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

Christiane Laine[a,*], Katariina Kemppainen[a], Lauri Kuutti[a], Antero Varhimo[a], Sari Asikainen[a], Antti Grönroos[b], Marjo Määttänen[a], Johanna Buchert[a], Ali Harlin[a]

[a] VTT Technical Research Centre of Finland, P.O. Box 1000, 02044 VTT, Finland
[b] VTT Technical Research Centre of Finland, Koivurannantie 1, 40400 Jyväskylä, Finland

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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.



## 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 et al., 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., 2013; 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 neighboring 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.

* Corresponding author. Tel.: +358 40 5473612.
*E-mail addresses:* christiane.laine@vtt.fi (C. Laine), katariina.kemppainen@vtt.fi (K. Kemppainen), lauri.kuutti@vtt.fi (L. Kuutti), antero.varhimo@vtt.fi (A. Varhimo), sari.asikainen@vtt.fi (S. Asikainen), antti.gronroos@vtt.fi (A. Grönroos), marjo.maattanen@vtt.fi (M. Määttänen), johanna.buchert@vtt.fi (J. Buchert), ali.harlin@vtt.fi (A. Harlin).

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**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 h in all cases.

| Trial nro | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Conditions | 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 |
| 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 |

## 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 (80 g/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 40 L Zirco reactor equipped with blade mixer according to Table 1. The primary extract was obtained by filtration in a self-constructed 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, 2008; Hausalo, 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 × 6.25) measured by Kjeldahl according to Kane (1986).

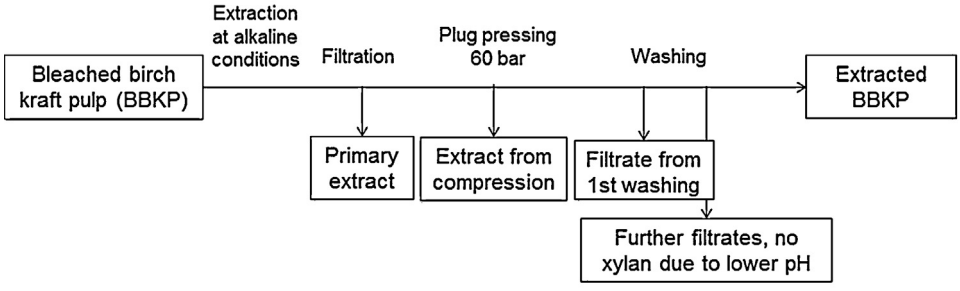


**Fig. 1.** Schematic presentation of the filtration and washing steps applied after the alkaline extraction of BBKP.