



# Fractionation and characterization of saccharides and lignin components in wood prehydrolysis liquor from dissolving pulp production

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## ABSTRACT

Saccharides and lignin components in prehydrolysis liquor (PHL) from kraft-based dissolving pulp production was characterized after being fractionated using membrane filtration. The results showed that the membrane filtration provided a method for organics fractionation with considerable recovery rate, but exhibited some disadvantages. Besides the limited ability in purifying oligosaccharides (OS) due to the overlaps of molecular weight distribution with lignin components, the membrane filtration could not improve the homogeneity of OS as indicated by the analysis of chemical compositions and the degree of polymerization (DP), which may be ascribed to the linear conformation of OS. The characterization of lignin components indicated a great potential for polymer industry because of the remarkable content of phenolic hydroxyl groups (PhOH), especially for low molecular weight (LMW) fraction. It was concluded the organics in PHL provided streams of value-added chemicals. However, the practical significance thereof can be realized and maximized only when they are successfully and completely fractionated.

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## 1. Introduction

The prehydrolysis-kraft process currently attracts widespread attention because it not only produces high grade dissolving pulp but also provides a potential way for high-value utilization of hemicellulose (Buranov & Mazza, 2010; Nabarlatz, Ebringerová, & Montané, 2007; Sun et al., 2005). This process fits perfectly into the forest biorefinery concept if these hemicellulosic oligosaccharides (OS) in prehydrolysis liquor (PHL) could be fully isolated and purified. However, the prehydrolysis step that serves the purpose of hemicelluloses extraction is ineluctably accompanied with the depolymerization of other component of biomass, namely lignin degradation. This makes the OS separation a challenging task because of the presence of lignin components (Bujanovic, Goundalkar, & Amidon, 2012; Tunc & van Heiningen, 2011).

It was reported the lignin reactions during prehydrolysis mainly involved the homolytic cleavage of aryl ether bonds, the generation of new phenolic units and condensation reactions occurred at extremely high temperature (Bardet, Robert, & Lundquist, 1985). These reactions release a diverse palette of degradation byproducts. Liu, Ni, Fatehi, and Saeed (2011) found that the depolymerized lignin in PHL had a lower average molecular weight but a significant increase of the phenolic hydroxyl groups (PhOH) compared to dioxane lignin. Similar result was reported by Leschinsky, Zuckerstätter, Weber, Patt, and Sixta (2008) that the extensive lignin degradation occurs during prehydrolysis through homolytic cleavage of the aryl-ether bonds, resulting in a strong increase of PhOH and a decrease in aliphatic hydroxyl groups. Another study of Leschinsky, Weber, Patt, and Sixta (2009) reported that the formation of the condensed lignin in PHL is characterized by a higher molecular weight and insoluble at low temperature. His study also indicated a broad distribution of molecular weight of lignin components in PHL. Besides these lignin oligomers, a variety of low molecular weight (LMW) aromatic compounds were present as a result of the cleavage of the  $\alpha$ -O-4 linkages of lignin. Goundalkar, Bujanovic, and Amidon (2010) demonstrated that vanillin and syringaldehyde were the major aromatic compounds in maple PHL. Besides these degradation byproducts of lignin, the dissolving organics in PHL

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also include furfurals and organic acids that are derived from carbohydrate degradation (Cara et al., 2012; Liu, Hu, Jahan, & Ni, 2013; Saeed et al., 2012), and therefore make the compositions of PHL more complicated.

Various methods have been developed for OS separation by removing non-saccharide contaminants, namely lignin components, e.g. polymer flocculation (Duarte, Ramarao, & Amidon, 2010), solvent extraction (Vázquez, Garrote, Alonso, Domínguez, & Parajó, 2005), adsorption by surface active materials (Liu, Fatehi, & Ni, 2012; Montané, Nibarlatz, Martorell, Torné-Fernández, & Fierro, 2006), ion exchange or chromatography techniques (Cara et al., 2012; Palm & Zacchi, 2004), membrane filtration (Al Manasrah, Kallioinen, Ilvesniemi, & Mänttari, 2012; Buranov & Mazza, 2010), and combination of these techniques (Chen, Wang, Fu, Li, & Qin, 2014; Shen, Kaur, Baktash, He, & Ni, 2013). However, their performances remain to be improved and currently far from the requirement of industrial application in terms of process cost and recovery yield as reviewed by Qing, Li, Kumar, and Wyman (2013). Although the separation strategies of OS from PHL were extensively studied, the characterization of the dissolving organics is rather limited. It is believed that a better understanding of the molecular information about the dissolving organics in PHL is of vital importance for biorefinery and will undoubtedly facilitate the OS separation.

The present work addresses the fractionation and characterization of organic compounds in PHL. This is an effort not only to provide fundamental information beneficial to OS purification, but also to wood biorefinery.

