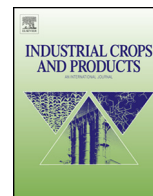




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Fractionation of technical lignin with ionic liquids as a method for improving purity and antioxidant activity

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ABSTRACT

Alder soda lignin, a by-product of the chemical processing of black alder wood, was fractionated using ionic liquids (ILs) based on the 1-butyl-3-methylimidazolium [Bmim] cation and the following anions: chloride ([Bmim]Cl), dimethylphosphate ([Bmim]Me₂PO₄), acetate ([Bmim]OAc) and tosylate ([Bmim]OTs). The aim was to obtain lignin fractions of improved purity for further application as antioxidants. The purity and properties of the IL lignin fractions were compared with those of other lignin fractions obtained using sequential extraction with organic solvents. The original lignin and the lignin fractions were characterized by analytical pyrolysis (Py-GC/MS/FID), size-permeation chromatography (GPC), electron paramagnetic resonance (EPR) spectroscopy and wet chemistry methods. The lignin treatment with [Bmim]DMP, [Bmim]OAc and [Bmim]OTs produced fractions with a lignin content of 98–99%. These fractions along with the *n*-propanol and methanol fractions obtained using sequential organic solvent extraction were enriched with certain structural features that had a positive impact on lignin antioxidant activity, according to the results from DPPH[•] and ORAC assays.

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1. Introduction

Lignin is one of the most abundant terrestrial biopolymers (Barros et al., 2015). As the organic constituent of photosynthesized plant biomass, the annual production of lignin on Earth has been estimated in the range of 5–36 × 10⁸ tons (Gellerstedt and Henriksson, 2008). The biological function of lignin, together with polysaccharides, is to generate resistant plant tissue structures, providing plants with mechanical strength and efficient water-conducting systems. Lignin also plays a significant role in plant defense against biodegradation (Vance et al., 1980; Vanholme et al., 2010). Lignin is an amorphous polyphenolic irregular polymer generated through the polymerization of three monomers, coniferyl, sinapyl and *p*-coumaryl alcohols, creating a heterogeneous composition of phenylpropanoid units (PPUs), namely *p*-hydroxyphenyl (H), guaiacyl (G) and syringyl (S) PPUs, differing in the degree of OCH₃ substitution on the phenolic ring (Vanholme et al., 2010; Fengel and Wegener, 1983). Lignin *in situ* is covalently linked

with hemicelluloses in the lignin-carbohydrate complex (Balakshin et al., 2011; You et al., 2015). As a by-product of the pulp and paper industries, lignin can be obtained in a large scale (about 70 million tons per year) (Espinoza-Acosta et al., 2016). During plant biomass processing, the significant *in situ* modification of the lignin structure occurs (Gellerstedt and Önerund, 2003; Sjostorm, 1993), and the chemical structure of “technical lignins” (functionality, molar mass, cross linking density, etc.) depends not only on the plant botanical origin and the environmental conditions of growth but also on the conditions of isolation from plant tissue (Espinoza-Acosta et al., 2016).

Currently, the aqueous alkaline treatment of biomass is the most popular delignification technology practiced industrially (Shatalov and Pereira, 2013; Lora and Glasser, 2002), and such technical lignins, such as kraft lignins and soda lignins, are available in large amounts. However, most industrial delignification operations associated with the paper industry incinerate the alkaline extract to produce energy and steam for the cooking process (Vishtal and Kraslawski, 2011). Factors such as the chemical heterogeneity of lignin structure, including significant variations in lignin PPU structure and functionality over molecular mass distribution (MMD), the presence of impurities of different origins (e.g. carbohydrates), and the high degree of polydispersity (Vishtal and Kraslawski, 2011;

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Matsushita, 2015; Crestini et al., 2011; Bikova et al., 2004), hinder the utilization of technical lignins in high-value-added applications. In addition, high purity lignins can be used in many industrial and consumer applications, such as the production of polyurethane foams, adhesives, and epoxies (Lora and Glasser, 2002). Some potential uses for industrial lignins have been proposed (Bos and Sanders, 2013; Yuan et al., 2013), including those based on the antioxidant and antimicrobial properties of lignin (Vinardell et al., 2008; Domenek et al., 2013).

