



Softwood kraft lignin for value-added applications: Fractionation and structural characterization



Marina Alekhina^{a,*}, Olga Ershova^a, Andreas Ebert^b, Sami Heikkinen^c, Herbert Sixta^a

^a Department of Forest Product Technology, Aalto University, School of Chemical Technology, P.O. Box 16300, Vuorimiehentie 1, Espoo FIN-00076, Finland

^b Research Division of Biopolymers, Fraunhofer IAP, Geiselbergstraße 69, 14476 Potsdam-Golm, Germany

^c Laboratory of Organic Chemistry, Department of Chemistry, University of Helsinki, A.I Virtasenaikio 1, P.O. Box 55, Helsinki FIN-00014, Finland

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ABSTRACT

This study focuses on a systematic, structural characterization of lignin samples fractionated from softwood industrial black liquor (BL). In addition to the isolation efficiency, the impact of fractionation and pulping severity on lignin structure was studied. BL samples from different chemical pulping stages were collected and the lignin was fractionated by sequential precipitation. While the alteration in structure and properties of the samples recovered from different delignification stages was only marginal, the spectroscopic characterization of the isolated lignin revealed significant alteration in its structure and functionalities as a function of the pH. Lignin samples precipitated at pH 10.5 exhibited the highest purity, as indicated by them having the lowest content of polysaccharides. In contrast, the samples precipitated at a pH of 2.5 revealed the highest carbohydrate content, rising from 9.7% at the beginning of cooking, to 36.8% at the end. At the same time, these lignin samples had the lowest M_w and the highest number of phenolic hydroxyl groups. Based on spectroscopic analysis, low M_w kraft lignin displayed an unusually high carboxyl content and a low methoxyl group content. All of the kraft lignin samples showed a reduction in the number of primary and secondary OH groups, which continuously decreased over the course of pulping. An opposite trend was observed with decreasing precipitation pH.

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1. Introduction

The use of renewable raw materials as a source of chemicals, materials, and energy is expected to increase in the foreseeable future due to the gradual depletion of fossil fuels. In this scenario, the development of new products and materials from lignocellulosic biomass in connection with emerging biorefinery strategies will be promoted. The concept of wood biorefinery comprises the selective separation of the three main polymeric wood components cellulose, hemicellulose, and lignin, and their subsequent utilization for the production of fuels, high value-added chemicals, and other related products. Cellulose and hemicellulose fractions can be readily used for the production of pulp, as a source of sugars for fermentation to produce pure chemicals, or as biofuels after further conversion processes. However, the efficient utilization of lignin presents an ongoing challenge (Ragauskas et al., 2014).

Lignin constitutes between 15% and 40% of the dry matter of woody plants. It is primarily a material that adds strength and

structure to the cell walls, controlling fluid flow, and protecting against the enzymatic degradation of other components. Lignin is a complex phenolic polymer built up through the oxidative coupling of C₆–C₃ (phenylpropane) units; namely, guaiacyl alcohol (G), syringyl alcohol (S), and 4-hydroxy phenyl alcohol (H), which form an irregular structure in a three-dimensional network inside the plant cell wall. The structural building blocks of lignin are joined together by ether linkages (C–O–C) or carbon–carbon bonds (C–C), while the major inter-unit linkage is of the β–O–4 type. In addition to the 20 different types of bonds present within lignin itself, lignin is also associated with the hemicelluloses, forming the so-called lignin–carbohydrate complexes (LCCs) (Garcia et al., 2009).

Technical or industrial lignin is generated in large quantities as a by-product of the chemical pulping of wood. During kraft pulping, about 90–95% of the lignin is chemically degraded to fractions that are soluble in aqueous alkali and thus these fractions form the major constituent of the black liquor (BL). Kraft lignin differs significantly from native lignin in its structure and chemical composition. Structural changes such as cleavage of α–O–4 and β–O–4 linkages lead to formation of lower molecular weight lignin and its dissolution in spent liquors. Additionally, undesirable impurities such as sulfurous compounds or carbohydrates are present in lignin derived

* Corresponding author. Tel.: +358 505672661.

E-mail address: marina.alekhina@aalto.fi (M. Alekhina).

from kraft fractionation process. (Marton, 1971; Rudholm, 1965; Santos et al., 2013; Sixta et al., 2006)

Currently, the pulp and paper industry produces an estimated 50 million tons of lignin annually (Higson and Smith, 2011). However, only about 2% of it (1.1 million tons) is commercially utilized for low-value products such as dispersing or binding agents and the rest is used for production of steam, heat and power (Higson and Smith, 2011). Although the energy aspect of lignin utilization is very important for the overall economic balance of the process, the potential of the valuable chemical properties and functionality of lignin has not yet been fully realized. Due to development of emerging lignocellulose biorefinery industry for production of biofuels and chemicals, even larger amounts of lignin will be generated in near future. For example, the U.S. Energy Security and Independence Act of 2007 mandates the development of 79 billion liters of second generation biofuels annually by 2022 (Ragauskas et al., 2014). Therefore, about 62 million tons of lignin will be produced annually in the United States alone. Without new product applications, the lignin produced worldwide would far exceed the current market (Ragauskas et al., 2014). Additionally, it should be mentioned that the total lignin availability in the biosphere exceeds 300 billion tons and increases by around 20 billion tons every year (Smolarski, 2012).

