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Extraction of xylan from wood pulp and brewer's spent grain

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Abstract

Hemicelluloses are potential raw materials for different types of biobased materials. Alkaline extraction of bleached birch kraft pulp yields pure, high molecular weight hemicellulose (xylan) and hemicellulose-poor pulp. In this work, the concentration of alkali and the extraction temperature were studied as parameters for xylan yield and mass balance in the extraction. Extraction at room temperature using 1 molar aqueous sodium hydroxide (NaOH) showed the highest value for the mass balance with 98.5 wt.-% on dry matter of pulp – 16.1 wt.-% xylan in the extract and 82.4 wt.-% extracted pulp. Recycling of 90% of the NaOH used for the extraction was demonstrated by ultrafiltration. The ultrafiltration process is thus a highly potential tool offering an economical way to simultaneously recycle chemicals and separate products from process liquids in xylan extraction and other biorefinery processes. The concept of alkaline extraction was also demonstrated for brewer's spent grain (BSG). Arabinoxylan comprised 80% of the carbohydrates in the alkaline extract of BSG. However, the selectivity of the extraction was poor as proteins, lipids and some lignin were also efficiently extracted from BSG in alkaline conditions.

Keywords

Xylan; birch kraft pulp; brewer's spent grain; alkaline extraction; sodium hydroxide; mass balance

Highlights

- Alkaline extraction of pure xylan from birch kraft pulp was optimized.
- The best conditions yielded 16.1 wt.-% xylan and 82.4 wt.-% extracted pulp.
- 90% of applied sodium hydroxide was recycled by ultrafiltration.
- In the extraction of BSG, lipids and protein were co-extracted with arabinoxylan.

1. Introduction

The potential use of wood xylan has been demonstrated in a variety of polymer applications thus substituting synthetic polymers. The use of hemicelluloses in general as additives in papermaking (e.g. as such or modified for barrier applications), food additives, thickeners, hydrogels, emulsifiers, coating color components, adhesives and cancer protective agents has been reported (Ebringerová, 1994; Ebringerová and Heinze, 2000; Gatenholm et al., 2004; Gröndahl et al., 2004, 2008; Kataja-aho et al., 2012; Laine et al., 2008, 2013, 2014; Pohjanlehto et al., 2011; Söderqvist Lindblad et al., 2004; Talja et al., 2011).

Hemicelluloses are the second most abundant plant material in nature being present in different kinds of wood or agro-based materials. Bleached birch kraft pulp (BBKP) as well as other bleached hardwood pulps represent attractive sources for the isolation of pure, linear xylan (Laine et al., 2013a, Varhimo et al., 2014). As compared to wood or other biomasses the bleached pulps are already delignified and contain practically only cellulose and deacetylated xylan. The economic feasibility of the process is improved as both co-produced fractions – hardwood pulp with reduced xylan content and isolated xylan – have potential value-added applications. Pulp xylans can be extracted rather easily in alkaline conditions. In addition to wood pulp, also other raw materials should be considered as potential sources of xylan. One interesting alternative is brewer's spent grain (BSG) which is the solid residue left after the processing of germinated and dried cereal grains (malt) for the production of beer and other malt products (malt extracts and malt vinegar). BSG contains high molecular weight arabinoxylans, both highly and poorly substituted (Kabel et al., 2002; Mandalari et al, 2005). Typical for BSG arabinoxylan is its ferulic and diferulic acid residues crosslinking neighbouring xylan chains and also lignin (Mandalari et al., 2005; Lam et al., 2001). BSG is currently mainly used mainly as cattle feed (Crawshaw, 2001) and value added applications for its components are actively being sought for.

This work demonstrates details on extraction parameters for xylan from BBKP including mass balances of the material throughout the process. Recycling of NaOH by ultrafiltration was included in the evaluation. The suitability of the alkaline extraction process for BSG xylan was also investigated.

2. Materials and Methods

Industrial bleached birch kraft pulp (*Betula pendula /Betula pubescens*) was obtained from a pulp mill in Finland. Brewer's spent grain was obtained fresh at 31% dry matter content from a Finnish large brewery and stored at -18°C prior to use.

2.1 Extraction of xylan from bleached birch kraft pulp

1.5 kg industrially bleached birch kraft pulp (d.m.) was extracted with either 1.0 M (40 g/L) or 2.0 M (80g/L) sodium hydroxide (NaOH) (diluted from 50 wt.-% NaOH, Algol Chemicals Oy, Finland) solution at 5% consistency and a selected temperature for 60 min in a 40L Zirco reactor equipped with blade mixer according to Table 1. The primary extract was obtained by filtration in a wire bottomed washing diffuser including circulation of the filtrate through the filter cake to obtain a fines-free extract. The primary extract was recovered by applying suction. Secondary extract – the filtrate from compression – was obtained by applying a pressure of 60 bar to the wet filter cake (piston press impregnator, MKH Press Oy, Jämsänkoski, Finland). Finally, the pulps were washed by dispersing them into fresh water at a consistency of 5% followed by thickening in a self-constructed wire-bottomed washing diffuser by applying suction. The washing cycle was repeated until the pH of the filtrate decreased to about 9. Only the first washing water was collected for analysis. The pulp yield was determined. The amounts of filtrates are shown in Table 1.

