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Sugarcane straw lignin obtained by sulfur dioxide-alcohol-water (SAW) fractionation: Effect of solvent

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ABSTRACT

Sugarcane straw (SCS) lignin is extracted by SO_2-Alcohol-Water (SAW) fractionation (155 °C, 1 h) using methanol, ethanol or isopropanol as pulping solvent (SO_2/Alcohol/Water = 12/44/44 wt%). The SAW fractionation removes 90–95% lignin from SCS of which only 30–45% is isolated as precipitated lignin after solvent evaporation. The precipitated and pulp residual lignin (5–10%) are analyzed for their degree of sulfonation (S/C9) while precipitated lignin is further analyzed in terms of molecular weight distribution (MWD) and alkoxylation reactions. Similar S/C9 values for methanol, ethanol and isopropanol lignin show that the degree of sulfonation is independent of fractionation solvent. However, the sulfonated lignin is comparatively less soluble in the methanol-based liquor compared to the corresponding lignins in the ethanol- and isopropanol-based liquors. The mass average molecular weight, M_w, is highest for isopropanol lignin (~3800) while the numbers for methanol and ethanol lignins are comparatively smaller but nearly equal in magnitude (~3000). Alkoxyl groups and nuclear magnetic resonance (NMR) analyses are performed to interpret the differences in lignin M_w and alkoxylation reactions. Different ether and ester type linkages are identified in NMR spectra confirming lignin alkoxylation. Lignin carbohydrate complexes (LCC) are also found in NMR spectra confirming that some of the detected carbohydrates are covalently bound to lignin.

1. Introduction

Lignin is the 2nd most abundant renewable material on earth with cellulose being the first (Hu et al., 2011; Min et al., 2013; Kuhad and Singh, 2007). In contrast to most other natural polymers, which have only one kind of inter-monomeric linkage, lignin contains many different carbon-to-carbon and ether linkages. It is almost impossible to isolate lignin in pure form because of strong physical and chemical linkages between lignin and the cell wall polysaccharides (Holtmam et al., 2003). Because condensation and degradation reactions occur during commercial pulping processes, and the dissolved lignin is mixed with soluble carbohydrate products and pulping chemicals, industrial lignins are hardly used for making value added products despite its high availability. Lignin can be separated from lignocellulosic biomass by mechanical or chemical means. Milled wood lignin (MWL) is considered similar to native lignin, and is obtained by aqueous dioxane extraction of finely ball milled biomass (Bjorkman, 1954, 1956). Modifications of MWL, including cellulolytic enzymatic lignin (CEL) (Chang et al., 1975) and enzymatic mild acidolysis lignin (EMAL) (Wu and Argyropoulos, 2003) have been introduced to decrease the amount of carbohydrate contamination. These extraction technologies produce lignin at low yields and are energy intensive because biomass milling is performed for hours to weeks (Guerra et al., 2006). Kraft and acid sulfite (AS) are two well-known chemical pulping processes that produce cellulosic pulp and a spent liquor stream rich in lignin. In the Kraft process, lignin undergoes major modifications and the lignin containing spent liquor is burnt in a chemical recovery cycle to meet energy requirements and recover the inorganic pulping chemicals (Kouisni et al., 2011). Kraft lignin can be recovered from the spent pulping liquor by acid precipitation (Kouisni et al., 2011). However, Kraft lignin is not as reactive as sulfite lignin, also called lignosulfonate, produced by pulping using excess SO_2 dissolved in an aqueous base (AS pulping). Lignosulfonates have many applications such as surfactants, dispersants, binder, emulsion agent etc. (Yang et al., 2007). The number of mills producing lignosulfonates has decreased over time because of the difficulty of the weaker sulfite pulp to compete with Kraft pulp. In contrast to Kraft and AS, organosolv pulping processes are suggested as a route to produce pure and sulfur-free lignin as an important coproduct. It has been reported that SO_2-ethanol-water (SEW) produces a lignin that can be easily separated from spent liquor stream without

