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An enzyme-catalysed bleaching treatment to meet dissolving pulp characteristics for cellulose derivatives applications

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HIGHLIGHTS

- Action of natural mediators examined for the first time in unbleached sulphite pulp.
- Violuric acid was the most efficient mediator for sulphite pulp biobleaching.
- Impact of enzymatic stage (L) was evaluated in comparison to conventional treatment.
- The efficiency of Po stage was assessed via H_2O_2 consumption and reaction time.
- Final good dissolving pulp properties were obtained by means of LMS.

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ABSTRACT

Bleached cellulose with good end-properties (~90% ISO brightness and 62% cellulose preservation) was obtained by using a totally chlorine-free biobleaching process (TCF). Unbleached sulphite cellulose was treated with *Trametes villosa* laccase in combination with violuric acid. This enzymatic stage (L) was followed by a chelating stage (Q) and then by a hydrogen peroxide stage reinforced with pressurized oxygen (Po), resulting to an overall LQPo sequence. The use of violuric acid was dictated by the results of a preliminary study, where the bleaching efficiency of various natural (syringaldehyde and *p*-coumaric acid) and synthetic mediators (violuric acid and 1-hydroxybenzotriazole) were assessed. The outstanding results obtained with laccase-violuric acid system fulfil most of the characteristics of commercial dissolving pulp, totally acceptable for viscose manufacturing or CMC derivatives, with the added advantage that the enzymatic treatment saved 2 h of reaction time and about 70% of hydrogen peroxide consumption, relative to a conventional sequence (Po).

1. Introduction

Most wood pulp produced – 1.86×10^8 ton (FAO, 2012) – is used in the paper and packaging industry but a substantial part is employed to obtain cellulose-based products with important applications in industrial sectors such as, pharmaceutical, textile, food and printing, among others. Cellulose-based products are classified into cellulose derivatives and regenerated cellulose (Köpcke et al., 2008) and the raw material typically used for the production of these products is low-yield chemical bleached pulp called dissolving-grade pulp. Dissolving pulp is defined by high content of cellulose (90–99%), small amounts of hemicellulose (2–4%) and only traces of residual lignin, extractives and minerals. Removing hemicelluloses from wood fibres is essential with a view to facilitating the processing of cellulose during the production of viscose. Hemicelluloses can affect the filterability of viscose, the xhantation of cellulose, and the strength of the end product (Christov and Prior, 1993). In addition, high brightness, low degree of polymerization and very uniform molecular weight distribution are also highly desirable qualities; in contrast fibre strength is not an issue.

According to FAO (2012), the current world production of dissolving-grade pulp is 4.22×10^6 ton; however, the demand for speciality cellulose has become apparent in recent years and prospective consumer markets indicate that this interest will continue in subsequent decades. This upturn in the dissolving pulp market is considered to be due to an increasing demand for textile materials in Asian countries, environmental and agricultural restrictions on cotton cultivation and the important point that dissolving pulp can be an environmentally friendly alternative to synthetic fibres.

Dissolving pulp has traditionally been obtained by the alkaline pre-hydrolysis kraft (PHK) process or acid sulphite process. However, these conventional pulping processes have some drawbacks relating to the quality of the final product and the pollution they

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generate. In view of these disadvantages, new industrial technologies such as organosolv pulping or the removal of hemicellulose by alkaline, nitren and cuen extraction have been developed and studied. In the same way, the enzymes have been used alone and in combination with alkaline extraction to develop effective alternatives to chemical processes (Bajpai and Bajpai, 2001; Ibarra et al., 2010; Jackson et al., 1998; Puls et al., 2006; Schild and Sixta, 2011; Wallis and Wearne, 1990). In addition, dissolving pulp is more expensive to obtain than paper-grade pulp in terms of chemical consumption, production rate, inventories and storage space (Hillman, 2006) and hence the interest to upgrade paper-grade pulps to dissolving quality pulps. Furthermore, the potential of a sulphite mill biorefinery, i.e. separation of lignocellulosic materials (LCM) with different properties into different streams and the further processing of these fractions to obtain high-value bioproducts, has become desirable.

In terms of bleaching treatments, chlorine-based chemicals were typically used in order to control cellulose degradation and achieve a desired viscosity level, but in response to environmental concerns these technology were largely abandoned. The new bleaching processes such as the elemental chlorine free (ECF) and the totally chlorine free (TCF) are based on oxygen-derived compounds. A typical ECF sequence comprises multi-stages, oxygen delignification (O), chlorine dioxide (D), alkaline extraction (E) and hydrogen peroxide (P) stages in any combinations, while a conventional TCF sequence includes an oxygen delignification (O) stage, an acid (A) stage, an ozone (Z) stage and a hydrogen peroxide (P) stage in different multi-positions. Also, biotechnology has provided highly promising results in delignifying or bleaching paper-grade pulps. In particular, the laccases are known to catalyse the oxidation of phenolic substrates; however the feasibility of laccase application may be improved in the presence of a redox mediator (viz. as a laccase–mediator system, LMS). The mediator acts as an intermediate to allow the enzyme to indirectly oxidize large molecules or even non-phenolic substrates. Mediator oxidation by laccase produces a high redox potential which dramatically expands the range of laccase-oxidizable compounds. LMS have been widely applied in alkaline pulps (Andreu and Vidal, 2011; Aracri and Vidal, 2011; Bourbonnais et al., 1997; Chakar and Ragauskas , 2004; Valls et al., 2013). To our knowledge, however, sulphite pulp processed with laccase plus a natural or synthetic mediator has not so far been reported. Moreover, as demand for dissolving pulp is estimated to increase during the next decades, the potential of LMS can offer a good alternative for traditional bleaching processes. With this aim, a biobleaching sequence using a laccase–mediator system in combination with a chemical bleaching stage was developed for efficient bleaching of softwood sulphite cellulose. In preliminary tests, two synthetic (violuric acid and 1-hydroxybenzotriazole) and two natural compounds (*p*-coumaric acid and syringaldehyde) were used as mediators and their bleaching responses assessed in terms of pulp and effluent properties. The mediator with the highest bleaching potential was selected for further use in an extended TCF biobleaching sequence.