2.2 Extraction of brewer's spent grain (BSG)

1.5 kg BSG (d.m.) was extracted with 1 M NaOH) (diluted from 50 wt.-% NaOH, Algol Chemicals Oy, Finland) solution at room temperature for one hour correspondingly to the pulp extraction. The extract was collected by centrifugation using 4000 rpm (Sorvall RC 12 BP, Thermo Fisher Scientific,Waltham, Massachusetts, USA). For the yield determination as well as for analysis, an

aliquot of the extracted pulp was washed with fresh tap water to neutral using centrifugation for the recovery.

2.3 Ultra- and diafiltration of alkaline extracts

Selected alkaline extracts were ultrafiltrated using LabStak M20 equipment (Alfa Laval AB, Sweden). Ten Alfa Laval-UFX5pHt membranes with an area of 0.018 m^2 were used yielding in total a membrane surface area of 0.180 m^2. The filtration temperature was 50°C, dropping only shortly to 33°C during addition of fresh feed liquor.

A selected concentrate was diafiltrated using the same equipment and membrane as for the ultrafiltration. Tap water was used for the dilution of the concentrate and diafiltration performed for concentration. This was repeated until the conductivity of the permeate was below 1 mS/cm.

2.4 Storage tests of xylan in alkaline extracts

100 mL portions of a selected alkaline concentrate were stored in closed glass bottles at 60°C in an oven for different periods of time. One reference sample was stored at room temperature for 6 weeks and the other in the refrigerator (4-8°C) until the whole sample set was analyzed.

2.5 Analytics

Carbohydrates and lignin content of the solids was determined after air drying. The samples were ground before analysis using Fritch Pulverizette 14 mill (Fritsch GmbH, Germany). After that, solid samples were hydrolyzed first with 72% (w/w) sulphuric acid (Fluka Chemie AG, Switzerland). for 60 min at 30°C and then autoclaved with 4% (w/w) sulphuric acid for 60 min. The resulting monosaccharides were determined by HPAEC with pulse amperometric detection (Dionex ICS 3000 equipped with CarboPac PA1 column or Dionex ICS 5000 equipped with CarboPac PA20 column, Dionex, USA) according to NREL method (NREL standard, Hausalo et al., 1995). The

polysaccharide content in the samples was calculated from the corresponding monosaccharides using a correction factor of 0.88 for pentoses and 0.9 for hexoses to account for anhydrosugars in the polysaccharides. Klason lignin content i.e. the insoluble residue from the hydrolysis was determined gravimetrically. Acid soluble lignin in the hydrolysate was detected at 215 and 280 nm using equation described by Goldschmid (1971).

For the determination of the **carbohydrates and lignin content of the extracts**, the alkaline extracts were filtered before neutralization to remove potential fines material while the neutralized samples were analyzed as such. After that, the samples were neutralized using diluted sulfuric acid. Then the samples were autoclaved with 4% (w/w) sulphuric acid for 60 min. The analysis was continued as described for the analysis of the solid samples.

The **protein content** of the samples was determined based on the total nitrogen (N X 6.25) measured by Kjeldahl according to Kane (1986).

Lipophilic extractives were determined gravimetrically after 5 h Soxhlet extraction by heptane prior to acid hydrolysis.

Molar mass distributions of the carbohydrates in the extracts was performed by size exclusion (SEC) measurements with MCX columns in 0.1M aqueous sodium hydroxide (NaOH) using Water 717 plus Autosampler, Waters 515 HPLC pump and Waters 2414 Refractive Index Detector. Molar mass distributions of the xylans were calculated from pullulan (5 900 – 708 000 g/mol) calibration using Waters Empower 2 program. Two parallel determinations were performed. The equipment and software were acquired from Waters Corporation, USA.

The recovered extracts were analysed for **pH** and **NaOH** (SCAN-N 33:94).

3. Results and discussion

3.1. Extraction of bleached birch kraft pulp (BBKP) at different parameters

A set of extractions of BBKP was performed to obtain data for mass balances to determine the optimum conditions for the extraction. The BBKP contained insignificant amounts of lignin (< 0.4 wt.-% of insoluble and < 0.1 wt.-% of acid soluble lignin). Different temperatures and sodium hydroxide (NaOH) concentration were applied as listed in Table 1. The applied filtration and washing steps are schematically shown in Figure 1. After the extraction, the pulp was filtered yielding the 'Extract' and the wet pulp cake. After that, plug pressing was applied yielding the 'Extract from compression' and the compressed pulp cake. After that, the pulp was washed yielding the 'Filtrates from washing' and the 'Extracted pulp'.

