Effect of reduced pulp xylan content on wet end chemistry and paper properties — a pilot scale study

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ABSTRACT: In this scale-up study, we examined the effects of using varying amounts of fibers with reduced xylan content in paper. Bleached birch kraft pulp was partially or fully replaced by alkali-extracted pulp, and the effects of this replacement on the wet end chemistry of the paper machine and the resulting paper properties were determined. Our results show that paper properties can be maintained or improved when optimizing the partial replacement of bleached birch kraft pulp with alkali-extracted pulp. The incorporation of alkali-extracted pulp in paper machine stock had a positive effect on first pass retention and retention of chemicals. However, careful optimization of chemical dosages is required because of the altered charge balance in the wet end.

Application: The results of this study can be applied to predict the implications of varying pulp xylan content on the wet end chemistry of the paper machine and the resulting paper properties.

Recently, the possibility of obtaining polymeric xylan as a side stream from an existing fiber line producing bleached hardwood kraft pulp has gained much interest. In general, xylan could be isolated by means of relatively simple process arrangements applying short alkaline extraction at room temperature [1-4]. The resulting xylan fraction represents a potential value-added product with several suggested end applications in areas such as papermaking, paper and board converting, the food industry, and even pharmaceuticals [5-9]. However, to maintain the process feasibility of this approach, it is a pre-requisite that the alkali-extracted pulp also remains applicable for papermaking.

The main difficulties related to the use of alkali-extracted pulp in papermaking include increased energy consumption in refining and somewhat altered fiber properties. Regardless of the wood species and pulping method, the reported characteristics of pulps with reduced hemicellulose content often include decreased pulp beatability and tensile strength, increased or similar tear strength, and comparable zero-span strength [10-14]. On the other hand, we recently showed that, by careful optimization of the extraction conditions, some of the negative effects on pulp quality can be prevented, and some of its properties may even be improved [4].

Another issue worth considering is that the fiber charge will be reduced together with the pulp xylan content. In softwoods and hardwoods, the fiber charge originates mainly from the 4-O-methyl-α-D-glucopyranosyluronic acid groups bound to the xylan backbone, and an anionic charge is generated through ionization of these groups under prevailing conditions [15]. Because the xylan-based anionic sites on fiber surfaces are the main retention sites for most papermaking additives, a reduced pulp xylan content is likely to have significant implications on the wet end chemistry of the paper machine.

In our previous work, we demonstrated that alkaline extraction of bleached kraft pulp reduces the amount of charged groups in fibers, which is then reflected in their ability to fix chemicals and fillers [16]. The aim of the present pilot scale study was to further clarify how alkali-extracted kraft pulp affects wet end chemistry and paper product quality. In addition, the present paper discusses the implications that varying pulp xylan content may have in the papermaking process.

MATERIALS AND METHODS

Elemental chlorine free (ECF)-bleached dried birch kraft pulp was obtained from a Finnish pulp mill. In order to prepare a pulp with reduced xylan content, 665 kg of this pulp was extracted with a mild solution of sodium hydroxide (0.56 M, 1 h at room temperature) as described in [4], and used as a fiber source in the paper machine stock. **Table I** shows the chemical compositions of the unextracted and alkali-extracted pulps.

	Unextracted	Alkali-extracted
Carbohydrate Composition		
Cellulose, %	74.6	80.7
Xylan, %	24.9	18.7
Glucomannan, %	0.5	0.6
Total, %	100	100

I. Relative carbohydrate compositions of unextracted and alkali-extracted bleached birch kraft pulps.

The unextracted and alkali-extracted pulps were refined to °SR 22 using a pilot-scale disc refiner with specific energy consumptions of 26.0 kWh/ton and 59.4 kWh/ton, respectively. The refined pulps were used as such or as mixtures to prepare stocks for a pilot paper machine producing fine paper with a basis weight target of 75 g/m² (**Table II**).

The pilot paper machine trials were conducted at Stora Enso Research Centre in Imatra, Finland. The pilot machine has a dilution-controlled headbox and a fourdrinier-type wire section. The temperature of the headbox was adjusted to 45°C. **Table III** lists the chemical doses and dosing points. The production rate was 60 m/min. The dried paper was reeled and cut into sheets.

The on-site precipitated calcium carbonate (PCC) used in this trial had a slightly anionic charge, scalenohedral crystal form, and a mean particle size around 2 μm, as determined by laser diffraction.

Pulp and paper properties

The relative carbohydrate composition of the pulps was determined after acid hydrolysis (SCAN CM 71:09 "Pulps - Carbohydrate composition"). The monosaccharide composition of the resulting hydrolysates was detected using high performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD).

The total organic carbon (TOC) in the wire water samples was determined using a TOC analyzer. Before the TOC analyses, the wire water samples were centrifuged for 15 min at 3000 rpm, corresponding to 2014 g. The turbidity of the wire water samples was measured with a Hach 2100P Turbidimeter (Hach; Loveland, CO, USA).

A Mütek SZP-06 system zeta potential device (BTG; Eclépens, Switzerland) was used to determine the zeta potential of the fibers, and a Mütek PCD-02 particle charge detector, using cationic poly-DADMAC as a titrant, was used to determine the cationic demand of the filtrates.