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further acidification by simple evaporation of ethanol (Retsina and Pylkkanen, 2013). However, lignin obtained by SEW fractionation contains sulfonate groups just as sulfite lignin. The degree of sulfonation (S/C9) of lignin obtained from various lignocellulosic feedstocks in SEW fractionation has been reported (Iakovlev and van Heiningen, 2012; Sklavounos et al., 2013; Yamamoto et al., 2014; You et al., 2017a) but no data is available regarding possible other modifications such as alkoxylation of the lignin. However, other lignin extraction studies involving alcohols and mineral acids (no SO_2) confirm the presence of lignin alkoxylation reactions (Bauer et al., 2012; Lancefield et al., 2017). Bauer et al. (2012) reports ethoxylation of ß-O-4 linkages in Miscanthus giganteus lignin extraction with 65–95% ethanol and 0.2 M HCl under reflux conditions. Similarly, extensive alkoxylation of beech, walnutshell and Douglas fir lignin is seen when treated with ethanol or butanol (95%, 0.2 M HCl) at different temperatures (Lancefield et al., 2017). These studies reveal that alkoxylation occurs at the alpha position of the lignin propyl side chain, and that the extent of alkoxylation depends on type of lignocellulosic feedstock, alcohol concentration and operating temperature. In view of these recent findings that lignin undergoes alkoxylation during organosolv fractionation, SCS lignin is extracted by SO_2-alcohol-water (SAW) fractionation and the effect of the solvent used (methanol, ethanol or isopropanol) on the structure of isolated lignin is investigated. It has been shown in our earlier study that SAW fractionation process can easily fractionate SCS into cellulose, hemicellulose with more than 90% lignin removal using methanol, ethanol or isopropanol (155 °C, 1 h, SO_2/alcohol/water = 12/44/44 wt%). However, ethanol and isopropanol are preferred solvents in SAW fractionation system because of their better delignification properties and less stringent safety regulation requirements (Sharazi and van Heiningen, 2017a). Also, the use of SCS in the fractionation processes to separate carbohydrates and lignin to be used in biochemical conversion processes is a logical choice because of its low cost and abundance (Goncalves et al., 2005; Moutta et al., 2012; Saska and Gray, 2006; You et al., 2016). Lignin obtained from this cheap and abundantly available raw material may be valuable if it is pure and has the properties necessary for polymer product development. Therefore, this study is focused on determining the purity and characteristics of lignin obtained from SCS using three different alcohols in the SAW fractionation process.

2. Material and methods

2.1. Fractionation and lignin separation

Sugarcane straw (SCS) obtained from the Thomaston, GA, biorefinery of API (American Process Inc.) was fractionated for 1 h at 155 °C at a liquor to feedstock ratio (L/F) of 4 L/kg. The composition of SCS, cooking liquor preparation and other fractionation conditions are the same as described earlier (Sharazi and van Heiningen, 2017a, 2017b). Spent liquors containing lignin and sugars were obtained by manually squeezing the fractionated SCS (75 mesh nylon bag). The remaining solid residue, called pulp, was washed with aqueous alcohol and water as described earlier (Sharazi and van Heiningen, 2017a). Methanol, ethanol and isopropanol spent liquors and pulps were designated as SO_2-methanol-water (SMW), SO_2-ethanol-water (SEW) and SO_2-isopropanol-water (SPW) respectively. 10 mL of SMW, SEW and SPW liquors were subjected to rotary evaporation to remove SO_2 and alcohol. After 50–60% mass reduction of the spent liquors by rotary evaporation, the remaining suspension was transferred into 50 mL Corning vials and deionized water (30–35 mL) was added to further precipitate lignin. The precipitated lignin was separated by centrifugation (4000 rpm, 10 min) while the rest of the lignin remained in solution as soluble lignin. The precipitated lignin samples were freeze dried (−80 °C) and then put into a vacuum oven dryer (vacuum $\sim 10^{-4}$ Torr) for at least 48 h. These precipitated lignin samples were analyzed for sulfur content, molecular weight distribution (MWD) and content of alkoxyl groups.