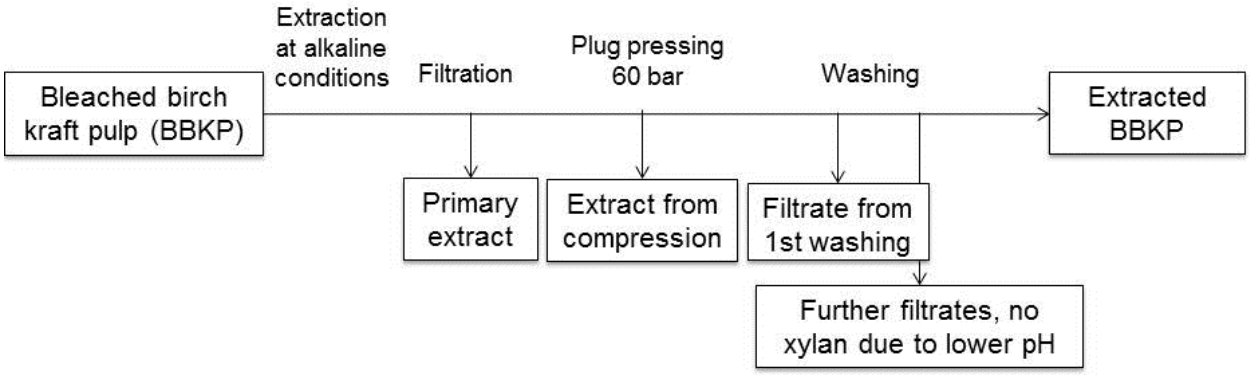


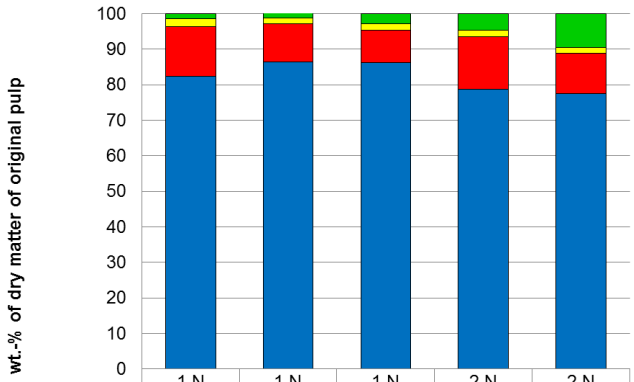
Figure 1. Schematic presentation of the filtration and washing steps applied after the alkaline extraction of BBKP.

Table 1. Parameters of alkaline extractions of bleached birch kraft pulp (1.5 kg per trial). The consistency was 5% and the extraction time 1 hour in all cases.

Trial nro	1	2	3	4	5
Conditions	1N NaOH, 20°C	1N NaOH, 40°C	1N NaOH, 75°C	2N NaOH, 20°C	2N NaOH, 75°C
Primary extract, kg	23.83	23.57	23.73	23.97	25.42
Extract from compression, kg	4.26	4.39	4.09	3.28	3.31

The mass balances over the alkaline pulp extractions are summarized in Figure 2. Insignificant losses (<2 wt.%) were observed for extractions using 1 mol/L NaOH at either 20 or 40°C. Higher temperature resulted in lower amounts of extracted xylan and non-identified losses of 2.9 wt.-%. Higher NaOH concentration induced unidentified losses already at 20°C (>4 wt.-%) and is therefore an unfavored option. The xylan yield was higher at 20°C when 1 mol/L NaOH was used compared to higher temperatures with the same NaOH concentration. In total, xylan accounting for 16.1 wt.-% of pulp and 62 wt.-% of the initial xylan in the pulp were extracted with 1 mol/L NaOH at 20°C. Slightly higher xylan yield was obtained with 2 mol/L NaOH concentration and 20°C yielding in total 16.8 wt.-% of pulp and 65 wt.-% of the initial xylan in the pulp. However, material losses were encountered (see above). Thus, 20°C or even lower temperatures and 1 mol/L NaOH are most favorable to obtain a high yield of xylan without loss of material. However, for practical reasons, low temperatures are not always applicable in industrial processes, because the typical processing temperatures for the pulp bleaching line are 60-90°C. Lower extraction yield for xylan could be accepted with low material losses at 40-60°C using 1 mol/L NaOH. In practice, xylan can also be extracted at lower alkaline charge than 1 mol/L. However, the xylan yield decreases with decreasing

alkalinity e.g. from 15-17 wt.% using 1 mol/L NaOH to 8-9 wt. % using 0.5 mol/L NaOH (Laine et al., 2013a).



