



A precise study on effects that trigger alkaline hemicellulose extraction efficiency



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HIGHLIGHTS

- Alkaline hemicellulose extraction efficiency of hardwood paper pulps.
- Xylan degradation in cold caustic extractions using synthetic white liquor.
- Uniformity and purity of alkaline extracted hardwood hemicelluloses.

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ABSTRACT

The conversion of paper-grade pulps into dissolving pulps requires efficient strategies and process steps to remove low-molecular noncellulosic macromolecules generally known as hemicelluloses. Current strategies include alkaline extractions and enzymatic treatments. This study focused on the evaluation of extraction efficiencies in alkaline extractions of three economically interesting hardwood species: beech (*Fagus sylvatica*), birch (*Betula papyrifera*), and eucalyptus (*Eucalyptus globulus*). Substrate pulps were subjected to alkaline treatments at different temperatures and alkalinities using white liquor as the alkali source, followed by analyses of both pulps and hemicellulose-containing extraction lyes. The extracted hardwood xylans have strong potential as an ingredient in the food and pharmaceutical industries. Subsequent analyses revealed strong dependencies of the extraction efficiencies and molar mass distributions of hemicelluloses on the process variables of temperature and effective alkalinity. The hemicellulose content of the initial pulps, the hardwood species, and the type of applied base played minor roles.

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1. Introduction

For the production of high-quality dissolving pulps, the most commonly applied processes are acid sulfite cooking and prehydrolysis Kraft (PHK) cooking. In both treatments, process conditions lead to the extraction and digestion of the major part of hemicelluloses and lignin, enabling the production of high-purity pulps with a uniform molecular weight distribution (Hinck et al., 1985). As an unwanted side effect, these treatments lead to cellulose degradation reactions due to hydrolytic cleavages and peeling reactions at high temperatures, directly affecting the overall process yield.

To produce paper-grade pulp, conventional Kraft cooking is the major process applied worldwide. During this process, effective

delignification is achieved through nucleophilic reaction of hydrogen sulfide ions with lignin molecules. The major part of hemicelluloses remains unaffected in the pulp matrix, increasing the overall process yield. Thus, both the cellulose and hemicellulose yields achieved in these cooking processes considerably exceed those achieved by sulfite and PHK cooking. In paper-grade pulps, the high hemicellulose content positively affects the physical strength properties of the paper product. In order to benefit from these high cellulose yields, a process that combines Kraft cooking with subsequent hemicellulose and lignin removal leads to the production of high-purity dissolving pulps, a process concept generally known as modified Kraft cooking (Gehmayer et al., 2011; Sixta et al., 2007). Several studies have focused on this strategy's potential for creating high-quality pulps for viscose production (Jackson et al., 1998; Köpcke et al., 2008). The overall approach includes alkaline treatments of paper-grade pulps followed by various enzyme treatments to enhance pulp reactivity and eventually

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a totally chlorine-free (TCF) bleaching sequence. The advantage of this process is that the cellulosic fraction remains largely unaffected and indicates a narrower molar mass distribution for the resulting pulps compared to dissolving pulps produced by conventional sulfite and PHK processes.

The challenge of extracting hemicelluloses from paper pulps for the production of dissolving pulps is twofold. First, the removal of hemicelluloses has to be almost quantitative, resulting in a high alpha-cellulose content with a narrow molar mass distribution in order to adjust pulp viscosity. Second, a high reactivity of the resulting pulps is required to ensure a stable rayon process. The alkaline treatment of the pulp substrates induces a partial conversion of the cellulose I allomorph to cellulose II. This has a direct effect on reactivity and accessibility to reagents. When dried, alkali-treated pulps with a high cellulose II content tend to exhibit collapsed interfibrillar spaces (Gehmayr et al., 2011) that lead to the formation of aggregates. These structural changes may be caused by radical reactions in the sodium-cellulose system (Bains et al., 1968) at even lower alkali concentrations as applied in alkaline hemicellulose extractions of Kraft pulps. Previous studies have described the formation of strong hydrogen bonds in cellulose systems, especially for cotton linters and sulfite pulps, which result in molecular aggregates. The aggregates exhibit a decreased surface area and pore volume, resulting in decreased pulp reactivity to esterification agents (El-Din and El-Megeid, 1994). This side effect is generally described as pulp hornification, and alternative solvents have been investigated to avoid this problem (Puls et al., 2006). Our study focused on alkaline extractions, because they seem to be more promising for prospective large-scale applications.

