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Short Communication

Structural variation of eucalyptus lignin in a combination of hydrothermal and alkali treatments

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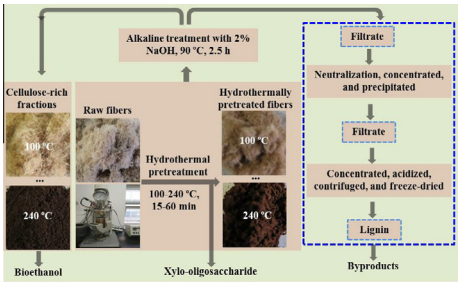
HIGHLIGHTS

- Hydrothermal and alkali treatments were combined to fractionate lignin.
- An increase in pretreatment severity facilitated the release of lignin.
- The β-O-4 linkage was cleaved gradually with the increased temperature.
- M_w of lignin decreased from 1630 to 510 g/mol as temperature increased.

GRAPHICAL ABSTRACT



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ABSTRACT

In this work, the structural features of the lignin isolated with 2% NaOH at 90 °C for 2.5 h from the hydrothermally pretreated eucalyptus fibers at different temperatures (100–200 °C) for different times (15–60 min) were thoroughly investigated. Results showed that the hydrothermal pretreatment facilitated the separation of alkali lignin from the pretreated fibers. It was found that the linkages of β-O-4, β-β, and β-5 decreased gradually with the increase of hydrothermal severity. Furthermore, decreased molecular weights (1630–510 g/mol), associated carbohydrates contents (1.99–0.05%) and aliphatic OH contents (3.37–0.65 mmol/g), and increased phenolic OH contents (0.71–2.98 mmol/g) and thermal stability of the alkali lignins were observed with the increase of the hydrothermal severity.

1. Introduction

As a promising alternative to the limited fossil fuels, bioethanol produced from lignocellulosic biomass can effectively relieve the increasing energy and environmental issues caused by the excessive consumption of fossil fuels. However, lignin is regarded as a vital factor that affects the production of bioethanol. For decades, numerous pretreatments, including physical, chemical, physico-chemical and biological methods, have been developed to overcome the biomass recalcitrance (Hendriks and Zeeman1, 2009). Among these pretreatments, hydrothermal pretreatment is very attractive because of its applicability for wet lignocellulose, high energy efficiency, no catalyst employment and low-corrosion potential (Gullón et al., 2012). It is an effective method for hemicelluloses recovery or conversion. More importantly, alkali solution can disrupt the plant cell walls by dissolving lignin and hemicelluloses, which is widely used to fractionate lignin from lignocellulosic materials.

A combined process based on hydrothermal and alkali treatment was considered as a promising method for utilization of lignocellulose with high efficiency, in which the hydrothermal

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pretreatment was aimed to remove hemicelluloses, followed by an alkali treatment with NaOH solution to remove lignin. After the combined process, cellulose was hydrolyzed to fermentable sugars for bioethanol production, while hemicelluloses was hydrolyzed to xylo-oligosaccharides for further use in food, nutraceutical and pharmaceutical industries (Vazquez et al., 2000). Alkali lignin isolated from the hydrothermally pretreated lignocellulose can also be applied in the fields of thermoplastics, thermosettings, elastomers, adhesives, and sealants (Feldman et al., 1992). The development of high valuable products from lignin can effectively improve the economics of the combined process. However, the potential application of the isolated lignin is significantly affected by its inherent complexity and heterogeneity, and the lignin structure could also be changed during the process (Ragauskas et al., 2014). Therefore, the knowledge of lignin structures is beneficial for evaluating of the utilization of lignin.

In the present work, alkali lignins were extracted from hydrothermally pretreated fibers with the objective to determine how the structure and chemical reactivity of eucalyptus lignin is altered during various pretreatment conditions. The structural features of the lignins obtained were thoroughly characterized by high-performance anion exchange chromatography (HPAEC), Fourier transform infrared (FT-IR), heteronuclear single quantum coherence (HSQC) and ^{31}P NMR spectroscopy, and gel permeation chromatography (GPC). In addition, thermogravimetric analysis (TGA) was also performed to determine the thermal behaviors of the lignins obtained.

2. Methods

2.1. Materials

Thermo-mechanical fibers obtained at 120 °C for 1–2 min from *Eucalyptus urophylla*, were kindly supplied by the State Key Laboratory of Pulp and Paper Engineering, South China University of Technology, China. The fibers were first dewaxed with methylbenzene/ethanol (2:1, v/v) in a Soxhlet apparatus for 3 h, and then were dried in an oven for 12 h at 60 °C. The composition of the dewaxed fibers was 45.0% cellulose, 21.7% hemicelluloses, 25.8% acid insoluble lignin, and 1.3% acid soluble lignin (Sluiter et al., 2008). All chemicals purchased were of analytical or reagent grade and used without further purification.