	1 N NaOH, 20 °C	1 N NaOH, 40 °C	1 N NaOH, 75 °C	2 N NaOH, 20 °C	2 N NaOH, 75 °C
Loss of material, %	1.5	1.3	2.9	4.7	9.6
Extracted xylan in compressed extract, %	2.1	1.7	1.8	1.8	1.6
Extracted xylan in extract, %	14	10.8	9.2	14.8	11.3
Extracted pulp, %	82.4	86.3	86.1	78.7	77.5

Figure 2. Mass balances for the different extraction trials for BBKP.

The loss of material cannot be explained by hydrolysis into oligo- and monosaccharides, because these would have been detected as xylose in the analysis of sugars after acid hydrolysis. Observed losses were probably caused by the degradation of carbohydrates by peeling and stopping reactions to carboxylic acids – the same reactions which take place during alkaline pulping (Sjöstöm, 1993). More detailed analysis of the extracts would be necessary to confirm this.

The carbohydrate concentration in the primary extracts and extracts from compression are shown in Table 2. All BBKP extracts contained mainly xylan composed of xylose units with less than 0.5% of other neutral monosaccharides which were low amounts of rhamnose and glucose. In earlier studies, analysis of a similar xylan using acid methanolysis and gas chromatography (Sundberg et al., 1996) showed that low amounts of 4-*O*-methyl glucuronic acid (MeGlcA) are present in the xylan accounting for approximately 2 wt.% of the monosaccharides (Laine, unpublished results). This means that the xylan is substituted at C-2 with one MeGlcA substituent

for approximately every 60 xylose residues. It is expected that the xylan in the present study has similar contents of MeGlcA. The total carbohydrate concentrations expressed as xylan were highest with the lowest temperature of 20°C for both, 1 mol/L and 2 mol/L NaOH extractions. Higher concentration (10 g/L) was obtained using 2 mol/L NaOH at 20°C. Interestingly, the extracts from compression showed mostly lower carbohydrate contents compared to the primary extracts. Extracts for the highest temperature (75°C) were an exception, as their extracts from compression contained higher xylan concentrations than the primary extracts. These results show that the dissolution and readsorption of hemicelluloses on pulp fibres are complex phenomena as reported earlier (Tammelin et al., 2009). Increased temperature favors adsorption as reported by Ban and van Heiningen (2011). After the first filtration, the samples cooled down to approximately 50°C, and the pulp probably released additional xylan that dissolved into the extract from compression.

The xylan in the extract from compression accounted for 11-17% of extracted xylan that was recovered in total in the primary extract and the extract from compression. This is a significant amount and therefore, compression of the wet pulp cake after recovery of the primary extract is recommended to increase the xylan yield.

The washing filtrates were in practice free of xylan. Due to the dilution with water, the pH dropped to pH 13.0 or lower for the pulp extracted with 1 mol/L NaOH and to13.2-13.3 for those extracted using 2 mol/L NaOH. The pH drop to 13 obviously induces readsorption of the xylan to pulp from solution. At pH 13.3, small amounts of xylan were still dissolved but accounted only for 2% of the total xylan extracted. Therefore, the xylan in the washing filtrates was not included in the mass balances shown in Figure 2.

The molar mass distributions of the xylan in the different extracts were rather similar, the mass average molar mass (M_w) ranging from 16,200-16,800 g/mol and a polydisperse index of 1.5-1.6 (Table 2).

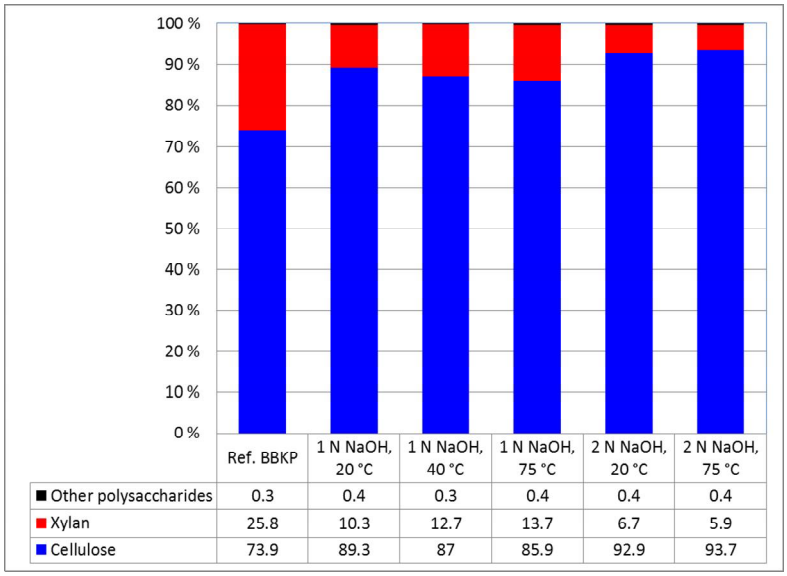
Table 2. Carbohydrate concentration, pH and molar mass distribution data of the alkaline extracts and 1st washing filtrate, announced as xylan in g/L. The total amount of xylan (anhydroxylose) was calculated, using a correction factor of 0.88 for xylose.