Cold alkaline extractions between 20 °C and 40 °C, known as cold caustic extractions (CCEs), have been used in several applications (Gehmayr et al., 2011), because they offer minimal cellulose losses. Previous studies have described the influence of process conditions on the hemicellulose extraction efficiency in alkaline extraction depending on pulp type (Sixta, 2006). Hemicelluloses extracted by alkaline treatments contain highly polymeric xylan. In the case of birch xylan (degree of polymerization (DP) ~200), a substituent is found at every tenth monomer at carbon C2 by 4-O-methyl-glucuronic acid (Teleman et al., 2001) and with additional 4-O- α -D-galactopyranosyluronic acid units (Shimizu and Samuelson, 1973). The degree of substitution with uronic acids is reduced through pulp production processes. Extensive research has been performed on the degradation reactions of birch hemicelluloses (Johansson and Samuelson, 1977a; Kolmodin and Samuelson, 1973), including peeling reactions (Ericsson et al., 1977; Johansson and Samuelson, 1977b). These reactions take place at reducing end groups (Machell and Richards, 1957; Richtzenhain, 1954; Mozdyniewicz et al., 2014) and form isosaccharinic acid as the main soluble product. The loss of reducing sugars by peeling is stopped by a reaction that leads to the formation of alkali-stable metasaccharinic acid. In the case of hardwood xylylans, peeling retardation occurs at substituted units. Hence, substitution with uronic acids hinders xylan peeling.

In addition to peeling reactions, random xylan chain scission may occur in alkaline pulp treatments. Hemicellulose degradation follows pseudo-zero-order kinetics at 160–180 °C (Collier, 1960), depending on alkalinity, the initial concentration of xylan, and its DP. Subsequently, the decrease in DP and quantity of hemicelluloses leads to an increase in acid formation through polysaccharide degradation (Mozdyniewicz et al., 2014). The situation changes in the presence of oxygen, with depolymerization reactions occurring already at 95 °C (Kolmodin and Samuelson, 1973). In the present study, xylan extractions were performed at moderate temperatures ranging from 0 °C to 80 °C. In this temperature range, xylan depolymerization reactions cannot be fully excluded, but they

are highly restricted. Peeling reactions also occur at these temperatures, although to a much smaller extent. Analyzing ratios of the beta and gamma fraction enables the determination of the extent of degradation products present as acid-soluble compounds. The quantification of beta and gamma cellulose in alkaline process lyes is achieved through the precipitation of the beta fraction by sulfuric acid and the subsequent determination of the dissolved molecules by measurement of the dissolved organic carbon (DOC).

An almost complete recirculation of alkaline process media ensures the economic efficiency of the entire extraction process, which requires large amounts of alkali. For recycling of the alkaline media, the dissolved hemicelluloses have to be removed and separated almost completely.

In this study, white liquor recovered from the cooking liquor in these processes was used as a treatment lye in order to simulate the integration of the alkaline extraction in Kraft cooking plants.

The present study investigated the influence of process conditions during alkaline extractions of hemicelluloses from hardwood Kraft pulps. It focused on the applicability of economically interesting hardwood species, namely beech (*Fagus sylvatica*), birch (*Betula papyrifera*), and eucalyptus (*Eucalyptus globulus*), using white liquor as the alkali source. Due to differences in both morphology and chemical composition between the different hardwood species, their behavior during alkaline extraction is not yet fully understood. Initial investigations revealed strong effects of temperature and alkalinity on the polysaccharides. The knowledge of these supramolecular interactions will enable the production of a dissolving pulp low in hemicellulose with high reactivity as well as the production of a hemicellulosic co-product of high quality.

2. Materials and methods

2.1. Starting pulps

Oxygen-delignified never-dried eucalyptus (*E. globulus*) Kraft pulp was supplied by ENCE (Spain) and was prepared from wood chips from Uruguay in the pulp mill in Huelva, Spain. Oxygen-delignified never-dried birch (*B. papyrifera*) Kraft pulp was also used. Both paper pulps are commercially available. Beech (*F. sylvatica*) pulp was prepared using a pilot scale digester according to a standard Kraft continuous batch-cooking protocol. The resulting brown stock was subsequently oxygen-delignified. The parameters of the pulps before alkaline treatments are given in Table 1.

2.2. Alkaline treatments

All alkaline treatments were performed according to Wallis and Wearne (1990) in a lab high-shear mixer or in polyethylene flasks.

Table 1
Parameters of oxygen-delignified Kraft pulps.

	Birch	Eucalyptus	Beech
Kappa number (–)	7.6	7.4	5.2
Brightness (%ISO)	66.4	67.7	61.6
Intrinsic viscosity [η] (mL g ⁻¹ odp)	925	880	925
Water retention value (%)	103	98	81
Carboxyl group content (μ mol 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
Weight average (kg mol ⁻¹)	420	514	540
Crystallinity (%)	57	56	52
Cellulose II content (%)	10	10	17

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