated in a laboratory disintegrator for 10,000 revolutions and then dewatered in a Büchner funnel. We added deionized water and NaOH to achieve a pulp consistency of 10% and pH 13. The pulp samples, 160 o.d. pulp/sample, were placed in plastic bags and kept for 10 min in a water bath at a temperature of 70ºC before mixing for 60 sec at 2,100 rpm. We washed the pulps to neutral pH after mixing.

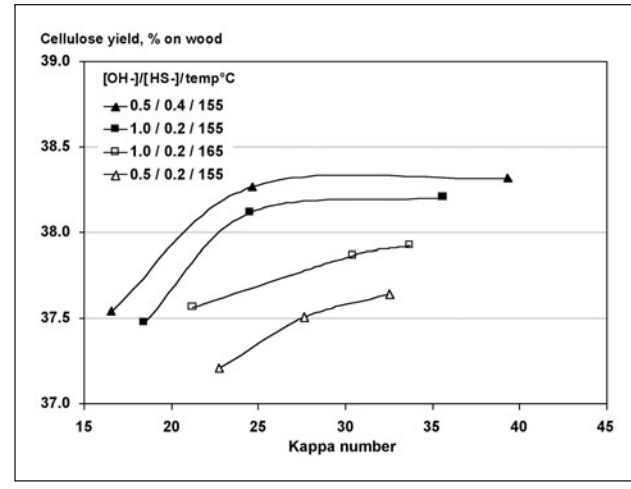
Before oxygen delignification, we disintegrated the reference pulps in a laboratory disintegrator for 10,000 revolutions (ISO 5263-1). The high-intensity mixed pulps were considered disintegrated by the mixing. Samples of 80 g o.d. pulp were

	D	Q	EP	D
Pulp consistency, %	10	4	10	10
ClO_2 charge, %	2.8			2.0
H_2O_2 charge, %			0.3	
EDTA, %		0.2		
$MgSO_4$, %			0.05	
Buffer, % of total weight sodium acetate/acetic acid				10
NaOH, %		Starting-pH > 4.8	1.5	
Temperature, ºC	70	90	70	70
Time, min	30	60	60	120

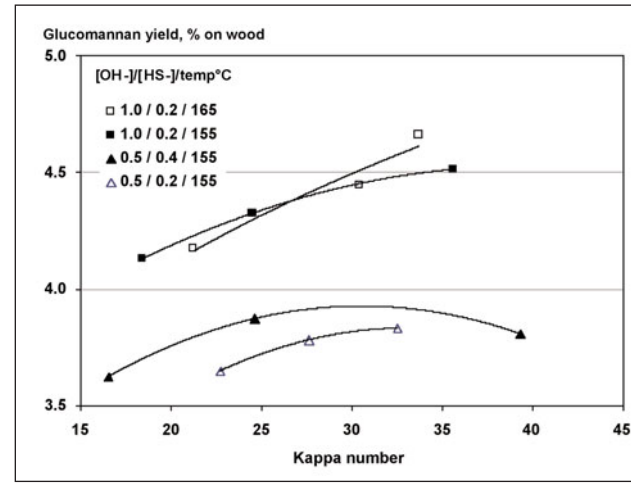
II. Conditions in bleaching.



1. Effect of pulping variables on total pulp yield.



2. Cellulose yield on pulp was affected by all variables tested.



3. Glucomannan yield was affected only by a change in alkali concentration.

brought to a 12% pulp consistency by adding deionized water, NaOH (2.7 weight-%) and $MgSO_4$ (0.5 weight-%) solutions. Next, the pulps were placed in stainless steel autoclaves. Oxygen gas of 6 bar was released into the autoclaves before they were put in a glycol bath at a temperature of 100ºC. After 10 min warming + 100 min reaction time, the autoclaves were cooled in a water bath. The pH of the residual liquor was between 11 and 12, the high-intensity-mixed pulps having a higher end-pH than the reference pulps.

The oxygen-delignified pulps were bleached according to (DQ)(EP)D under the conditions seen in **Table II**. The bleaching was performed in plastic bags and the pulps were washed between the stages.