Trial nro		1	2	3	4	5
Conditions		1N NaOH, 20°C	1N NaOH, 40°C	1N NaOH, 75°C	2N NaOH, 20°C	2N NaOH, 75°C
Primary extract	pH	13.9	13.6	13.9	14	14
	Xylan, g/L	9.1[a]	7.1	6	10.0[a]	7.2
	Mw, g/mol	18 800	n.d.	17 600	17 000	17 800
	PD	1.5	n.d.	1.5	1.6	1.5
Extract from compression	pH	13.9	13.6	13.9	13.9	14
	Xylan, g/L	7.7[a]	5.9	6.9	8.7[a]	7.6[a]
	Mw, g/mol	18 800	n.d.	16 200	16 900	17 000
	PD	1.6	n.d.	1.6	1.6	1.6
1st washing filtrate	pH	12.9	12.9	12.9	13.3	13.2
	Xylan, g/L	< 0.1	< 0.1	< 0.1	0.14	< 0.1
	Mw, g/mol	n.d.	n.d.	n.d.	n.d.	n.d.
	PD	n.d.	n.d.	n.d.	n.d.	n.d.

[a] The samples contained minor amounts of glucose and partly also rhamnose, in total below 0.5% of the xylan content.

n.d. - Not determined; Mw - Mass average molar mass; PD – Polydispersity

The composition of extracted BBKP (Figure 3) shows that the proportion of xylan in the polysaccharides was reduced from 25.8% down to 5.9 wt.% at the most drastic conditions (2 mol/L NaOH, 75°C) and to 6.7 wt.% at lower temperature (2 mol/L NaOH, 20°C). The xylan content in the pulp extracted with 2 mol/L NaOH was slightly lower than the reported residual xylan content of 7.5 % in birch kraft pulp after extraction using 2.5 mol/L NaOH at 23°C (Froschauer et al., 2013) and slightly higher than the reported residual xylan content of 5.7% in TCF bleached *Eucalyptus globulus* kraft pulp after extraction using 2.25 mol/L NaoH at 30°C for 30 minutes (Sixta and Schild, 2009). The obtained results are thus in agreement with earlier results on cold caustic extraction (CCE) of pulps and the residual xylan content appears to remain in a rather narrow range independent on the hardwood pulp quality.



	Ref. BBKP	1 N NaOH, 20 °C	1 N NaOH, 40 °C	1 N NaOH, 75 °C	2 N NaOH, 20 °C	2 N NaOH, 75 °C
Other polysaccharides	0.3	0.4	0.3	0.4	0.4	0.4
Xylan	25.8	10.3	12.7	13.7	6.7	5.9
Cellulose	73.9	89.3	87	85.9	92.9	93.7

Figure 3. Carbohydrate composition of the unextracted pulp (Ref.) and the extracted pulps at different conditions.

3.2. Extraction of brewer's spent grain (BSG)

The mildest extraction conditions which produced the best total yield for BBKP were tested for another raw material – brewer's spent grain (BSG), which also contains a high proportion of xylan, more specifically arabinoxylan. Based on the content of xylose and arabinose, BSG contained 23.3% or arabinoxylan, which is slightly less than the xylan content of BBKP (25.8%). BSG was extracted at 20°C with 1 mol/L NaOH for 1 hour. The residue was washed and centrifuged to obtain the neutral extracted BSG. This is more favorable than filtration for the BSG due to higher filtration resistance of the material.

56 wt.-% of the BSG dry matter was recovered as the neutral residue and 37% in the extract. This accounts for 93 % of the starting material. The losses were most probably partly due to the washing steps during centrifugation and therefore the yield can be regarded as satisfactory.

The alkaline extract was found to contain proteins and carbohydrates as the major BSG components (Table 3). Carbohydrates were present in the extract as poly- and oligosaccharides since no monosaccharides were detected. Lignin was a minor compound in the extract. A considerable part of the dry matter in the extract was NaOH. The unidentified part of the extract was probably mainly composed of lipids as the lipid content of the BSG was efficiently reduced from 10.6% to 0.9% during the extraction.