2. Methods

2.1. Raw material

Unbleached sulphite cellulose obtained from a mixture of 60% spruce (*Picea abis*) and 40% pine (*Pinus sylvestris*) and cooked at Domsjö mill (Sweden), was used as raw material. Prior to bleaching treatments, fibre samples were conditioned at pH 4 adjusted with H_2SO_4, stirred at 2% pulp consistency for 30 min and washed with de-ionized water in a glass filter funnel. This step was needed to remove contaminants and metals, and also to bring the pulp to the pH required for enzymatic treatment. The main characteristics of the starting pulp were as follows: 4.2 ± 0.2 kappa number, 61.25 ± 0.6% ISO brightness, 511 ± 11 mL/g viscosity. Carbohydrate composition, as determined by high-performance liquid chromatography (HPLC), were as follows: 90.2 ± 0.38% glucan, 4.3 ± 0.1% mannan, 2.1 ± 0.0% xylan, 0.8 ± 0.0% glucuronic acid, 0.2 ± 0.0% arabinan and 0.04 ± 0.01% acetyl groups.

2.2. Enzyme and mediators

Commercial laccase from *Trametes villosa* was used in combination with the natural mediators syringaldehyde (SA) and *p*-coumaric acid (*p*CA), and the synthetic mediators 1-hydroxybenzotriazole (HBT) and violuric acid (VA). The enzyme was supplied by Novozymes® (Denmark) and the mediators were purchased from Sigma–Aldrich. Laccase activity was determined by monitoring the oxidation of ABTS 2,2′azino*bis*(3-ethylbenzthiazoline-6-sulphonate) in 0.1 M sodium acetate buffer at pH 5 at 25 °C. One activity unit is defined as the amount of laccase required to convert 1 μmol/min of ABTS to its cation radical (ε_{436} = 29,300 M^{-1} cm^{-1}).

2.3. Preliminary bleaching tests: selection of the mediator

Unbleached sulphite cellulose was treated with a laccase–mediator system (LMS) consisting of the enzyme and either a synthetic compound (HBT or VA) or a natural compound (SA or *p*CA). All treatments, at 5% pulp consistency, were conducted in an oxygen pressurized reactor (0.6 MPa), at stirring rate of 30 rpm, using 50 mM sodium tartrate buffer at pH 4, a dose of 20 U/g odp (oven dried pulp) of laccase and one of 1.5% odp of each mediator at 50 °C for 4 h. A few drops of the surfactant Tween 20 (0.05% w/v) were also added. The enzymatic conditions were similar to those previously used by Valls et al. (2012) with eucalyptus pulp. The sequence was completed with a chemical bleaching stage involving alkaline peroxide bleaching procedure. Fibre samples, at 5% consistency, were treated with 2% odp H_2O_2, 1.5% odp NaOH, 1% odp DTPA (diethylenetriaminepentaacetic acid) and 0.2% odp $MgSO_4$ in a Datacolor Easydye AHIBA oscillating individual reactor at 90 °C for 2 h (Andreu and Vidal, 2011; Aracri et al., 2009; Fillat et al., 2010). After each stage, residual liquors were collected for subsequent analysis, and pulp samples filtered and extensively washed for further processing. A laccase control sequence (K_LP) was conducted in parallel under the same conditions but with no presence of mediator. A conventional hydrogen peroxide bleaching sequence, i.e. a P stage applied directly to the starting pulp, was also performed in order to compare the bleaching efficiency of the laccase–mediator system in combination with a hydrogen peroxide bleaching stage.

A xylanase stage (X) was described as a pre-trial test to assess the efficiency of the enzyme on sulphite cellulose. The enzyme used was a commercial xylanase (Pulpzyme HC) supplied by Novozymes®. The X stage used 3 U/g odp xylanase at 10% consistency adjusted with Tris–HCl buffer at pH 7 at 50 °C for 2 h. After treatment, liquors were recovered and the resulting pulp was extensively washed as reported elsewhere for eucalyptus pulp (Valls et al., 2010).

2.4. Extended biobleaching sequence: influence of the H_2O_2 dose and reaction time reduction

An extended TCF biobleaching sequence including a laccase–mediator treatment was applied to the initial pulp. The sequence was designated LQPo/P, where L denotes the enzymatic treatment, Q a chelating stage and Po/P a hydrogen peroxide stage lasting 6 h – the first four reinforced with pressurized oxygen and then followed by a depressurization where oxygen is removed.