Bioresource Technology 118 (2012) 30–36

Contents lists available at SciVerse ScienceDirect

Bioresource Technology

journal homepage: www.elsevier.com/locate/biortech

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

Iwona Cybulska [a,*], Grzegorz Brudecki [a], Kurt Rosentrater [b], James L. Julson [a], Hanwu Lei [c]

[a] Department of Agricultural and Biosystems Engineering, South Dakota State University, Brookings, SD 57007, United States
[b] Department of Agricultural and Biosystems Engineering, Iowa State University, Ames, IA 50011, United States
[c] Bioproducts, Sciences and Engineering Laboratory, Department of Biological Systems Engineering, Washington State University, Richland, WA 99352, United States

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.

ARTICLE INFO

Article history:
Received 16 March 2012
Received in revised form 14 May 2012
Accepted 16 May 2012
Available online 24 May 2012

Keywords:
Lignin
Organosolv pretreatment
Phenolic structures
Vanillin
Ionization difference spectra

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 ^{1}H 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

* Corresponding author. Tel.: +1 605 688 4710; fax: +1 605 688 6764.
E-mail addresses: iwonacybulska@op.pl, iwona.cybulska@sdstate.edu (I. Cybulska).

0960-8524/$ - see front matter © 2012 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.biortech.2012.05.073

as a result of ether bond cleavage, producing highly phenolic organosolv lignin (Xu et al., 2006). In addition to being highly phenolic, organosolv lignin is considered relatively pure (i.e. low in carbohydrates, free of sulfur, and low in ash), low molecular weight and highly hydrophobic (Pye and Lora, 1991). Generally, organosolv lignin contains less contaminants than lignin obtained from other processes, such as kraft or sulfite (Lora and Glasser, 2002).

The majority of lignin obtained from pulping processes has been used as fuel to generate energy needed for recovery of other chemicals, due to its high energy content (Kleppe, 1970). However, lignin offers a vast range of potential applications in many industries, beyond that of just a combustion fuel. For example, kraft and sulfite lignin has been used as binders and dispersants (Lora and Glasser, 2002). Organosolv lignin offers additional utilization possibilities, primarily because they are sulfur-free (organosolv processing can eliminate emissions of sulfur compounds during heat processing) and highly phenolic (with a wide range of possible oxidation products) (Lora and Glasser, 2002; Pye and Lora, 1991). One of the potential organosolv lignin applications is production of resins. Using lignin in production of phenolic resins (utilized in plastics manufacture) offers advantages such as limiting the use of toxic formaldehyde, and improved wear behavior. Organosolv lignin has also shown beneficial features when used as a material for oriented strand board binders. Epoxy resins are yet another potential lignin application (e.g. printed circuit board production). Furthermore, organosolv lignin derivatives (modified with alkylene oxides) have been used to produce polyurethane and isocyanurate resins (Lora and Glasser, 2002).

Highly phenolic lignin processing can yield a variety of commercially important compounds, such as vanillin, guaiacol, vanilic acid, acetovanillone, 5-carboxyvanillin, vanillil, vanillovanillone, and syringaldehyde (Pearl, 1967). Vanillin is commonly used as food (e.g. ice cream, bakery products, candy) and beverage additives (as flavoring and scent). It is also a substrate for production of many other chemicals, including papaverine (heart medication), hydrazones (herbicide), trimethoprim (antibacterial agent). Vanillin has been widely produced from guaiacyl units occurring in lignin from kraft and sulfite processes. However, utilizing both kraft lignin and lignin sulfonates resulted in toxic by-products, and was phased out in the late 1980s due to environmental issues and availability of petroleum-based vanillin products (Hocking, 1997; Schulz, 1940). Organosolv lignin is free of sulfur, and thus do not generate hazardous by-products, and could result in an opportunity for sustainable vanillin production (Gogotov et al., 1996).