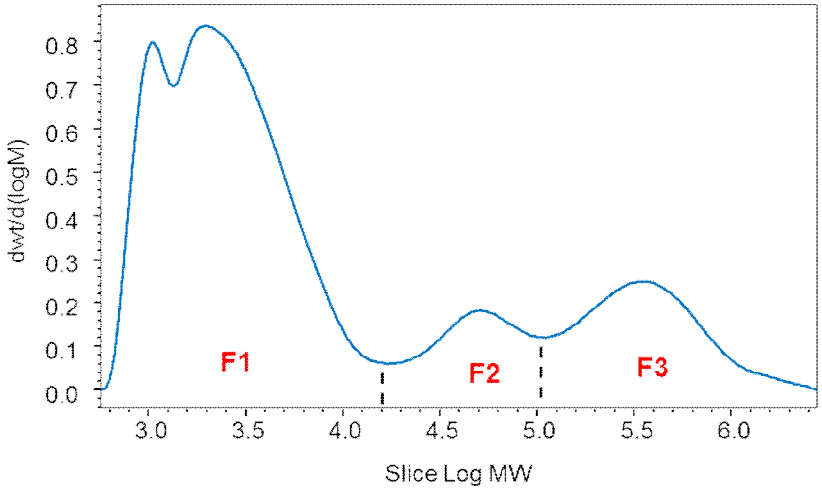
Table 3. Composition of BSG, extracted BSG and the alkaline extract. The carbohydrates are announced as anhydrosugars.

Composition (% of dry matter)	BSG	Extracted BSG	Extract
Carbohydrates	41.4	65.7	12.1
Glucose	16.4	41.5	1.7
Xylose	17.1	16.2	6.6
Arabinose	6.2	6.0	3.1
Galactose	1.1	1.1	0.5
Mannose	0.5	0.9	0.2
Rhamnose	0.0	0.0	0.0
Protein	22.6	1.8	15.3
Insoluble lignin	14.8	12.6	NA
Acid soluble lignin	4.8	0.6	3.0
Lipophilic extractives	10.6	0.9	NA
Ash	4.1	5.5	NA
NaOH	NA	NA	50.9
Other	1.7	12.9	18.7

NA – not analyzed.

Most of the extracted carbohydrates were arabinoxylan (80% of all carbohydrates) next to glucose-containing carbohydrates (starch) and apparently some galactoglucomannans (Table 3). Based on the molar ratio of arabinose and xylose, it appears that the xylan extracted from BSG had a relatively higher degree of substitution than in the original BSG. The molar mass distribution

(MMD) was multimodal. Figure 4 presents the MMD obtained by refractive index (RI) detection showing the data for the whole sample as well as for the major fractions. It should be noted that RI detection also shows lignin and protein. The fractions showed weight average molar mass of 3,000, 56,000 and even 449,500 g/mol. Mandalari et al. (2005) found two distinct peaks of arabinoxylan extracted with 1 M KOH from alcohol insoluble residue of BSG with molar mass ranges of 100,000-2 000,000 g/mol and 2,000-7,600 g/mol.



Sample	Mn	Mw	PD
BSG extract	2 600	91 400	35.2
F1	1 900	3 000	1.6
F2	46 200	56 300	1.2
F3	297 700	449 500	1.5

Figure 4. Molar mass distribution and molar mass values for the BSG extract as well as the major fraction indicated in the distribution.

The composition of the extracted BSG was compared to the unextracted BSG (Table 3). Nearly all the proteins, lipophilic extractives and acid soluble lignin were extracted (>93% extraction yield based on the mass yield and composition of the residue), as well as a significant portion of acid insoluble lignin (52% extraction yield) leaving a residue rich in carbohydrates, mainly cellulose.

Less than 50% of arabinoxylan could be extracted in these conditions showing the differences between BBKP xylan and BSG arabinoxylan. As a comparison, Vieira et al. (2014) were able to remove 75-82% of arabinoxylan from BSG by three sequential alkaline extractions using up to 4 M KOH. It can be concluded that alkaline extraction performed in the conditions optimized for BKKP is better suited to extract proteins and lipids than xylan from BSG.

3.3. Concentration of polymeric xylan and recycling of NaOH by ultrafiltration

The xylan in the extract from BBKP was in a rather low concentration (max 1 wt.% in the extract). At the same time, the extract contained high amounts of NaOH. Thus, ultrafiltration was used to recycle NaOH and to concentrate the product. Two ultrafiltration trials were run using 5 kDa membranes in Labstak equipment. The tested membranes were UFX5 pHt UF membranes (polysulphone permanently hydrophilic on polypropylene support material). Elevated temperature was used to reduce the viscosity of the extract.

