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Reactive organosolv lignin extraction from wheat straw: Influence of Lewis acid catalysts on structural and chemical properties of lignins

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ABSTRACT

Lewis acids have been studied as catalysts in the organosolv treatment of wheat straw. Fractionation of the lignocellulosic biomass and fragmentation of lignin have been performed in aqueous ethanol in the presence of $FeCl_2$, $CuCl_2$, $FeCl_3$, $Ga(OTf)_3$, $ZrOCl_2$ or $Sc(OTf)_3$. The lignins were characterised in terms of molecular weight, β—O—4 linkage content and chemical functions through size exclusion chromatography; thioacidolysis; ^{31}P and ^{13}C NMR spectroscopies. The degree of delignification and the yield of Klason lignin increased with the hardness of the Lewis acid. About half of the delignification products were water-soluble monomers and oligomers. The nature of the Lewis acid influenced also the characteristics of the precipitated lignins. The molecular mass, the amount of OH groups and of aliphatic C—O bonds decreased as cation hardness increased.

1. Introduction

Lignin is a polyphenolic amorphous material derived primarily from the dehydrogenative radical polymerization of monolignols (*p*-coumaryl-, coniferyl- and sinapyl-alcohols). Each of these monolignols results in a different type of lignin units: *p*-hydroxyphenyl (H), guaiacyl (G), and syringyl (S) units, respectively, which vary according to growing place, maturity and localization in the cell. Lignin generally shows an irregular structure with a highly condensed cross-linked polymer network. Lignin composition varies in different groups of vascular plants, being G-, GS-, and HGS-type lignin characteristic for softwoods (woody gymnosperms), hardwoods (woody angiosperms), and grasses plants, respectively. These native lignins include both condensed inter-unit linkages (5-C-5′, 4-O-5′, and 5–5′) and aryl ether linkages (β—O—4, β—β and β—5), the β—O—4 bonds being the most frequent in natural lignins (Fig. 1) (Gösta and Knut, 2010).

The characteristics of extracted lignins (technical lignins) are dependant both on biomass resource and extraction process. Lignin obtained as a by-product of the kraft pulping has high sulphur content and is primarily burned for thermal energy production and sulphur recycling. Organosolv process was developed in the 70–80s as an efficient and sulphur-free way to produce high-quality pulp from northern hardwoods (Berlin et al., 2013; Pye and Lora, 1991). In this process, biomass is treated with an aqueous solution of organic solvent (e.g. ethanol) at high temperature with or without a catalyst (sulphuric or other acids). This pre-treatment achieves an efficient fractionation of the cellulose-hemicellulose-lignin matrix in three separate streams containing cellulose, hemicellulose-derived products and lignin-derived products. The recovered insoluble cellulosic substrate is more susceptible to enzymatic hydrolysis and the solubilised organosolv lignins are recognised as high-quality technical lignins (Stephen et al., 2012). Lewis acids have been proposed to improve fractionation of lignocellulose by acidolysis (Lachenal et al., 2004) and organosolv pulping (Yawalata and Paszner, 2004). Recently, while studying the pre-treatment for enzymatic degradation of cellulose, Kim et al., 2010 have shown that using Lewis acids during organosolv process allows an effective dissolution of hemicelluloses contained in the straw, liberating lignin–although the authors did not specifically isolate and characterise it. Recently Huijgen et al. studied, among others, a $MgCl_2$-catalyzed organosolv fractionation process which seemed to more selectively improve delignification of willow wood (Huijgen et al., 2011).