Conditions in bleaching

We analyzed kappa number according to SCAN-C 1:77R, and pulp viscosity to ISO 5351. The carbohydrate monomers were analyzed using a sample preparation according to TAPPI T 249 cm-85 "Carbohydrate composition of extractive-free wood and wood pulp by gas-liquid chromatography," followed by IC-analysis. We calculated the amount of the different polymers in pulp according to Janson [26].

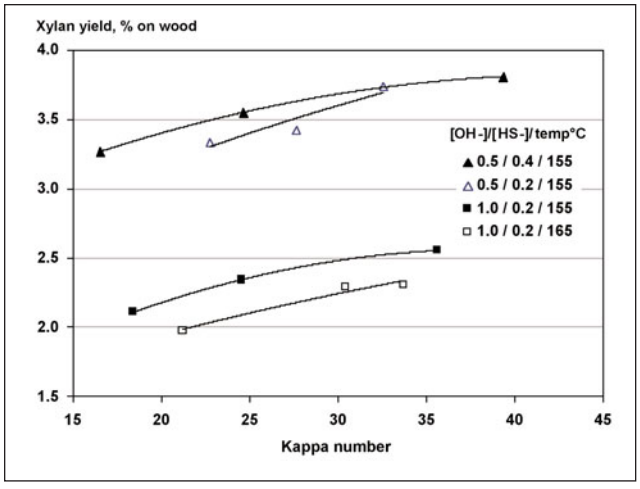
To test the strength of the bleached pulps, they were PFI-beaten between 0 and 4,000 revolutions, according to ISO 5264-2, and sheets were made according to ISO 5269-1. We analyzed the tear and tensile strengths according to ISO 1924-2 and ISO 1974, respectively. We conducted the zero-span tensile tests on sheets made of pulp beaten to 4,000 revolutions in the PFI mill. Curl and fiber length were also measured on a FiberLab3™.

RESULTS

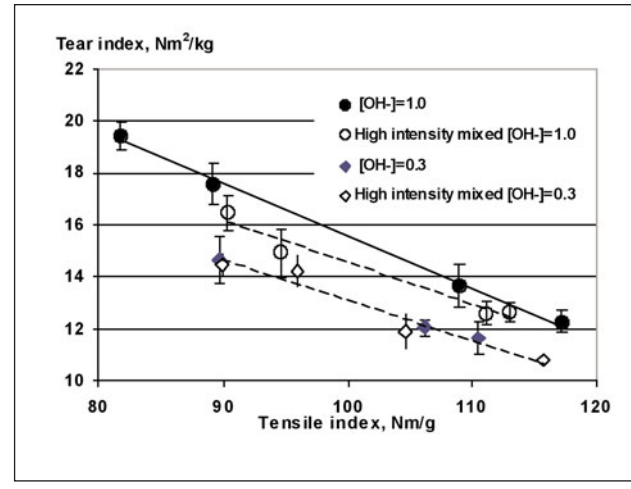
Influence of cooking parameters on pulp yield and carbohydrate composition

The influence of varied hydroxide ion, hydrogen sulfide ion, and temperature in a kraft cook on the total yield is shown in **Fig. 1**. As can be seen, at a certain degree of delignification, the difference in yield between the cooking conditions that led to the highest and the lowest yield was around 2%-units. According to this figure, it seems that hydrogen sulfide ion concentration and temperature had the largest effects on pulp yield, whereas cooking at 0.5 or 1.0 M hydroxide ion concentration did not affect the total yield. However, not only the amount but the composition of the carbohydrates in pulp were affected, and the two levels of alkalinity produced pulps with different carbohydrate composition, as is apparent in Fig. 1.

Figure 2 shows the cellulose yield in the pulp. A higher sulfide ion concentration gave a higher cellulose yield. Increasing the delignification rate by cooking at a higher alkali concentration was also beneficial for the cellulose yield, whereas increasing the temperature resulted in a lower cellulose yield.



4. A higher hydroxide ion concentration gave a lower xylan yield.



5. Tear index vs. tensile index; solid lines indicate values for pulps not high-intensity mixed, dashed lines after mixing. Error bars indicate standard variation in test procedure at 95%.

