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Improvement of ultrafiltration performance by oxidation treatment in the recovery of galactoglucomannan from wood autohydrolyzate

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ABSTRACT

The possibility to enhance ultrafiltration in the recovery of galactoglukomannan (GGM) from wood autohydrolysate with the gas-phase pulsed corona discharge (PCD) oxidation was studied. The filtration capacity, membrane fouling, and purity of hemicelluloses in the membrane concentrates were used as criteria to evaluate the benefits of the hybrid separation process. The results showed that the PCD oxidation significantly improved the filterability of the wood autohydrolyzate, although its effect on the fouling of the very hydrophilic cellulose-based UF membranes was low. The positive influence on filterability can be at least partly explained by the decreased viscosity of the oxidized autohydrolyzates. Oxidation modified the structure of the lignin but its effect on the lignin molar mass was small. As a result of oxidation, the average molar mass of hemicelluloses was also slightly decreased. Therefore, the influence of oxidation on the purity of the concentrated hemicellulose fractions was not as high as expected. However, oxidation removed lignans and lipophilic wood extractives, which have some influence on the purity of the produced hemicellulose fractions.

1. Introduction

Hemicelluloses are the second most common group of polysaccharides in nature. Globally, pulp mills treat approximately 70 Mt of hemicelluloses annually. Typically, hemicelluloses are not utilized in the most efficient way in the mill and they are usually incinerated in the recovery boiler although their heating value is relatively low. Therefore, hemicelluloses are a huge, existent raw material source for future oil-free economy.

Galactoglucomannans (GGMs) are the predominant hemicelluloses in the soft woods and their recovery and refining to value added products have recently attracted the attention of researchers [1–3]. One of the promising methods to extract GGMs from wood material is pressurized hot water extraction [4–8]. During the extraction other wood compounds are also dissolved into the wood autohydrolyzate and, therefore, further fractionation and purification is needed before the hemicelluloses can be further processed to compounds substituting oil-based compounds. Typically, wood autohydrolyzates contain phenolic compounds such as lignin and its degradation products, and lignans. In addition, small amounts of organic acids and wood lipophilic extractives are present. Lipophilic extractives and lignans have low molar masses, which makes application of membrane technology, in particular ultrafiltration (UF), theoretically feasible in recovery and purification of dissolved high molar mass hemicelluloses [9–14]. The approach, however, often suffers from a noticeable decrease in filtration capacity making the process uneconomical [13,15]. In addition, UF is not selective as regards hemicelluloses, as other high molar mass compounds, such as lignin, are retained simultaneously.

The feasibility of the UF process may be improved by using a proper hydrophilic membrane [16,17], controlling filtration conditions (e.g. high shear rate on the membrane surface to reduce concentration polarization, and thus, usually also membrane fouling), and by applying suitable pre-treatment to the feed solution [13–15]. Lignin and wood extractives have shown to be potential foulants when wood originating solutions are treated. Various pre-treatment processes are able to degrade, inactivate, or remove these foulants prior to UF. Oxidation of the foulants is an attractive fouling management alternative, because it might lead to small molar mass lignin compounds permeating the membrane and offers the possibility to valorize lignin recovered from the

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permeate fraction. Moreover, the waste amount produced in the hybrid process combining oxidation and ultrafiltration is easier to minimize compared to a process combining adsorbents and ultrafiltration. Oxidation might also separate lignin from hemicellulose–lignin complexes and thus enable improvement of purity of the concentrated high molar mass hemicellulose fraction.

Different oxidation methods, for instance wet oxidation [18,19] and ozonation [20,21] have been studied in the degradation of lignin present in different biomass based solutions. Recently, oxidation with the pulsed corona discharge (PCD) method has also proven to decompose lignin in aqueous solutions [22] at an energy efficiency exceeding the one of traditional ozonation; this is due to utilizing short-living oxidants [23]. The degradation of lignin to vanillin and syringaldehyde as oxidation products has been presented as a possible perspective to valorize lignin using the PCD treatment [22]. In the PCD oxidation, only a small energy input is needed to generate ozone and hydroxyl radicals from oxygen and water and, therefore, less energy is needed compared to ozonation. Koivula et al. [13] showed earlier that pretreatment of spruce autohydrolyzates with PCD oxidation significantly improved the flux through a hydrophobic polysulphone membrane and reduced membrane fouling. However, the effect of PCD oxidation on the composition and properties of the wood autohydrolyzate was not examined in details. Furthermore, the effect of oxidation on the filtration performance of hydrophilic membranes, which generally have a lower fouling tendency in the treatment of wood originating solutions, was not studied.