2.2. Lignin fractionated by the combination of hydrothermal and alkali treatments

The hydrothermal pretreatment was conducted in a laboratory-scale reactor (Parr Instrument Company, Moline, USA) with a maximal volume of 1000 mL. The dewaxed fibers (15.0 g) were dispersed in 450 mL distilled water and transferred to the reactor. Then the reactor was heated to 100, 120, 140 and 160 °C for 60 min, 180 °C for 15, 30, 45 and 60 min, 200, 220 and 240 °C for 30 min, respectively, at a heating rate of about 4 °C/min. The pretreated fibers were washed with hot water thoroughly and dried in an oven at 60 °C for 12 h. Then the pretreated fibers were treated with 2% NaOH at 90 °C for 2.5 h with a solid-to-liquid ratio of 1:30 (g/mL) and filtered. Afterwards, the liquid stream was adjusted to pH 5.5–6.0 with HCl, concentrated to about 60 mL on a rotary evaporator under reduced pressure. The concentrated liquid was poured into 180 mL 95% ethanol to recover hemicelluloses. Next, the filtrate was concentrated to about 30 mL and mixed with 150 mL pH 2.0 HCl solution to precipitate lignin. The lignin obtained was freeze-dried and labeled as $L_{100\text{-}60}$, $L_{120\text{-}60}$, $L_{140\text{-}60}$, $L_{160\text{-}60}$, $L_{180\text{-}15}$, $L_{180\text{-}30}$, $L_{180\text{-}45}$, $L_{180\text{-}60}$, $L_{200\text{-}30}$, $L_{220\text{-}30}$, and $L_{240\text{-}30}$, respectively. The control lignin fraction AL obtained without hydrothermal pretreatment was also fractionated for a comparison.

2.3. Analysis procedures

The associated carbohydrates in the lignins obtained were determined by HPAEC. The molecular weights of the lignin fractions were determined by GPC. The operation conditions were described in detail in Supporting information. FT-IR spectra of all lignin fractions were recorded on a Bruker spectrophotometer in the range of 2000–800 cm^{-1} with a resolution of 4 cm^{-1}. KBr disk containing 1% finely ground lignin was used for determination. HSQC NMR spectra were detected on a Bruker AVIII 400 MHz spectrometer at 25 °C using DMSO-d_6 as solvent, and 60 mg lignin was dissolved in 0.5 mL DMSO-d_6. ^{31}P NMR spectra were also determined according to a previous literature (Wen et al., 2013a), in which phenolic hydroxyl, aliphatic hydroxyl and carboxyl groups of the lignin obtained were quantitated. Thermal analysis of the lignin fractions isolated was performed using TGA and differential thermogravimetric (DTG) on a simultaneous thermal analyzer (TGA Q500, USA). About 8–10 mg lignin was heated in a platinum crucible from room temperature to 700 °C at a heating rate of 20 °C/min under nitrogen atmosphere.

3. Results and discussion

3.1. Yield of the isolated lignin and the content of associated carbohydrate

Table 1 shows the yields of lignin based on the initial weight of the raw fibers and its associated carbohydrate contents. In this work, only 1.84% of lignin was extracted from the unpretreated

Table 1
Yield of lignin and its associated carbohydrate content.

Lignin fractions	Lignin yield[a]	Arabinose	Galactose	Glucose	Xylose	Mannose	Total sugars[b]
AL	1.84	0.11	0.05	0.16	0.10	0.09	0.51
$L_{100\text{-}60}$	1.84	0.30	0.33	0.41	0.62	0.33	1.99
$L_{120\text{-}60}$	3.31	0.05	0.14	0.06	1.22	0.07	1.54
$L_{140\text{-}60}$	4.28	0.05	0.09	0.07	0.86	ND	1.07
$L_{160\text{-}60}$	8.41	ND[c]	0.09	0.07	0.77	ND	0.93
$L_{180\text{-}15}$	7.18	ND	0.06	0.10	0.67	ND	0.83
$L_{180\text{-}30}$	8.14	ND	0.04	0.08	0.43	ND	0.55
$L_{180\text{-}45}$	8.12	ND	0.03	0.12	0.10	ND	0.25
$L_{180\text{-}60}$	8.27	ND	0.07	0.09	0.18	ND	0.34
$L_{200\text{-}30}$	12.22	ND	0.03	0.08	0.16	ND	0.27
$L_{220\text{-}30}$	13.94	ND	ND	0.11	ND	ND	0.11
$L_{240\text{-}30}$	16.36	ND	ND	0.05	ND	ND	0.05

[a] Based on the initial weight of the raw fibers (%, w/w).
[b] Based on the dry mass of lignin (%, w/w).
[c] ND, not detectable.