



## Characteristics of wheat straw lignins from ethanol-based organosolv treatment



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### ARTICLE INFO

#### Article history:

Received 16 January 2014

Received in revised form 28 April 2014

Accepted 3 May 2014

#### Keywords:

Lignin

Wheat straw

Organosolv

Residual carbohydrates

Functional groups

Thermal behavior

### ABSTRACT

Non-purified lignins resulting from ethanol-based organosolv fractionation of wheat straw were characterized for the presence of impurities (carbohydrates and ash), functional groups (hydroxyl, carboxyl and methoxyl), phenyl-propanoid structural moieties, molar mass distribution and thermal behavior. In accordance with its herbaceous nature, the syringyl/guaiacyl-ratio of the wheat straw lignins was substantially lower than of Alcell lignin. In addition, the content of *p*-hydroxyphenyl and carboxyl groups is substantially higher for the wheat straw lignins. The non-purified organosolv lignins had a high purity with 0.4–5.2% carbohydrate impurities, both originating from lignin to carbohydrate complexes and residual organosolv liquor. The use of H<sub>2</sub>SO<sub>4</sub> in the organosolv process improved the lignin yield, but at low acid doses increased the carbohydrate impurities. For applications where a low amount of carbohydrates is important, lignin from a high-temperature autocatalytic organosolv process was found to be preferred. The highest content of total hydroxyl groups was determined when lignins were produced using 30 mM H<sub>2</sub>SO<sub>4</sub> as catalyst or 50% w/w aqueous ethanol as solvent for the organosolv process. Aliphatic hydroxyl groups, the most predominant type of hydroxyl groups present originating for a substantial part from residual carbohydrates, were found to decrease with reaction time and ethanol proportion of the organosolv solvent. The correlations between organosolv process conditions and lignin characteristics determined can facilitate the use of organosolv lignins in value-added applications such as in polymers and resins and as a feedstock for bio-based aromatics.

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### 1. Introduction

Lignin is the most abundant aromatic biopolymer in nature consisting of phenylpropane units that originate from three aromatic alcohol precursors (monolignols); i.e., *p*-coumaryl, coniferyl and sinapyl alcohol (Fengel and Wegener, 2003; Ghaffar and Fan, 2013). The cross-linked phenolic substructures that originate from these monolignols are defined as *p*-hydroxyphenyl (H, from coumaryl alcohol), guaiacyl (G, from coniferyl alcohol) and syringyl (S, from sinapyl alcohol) structural moieties (Fengel and Wegener, 2003; Buranov and Mazza, 2008). Cereal straw lignin is a GSH-type lignin containing all three monolignols (Dence and Lin, 1992). The composition of degradation products of lignins from wheat straw by thioacidolysis shows that the proportion of H, G, and S is 5, 49, 46% (Buranov and Mazza, 2008). During the biological lignification process, the monolignols form a complex network closely

associated with hemicelluloses. Hydroxycinnamic acids (ferulic and *p*-coumaric) act as cross-linking agent between lignin and carbohydrates forming so-called lignin–hydroxycinnamate–carbohydrate complexes (Sun, 2010). The major inter-unit linkages within lignin are of an ether type with around 50% β-O-4 ether linkages (Ghaffar and Fan, 2013).

Lignin's aromatic nature makes it a potential renewable source of (aromatic) chemicals and performance products (Hu, 2002; Lora and Glasser, 2002; Bozell et al., 2007; Stewart, 2008; Zakzeski et al., 2010). Potential applications of lignins from various sources include the production of chemicals such as phenol(ics) and BTX (benzene, toluene and xylene) (Zakzeski et al., 2010). The use of lignin in various material applications has been studied such as phenolic resins (Da Silva et al., 2013; Lora and Glasser, 2002; Stewart, 2008), polyurethanes (Lora and Glasser, 2002; Pan and Saddler, 2013), epoxy resins (Lora and Glasser, 2002; Stewart, 2008), and carbon fibers (Hu, 2002; Pan, 2013). Finally, the use of lignin as antioxidant has been reported (Dizhbite et al., 2004; Pan et al., 2006; El Hage et al., 2012). In spite of the various potential applications, the current industrial use of lignin is still limited due to

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limited industrial supply and challenging lignin properties such as its complex and non-uniform chemical structure (Vishtal and Kraslawski, 2011). However, the expected substantial increase in available technical lignins from pulp and paper processes, ligno-cellulosic biofuels production and biorefineries as well as lignin's unique chemical structure warrant additional research to develop (new) outlets (Vishtal and Kraslawski, 2011).

The desired lignin characteristics depend on the application. Monteil-Rivera et al. (2013) provide an interesting discussion on the required lignin properties for various applications. For example, molar mass (polydispersity) and (total) OH content are physico-chemical lignin characteristics that are important for the use of lignins in lignin-polymer blends. For many applications, lignins having a high purity, i.e. low in ash, residual carbohydrates etc. are preferred. Isolation of lignin from lignocellulosic biomass e.g. by using organic solvents (organosolv) enables production of such high-purity lignins (Pan, 2013).

Organosolv fractionation is considered to be a promising biorefinery approach given the coproduction of cellulose products (e.g., fibers or enzymatically digestible cellulose), high-purity lignin and hemicellulose-derived products such as xylose, furfural and acetic acid (Zhao et al., 2009; Pan, 2013). Coproduction of these materials seems critical to improve the cost-effectiveness of biorefinery schemes for second generation biofuels such as bioethanol. Organosolv processes currently operated at pilot-scale include the ethanol-based process of Lignol in Burnaby, BC, Canada (former Alcell® process) (Arato et al., 2005) and the acetic and formic acid-based process from CIMV in Pomacle, Champagnes-Ardennes, France (Delmas et al., 2011).