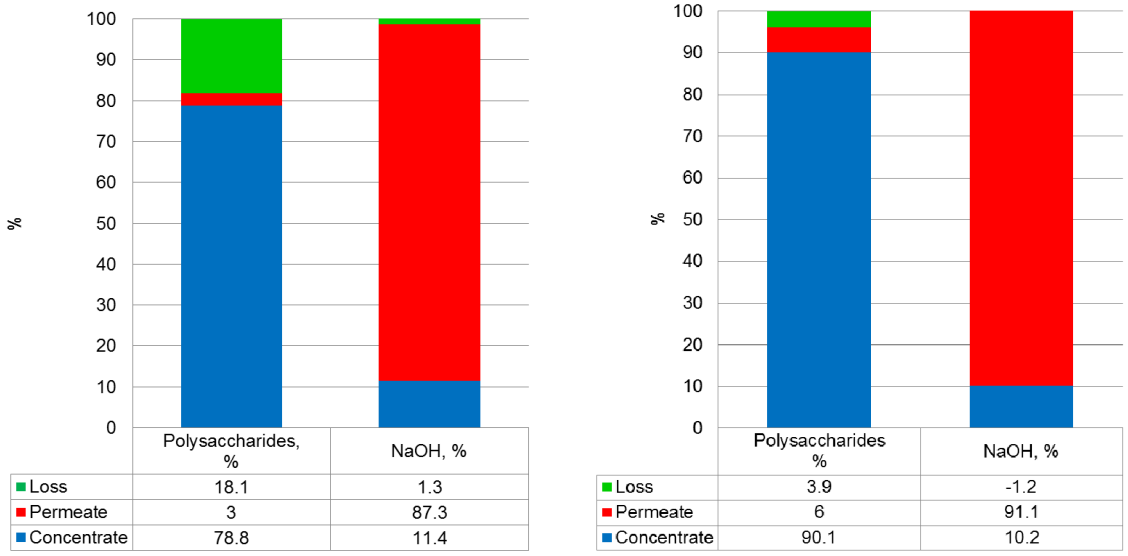


Figure 5. Mass balances of two ultrafiltration trials of the extract from 1 mol/L NaOH / 20°C (trial 1, left) and 1 mol/L NaOH / 75°C (trial 2, right).

It was technically possible to concentrate the extracts by a concentration factor of 8.6 and 10.5 for the extract obtained at room temperature using 1 mol/L and 2 mol/L NaOH, respectively. 87- 91 % of the NaOH was filtered to the permeate with minor amounts of xylan. These results are promising for the economy of the extraction process.

For the second ultrafiltration, online data of the ultrafiltration during the trial was collected (Figure 6). A total of 23.6 kg of primary extract was fed at a volume flow rate of 9 L/min to the equipment, starting with 7.6 kg of the extract and three further additions of 5.0-5.8 kg of the same extract. The feed pressure was 5-13 bar, and the pressure difference mainly 2 bar. The filtration was stopped when the pressure difference reached 5 bar at the end of the filtration. A concentration factor of 10.5 was reached. In this trial, the recovery of NaOH to the permeate and the recovery of xylan in the concentrate was as high as 90% for both. The flux remained satisfactory decreasing slowly from 70 to 40 L/(m^2h) during the trial. The ultrafiltration was terminated when the pressure difference reached 5 bar. The obtained flux is slightly lower than fluxes of 70-100 L/(m^2h) reported for ultrafiltration of paper mill waters using a tubular polysulfone membrane (Nuortila-Jokinen and Nyström, 1996), but still on a reasonable level. The final concentration of xylan in the concentrated extract was 5 wt.-%. It is expected that optimization of the ultrafiltration will allow even higher concentration of xylan and consequently also higher amounts of NaOH would be recycled.

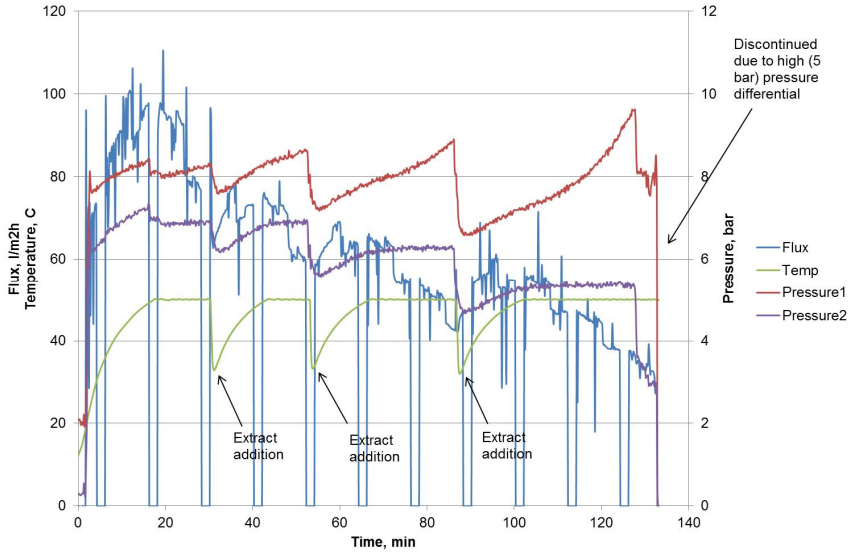


Figure 6. Data recorded during the 2nd ultrafiltration trial.