The production of effective naturally derived antioxidants based on technical lignins is currently considered a prospective avenue for the valuable application of these polyphenolic polymers (Espinoza-Acosta et al., 2016; Ponomarenko et al., 2015a,b). The antioxidant properties of lignins have been verified for a variety of polymeric composite materials, animal feeds, and biological systems (Arshanitsa et al., 2013; Lu et al., 1998; Krizkova et al., 2000; Pouteau et al., 2003; Dizhbite et al., 2004; Carmen et al., 2004; Kosikova et al., 2006; Pan et al., 2006; Vinardell et al., 2008; Kaur and Uppal, 2015). The technical application of lignins as antioxidants is prospective as different materials, food products, means for human health care, etc., undergo oxidative degradation. To protect their properties and prolong their life spans, antioxidants should be added to almost all oxidizable organic substrates. The antioxidant demand has permanently increased in the last 10 years. In 2013, the antioxidant market was 1.5 billion American dollars (USD) per year. In 2014, the global demand for antioxidants was valued at approximately 2.25 billion USD per year and is expected to reach USD 3.25 billion by 2020. According to a recent study by Grand View Research, Inc., the global natural antioxidants market is expected to reach USD 4.14 billion by 2022 (<http://www.marketresearchstore.com/report/antioxidants-market-for-pharmaceuticals-food-z38119>). There is an increasing public awareness regarding the application of synthetic antioxidants not only for food and personal care but also for the stabilization of polymeric materials. Due to the biodegradability and significantly lower toxicity of these compounds, the application of natural antioxidants is of high importance not only for health care and cosmetics but also for the food industry in connection with problems of food safety and packing materials, such as plastic containers, films and bags, which come in contact with food (Sanches-Silva et al., 2014; Ambrogi et al., 2011). The “technical lignins” are promising antioxidants for a variety of polymeric composite materials, animal feeds, and biological systems (Lu et al., 1998; Krizkova et al., 2000; Pouteau et al., 2003; Dizhbite et al., 2004; Carmen et al., 2004; Kosikova et al., 2006; Pan et al., 2006; Vinardell et al., 2008) and are effective, environmentally friendly and safe for human consumption, however, the production of these materials requires thorough purification and fractionation to improve their compatibility with defense substrates and promote a stabilizing effect. Lignin purified fractions with well-defined molecular weight were obtained from industrially processed lignin using flocculation (Piazza et al., 2014) and ultrafiltration (Sevastianova et al., 2015) methods. Reducing the molecular and structural heterogeneity of lignin by sequential extraction using organic solvents and mixtures of increasing hydrogen-bonding capacity has been reported as a prospective methodology for the selective fractionation and production of lignin fractions with distinct group functionalities over MMD and lower polydispersity and heterogeneity for industrial application. A number of organic solvents have been suggested for the fractionation of technical lignins (Arshanitsa et al., 2013; Ropponen et al., 2011), including acetone and an ethyl acetate-water mixture (Vanholme et al., 2010).

Recently more environmentally friendly processes for the fractionation and purification of technical lignin were suggested, including the procedure based on the ultrasonic extraction and hot water treatment, which is very efficient for the removal of inor-

ganic and carbohydrates impurities from the industrial kraft lignins (Fang et al., 2015). Ionic liquids (ILs) have also become popular for the fractionation, dissolution and purification of biomass components (Espinoza-Acosta et al., 2016). The absence of volatility is one of the most important benefits of ionic liquids, offering much lower toxicity than low-boiling-point solvents. In addition, ILs have excellent properties, such as poor electricity conduction, non-ionizing (e.g. non – polar) activity, high viscosity, low vapor pressure, low combustibility, excellent thermal stability, wide liquid regions and favorable solvating properties, for a range of polar and non-polar compounds (Tang et al., 2012).

In the present study, a technical lignin obtained from the soda pulping of black alder wood was treated using 1-butyl-3-methylimidazolium-based ILs of different anions: [Bmim]Cl, [Bmim]Me₂PO₄, [Bmim]OTs, and [Bmim]OAc. The type of anion in the ionic liquid influences strongly the solubility of lignin, similarly to the dissolution of cellulose (Brandt et al., 2013). The choice of the anions in the present research had in purpose to provide a broad range of the polarity of ILs. The values of Kamlet-Taft β parameter for the ILs used in current study varied between 0.80 to 1.20 in the following order: [Bmim]OTs (0.80) < [Bmim]Cl (0.84) < [Bmim]Me₂PO₄ (1.12) < [Bmim]OAc (1.20) (Brandt et al., 2011; Spange et al., 2014). All used ionic liquids are miscible with water which is important for the developing of the effective lignocellulosic biomass pretreatment process using an ionic liquid – water mixtures (Fu and Mazza, 2011; Brandt et al., 2011; Yan et al., 2015). The aim was to obtain lignins of high purity for further application as antioxidants. For the best of our knowledge, the antioxidant properties of lignin isolated or purified using ILs are almost not studied. In the only research carried out by Ross et al. (2012) it was found that lignins extracted with ionic liquid 1-ethyl-3-methylimidazolium acetate from wheat straw, triticale straw and flax shives had the much lower antioxidant activity in DPPH• assay in comparison not only with known strong flavonoid antioxidant rutin and quercetin but also with commercial organosolv lignin.

In the present work, the purity and antioxidant properties of the IL lignin fractions were compared with those of other lignin fractions obtained using sequential extraction with organic solvents of increasing polarity (Arshanitsa et al., 2013; Ponomarenko et al., 2014). The composition and structural properties of the fractions obtained from soda lignin were examined using Py-GC/MS/FID, GPC and EPR methods, emphasizing the structural features (structural descriptors) of lignins, which have a definite impact on the antioxidant activity of these compounds in processes associated with proton-coupled electron transfer (PCET) and sequential proton loss electron transfer (SPLET) mechanisms (Ponomarenko et al., 2015a,b). The presence of carbohydrate admixtures, the O-containing groups in side chains (mainly –CHO and –CO groups), as well as the increased size of the π – conjugated systems, have a strong negative effect on the lignins antioxidants activity, whereas increasing portions of methoxylated phenyl propane units (PPU) and PPU with α-CH₂ groups will enhance it. The antioxidant activity of the obtained lignin samples was assessed using the free radical DPPH• and kinetic ORAC test, which characterizes the antioxidant potential in preventing fluorescein oxidation.

Soda-based delignification methods are primarily used for cooking annual crops and hardwoods. Soda lignins are sulfur-free, with a chemical composition resembling that of lignin *in situ* compared with kraft lignins and lignosulfonates. The absence of sulfur in soda lignins is an important factor, considering the subsequent application of these molecules as antioxidants in polymeric and biological systems, including health care. Soda lignins are proposed for use in areas that require lignins of high purity, namely for the production of phenolic resins (Gosselink et al., 2004a; Tejado et al., 2007), synthesis of polymers (Wormeyer et al., 2011), and produc-

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