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Multivariate data examination in evaluation of the effect of the molecular mass of lignin and hemicelluloses on ultrafiltration efficiency

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ABSTRACT

In this study, multivariate examination was used to show the influence of birch extract characteristics on filtration performance in the ultrafiltration based hemicellulose recovery process. Different pretreatments based on adsorption, flocculation or oxidative degradation by enzyme, and a combination of degradation and adsorption, were performed to change the extract characteristics. It was clearly demonstrated that in addition to the total concentration of lignin or carbohydrates in the treated wood extract, also their size has a significant effect on filtration efficiency. Both the ligneous and hemicellulosic compounds, having a negative impact on filtration capacity, seemed to be small enough to enter the membrane skin layer. Thus, in the development of pretreatment processes to enhance filtration efficiency in the recovery of hemicelluloses in biorefineries with ultrafiltration, the focus should not be strictly on maximal removal, but also the size of the lignin molecules has to be considered. From the tested pretreatment methods, the highest increase of flux was achieved with laccase treatment combined with adsorption on bentonite because it decreased the amount of harmful-sized compounds and increased the amount of large compounds, which were favourable to the higher flux.

1. Introduction

Ultrafiltration is a potential technique for the recovery of hemicelluloses from wood extracts [1–3]. However, fouling challenges are often reported when wood-derived solutions, or solutions with similar content, have been ultrafiltered [4–7]. Based on the literature, potential foulants are lignin and wood extractives [5,8–10]. The removal of these compounds prior to ultrafiltration has been shown to improve filtration performance [11,12].

Lignin can be removed for instance by adsorption on activated carbon [13,14], polymeric adsorbents [15–17], or bentonite (phenol removal) [18]. However, the tested pretreatments have shown not to be specific to lignin but they remove also other compounds from the extracts. For instance, Koivula et al. [12] have reported that pretreatment with XAD adsorbents decreased the lignin amount in wood extract but also caused significant hemicellulose losses. Also Schwartz and Lawoko [16] noticed XAD4 adsorbent treatment to decrease the amount of monosaccharides in addition to the efficient removal of acid-soluble lignin from wood extract. The monosaccharides were, however, mostly recovered from the adsorbent by water wash, whereas acid-soluble lignin remained attached to the adsorbent. In addition, Liu et al. [19] reported on hemicellulose losses during the removal of lignin from prehydrolysis liquor by activated carbon.

In order to decrease the adsorption of hemicelluloses, the amount of adsorbent should be optimised. Notable improvement in filtration capacity does not necessarily require the total removal of foulants. However, the hemicellulose losses during the adsorption process might not be controlled merely by optimising the adsorbent amount because part of the ligneous material present in the extracts is chemically bound with hemicelluloses [20–22]. For instance, Tunc and van Heiningen [23] have shown that in hardwood extract, lignin was bound especially to low molecular mass hemicelluloses. Thus, to minimise hemicellulose losses in the pretreatment, the linkages between lignin and hemicelluloses should be broken prior to adsorption.

In addition to the changes in extract composition, pretreatment also causes changes in the molecular mass distribution of the extract. For instance Koivula et al. [12] have shown that the XAD adsorbent removed most efficiently the highest molecular mass lignin when pine/eucalyptus extract was treated. Gütsch and Sixta [13] have also reported that high-molecular mass lignin was removed first, and low-molecular mass lignin after that, when

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activated carbon was used in lignin removal from wood autohydrolysate. Therefore, if the aim is to remove high-molecular mass lignin instead of low-molecular weight lignin, the amount of activated carbon should be fixed, enabling the adsorption capacity to be fulfilled after the high-molecular mass lignin has been adsorbed, leaving no "empty space" for the low-molecular mass lignin.

Earlier studies have shown that pretreatment removing lignin and wood extractives decreases membrane fouling and improves filtration capacity [11,12]. However, the overall changes in the treated wood extract derived from improvements in the filtration process have not been discussed in detail. Therefore, this study examines the influence of molecular mass distribution changes caused by pretreatment on filtration performance and evaluates the effect of the pretreatment on extract content. Multivariate examination was used to enable comprehensive examination of this complex phenomenon.

2. Materials and methods

2.1. Wood extract

Extraction was made with birch wood chips and water at 20 bar and 173 °C (maximum temperature during extraction) for 70 min, similarly to the efforts of Kilpeläinen et al. [24]. The original, untreated wood extract contained 35 g/l organic material. Of the total organic material, 22 g/l were carbohydrates and 4 g/l lignin. The other organic material present in the wood extracts consisted of, for instance, wood extractives, acetic acid and degradation products of carbohydrates, e.g. furfural and hydroxymethylfurfural [15].