The fiber properties and pulp fines contents were determined using an L & W FiberTester (Lorentzen & Wettre; Stockholm, Sweden). The water retention value (WRV) and Schopper-Riegler (SR) number were determined according to standard methods ISO 23714 ("Pulps – Determination of water retention value [WRV])" and SCAN-C 19:65 ("Pulps – Determination of drainability – Part 1: Schopper-Riegler method"). The physical testing of the paper sheets was performed according to EN ISO 5269-1:1998 ("Pulps - Preparation of laboratory sheets for physical testing - Part 1: Conventional sheet-former method"). The z-directional strength of the paper samples was performed using a Scott bond method according to TAPPI T 569 ("Internal bond strength [Scott type]"). The ash content of the paper samples was determined according to TAPPI T 211 ("Ash in wood, pulp, paper, and paperboard: combustion at 525°C"). Formation of paper samples was determined with Ambertec Beta Formation tester (Ambertec; Espoo, Finland) according to SCAN-P 92:09 ("Paper and board – Beta-radiation based grammage formation measurement – Point source method").

The determination of $Cobb_{60}$ was performed according to the standard method ISO 535:1991 ("Paper and board – Determination of water absorptiveness – Cobb method"). The Hercules size test (HST) was performed according to TAPPI T 530 om-07 ("Size test for paper by ink resistance [Hercules-type method]"). The HST measurements were performed using a Hercules sizing tester (Hercules; Wilmington, DE, USA) with neutral green ink (naphtol green B, standard Fluka quality for microscopy and complexometry) and 85% reflectance.

Atomic force microscope (AFM) images were captured of

	100/0	75/25	50/50	25/75	0/100
Unextracted pulp, %	100	75	50	25	0
Alkali-extracted pulp, %	0	25	50	75	100

II. Mixing ratios of unextracted and alkali-extracted pulp in pilot trial.

Additive	Trade Name	Added Amount, %	Dosing Point
Cationic starch (wet end)	Raisamyl 50021	0.4	Mixing chest outlet
Alkyl ketene dimer (AKD)	EKA DR28HF	0.15	Level box outlet
Precipitated calcium carbonate (PCC)	On-site PCC	24	Between level box and fan pump
Cationic starch (retention)	Raisamyl 50021	0.15	Fan pump inlet (short circulation)
Cationic polyacrylamide (C-PAM)	Percol 47	0.015	After cyclone (short circulation)
Bentonite	Hydrocol SH	0.15	Before headbox (short circulation)

III. Chemical additives used in pilot trial.

freeze-dried fibers attached to a microscope glass plate using a Bruker Dimension 3100 atomic force microscope (Bruker; Billerica, MA, USA) operated in the tapping mode, using low spring constant silicon probes (k = 7.0 N/m, tip radius <10 nm). The typical scanning frequency was 0.5 Hz.

A light microscope was used for visual imaging of the pulps. Before the analysis, the samples were subjected to Simons' staining [17] where blue (Potamine sky blue) and orange (Potamine fast orange 6 RN) dyes were used.

Chemical retention

The determination of the retention of alkyl ketene dimer (AKD) and of starch was based on their concentrations in the headbox pulp and in the wire water samples. Before the analyses, the pulp and wire water samples were filtrated using a black ribbon filter paper (Whatman, Grade 40; GE Healthcare Life Sciences; Little Chalfont, Buckinghamshire, UK). The filter papers were then dried together with the solids separated from the samples and analyzed for their AKD and starch content. Both determinations were based on the assumption that all of the substance to be analyzed was adsorbed in the solid fraction (i.e., no substance remained in the water phase).

The determination of AKD from filter cakes and paper samples was performed using solvent extraction and gas chromatography as described by Laitinen [18]. The determination of starch from filter cakes was performed according to TAPPI T 419 om-11 ("Starch in paper").

