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Integration of a kraft pulping mill into a forest biorefinery: Pre-extraction of hemicellulose by steam explosion versus steam treatment

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HIGHLIGHTS

- Steam explosion and steam pre-treatments were carried out before kraft pulping.
- The rate of extraction of hemicelluloses was similar with both pre-treatments.
- Steam explosion enhanced delignification more efficiently.
- Pre-treatments reduced paper mechanical properties owing to the fiber morphology.
- Paper optical properties were boosted when pre-treatments were carried out.

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ABSTRACT

Growing interest in alternative and renewable energy sources has brought increasing attention to the integration of a pulp mill into a forest biorefinery, where other products could be produced in addition to pulp. To achieve this goal, hemicelluloses were extracted, either by steam explosion or by steam treatment, from *Eucalyptus globulus* wood prior to pulping. The effects of both pre-treatments in the subsequent kraft pulping and paper strength were evaluated. Results showed a similar degree of hemicelluloses extraction with both options (32–67% of pentosans), which increased with the severity of the conditions applied. Although both pre-treatments increased delignification during pulping, steam explosion was significantly better: 12.9 kappa number vs 22.6 for similar steam unexploded pulps and 40.7 for control pulp. Finally, similar reductions in paper strength were found regardless of the type of treatment and conditions assayed, which is attributed to the increase of curled and kinked fibers.

1. Introduction

Integration of a lignocellulose biorefinery into a pulp mill is a feasible possibility to add value to the production of pulp, a product considered as a commodity with a moderate added value. The integrated biorefinery-pulp mill would bring forth products of higher added-value, such as furfural, carbon fibers, biopolymers or biofuels, in addition to pulp (Helmerius et al., 2010).

One strategy to accomplish this integration is to use a fraction of hemicelluloses which, in a conventional kraft cooking, are dissolved into the cooking liquor and burned in the recovery boiler jointly with the lignin degradation products. While, combustion of the non-cellulosic compounds provides the necessary supply of energy to maintain the pulp mill or even to have a surplus, removal of hemicelluloses prior to cooking does not necessarily affect the final energy balance because their heating value is approximately half that of lignin, and cooking pre-extracted chips requires considerably less energy than cooking normal chips, as the cooking time of the former is significantly shorter (Martín-Sampedro et al., 2011a). The removed hemicelluloses could be hydrolyzed into sugars and then fermented to ethanol or derived to other value-added products. These compounds are considered promising platform chemicals in the synthesis of many other valuable products (Tuck et al., 2012).

Hemicelluloses extraction has been done by a variety of methods such as autohydrolysis, steam explosion, acid hydrolysis or alkali extraction. However, steam explosion and autohydrolysis pre-treatments only use water/steam at high temperature causing the formation of acetic acid from the acetylated wood component, which catalyzes hydrolytic reactions in the wood polymers. Thus, these hydrothermal pre-treatments can be considered as a green and competitive technology to remove hemicelluloses in hardwood, since reaction media contain only lignocellulosic feedstock

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and water, which prevents corrosion problems and the formation of neutralization sludges (Garrote et al., 1999; Martín-Sampedro et al., 2011a).

The effect of these hydrothermal pre-treatments on a subsequent pulping process has been studied using a diversity of raw materials. Autohydrolysis has been applied as a pre-treatment on kraft, soda or ethanol–water pulping using pine (Kautto et al., 2010; Saukkonen et al., 2012), a mixture of maple, poplar and birch (Li et al., 2010), eucalyptus (Chirat et al., 2012; Mendes et al., 2009; Vila et al., 2011, 2012), aspen (Al-Dajani et al., 2009), birch (Helmerius et al., 2010), bagasse (Hamzeh et al., 2013) and *Leucaena leucocephala* K360 (Feria et al., 2012). Although in less extent than autohydrolysis, steam explosion pre-treatment has also been studied using different raw materials such as pine (San Martin et al., 1995), Norway spruce (Jedvert et al., 2012), a mixture of marple, birch and aspen (Ahvazi et al., 2007), *Hesperaloe funifera* (Martín-Sampedro et al., 2012b) and eucalyptus (Martín-Sampedro et al., 2011a,b). With both pre-treatments, hemicelluloses removal results in an improvement of the delignification rate, which reduces the cooking time and/or the chemical charge required for an equal target of kappa number, and enhances the subsequent bleaching process. In some cases, it has also been observed a decrease in pulp viscosity, due to the reduction of the cellulose polymerization degree and a general loss of mechanical properties. Nevertheless, the loss of pulp mechanical properties is moderate when the xylan removal is limited (Chirat et al., 2012), and the pulp viscosity could be maintained if pre-extracted chips are cooked at milder conditions than non-extracted wood (Vila et al., 2012). Finally, the decrease in pulp yield observed could be explained by the hemicellulose removal and an increase of the peeling reactions of a more exposed cellulose (Chirat et al., 2012).

