



Short Communication

Improvement membrane filterability in nanofiltration of prehydrolysis liquor of kraft dissolving pulp by laccase treatment

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HIGHLIGHTS

- Laccase treatment facilitated subsequently nanofiltration by lignin removal.
- Laccase treatment resulted in the increase of membrane filterability.
- Hemicellulosic sugars was concentrated and purified by proposed process.

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ABSTRACT

In this work, laccase treatment was employed to enhance nanofiltration process by lignin removal. Results showed that the membrane filterability was increased in terms of deionized water flux and PHL filtration process. On the other hand, the hemicellulosic sugars were negligible affected and can be concentrated to 172 g/L, which was increased about 300% from the original one. The combined laccase-nanofiltration process provides an alternative approach to utilize hemicellulosic sugars of PHL in an environmentally friendly way.

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1. Introduction

Biorefinery concept attracts numerous interesting to produce bio-chemical and bio-energy from lignocelluloses with the potential of displacing fossil-based sources (Luterbacher et al., 2014). Fractionation of hemicellulose and destructure of compact cell wall is considered as a critical step (Himmel et al., 2007). For kraft based dissolving pulp production process, the hot water/steam pre-extraction was conducted to produce high purity of cellulose by dissolving hemicellulose into prehydrolysis liquor (PHL), which fits well into biorefinery concept. The dissolved hemicellulosic sugars make PHL a potential source for value-added products production (Saadatmand et al., 2013; Saeed et al., 2012; Yang et al., 2013).

Purification and concentration of hemicellulosic sugars is a vital process for practical utilization of PHL due to its low concentration

(6 wt%) (Shen et al., 2011). Membrane filtration was adapted to fulfill this demand though molecular sieving and electrostatic repulsion (Hu et al., 2010). To date, membrane technology has been used in many industrials, such as pulping industry of aqueous systems, desalination and fruit juice industry (Gautam and Menkhaus, 2014; Pabby et al., 2008). Moreover, nanofiltration has also been applied to concentrate the dissolved organics from pre-extraction liquor of biomass (Amidon et al., 2008; Liu et al., 2008).

However, foulant in PHL is one of the key limitations for nanofiltration commercialization. The lignin with relatively high molecular weight was considered as the main foulant that decreasing membrane filterability and lifetime. Therefore, treatment of PHL prior to nanofiltration might be one of efficient ways to improve its filterability. Numbers of studies have been carried out on this purpose. For example, Koivula et al. (2011) evaluated various pre-treatment methods to manage fouling in ultrafiltration of wood hydrolysates and found that the pulsed corona discharge treatment is effective for polysulfone membrane. Shen et al. (2013) reported that the activated carbon treatment of PHL improved membrane filterability when using a combined process to concentrate

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dissolved organics from PHL. Similarly, Ahsan et al. (2013) also employed activated carbon to remove lignin for nanofiltration and reverse osmosis of acetic acid from PHL.

Recently, laccase treatment captured attentions to remove lignin from the extraction liquor for its high selectivity and environmentally friendly manner. For example, Jurado et al. (2009) revealed that laccase treatment can remove phenolic compounds when studying bioconversion of steam explosion wheat straw. Ludwig et al. (2013) reported that immobilized laccase treatment can remove 80% of phenolic materials from pre-extraction liquor of wheat straw. Our previous study showed that the lignin molecular weight was increased after laccase treatment of PHL, thus enhancing lignin removal (Wang et al., 2014).

The objective of this work is to enhance the membrane feasibility in nanofiltration of PHL by laccase treatment. The membrane flux before and after filtration was determined to evaluate the feasibility. Mass balance of nanofiltration was summarized and an integration of laccase-nanofiltration into dissolving pulp production process was proposed.

2. Methods

2.1. Materials

The industrially produced PHL was collected from a dissolving pulp mill in Eastern Canada based on the kraft technology using mixture wood of maple (70 wt%), poplar (20 wt%) and birch (10 wt%). The chemical components of PHL were list in Table 1 (Wang et al., 2014).

The laccase (*Trametes versicolor*) was purchased from Sigma-Aldrich with activity of 12.0 U/mg determined by UV spectrometric method at 420 nm (Wang et al., 2014). The nanofiltration membrane with molecular weight cut off of 160–200 and pH range of 3–10 was supplied by Alfa Laval Company.