Varying cooking temperature had no effect on the glucomannan yield and neither did a change in hydrogen sulfide concentration have a significant effect (**Fig. 3**). Increasing the alkali concentration resulted in a pulp with a higher amount of glucomannan, due to increased delignification rate and thereby less time for glucomannan degradation to occur.

The xylan yield was even more sensitive to the alkali concentration than the glucomannan yield, as seen in **Fig. 4**. However, contrary to the glucomannan case, an increased hydroxide ion concentration led to a decreased xylan yield. Increased cooking temperature decreased the xylan yield slightly as well.

Influence of hemicellulose composition on endurance

Table III presents the content of the carbohydrate species, kappa number and viscosity of pulp obtained by cooking at different hydroxide ion levels, 1.0 mol/L and 0.3 mol/L. The total hemicellulose content was 0.7%-units higher for the pulp cooked at high [OH-], but the proportions between xylan and glucomannan differed substantially.

Relative carbohydrate composition, %	High [OH-]	Low [OH-]
Cellulose	83.9	84.6
Glucomannan	9.5	7.0
Galactan+arabinan	0.9	0.7
Xylan	5.7	7.6
Total amount of hemicellulose	16.1	15.4
Ratio $\frac{Cellulose}{Hemicellulose}$	5.21	5.49
Kappa number	32.7	31.5
Viscosity, mL/g	1110	850

III. Relative carbohydrate composition in pulp produced at different levels of hydroxide ion concentration.

In **Fig. 5** the results of the strength testing are presented as tear index vs. tensile index for the two pulps. To evaluate their ability to endure mechanical treatment, the pulps were mixed at high intensity. As can be seen, the pulp cooked at high [OH-] dropped to a lower tear strength level after the mechanical treatment. The strength of the pulp cooked at low [OH-] however, was not affected by the high-intensity mixing.

The fiber strength was estimated by measuring dry and rewetted zero-span tensile index, shown in **Table IV**. The ratio between dry and rewetted zero-span tensile indices gives an indication of the extent of local damage, the higher the value the less the damage. As can be seen in the table, the low-alkalinity pulp had a lower rewetted zero-span tensile index. However, as the pulps were subjected to high-intensity mixing, the rewetted zero-span tensile index and the ratio between rewetted and dry tensile indices were about the same for the high- and low-alkalinity cooked pulps.

DISCUSSION

The hypothesis behind this study was that pulps with different hemicellulose compositions react differently when subjected to mechanical treatment. The carbohydrate composition of the pulp is determined by the cooking conditions used. Cellulose is relatively resistant to alkaline degradation reactions [27-29]. As seen in Fig. 2, the cellulose yield varied only within 1%-unit by the variation in cooking parameters in our study. The hemicelluloses, glucomannan and especially xylan, are more affected by changes in cooking conditions. About three-quarters of the glucomannan present in wood is

		High [OH-]	Low [OH-]
***Not* high-intensity mixed**	**Dry zero-span index**, Nm/g	193 ±4.0	190 ±5.4
	Rewetted zero-span index, Nm/g	193 ±5.3	174 ±5.1
	Ratio $\frac{rewetted}{dry}$ **%**	100%	92%
After high-intensity mixing	**Dry zero-span index**, Nm/g	200 ±2.9	196 ±4.1
	Rewetted zero-span index, Nm/g	178 ±3.3	172 ±3.5
	Ratio $\frac{rewetted}{dry}$ **%**	89%	88%

IV. Fiber strength was measured as zero-span tensile index. Error at 95% confidence interval.

dissolved and degraded early in the cook, but the remaining quarter is quite stable in kraft cooking conditions [27]. Higher hydroxide ion concentration or higher temperature increases the rate of degradation, but at a certain degree of delignification the differences in glucomannan content due to changes in cooking parameters are small [29]. Lignin-carbohydrate complexes enriched in galactoglucomannan are easily removed from wood, whereas the remaining glucomannan, chemically bonded to lignin, is very hard to remove, even by harsh oxygen delignification [30].