RESULTS AND DISCUSSION

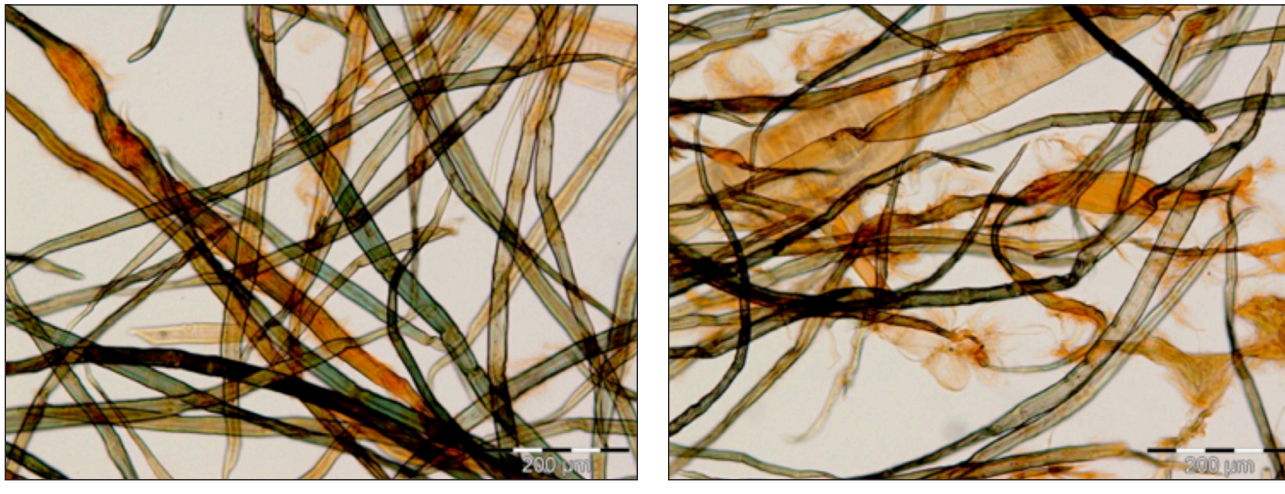
Pulp properties

Table IV shows some characteristics of the unextracted and alkali-extracted pulps refined to °SR 22. The alkaline extraction procedure used here yields pulp with increased fiber width, curl, and WRV; slightly decreased fiber length; and about 45% lower fines content compared to the unextracted pulp. Before refining, primary fines contents of 1.66% and 0.38% were determined for the unextracted and alkali-extracted pulps, respectively. Thus, in spite of the remarkably higher refining intensity required for alkali-extracted pulp, the amount of secondary fines formed during refining was fairly similar in both pulps (i.e., 1.04% in the unextracted pulp and 1.12% in the alkali-extracted pulp). The decreased content of primary fines in the alkali-extracted pulp was caused by pulp washing applied after extraction [4].

Length-weighted Property	Unextracted	Alkali-extracted
Fiber length, mm	0.96 (0.01)	0.93 (0.00)
Fiber width, μm	19.9 (0.00)	20.5 (0.00)
Fines content, %	2.7 (0.00)	1.5 (0.00)
Curl, %	11.2 (0.44)	14.6 (0.09)
Water retention value, g/g	1.69 (0.01)	1.85 (0.04)

IV. Some characteristics of unextracted and alkali-extracted bleached birch kraft pulps at °SR 22. Fiber characteristics were determined as duplicates (standard deviation given in brackets).

The reduced content of fines and xylan in alkali-extracted pulp should generally cause the WRV to decrease [2,19], but exactly the opposite behavior was observed here. The present results are in agreement with our previous observations for alkali-extracted laboratory pulp and for unbeaten pilot scale pulp [4,16]. The most likely reason for the increased WRV and fiber width could be increased fiber swelling, probably caused by an exchange of counter ions at negatively charged sites from hydrogen form to sodium form. Ion exchange generates osmotic pressure within the fiber wall, causing entry of additional water into the wall and the accompanying swelling and plasticization of the fiber wall [20]. This assumption is strongly supported by the microscopic images of beaten pulps after Simon's staining (**Fig. 1**), showing the accessibility of



1. Unextracted fibers (left) and alkali-extracted fibers (right) after Simons' staining.

fibers to high molecular weight (orange) and low molecular weight (blue) dyes.

According to Fig. 1, the alkali-extracted pulp has a higher accessibility to the high-molecular weight orange dye than the unextracted pulp. This is seen as a larger proportion of orange-colored material in Fig. 1, and indicates a less compact fiber wall structure with increased porosity, probably because of swelling and dissolution of xylan from the cell wall and some mechanical damage induced by more intensive refining. Figure 1 also shows there is more orange-dyed fibrillar material on the surfaces of the alkali-extracted fibers.

AFM measurements performed on unbeaten fibers before and after alkaline extraction revealed that the surface of the alkali-extracted pulp is rougher than that of the unextracted pulp. **Table V** shows the average roughness and root mean square roughness values obtained through analysis of several samples.

Sample	Average Roughness, nm	Root Mean Square Roughness, nm
Unextracted	40 (19)	51 (19)
Alkali-extracted	57 (24)	70 (23)

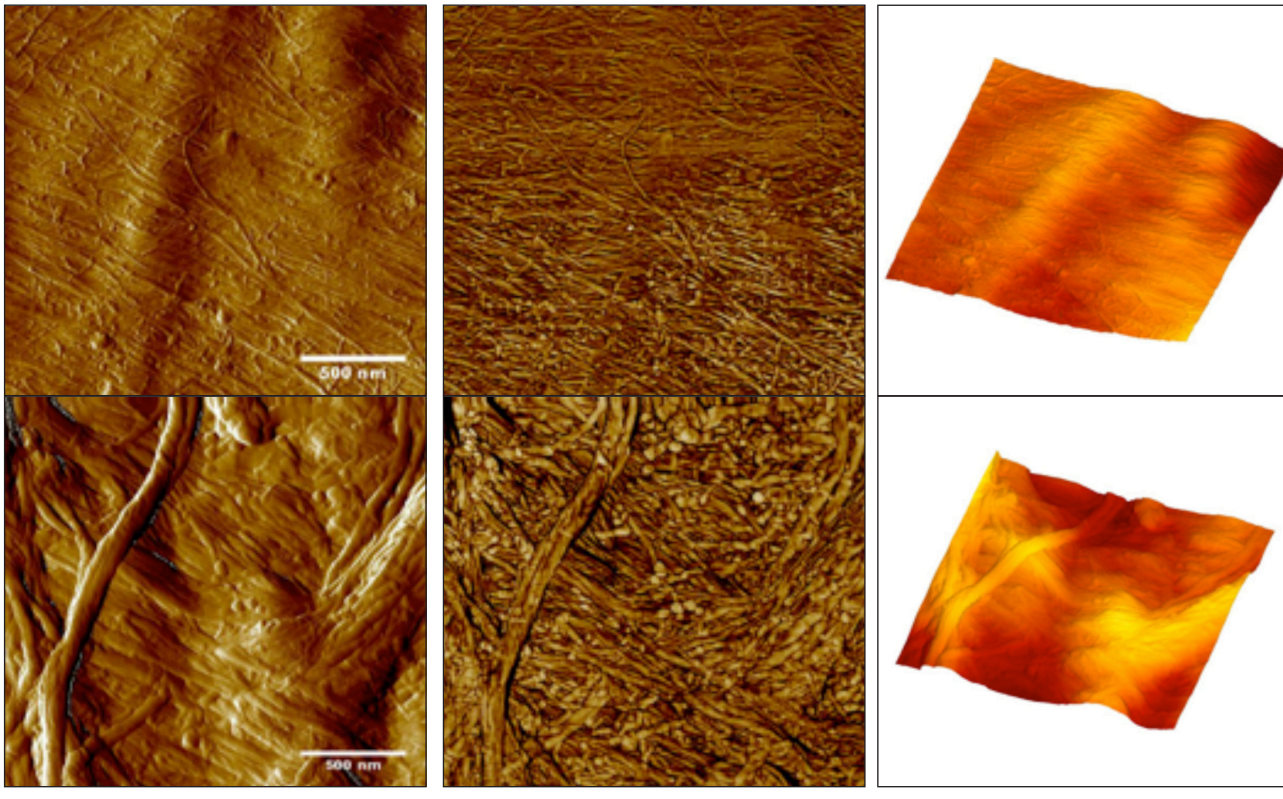
V. Average roughness and root mean square roughness values for unextracted and alkali-extracted pulp (standard deviation given in brackets).

