Aqueous organic solvent fractionation as means to improve lignin homogeneity and purity

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ABSTRACT

Lignin's heterogeneous polymeric structure limits its utilisation in high-value applications. This paper describes a protocol for kraft lignin precipitation fractionation from aqueous ethanol, acetone and propyleneglycol monomethyl ether solution by adding water as nonsolvent. The solvent-insoluble fractions possessed high molar mass (Mw 4300–18900 g/mol), high polydispersity (2.2–5.6), high nitrogen (0.15–0.43%) and low sulphur (0.7–1.5%) content. Even lignin aggregation was observed in acetone-based process. The molar mass of the precipitated fractions depended on the amount of water added in the precipitation step. The highly soluble lignin fractions possessed very low molar mass (Mw 1100–1200 g/mol), more free phenolic hydroxyl groups (3.95–4.05 mmol/g), carboxylic acid groups (0.56–0.71 mmol/g), higher amount of sulphur (1.6k2.9%) and more carbohydrates (5.3–6.1%) than other lignin fractions. The presented protocol provides a selection of green solvents for a simple and easily scalable and tunable lignin fractionation process to produce lignin with constant quality and high purity.

1. Introduction

Lignin is the second most abundant natural polymer after cellulose and it composes of ca. 20–30% of wood and most other lignocellulosic biomasses (Boerjan et al., 2003; Ragauskas et al., 2014). Lignin is considered as the most promising aromatic raw material to replace petrochemical-based feedstocks (Ragauskas et al., 2014). Currently, worldwide chemical wood pulping industry produces ca. 70 Mt of lignin which is mostly incinerated to generate energy. Novel technological solutions provide means to recover part of lignin from the existing process streams without impeding the energy or chemical balances of the mills (Tomani, 2010). In addition to pulping industry also lignocellulosic ethanol production is expected to produce another 62 million tons of lignin as side streams by 2022 (Ragauskas et al., 2014) These volumes illustrate the high availability of technical lignins, and it is expected that lignin will become a commercially relevant feedstock for a range of materials (Gellerstedt, 2015; Ragauskas et al., 2014).

Lignin is composed mostly of three types of phenyl propane units, i.e. *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) units, which differ by the number of methoxyl groups attached on the aromatic ring. H units have no methoxyl groups, G units possess one methoxyl group and S units possess two methoxyl groups attached on the aromatic ring. The relative content of these units depend mostly of plant species, as softwood lignin is composed mostly of G and some H units, hardwood lignin contains both G and S units and minor amount of H units and herbaceous lignins contain all three units in remarkable quantities (Vanholme et al., 2010). The phenyl propane units in lignin are interlinked via different, mostly ether, linkages (Boerjan et al., 2003). There is significant variation in lignin interunit linkages within trees and even cell wall layers (Vanholme et al., 2010) which indicates that lignin is inherently heterogeneous polymer. Furthermore, in chemical pulping processes the heterogeneity is increased due to incomplete impregnation of the chemicals in the feedstock. The heterogeneity is a challenge when lignin is used in material applications where constant molecular size, functionality and reactivity are required (Chatterjee and Saito, 2015; Gellerstedt, 2015; Norberg et al., 2013; Teng et al., 2013).

Ultrafiltration (Brodin et al., 2009; Norgren and Lindström, 2000; Sevastyanova et al., 2014; Toledano et al., 2010a, 2010b), solvent fractionation (Boeriu et al., 2014; Cui et al., 2014; Duval et al., 2015; Li and McDonald, 2014; Lovell and Hibbert, 1941; Mörck et al., 1986; Ni and Hu 1995; Ropponen et al., 2011; Sadeghifar and Argyropoulos, 2016) and their combinations (Helander et al., 2013) are potential techniques to decrease the heterogeneity of lignin isolates. Ultrafiltration provides an efficient method to control the

molar mass distribution of lignin by the selection of membranes with suitable cut-offs (Brodin et al., 2009; Sevastyanova et al., 2014; Toledano et al., 2010a, 2010b). A major advantage of this method is that the technology can be applied directly to cooking liquor at pulp mill without a need to adjust pH or temperature (Sevastyanova et al., 2014). On the other hand, the poor solubility of some lignins (e.g. hydrolysis lignin from ethanol production plant), fouling of the membranes and expensive instrumentation are major limitations for ultrafiltration.

Solvent fractionation is based on partial solubility of polymers into solvents. Several solvent fractionation methods have been developed to produce polymer fractions with narrow distribution of molar mass, branching or chemical composition (Francuskiewicz, 1994). Solvent fractionation of lignin can be performed either by selective dissolution of solid lignin or selective precipitation of dissolved lignin. In the pioneering work by Lovell and Hibbert (1941), lignin was first dissolved in methanol followed by fractionation using two immiscible solvents, carbon tetrachloride and chloroform. Later, Mörck et al. (1986) developed a sequential fractionation process using dichloromethane (DCM), isopropanol, methanol and methanol-DCM mixture to extract lignin fractions. Similar strategies have been implemented over the years and the methods are based on organic solvents such as DCM, isopropanol, methanol, ethanol, acetone, diethyl ether, dioxane, tetrahydrofuran, butanone and hexane as pure solvents or as mixtures. (Arshanitsa et al., 2013; Dodd et al., 2015; Duval et al., 2015; Jiang et al., 2017; Li and McDonald, 2014; Passoni et al., 2016; Ropponen et al., 2011) However, apart from the protocol designed by (Duval et al., 2015) these fractionation methods are based on solvents that are classified as problematic or even hazardous (Prat et al., 2016) and therefore should be replaced with safer alternatives. On the other hand, the protocol by (Duval et al., 2015) utilizes four different solvents (ethyl acetate, ethanol, methanol and acetone) sequentially, which makes it complicated to scale up especially when chemical recycling needs to be considered.

