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Lignin profiling in extracted xylans by size-exclusion chromatography

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ABSTRACT

Utilization of the polymeric parts of lignocellulose is expected to gain increasing importance in future biorefinery scenarios. In that respect, a particular focus is placed on hemicelluloses from different wood species gained from an industrially feasible upgrading step in the production of dissolving pulps from paper pulps. During alkaline post-extractions for hemicellulose removal, residual lignins are extracted as well. They are either covalently linked to the extracted hardwood xylans or simply co-dissolved in the alkaline lye. In order to better describe the lignin in xylan containing lyes, a method for lignin profiling was set up by hyphenating size-exclusion chromatography of xylans with UV detection which facilitates visualization of the residual lignin distribution. Simultaneous lignin quantification was achieved with lignin standards prepared from Kraft cooking liquors. The setup presented may serve as advanced characterization for novel xylan products.

1. Introduction

Using alkaline process lyes to remove non-cellulosic macromolecules from pulp is a simple and suitable technique for the production of high purity dissolving pulps with a uniform molar mass distribution (Jayme and Roffael, 1969; Wallis & Wearne, 1990) out of lower-value paper pulps (Jackson, Heitman, & Joyce, 1998). This process can be applied to paper pulps created by alkaline Kraft cooking, which is the dominant technology worldwide for producing this type of pulp. As the extraction process can be integrated into paper pulp production lines internationally, it has enormous potential in the field of biorefinery in order to benefit from non-cellulosic carbohydrate polymers alternatively to their energetic utilization through combustion (van Heiningen, 2006).

In alkaline extractions of hemicelluloses from pulps, physical phenomena, such as the swelling behavior of pulps and the dissolution characteristics of hemicelluloses, lead to high-yield and selective cellulose purification (Rydholm, 1965). Alpha-cellulose losses are low due to hindered alkaline cellulose degradation reactions when temperatures are low (Glaus & Van Loon, 2008; Mozdyniewicz et al., 2013; Rydholm, 1965; Schild, Sixta, & Testova, 2010). Good extraction results are achieved when hardwood pulps are used due to the alkaline dissolution characteristics of hardwood xylans (Gehmayr, Schild, & Sixta, 2011). Several studies have already focused on using this strategy in order to provide pulps for viscose fiber production (Hamelinck, 2004; Jayme & Roffael, 1969). In large scale operations, the alkaline extractions lead to the production of pulps with low hemicellulose concentrations, on the one hand, and caustic effluents with high concentrations of dissolved hemicelluloses on the other. In paper pulps, these highly polymeric hemicelluloses positively affect the paper properties (Köpcke, Ibarra, & Ek, 2008) and can be employed to achieve high overall process yields.

In alkaline Kraft processes, hardwood xylans remain almost unaffected in terms of their degree of polymerization (DP) referring to acidic pulping processes, slightly depending on the hardwood source applied (Pinto, Evtuguin, & Neto, 2005; Sixta, 2006; Mais & Sixta, 2004). Only their substitution with acetyl groups is reduced, leading to the release of acetic acid in the cooking liquors. Therefore, the extracted hardwood xylans prepared by Kraft cooking show a high average molar mass in contrast to acidic cooking trials. Consequently, they demonstrate interesting rheological behaviors and hence have a high commercial potential. Additionally, the almost complete recirculation of the alkaline solutions without hemicelluloses for their further utilization in Kraft cooking, oxygen delignification or alkaline post extractions improves the cost- and resource-effectiveness of the process (Sixta, Promberger, Borgards,

Abbreviations: PHK, prehydrolysis Kraft cooking; DOC, dissolved organic carbon; EA, effective alkalinity; CBC, continuous batch cooking; η, intrinsic viscosity (CUEN viscosity).

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Table 1
Parameters of oxygen-delignified Kraft pulps used.

	birch	eucalyptus	beech
Kappa number (–)	7.6	7.4	5.2
Brightness (%ISO)	66.4	67.7	61.6
[η] (ml g^{-1} odp)	925	880	925
Water retention value (%)	103	98	81
Carboxyl content (μmol g^{-1})	109.6	126.7	66.7
Glucan (%)	76.0	77.5	83.7
Xylan (%)	23.8	22.1	16.1
Mannan (%)	0.2	0.0	0.2
Arabinan (%)	0.0	0.0	0.0
Rhamnan (%)	0.0	0.0	0.0
Galactan (%)	0.0	0.2	0.0
Crystallinity (%)	57	56	52
Cellulose II content (%)	10	10	17

& Möslinger, 2007). In sum, the process step of alkaline hemicellulose removal from hardwood paper pulps provides a tool enabling the pulp manufacturer to benefit from a product with additional economic value and represents an alternative way to benefit from the chemical diversity of the wood resource (Schild et al., 2010). In a high-value hemicellulose co-product, purity and uniformity have to be guaranteed. The chain lengths of glycosidic macromolecules, which is one parameter that affects the rheological behavior of the product, can easily be monitored by size-exclusion chromatography. The differences in rheological behavior as dependent on chain lengths, substitution patterns and the ionic state of the inclosing carboxyl groups have already been determined (Ebringerova & Heinze, 2000). From monomeric xylose, other bulk products, such as furfural, acetic acid, xylitol and ethanol can be produced (Glaus & Van Loon, 2008; Köpcke et al., 2008).

