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Potential of hot water extraction of birch wood to produce high-purity dissolving pulp after alkaline pulping

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HIGHLIGHTS

- Hot water extractions followed by SAQ pulping produce high-purity cellulose pulps.
- Below a xylan content of 3% in pulp, the cellulose yield dramatically decreases.
- Sodium borohydride increases the cellulose yield.
- After intense hot water extractions, amorphous cellulose is degraded during pulping.

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ABSTRACT

The potential of hot water extraction of birch wood to produce highly purified dissolving pulp in a subsequent soda-anthraquinone pulping process was evaluated. After intermediate extraction intensities, pulps with low xylan content (3–5%) and high cellulose yield were successfully produced. Increasing extraction intensity further decreased the xylan content in pulp. However, below a xylan content of 3%, the cellulose yield dramatically decreased. This is believed to be due to cleavage of glycosidic bonds in cellulose during severe hot water extractions, followed by peeling reactions during alkaline pulping. Addition of sodium borohydride as well as increased anthraquinone concentration in the pulping liquor increased the cellulose yield, but had no clear effects on pulp purity and viscosity. The low intrinsic viscosity of pulps produced after severe extraction intensities and soda-anthraquinone pulping corresponded to the viscosity at the leveling-off degree of polymerization, suggesting that nearly all amorphous cellulose had been degraded.

1. Introduction

The concept of a wood biorefinery is envisioned as the selective separation of wood components for the production of high value-added products. Within this context, hot water treatment of wood (autohydrolysis) prior to pulping operations is recognized as a potential step to extract the hemicelluloses and convert them into films, fuels or food additives, among others (Girio et al., 2010; Hansen and Plackett, 2008; Parajó et al., 2004). Autohydrolysis of wood is typically conducted under mild conditions to minimize the degradation of extracted hemicelluloses (Testova et al., 2011; Tunc and van Heiningen, 2009). The extraction of high-molar mass hemicelluloses may also be enhanced by controlling the pH during a hot water extraction (Song et al., 2011).

In addition to hemicelluloses, a part of the lignin is dissolved in the water extract, whereas the lignin in the wood residue is structurally altered (Leschinsky et al., 2008; Rauhala et al., 2011). Delignification of the wood residue under alkaline conditions is facilitated and succeeds under milder conditions than those used for delignification of untreated wood (Rauhala et al., 2011; Yoon and van Heiningen, 2008). Compared with pulps produced from untreated wood, pulps that are produced from water extracted wood generally show reduced papermaking properties, owing to the lower amount of hemicelluloses (Helmerius et al., 2010; Yoon and van Heiningen, 2008). The presence of hemicelluloses enhances the formation of bonds between cellulose fibers, giving the pulp superior mechanical performance. A low hemicellulosic content is thus not desired in the production of high-quality paper pulps, whereas it is required in the production of dissolving-grade pulps.

Dissolving pulps, with a high cellulose content (over 90% of the dry mass) of uniform degree of polymerization (DP) and low amounts of inorganic and organic non-cellulosic compounds, are used to manufacture regenerated fibers (to make textiles or films) as well as a variety of cellulose ether and cellulose ester products

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(Sixta, 2006). Dissolving pulps are produced by the prehydrolysis kraft (PHK) process, in which wood is steamed prior to pulping to remove part of the hemicelluloses, or by the acid sulfite process. Post-treatments to reduce the amount of residual hemicelluloses in the pulp include a hot caustic extraction (HCE) and/or cold caustic extraction (CCE). These purification steps contribute to a considerable increase in production costs (Sixta, 2006). Acetate-grade pulps are the highest purity dissolving pulps, with a xylan content lower than 2%, a cellulose content higher than 97%, and an intrinsic viscosity between 600 and 800 mL/g (Sixta, 2006).

Refining steps to produce highly purified dissolving pulps might not be necessary if hot water extractions at elevated temperatures are applied before pulping. This is because at temperatures above 180 °C, hot water extractions induce a quantitative removal of hemicelluloses from wood, with only minor losses in cellulose yield (Borrega et al., 2011a; Mok and Antal, 1992). However, hydrolytic cleavage of both hemicelluloses and cellulose appears to occur even at relatively mild extraction intensities (Lin, 1979). The formation of new reducing end-groups in cellulose chains may then promote degradation by peeling reactions during an alkaline pulping process (Alén, 2000).

Aldehyde end-groups in carbohydrates can be stabilized by reduction to alditols or oxidation to aldonic acids. Stabilization of carbohydrates diminishes the extent of peeling reactions, which in turn increases the pulp yield. Anthraquinone (AQ) is an oxidant, often used in chemical pulping, that stabilizes carbohydrates and improves the rate of delignification. Furthermore, in the case of hardwoods, a non-sulfur soda-anthraquinone (SAQ) process may produce pulps in higher yield and similar bleachability than those produced by conventional kraft pulping, while being friendlier to the environment (Francis et al., 2008).