A fractional precipitation fractionation scheme for lignin was first proposed by Cui et al. (2014) who dissolved kraft lignin in acetone and then added hexane gradually to precipitate lignin fractions from the solution. Mixing two miscible solvents allowed the flexible manipulation of the yield and molecular composition of each lignin fraction and hence provided an attractive approach for lignin fractionation. However, hexane is a hazardous chemical (Prat et al., 2016), which should be substituted with a less harmful solvent. A similar approach was applied by Sadeghifar et al. (2017), who dissolved organosolv lignin into aqueous acetone followed by controlled lignin precipitation fractionation with water addition.

In this paper, we demonstrate a solvent fractionation method to separate kraft lignin in homogeneous fractions using three different green aqueous solvents: ethanol, acetone and propyleneglycol monomethyl ether (PGME). The lignin precipitation fractionation was performed by first dissolving lignin in aqueous solvent followed by addition of water to controlled precipitation of lignin. The chemical structures of the produced lignin fractions were characterised to assess the performance of the process. This fractional precipitation procedure provides an easily controllable process to manipulate the yield and structural composition of produced lignin fractions without the use of harmful or hazardous solvents or expensive instrumentation.

2. Materials and methods

2.1. Kraft lignin and its characterization

Dry softwood kraft lignin (dry matter 95%) was an industrial kraft lignin precipitated from softwood black liquor and kindly gifted by Metsä Fibre. Klason lignin content was determined gravimetrically after acid hydrolysis of the sample (Allsopp and Misra, 1940), and the hydrolysate was analysed to determine the acid soluble lignin using UV spectroscopy (Goldschmid, 1971) and carbohydrates using HPAEC-PAD (Tenkanen and Siika-Aho, 2000).

Elemental analysis (C, H, N and S) was determined from 20 to 30 mg of ground and dried (105 °C for overnight) using FLASH 2000 series elemental analyzer (Thermo Scientific, Bremen, Germany).

UV absorption coefficient for the unfractionated kraft lignin was determined using Hitachi U-2000 (Tokyo, Japan) UV spectrophotometer. The absorptivity value was defined by dissolving 13.5 mg of lignin (o.d.) in 1000 ml NaOH solution (0.1 M) at room temperature. The absorbance at 280 nm (0.350 ± 0.020) designates the absorptivity value of $25.91 \cdot g^{-1} \cdot cm^{-1}$, which was applied to determine the concentration of dissolved lignin.

For the molar mass measurements, the samples were dissolved in 0.1 M NaOH and filtered (0.45 μm).The molar mass measurements were performed with size exclusion chromatography (SEC) using 0.1 M NaOH eluent (pH 13, 0.5 ml/min, T = 25 °C) and PSS MCX 1000 & 100000 Å columns. The elution curves were detected using Waters 2998 Photodiode Array detector at 280 nm. The molar mass distributions (MMD), number average molar mass (M_n), weight average molar mass (M_w) and polydispersity (PD) were calculated against polystyrene sulphonate standards (eight standards with a range of 3420–148500 g/mol) and using Waters Empower 3 (Milford, MA, USA) software.

The number of hydroxyl groups were determined with ^{31}P NMR spectroscopy by using the procedure by Granata and Argyropoulos (Granata and Argyropoulos, 1995) and using a Bruker 500 MHz (Billerica, MA, USA) spectrometer. 1024 scans with pulse delay of 5 s, 90° pulse, line broadening of 2 and default baseline correction were used in spectral collection. The quantification limits applied were 150–145 ppm for aliphatic OH groups, 145-140.5 ppm for 3 and 5-subsituted phenolic OH groups, 140.5-138.5 ppm for guaiacylic OH groups, 138.5–137 ppm for p-hydroxyphenyl groups and 136–134 ppm for carboxylic acid groups.

2.2. Solvent fractionation of lignin

Lignin fractionation followed the scheme in Fig. 1: 10 g (o.d.) of kraft lignin was mixed with 100 ml of aqueous ethanol (80% by volume), acetone (60% by volume) or PGME (60% by volume) solution. The dispersion was mixed in an erlenmeyer flask under magnetic stirring for 20 min at room temperature. The solution was centrifuged for 20 min and the supernatant was recovered. The insoluble lignin fraction was washed twice with aqueous solvent of same concentration, dried (in vacuum at 40 °C for 16–72 h) and weighed.

A predefined volume of supernatant from the first fractionation stage was placed in Erlenmeyer flask followed by water addition to reach the desired solvent concentration (70% for ethanol and 50% for acetone or PGME). This solution was mixed for 20 min to allow lignin to precipitate followed by centrifugation and recovering the supernatant. The precipitate was washed twice with aqueous solvent, dried (40 °C vacuum) and weighed. Again, a predefined volume of supernatant was replaced in Erlenmeyer flask followed by water addition to precipitate a new fraction of lignin. These steps were repeated until solvent concentration of 50% was reached. At this stage the lignin concentration was so low that the precipitation fractionation was not practical to continue further. A new fractionation sequence was started by mixing 10 g of lignin with aqueous solvent (50% by volume) and repeating the fractionation as explained above. This way, the solvent volumes and lignin concentrations remained at practical level until solvent concentra-