The roughness values in Table V have relatively high standard deviations and thus can only be taken as rough estimates. A better insight into the differences in surface structure between the pulps can be obtained from **Fig. 2**, which reveals a structural change, particularly in the P layer. The dissolution of xylan seems to cause partial liberation of surface fibrils and partial swelling of fibers, which increases the microroughness of the alkali-extracted pulp compared to the unextracted pulp.

Based on the above and previously reported results, we assume that mainly the surface xylan has been removed in this case because of the relatively low alkali concentration. Kraft pulps typically have a high surface xylan content [21,22], and the amount of extractable xylan is determined chiefly by the alkali concentration. At most, about an 80% reduction in the pulp xylan content can be reached using a 9% NaOH solution in extraction. On the other hand, the remaining 20% cannot be leached out from the cell wall, and is considered to be inaccessible xylan, probably bound to cellulose fibril aggregates [23,24].

Wet end chemistry results

Table VI shows the important characteristics of the papermaking stocks with a varying mixing ratio of unextracted and alkali-extracted pulp. It is evident that, when the portion of alkali-extracted pulp in the furnish is increased, the zeta potential of the headbox stock is shifted to less negative values,



2. Atomic force microscope amplitude, phase, and topography images of unextracted (top panels) and alkali-extracted (bottom panels) fiber surfaces before refining (image area 2 µm × 2 µm).

Mixing Ratio, %/%	Machine Chest		Headbox			Wire Water			
	Water Retention Value, g/g	°SR	pH	Consistency, g/L	ζ-Potential, mV	Turbidity, NTU	Consistency, mg/L	Total Organic Carbon, ppm	Cationic Demand, mekv/L
100/0	1.69	19.0	9.4	7.1	-22.3	1.62	0.53	22.8	-0.012
75/25	1.71	20.0	9.3	6.9	-21.9	0.78	0.40	17.8	- 0.006
50/50	1.76	19.0	9.2	6.9	-19.1	0.40	0.39	13.4	-0.003
25/75	1.79	18.5	9.1	6.8	-17.1	0.43	0.35	10.7	-0.001
0/100	1.81	19.0	9.0	6.7	-14.9	0.45	0.36	7.8	-0.001

VI. Properties of the pulp and process water samples from machine chest, headbox stock, and wire section. Mixing ratio = % unextracted pulp/% alkali-extracted pulp.

and the cationic demand of the wire water samples approaches zero. At mixing ratios of 25/75 and 0/100, there is virtually no cationic demand left in the wire water samples (Table VI).

The main reason behind the observed changes in zeta potential and cationic demand with an increasing amount of alkali-extracted pulp in furnish is the reduced charge density of alkali-extracted pulp fines in particular [16]. The adsorption of starch onto fines and filler particles is favored over adsorption onto the fiber fraction, mainly because of the larger specific surface area and surface charge of fines [25,26]. Thus, when unextracted pulp is replaced by alkali-extracted pulp, the consumption of cationic starch and retention aid by the anionic material in the wire water will be decreased. Simultaneously, the adsorption of cationic starch and retention polymer onto the fiber fraction is facilitated, causing the zeta potential to become less negative. Furthermore, the adsorption of cationic additives on the fiber surface is probably favored by the rougher surface structure of the alkali-extracted pulp [27].

Table VI shows that wire water turbidity, solids content, and TOC content are decreased with an increasing proportion of alkali-extracted pulp. These results demonstrate that the amount of non-retained material in the wire water decreases when the proportion of alkali-extracted pulp in the furnish is increased. The reason for this seems to be the improved overall retention efficiency.