In this study, hot water extractions of birch wood under a wide range of intensities are conducted to investigate the potential to produce dissolving-grade pulps in a subsequent SAQ pulping process, without the need for additional purification steps. The yield, chemical composition and viscosity of the pulps before bleaching is determined and related to the intensity of the hot water extraction. The effects of carbohydrate stabilization agents on minimizing peeling reactions during pulping are also reported. Finally, the impact of extraction intensity on cellulose depolymerization is analyzed by determining the molar mass distribution of selected pulp samples.

2. Experimental

2.1. Wood material

Birch wood chips were delivered from a pulp mill in Finland. The chips were screened (SCAN-CM 40:01) upon delivery and subsequently stored in a freezer. The dry matter content was determined by oven-drying representative samples at 103 °C overnight.

2.2. Hot water extractions

Hot water extractions were conducted in a 10 L batch reactor equipped with a heat-exchanger and temperature control. About 1 kg of chips (oven-dry mass) was placed in the reactor, together with a predetermined amount of deionized water to reach a liquid to wood (L:W) ratio of 3:1 g/g. A high-pressure pump was used to continuously re-circulate the water through the chip bed. The temperature in the reactor was raised to the setup temperature, and after an isothermal treatment time, the water extract was drained through a bottom valve. The reactor was then rapidly cooled, and the wood residue was recovered and stored in the freezer. The wood yield was determined gravimetrically after oven-drying representative samples at 103 °C overnight.

The intensity of any hot water extraction is often described by the *P*-factor. This intensity factor uses an Arrhenius-type expression to account for the combined time–temperature effect, with an activation energy of 125.6 kJ/mol corresponding to the removal of fast-reacting xylan (Sixta, 2006). Owing to the severe conditions applied in this study, the intensity of any hot water extraction was described by a modified *P*-factor. An activation energy of 180 kJ/mol, corresponding to the removal of the recalcitrant xylan fraction in birch wood (Borrega et al., 2011a), was used to compute the modified *P*-factor, from here on denoted as P_{Xs}. An increase in P_{Xs} corresponds to an increase in autohydrolysis intensity. The experimental parameters for the hot water extractions are summarized in Table 1.

2.3. Alkaline pulping

Pulping experiments were conducted in an oil-bath reactor, containing 8 rotating autoclaves of 225 mL each. A predetermined amount of wood chips, corresponding to 25 g of initial oven-dry wood, were placed in each autoclave. An aqueous solution containing caustic soda (NaOH) and AQ was added, reaching a L:W ratio of 3:1 g/g. The amounts of soda and AQ were 22% and 1% on initial oven-dry wood mass, respectively. Each pulping trial was conducted in duplicate. The temperature in the reactor was raised to 150 °C and kept constant for 60 min, reaching an *H*-factor of about 200 h. The *H*-factor is an intensity factor that combines the effect of pulping temperature and time into a single variable (Vroom, 1957). The pulping was stopped by submerging the autoclaves in an ice-water bath. The black liquor was drained and the pulp was thoroughly washed with warm water. The pulp yield was determined by oven-drying representative samples after screening in a laboratory 0.35 mm plate screener.

A few selected wood residues from the hot water extractions were subjected to SAQ pulping with 22% NaOH and 0.1% AQ. The effect of carbohydrate stabilizing agents such as anthraquinone-2-sulfonic acid sodium salt (AQS) and sodium borohydride (BH) was then tested by adding either one of these chemicals to the SAQ pulping liquor. The amount of AQS and BH added was 1%, based on initial oven-dry wood mass. The pulping experiments were conducted following the same procedure described above.

2.4. Analytical determinations

Chemical composition (carbohydrates, Klason lignin and ASL) of wood and pulp samples was determined after a two-stage total hydrolysis, according to the analytical method NREL/TP-510-42618 issued by the U.S. National Renewable Energy Laboratory (NREL). The ASL was measured in a Shimadzu UV-2550 spectrophotometer at a wavelength of 205 nm, and using an absorption coefficient of 110 L/(g cm) (Swan, 1965). The monosaccharides were determined by high performance anion exchange chromatography with pulse amperometric detection (HPAEC-PAD) in a Dionex ICS-3000 system. Based on the amount of individual monosaccharides, cellulose and xylan content in wood and pulp samples was calculated with the Janson formula (Janson, 1974). With this formula, cellulose is defined as the content of anyhydroglucose in the sample after subtracting the contribution of glucose to glucomannan, and xylan is defined as the content of anyhydroxylose including uronic acid substituents. The kappa number and intrinsic viscosity of the pulps were determined according to the SCAN-C 1:100 and SCAN-CM 15:99 methods, respectively. The intrinsic viscosity at the LODP was determined after hydrolyzing three pulp samples in 2 M aqueous hydrochloric acid (HCl) at 80 °C, following the procedure described by Håkansson et al. (2005).