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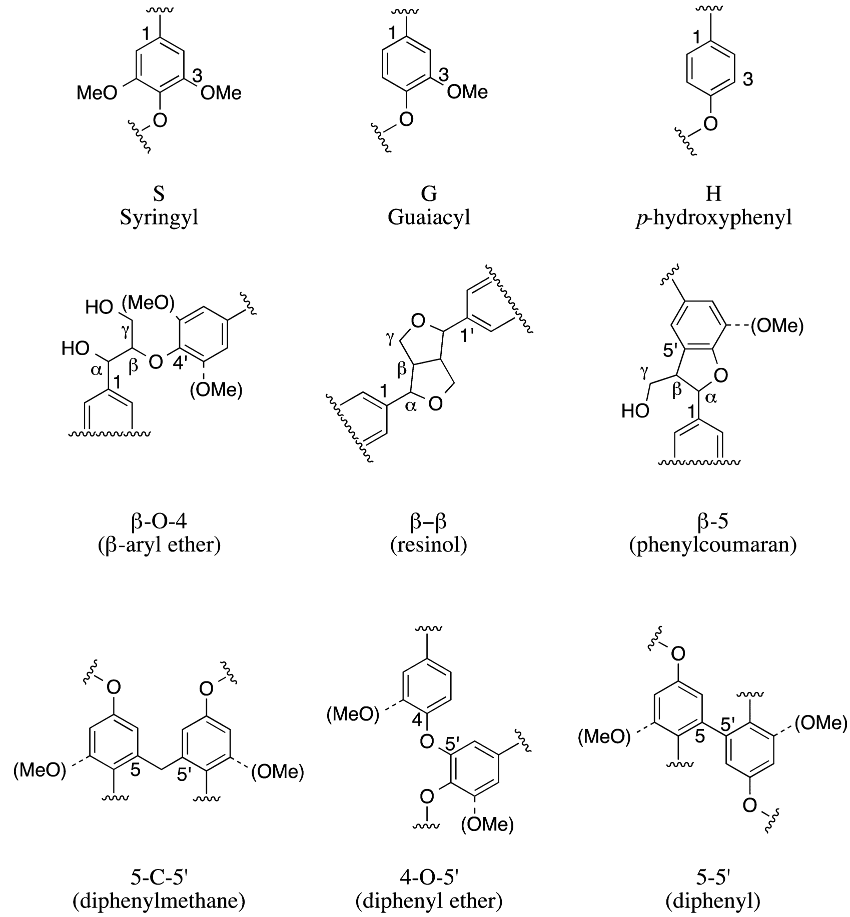

Fig. 1. Main inter-units linkages and building blocks found in lignin.

Disruption of linkages in lignin represents a potential route for the production of a wide range of phenolic compounds for adhesives, resins, flavours, biochemicals and biofuels (Stewart, 2008; Sun, 2010; Thakur et al., 2014; Wang et al., 2009). The catalyst and the process for catalytic fragmentation of lignins have to be chosen according to the structural and chemical properties of the lignin to be fragmented (Zakzeski et al., 2012; Zakzeski and Weckhuysen, 2011).

In this context, the present paper evaluates the interest of Lewis acid catalysed organosolv fractionation of wheat straw. Transition metal salts are known to be effective catalysts of oxidative degradation of lignin (Zakzeski et al., 2010). The present process is expected to couple fractionation and fragmentation. The impact of several transition metal salts on the structural and chemical characteristics of the technical lignins obtained is addressed.

2. Materials and methods

2.1. Materials

The straw used in this study was collected from a single harvesting of soft wheat (*Triticum aestivum*) from a local organic farm. The straw stock, which was collected in summer 2010, consists of 90 kg in 6 bales. Straw drying was performed at room temperature on field. The straw was subjected to a succession of knife mill grindings, first with a 5 cm grid, then with a 1 cm grid. The composition of the straw was cellulose 44.3%, hemicelluloses 24.5% (xylose 19.1%, arabinose 3.3%, galacturonic acid 1.1%), lignin 22.34%, proteins 3.1%, and ashes 3.4%. The metal salts and reagents were purchased from Sigma–Aldrich. Gallium triflate was purchased from Strem.

2.2. Pulping

The process is a classical organosolv process. In a typical experiment, 40 g of wheat straw was mixed in 1.25 L of aqueous ethanol (EtOH 65%, H_2O 35%) with 8 mmol L^{-1} catalyst in a 2 L autoclave (Autoclave France®). A benchmark experiment was carried out by using 4.4 mmol L^{-1} H_2SO_4 in the same conditions. The mixture was stirred during 2 h at 160 °C. Upon completion of the reaction, the reactor was cooled down to room temperature. Pulp and black liquor were separated from the reaction mixture using a nylon filter. The pulp was washed three times with 300 mL of an aqueous ethanol solution at 60 °C and the washes combined with the black liquor. Three volumes of water were added to the resulting liquor in order to precipitate the lignin. The solution obtained was centrifuged at 20 °C with 4950 rpm for 20 min and filtered under vacuum using Whatman® No 1 filters. The precipitate was washed with water and dried at 50 °C for 72 h. In this paper, the precipitate is defined as lignin fraction and the filtrate as aqueous ethanol fraction in which extractible compounds were dissolved.

2.3. Lignin characterization

The different lignins are characterised by the common procedure described in literature (Tamminen, 1999).

2.3.1. Klason method

The carbohydrate and lignin compositions of the extracted lignins were measured using a Klason method (Sluiter et al., 2008) in conditions optimised for the analysis of sugars (Renard et al., 1998). The dried samples (100 mg) were treated with 1.25 mL of