Table VII shows machine data for first pass retention and filler retention, together with the retention values determined in the headbox for both cationic starch and AKD. With respect to chemical retention, the optimal mixing ratio of unextracted and alkali-extracted pulp is 25/75. At this mixing ratio, the highest retention levels are obtained for all components (i.e., filler, starch, and AKD). Whenever a portion of alkali-extracted pulp was included in the papermaking, filler retention in particular increased to a significantly higher level than when only unextracted birch kraft pulp was used. The increased filler retention was obvious in the first pass retention, but even more so in the retention of starch and AKD, both of which were increased by more than 10% units at a mixing ratio of 25/75. The results are in accordance with findings that a major

Mixing Ratio, %/%	First Pass Retention, %	Filler, %	Starch, %	AKD, %
100/0	92.5	76.3	79.8	75.8
75/25	94.1	81.2	85.7	84.9
50/50	94.2	81.0	89.3	85.1
25/75	94.7	87.8	90.7	86.8
0/100	94.6	82.1	88.6	86.5

VII. First pass retention and retention of filler, starch and alkyl ketene dimer (AKD) for different mixing ratios of unextracted and alkali-extracted pulp. Retention values for starch and AKD are based on their concentrations in headbox stock and wire water. Mixing ratio = % unextracted pulp/% alkali-extracted pulp.

part of the cationic polyelectrolytes and a large proportion of PCC typically are adsorbed onto the fines fraction [25,28,29]. However, together with our previously published laboratory results [16], the present results strongly suggest that the less charged fines in alkali-extracted pulp consume less cationic additives, and adsorption onto the fiber fraction is simultaneously favored by the increased roughness of the fiber surfaces.

Besides the amount and type of fines, the presence of a sufficient amount of anionic charge is equally important for the retention of cationic polyelectrolytes. The results in Table VII suggest that for a mixing ratio of 0/100, the cationic load in the system is likely to be too high because the filler retention is notably lower at a mixing ratio of 25/75. In other words, there are probably not enough anionic sites left for the efficient attachment of cationic additives. Thus, the driving force for retention diminishes, and the originally negatively charged particles may ultimately obtain steric or positive electrostatic repulsion forces to dominate the particle interactions. Obviously, this must lead to decreased filler retention, which is in turn reflected in the retention of AKD and starch, because a significant portion of these is typically adsorbed onto the filler surface [26,30].

Another consequence that follows from the replacement of the unextracted pulp with alkali-extracted pulp is the increased WRV of the machine chest furnish, which includes wet end starch. A steady increase from 1.69 g/g to 1.81 g/g can be seen as the proportion of alkali-extracted pulp in the papermaking furnish is raised (Table VI). This is to be expected because the corresponding WRVs of the pulps without any wet end starch dosing were 1.69 g/g and 1.85 g/g, respectively. During the trial, no significant differences in steam consumption at the drying section were observed, but the dry matter content determined after third press was slightly reduced, from 41.2% to 39.8%, when unextracted pulp was fully replaced by alkali-extracted pulp.

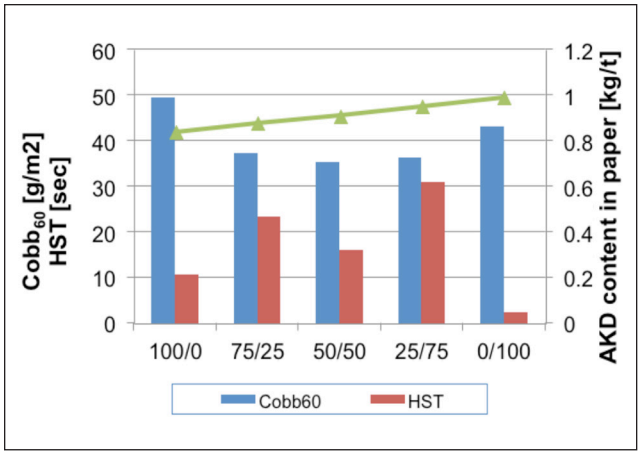
Sizing performance

Figure 3 shows the effect of replacing some of the ordinary birch kraft fibers with alkali-extracted fibers on AKD sizing, evaluated by means of $Cobb_{60}$ and HST sizing tests, and by the amount of AKD determined from paper samples. According to our results, the AKD content of paper is linearly increased when the proportion of alkali-extracted pulp is increased. When replacing all of the unextracted pulp with alkali-extracted pulp, the AKD content of paper was increased by 15%. However, in all of the paper samples, the AKD content seemed to be somewhat lower than could be expected based on the retention values determined in the headbox (Table VII).

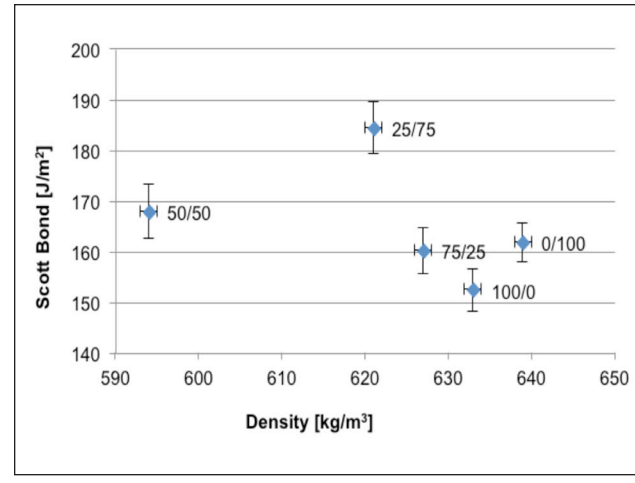
The water absorption capacity of paper (measured as the

