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Purification and concentration of lignin from the spent liquor of the alkaline oxidation of woody biomass through membrane separation technology

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ABSTRACT

Lignocellulosic plant biomass is a renewable and abundant source for the production of bio-based fuels, chemicals and chemical building blocks. Efficient fractionation and conversion of these feedstocks are an essential step in the valorization of the cellulose, hemicellulose and lignin fractions. The use of a new two-stage alkaline oxidation (AlkOx) process has been investigated for the pretreatment of softwood in presence of sodium carbonate.

Within this study, the use of commercial polymeric and ceramic ultrafiltration membranes for the purification and concentration of lignin from the spent liquor of the AlkOx process has been evaluated enabling further valorization thereof. Higher permeation fluxes were observed, ranging from 30 to 139 L/m^2 h, depending on the hydrophilicity, pore size and structure/chemistry of the membrane. High lignin retentions have been obtained for all membranes. Diafiltration of the spent liquor using the ESP04 membrane enables the purification of the lignin fraction with an efficient removal of the impurities originating from both the lignocellulosic material and the pretreatment.

The integration of both processes allows the co-valorization of the lignin fraction, besides the primary C5/C6 sugar fraction produced in the two-stage alkaline oxidation of softwood. Also some preliminary techno-economic calculations have been realized on the membrane separation process to asses the economic potential of this technology.

1. Introduction

Up to recently, development of lignocellulosic biorefineries has mainly focused on biofuels, preferring non-wood feedstocks with high carbohydrate contents, such as bagasse, sweet sorghum, corn stover and grasses (Smolarski, 2012). There has also been some focus on advanced wood-based biorefineries, although much more substantial amounts of wood are currently used for the pulp and paper production and different mechanical wood products. Consequently, wood-based chemicals have typically been produced only as pulping by-products; major examples include lignosulphonates, turpentine, and tall oil (for fatty acids, resin acids and phytosterols).

Wood and other lignocellulosics are composed of three main components, cellulose, hemicellulose and lignin (in addition to various extractives in small quantities) (Ayyachamy et al., 2013; Mussatto, 2016). Once extracted, cellulose and hemicellulose can be hydrolysed to C5 and C6 sugars, to be further processed to various biobased chemicals and biofuels (e.g. ethanol). Lignin, the second most abundant terrestrial polymer after cellulose, representing 20–30 wt.% of wood, is currently used in limited amounts only. Kraft and sulphite pulping are the two dominating process technologies used in pulp and paper industry, producing between 40 and 50 million tons per year of lignin (Toledano et al., 2010a). Currently the Kraft lignin rich black liquor is combusted in the recovery boiler to recycle the cooking chemicals and to produce energy. Lignosulphonates on the other hand are commercially used as raw material in low or medium value products without or with minimal purification treatment, such as industrial detergents,

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concrete additives, cement dispersants, asphalt emulsifiers, compressed material binders, plasticizers, stabilizers, glue adhesives and feedstock for chemical processing (e.g. vanillin). (Gellerstedt, 2015; Gellerstedt et al., 2013; Restolho et al., 2009). The world's lignosulfonate industry is dominated by BorregaardLignoTech and Tembec.

Lignocellulosic raw materials may serve as an abundant resource of chemicals. In future biorefineries, utilization of all major components of wood, especially lignin, as building blocks for value added products is of utmost importance.The challenges associated arise from the recalcitrant nature of lignocellulosics, where cellulose and hemicellulose are tightly linked with lignin making the structure of plant cell walls difficult to loosen and made accessible for further utilization of the biomass components. Pretreatment of lignocellulosics is therefore a key aspect for utilization of the main biomass components in future biorefineries (Mussatto, 2016). A variety of pretreatment methods, allowing fractionation of biomass components in their polymeric form, have been developed during the past decades but only a few ones have reached the commercialization phase (Galbe and Zacchi, 2012; Jørgensen et al., 2007; Mussatto, 2016). Lignin can be recovered from a biotechnical biorefinery process either after hydrolysis of carbohydrates as hydrolysis lignin, or from the liquid phase of a fractionating pretreatment process. Hydrolysis lignin can be highly impure, containing residual carbohydrates, small amount of enzymes adsorbed to the fibres, and in the case of a simultaneous saccharification and fermentation process also yeast. The so-called cooking techniques on the other hand delignify biomass at least partially, resulting in a liquid phase, or cooking liquor, containing lignin in solution. Typical processes of this kind are various organosolv techniques (Rovio et al., 2012). Since production of highly hydrolysable material from woody feedstocks by organosolv methods is challenging, especially from softwood, an alkaline oxidation strategy has been developed (Kallioinen et al., 2013). In this method, biomass is processed with Na_2CO_3 in the presence of oxygen, resulting in a fibre fraction easy to hydrolyse by enzymes and a liquid fraction, containing partially oxidized lignin and small organic acids as degradation products of mainly hemicellulose (Rovio et al., 2012).

