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Membrane filtration of kraft lignin: Structural charactristics and antioxidant activity of the low-molecular-weight fraction

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ABSTRACT

Lignin, which is the second most abundant biomass component and has carbon-rich phenolic content, is a promising renewable raw material for multiple applications, such as carbon fibers, adhesives, and emulsifiers. To use lignin efficiently, it is important to ensure its purity and homogeneity. As a result, the separation of lignin into fractions with high purity and narrow molecular-weight distributions is likely a prerequisite for several applications. Ultrafiltration using ceramic membranes has many advantages, including enabling direct lignin extraction from Kraft pulp cooking liquors without pH and temperature adjustment. One challenge with membrane filtration using such a system is the potential for reduced membrane performance over time, which is associated with fouling.

In this study, LignoBoost Kraft lignin was fractionated using a ceramic membrane with a molecular weight cut-off of 1 kDa. The separation behavior during ultrafiltration fractionation was investigated and the antioxidant properties of the recovered low-molecular-weight (low-MW) lignin samples were evaluated.

Using this model system, the permeate fluxes were unstable during the 100 h of membrane operation. However, a decrease in the average MW in the permeate over time was observed. The shift in MW was most pronounced for virgin membranes, while a more stable MW distribution was evident for membranes subjected to multiple cleaning cycles. According to 2D NMR analysis, low-MW lignin that was recovered after 100 h of operation, consisted of smaller lignin fragments, such as dimers and oligomers, with a high content of methoxy-groups. This was confirmed using the size exclusion chromatography method, which indicated an weigh average molecular weight in the range of 450–500 Da. ^{31}P NMR spectroscopy showed that, despite the lower total content of phenolic OH groups, the low-MW sample had a higher proportion of non-condensed phenolic OH groups. The results of the antioxidant tests demonstrated the strong potential of lignin and its low-MW fraction as a natural antioxidant, particularly for lipid-containing systems. The low-MW lignin fraction showed better antioxidant activity than the non-fractionated LignoBoost lignin in the kinetic oxygen radical absorbance capacity (ORAC) test and demonstrated three-fold stronger inhibition of the substrate (fluorescein) than the reference antioxidant Trolox (a water-soluble derivative of vitamin E).

1. Introduction

Replacing fossil raw materials with renewable materials has become a primary focus of many research efforts. As a result, there is growing interest in lignocellulosic material, an abundant and renewable resource for the production of biofuel and high value bioproducts, as a feasible alternative (Luterbacher et al., 2014; Ragauskas et al., 2014). Lignocellulose biomass is composed of three main components: cellulose, hemicelluloses and lignin. Lignin is the most abundant biopolymer after cellulose, corresponding to 15–30% of the wood weight of softwood and approximately 20% of that of hardwood. Its structure consists of a phenyl propane (C6–C3) units joined together through various interunit linkages, e.g., ether linkages (C—O—C) or carbon-carbon bonds (C—C). These interunit linkages impart heterogeneous complex

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structures to the lignin (Adler, 1957; Crestini et al., 2011; Lin and Dence, 1992; Sarkanen and Ludwig, 1971).

Technical lignin is a byproduct of the pulp and paper and biorefinery industries, where the Kraft and sulfite processes generates approximately 70 million tons of lignin annually (Lora and Glasser, 2002; Tomani, 2010). During the Kraft pulping process, lignin is degraded and solubilized in a strong alkaline aqueous solution, forming (together with degraded hemicelluloses and spent cooking chemicals) a black liquor (BL) (Marton, 1971; Sjöström, 1981). As a result, the chemical structure of Kraft lignin in terms of molecular weight (Mw), content of functional −OH and −COOH groups and cross-linking density differ significantly from that of the lignin structure in the original plants, depending to a large extent on the conditions during the pulping process (Gellerstedt and Lindfors, 1984; Robert et al., 1984). The generated Kraft lignin is today used almost exclusively for energy production to cover the energy demand of the Kraft pulp process, however increasing energy efficiency of the Kraft pulp process enables the extraction of excess Kraft lignin for uses in value-added applications (Loutfi et al., 1991; Wallberg et al., 2005; Wallberg and Jönson, 2003).

To use lignin efficiently, an important step is the separation of lignin. Three methods for extracting lignin can be found in the literature. One method is precipitation of the lignin from the BL by acid (Alen et al., 1979; Passinen, 1968). In 1910, Hough patented a method in which lignin can be precipitated by acidification of spend liquors from the alkaline pulping process using sulfuric acid. To improve dead-end filtration and prevent any possibility of colloid formation (which would interfere with the downstream separation steps), the precipitation step was performed at higher temperature (Hough, 1910). A recent development is the LignoBoost process, where through displacement washing, a lignin with a higher purity can be produced. In this method, after the precipitation of lignin, the material is filtered, and the filtrate cake is re-dispersed at a low pH (2–4). The newly formed suspension can easily be filtered and washed by displacement washing (Tomani, 2010; Öhman and Theliander, 2006; Öhman et al., 2007). A third technique that has been suggested is membrane separation by ultrafiltration (Colyar et al., 2008; Helander et al., 2013; Jönsson et al., 2008; Sevastyanova et al., 2014; Toledano et al., 2010; Wallberg and Jönsson, 2003).