Mixing Ratio, %/%	100/0	75/25	50/50	25/75	0/100
Grammage, g/m²	77.9	76.5	75.5	77.6	76.1
Ash content, %	19.5	20.7	21.1	21.0	21.6
Thickness, µm	123	122	127	125	119
Density, kg/m³	633	627	594	621	639
Bulk, cm³/g	1.58	1.59	1.68	1.61	1.56
Specific formation number, √g/m	0.41	0.46	0.44	0.46	0.45
Elongation, %	1.79 (0.24)	1.92 (0.19)	1.89 (0.18)	2.38 (0.19)	1.99 (0.15)
Tensile index, Nm/g	27.99 (1.68)	27.37 (1.20)	27.95 (1.10)	26.44 (1.06)	24.78 (0.77)
Tensile stiffness index, mNm/kg	4.35 (0.15)	4.14 (0.12)	4.18 (0.14)	3.77 (0.13)	3.80 (0.10)
Elastic modulus, MPa	2757 (97.98)	2597 (77.46)	2480 (80.62)	2340 (77.46)	2427 (63.25)
Fracture toughness index, kJ/kg	354 (66.34)	373 (56.91)	376 (50.61)	459 (57.38)	353 (39.97)
Tear index, mNm²/g	4.91 (0.19)	4.71 (0.16)	5.31 (0.16)	5.19 (0.32)	4.95 (0.58)
Bendtsen air permanence, µm/Pa s	32.29 (2.39)	36.48 (2.71)	34.80 (1.61)	32.20 (2.49)	38.75 (3.04)
Bendtsen roughness, ml/min	778 (71.1)	692 (72.7)	896 (75.9)	952 (69.7)	675 (45.9)
Scott bond,* J/m²	152 (9.43)	160 (10.13)	168 (12.19)	184 (11.65)	162 (8.51)
Y-value, %	93.43	93.32	93.46	93.57	93.46
ISO brightness, %	88.68	88.71	88.99	89.26	89.21
Opacity, %	86.30	85.73	85.84	86.00	86.71
Light scattering coefficient, s, m²/kg	54.02	54.27	56.96	56.75	58.86
Light absorption coefficient, k, m²/kg	0.13	0.13	0.13	0.13	0.14
* Top side.					

VIII. Properties of paper samples containing a varying amount of alkali-extracted pulp (standard deviation given in brackets). The strength properties are given as a geometric machine direction/cross direction mean. Mixing ratio = % unextracted pulp/ % alkali-extracted pulp.



3. Water absorption capacity ($Cobb_{60}$), Hercules size test sizing response, and AKD content of paper samples containing a varying proportion of alkali-extracted pulp.



4. Scott bond strength vs. density of paper samples containing a varying amount of alkali-extracted pulp.

$Cobb_{60}$ value) showed a fairly good agreement with the amount of AKD. However, for a mixing ratio of 0/100, there seemed to be the highest amount of AKD in paper (0.99 kg/ton), but the Cobb sizing level was notably lower than for a mixing ratio of 50/50, for example. Cobb measurements were repeated after oven curing the sheets (105°C, 15 min), but curing did not improve the sizing efficiency.

The HST size test measures the penetration of ink into the paper structure, and is even more sensitive to small-scale paper defects than the Cobb test. The results of the HST tests (Fig. 3) revealed a difference in the performance of AKD for mixing ratios of 25/75 and 0/100 more clearly than one would expect based solely on the $Cobb_{60}$ measurements. HST shows nearly no resistance for neutral green ink for a mixing ratio of 0/100, even though the amount of AKD in paper was the highest in this case.

The most probable reason for the observed sizing behavior is that the size is unevenly distributed in paper made of 100% alkali-extracted pulp, which in turn is most likely a consequence of overloading the system with cationic additives. AKD particles are known to be retained by carboxyl groups, and if these are already blocked when AKD is applied, poor sizing performance can be expected [31]. Another plausible explanation for this behavior can be that a higher amount of AKD is adsorbed onto PCC filler surfaces when using only alkali-extracted pulp. The AKD adsorbed onto a filler surface is not able to form bonds with the cellulose hydroxyl groups, which may lead to a false orientation of the hydrophobic chains and cause a size reversion to take place [32,33].

Physical properties

Table VIII shows the physical and optical properties of the paper samples. Our results indicate that the addition of alkali-extracted pulp in paper machine stock together with unextracted pulp has only a minor effect on the common features of pulps with low hemicellulose content: a decreased tensile and tensile stiffness index together with an increased tear index [34-37]. Tensile strength and tensile stiffness index show a notable decrease only for 100% alkali-extracted pulp (Table VIII), while tear index remains practically at the original level. This is likely a result of the reinforcing effect, a phenomenon that is known from mixtures of mechanical and chemical pulps [38,39]. It seems that, when a pulp mixture contains unextracted pulp, the unextracted fibers are able to form a continuous load-carrying network and therefore no decrease is seen in tensile properties. However, if the portion of alkali-extracted pulp is further increased close to 100%, the load-carrying network of unextracted fibers is lost. In addition, the different swelling properties of the two fiber types will have an effect on the activation of fibers during paper drying/consolidation, entailing additional effects on sheet bonding and strength properties with mixtures of alkali-extracted and unextracted pulps [40].

