



## Colloidal behaviors of lignin contaminants: Destabilization and elimination for oligosaccharides separation from wood hydrolysate



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### ABSTRACT

Oligosaccharides (OS) production using wood prehydrolysis liquor (PHL) is a crucial subject with significant economic and environmental benefits for wood biorefinery. However, this is a challenging task due to the presence of a diverse palette of lignin-derived contaminants. In this work, lignin contaminants were classified into macro-lignin particles (MLPs), amphiphilic lignin derivatives (ALDs) and small lignin fragments (SLFs) based on their colloidal and molecular behaviors. Accordingly, a process was developed to destabilize ALDs and MLPs synergistically by applying polycations at an elevated pH, which achieved 57.8% lignin removal. The remaining SLFs were adsorbed by macroporous resin with pore size of 20 nm at least, leading to 95.2% of final lignin removal and 66.6% of OS recovery. This study has both scientific and practical significance for wood biorefinery because of the low cost of chemicals employed and the regeneration ability of macroporous resin.

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### 1. Introduction

The growing commercial importance of non-digestible oligosaccharides (OS) in pharmacy, nutraceuticals, and food industries is encouraging the identification of renewable and inexpensive xylan-rich sources such as lignocellulosic biomass for OS production [1,2]. This is in harmony with the concept of biorefinery, which is to refine the lignocellulosic biomass into a spectrum of more profitable bio-based products [3–5] and bioenergy [6–8]. In this context, prehydrolysis of wood was introduced to the conventional pulping process to extract the hemicellulosic OS for value-added products, while the residual solid could still be processed into wood products, such as paper and dissolving pulp [9–11]. This process is now being widely used in China by using poplar wood as raw materials that have remarkable hemicellulose content from 16.6% to 23.24% [12]. However, OS separation from prehydrolysis liquor (PHL) is very challenging because of the fact that PHL contains not only OS but a diverse palette of degradation byproducts of lignocellulose, mainly lignin-derived degradation products [13,14]. To our knowledge, the production of OS from PHL has not been industrialized at present, making the PHL one of waste water sources in pulp mills.

Various approaches had been developed to remove lignin contaminants from PHL for OS separation, e.g. solvent extraction [4], adsorption by surface active materials [15], anion-exchange or size-exclusion chromatography techniques [2], membrane filtration [16–18], and salt/polymer/polyelectrolyte flocculation [19–21]. However, their performance on OS separation remains to be improved in the terms of process cost, recovery yield and especially lignin selectivity as reviewed by Qing et al. [22]. Recently, a method featured by specific lignin removal from PHL was proposed by Chen et al. [20], but the recovery yield was still low, only 29–36% as reported. To design an effective OS separation process, it is necessary to investigate the chemical structure, molecular size and interfacial behaviors of lignin contaminants. Further, most biorefinery plants currently focus on the utilization of cellulose and hemicelluloses, whereas the lignin in PHL is deemed as waste due to the lack of properties information. It is believed that a better understanding of lignin not only facilitates the OS separation, but more importantly, will boost value-added applications in current and future biorefinery. However, literatures in this aspect are really limited so far. The study of Leschinsky et al. [23] showed that a portion of lignin was dissolved at high temperature during prehydrolysis but became insoluble upon cooling. This lignin fraction is characterized by high molecular mass, and is the source of turbidity of PHL, and hereby is denoted by macro-lignin particles (MLPs). Despite the hydrophobic and aromatic nature of native lignin of wood, it was reported that the majority of depolymerized lignin molecules in PHL were quite amphiphilic due to the

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liberation of phenolic groups resulted primarily from the hemolytic cleavage of aryl ether bonds in  $\beta$ -O-4 bonds structure under prehydrolysis conditions [24,25]. This lignin fraction was denoted by amphiphilic lignin derivatives (ALDs) that are actually used as surfactant [26–28] or polyelectrolyte [21,29,30]. The extensive degradation of lignin leads to small aromatic molecules which are therefore denoted as small lignin fragments (SLFs). SLFs are rich in carboxyl groups and phenolic hydroxyl groups (PhOH) [31]. The study of Aimi et al. showed SLFs tended to attach to high molecular weight oligosaccharides and form lignin-carbohydrate complex [32]. Please note that the lignin classification mentioned above is malleable rather than absolute, and the purpose of classification is to guide the OS separation from lignin contaminants.

The present work focused on the colloidal behaviors of lignin contaminants in PHL, hoping to provide a primary explanation for lignin destabilization mechanisms. In addition, process was developed accordingly to eliminate lignin selectively for OS separation.

## 2. Material and methods

### 2.1. Materials

The fast-growing poplar 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 Northern China. Poplar wood chips were prepared from debarked wood logs harvested from the southwest region of Shandong province, China. The wood chips were then screened to remove all particles greater than 38 mm and less than 6 mm in length. The thickness of the accepted chips ranged from 1 to 5 mm. The wood chips were then air-dried to the solid content of approximate 89% for prehydrolysis. Folin–Ciocalteu’s phenol reagent for determination of PhOH content and *N,O*-Bis(trimethylsilyl) trifluoroacetamide (BSTFA) for gas chromatography derivatization were purchased from Sigma–Aldrich, Inc. Polydiallyldimethylammonium chloride (*p*-DADMAC) was provided by Ashland Inc. with electric charge density of 2 mEq/g and molecular weight of 100–1000 kDa. Polyaluminium chloride (PAC) used in the present study was purchased from Aspirit Chemical Co., Ltd., Qingdao, China. Dextran with weight average molecular weight from 0.18 to 33.5 kD (American Polymer Standards Corporation, Mentor, OH) was used as standard for the size exclusion chromatography (SEC) analysis. Macroporous adsorption resins CAD-40, D101, DM301, S-8, and X-5 were generally provided by Huizhu Resin Co., Ltd., Shanghai, China.