This work compares lignin extracted from three types of feedstock (prairie cordgrass, switchgrass and corn stover) using organosolv treatment (clean fractionation). The extracted lignin samples were characterized by their original fractional yield, Klason lignin content, solubility in various organic solvents, and contamination by carbohydrates and ash. Spectroscopic methods were also employed to analyze phenolic functional group occurrence and configuration. These included UV–vis ionization difference spectra method and ^{1}H nuclear magnetic resonance (NMR) spectroscopy. Additionally, nitrobenzene oxidation was performed to evaluate guaiacyl unit content, and possible lignin application was examined by measuring vanillin yield. The main purpose of this research was to compare lignins of various origins based on their purity and possible industrial application.

2. Methods

2.1. Materials

Prairie cordgrass (PCG), switchgrass (SG) and corn stover (CS) were used as feedstocks for lignin extraction in this study. All of these materials were obtained locally near Brookings, South Dakota. Prior to processing, all of the samples were ground using a laboratory mill (Model 3375-E15, Thomas Scientific, USA) to pass through a 1 mm screen. Composition of each material, including structural carbohydrates, lignin, ash and moisture content, was measured according to NREL/TP-510-42618 procedure (Sluiter et al., 2008c). All reagents and solvents used in this study were of analytical grade.

2.2. Organosolv pretreatment (clean fractionation)

The clean fractionation process used in this study was based on the National Renewable Energy Laboratory (NREL) optimized process (Black et al., 1998). Ethyl acetate was used as lignin solvent and was mixed with ethanol and water in various ratios. A catalyst (sulfuric acid) was added to the process to initiate ether bond cleavage and improve lignin extraction. The clean fractionation conditions, including temperature, solvent composition and catalyst amount, were optimized for each of the materials using Response Surface Methodology. One of the primary response variables was lignin recovery, which was based on the gravimetric measurement. Optimizations performed for each grass have been presented in different studies (unpublished results). Predetermined optimal conditions of the clean fractionation for each material can be found in Table 2.

The pretreatment was performed in a custom-made experimental set-up, which included an aluminum heating block that held six stainless steel reactor tubes (each of 250 mL capacity). Each reactor tube was equipped with a pressure gauge and a thermocouple. Thermocouples were connected to a temperature controller (Autotune Temperature Controller C9000A Series, Omega, Stamford, CT) monitored by LabView computer software version 8.2 (National Instruments, Austin, TX).

Raw biomass (10 g, dry mass) was loaded into the reactors and treated with the solvent mixture at optimal temperature for 20 min. Liquid-to-solid ratio (%w/w) was 10:1. After the treatment, the slurry was filtered to separate liquid from solid fraction. The cellulose (solid) fraction was washed with approximately 2 L of water to remove solvent residues, and subsequently enzymatically hydrolyzed and fermented to ethanol (Dowe and McMillan, 2008; Selig et al., 2008). The liquid fraction was then separated into two phases: organic (containing lignin dissolved in ethyl acetate and ethanol) and aqueous (containing hemicellulose dissolved in water and ethanol). Lignin was reprecipitated by solvent evaporation, weighed, and stored for analysis.

2.3. Lignin analyses and characterization

2.3.1. Klason lignin, contaminants, and ash analyses

Lignin purity was evaluated by measuring Klason lignin (acid insoluble lignin) content and the amount of contaminants present in the extracted samples. The analysis was carried out by sulfuric acid hydrolysis according to NREL's standard procedure (Sluiter et al., 2008c). Carbohydrate contamination was measured by analyzing the hydrolyzate using High Performance Liquid Chromatography (Agilent HPLC 1200 Series) (Sluiter et al., 2008b). Ash content was also analyzed according to NREL's standard procedure (Sluiter et al., 2008a).

2.3.2. Solubility

Another characteristic of lignin is solubility in various organic solvents. The choice of solvents evaluated in this study was based on literature (Gosselink et al., 2004; Lin and Dence, 1992; Sarkanen and Ludwig, 1971), and included dimethyl sulfoxide (DMSO), dioxane, methanol, ethanol, ethyl acetate, and MIBK. Solutions were prepared in 100 mL volumetric flasks, using 0.05 g of each lignin type. The solutions were kept at 40 °C with constant agitation for