## 2. Materials and methods

### 2.1. Materials

The fast-growing aspen species, *Populus × euramericana* 'Neva', was selected as raw materials in the present study because it is widely used in dissolving pulp mills through prehydrolysis kraft process in North China. Poplar wood chips were prepared from debarked wood logs harvested from the southwest region of Shandong province, China. Microporous membrane made of mixed cellulose esters with pore size of 0.45  $\mu\text{m}$  and Ultracel regenerated cellulose membrane with molecular weight cut off (MWCO) 1.0, 3.0, 10.0, 30.0 kD were provided by Merck Millipore, Billerica, MA. All chemicals were analytical-reagent grade from Sigma-Aldrich, Inc. The chemicals included 2 N Folin-Ciocalteu's phenol reagent and 3,5-dinitrosalicylic acid (DNS), anhydrous sodium carbonate, and 4-hydroxybenzoic acid. Dextran with weight average molecular weight from 0.18 to 36.3 kD (American Polymer Standards Corporation, Mentor, OH) was used as standard samples for the size exclusion chromatography (SEC) analysis. Xylose and xylooligosaccharides (XOS) purchased from Megzyme Ireland with degree of polymerization (DP) from 2 to 6 were used as standard for high performance anion exchange chromatography with pulsed amperometric detector (HPAEC-PAD) to get DP profile of saccharides in PHL.

### 2.2. Prehydrolysis and PHL preparation

The prehydrolysis was carried out in a 23 L pulp digester, using 1.0 kg of oven-dried poplar chips. Deionized water was added in order to reach 6:1 of liquid to wood ratio. The digester temperature was ramped from room temperature to 170 °C and held for 60 min. This is a representative reaction severity widely applied in industrial process that corresponds to P-factor of 550 (Duarte, Ramarao, Amidon, & Ferreira, 2011). At the end of prehydrolysis, the digester was cooled, depressurized and the reaction mixture

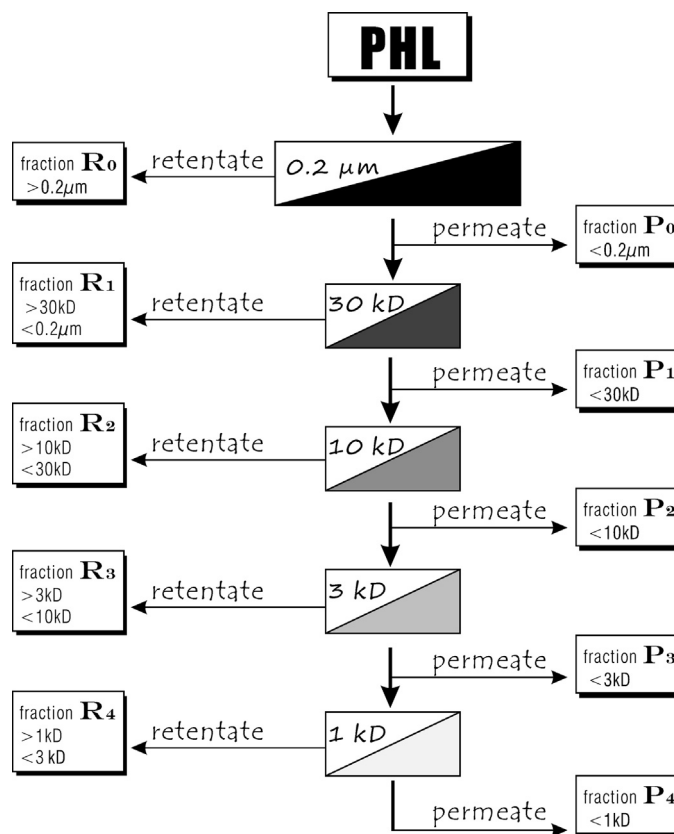


Fig. 1. Flow diagram for the fractionation of PHL by MF and UF.

was withdrawn. The composition of aspen wood before and after treatment as well as the PHL composition were listed in Table 1.

### 2.3. Fractionation by membrane filtration

Batch filtration processing was conducted to fractionate the organics in PHL according to the scheme in Fig. 1. Prior to ultrafiltration (UF), the PHL was subjected to microfiltration (MF) using 0.45  $\mu\text{m}$  membrane to eliminate insoluble particles. The UF was performed in dead-end mode using a stirred cell (Millipore) at ambient temperature and 0.3 MPa by compressed nitrogen. Flat sheet Millipore membranes with an effective membrane area of 40  $\text{cm}^2$  were employed. A magnetic stirrer bar was employed at a stirring rate of 100 rpm. Reverse stirring was also applied every 10 min to ensure that the feed solution was well mixed. The nominal MWCO of membranes used was 30, 10, 3 and 1 kD, respectively. The PHL starting volume was approximately 150 mL. In each UF step, the volume concentration ratio was controlled to be 10, and the permeate was collected and filtered using the next lower MWCO membrane.

### 2.4. Analytical methods

The reducing sugar in solution was determined using DNS method (Miller, 1959). While a strict definition of an OS is not established, saccharides with DP greater than 2 but soluble in PHL were considered as OS in present study. The OS content was measured by an indirect method based on quantitative acid hydrolysis of the liquid samples with 4% w/w of  $\text{H}_2\text{SO}_4$  at 121 °C for 60 min according to technical report from NREL (Sluiter et al., 2006). The OS concentration was expressed as the increase of monosaccharides (MS) which were determined by HPAEC-PAD. This system

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