### 2.2. Prehydrolysis for PHL preparation

PHL was prepared in laboratory as described elsewhere [20]. Prehydrolysis was carried out in a digester with capacity of 23 L. The digester was heated electrically and rotated at 2 rpm for mixing. About 1.0 kg (on oven-dried basis) of wood chips was placed in the digester and 6 L of deionized water was added. The digester temperature was ramped to 170 °C and held for 60 min. This is a representative reaction severity in industrial process that corresponds to P-factor of 550 [11]. At the end of the treatment, the digester was depressurized, cooled and the reaction mixture was withdrawn. About 4.2 L PHL was separated and collected from the hot water treated wood chips. The chemical compositions of poplar wood before and after prehydrolysis as well as the PHL compositions in terms of carbohydrate and lignin were listed in Table 1.

**Table 1**

Chemical compositions of poplar wood before and after prehydrolysis as well as the compositions of the PHL in terms of carbohydrates and lignin.

Untreated wood (1.0 kg)	Residual solid (0.81 kg)	PHL (6.0 L) <sup>g</sup>	
		Oligosaccharides (18.89 g/L)	Monosaccharides (2.46 g/L)
Arabinan 0.38%	Arabinan nd <sup>a</sup>	AOS <sup>b</sup> 5.7%	Arabinose 24.9%
Galactan 0.71%	Galactan nd	GalOS <sup>c</sup> 7.6%	Galactose 15.9%
Glucan 40.7%	Glucan 49.2%	GluOS <sup>d</sup> 8.9%	Glucose 10.8%
Xylan 16.4%	Xylan 5.3%	XOS <sup>e</sup> 70.5%	Xylose 40.2%
Mannan 3.8%	Mannan 1.7%	MOS <sup>f</sup> 7.2%	Mannose 8.1%
Lignin 23.5%	Lignin 26.1%	Lignin 7.12 g/L	

<sup>a</sup> Not detected.

<sup>b</sup> Arabinooligosaccharides.

<sup>c</sup> Galctooligosaccharides.

<sup>d</sup> Glucooligosaccharides.

<sup>e</sup> Xylooligosaccharides.

<sup>f</sup> Mannoooligosaccharides.

<sup>g</sup> Theoretical volume of PHL.

### 2.3. OS separation from PHL

Several methods were tried to isolate MLPs from PHL, including centrifugation at 5000 rpm for 5 min, microfiltration using 0.45  $\mu$ m regenerated cellulose membrane, and salting out by using anhydrous sodium sulfate. In addition, alkaline treatment was also investigated to destabilize the MLPs at pH 8.9 using sodium hydroxide. The PHL after MLPs removal was then subjected to polyelectrolyte treatment to precipitate ALDs. Polyelectrolyte treatment was performed by using inorganic polyelectrolyte PAC or organic polyelectrolyte *p*-DADMAC with various dosage in a wide range of pH ranged from 2 to 11 at ambient temperature. After ALDs precipitation by PAC, batch adsorption experiments were conducted to remove SLFs from PHL by using a variety of macroporous resins with different properties. The procedure of the absorption experiments involved neutralization of PHL by sulfuric acid, introduction of 5.0 g adsorbent into flask filled with 100 mL of the neutralized sample, and stirring at 25 °C and 100 rpm in a shaking incubator for adsorption equilibrium. Once equilibrium was reached, the samples were taken for lignin and OS determination.

### 2.4. Analysis

The turbidity of samples was measured in nephelometric turbidity units (NTU) according to EPA Method 180.1. The lignin in PHL and wood chips was quantified in terms of acid-insoluble lignin (Klason lignin) and acid-soluble lignin. Klason lignin and acid soluble lignin in wood were determined according to Tappi methods T 222 om-98 and UM 250, respectively. The OS was measured by an indirect method based on quantitative acid hydrolysis of samples with 4% w/w of H<sub>2</sub>SO<sub>4</sub> at 121 °C for 60 min according to technical report from NREL (Sluiter et al., 2006). The OS concentration was expressed as the increase in sugar monomers, as analyzed by high performance liquid chromatography (HPLC) Shimadzu LC-20T equipped with a refraction index detector and a CARBOsep CHO-682 column (7.8 × 300 mm, 7  $\mu$ m) with pure water as eluent at 0.4 mL/min and 80 °C. Particle size and zeta potential of lignin molecules in PHL were measured by dynamic light scattering (DLS) analyzer equipped with a laser Doppler microelectrophoresis (Zetasizer Nano ZS90, Malvern Instruments, UK) at 25 °C. All the dilutions required for DLS analysis were made with 20 mM NaCl solution in order to ensure a good conductivity of the solution. The PhOH content of lignin in PHL was determined according to Folin–Ciocalteu assay [33] with a minor modification that 70%

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