Unexpectedly, the Scott bond showed a considerable increase for a mixing ratio of 25/75 (Table VIII), and therefore, it was plotted against sheet density. **Figure 4** shows that for mixing ratios of 50/50 and 25/75 in particular, high bonding strength was obtained for a relatively low sheet density. This is interesting since the alkali-extracted pulp had a lower fines content than the unextracted pulp. Fines are known to contribute positively to bonding strength. On the other hand, Fig. 1 shows the presence of a higher amount of fibrils on the surface of the alkali-extracted fibers and it has been previously reported that alkaline extraction increases wet fiber flexibility [41]. According to the literature, both of these phenomena increase the relative bonded area [42]. In general, an increase in fiber flexibility leads to an increase in the area of interfiber contact, thus having an effect on the number of interfiber bonds in the fiber network.

The higher starch retention in papers containing alkali-extracted pulp (Table VI) very probably contributes to the observed increase in internal bond strength. The addition of wet end starch improves paper strength through the formation of additional hydrogen bonds between the hydroxyl

groups in the cationic starch and fiber surface during drying. The limit of strength improvement obtained by addition of starch is reached when the bonds become stronger than the fibers themselves.

The fact that the internal bond strength is increased by the addition of alkali-extracted pulp, while the tensile index remains unchanged or is slightly decreased, indicates that the increased fiber wall porosity in alkali-extracted pulp does not favor the penetration of starch into the fiber wall. Several authors have reported that the in-plane strength properties (i.e., tensile strength and strain at break) are affected most by starch that is able to penetrate into the fiber wall, while the z-direction strength is affected independently of the location of the adsorbed starch [43,44].

CONCLUSIONS

In this pilot scale study, alkali-extracted pulp with reduced xylan content was used to partially or fully replace bleached birch kraft pulp as the raw material in papermaking. Based on this study, the following conclusions can be drawn:

- Alkaline extraction of birch kraft pulp results in a rougher and more fibrillar fiber surface, which seems to be beneficial for the retention of cationic additives.
- The electrostatic charge balance in the wet end is altered when the xylan content in the furnish varies, and the chemical dosing strategies need to be reconsidered to achieve efficient retention.
- With respect to chemical retention, better results were obtained for mixtures of alkali-extracted and unextracted pulp than for either of these pulps alone. Consequently, the performance of both AKD and wet end starch was improved.
- The paper strength properties can be maintained at their original level, providing that the proportion of alkali-extracted pulp is 50% or less.
- The z-direction strength of the paper is increased by about 20% when 75% of the unextracted pulp is replaced by alkali-extracted pulp.

This study thus demonstrates that alkali-extracted birch pulp could be used in papermaking stock without losing the physical or mechanical properties of paper. Even a small addition of extracted pulp seems to favor the retention of chemicals by changing the electrostatic charge balance in the wet end. **TJ**

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LITERATURE CITED

1. Pekkala, O., U.S. pat. 2008/0295986 A1 (Dec. 4, 2008).
2. Fuhrmann, A. and Krogerus, B., *TAPPI PEERS Conf.*, TAPPI PRESS, Atlanta, GA, USA, 2009, Conf. CD, p. 2668.
3. Talja, R.A., Fuhrmann, A., Krogerus, B., et al., *7th Bienn. Johan Gullichsen Colloq.*, Paper Engineers' Association, Helsinki, Finland, 2009, p. 77.
4. Saukkonen, E., Lyytikäinen, K., and Backfolk, K., *TAPPI J.* 11(4): 37(2012).
5. Lee, H.L., Lee, S.H., Youn, H.J., et al., *Int. Symp. Wood, Fiber Pulping Chem., 15th*, Papirindustriens Tekniske Forening, Oslo, Norway, 2009, Conf. CD.
6. Bindgård, L., *TAPPI Eur. PLACE Conf., 13th*, TAPPI PRESS, Atlanta, 2011, p. 28.
7. Laine, C., Harlin, A., Hartman, J., et al., *Ind. Crops Prod.* 44(1): 692(2013).
8. Li, X., Shi, X., Wang, M., et al., *Food Chem.* 126(2): 520(2011).
9. da Silva, A.E., Marcelino, H.R., Gomes, M.C.S., et al., in *Products and Applications of Biopolymers* (J. Verbeek, Ed.) Intech, Rijeka, Croatia, 2012, Chap. 4, pp. 61-84.
10. Vaaler, D., Ljones, S., Ribe, E., et al., *Eur. Workshop Lignocellul. Pulp, 7th*, Åbo Akademi, Turku, Finland, 2002, p. 147.
11. Colodette, J., Muguet, M., Juste, V., et al., *Nord. Wood Biorefin. Conf., 3rd*, Innventia AB, Stockholm, Sweden, 2011, p. 119.
12. Yoon, S.-H. and van Heiningen, A., *TAPPI J.* 7(7): 22(2008).
13. Kautto, J., Saukkonen, E., and Henricson, K., *BioResources* 5(4): 2502(2010).
14. Duarte, G.V., Ramarao, B.V., Amidon, T.E., et al., *Ind. Eng. Chem. Res.* 50(17): 9949(2011).
15. Sjöström, E., *Nord. Pulp Pap. Res. J.* 4(2): 90(1989).
16. Lyytikäinen, K., Saukkonen, E., Kajanto, I., et al., *BioResources* 6(1): 219(2011).
17. Yu, X., Minor, J.L., and Atalla, R.H., *TAPPI J.* 78(6): 175(1995).
18. Laitinen, R., "Development of LC-MS and extraction methods for the analyses of AKD, ASA and rosin sizes in paper products," Doctoral thesis, Lappeenranta University of Technology, Lappeenranta, Finland, 2007.
19. Turt, V., Co, A., and Genco, J.M., *TAPPI Eng. Conf.*, TAPPI PRESS, Atlanta, 1994, p. 273.
20. Scallan, A.M. and Grignon, J., *Sven. Papperstidn.* 82(2): 40(1979).
21. Sjöberg, J. and Dahlman, O., *Eur. Workshop Lignocellul. Pulp, 6th*, Universite Bordeaux 1, Bordeaux, France, 2000, p. 583.
22. Dahlman, O., Jacobs, A., and Sjöberg, J., *Cellulose* 10(4): 325(2003).
23. Teleman, A., Larsson, P.T., and Iversen, T., *Cellulose* 8(3): 298(2001).
24. Köpcke, V., "Conversion of wood and non-wood paper-grade pulps to dissolving grade pulps," Doctoral thesis, Royal Institute of Technology, Stockholm, Sweden, 2010.
25. Wågberg, L. and Björklund, M., *Nord. Pulp Pap. Res. J.* 8(4): 399(1993).
26. Hedborg, F. and Lindström, T., *Nord. Pulp Pap. Res. J.* 8(3): 319(1993).
27. Kang, T. and Paulapuro, H., Japan *Tappi J.* 60(8): 1202(2006).