Therefore, the aim of this study was to discover the influence of PCD oxidation pretreatment on the performance of a membrane-based recovery and purification process for hemicellulose (galactoglucomannan), when hydrophilic membranes are applied. The filtration capacity, membrane fouling, and purity of hemicelluloses in membrane concentrates were used as criteria to evaluate the benefits of the hybrid separation process. The effect of oxidative treatment on the autohydrolyzate composition and properties were analyzed and the filtration results explained based on the analysis results.

2. Materials and methods

2.1. Wood autohydrolyzate

Wood extract (autohydrolyzate) was prepared by the treatment of 29.4 kg of dry spruce saw dust with water in a 300 L flow-through extraction vessel at the volumetric flow rate of 14 L/min. The extraction temperature and time were 170 °C and 52 min. The total amount of wood autohydrolyzate was 728 kg, making the water/wood ratio approx. 25. The extraction equipment is described in detail by Kilpeläinen et al. [24].

The extracted liquor contained 2.6 g/L of organic carbon and about 3.8 g/L of carbohydrates. The proportion of monomeric sugars was less than 10% of the total carbohydrates. The average molar mass of hemicellulose was approximately 7 kDa. Due to autohydrolyses and cleavage of acetic acid during the extraction in hot water the pH of wood autohydrolyzate was 4.1. Lignin was expectedly the main impurity in the wood autohydrolyzate. Its content was evaluated by the UV absorbance at 280 nm comprising 0.6 g/L. The liquor also contained about 28 mg/L of lipophilic extractives, 44 mg/L of lignans, 440 mg/L of organic acids and less than 10 mg/L of furan compounds.

2.2. Membrane filter and membranes

In order to minimize membrane fouling, hydrophilic cellulose based UF membranes (water–air interface contact angles below 15°) in a high shear rate membrane filter were used in this study [16,17]. According to the manufacturers, the cut-off values of the membranes used were 30 and 10 kDa for the UC030 (Microdyn-Nadir) and the RC70PP (Alfa Laval) membranes, respectively. The membranes were selected based on earlier experience of the filterability of membranes with similar types of solutions [12,13,16]. A high shear rate cross-rotational (CR) filter was used, because it enables a high turbulence on the membrane surface, thus reducing the effect of concentration polarization [25].

2.3. Filtration experiments

All filtrations were made in the concentration mode to volume reduction factors (VRF) numerically presented in Fig. 1. During the filtration the permeate was collected in a separate vessel, and the concentrate was recirculated back into the feed tank. The pressure, temperature and rotor velocity were kept constant during filtrations. Filtrations were made at a pressure of 1 bar and 2 bar with the 30 kDa and the 10 kDa membrane, respectively. The rotor velocity in the CR-filter was approximately 9 m/s and the temperature 65 °C.

Sequential filtrations were carried out by filtering the previous stage concentrate or permeate using the same or a lower cut-off membrane as shown in Fig. 1. Based on the cut-off values 10 and 30 kDa, two kinds of hemicellulose fractions were recovered by the membranes used. Oxidation treatment was applied to three solutions (Fig. 1):

1. The original wood autohydrolyzate prior to the filtration with the 30 kDa membrane (UC030 III PCD).
2. The 30 kDa membrane concentrate prior to further concentration filtration with the 30 kDa membrane (filtration UC030 II PCD).
3. The 30 kDa membrane permeate (UC030 I) which was at first pre-concentrated by the 10 kDa membrane (RC70PP I) prior to further concentration filtration with the 10 kDa membrane (Filtration RC70PP II PCD).

Membrane performance was evaluated by measuring the permeate flux, pure water permeabilities before (PWP_b), and after (PWP_a) the filtration of wood autohydrolysate and by analyzing the collected samples. Fouling was calculated from the pure water permeabilities and presented as a per cent difference in pure water fluxes before and after the wood autohydrolyzate filtration (Eq. (1)).

2.4. Oxidative treatment

Oxidative treatment was studied with the aim of improving the filtration efficiency and the hemicellulose fraction purity. A schematic diagram of the experimental set-up is shown in Fig. 2. The system consists of a pulse generator (power supply) and a simple reactor described earlier [23]. The power supply generates the discharge pulses of voltage pulse amplitude 20 kV, the current 380–400 A, and 100 ns in duration at pulse repetition frequency of 840 pulses per second (pps). The energy delivered to the reactor was calculated as an integral product of voltage and current peak areas. The maximum delivered energy was 250 W at the maximum pulse repetition frequency (840 pps). The energy consumption efficiency of the pulse generator was 67%.

An autohydrolyzate solution in the amount of 40 L was circulated from the reservoir tank through the reactor by a pump. The autohydrolyzate passed from the top of the reactor through a perforated plate and spread between the electrodes. The autohydrolyzate passed through the PCD zone where the target compounds reacted with hydroxyl radicals, ozone, and other