Besides hemicelluloses, residual lignins that remain in the pulps after pulping and oxygen delignification are also removed under alkaline conditions in cold and hot caustic extractions. This removal of lignins may be either due to the general solubility of Kraft lignins in alkali or due to co-extraction, as lignins can be bound to xylans with covalent linkages. The present study was set up to profile these lignins during size-exclusion chromatography by hyphenation with UV detection. This experimental strategy should show possible correlations between lignin content and lignin localization along the xylan molar mass. The application of self-prepared lignin standards with similar structural properties to residual lignins in Kraft pulps additionally allows lignin quantification within reasonable limits (although we have to expect a slight difference in the extinction coefficient between residual lignin and precipitated lignin which was additionally treated in a simulated oxygen stage). All these data can be further used to define subsequent purification strategies or bleaching conditions. A minimal intake of bleaching chemicals positively impacts the cost- and resource-effectiveness of the processes and lowers the amount of wastewater effluents, which is a key parameter in all pulp-producing processes.

2. Materials and methods

2.1. Starting pulps

Commercially available never-dried eucalyptus (*Eucalyptus globulus*) Kraft pulp after oxygen delignification was kindly supplied by ENCE from the pulp mill in Huelva, Spain. The corresponding pulp was prepared from wood chips from Uruguay. Oxygen delignified never-dried birch (*Betula papyifera*) Kraft pulp was also used. Beech (*Fagus sylvatica*) paper pulp was provided by Lenzing AG using a pilot scale digester applying a Kraft CBC protocol. The resulting pulp was oxygen-delignified as well. The initial pulps for subsequent alkaline treatments reflect the parameters given in Table 1.

2.2. Alkaline post-extraction of pulps

80 g atro paper pulp according to Table 1 was subjected to alkaline treatments in polyethylene flasks (Jayme & Schenck, 1949) with 30-min residence time at 10% volumetric consistency. As the method was developed to quantify alkaline extractable residual lignins in a hemicellulosic co-product, extractions were performed similarly to process conditions. Therefore, synthetic white liquor was used as an alkali source for all extractions, which consisted of sodium hydroxide, sodium sulfide and sodium carbonate. As caustic lye typically used in Kraft paper pulp mills, white liquor with 30% sulfidity and 90% causticizing degree was utilized. Treatment temperatures were varied between 20 °C and 80 °C and effective alkalinities between 40 g l^{-1} and 120 g l^{-1}. In order to separate pulps from the hemicellulose-containing lyes, the obtained pulp suspension was filtered through a glass frit. After washing them with a 20 g l^{-1} white liquor and hot water, the pulps could be used for analyses.

2.3. Preparation of lignin standards

The alkali-soluble technical lignins of the three hardwood species used in this study were precipitated from Kraft black liquors by acidification with concentrated sulfuric acid (H_2SO_4). After centrifugation and washing with 0.06 mol l^{-1} H_2SO_4 and deionized water, the lignins were dried at 50 °C overnight, and their dry content was determined. The dried lignins were then treated with 2% w/w sodium hydroxide solutions under oxygen pressure in a stirred reactor to simulate the typical oxygen delignification of paper pulps. After precipitation, washing, drying and determination of the dry content, the obtained lignins were treated with a 100 g l^{-1} white liquor similar which replicates conditions used in caustic hemicellulose extractions at elevated temperatures. For this purpose, highly concentrated white liquor was used as an alkali source in a stir reactor under atmospheric conditions. After precipitation, washing and drying, lignin standards were prepared in 100 g l^{-1} white liquor with a concentration range of 10–3000 mg l^{-1}.

2.4. Analytical methods

The Kappa numbers of the alkaline treated pulps were determined according to TAPPI T 236 cm-85 (1993a). Lignin contents in pulps were calculated out of Kappa numbers according to the equation: lignin content = Kappa number × 0.16 (Li & Gellerstedt, 1998). The sugar content in pulps was measured by high-performance anion-exchange chromatography with pulsed amperometric detection after a two-stage total hydrolysis (Wright & Wallis, 1996). The hemicellulose content in the caustic solutions was determined by dissolved organic carbon (DOC) measurement according to EN 1484 by applying already established conversion factors (Hamelinck, 2004).

2.5. Method for lignin profiling

The molar mass distributions of the dissolved hardwood xylans were determined by size-exclusion chromatography after dissolution in 0.5 mol l^{-1} sodium hydroxide (Guerra, Lucian, & Argyropoulos, 2008). The chromatographic system consisted of three PSS MCX 1000 Å, 300 × 8 mm analytical columns (PSS, Mainz, Germany) with refractive index (RI) detection at a flow rate of 1 ml min^{-1}. The pre-column was a PSS MCX 1000 Å, 50 × 8 mm. For RI detection an Shodex RI-101 detector was used and viscosity detection was done with a WGE eta 2010 detector. Calibration was carried out with a set of pullulan standards (Showa Denko, Japan), dextran standards (PSS, Mainz, Germany) and cello-oligomers (Fluka, Merck, Germany). The UV detector used was a Kontron