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Hemicelluloses removal in autohydrolysis pretreatment enhances the subsequent alkali impregnation effectiveness of poplar sapwood

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HIGHLIGHTS

- Poplar sapwood with different hemicelluloses content by autohydrolysis was got.
- The autohydrolyzed poplar sapwood was subjected to alkali impregnation.
- Porosities of the fiber cell walls were increased due to the hemicelluloses removal.
- Hemicelluloses removal raised alkali impregnation effectiveness of poplar sapwood.

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ABSTRACT

This work is aimed at investigating the influence of changes in the content of hemicelluloses of the autohydrolyzed poplar sapwood on the subsequent alkali impregnation for chemi-mechanical pulping (CMP). An alkali impregnation process was conducted using the autohydrolyzed poplar sapwood with different content of hemicelluloses as raw materials. The results showed that both the amount of NaOH consumption and swelling degree of poplar sapwood increased with the removal of hemicelluloses, thus enhancing the alkali impregnation effectiveness. The hemicelluloses removal can also shorten the alkali impregnation time for the autohydrolyzed poplar sapwood to achieve the similar impregnation effectiveness of unautohydrolyzed poplar sapwood. All of these can be attributed to the fact that the hemicelluloses removal would result in the exposure of more free hydroxyl groups on the cellulose and an increase in the porosity of the fiber cell walls.

1. Introduction

As a fractionation method of biomass chemical composition, autohydrolysis pretreatment has been widely studied by many researchers due to its cost-effectiveness in the removal of hemicelluloses. Yoon et al. (2008) found that autohydrolysis of loblolly pine chips could lead to the removal of a great part of hemicelluloses, with a minor dissolution of lignin and celluloses. Duarte et al. (2011) studied the influence of autohydrolysis on the mechanical properties of sugar maple kraft pulp fibers. They noticed that the fiber lengths had little change, while the fines content was reduced, and the tensile and burst strengths of the corresponding handsheets also had significant losses after autohydrolysis pretreatment. When autohydrolysis pretreatment was applied to chemi-thermomechanical pulping (CTMP) (i.e., one kind of chemi-mechanical pulping (CMP)), it could be beneficial not only to the high-value utilization of hemicelluloses in wood raw materials but also to the reduction of refining energy consumption with acceptable variation of pulp properties (Hou et al., 2014).

During autohydrolysis pretreatment, hydronium ions can react with the acetyl groups on the side chains of the xylan in hardwood, and the resultant acetic acid will act as the catalytic agent to further promote more removal of the acetyl groups (Gütsch et al., 2012; Li et al., 2014). The content of hemicelluloses in the autohydrolyzed wood chips will be reduced significantly, and thus inevitably affect the subsequent alkali impregnation in CMP using the autohydrolyzed wood chips as raw materials.

Alkali impregnation is an important process commonly used in CMP. A homogeneous impregnation determines the chemical distribution in the interior of wood matrix, which affects the properties of resultant pulp (Bengtsson and Simonson, 1984; Malkov et al., 2003; Zanuttini and Marzocchi, 2003). Zanuttini and Marzocchi (2003) confirmed that the wood alkali swelling, which increased with the reinforcement of the alkaline action, could

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determine the strength and optical properties of chemi-mechanical pulp. In addition, the energy consumption of further refining in CTMP was also drastically reduced by alkali impregnation (Stationwala, 1994; Shen et al., 2002).

An alkali impregnation process involves both mass transfer and chemical reaction. There are three factors influence the mass transfer in wood chips (Malkov, 2002; Bao and Lv, 1992), which relate to the properties of wood itself, impregnation liquor properties and the process conditions. Among them, the most important factors are the structure of wood capillaries and wood chemical composition (Malkov, 2002). While for the chemical reaction, the alkali added would react mainly with the acetyl groups and other weak acidic groups of wood (Katz et al., 1981). These reactions, which are expected in the alkali impregnation process, are favorable for the subsequent refining and defibrillation in CTMP (Zanuttini and Marzocchi, 1997; Sixta, 2006). The direct relationship between wood fiber swelling and the content of acetyl groups has been established by Zanuttini and his co-workers (Zanuttini et al., 1998, 2003). They also found that the deacetylation reaction accounted for the most of the alkali consumption in the alkali impregnation, and that the swelling caused by the alkali impregnation was related to the acetyl groups, which mainly come from the hemicelluloses chains, rather than acidic groups. Evidently, the content of hemicelluloses, in great part, determines the alkali impregnation effectiveness.