Characterization of lignins produced including dependency on the organosolv process conditions is a prerequisite for the development of value-added lignin applications and, thereby, an economically viable organosolv biorefinery concept. In the literature, lignins extracted by ethanol-based organosolv processes have been widely studied for various types of biomass such as loblolly pine (Sannigrahi et al., 2010), switchgrass (Hu et al., 2012), flax (Buranov et al., 2010; Monteil-Rivera et al., 2013), fiber hemp (Zomers et al., 1995; Monteil-Rivera et al., 2013) and wheat straw (Monteil-Rivera et al., 2013). Characterization of organosolv lignins including correlation to organosolv process conditions have been reported for bagasse (Vallejos et al., 2011), hybrid poplar (Pan et al., 2006), olive tree pruning (Toledano et al., 2011) and Miscanthus (El Hage et al., 2010). However, in most studies washed or otherwise purified lignins have been used in order to remove non-bonded impurities and to be able to study the chemistry occurring during the organosolv process. Whether the lignin product will be washed or otherwise purified in an industrial organosolv process depends on the economic trade-off between potentially improved lignin application possibilities and additional costs for the purification step. In this study, we focused on non-purified organosolv wheat straw lignins.

The objective of this paper is to characterize non-purified lignins resulting from an earlier study in which we reported on ethanol-based organosolv pretreatment of wheat straw for enzymatic cellulose hydrolysis (Wildschut et al., 2013). Wheat straw is an attractive low-cost feedstock for the production of bio-based chemicals because of its annual renewability and abundance, being an agricultural residue from the production of cereals (Buranov and Mazza, 2008; Sun, 2010). In this study, selected wheat straw lignins will be analyzed for their composition (carbohydrate and ash impurities), physical properties as molar mass distribution (SEC), thermal degradation (TGA) and glass-transition temperature (DSC), as well as hydroxyl, carboxyl and methoxyl functional groups (both by wet chemical methods and <sup>31</sup>P-NMR). The influence of the organosolv process conditions on the lignin characteristics will be assessed. Alcell® lignin, an

ethanol organosolv hardwood lignin, will be used as a reference lignin.

## 2. Materials and methods

### 2.1. Lignin samples

Lignin samples from an earlier study (Wildschut et al., 2013), in which lignin was isolated from wheat straw using an ethanol-based organosolv process, were selected for characterization such that the influence of the main process parameters of the organosolv process on the lignin characteristics could be assessed. In addition, the optimum process conditions for enzymatic cellulose digestibility and lignin yield were included (Wildschut et al., 2013). Table 1 gives an overview of selected lignin samples including the organosolv process conditions used. In addition to the wheat straw organosolv lignins, Alcell® (here and further Alcell) lignin was included in all lignin characterizations as a reference material. Alcell ethanol-water organosolv lignin from mixed hardwoods was obtained from Repap Technologies, Canada.

The methods used for the organosolv delignification experiments as well as the analysis method used to determine the lignin content of the resulting wheat straw pulp and thereby the delignification degree have been reported earlier (Wildschut et al., 2013). The summative composition of the wheat straw was (% w/w, dry basis): glucan, 35.4; xylan, 19.8; arabinan, 2.1; galactan, 1.4; lignin, 17.6; ash, 3.5; extractives, 10.2 (Wildschut et al., 2013). The elemental composition was (%): C 47.3, H 6.4, N 0.7, and O 44.6 (Wildschut et al., 2013). The liquids resulting from the organosolv process, i.e. the “organosolv liquor” and the solution resulting from pulp washing, were combined and added to chilled water to separate the dissolved lignin by precipitation (4 °C, 3:1 w/w dilution ratio H<sub>2</sub>O: organosolv liquor). Precipitated lignin particles were sedimented by centrifugation, the liquor was decanted and the lignin was dried. No further purification steps, such as washing, were applied on the lignin. For more details on the lignin isolation procedure, we refer to Huijgen et al. (2010). Analysis of the sugar content of the combined liquors was performed by High Performance Anion Exchange Chromatography with Pulsed Amperometric Detection (HPAEC-PAD) after post-hydrolysis of oligomeric sugars present, as described earlier (Huijgen et al., 2012).

### 2.2. Lignin composition

The dry matter content (DM) was measured using a halogen moisture analyzer (Mettler Toledo HR83, Columbus, OH). The ash content was determined in duplicate using thermogravimetric analysis under air (Mettler Toledo TGA 850, Columbus, OH). 10 mg of sample was heated with 10 °C/min to 900 °C, including an isothermal interval at 105 °C to determine the dry weight of the sample.

The residual carbohydrate content of the lignin samples was determined using an analytical procedure for summative composition analysis of lignocellulosic biomass, which has been reported in earlier work (Huijgen et al., 2011, 2012) and is based on the standard Laboratory Analytical Procedures (LAP) of NREL (Golden, CO) (National Renewable Energy Laboratory (NREL), 2009). The lignin samples were finely crushed to powder and hydrolyzed in two steps: (1) 12 M (72% w/w) H<sub>2</sub>SO<sub>4</sub> (30 °C, 1 h) and (2) 1.2 M H<sub>2</sub>SO<sub>4</sub> (100 °C, 3 h). The acid-insoluble lignin (AIL) content was defined as the amount of ash-free Klason lignin (i.e., the solid residue corrected for its ash content according to NREL/TP-510-42618 (National Renewable Energy Laboratory (NREL), 2009)). The hydrolysate was analyzed for acid-soluble lignin (ASL, UV-absorption at 205 nm) as well as monomeric sugars

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