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Changes of anionic groups in alkaline peroxide-impregnated aspen chemithermomechanical pulp during subsequent alkaline peroxide bleaching

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ABSTRACT

The effect of alkaline peroxide bleaching on the total anionic groups (AGs) and surface AGs in aspen chemithermomechanical pulp (CTMP) fibers was investigated. Alkaline treatment, especially alkaline peroxide bleaching resulted in the formation of new AGs and surface AGs in the CTMP fibers. The carboxylic groups in uronic acid units, including 4-*O*-methylglucuronic acid, galacturonic acid, and glucuronic acid units were the main contributors to the AGs in the fibers. However, the oxidized lignin accounting for more than 30% of the total AGs in the bleached CTMP fibers, was the main origin of the new AGs formed during the peroxide bleaching. In addition, the new AGs were also formed by extensive deesterification of the residual esterified uronic acids in pectins and lignin-carbohydrate complexes (LCCs). Although some uronic acid units were dissolved in the process water, both the total AGs and surface AGs in the fibers increased after alkaline peroxide bleaching.

1. Introduction

Anionic groups (AGs) can originate from the wood used as raw material in pulp manufacture or be generated during pulping, bleaching, and papermaking (Sjöström, 1989), which are the most important groups in pulp because they can significantly affect fiber swelling, beatability, paper strength properties, and interactions with paper chemicals (Barzyk, Page, & Ragauskas, 1997; Fardim, Moreno, & Holmbom, 2005; Konn, Pranovich, Fardim, & Holmbom, 2007; Laine & Stenius, 1997; Zhang, Sjögren, Engstrand, & Htun, 1994). Carboxyl groups are the main AGs present in all papermaking fibers. In native wood, most of the carboxyl groups originate from uronic acid units. In both softwood and hardwood, the main uronic acids are 4-O-methylglucuronic acid units bound to xylans and galacturonic acid units in pectins (Willför, Sundberg, Hemming, & Holmbom, 2005; Willför, Sundberg, Pranovich, & Holmbom, 2005).

During pulping and alkaline peroxide bleaching of CTMP, new AGs can be formed, and bleached CTMP contains more AGs than any other papermaking fibers (Fardim, Moreno, & Holmbom, 2005). The formation of new AGs during pulping and bleaching of CTMP depends on the wood materials and process conditions. Pectins are the important wood components to form new AGs during CTMP pulping and bleaching, because they can form new free uronic acids by deesterification under alkaline conditions. In addition, the pectins can also be degraded by polygalacturonic chain-splitting according to the β-elimination mechanism under alkaline conditions (Kiss, 1974; Renard & Thibault, 1996). The degraded pectins form new uronic acid units in the fibers or dissolve in the process water during pulping and bleaching of CTMP. The degradation and dissolution of pectins depends on the pretreatment conditions. About 2%–10% of the total pectins in the wood were dissolved in the process waters during CTMP pulping (Konn, Pranovich, & Holmbom, 2006). The alkalinity is the most important factor that affects the deesterification of pectins during impregnation stage in CTMP pulping. In the alkaline peroxide impregnation stage of spruce chips, increasing NaOH dosage from 1% to 2% could result in the deesterification of pectins from 50–60% to 70–80% (Konn et al., 2006). Hafrén and Daniel (2003) reported that the deesterification of pectins was not complete during CTMP pulping of spruce, and the residual esterified galacturonic acid units were specifically localized on the surface of unbleached CTMP. In addition, it was believed that new AGs could also be created in the fiber materials duo to lignin oxidation in the alkaline peroxide impregnation of spruce CTMP (Konn et al., 2007).

The AGs would no doubt be influenced by the subsequent alkaline peroxide bleaching. The AGs content in thermomechanical pulp (TMP) increases during peroxide bleaching, which is the results of deesterification of esterified uronic acid units in pectin and lignin-carbohydrate complexes (LCCs), and the generation of new carboxyl groups during lignin oxidation (Pranovich, Sundberg, & Holmbom, 2003). The study by Fardim and Holmbom (2005) showed that the main origins of AGs are the 4-*O*-methylglucuronic

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acid units, galacturonic acid units, sulfonic acid groups and oxidized lignin in the alkaline peroxide bleached CTMP from spruce and aspen. However, the changes of AGs and surface AGs in the fibers of CTMP during alkaline treatment and alkaline peroxide bleaching have not been well understood.

Nowadays, fast-growing aspen such as *Populus* × *euramericana* 'Guariento' or *Populus* × *euramericana* 'Neva' is regarded as one of the most suitable hardwood species grown in North China. The aspen has been widely planted and the use in the kraft and mechanical pulp production has increased in China in recent years (Xu et al., 2010). Many Chinese pulp and paper mills including Huatai, Sunpaper and Tralin have already established large aspen plantations and several modern production lines of aspen bleached CTMP (Yang, Lu, & Ni, 2006).

The aim of this study was to investigate the origin, formation and changes of total and surface AGs in fibers during the only alkaline treatment and alkaline peroxide bleaching of aspen CTMP. The dissolution of uronic acid units, the extensive deesterification of uronic acid units and the oxidation of lignin during alkaline peroxide bleaching of aspen CTMP were discussed in detail.