Xylan is the component in wood most easily manipulated by varying the cooking parameters. It is sensitive to changes in hydroxide ion concentration [27, 29, 32]. This study shows also a decrease in xylan content when the alkalinity of the cook was increased. As a consequence, at low hydroxide ion concentrations in the kraft cook, a pulp with higher amount of xylan and lower amount of glucomannan is obtained. Conversely, at high hydroxide ion concentration the pulp will have more glucomannan and less xylan.

To study the ability of fibers to endure mechanical treatment, we used two pulps; one produced at high hydroxide ion concentration, the other at low concentration. The cooking time was the same in the two cooks, and so to have the same degree of dezincification, the cooking temperatures in the two cooks were 147ºC and 164ºC, respectively. In accordance with previous studies [32], the pulp cooked at high alkalinity had higher tear strength at a given tensile index (Fig. 5). After the high-intensity mixing, this pulp lost in strength, whereas the pulp cooked at low alkalinity was not affected. This is an indication that the pulp from the low-alkalinity cook was not sensitive to mechanical treatment. The zero-span tensile strength data in Table IV also indicate that the pulp cooked at high alkalinity did not endure mechanical treatment as well as the pulp cooked at low alkalinity. The rewetted zero-span tensile index is sensitive to local damage to the fiber wall, and will normally be lower than the dry zero-span tensile strength index [33-34]. The ratio between dry and rewetted zero-span tensile indices gives an indication of the extent of local damage, and the higher the value the less the damage. As the pulps were subjected to high-intensity mixing, the rewetted zero-span tensile index of the pulp cooked at high alkalinity dropped down to the level of the pulp cooked at low alkalinity. This again was an indication that pulp from the high-alkalinity cook did not endure mechanical treatment as well as the pulp cooked at low alkalinity.

If we adopt the theory that the mechanical treatment has disrupted the fibril structure of the fiber wall, thus reducing the fiber strength, as proposed by Robertsén and Joutsimo, our results imply that the strength of the pulp with a lower xylan content decreased due to defects of the fiber wall caused by the high-intensity mixing. Paavilainen has seen a relationship between higher xylan content and higher fiber flexibility [31]. Increased alkali charge decreased the amount of xylan in the pulp. As the pulps were subjected to mechanical treatment in a PFI mill, the lower the xylan content, the more pronounced was the reduction in fiber length. It is conceivable that a higher amount of xylan in the fiber renders it more flexible and thereby more resilient when subjected to mechanical stresses.

CONCLUSIONS

By applying the appropriate cooking parameters in a kraft cook it was possible to obtain pulps with different hemicellulose composition. The pulp with higher xylan content had a lower strength, measured as tear vs. tensile index, but mechanical treatment did not affect the strength level. The pulp fibers with lower xylan content acquired more local fiber wall defects, measured as rewetted zero-span tensile index, when high-intensity mixed and the mechanical treatment also caused loss of tear strength at given tensile strength. Thus, fibers with higher xylan content seem to be able to endure mechanical treatment better than fibers with lower xylan content. **TJ**

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INSIGHTS FROM THE AUTHORS

Studies on strength delivery and related fields have so far concentrated on finding the locations in the mill where fibers are damaged and what the damage is. However, fibers will invariably encounter mechanical stresses along the fiber line. In this article we used the concept of vulnerability of fibers to mechanical treatment.

We hypothesized that fibers with different properties have different abilities to withstand mechanical forces as they are discharged from the digester and transported through valves, pumps and various washing and bleaching equipment. In this article, we present results from studies on the vulnerability of pulps with large difference in carbohydrate composition.

In a previous study, we evaluated the vulnerability of pulps manufactured at different sodium ion concentrations. Other researchers have proposed that pulps with a high strength level are more sensitive to strength loss. Our present study supports this assumption, as the high-strength pulp lost strength upon mechanical treatment. However, in our other study the high-strength pulp was less sensitive to mechanical treatment. This implies that many different factors influence the vulnerability of fibers and it would be of interest to find out what chemical or physical characteristics of the fiber wall make them more resilient.

From a mill point of view, our article shows the deficiency in evaluating only the brown stock pulp strength and not considering the vulnerability to mechanical treatment. Pulps with different brown stock pulp strength may well be quite equal in strength after being transported through the entire fiber line.

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