As lignin is nowadays considered as a valuable chemical, its recovery from cooking liquor promises a commercial benefit compared to energy generation by burning (Abels et al., 2013). However, producing high value lignin products is challenging, and calls for efficient technologies for separation of lignin after the pretreatment step (Ragauskas et al., 2014, 2006). As most chemicals in petroleum refineries are volatile, separation schemes are dominated by distillation. By contrast, most compounds derived from biomass are non-volatile and process streams are typically dilute, which implies that large volumes of water/solvent need to be evaporated. Whereas research techniques such as size-exclusion chromatography are excellent tools for producing small quantities of pure biomass substances, these processes are difficult to scale up and production levels remain limited (Ragauskas et al., 2006). Energy-efficient separation and purification of bio-based chemicals at the industrial scale remains, therefore, a challenge.

Membrane separation can be integrated in the production loop and offer tremendous potential to reduce energy consumption, and to simplify the recovery, fractionation, purification and concentration of valuable intermediate and final products from complex biomass liquors or hydrolysates (He et al., 2012; Lipnizki, 2014; Restolho et al., 2009). Membrane processes, mainly ultrafiltration (UF) and nanofiltration (NF) have been used in pulp and paper mills since the late 1960s (Jönsson et al., 2008). The rising demand for environmental protection, energy savings and recovery of valuable products accelerated however their application in the pulp and paper industry, both at laboratory, pilot and industrial scale (Abels et al., 2013; Restolho et al., 2009). Besides wastewaters and effluents treatments, membrane filtration can be used to extract various components from black liquor. Both UF and NF of black liquor have been investigated, although UF has been more extensively studied (Alexandri et al., 2016; Alriols et al., 2010; Bhattacharjee et al., 2006; García et al., 2011; Humpert et al., 2016; Jönsson et al., 2008; Keyoumu et al., 2004; Mänttäri et al., 2015; Niemi et al., 2011). However, efforts towards the more efficient use of wood and hence lignin as a valuable product have awakened the interest in the use of membrane processes to improve the purity of lignin as well as to concentrate and fractionate lignin by molecular weight for specific applications, as demonstrated in several works found in literature (Afonso, 2012; Arkell et al., 2014; Bhattacharya et al., 2005; Colyar et al., 2008; Fälth et al., 2001; Fernández-Rodríguez et al., 2015; Humpert et al., 2016; Jönsson et al., 2008; Jönsson and Wallberg, 2009; Leberknight and Menkhaus, 2013; Restolho et al., 2009; Tanistra and Bodzek, 1998; Toledano et al., 2010a, 2010b; Wallberg et al., 2003; Weinwurm et al., 2016). In all these studies, various methods of filtration and operation parameters have been considered and the costs associated with the application of membrane technology have been evaluated. In any case, the results of all these studies depend on the liquor used as feedstock, since the composition and molecular weight distribution of the components within the liquor depend on the pulping process utilized (Fernández-Rodríguez et al., 2015). Overall, it can be stated that the main benefits of membrane processes in these applications are the possibility of withdrawal of the liquor at any position, without adjustment of the pH or temperature, and the possibility to obtain lignin with defined properties, particulcarly specific molecular weight, as determined by the membrane cut-off (MWCO), and low polydispersity, enabling the use in high value-added applications as polymer formulations or as low molecular weight compounds (Alriols et al., 2010; Jönsson et al., 2008; Toledano et al., 2010a, 2010b).

The economic competitiveness of the products obtained from a lignocellulosic biorefinery is highly dependent on the separation and purification technologies used and the process energetic efficiency (García et al., 2011). From this point of view, a number of membrane processes for lignin applications have been subject to a techno-economic assessment to establish mass and energy balances, to optimize the process in terms of yield, solvent recovery and energy consumption and finally to make a cost estimation of the UF/NF process (Alriols et al., 2010; Arkell et al., 2014; García et al., 2011; Jönsson et al., 2008; Jönsson and Wallberg, 2009).

Besides the numerous studies reported in literature, the evolution of patent publications for membranes in biorefinery is increasing indicating the high attention given to this topic (Abels et al., 2013). Only in 2015 32 patents related to UF or NF and lignin have been filed. Most of these patents deal with the purification of lignin from different cooking liquors using either UF or NF (Espacenet Patent Search). In addition, Borregaard Industries possesses the most important plant for lignosulphonates concentration by UF since 1981. This plant allows producing a concentrate stream enriched in lignosulphonates (approximately 95% of purity) with a low percentage of sugars and salts. High value-added products as vanillin can be obtained from this company from these lignosulphonates after using an UF stage, demonstrating the benefits of this technique (Fernández-Rodríguez et al., 2015).

In this work, spruce chips (*Picea abies*) were treated with Na_2CO_3 in the presence of oxygen (AlkOx process). The applicability of membrane separation technologies was investigated for the purification and concentration of the lignin in the spent liquor SL2 issued from the AlkOx process. Thereto, the separation efficiency of commercial polymeric and ceramic UF membranes has been evaluated. Based on the results of these screening trials, the most promising membrane was selected for longer term trials aiming at a proof-of-concept of membrane-based purification of lignin, with efficient

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