Membrane separation is a versatile operation that has found application in a wide range of sectors, e.g., the food industry, water purification and the pharmaceutical industry. For lignin separation using membrane filtration, several studies can be found in the literature, e.g., concentration or recovery of byproducts from BL (Brodin et al., 2009; Dafinov et al., 2005; Kevlich et al., 2017; Keyoumu et al., 2004; Tanistra and Bodzek, 1998; Wallberg et al., 2003). The cost of lignin separation by applying ultrafiltration to BL streams in pulp mills has also been estimated (Jönsson and Wallberg, 2009; Wallberg et al., 2005).

Relative to other separation methods, membrane filtration has several advantages, e.g., it is possible to utilize ultrafiltration for lignin separation directly from a BL stream without temperature or pH adjustment (Wallberg and Jönsson, 2006). Such partial lignin separation will decrease the organic load on the recovery boiler system, which is often a bottleneck in the pulp mill (Hill et al., 1988; Wallberg and Jönsson, 2006). Additionally, fractionation using membranes with different molecular cut-offs produces lignin with more well-defined molecular mass, lower polydispersity and tailored properties (Sevastyanova et al., 2014). Thus, ultrafiltration of Kraft lignin can provide a pathway for upgrading lignin, opening new routes for the production of high-value materials and chemicals from this lignin source.

Lignin as a source of phenolic units, including various aromatic and aliphatic hydroxyl groups, is one of the best candidates for modification and various applications (Espinoza-Acosta et al., 2016), e.g., in the production of vanillin (Tarabanko et al., 1995) and phenols; as a dispersant in cement and gypsum blends (Matsushita et al., 2008; Yang et al., 2007), an emulsifier (Boeriu et al., 2004) an adsorbent (Mohan et al., 2006; Podkościelna et al., 2015), a carbon fiber precursor (Kadla et al., 2002; Kubo and Kadla, 2005), and an antioxidant (Espinoza-Acosta et al., 2016); and co-reagent in phenol-formaldehyde resins (Jönsson et al., 2008; Mansouri and Salvadó, 2006; Sarkar and Adhikari, 2000; Tejado et al., 2007; Villar et al., 2001) and thermoplastics synthesis (Wang et al., 2016).

As a polyphenol, lignin has a strong potential as an antioxidant to prevent oxidation reactions in biofuels, animal feeds and polymeric composite materials (Gulcin, 2012; Salem et al., 2014; Sindhi et al., 2013). The complex structure of lignin, composed of aromatic rings with hydroxy and methoxy functional groups, is responsible for this antioxidant potential due primarily to the termination of the oxidation propagation reaction through hydrogen donation (Jamshidian et al., 2012; Lu et al., 1998; Malík and Kröhnke, 2006). As a result of recent observations of possible cytotoxic and carcinogenic effects of synthetic antioxidants, i.e., butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT), tert-butylhydroquinone (TBHQ) and propyl gallate (PG) at high dosages (Carocho and Ferreira, 2013; Gulcin, 2012), an attention towards the use of naturally occurring antioxidants (Gulcin, 2012), including lignin, is growing. The antioxidant activity of technical lignin is well established (Boeriu et al., 2004; Dizhbite et al., 2004; KoŠíková et al., 2006; Lu et al., 1998; Pan et al., 2006; Pouteau et al., 2003), however, the application of technical lignins as a natural antioxidants has not been implemented in the industrial sector mainly due to the high non-homogenous complex structure and high polydispersity of lignin (García et al., 2009; Hussin et al., 2015). Typically, purification and fractionation steps are necessary to improve the compatibility of lignin material with various substrates and enhance its stabilizing effect (García et al., 2010; García et al., 2009; Hussin et al., 2015; Lauberts et al., 2017; Ponomarenko et al., 2014; Ponomarenko et al., 2015b). Although, to predict the antioxidant properties of lignin material, several different tests should be applied, mainly due to the different reaction kinetics of lignin material in different systems.

The aim of this study was to investigate the separation behavior during fractionation of dissolved LignoBoost Kraft lignin using a ceramic membrane with molecular weight cut-off of 1 kDa and to evaluate the structural characteristics and properties of the fractions obtained (low-MW fractions), including their antioxidant activity in different systems.

The changes in MW and composition of lignin in the permeate were monitored over four days of membrane operation. A detailed structural characterization of lignin material was performed by nuclear magnetic resonance spectroscopy (NMR) analysis (2D-NMR and ^{31}P NMR), analytical pyrolysis (pyrolysis-gas chromatography-mass spectrometry (Py-GC/MS) and size-exclusion chromatography (SEC). To evaluate the antioxidant activity of the low-MW Kraft lignin fraction and original LignoBoost lignin, the radical scavenging activity towards DPPH· and ABTS· radicals and the oxygen radical absorbance capacity (ORAC) were tested. In addition, the Oxipres test, which evaluates the inhibitory properties of lignin in the oxidation of rich-in-lipids substrates, e.g., vegetable oils, bio-diesel, and cosmetic creams, was performed. These characteristics are expected to provide guidance on the optimization of the lignin fractionation using ultrafiltration and on possible applications of lignin as a natural antioxidant.

2. Experimental

2.1. Materials

The LignoBoost Kraft lignin powder used in this study was produced from Nordic softwood and kindly supplied from a plant in northern Europe.

Sodium hydroxide (Sigma Aldrich, Germany) was used to dissolve lignin, and sulfuric acid (> 95%) (Fisher Scientific, UK) was used for the precipitation of the fractionated products. Sodium chloride (Sigma