Comparative study of organosolv lignin extracted from prairie cordgrass, switchgrass and corn stover

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HIGHLIGHTS

- Organosolv lignin extracted from three feedstocks was analyzed.
- Lignin origin influences its properties.
- Examined lignins were found low in contaminants.
- Examined lignins were found highly phenolic and applicable in vanillin production.

ABSTRACT

Lignin extracted from prairie cordgrass, switchgrass, and corn stover (using ethyl acetate–ethanol–water organosolv pretreatment) was analyzed and characterized using several methods. These methods included analysis of purity (by determination of Klason lignin, carbohydrate, and ash contents), solubility (with several organic solvents), phenolic group analysis (ultraviolet ionization difference spectra, and nitrobenzene oxidation), and general functional group analysis (by 1H NMR). Results showed that all the examined lignin samples were relatively pure (contained over 50% Klason lignin, less than 5% carbohydrate contamination, and less than 3% ash), but switchgrass-derived lignin was observed to be the purest. All the lignins were found to contain high amounts of phenolic groups, while switchgrass-derived lignin was the most phenolic, according to the ionization difference spectra. Nitrobenzene oxidation revealed that all the lignin samples contained available guaiacyl units in high amounts.

1. Introduction

Lignin represents the most abundant natural phenolic polymer (Lora and Glasser, 2002). It occurs in lignocellulosic plants and plays a major role in maintaining their rigidity and resistance against environmental conditions (Brown, 2003). Lignin is known as an effluent from paper making processes, such as kraft or sulfite pulping (Madakadze et al., 1999).

The monomers which undergo polymerization and contribute to lignin's complex structure include p-hydroxycinnamyl (coumaryl), coniferyl and sinapyl alcohols. These correspond to three main structural (phenylpropanoid) units of lignin polymer: p-hydroxyphenyl, guaiacyl, and syringyl, respectively (Lin and Dence, 1992). Depending on the material, these structural units occur in different proportions. Softwood lignin tends to contain mostly coniferyl alcohol-derived units, while for herbaceous lignin, coumaryl alcohol-derived units are more typical (Gosselink et al., 2004). Main functional groups observed in lignin structures include hydroxyl (partly phenolic), methoxyl, carbonyl, and carboxyl (Gosselink et al., 2004). Polymerization of coumaryl groups results in formation of aryl-ether bonds (α and β), which among ester and ketal bonds occur most commonly in lignin polymers (Xu et al., 2006).

The organosolv pretreatment originated from an organosolv pulping process, and represents an alternative to traditional pulping methods. The principle is based on lignin solubility in certain organic solvents (e.g. alcohols, organic acids, ketones) (Taherzadeh and Karimi, 2008; Zhao et al., 2009). In the 1990s, the organosolv process was applied specifically as a biomass pretreatment method in ethanol production. Two processes (ALCELL™ and Lignol) were demonstrated on a commercial scale, both using ethanol as a lignin solvent (Arato et al., 2005; Pye and Lora, 1991).

Organosolv pretreatment cleaves mainly α-aryl ether bonds, while the β-aryl ether bonds are cleaved to a lesser extent (Meshgini and Sarkanen, 1989). New phenolic groups are formed...