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Combination of alkaline and enzymatic treatments as a process for upgrading sisal paper-grade pulp to dissolving-grade pulp

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ABSTRACT

A sequence of treatments consisting of an initial xylanase treatment followed by cold alkaline extraction and a final endoglucanase treatment was investigated as a process for upgrading non-wood paper-grade pulps to dissolving-grade pulps for viscose production. Five commercial dried bleached non-wood soda/AQ paper pulps, from flax, hemp, sisal, abaca, and jute, were studied for this purpose. Commercial dried bleached eucalyptus dissolving pulp was used as reference sample. Sisal pulp showed the highest improvement in Fock's reactivity, reaching levels nearly as high or even higher than that of eucalyptus dissolving pulp (65%), and a low hemicellulose content (3–4%) when was subjected to this sequence of treatments. The viscosity, however, decreased considerably. A uniform and narrow molecular weight distribution was observed by size exclusion chromatography. ^{13}C nuclear magnetic resonance spectroscopy and Raman microspectroscopy revealed that the cellulose structure consisted of cellulose I.

1. Introduction

Despite wood is still by far the main source for pulp and paper production, non-wood fibers occupy small niche markets providing special properties to a range of high added value products (Moore, 1996). However, where wood-based fibers are not available, as in the developing world, they are the major source for the pulp and paper industry (Moore, 1996). Moreover, there is a growing need in different world organizations to consider alternative agricultural strategies that move an agricultural industry entirely focused on food production to one that also supplies the needs of other industrial sectors, such as pulp and paper, and cellulose-based products (van Dam et al., 1994). In addition of cereal straw, the leading non-woody plant, other sources such as flax, hemp, sisal, abaca or jute could become an important crop in this transformation.

Dissolving-grade pulps are used as raw material in the manufacture of different cellulose-derived products, including viscose rayon, the first commercially manufactured regenerated cellulose fiber. In the viscose process, cellulose is treated with carbon disulfide in the presence of a base to produce cellulose xanthate (Treiber, 1985). In contrast to paper-grade pulps, dissolving pulps must contain a high content of cellulose (90–99%), low content of hemicelluloses (2–4%), and traces of residual lignin, extractives and minerals. A cellulose predominantly consisted of cellulose I with a uniform molecular weight distribution is also desired (Sixta, 2006).

Hemicelluloses are undesirable impurities in dissolving pulps, affecting the cellulose processability, e.g. the filterability and the xanthanation in the viscose process, and properties of the cellulose-end products such as the viscose strength (Christov and Prior, 1993). Most of the hemicellulose is reduced from wood by acid sulfite and pre-hydrolysis kraft processes, the two major methods used to produce dissolving pulps. However, the manufacture of these pulps demands higher costs than the commonly used paper pulps. For this reason, other alternatives have been studied; among them the conversion of paper pulps to dissolving pulps by selective reduction of the hemicellulose (Wallis and Wearne, 1990; Jackson et al., 1998; Bajpai and Bajpai, 2001; Puls et al., 2006; Köpcke et al., 2008). Different methods have been developed for this purpose, including alkaline, nitren, and cuen extraction (Wallis and Wearne, 1990; Puls et al., 2006). In the same way, the use of xylanases, alone or in combination with alkaline extraction, has been also demonstrated (Jackson et al., 1998; Bajpai and Bajpai, 2001; Köpcke et al., 2008).

Reactivity is often the most significant quality parameter of dissolving pulps. High cellulose reactivity improves the homogeneity and quality of cellulose-end products and lower the demands of reactants, e.g. use of carbon disulfide in the viscose manufacture, reducing production costs and the environmental impact.

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However, increasing the accessibility and reactivity of cellulose is not a simple task. Cellulose has a compact fibrillar structure as a result of intra- and intermolecular hydrogen bonds and hydrophobic interactions (Fengel and Wegener, 1984). Various treatments have been assessed to increase the reactivity of the cellulose (Krässig, 1993), including the use of enzymes such as monocomponent cellulases (Henriksson et al., 2005; Kvarnlöf et al., 2006; Engström et al., 2006; Köpcke et al., 2008).

After showing the feasibility of upgrading eucalyptus and birch paper kraft pulps to dissolving pulps by combining alkaline extraction with xylanase and endoglucanase treatments (Köpcke et al., 2008), these treatments are investigated and optimized on flax, hemp, sisal, abaca and jute soda/AQ paper-grade pulps for the same purpose. The treatment effects on pulps are evaluated in terms of reactivity, according to Fock's method, viscosity, and hemicellulose content. The molecular weight distribution is recorded by size exclusion chromatography (SEC). The supramolecular structure is studied by ^{13}C nuclear magnetic resonance spectroscopy (^{13}C-CP/MAS NMR) and Raman microspectroscopy.

2. Methods

2.1. Pulp samples

Commercial dried ECF-bleached soda/AQ paper-grade pulps from flax (*Linum usitatissimun*), hemp (*Cannabis sativa*), sisal (*Agave sisalana*), abaca (*Musa textilis*), and jute (*Corchorus capsuloris*), provided by Celesa (Spain), were investigated. The results were compared with those of a commercial dried TCF-bleached sulfite pulp from eucalyptus (*Eucalyptus globulus*), provided by Sniace (Spain). In general, these pulps presented a low kappa number (0.6–1), high brightness (near 90%) and alpha cellulose content around 88–91%. The viscosity values were different, depending on the pulp (530 mL g^{-1} for *E. globulus* sulfite pulp, and 802, 683, 654, 1195 and 692 mL g^{-1} for flax, hemp, sisal, abaca and jute soda/AQ pulp). Prior to the treatments, the dried sheets were maintained in deionized water for 24 h, disintegrated in Lorentzen & Wettre equipment at 1.5% consistency and 30,000 revolutions, according to the ISO standard 5263-1:2004, and were finally filtrated.