2.2. Pretreatment

Different pretreatments based on adsorption, flocculation or oxidative degradation (by enzyme) were carried out for birch extract prior to filtration with a tight ultrafiltration membrane (Table 1). Also the combination of degradation and adsorption was studied. First, small scale experiments were performed to determine an adequate substance to extract phase ratio (p.r.). After small scale experiments, UV absorbance (at 205 nm) was measured to detect lignin, and the p.r. used in the actual pretreatment experiments was selected based on the decrease in the UV absorbance value. With XAD adsorbents, small scale experiments have been performed in earlier studies and are thus not included here [12].

2.3. Filtration

Filtrations were carried out with a dead-end laboratory-scale filter cell (Amicon 8400) and UFX5pHt membrane (Polysulphone, 5 kDa, Alfa Laval). The membranes were soaked in a 0.1% NaOH solution for 15 min and rinsed with pure water before use. The pure water flux was measured before and after the filtration of the extract. The aim in the filtration was to continue until there was 100 g of the concentrate, that is, until 200 g of permeate was formed. The mass of feed solution was 300 g, and thus, a volume reduction factor (VRF, ratio of the feed and concentrate volumes) of 3 was achieved. If the VRF value of 3 could not be achieved, filtration was ended when the flux value fell below 5 kg/(m^2 h). Pure water flux (PWF) measurements and extract filtrations were carried out at 60 °C and 3 bar (PWF) and 5.5 bar (extract). PWF was measured until it remained stable, and PWF values presented in this study are average values of three stable PWF values. A magnetic stirrer with the tip linear velocity of 1.5 m/s was used to decrease the concentration polarisation. Three samples were collected from each filtration: feed, permeate and concentrate.

2.4. Analysis

The amount of lignin was determined by UV absorbance at 205 nm according to TAPPI UM 250 method [25]. The amount of total carbohydrates was analysed as monosaccharides using gas chromatography (Varian 8200) and acid methanolysis as sample treatment [26]. Wood extractives were analysed from silylated samples by gas chromatograph [9].

The molecular size distribution of hemicelluloses and lignin was determined by a size exclusion chromatography (SEC) system. The system was Waters 600E (Waters, Milford, MA) equipped with a Waters 2414 refractive index (RI) detector, a Waters 486 UV absorbance detector and a column packed with 30 cm of Superdex 30 and 30 cm of Superdex 200 (GE Healthcare, Uppsala, Sweden). The eluent was a 125 mM NaOH solution of a flow rate of 1 ml/min. To calibrate the system, standards of polyethylene glycol with molecular masses 0.4, 4, 10 and 35 kg/mole (Merck Schuchardt OHG, Hohenbrunn, Germany) were used. The samples were pretreated before injection into the SEC column; the samples were heated to 65 °C in a water bath and kept at that temperature for at least 15 min before the samples were filtered through a 0.2 μm filter, filled into vials and inserted into the autosampler. The RI detector detects both carbohydrates and lignin, but since the amount of lignin compared to the amount of carbohydrates is so small, the RI profile can be dealt with as a carbohydrate profile in later discussion. Also, the sensitivity of the UV detector is higher towards lignin than carbohydrates, which confirms the interpretation of the analysis results.

2.5. Mathematical tools

Due to the multivariate nature of the data sets, multivariate approaches were applied in their interpretation. Principal component analysis (PCA) formed the main core of the data-analyses, in

Table 1
Pretreatment methods to remove/degrade lignin in birch extract prior to ultrafiltration.

Pretreatment	*x* to extract p.r.[a] (small scale)	*x* to extract p.r. (actual experiment)	*t* (min)	*T* (°C)	Separation
Adsorption on activated carbon (granulated)	0.05, 0.1 and 0.2	0.2	180	60	Vacuum filtration with paper filter (S&S 604 Rundfilter)
Adsorption on bentonite (powder, Hydrocol)	0.01, 0.03, 0.05, 0.1 and 0.2	0.05	60	60	Centrifugation 15 min 20,000 rpm
Adsorption on XAD16 and XAD7 (Rohm & Haas)	0.005, 0.02, 0.05, 0.1 and 0.15	0.15	60	60	Vacuum filtration with paper filter (S&S 604 Rundfilter)
Enzymatic degradation by laccase (Novozym) combined with adsorption on bentonite	Laccase to extract: 0.01, 0.05; bentonite to extract: 0.1	0.01; 0.1	60 (Laccase) + 30 (Bentonite)	60	Centrifugation 15 min 20,000 rpm

x amount of adsorbent/enzyme.
[a] p.r. phase ratio.