3.4. Stability of polymeric xylan in the alkaline extract during storage

Storage stability of the alkaline extract was studied. The accelerated ageing was done with a selected concentrated extract in an oven at 60°C for a time range from 2 hours up to one month. The xylan content in the samples was compared to a sample stored in the cool room at 4-8°C (Figure 7). In addition, one sample was stored at room temperature for 6 weeks. The xylan content was analyzed as xylose after hydrolysis. This means that the analysis included possible monomeric or oligomeric xylose.

The xylan in the alkaline extract was stable only for some hours at 60°C. During one day, 10% xylan loss occurred and 28% of the xylan was degraded after one months. However, when xylan was stored at room temperature for 6 weeks, only 7% of the xylan was degraded. At 60 °C the mass average molar mass (Mw) of the sample decreased slightly from 15 700 to 14 300g/mol during one month with the polydispersity remaining at 1.6. The analysis of the degradation products was not included in this study, but it is assumed that carboxylic acids are formed as discussed above.

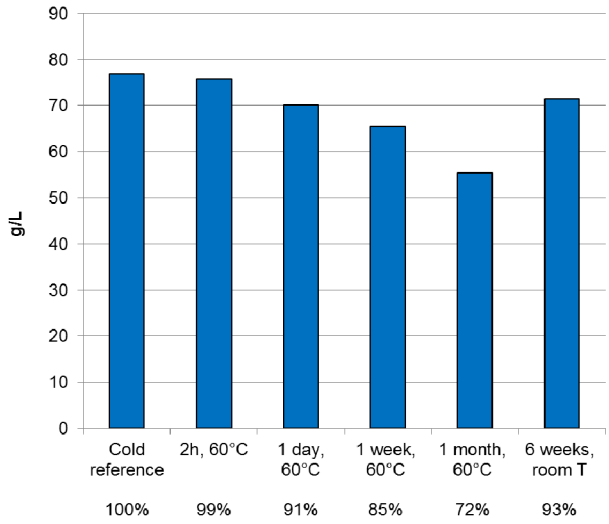


Figure 7. Xylan concentration in samples during accelerated aging at elevated temperatures announced as xylose after hydrolysis.

3.5 Diafiltration

As shown above, the xylan degraded gradually in alkaline solution. For longer storage, it is thus favorable to store xylan in neutral conditions. Therefore, the concentrated alkaline extract was diafiltered using the same ultrafiltration equipment as for the concentration of the alkaline extract. The final permeate conductivity was < 1 ms/cm and the xylan content in the concentrate was 3.5wt.-%. During the diafiltration, the pH decreased slowly due to dilution with neutral tap water. Already at a pH between 13.5 and 13, the xylan was not soluble anymore and a milky dispersion of light color was formed. A total of 88 % of the xylan could be recovered in the dispersed form. The xylan quality was comparable to that of the xylan in our previous study (Laine et al., 2013).

4. Conclusions

The mass balances for the extraction of xylan from BBKP showed that only minor material losses occur at conditions typically used for cold caustic extraction (CCE). Concentration performed by ultrafiltration enabled recycling of 90% of NaOH. Up to 16 wt-% on pulp of pure xylan was extracted of which 90% was recovered as concentrated alkaline extract. The alkali-stability of xylan in 1 M NaOH solution was acceptable at room temperature but already few % degraded at storage at elevated temperatures during 1 day. Diafiltration of the concentrated alkaline extract produced a milky xylan dispersion of light color. In total, the xylan yield for the neutral dispersion was 11.2 wt-% on pulp through the whole process (extraction, ultrafiltation and diafiltration) corresponding to 43% of the xylan in BBKP. The remaining extracted pulp could be a valuable raw material for e.g. dissolving pulp or cellulose derivatives.

Although BSG is also a potential source of xylan, the alkaline extraction conditions optimized for bleached kraft pulp were less suitable for it. Alkaline extraction of BSG was shown to efficiently co-extract protein and lipids, as well as some lignin with arabinoxylan. The complexicity of BSG composition makes selective extraction of arabinoxylan more challenging compared to BBKP.

Further development of the promising approaches will most probably even further improve the yields from BKPP. The demonstrated fractionation process has potential for industrial use when production of both – the isolated xylan and the extracted pulp is the target. Economic and technical feasibility studies are nevertheless still necessary. The feasibility is dependent on the specific mill boundary condition, on the achievable prices for the products as well as the production volumes. The concept of alkaline extraction followed by recovery of the alkali to the permeate and the high molar mass components to the concentrate is a highly potential tool that can be applied more generally for biomass fractionation. This demands still development work to establish the ultrafiltration process in this new application area.

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4