2.2. Enzymes

Monocomponent endoglucanase preparation (Novozyme 476) and xylanase preparation (Pulpzyme HC), both supplied by Novozymes Denmark, were used. Novozyme 476 is produced from a genetically modified *Aspergillus* species. The cellulolytic activity was determined by the manufacturer and expressed in Endo Cellulase Units (ECU) per unit mass of material as 5000 ECU g^{-1}. Pulpzyme HC is produced from a genetically modified *Bacillus* species. The xylanase activity was determined by the manufacturer and expressed in Endo Xylanase Units (EXU) per unit mass of material as 1000 EXU g^{-1}.

2.3. Enzymatic and chemical treatments

Enzymatic treatments were carried out according to Köpcke et al. (2008) on 10 g (dry weight) of pulp at 3% pulp consistency in phosphate buffer solution (11 mM NaH_2PO_4 and 9 mM Na_2HPO_4), pH 7 (the optimal pH of the enzymes, as described by the manufacturer Novozymes). For a homogeneous distribution, the enzymes were added to the buffer and then to the pulp. The enzymatic treatments were performed in plastic bags in a water bath at 50 °C for Novozyme 476 and 60 °C for Pulpzyme HC (the optimal temperatures of the enzymes, as described by the manufacturer Novozymes). The pulps were kneaded every 30 min. After treatment, the enzymes were denatured by filtration on a Büchner funnel and mixed with deionized water at 90 °C. The treated pulps were placed in a 90 °C water bath for 30 min and subsequently filtered and washed with 1000 mL of deionized water. As a control, pulps were treated under identical conditions without enzymes.

The effects of Novozyme 476 dosage and incubation time on the different pulps were investigated, as described in previous study (Köpcke et al., 2008). Different enzyme dosages were tested (0, 50, and 250 ECU g^{-1} dry weight pulp), keeping the incubation time constant at 1 h. In the same way, different incubation times were considered (0, 15, 30, 45, 60, and 120 min), keeping the enzyme dosage constant at 250 ECU g^{-1} dry weight pulp.

Similarly, in order to optimize the removal of xylan by enzymatic treatment, different dosages of Pulpzyme HC were tested (0, 10, 80, 500, and 1000 EXU g^{-1} dry weight pulp), with incubation time of 2 h.

Chemical treatment consisted of an alkaline extraction with 9% NaOH solution at room temperature for 1 h and 4% pulp consistency (Köpcke et al., 2008). Extracted pulps were filtered and washed with deionized water until the filtrate pH was neutral.

2.4. Reactivity measurements

The reactivity of the treated pulps was analyzed according to a slightly modified version of Fock's method (Fock, 1959; Henriksson et al., 2005). This test is a micro-scale process similar to the viscose process. The test was carried out in two steps. Prior to Fock's analysis, the treated pulps were dried at 50 °C.

2.4.1. Step 1. Preparation of viscose from treated pulps and collection of regenerated cellulose

0.5 g of pulp samples were weight in a 100 mL Erlenmeyer with a stopper. Fifty milliliters of 9% NaOH and 1.3 mL of CS_2 were added, and the solutions were stirred with a magnetic stirrer (300 rpm) for 4 h at room temperature. The solution was diluted to 100 g using deionized water and carefully shaken. The solution was then left for 2 h in order to allow any undissolved cellulose to settle. An aliquot (10 mL) from the upper clear solution was then transferred to another 100 mL Erlenmeyer flask and neutralized using 29% H_2SO_4. The yellow solution turned transparent and was left overnight in a fume cupboard.

2.4.2. Step 2. Oxidation and titration of the regenerated cellulose

The regenerated cellulose samples were mixed with 20 mL of 68% H_2SO_4 and stirred with a magnetic stirrer for 1 h. The milky solution was diluted to 50 mL with deionized water. Ten milliliters of 1 N $K_2Cr_2O_7$ was added, and the solution was refluxed for 1 h to fully oxidize the regenerated cellulose and thereby clear the solution. The solution was transferred to a 100 mL measuring and diluted with deionized water. Forty milliliters of the solution was then transferred to a 250 mL beaker containing 0.5 g of KI, stirred with a magnetic stirrer, and titrated with 0.1 N of $Na_2S_2O_3$. When the brown solution started to change the color, 1.5 g of starch was added, and the solution turned blue-violet. The titration continued until all of the I_2 was reduced and the solution turned pale blue. The volume of $Na_2S_2O_3$ required in each case was determined.

Reactivity measurements were carried out in triplicate and expressed as the regenerated cellulose yield (Eq. (1))

$$X = (100)9.62^{a}\frac{M(V_1C_1 - (V_2C_2100/40^{b})/6)}{4Y} \quad (1)$$

where, X is the reacted cellulose (%), Y is the weight of sample (g), M is the molecular mass of glucopyranosyl residue, $C_6H_{10}O_5$ (162 g mol^{-1}), V_1 is the volume of added $K_2Cr_2O_7$ (L), V_2 is the volume of titrated $Na_2S_2O_3$ (L), C_1 is the concentration of $K_2Cr_2O_7$