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Structural transformation of hemicelluloses and lignin from triploid poplar during acid-pretreatment based biorefinery process

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ABSTRACT

In order to understand the behaviors of hemicelluloses and lignin under the given acidic conditions with increasing severity, the structural characteristics were elucidated in detail by both wet chemistry methods and spectroscopic analyses in this study. Although acidic pretreatment significantly hydrolyzed the glycosidic linkages in xylan backbone and then reduced the molecular weight of xylan from 89,600 to 19,630 g/mol, a slightly increased amount of glucuronic acid was observed, probably attributing to the maintenance of ester bonds. The serious structural variation occurred in lignin macromolecule was evidenced by the extensive degradation of β -O-4 ether linkages and resinol substructure, together with the changes in the ratios of the three monolignols in ester-bond, ether-bond and non-condensed phenolic compounds. At the most severity, obvious condensation reactions introduced the clear shift of C₂ and C₅ correlations and the absence of C₆ correlation in guaiacyl units by 2D HSQC analysis.

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1. Introduction

Hemicelluloses and lignin, the abundant natural polymeric materials, are extremely complicated and not efficiently utilized in the field of biomass. As the concept of "BIOREFINERY" is extensively prevalent recently, the full utilization of the whole components of biomass is attracting more and more attention by the governments and the researchers, especially for the applications of hemicelluloses and lignin (Lynd et al., 2008). Unlike the most natural polymers, hemicelluloses are heteroglycans with various different sugar units, arranging in different proportions with an equatorial configuration. Hemicelluloses include xyloglucans, xylans, mannans, glucomannans, and β -(1 \rightarrow 3, 1 \rightarrow 4)-glucans, biosynthesized by glucosyltransferases located in the golgi membranes (Scheller and Ulvskov, 2010). The most important biological role of hemicelluloses is contributed to the cross-linked interaction with cellulose and lignin, strengthening the cell wall and embedding the crystalline cellulose elementary fibrils. Lignin is the most abundant and complex aromatic polymer found in the plant cell walls, considering as a primary factor limiting cell wall degradability by rumen microbes. The concise comprehensive definition of lignin requires almost half a page in length. Briefly, lignin is built from three basic monolignols (p-coumaryl, coniferyl and sinapyl alcohols) connected by the various interunit bonds, such as several types of ether (e.g. β -*O*-4, α -*O*-4, and 4-*O*-5) and carbon–carbon (e.g. β - β , β -5, and 5-5) linkages mediated by laccases and peroxidases (Ralph et al., 2004a).

Research activities in the hemicellulosic applications are mainly focused on utilizing their native or modified forms in various areas as biopolymers, including food and non-food applications. A sustainable film was made of glucuronoxylan from aspen wood with 35 wt.% sorbitol and exhibited an oxygen permeability of $0.21 \text{ cm}^3 \mu \text{m} \text{m}^{-1} \text{d}^{-1} \text{kPa}^{-1}$ at 50% RH (relative humility), which was similar to the value of a poly(vinyl alcohol) (PVOH) film under the same condition (Grondahl et al., 2004). Due to the unique geland film-forming properties as well as biocompatibility and biodegradation of these polysaccharides, the application potential has recently been intensified in drug delivery, cellular therapy, encapsulation and emulsification (Hansen and Plackett, 2008), Lignin has been traditionally viewed as a low-value by-product of pulping and papermaking, and a formidable barrier to efficient enzymatic breakdown of lignocellulosic material to sugars. As an environmentally friendly and natural compound, new applications of lignin in biomaterials, fuels, biostabilisers, etc., have been recently proposed (Lora and Glasser, 2002). Serving as the adjunct crosslinker, lignin should be an obvious candidate in resin industry, although its chemical heterogeneity and impurity limit the crosslinking process. In 2000, the Lenox® lignin-epoxy resins for moulded composites reached ~350 kL/annum at their peak (Stewart, 2008). In order to eventually become an economical process, the

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