2. Experimental

2.1. Materials

Aspen (a mixture of *Populus* × *euramericana* 'Guariento' and *Populus* × *euramericana* 'Neva') unbleached CTMP was prepared in Huatai Group (Dongying, China). The aspen chips were steamed for 30 min at 100 °C after being washed thoroughly. The compressed chips were impregnated in the liquor of 2.5% H_2O_2 (on o.d. wood), 3% NaOH (on o.d. wood) and 2.5% Na_2SiO_3 (on o.d. wood) at 85 °C for 30 min and then subjected to two-stage refining. First stage refining was carried out at a conical-disc refiner (RGP 82 CD, Metso), which disc diameter is 2080 mm, and the second stage refining was carried out at a single-disc refiner (RGP 268 SD, Metso), which disc diameter is 1728 mm. The refined pulp was washed and then concentrated to about 20% consistency before use. The pH of the pulp was 8.3 and no residual peroxide was found in the pulp. All chemical reagents used in the experiment were analytic grade.

2.2. Alkaline peroxide bleaching

The peroxide bleaching was conducted in plastic bags in a thermostatic water bath under the following conditions: 4.0% H_2O_2 (on o. d. pulp), 3.0% NaOH, 3.0% Na_2SiO_3, 0.05% $MgSO_4$, 10% pulp consistency, 70 °C and 90 min. At the end of the bleaching, the pulp was washed twice with deionized water in a Buchner funnel with a 200-mesh screen. For the alkali-treated pulp, the pulp was treated as peroxide bleaching process, but no H_2O_2 was added.

2.3. Extraction

The unbleached, alkali-treated and bleached pulps were extensively washed with distilled water at 60 °C to remove all dissolved and colloidal substances. It was then extracted with acetone–water (9:1, v/v) to remove extractives and then washed with EDTA and 0.01 M HCl solution to remove metal ions (Fardim et al., 2005).

2.4. Conversion of AGs to sodium salt form

The AGs were converted to sodium form by treatment with 2 mM $NaHCO_3$ solution and stirring for 30 min followed by filtration. The pulps were then washed with deionized water until the conductivity of the filtrate was lower than 5 μS cm^{-1}. The fully washed pulps were then used for MB (methylene blue) sorption to measure the AGs (Fardim et al., 2005).

2.5. MB sorption

MB sorption method, which is based on the replacement of AG counter-ions by the cationic dye, was used for determination of the total AGs content (Fardim & Holmbom, 2003). About 100 mg of o.d. pulp was used for every test and a sorption time of 20 min at 500 rpm agitation was used.

2.6. Determination of uronic acid units in fibers

The uronic acid units in the fibers were determined by gas chromatography (GC) after methanolysis as described by Sundberg, Sundberg, Lillandt, and Holmbom (1996). All the results were calculated on an extractive-free and freeze-dried pulp basis.

2.7. XPS analysis

The surface AGs were determined by XPS analyses on MB-labeled samples. X-ray photoelectron spectra of fiber surfaces were obtained with Thermo Scientific K-Alpha XPS spectrometer (ThermoFisher Scientific, East Grinstead, UK) with a monochromatic Al Kα X-ray source. The samples were run at a take-off angle (relative to the surface) of 90°, and the analyzed area was 400 μm × 400 μm. Charge compensation was provided by utilizing the flood gun provided with the instrument. Low resolution (pass energy 150 eV) was used for survey spectra and characterization of the fiber surface elements composition. The relative concentrations of C, O, S, and N (in at.%) on the fiber surfaces were measured using a pass energy of 150 eV in a snapshot mode, collection time optimized for signal-to-noise. The estimation of surface AGs was calculated according to Eq. (1) by Fardim et al. (2005).

$$\mathrm{SAG} = \left[\frac{\mathrm{S}\times 32.06}{\mathrm{C}\times 12.00 + \mathrm{O}\times 15.99 + \mathrm{N}\times 14.00 + \mathrm{S}\times 32.06}\right] \times \left[\left(\frac{1}{32.06}\right)\times 10,000\right] \quad (1)$$

2.8. Distribution of AGs by ToF-SIMS imaging

The pulps after extraction and metal ions removal were treated with 2 mM $MgCl_2$ with stirring for 30 min, and then the pulps were washed with the deionized water until the conductivity of the final filtrate was less than 2.0 μS cm^{-1}.

The surface distribution of AGs was analyzed using ToF-SIMS imaging by monitoring the distribution of characteristic Mg^{2+} on a raster size of 200 μm × 200 μm. All measurements were conducted on a ToF-SIMS IV (Münster, Germany). A Bi liquid metal ion gun was used and spectra were obtained in a high spatial resolution mode (Sodhi, 2004) using the Bi_3^+ cluster as the primary ion species.

3. Results and discussion

3.1. Total AGs and uronic acid units in fibers

MB sorption method was reported to be a straight-forward and repeatable method for total AGs of the fibers (Fardim & Holmbom, 2003). Because the wood chips were impregnated with alkaline peroxide instead of alkaline sulfite in the study, the sulfonic acid group did not exist in CTMP used. As shown in Table 1, the amount of AGs in the unbleached CTMP fibers was 195 μmol/g. Alkali treatment and alkaline peroxide bleaching increased AGs to 230 μmol/g and 275 μmol/g, respectively. That is to say, alkali