In Xu's study (Xu et al., 2016), the effect of autohydrolysis pretreatment on the subsequent alkali impregnation of poplar wood chips was explored. However, how did the content of hemicelluloses remained in the autohydrolyzed wood chips affect the subsequent alkali impregnation effectiveness was not studied in detail. In this paper, the autohydrolyzed poplar sapwood with different content of hemicelluloses was selected as raw materials to perform an alkali impregnation. Both the amount of NaOH consumption and alkali swelling degree of the sapwood were determined to characterize the change in the alkali impregnation effectiveness. The mechanism of hemicelluloses removal by autohydrolysis pretreatment affecting the subsequent alkali impregnation effectiveness was then investigated. The objective of this work is to improve the performance in CMP using the autohydrolyzed poplar wood chips as raw materials.

2. Materials and methods

2.1. Materials

A 100 mm length (longitudinal direction) poplar stem wood disc with a diameter of 28.8 cm was obtained from a freshly felled 7-year-old poplar in Tangshan, China. After being debarked, the disc was then air-dried at room temperature until the moisture content was reduced to approximately 10%. The sapwood portion was selected and then cut in the form of 30 mm (longitudinal) × 30 mm (radial) × 10 mm (tangential) pieces. After being picked out the knots, the poplar sapwood chips were washed with deionized water and then air-dried.

2.2. Autohydrolysis pretreatment

The autohydrolysis pretreatment was performed with a 6 L digester (M/K systems Inc., USA) equipped with a centrifugal pump for liquor circulation. The poplar sapwood chips equivalent to 100g of the oven-dry weight were added in the digester, and then mixed with the preheated deionized water at a solid/ liquid ratio of 1:10 kg/L. More details were given in the literature reported by Hou et al. (2014)).

The combined hydrolysis factor (CHF) was used to quantify the intensity of autohydrolysis pretreatment of the poplar sapwood by the following expression (Zhu et al., 2012):

$$CHF = t \times \exp(25.6 - 11000/T) \quad (1)$$

where t is the autohydrolysis time in min, and T is the autohydrolysis temperature in Kelvin.

In order to obtain the autohydrolyzed poplar sapwood chips with different hemicelluloses contents, four different CHFs were chosen, and the corresponding autohydrolysis temperature and time are listed in Table 1. The autohydrolyzed poplar sapwood chips were taken out of the digester after the autohydrolysis pretreatment was terminated, and then washed thoroughly with deionized water until the filtrate was colorless and its pH was neutral. After being air-dried at room temperature, the autohydrolyzed poplar sapwood chips were collected in plastic bags.

2.3. Preparation of the poplar sapwood meal

According to the literatures published (Beatson et al., 1985; Zanuttini and Marzocchi, 1997; Zanuttini et al., 1998), to minimize the mass and heat transfer resistance and to lower the impact of wood capillaries structure on the alkali impregnation, a certain amount of unautohydrolyzed and autohydrolyzed poplar sapwood chips was selected and ground to the meal. The meal was prepared using a Wiley-type mill (NO. 2, Arthur H. Thomas Co., USA), and then screened to obtain the 40/60 mesh fraction, finally collected in a plastic bag for later use.

2.4. Analysis of chemical composition of the autohydrolyzed sapwood chips

2.4.1. Pentosan content

The pentosan content, which was used to characterize the hemicelluloses content of the autohydrolyzed poplar sapwood chips, was determined according to TAPPI T223 cm-01.

2.4.2. Content of acetyl groups

In order to determine the content of acetyl groups of the autohydrolyzed poplar sapwood chips, it is necessary to convert the acetyl groups to acetic acid. A series of preparations were carried out according to NREL-510-42618. For this conversion method, a two-step sulfuric acid hydrolysis (i.e., 72% sulfuric acid at 30 °C for 60 min for the primary hydrolysis and 4% sulfuric acid at 121 °C for 60 min for the secondary hydrolysis) was conducted. After being filtrated and purified, the hydrolyzed liquid was collected to determine the content of acetyl groups. The content of acetyl groups was determined according to the literature method (Cui et al., 2014) using an ion chromatography unit (Dionex-IC5000, Thermo Fisher Scientific, USA) equipped with an IonPac AS11-HC analytical column (4 × 250 mm).

2.4.3. Lignin content

The lignin content of the autohydrolyzed sapwood chips, including the acid-insoluble and acid-soluble lignin, was determined according to NREL-510-42618. The acid-soluble lignin was determined by measuring the absorbance of the filtrate at a wavelength of 240 nm on a UV–visible spectrophotometer (UV-2550, Shimadzu, Japan), in which the test sample was first extracted by alcohol and then hydrolyzed by using a two-step acid hydrolysis. After the acid hydrolysis, the residue was washed and dried to determine the content of the acid-insoluble lignin.