The structure and properties of lignin differ depending on its origin, pulping conditions, and isolation methods. The severity of the kraft pulping process can influence the structure of dissolved lignin. Baptista et al. (2008) reported that the structure of both the residual and dissolved lignin were influenced by the extent of delignification. In contrast, Robert et al. (1984) did not identify any major changes in the chemical structure of lignin as a function of cooking time, which may be attributed to the difference in the delignification rates. The results of their study tend to indicate that the majority of the chemical reactions during kraft cooking take place in the solid phase, thus resulting in comprehensive changes in the lignin structure.

Different methods have been proposed for the fractionation of technical lignin. The three main approaches include fractionation based on solubility in organic solvents (Saito et al., 2014), selective acid precipitation at reduced pH values (Mussatto et al., 2007), and membrane ultrafiltration (Toledano et al., 2010). In addition, the recent implementation of commercial processes—such as LignoBoost (Öhman et al., 2006), or the process for the production of Indulin AT—has demonstrated the successful manufacture of kraft lignin from BL with relatively high purity. With these processes, it will be easier for kraft pulp mills to incorporate the isolation of lignin from the excess thick liquor.

Due to its aromatic structure, lignin can be an attractive source of aromatic compounds and can be used as starting material for a series of useful products. Several types of lignin and its derivatives are successfully used in the production of vanillin, phenols, benzene, adhesives, dispersants, emulsifiers, chelants, antioxidants, pesticides, fertilizers, vegetal charcoal, concrete additives, and as a component for resins and thermoplastics (Gargulak and Lebo, 1999). In addition to the competing energy value of lignin, other challenges, including heterogeneity, especially the broad distribution of the molecular weight, and undesirable organic and inorganic impurities (sulfurous compounds and carbohydrates, respectively) associated with technical lignin isolated from BL, limit its utilization in high value-added applications.

To further advance the utilization of lignin in new applications or products, better knowledge is required on the sourcing, the separation process, and their impact on the structural and chemical characteristics of the obtained materials. Several studies in the field of lignin separation by acid precipitation have been performed earlier. However, the majority of the studies deal with fractionation of BL derived from pulping of hardwood species and annual plants.

Table 1

Physicochemical properties of industrial black liquors derived from different cooking stages.

Properties	Initial	Bulk	Residual
Density, [kg/m ³]	1.128	1.130	1.134
pH	13.94	13.86	13.82
TDS ^a , [g/L]	218.0	249.6	252.8
TOC ^b , [g/L]	55.0	69.9	77.6
TC ^c , [g/L]	58.4	72.7	80.6
RA ^d , [g NaOH/L]	28.8	26.9	26.3
Lignin, [g/L]	56.3	69.6	71.1
Carbohydrates, [g/L]	3.6	4.0	3.8
Arabinose, [mg/L]	1025	1395	1400
Xylose, [mg/L]	1680	1975	1545
Galactose, [mg/L]	755	605	745
Glucose, [mg/L]	65	35	50
Mannose, [mg/L]	50	30	45

^a TDS – Total dissolved solids.

^b TOC – Total organic carbon.

^c TC – Total carbon.

^d RA – Residual alkali.

Softwoods represent the principal lignocellulosic in northern hemisphere, and therefore, their utilization is of interest.

Additionally, the major part of the work published earlier is focusing on isolation of lignin from BL by gradual acid precipitation. In contrast to the earlier research, this work combines fractionation according to pH with collection of BL at different stages of the pine kraft pulping. The effect of BL fractionation on the lignin yield, structure and purity was studied. The fractionation was coupled with comprehensive characterization of obtained fractions using advanced analytical techniques. Fractionated kraft lignin samples were quantified and comparatively characterized in terms of yield, chemical composition, molecular weight, and functional groups.

2. Material and methods

2.1. Materials

Samples of industrial pine kraft BL were supplied by Metsä Fiber, from its Rauma (Finland) pulp mill. This pulp mill operates according to the Superbatch cooking process, in which the temperature is ramped from 90 °C (impregnation time, 58 min) to 162 °C over a period of 52 min and then held at this temperature for 59 min. The kappa number of the produced pulp was 29.1. BL samples were collected at different stages of delignification: initial (*H*-factor = 185), bulk (*H*-factor = 550) and residual delignification (*H*-factor = 670) phases. The original characteristics of BL are shown in Table 1. Density was determined by measuring the weight of the BL in a known volume. Total dissolved solids (TDS) were determined by using a method based on TAPPI T264 cm-97. The lignin concentration was measured using a UV-vis spectrometer (UV-2550, Shimadzu) at 280 nm, an absorptivity constant of 24.6 g/L was used (Fengel et al., 1981). The carbohydrate content was determined according to NREL/TP-510-42618. Total organic carbon (TOC) and total carbon (TC) were measured in the BL using a TOC-V_{CPH} analyzer (Shimadzu) according to SFS-ISO 8245. The residual alkali content of BL was determined with an automatic titrator according to SCAN-N 33:94. All BL characteristics are averages of at least three measurements.

Pine wood chips for dissolved wood lignin (DWL) preparation were supplied by Metsä Fiber, Finland. Pine DWL was prepared according to (Fasching et al., 2008) and used as a reference showing properties close to those of native lignin. Deuterated chloroform (CDCl₃) containing 0.03% tetramethylsilane (TMS) (used as internal standard) and Chromium(III) acetylacetonate (Cr(acac)₃) (relaxation agent) were purchased from (St. Louis,

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