2.2. Laccase treatment of PHL

Laccase solution was added into the flask containing PHL, and then shook in a water bath at 36 °C for 3 h. The laccase concentration was set at 2 U mL⁻¹. Once the reaction was completed, the liquor was centrifuged at 4000 rpm for 15 min to collect the supernatant, i.e. treated PHL. The original PHL was also centrifuged at 4000 rpm for 15 min to collect the supernatant as the control, i.e. original PHL.

2.3. Nanofiltration

Nanofiltration was conducted in a flow cell with a membrane area of 0.0015 m². 30 g of PHL was added into the flow cell for a batch experiment. The nanofiltration condition was set at a constant pressure of 500 psi and stirrer speed of 500 rpm. The experiment was ended at volume reduction factor (VRF, i.e. initial feed volume divide retentate volume) of 3. Then, the concentrated liquor was collected from the flow cell. Before and after each experiment, the nanofiltration system was flushed with deionized water to calculate the flux (kg/m² h) according to Eq. (1).

$$\text{Flux} = \frac{w}{A \times t} \quad (1)$$

Table 1
Composition of the original PHL.

	Xylose	Arabinose	Galactose	Glucose	Mannose	Total sugars	Acetic acid	Lignin
Mono-	5.36	1.58	0.85	0.95	0.43	9.87	11.3	12.2
Oligo-	40.7	0.00	1.62	4.45	4.92	52.3		

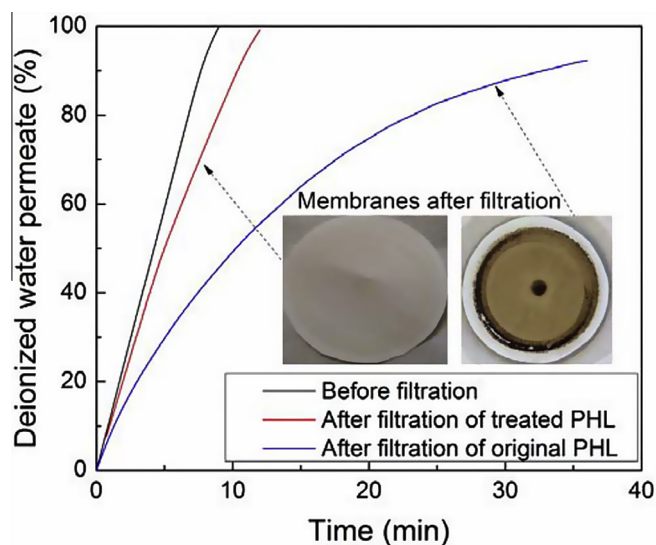


Fig. 1. Deionized water permeate as a function of filtration time before and after filtration of PHLs.

where, w is the permeate weight at the end of filtration (g), A is the area of membrane (0.0015 m²), and t is the time to finish the filtration (h).

2.4. Analytical method

Quantitative determination of dissolved organics, i.e. oligosugars, monosugars, acetic acid and lignin was conducted based on the ion chromatography (IC), Varian 300 NMR-spectrometer and UV-Vis spectrometric method. The procedures have been published (Saeed et al., 2012; Liu et al., 2013).

Prior to sugar analysis, the PHL was hydrolyzed in a Parr reactor (Neslab Instruments, Inc., Portsmouth, NH, USA) under condition of sulfuric acid of 4%, 121 °C and 1 h. The monosugars were corresponding to the sugar content in the PHL before the acid hydrolysis, while the oligosugars were calculated from the difference with and without the acid hydrolysis. The acetic acid content was determined by preparation of PHL with D₂O at ratio of 1:4 (m/m). The lignin content of the PHL was determined at 205 nm after dilution.

3. Results and discussion

3.1. Deionized water flux

The membrane filterability of deionized water before and after filtration of treated and original PHLs were present in Fig. 1. It can be seen that the membrane filterability of the one after filtration was decreased greatly in comparison with that of before filtration due to the fouling problem. As expected, the filterability of laccase treated PHL was much better than the original PHL. Furthermore, the photographs in Fig. 1 clearly showed that the precipitated foulant of treated PHL was much less than the original one. All these confirmed that the laccase treatment facilitated subsequently nanofiltration through lignin removal.

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