2.2. Lignin yield and sulfur analysis

The amount of lignin remaining in the pulp, called residual lignin, was calculated from the kappa number and pulp yield (Sharazi and van Heiningen, 2017a). The amount of lignin in the spent liquors (soluble + precipitated) was calculated from the difference between the original lignin content in SCS (19.8%) and that in the pulp. Precipitated lignin was gravimetrically measured after rotary evaporation of spent liquor (Section 2.1) and this amount was subtracted from total lignin in spent liquor to quantify the amount of soluble lignin. Original SCS and pulps were ground in a Wiley mill before total sulfur analysis. The amount of sulfur in these solids and in the precipitated lignin samples was determined after digesting the solids following the EPA-3051 method (EPA, 2007) and then analyzing it for sulfur using inductively coupled plasma-optical emission spectrometry (ICP-OES).

2.3. Lignin sugar content

The amounts of different sugars in precipitated lignin samples were determined by standard two step hydrolysis (72% H_2SO_4, 30 °C, 1 h and 4% H_2SO_4, 121 °C, 1 h). The liquor obtained from precipitated lignin hydrolysis was filtered (0.45 µm PTFE filter) and analyzed by high performance anion exchange chromatography with pulsed amperometric detection (HPAEC-PAD). The instrument was equipped with a Dionex CarboPac PA1 (4 × 250 mm) column (30 °C), CarboPac PA1 (4 × 50 mm) guard column, IonPac NG1 (4 × 35 mm) guard column, GP50 Pump, ED40 Detector (gold electrode), and an AS50 Autosampler. The eluent flow rate was 1.0 mL/min (degassed Milli-Q H_2O at 0.7 mL/min + 300 mM NaOH from the post column at 0.3 mL/min).

2.4. Size exclusion chromatography (SEC)

Molecular weight distributions of the precipitated lignin samples (Section 2.1) were obtained by dissolving 5 mg of lyophilized samples in a 2 mL of DMSO + 0.5% LiBr (w/w) solution. After filtration of the samples through 0.45 µm PTFE filters, size exclusion chromatography (SEC) was performed with an Agilent 1260 Infinity system. The equipment consisted of an isocratic pump (G1310B), a micro degasser (G1379B) and a standard autosampler (G1329B). The detection system included a UV detector (G1314B) in series with a refractive index detector (G1362A). The mobile phase was DMSO + 0.5% LiBr set to a constant flow rate of 0.5 mL/min for a total run time of 65 min. The injection volume was 100 µL. The separation system consisted of PSS GRAM Precolumn, PSS GRAM 100 Å and PSS GRAM 10 000 Å analytical columns thermostated at 60 °C and connected in series. The pullulan standards with nominal masses of 708 kDa, 337 kDa, 194 kDa, 47.1 kDa, 21.1 kDa, 9.6 kDa, 6.1 kDa, 1.08 kDa and 342 Da were used for standard calibration.

2.5. Nuclear magnetic resonance (NMR)

All NMR spectra were recorded on a Bruker Avance II 400 (resonance frequencies 400.13 MHz for ^{1}H and 100.63 MHz for ^{13}C) equipped with a 5 mm observe broadband probe head (BBFO) with z–gradients at room temperature with standard Bruker pulse programs. 20–40 mg of the samples (precipitated lignin) were dissolved in 0.6 mL of a mixture of deuterated DMSO: Pyridine = 4:1. Chemical shifts are given in ppm, referenced to residual DMSO-d_6 signals (2.49 ppm for ^{1}H, 39.6 ppm for ^{13}C). HSQC experiments were acquired in edited mode with a relaxation delay of 0.5 s using adiabatic pulse for inversion of ^{13}C and GARP-sequence for broadband ^{13}C-decoupling, optimized for ^{1}J (CH) = 145 Hz. The mixing time for HSQC-TOCSY experiments was set to 100 ms whereas the HMBC was optimized to a heteronuclear long-range coupling constant of 8 Hz.