As all hydrothermal pre-treatments (stem treatment, hot water treatment, steam explosion, etc.) lead to a similar release of acids from acetylated wood components which catalyze hydrolytic reactions in the wood polymers (autohydrolysis), the main difference between steam treatment (sometimes called autohydrolysis treatment) and steam explosion is the rapid decompression that takes place at the end of steam explosion but not in steam treatment. This decompression forces the fibrous material to "explode" into separated fibers and fiber bundles, generating a solid fraction with a more open structure (Ahvazi et al., 2007; Martín-Sampedro et al., 2011a,c) that may enhance the efficient diffusion of cooking liquor into the fibers. Although both pre-treatments have been studied in different articles, as mentioned above, a comparison between them has not been previously reported. Therefore, the main objective of this study is to compare the effect of steam explosion and steam treatment on the subsequent kraft pulping of *Eucalyptus globulus*, in order to elucidate the separate effect of the steam treatment (causing autohydrolysis in both pre-treatments) and of the "explosion". Furthermore, the influence of the severity factor on the subsequent pulping process and pulp quality was also studied with both pre-treatments.

2. Experimental

2.1. Raw material

E. globulus chips were kindly provided by La Montañanesa pulp mill (Torraspapel – Lecta Group, Spain). The material was air dried and then homogenized in a single stock (by conditioning inside polyethylene bags) to avoid differences in composition and water content. The chips were stored in polyethylene bags at 25 °C.

2.2. Steam explosion and steam treatments

Steam explosion and steam treatments were performed in a 26 L stainless steel digester (manufactured by Cadepla S.L.) capable of temperatures to 190 °C and a pressure of 1.37 MPa (14 kg-f cm^{-2}). The digester was connected to a blowing tank into which chips were discharged at the end of the treatment. It was also equipped with electrovalves for steam admission, and a ball valve of discharge. The steam generator was a Babcock Wanson VAP 250RR boiler, with a maximum steam production rate of 270 kg h^{-1} and a working pressure of 1.37 MPa.

According to previous reports (Martín-Sampedro et al., 2011a; Martín-Sampedro et al., 2011c), chips were immersed in water at 25 °C for 16 h in order to improve the efficiency of the subsequent steam pre-treatments. In all of the experiments, 500 g of *E. globulus* chips were treated with steam at 183 °C (10 kg-f cm^{-2}). The variable operational conditions were: number of cycles of treatment (one or two), duration of the first cycle (5 or 10 min), and discharge pressure (6 kg-f cm^{-2} for steam explosion treatments or atmospheric pressure for steam treatments). When a second cycle was carried out, the pre-treated chips obtained in the first cycle were washed with cold water and then subjected to a second cycle of 3 min following the same procedure as in the first cycle. After treatment, the samples were thoroughly washed with water, dried at room temperature and stored in sealed polyethylene bags.

The severity factor of each treatment was calculated according to the following equation (Eq. (1)) defined by Overend and Chornet (1987).

$$S_0 = \log\left(e^{\frac{T-100}{14.75}t}\right) \quad (1)$$

in which T is the temperature (°C) and t the duration of the treatment (min).

Water retention, or hydration, capacity of the treated and untreated chips was defined as the weight of water absorbed by the chips after being immersed in water at 25 °C for 6 h. It was expressed as grams of water per 100 g of oven dry wood, according to the following equation:

$$WR = \frac{W_w - W_d}{W_d} \cdot 100 \quad (2)$$

where W_w was the weight of the wood chips after the water immersion; then, wood chips were dried at 104 °C during 24 h, and weighted again (dry weight, W_d).

2.3. Chemical analysis

In order to carry out the chemical analysis, all the samples were dried at room temperature and then milled in a Wiley mill. The samples were sieved using standard sieves to obtain 20 g of wood meal sized between 0.30 and 0.40 mm. Acetone extractives (UNE-EN ISO 14453), hot water extractives (UNE 57-013-82), lignin content (TAPPI T 222 om-88), holocellulose content (Wise et al., 1946) and pentonsans content (TAPPI T 223 cm-84) were then measured in the wood meal. All determinations were duplicated.

2.4. Kraft cooking process

Kraft cooking was performed over control (non-treated), steam exploded and steam unexploded chips in pressurized 1-liter reactors. Four reactors were placed in a 20 L rotatory pressurized vessel that contained hot water for indirect heating of the reactors. The rotatory vessel had a jacket-type electrical heater controlled by a computer to set the cooking temperature. Cooking conditions were: 150 g of dry chips, 4 L/kg liquor to wood ratio, 16% active