28. Wågberg, L., *Nord. Pulp Pap. Res. J.* 15(5): 586(2000).
29. Liimatainen, H., Haapala, A., and Niinimäki, J., *TAPPI J.* 8(9):38(2009).
30. Voutilainen, P., *Int. Pap. Coat. Chem. Symp.*, CPPA, Montreal, QC, Canada, 1996, p. 195.
31. Isogai, A., Kitaoka, C., and Onabe, F., *J. Pulp Pap. Sci.* 23(5): J215(1997).
32. Novak, R. and Rende, D., *Papermakers Conf.*, TAPPI PRESS, Atlanta, 1993, p. 437.
33. Bartz, W., Darroch, M., and Kurrle, F., *Papermakers Conf.*, TAPPI PRESS, Atlanta, 1994, p. 173.
34. Kettunen, J., Laine, J.E., Yrjälä, I., et al., *Pap. Puu* 64(4): 205(1982).
35. Molin, T. and Teder, A., *Nord. Pulp Pap. Res. J.* 17(1): 14(2002).
36. Rydholm, S., *Pulping Processes*, Interscience Publishers, New York, 1967, pp. 1152-1166.
37. Spiegelberg, H.L., "The effect of hemicelluloses on the mechanical properties of individual pulp fibers," Doctoral thesis, Lawrence University, Appleton, WI, USA, 1966.
38. Ritala, R., *Nord. Pulp Pap. Res. J.* 2(2): 15(1987).
39. Ritala, R. and Huiku, M., *9th Fundamental Research Symposium*, Mechanical Engineering Publications Ltd., London, UK, 1989, pp. 195-218.
40. Retulainen, E., "The role of fibre bonding in paper properties," Doctoral thesis, Helsinki University of Technology, Helsinki, Finland, 1997.
41. Saukkonen, E., "Hemicellulose extracted kraft pulp as a raw material of paper," Master's thesis, Lappeenranta University of Technology, Lappeenranta, Finland, 2009.
42. Toven, K. and Johnsen, P., *Prog. Pap. Phys. Semin.*, Syracuse, New York, 2002, CD.
43. Brännvall, E., Eriksson, M.E., Lindström, M.E., et al., *Nord. Pulp Pap. Res. J.* 22(2): 244(2007).
44. Eriksson, M., Pettersson, G., and Wågberg, L., *Nord. Pulp Pap. Res. J.* 20(3): 270(2005).

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Alkaline extraction of kraft pulp has previously been investigated to convert paper grade pulps to dissolving grade pulps. However, when extracting the fibers under lower alkaline conditions, the resulting fibers could be used as a functional fiber component in papermaking furnishes. Therefore, we have chosen this topic to give new insights into the effects of alkaline extraction on fiber and paper properties.

In our previous study, we examined the effects of alkaline extraction of bleached birch kraft pulp on the resulting pulp properties as a function of extraction time. In the present study, we have continued this work by using extracted pulp as a raw material for papermaking. The present work focused on the wet end chemistry of the paper machine.

The interpretation of results was made more difficult by the fact that a considerable amount of primary fines was lost during washing of the alkali-extracted pulp. However, the conclusions of the present study are well supported by our previous study, which was made in laboratory conditions with comparable fines contents, and also by other results given in this study.

It was surprising that even a small addition of alkali-extracted pulp changes the electrostatic charge balance in the wet end in a way that is beneficial for retention. Another interesting finding was that some properties, such as internal bond strength, were substantially improved by the incorporation of alkali-extracted pulp into papermaking stock, which provides an opportunity for producing tailor-made pulps suitable for certain applications.

Based on our results, mills can predict what implications the varying pulp xylan content has in the papermaking process. The next step in our research is to find alternative fiber modification routes and clarify the effects of the selected routes on pulp and paper properties.

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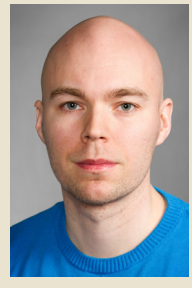
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